### 70th International Symposium on Molecular Spectroscopy

**The proceedings from the 70th International Symposium on Molecular Spectroscopy, held June 22-26, 2015 in Champaign, IL**

**Abstract**

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrieved as an official Department of the Army position, policy or decision, unless so designated by other documentation.

**Subject Terms**

international, symposium, molecular spectroscopy

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**Table:**

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<th>2. REPORT TYPE</th>
<th>3. DATES COVERED (From - To)</th>
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<th>6. AUTHORS</th>
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<tr>
<td>Benjamin J. McCall</td>
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<table>
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<tr>
<th>7. PERFORMING ORGANIZATION NAMES AND ADDRESSES</th>
</tr>
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<tbody>
<tr>
<td>University of Illinois - Urbana</td>
</tr>
<tr>
<td>1901 S. First Street, Suite A</td>
</tr>
<tr>
<td>Champaign, IL 61820 -7406</td>
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<td>U.S. Army Research Office</td>
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<tr>
<td>P.O. Box 12211</td>
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<td>Research Triangle Park, NC 27709-2211</td>
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<td>The proceedings from the 70th International Symposium on Molecular Spectroscopy, held June 22-26, 2015 in Champaign, IL</td>
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<td>b. ABSTRACT UU</td>
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<table>
<thead>
<tr>
<th>19a. NAME OF RESPONSIBLE PERSON</th>
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<tbody>
<tr>
<td>Benjamin McCall</td>
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<table>
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ABSTRACT

The proceedings from the 70th International Symposium on Molecular Spectroscopy, held June 22-26, 2015 in Champaign, IL.
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<th>Time</th>
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<td>MG Structure determination</td>
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<td>100</td>
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<td>TG Large amplitude motions, internal rotation</td>
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2015 International Symposium on Molecular Spectroscopy

University of Illinois at Urbana-Champaign

Supported by:
The U.S. Army Research Office
Welcome to the 70th International Symposium on Molecular Spectroscopy
June 22-26, 2015
Urbana-Champaign, IL

On behalf of the Executive Committee, I extend a heartfelt welcome to all the attendees of the 70th Symposium and welcome you to the University of Illinois at Urbana-Champaign.

The Symposium presents research in fundamental molecular spectroscopy and a wide variety of related fields and applications. The continued vitality and significance of spectroscopy is annually re-affirmed by the number of talks, their variety, and the fact that many are given by students. These presentations are the heart of the meeting and are documented by this Abstract Book. Equally important is the information flowing from informal exchanges and discussions. As organizers, we strive to provide an environment that facilitates both kinds of interactions.

The essence of the meeting lies in the scientific discussions and your personal experiences this week independent of the number of times that you have attended this meeting. It is our sincere hope that you will find this meeting informative and enjoyable both scientifically and personally, whether it is your first or 50th meeting. If we can help to enhance your experience, please do not hesitate to ask the Symposium staff or the Executive Committee.

Ben McCall
Symposium Chair

SCHEDULE OF TALKS

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<th>Tuesday (T)</th>
<th>Wednesday (W)</th>
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<th>Friday (F)</th>
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ABSTRACTS

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VENUE AND SPONSOR INFORMATION Follows AUTHOR INDEX
Mini-Symposia

ACCELERATOR-BASED SPECTROSCOPY
Organized by Jos Oomens (Radboud University, Nijmegen) and Jennifer van Wijngaarden (University of Manitoba). This mini-symposium will highlight spectroscopic techniques and the latest results from research conducted at synchrotron and free electron laser facilities. Invited Speakers: Robert Georges (Université de Rennes), Terry McMahon (University of Waterloo), Gaël Mouret (Université du Littoral Côte d’Opale), and Gert von Helden (Fritte-Haber-Institut, Berlin, Germany)

SPECTROSCOPY IN THE CLASSROOM
Organized by Stephen Cooke (Purchase College, SUNY) and Andrea Minei (College of Mount St. Vincent). This mini-symposium will focus on pedagogic innovation in molecular spectroscopy including affordable experiments, teacher resources, misused scientific terms, and perspectives on education in our field. Invited Speakers: Geoffrey A. Blake (California Institute of Technology) and Colin Western (University of Bristol)

HIGH-PRECISION SPECTROSCOPY
Organized by Mike Heaven (Emory University) and Trevor Sears (Brookhaven National Lab). This mini-symposium will cover all aspects of frequency comb generation, metrology and precision spectroscopy. Invited Speakers: Thomas K. Allison (Stony Brook University), Ian Coddington (National Institute of Standards and Technology), David Long (National Institute of Standards and Technology), Hiroyuki Sanada (Keio University), and Wim Ubachs (VU University Amsterdam)
The three Rao Prizes for the most outstanding student talks at the 2014 meeting will be presented. The winners are Grant Buckingham, University of Colorado; Kathryn Chew, Yale University; and Yu-Huan Huang, National Chiao Tung University. The Rao Prize was created by a group of spectroscopists who, as graduate students, benefited from the emphasis on graduate student participation, which has been a unique characteristic of the Symposium. This year three more Rao Prize winners will be selected.

The award is administered by a Prize Committee chaired by Gary Douberly, University of Georgia, and comprised of David Anderson, University of Wyoming; Brooks Pate, University of Virginia; Rebecca Peebles, Eastern Illinois University; Jennifer van Wijngaarden, University of Manitoba; and Tim Zvier, Purdue University. Any questions or suggestions about the Prize should be addressed to the Committee. Anyone (especially post-docs) willing to serve on a panel of judges should contact Gary Douberly (douberry@uga.edu).

The Miller Prize for the best presentation given by a recent PhD at the 2014 meeting will be presented. The winner, Christopher Leavitt (University of Georgia), will give a lecture on Wednesday.

The Miller Prize winner and his or her co-authors will be invited to submit an article to the Journal of Molecular Spectroscopy based on the research in the prize-winning talk. After passing the normal review process, the article will appear in the Journal with a caption identifying the paper with the talk that received the Miller Prize.

The award is administered by a Prize Committee chaired by Michael Heaven, Emory University and comprised of Frank De Lucia, The Ohio State University; Jinjun Liu, University of Louisville; David Perry, The University of Akron; Cristina Pizzarnini, University of Bologna; Scott Reid, Marquette University; Trevor Sears, Brookhaven National Laboratory; Jaime Stearns, Air Force Research Laboratory; Tim Steinle, Arizona State University; and Susanna Widicus Weaver, Emory University. Any questions or suggestions about the Prize should be addressed to the Committee. Anyone willing to serve on a panel of judges should contact Michael Heaven (mheaven@emory.edu).

Information

ACCOMMODATIONS
The check-in for dormitory accommodations is located in Bousfield Hall, 1214 South First Street, opens at noon on Sunday, June 21st, and remains open 24 hours a day through the Symposium. Hotel information is listed on the ISMS website.

PARKING
Parking permits are for lot E14 (see map at end of book). Please purchase parking as part of your check-in process at the dorm. If you need to purchase meter hang-tags for parking near the meeting rooms, you can do so at the registration desk.

REGISTRATION
The registration desk is located in Room 165 Noyes Lab, and is open on Sunday from 4:00-6:00 PM, and Monday through Friday from 8:00 AM-4:30 PM. Refreshments will be available from 8:00 AM-4:30 PM.

CHEMISTRY LIBRARY
The Chemistry Library will be open and available for your use during Symposium hours. The library has a number of computers, desks and tables to work at, and comfy chairs (and books!).

READY ROOM/STATION
We have set up Noyes Lab 164 as a “Ready Room” with computers that you can use to test your powerpoint presentation. If you have any problems, we will also have a staffed “Ready Station” in Noyes Lab 165 (right next to registration) where you can come for assistance.

COMPUTER Lab (VizLab)
Noyes Lab 151 is a small computer lab with Apple computers that is available for your use during the meeting. Please look in your packet for an access code to enter the room.

INTERNET ACCESS/Wi-Fi
Each attendee will receive a login and password to access campus WiFi (SSID: IllinoisNet or UIUICNet) as a guest. This access should work in most locations through campus. Please read the Internet Acceptable Use Policy below.

AUDIO/VIDEO INFORMATION
Each session room is equipped with a computer, onto which presentation files will be pre-loaded by Symposium staff. To submit your presentation file, you must go to the Manage Presentations link on our web site and follow the instructions. All files must be submitted by 11:59 PM CDT THE DAY BEFORE your presentation session. All submitted files will be loaded onto the presentation computer one half-hour prior to the beginning of the session.

ACKNOWLEDGMENTS
The Symposium Chair wishes to acknowledge the hard work of numerous people who made this meeting possible. First and foremost is the Symposium Coordinator Brijgit McCall, who has smoothly and single-handedly taken care of almost all of the electronic and logistical aspects of the meeting. Second are our student assistants, Brad Gibson, Charlie Markus, and Scott Dubowsky, who have handled innumerable important details to ensure the sessions and exhibitions go well. The other students in my group also play vital roles in monitoring the audiovisual systems and other aspects of the meeting. I wish to acknowledge the hospitality of the Chemistry Department and the School of Chemical Sciences (as well as the School of Molecular and Cell Biology) in tolerating our takeover of their buildings.
LIABILITY

The Symposium fees DO NOT include provisions for the insurance of participants against personal injuries, sickness, theft, or property damage. Participants and companions are advised to obtain whatever insurance they consider necessary. The Symposium organizing committee, its sponsors, and individual committee members DO NOT assume any responsibility for loss, injury, sickness, or damages to persons or belongings, however caused. The statements and opinions stated during oral presentations or in written abstracts are solely the author’s responsibilities and do not necessarily reflect the opinions of the organizers.

DISCLAIMER

The views, opinions, and/or findings contained in this report are those of the authors and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

INTERNET ACCEPTABLE USE POLICY

Each attendee will receive a login and password to access campus WiFi (SSID: IllinoisNet or UIUCNet) as a guest. Guest accounts are intended to support a broad range of communications. Professional and appropriate etiquette is required. Anonymous access and posting through guest accounts is forbidden. All users must accept that their identity may be associated with any content they provide while using the service. By accessing the campus WiFi network, you expressly acknowledge and agree to the following:

Use of the guest account service is at your sole risk and the entire risk as to satisfactory quality and performance is with you. You agree not to use the guest account intentionally or unintentionally to violate any applicable local, state, national or international law, including, but not limited to, any regulations having the force of law. To the extent not prohibited by law, in no event shall the university be liable for personal injury, or any incidental, special, indirect or consequential damages whatsoever, including, without limitation, damages for loss of profits, loss of data, business interruption or any other commercial damages or losses, arising out of or related to your use or inability to use the guest account, however caused, regardless of the theory of liability (contract, tort or otherwise) and even if the university has been advised of the possibility of such damages. The use of the guest account is subject, but not limited to, all University policies and regulations detailed at the Campus Administrative Manual (http://www.cam.illinois.edu). See the University’s Web Privacy Notice (http://www.vpaa.uiuc.edu/policies/web_privacy.cfm) for all applicable laws and policies.
Journal of Molecular Spectroscopy Review Lecture
1:30 – 2:10
PHYSICS BEYOND THE STANDARD MODEL: FROM MOLECULAR HYDROGEN SPECTROSCOPY. Wim Ubachs, Edelk John Salumbides, Julija Bagdonaite

MF. Mini-symposium: High-Precision Spectroscopy
Monday, June 22, 2015 – 1:30 PM
Room: 116 Roger Adams Lab
Chair: Michael Heaven, Emory University, Atlanta, GA, USA

MF01
Journal of Molecular Spectroscopy Review Lecture
1:30 – 2:10
PHYSICS BEYOND THE STANDARD MODEL: FROM MOLECULAR HYDROGEN SPECTROSCOPY. Wim Ubachs, Edelk John Salumbides, Julija Bagdonaite

MF02
PRECISION SPECTROSCOPY OF highly-excited vibrational levels of H₂. Ming Li Niu, Edelk John Salumbides, Wim Ubachs

MF03
BOUNDS ON THE NUMBER AND SIZE OF EXTRA DIMENSIONS FROM MOLECULAR SPECTROSCOPY. Edelk John Salumbides, Bert Schellekens, Beatriz Gato-Rivera, Wim Ubachs

MF04
CONTINUOUS SUPERSOPNUS EXPANSION DISCHARGE SOURCE FOR HIGH-PRECISION MID-INFRARED SPECTROSCOPY OF COLD MOLECULAR IONS. Tatsuya Tanaka, Michael Patambo, Benjamin J. McCall

MF05
PROGRESS TOWARDS A HIGH-PRECISION INFRARED SPECTROSCOPIC SURVEY OF THE H⁺ ion, Adam J. Perry, James N. Hodges, Charles R. Markas, G. Stephen Kocheril, Paul A. Jenkins II, Benjamin J. McCall

Intermission

MF06
HIGH PRECISION INFRARED SPECTROSCOPY OF OH⁻: Charles R. Markas, Adam J. Perry, James N. Hodges, G. Stephen Kocheril, Paul A. Jenkins II, Benjamin J. McCall

MF07
TOWARD TWO-COLOR SUB-DOPPLER SATURATION RECOVERY KINETICS IN CN (X, v = 0, J), Hong Xu, Damien Forthomme, Trevor Sears, Gregory Hall, Paul Dagdugian

MF08
AN EMPIRICAL DIPOLE POLARIZABILITY FOR Hₑ FROM A FIT TO SPECTROSCOPIC DATA YIELDING ANALYTIC EMPirical POTENTIALS FOR ALL ISOTOPOLOGIES OF Hₑ⁻. Young-Sang Cho, Robert J. Le Roy, Nikesh S. Dattani

MF09
ANALYTIC EMPirical POTENTIALS FOR BeH⁺, BeD⁺, and BeT⁺ INCLUDING UP TO 4TH ORDER QED IN THE LONG-RANGE, AND PREDICTIONS FOR THE HALO NUCLEONIC MOLECULES (1)BeH⁺ and (1)BeH⁺⁺, Lena C. M. Li Chun Fong, Gregorius Lach, Robert J. Le Roy, Nikesh S. Dattani

MF10
ANALYTIC EMPirical POTENTIAL AND ITS COMPARISON TO STATE OF THE ART ab initio CALCULATIONS FOR THE 6– Excited (1Σ⁺)–STATE OF Li⁺. Nikesh S. Dattani, Robert J. Le Roy

MF11
PRECISION SPECTROSCOPY OF TRAPPED HİF⁺ WITH A COHERENCE TIME OF 1 SECOND. Kevin Cossel, William Caiminescu, Matt Glass, Dan Gresh, Yui Zhou, Jun Ye, Eric Cornell

MF12
BROADBAND FREQUENCY COMB AND CW-LASER VELOCITY MODULATION SPECTROSCOPY OF T²H⁺. Dan Gresh, Kevin Cossel, Jun Ye, Eric Cornell

MF13
PURE MW DATA FOR = 0 – 6 OF PM GIVE VIBRATIONAL SPACINGS AND A FULL ANALYTIC POTENTIAL ENERGY FUNCTION. N. He (Chih) Yao, Corey Evans, Nick Walker, Robert J. Le Roy
MH. Linelists
Monday, June 22, 2015 – 1:30 PM
Room: B102 Chemical and Life Sciences
Chair: Shanshan Yu, California Institute of Technology, Pasadena, CA, USA

MH01
1:30 – 1:45

MH02
HITRAN Online: A NEW STRUCTURE AND INTERFACE FOR HITRAN LINE LISTS AND CROSS SECTIONS , Christian Hill, Laurence S. Rothman, Ioulit E. Gordon, Roman V Kochanov, Piotr Wcislo, Jonas Wilzewski
1:47 – 2:02

MH03
2:04 – 2:19

MH04
CPU-ACCELERATED INTENSITIES: A NEW METHOD OF COMPUTING EINSTEIN-A COEFFICIENTS, Ahmed Faris Al-Refaie, Sergei N. Yurchenko, Jonathan Tennyson
2:21 – 2:31

MH05
LINE SHAPE PARAMETERS FOR NEAR INFRARED CO2 BANDS IN THE 1.61 AND 2.06 MICRON SPECTRAL REGIONS, V. Malathy Devi, D. Chris Benner, Kenyoon Sung, Linda Brown, Timothy J Crawford, Mary Ann H. Smith, Aftan Muntz
2:33 – 2:48

MH06
RELIABLE IR LINE LISTS FOR SO2 AND CO2 ISOTOPOLOGUES COMPUTED FOR ATMOSPHERIC MODELING ON VENUS AND EXOPLANETS, Xinjian Huang, David Schwenke, Timothy Lee, Robert R. Gamache
2:50 – 3:05

MH07
LASER SPECTROSCOPIC STUDY OF CaH IN THE Σ+2 AND DΣ+2 STATES, Kenzaki Watanabe, Kanako Uchida, Kaori Kobayashi, Fusakazu Matsushima, Yoshiki Kobayashi
3:07 – 3:22

Intermission

MH08
ADDITIONAL MEASUREMENTS AND ANALYSES OF H3O2 AND H5O2, John Pearson, Shanshan Yu, Adam Walters
3:41 – 3:56

MH09
EXPERIMENTAL LINE LISTS OF HOT METHANE, Robert J. Hargreaves, Peter F. Bernath, Jeremy Bailey, Michael Dulick
3:58 – 4:13

MH10
EXPERIMENTAL TRANSITION SPECTRA OF HOT AMMONIA IN THE INFRARED, Christopher A. Brails, Robert J. Hargreaves, Michael Dulick, Peter F. Bernath
4:15 – 4:30

MH11
HYPERSONIC POST-SHOCK CAVITY RING-DOWN SPECTROSCOPY, Nikolai Sars-David, Samir Kassi, Abdelmassoud Besnard, Robert Georges
4:32 – 4:47

MH12
CH2D NEAR INFRARED CAVITY RING-DOWN SPECTRUM REANALYSIS AND IR-IR DOUBLE RESONANCE, Shuyee Yang, George Schwartz, Kevin Lehmann
4:49 – 5:04

MH13
A NEW LINE-LIST FOR HOT FORMALDEHYDE, Ahmed Faris Al-Refaie, Sergei N. Yurchenko, Jonathan Tennyson, Andrea Yachtmenner
5:06 – 5:21

MH14
THE MICROWAVE SPECTROSCOPIC OF AMINOACETONITRILE IN THE VIBRATIONAL EXCITED STATE, Chiho Fujita, Hiroyuki Ozeki, Kaori Kobayashi
5:23 – 5:38

MH. Ions
Monday, June 22, 2015 – 1:30 PM
Room: 274 Medical Sciences Building
Chair: Mark Johnson, Yale University, New Haven, CT, USA

MI01
ROTATIONAL ACTION SPECTROSCOPY VIA STATE-SELECTIVE HETERO ATOMIC ATTACHMENT, Lars Kluge, Alexander Stoffels, Sandra Brinken, Oskar Avanuy, Stephan Schlemmer
1:30 – 1:45

MI02
SYMMETRY BEYOND PERTURBATION THEORY: FLOPPY MOLECULES AND ROTATION-VIBRATION STATES, Hanno Schmiedt, Stephan Schlemmer, Per Jensen
1:47 – 2:02

MI03
STUDYING ROTATION/TORSION COUPLING IN H2 O USING DIFFUSION MONTE CARLO, Melanie L. Maher, Zhou Lin, Anne B McCoy
2:04 – 2:19

MI04
HIGH J ROTATIONAL LINES OF 13C ISOTOPOLOGUES OF HCO+ MEASURED BY USING EVENSON-TYPE TUNABLE FIR SPECTROMETER, Mari Sumiki, Ryo Osishi, Yoshiko Moriwaki, Takayoshi Amatatsu
2:21 – 2:36

MI05
UV-HOLE BURNING SPECTROSCOPY OF A PROTONATED ADENINE DIMER IN A COLD QUADRUPOLE ION TRAP, Hysuk Kang
2:38 – 2:48

MI06
SPECTROSCOPIC INVESTIGATION OF PROTON-COUPLED ELECTRON TRANSFER IN WATER OXIDATION CATALYZED BY A RUTHENIUM COMPLEX, [Ru(pp)/ppy][HCO2]/2, Erin M. Duffy, Brett Marsh, Jonathan Yoss, Elimele Garand
2:50 – 3:05

MI07
PROBING SOLVATION SHELS OF Ni(H2O)62+ (n=4-10) AND Ni(OH)2 O+ (n=2-5) WITH CRYOGENIC IR VIBRATIONAL SPECTROSCOPY. , Jonathan Yoss, Brett Marsh, Jia Zhou, Elimele Garand
3:07 – 3:22

MI08
MICROSOLVATION OF THE Mg2SO4.2H2O CATION: CRYOGENIC VIBRATIONAL SPECTROSCOPY OF (Mg2+)(SO4)2-(H2O)n (n=1-11), Patrick J. Keleher, Joseph W DePalma, Christopher J. Johnson, Joseph Fournier, Mark Johnson
3:24 – 3:39

MI09
CAPTURE AND STRUCTURAL DETERMINATION OF ACTIVATED INTERMEDIATES IN NICKEL CATALYZED CO2 REDUCTION, Stephanie Craig, Fabian Menges, Aaron Weik, Joseph Fournier, Niklas Tötsch, Mark Johnson
3:58 – 4:13

MI10
THRESHOLD IONIZATION SPECTROSCOPIC CHARACTERIZATION OF Li+ ATOM REACTION WITH ISOPRENE, Wenjin Cao, Dong-Sheng Yang
4:15 – 4:30

MI11
CO-PROMOTED BOND ACTIVATION OF ETHYLENE PROBED BY MASS-ANALYZED THRESHOLD IONIZATION SPECTROSCOPY, Yuchen Zhang, Sudeep Kumari, Wenjin Cao, Dong-Sheng Yang
4:32 – 4:47

MI12
STRUCTURE DETERMINATION OF CISPLATIN-AMINO ACID ANALOGUES BY INFRARED MULTIPLE PHOTON DISOCIATION ACTION SPECTROSCOPY, Chenchen He, Xun Bao, Yanlong Zhu, Stephen Strobehn, Brett Kimnani, Y-W Noi, C S Chow, M T Rodgers, Junhan Gao, J. Oomens
4:49 – 5:04

MI13
STRUCTURAL EFFECTS OF CYTIDINE 2′-DEOXYMODIFICATIONS AS DETERMINED BY BMFPd ACTION SPECTROSCOPY, Lucas Hawley, Chenchen He, Lin Fan, Raman Wu, Bo Yang, M T Rodgers, Giel Berden, J. Oomens
5:06 – 5:21

MI14
GAS-PHASE CONFORMATIONS AND ENERGETICS OF SODIUM CATIONIZED 2′-DEOXYGUANOSINE AND GUANOSINE: BMFPd ACTION SPECTROSCOPY AND THEORETICAL STUDIES, Yanling Zhu, Lucas Hawley, Chenchen He, Xun Bao, M T Rodgers, Junhan Gao, J. Oomens
5:23 – 5:38

MI15
UNRAVELING PROTON TRANSFER IN STEPWISE HYDRATED N-HETEROCYCLIC ANIONS, John T. Kelly, Nathan I Hammer, Kit Bowen, Gregory S. Tschumper
5:40 – 5:55
M. Small molecules
Monday, June 22, 2015 – 1:30 PM
Room: 217 Noyes Laboratory
Chair: Leah C O’Brien, Southern Illinois University, Edwardsville, IL, USA

MJO1
DEPARTURBATION ANALYSIS FOR THE \( A^3\Pi \) AND \( \nu^3 \Sigma^+ \) STATES OF \( \text{C}_2 \), Jun Tang, Wang Chen, Kentarou Kaseguchi
1:30 – 1:45

MJO2
HIGH-RESOLUTION LASER SPECTROSCOPY OF THE \( A^3\Pi \leftarrow \nu^3 \Sigma^+ \) LIMIT OF \( \text{ICl} \), State of \( \Pi \), Takao Tsuchiya, Nobuo Nishimiya, Robert J. Le Roy
1:47 – 2:02

MJO3
HIGH-RESOLUTION LASER SPECTROSCOPY FOR ABOSORPTION TO LEVELS LYING NEAR THE DISSOCIATION LIMIT OF THE \( A^3\Pi \), State of \( \Pi \), Tokio Yukiya, Nobuo Nishimiya, Robert J. Le Roy
2:04 – 2:19

MJO4
THE NEAR-INFRARED SPECTRUM OF NCI: ANALYSES OF THE (0,1), (1,0), & (2,1) BANDS OF SYSTEM a AND THE (1,0) BAND OF SYSTEM H. Jack C H urine, Courtney N Gipson, Ethan M Grames, James E O’Brien, Leah C O’Brien
2:21 – 2:36

MJO5
ANALYSIS OF EMISSION SPECTRA OF YTTRIUM MONOIODIDE PRODUCED BY PHOTODISSOCIATION OF \( \text{Y}_3 \), Wenting Wendy Chen, Thomas C. Galvin, Thomas J. Houlihan, Jr., and Gary Eden
2:38 – 2:53

MJO6
GENERATION OF VIBRATIONALLY EXCITED HCP FROM A STABLE SYNTHETIC PRECURSOR, Alexandre W Hui, Jun Jiang, Trevor J Erickson, Carrie Womack, Matthew Nasa, Christopher Cummins, Robert W Field
2:55 – 3:05

Intermission

MJO7
DPF ANALYSES YIELD FULLY ANALYTICAL POTENTIALS FOR THE \( B^1\Pi \), “BARRIER” STATES OF \( \text{B}_2 \) and \( \text{Li}_2 \) AND AN IMPROVED GROUND-STATE WELL DEPTH FOR \( \text{H}_2 \), Kai Slaughter, Nikesh S. Dattani, Claude S. Amiot, Amanda J. Lee, Robert J. Le Roy
3:24 – 3:39

MJO8
LASER SPECTROSCOPY OF THE PHOTODISSOCIATION OF \( \text{Rb-Ar} \) AND \( \text{Rb-Kr} \) THERMAL PAIRS: STRUCTURE OF THE \( \text{Rb}_2 \)-RARE GAS \( \Lambda^3\Pi \) STATE NEAR THE CLASSICAL LIMIT, Audrey E. Millison, William Goldshlag, Kylie T Raymond, and Gary Eden
3:41 – 3:56

MJO9
COLLISION-INDUCED ABSORPTION WITH EFFECTS ON ANISOTROPIC INTERACTIONS: THEORY AND APPLICATION TO \( \text{H}_2 \) \& \( \text{N}_2 \), Tin Tjan, Charlotte Millet, Katheleen Hunt, Ad van der Avoird, Gerrit Groenenboom
3:58 – 4:13

MJO10
PHOTO-DISSOCIATION RESONANCES OF JET-COOLDED \( \text{NO}_2 \) AT THE DISSOCIATION THRESHOLD BY CW-FLD WITH THE DUO PROGRAM, Patrick Dupré
4:15 – 4:30

Post-Deadline Abstract

TA. Metal containing
Tuesday, June 23, 2015 – 8:30 AM
Room: 116 Roger Adams Lab
Chair: Jacob Stewart, Emory University, Atlanta, GA, USA

TA01
BONDING AT THE EXTREME: DETECTION AND CHARACTERIZATION OF THORIUM DIMER, \( \text{Th}_2 \), Timothy Steimle, Seth Muscarella, Dainan L. Kokkin
8:30 – 8:45

TA02
THE QUINTESSENTIAL BOND OF MODERN SCIENCE: THE DETECTION AND CHARACTERIZATION OF DIATOMIC GOLD SULFIDE, \( \text{AuS} \), Dainan L. Kokkin, Raashan Zhang, Timothy Steimle, Bradley W Pearlman, Ian A Wyse, Thomas D. Varberg
8:47 – 9:02

TA03
LASER SPECTROSCOPY OF RUTHENIUM CONTAINING DIATOMIC MOLECULES: \( \text{RuH}_2 \) AND \( \text{RuF}_2 \), Allan G. Adam, Ricarda M. Konder, Nicole M. Nickerson, Colan Linton, D. W. Tokaryk
9:04 – 9:19

TA04
OPTICAL ZEEMAN SPECTROSCOPY OF CALCIUM FLUORIDE, \( \text{CaF}_2 \), Dainan L. Kokkin, Jack Delvin, Michael Tarbutt
9:21 – 9:36

TA05
ELECTRONIC TRANSITIONS OF YTTRIUM MONOPHOSPHIDE, \( \text{YI}_3 \), Chuan-Sheng Cheng, Biu Wo Li, MAN-CHOR Chan
9:38 – 9:53

TA06
ROTATIONALLY RESOLVED SPECTROSCOPY OF THE \( B^1\Pi \leftarrow \nu^1 \Sigma^+ \) AND \( C^1\Sigma^+ \leftarrow \nu^1 \Sigma^+ \) ELECTRONIC BANDS OF \( \text{CaF}_2 \), Michael Sullivan, Jacob Stewart, Michael Hearen
9:55 – 10:10

Intermission

TA07
HIGH RESOLUTION LASER SPECTROSCOPY OF NICKEL MONOBORIDE, \( \text{NiB} \), B. S. Goudreau, Dainan L. Kokkin, D. W. Tokaryk, Allan G. Adam
10:29 – 10:44

TA08
MOLECULAR LINE LISTS FOR SCANDIUM AND TITANIUM HYDRIDE USING THE DUO PROGRAM, Leonardo Leão, Sergei N. Yurchenko, Jonathan Tennyson
10:46 – 11:01

TA09
UV SPECTROSCOPY ON GAS PHASE Cu(I)-BIPYRIDYL COMPLEXES, Shuang Xu
11:03 – 11:18

TA10
ANION PHOTOELECTRON SPECTROSCOPY OF \( \text{NbW}^- \) AND \( \text{W}_2^- \), D. Alex Schrepper, Melissa A. Baudhuin, Doreen Leopold, Sean M. Casey
11:20 – 11:35

Intermission

TA01
DEPARTURBATION ANALYSIS FOR THE \( A^3\Pi \) AND \( \nu^3 \Sigma^+ \) STATES OF \( \text{C}_2 \), Jun Tang, Wang Chen, Kentarou Kaseguchi
1:30 – 1:45

TA02
HIGH-RESOLUTION LASER SPECTROSCOPY OF THE \( A^3\Pi \leftarrow \nu^3 \Sigma^+ \) SYSTEM OF \( \text{ICl} \) IN 0.7 \( \mu \text{m} \) REGION, Nobuo Nishimiya, Tokio Yukiya, Masao Suzuki, Robert J. Le Roy
1:47 – 2:02

TA03
ANALYSIS OF EMISSION SPECTRA OF YTTRIUM MONOIODIDE PRODUCED BY PHOTODISSOCIATION OF \( \text{Y}_3 \), Wenting Wendy Chen, Thomas C. Galvin, Thomas J. Houlihan, Jr., and Gary Eden
2:04 – 2:19

TA04
GENERATION OF VIBRATIONALLY EXCITED HCP FROM A STABLE SYNTHETIC PRECURSOR, Alexandre W Hui, Jun Jiang, Trevor J Erickson, Carrie Womack, Matthew Nasa, Christopher Cummins, Robert W Field
2:55 – 3:05

TA07
HIGH-RESOLUTION LASER SPECTROSCOPY OF NICKEL MONOBORIDE, \( \text{NiB} \), B. S. Goudreau, Dainan L. Kokkin, D. W. Tokaryk, Allan G. Adam
10:29 – 10:44

TA08
MOLECULAR LINE LISTS FOR SCANDIUM AND TITANIUM HYDRIDE USING THE DUO PROGRAM, Leonardo Leão, Sergei N. Yurchenko, Jonathan Tennyson
10:46 – 11:01
## TB. Mini-symposium: Accelerator-Based Spectroscopy

**Chair:** Jennifer van Wijngaarden, University of Manitoba, Winnipeg, MB, Canada

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<thead>
<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>8:30 – 9:00</td>
<td><strong>INVITED TALK</strong> JET-COOLED SPECTROSCOPY ON THE AILES INFRARED BEAMLNE OF THE SYNCHROTRON RADIATION FACILITY SOLEIL, Robert Georges</td>
</tr>
<tr>
<td>9:05 – 9:20</td>
<td><strong>TB02</strong> LOWEST VIBRATIONAL STATES OF ACRYLONITRILE, Zbigniew Kisiel, Marie-Aline Martin-Drumel, Olivier Pirali</td>
</tr>
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<td>9:22 – 9:37</td>
<td><strong>TB03</strong> FIR SYNCHROTRON SPECTROSCOPY OF HIGH TORSIONAL LEVELS OF CD$_3$OH: THE TAU OF METHANOL, Ronald M. Lee, Li-Hong Xu, Brant E Billinghurst</td>
</tr>
<tr>
<td>9:39 – 9:54</td>
<td><strong>TB04</strong> FAR-INFRARED SYNCHROTRON-BASED SPECTROSCOPY OF PROTON TUNNELLING IN MALONALDEHYDE, D. A. Goodwin, D. W. Tokaryk, Stephen Cary Ross</td>
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<tr>
<td><strong>Intermission</strong></td>
<td></td>
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<tr>
<td>10:13 – 10:43</td>
<td><strong>TB05</strong> THE DISCRETE NATURE OF THE COHERENT SYNCHROTRON RADIATION, Stefano Tammaro, Olivier Pirali, P. Roy, Jean François Lampin, Gaël Ducourneau, Arnaud Cuisset, Francis Hindle, Gaël Mouret</td>
</tr>
<tr>
<td>10:48 – 11:03</td>
<td><strong>TB06</strong> LOW-TEMPERATURE COLLISIONAL BROADENING IN THE FAR-INFRARED CENTRIFUGAL DISTORTION SPECTRUM OF CH$_4$, Vincent Bouchaud, Jean Vander Auwera, Laurent Manceron, F. Kwabia Tchana, Tony Gabard, Badr Amyay, Mbaye Faye</td>
</tr>
<tr>
<td>11:05 – 11:20</td>
<td><strong>TB07</strong> HYDROGEN AND NITROGEN BROADENED ETHANE AND PROPANE ABSORPTION CROSS SECTIONS, Robert J. Hargreaves, Dominique Appadoo, Brant E Billinghurst, Peter F. Bernath</td>
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## TC. Mini-symposium: Spectroscopy in the Classroom

**Chair:** S. A. Cooke, Purchase College SUNY, Purchase, NY, USA

<table>
<thead>
<tr>
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<tr>
<td>8:30 – 9:00</td>
<td><strong>INVITED TALK</strong> PGOPHER IN THE CLASSROOM AND THE LABORATORY, Colin Western</td>
</tr>
<tr>
<td>9:22 – 9:37</td>
<td><strong>TC03</strong> RESEARCH AT A LIBERAL ARTS COLLEGE: MAKE SURE YOU HAVE A NET FOR YOUR HIGH WIRE ACT, Mark D. Marshall, Helen O. Leung</td>
</tr>
<tr>
<td>9:39 – 9:54</td>
<td><strong>TC04</strong> A SPECTROSCOPY BASED P-CHEM LAB, INCLUDING A DETAILED TEXT AND LAB MANUAL, John Musgrove</td>
</tr>
<tr>
<td><strong>Intermission</strong></td>
<td></td>
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<tr>
<td>10:13 – 10:28</td>
<td><strong>TC05</strong> HOW WE KNOW: SPECTROSCOPY IN THE FIRST YEAR AND BEYOND, Kristopher J Ooms</td>
</tr>
<tr>
<td>10:30 – 10:40</td>
<td><strong>TC06</strong> EXPANDED CHOICES FOR VIBRATION-ROTATION SPECTROSCOPY IN THE PHYSICAL CHEMISTRY TEACHING LABORATORY, Joel R Schmitz, David A Dobson</td>
</tr>
<tr>
<td>10:42 – 10:57</td>
<td><strong>TC07</strong> SPECTROSCOPIC CASE-BASED STUDIES IN A FLIPPED QUANTUM MECHANICS COURSE, Steven Shipman</td>
</tr>
<tr>
<td>10:59 – 11:09</td>
<td><strong>TC08</strong> THE H-ATOM SPECTRUM: NOT A CLASSROOM DEMONSTRATION ..., Wolfgang Jäger</td>
</tr>
<tr>
<td>11:11 – 11:26</td>
<td><strong>TC09</strong> RAMAN INVESTIGATION OF TEMPERATURE PROFILES OF PHOSPHOLIPID DISPERSIONS IN THE BIOCHEMISTRY LABORATORY, Norman C. Craig</td>
</tr>
<tr>
<td><strong>Post-Deadline Abstract</strong></td>
<td><strong>TC10</strong> ONLINE AND CERTIFIABLE SPECTROSCOPY COURSES USING INFORMATION AND COMMUNICATION TOOLS. A MODEL FOR CLASSROOMS AND BEYOND, Mangala Sunder Krishnan</td>
</tr>
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TD. Conformers, isomers, chirality, stereochemistry

Tuesday, June 23, 2015 – 8:30 AM
Room: 274 Medical Sciences Building

Chair: Emilio J. Cocinero, Universidad del País Vasco (UPV-EHU), Leioa, Spain

TD01 8:30 – 8:45
A JOINT THEORETICAL AND EXPERIMENTAL STUDY OF THE SiH2O2 ISOMERIC SYSTEM,
Michael C McCarthy, Jürgen Gauss

TD02 8:47 – 9:02
A MINTY MICROWAVE MENAGERIE: THE ROTATIONAL SPECTRA OF MENTHONE, MENTHOL, CARVACROL, AND THYMOL, David Schmitz, V. Alvin Shubert, Thomas Betz, Barbara Michela Giuliano, Melanie Schnell

TD03 9:04 – 9:19
THE ROTATIONAL SPECTRUM AND CONFORMATIONAL STRUCTURES OF METHYL VALERATE, Ha Vinh Luan Nguyen, Wolfgang Stahl

TD04 9:21 – 9:36

TD05 9:38 – 9:53
UNRAVELLING THE CONFORMATIONAL LANDSCAPE OF NICOTINOIDS: THE STRUCTURE OF COTinine BY BROADBAND ROTATIONAL SPECTROSCOPY, Iciar Uriarte, Patricia Ercilla, Emilio J. Cocinero, Cristobal Perez, Elena Caballero-Mancebo, Alberto Lasarri

TD06 9:55 – 10:10
CONFORMATIONALLY RESOLVED STRUCTURES OF JET-COOLED PHENACETIN AND ITS HYDRATED CLUSTERS, Cheol Joo Moon, Ahreum Min, Ahreum Ahn, Myong Yong Choi

TD07 10:12 – 10:27
CONFORMATIONAL STRUCTURES OF JET-COOLED ACETAMINOPHEN-WATER CLUSTERS BY IR-DIP SPECTROSCOPY AND COMPUTATIONAL CALCULATIONS, Ahreum Min, Ahreum Ahn, Cheol Joo Moon, Myong Yong Choi

Intermission

TD08 10:46 – 11:01
THE INHERENT CONFORMATIONAL PREFERENCES OF GLUTAMINE-CONTAINING PEPTIDES: THE ROLE FOR SIDE-CHAIN BACKBONE HYDROGEN BONDS, Patrick S Walsh, Carl McBurney, Samuel H. Gellman, Timothy S. Zwier

TD09 11:03 – 11:18
APPLICATIONS OF STRUCTURAL MASS SPECTROMETRY TO METABOLICOS: CLARIFYING BOND SPECIFIC SPECTRAL SIGNATURES WITH DITOPE EDITED SPECTROSCOPY, Olga Gerlach, Conrad T. Wolfe, Joseph Foumiere, Sean Colvin, Mark Johnson, Scott Miller

TD10 11:20 – 11:35
ALKALI METAL-GLUCOSE INTERACTION PROBED WITH INFRARED PRE-DISSOCIATION SPECTROSCOPY, Steven J. Kriegel, Brett Marsh, Jia Zhou, Etienne Garand

TD11 11:37 – 11:52
PROBING THE CONFORMATIONAL LANDSCAPE OF A POLYETHER BUILDING BLOCK BY RAMAN JET SPECTROSCOPY, Sebastian Bocklitz, Martin A. Suhm
TF. Mini-symposium: High-Precision Spectroscopy
Tuesday, June 23, 2015 – 1:30 PM
Room: 116 Roger Adams Lab
Chair: Trevor Sears, Brookhaven National Laboratory, Upton, NY, USA

TF01
INVITED TALK
COMB-REFERENCED SUB-DOPPLER RESOLUTION INFRARED SPECTROSCOPER, Hiroyuki Sasada
1:30 – 2:00

TF02
SUB-DOPPLER RESOLUTION SPECTROSCOPIC OF THE FUNDAMENTAL VIBRATION BAND OF HCl WITH A COMB-REFERENCED SPECTROMETER, Kenji Honda, Hideyuki Sera, Masashi Abe, Hiroyuki Sasada
2:05 – 2:20

TF03
OBSERVATION AND ANALYSIS OF THE A1–A3 SPLITTING OF CH3D, Masashi Abe, Hideyuki Sera, Hiroyuki Sasada
2:22 – 2:37

TF04
HIGH RESOLUTION SPECTROSCOPY OF NAPHTHALENE CALIBRATED BY AN OPTICAL FREQUENCY COMB, Akiko Nishiyama, Kazuki Nakashima, Ayumi Matsuha, Masatoshi Misono
2:39 – 2:54

TF05
OPTICAL FREQUENCY COMB FOURIER TRANSFORM SPECTROSCOPIC WITH RESOLUTION EXCEEDING THE LIMIT SET BY THE OPTICAL PATH DIFFERENCE, Aleksandra Foltynowicz, Lucie Rutkowski, Alexander C Johannson, Amir Khodabakhsh, Piotr Maslowski, Grzegorz Kowzan, Kevin Lee, Martin Fernmann
2:56 – 3:11

TF06
POST-DEADLINE ABSTRACT
METROLOGY WITH AN OPTICAL FEEDBACK FREQUENCY STABILIZED CRDS, Sanje Kurki, Johannes Burkari
3:13 – 3:23

INTERMISSION

TF07
INVITED TALK
CAVITY ENHANCED ULTRAFAST TRANSIENT ABSORPTION SPECTROSCOPY, Thomas K Allison, Melanie Roberts, Reber, Yuening Chen
3:42 – 4:12

TF08
NOISE-IMMUNE CAVITY-ENHANCED OPTICAL FREQUENCY COMB SPECTROSCOPY, Lucie Rutkowski, Amir Khodabakhsh, Aleksandra C Johannson, Aleksandra Foltynowicz
4:17 – 4:32

TF09
A NEW BROADBAND CAVITY ENHANCED FREQUENCY COMB SPECTROSCOPIC TECHNIQUE USING GHz VERNIER FILTERING, Stéphanie Merville, Lucie Rutkowski, Georgi Dobrev, Patrick Crouzet
4:34 – 4:49

TF10
A DECADE-SPANNING HIGH-RESOLUTION SYNCHRONOUS OPTICAL SAMPLING BASED TERAHERTZ TIME-DOMAIN SPECTROMETER, Jacob T Good, Daniel Holland, Ian A Finnan, Brandon Carroll, Marco A Allodi, Geoffrey Blake
4:51 – 5:06

TF11
DOPPLER-LIMITED SPECTROSCOPY WITH A DECADE-SPANNING TERAHERTZ FREQUENCY COMB, Ian A Finnan, Jacob T Good, Daniel Holland, Brandon Carroll, Marco A Allodi, Geoffrey Blake
5:08 – 5:23

TF12
DUAL COMB RAMAN SPECTROSCOPY ON CESIUM HYPERFINE TRANSITIONS-TOWARD A STIMULATED RAMAN SPECTRUM ON CF2, MOLECULE, Tie-Wei Liu, Yen-Chu Hsu, Wang-Yau Cheng
5:25 – 5:40

TG. Large amplitude motions, internal rotation
Tuesday, June 23, 2015 – 1:30 PM
Room: 100 Noyes Laboratory
Chair: Kaori Kobayashi, University of Toyama, Toyama, Japan

TG01
THE BAND OF CH3(CHO) FROM 770-880 cm–1, Adam M Daly, Brian Drouin, John Pearson, Peter Groner, Keeyoon Sung, Linda Brown, Arlan Mantz, Mary Ann H Smith
1:30 – 1:45

TG02
LOW-TEMPERATURE HIGH-RESOLUTION INFRARED SPECTRUM OF ETHANE-1D, C2H2D: ROTATIONAL ANALYSIS OF THE 217 BAND NEAR 805 cm–1 using ERHAM, Peter Groner, Adam M Daly, Brian Drouin, John Pearson, Keeyoon Sung, Linda Brown, Arlan Mantz, Mary Ann H Smith
1:47 – 2:02

TG03
MICROWAVE SPECTROSCOPY OF THE EXCITED VIBRATIONAL STATES OF METHANOL, John Pearson, Adam M Daly
2:04 – 2:19

TG04
FIRST HIGH RESOLUTION ANALYSIS OF THE 117 BAND OF PROPANE AT 921.4 cm–1: EVIDENCE OF LARGE-AMPLITUDE-MOTION TUNNELLING EFFECTS, Agnes Perrin, F Kwabia Tchana, Jean-Marie Flaud, Laurent Manceron, Jean Demaison, Natalja Vogt, Peter Groner, Walter Lafferty
2:21 – 2:36

TG05
TORSIONAL STRUCTURE IN THE 491 cm–1 BAND OF PROPANE AT 921.4, Meng Huang, Anne B McCoy, Terry A Miller
2:38 – 2:53

TG06
UPDATE OF THE ANALYSIS OF THE PURE ROTATIONAL SPECTRUM OF EXCITED VIBRATIONS OF CH2(CH2CN)3, Adam M Daly, John Pearson, Shanshan Yu, Brian Drouin, Celina Bermudez, José L Alonso
2:55 – 3:10

INTERMISSION

TG07
UNUSUAL INTERNAL ROTATION COUPLING IN THE MICROWAVE SPECTRUM OF PINACOLONE, Yue Yue Zhao, Ha Vinh Lam Nguyen, Wolfgang Stahl, Jon T Hougen
3:29 – 3:44

TG08
THE COMPLETE ROTATIONAL SPECTRUM OF CH3,NO UP TO 376 GHz, Zbigniew Kisiel, Lucie Kolesnikova, José L Alonso, Ivan Medvedev, Sarah Forman, Manfred Winniewski, Frank C de Lucia
3:46 – 4:01

TG09
GAS PHASE CONFORMATIONS AND METHYL INTERNAL ROTATION FOR 2-PHENYLETHYL METHYL ETHER AND ITS ARGON VAN DER WAALS COMPLEX FROM FOURIER TRANSFORM MICROWAVE SPECTROSCOPY, Rami M Gursangui, Michael Tabergen
4:03 – 4:18

TG10
A COMPARISON OF BARRIER TO METHYL INTERNAL ROTATION OF METHYLSTYRENE: MICROWAVE SPEC-TROSCOPIC STUDY, Rami M Gursangui, Michael Tabergen
4:20 – 4:30

TG11
MICROWAVE SPECTRA AND AB INITIO STUDIES OF THE NE-ACETONE COMPLEX, Jean Gao, Javin Thomas, Yutjie Xu, Wolfgang Jager
4:32 – 4:47

TG12
THE EFFECTS OF INTERNAL ROTATION AND 1/8 QUADRUPOLE COUPLING IN N-METHYLMACETAMIDE, Raphaela Kamminger, Konrad Bibl, Ha Vinh Lam Nguyen, Wolfgang Stahl
4:49 – 5:04

TG13
A NEW HYBRID PROGRAM FOR FITTING ROTATIONALLY RESOLVED SPECTRA OF METHYLAMINE-LIKE MOLECULES: APPLICATION TO 2-METHYLMALONALDEHYDE, Isabelle Kliener, Jon T Hougen
5:06 – 5:21

TG14
DETERMINATION OF TORSIONAL BARRIERS OF ITACONIC ACID AND N-ACETYLETHANOLAMINE USING CHIRPED- PULSED FTMW SPECTROSCOPY, Josuah R Bailey, Timothy J McMahon, Ryan G Bird, David Pratt
5:23 – 5:38
TH. Radicals
Tuesday, June 23, 2015 – 1:30 PM
Room: B102 Chemical and Life Sciences
Chair: Bernadette M. Broderick, University of Georgia, Athens, GA, USA

TH01
Branch Simulation of the Photoelectron Spectrum for Methoxy Radical, Lan Cheng, Marissa L. Weichman, Jongjin B. Kim, Takatoshi Ichino, Daniel Neumark, John F. Stanton
1:30 – 1:45

TH02
Jahn-Teller Coupling in the Methoxy Radical: Insights into the Infrared Spectrum of Molecules with Vibronic Coupling, Breana Johnson, Edwin Sibert
1:47 – 2:02

TH03
Re-Evaluation of HO$_2$ Structure Using Millimeter-Submillimeter Spectroscopy, Lujiao Zou, Brian Hays, Susanna L. Widicus Weaver
2:04 – 2:19

TH04
On the Stark Effect in Open Shell Complexes Exhibiting Partially Quenched Electronic Angular Momentum, Gary E. Douberly, Christopher P. Moradi
2:21 – 2:36

TH05
Infrared Laser Spectroscopy and AB Initio Computations of OH- (D$_2$O), Complexes in Helium Nanodroplets, Joseph T. Brice, Christopher M. Leavitt, Christopher P. Moradi, Gary E. Douberly, Frederico J. Hernandez, Gustavo A Pinto
2:38 – 2:53

TH06
Vibrational-Torsional Coupling Revealed in the Infrared Spectrum of HE-Solvated n-Proply Radical, Christopher P. Moradi, Bernadette M. Broderick, Jay Agarwal, Henry F. Schaefer III., Gary E. Douberly
2:55 – 3:10

TH07
Vibronic Spectroscopy of Hetero Dihalo-Benzyl Radicals Generated by Corona Discharge Ret-Cooled Chlorofluorobenzyl Radicals, Young Yoon, Sang Lee
3:12 – 3:27

TH08
3:29 – 3:44

Intermission

TH09
Analysis of Rotationally Resolved Spectra to Non-Degenerate ($\omega_a'$) Upper-State Vibronic Levels in the $\bar{A}_g'^{-} \rightarrow \bar{X}_g^0$ Electronic Transition of NO$_3$, Mourad Roudjane, Terrance Joseph Codd, Ming-Wei Chen, Henry Tran, Dmitry G. Melnik, Terry A. Miller, John F. Stanton
4:03 – 4:18

TH10
Analysis of Rotationally Resolved Spectra to Degenerate ($\omega_a$') Upper-State Vibronic Levels in the $\bar{A}_g'^{-} \rightarrow \bar{X}_g^0$ Electronic Transition of NO$_3$, Henry Tran, Terry A. Miller
4:20 – 4:35

TH11
Rovibronic Variational Calculations of the Nitrate Radical, Bryan Changala, Joshua H Ratibhan, John F. Stanton
4:37 – 4:52

TH12
Vibronic Structure of the $\tilde{X}_g^0 \tilde{A}_g^0$ State of NO$_3$, Masami Fukushima
4:54 – 5:09

TH13
High-Resolution Laser Spectroscopy of $\tilde{A}_g^0 \tilde{X}_g^0$ Radical: Vibrationally Excited States of the $\tilde{A}_g^0 \tilde{X}_g^0$ State, Robert Tada, Shunji Kasahara, Takatoshi Ichino, Eizi Hirota
5:11 – 5:26

TH14
Structural Characterization of Hydroxyl Radical Adducts in Aqueous Media, Imamjens Jang, G. N. B. TroIPS
5:28 – 5:43

Intermission

TH01
Multiscale Spectroscopy of Diffusing Molecules in Crowded Environments, Ahmed A. Heikal
1:30 – 1:45

TH02
Investigating the Role of Human Serum Albumin on the Excited State Dynamics of Indocyanine Green Using Shaped Femtosecond Laser Pulses, Mouni Nazari, Arkaprabha Konar, Marie Kaniecki, Vadim V. Leozovoy, Marcos Danus
1:47 – 1:57

TH03
Ultrafast Spectroscopic and AB Initio Computational Investigations on Solvent-Induced Dynamics of Neutral and Deprotonated Tyrosine, Takashige Fujimota, Marek Z. Zigurski
1:59 – 2:14

TH04
2:16 – 2:31

TH05
Ultrafast Dynamics in DNA and RNA Derivatives Monitored by Broadband Transient Absorption Spectroscopy, Matthew M. Bisson, Carlos E. Crespo-Hernández
2:33 – 2:48

TH06
Can Femtosecond Transient Absorption Spectroscopy Predict the Potential of Small Molecules as Perspective Donors for Organic Photovoltaics?, Regina DiScipio, Genevieve Suere, Carlos E. Crespo-Hernández
2:50 – 3:05

TH07
Molecule-Like Case Nanoclusters Passivated with Strongly Interacting Ligands: Energy Level Alignment and Photoinduced Ultrafast Charge Transfer Processes, Yizhou Xie, Meghan B Trumis, Bill Pandit, Rashdeh Sarhad, Jiajun Liu
3:07 – 3:22

TH08
3:24 – 3:39

TH09
Ultrafast Terahertz Kerr Effect Spectroscopy of Liquids and Binary Mixtures, Marco A. Allday, Ian A. Pineram, Geoffrey Blake
3:58 – 4:13

TH10
Ultrafast Terahertz Kerr Effect Spectroscopy of Aromatic Liquids, Ian A. Pineram, Marco A. Allday, Geoffrey Blake
4:15 – 4:30

TH11
Vibrationally-Resolved Kinetic Isotope Effects in the Photo-Transfer Dynamics of Ground-State Tropolone, Kathryn Czer, Zachary Veresky, Patrick Vaccaro
4:32 – 4:47

TH12
Characterization of CB1/CB2 Photolysis by Velocity Map Imaging, W. G. Merrif, Amanda Caste, Benjamin C. Huang, Robert J. Maloney, Fleming Cram
4:49 – 5:04

TH13
Reversibility of InterSystem Crossing in the $\tilde{a}_g$ (000) and $\tilde{a}_g$ (010) States of Methylene, CH$_2$, Ash T. Le, Trevor Sears, Gregory Hall
5:06 – 5:21

TH14
Efficient Super Energy Transfer Collisions through Reactive-Complex Formation: H + SO$_2$, Jonathan M. Smith, Michael J. Wilhelm, Jianping Mu, HAI-LUNG Dai
5:23 – 5:38

TH15
Fourth-Order Vibrational Transition State Theory and Chemical Kinetics, John F. Stanton
5:40 – 5:55
TJ. Rydberg Atoms and Molecules
Tuesday, June 23, 2015 – 1:30 PM
Room: 217 Noyes Laboratory
Chair: Brian DeMarco, University of Illinois, Urbana, IL, USA

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TJ01 T. J. Rydberg Atoms and Molecules 1:30 – 1:45
PRECISION SPECTROSCOPY IN COLD MOLECULES: THE FIRST ROTATIONAL INTERVALS OF He$^+_3$ BY HIGH-RESOLUTION SPECTROSCOPY AND RYDBERG-SERIES EXTRAPOLATION, Paul Jansen, Luca Semeria, Simon Schneidgger, Frederic Merkt

TJ02 1:45 – 2:00
MICROWAVE SPECTROSCOPY OF THE CALCIUM 4enf → 4(n+1)d, 4enp, 4exh, 4exr, AND 4enk TRANSITIONS, Jirikan Nunkaw, Tom Gallagher

TJ03 2:00 – 2:14
PHASE DEPENDENCE IN ABOVE THRESHOLD IONIZATION IN THE PRESENCE OF A MICROWAVE FIELD, Vincent Castiglione, Eric Magnussen, Tom Gallagher

TJ04 2:14 – 2:26
MICROWAVE TRANSITIONS BETWEEN PAIR STATES COMPOSED OF TWO Rb RYDBERG ATOMS, Jonathan Lee, Tom Gallagher

TJ05 2:26 – 2:43
HIGH-RESOLUTION SPECTROSCOPY OF LONG-RANGE MOLECULAR STATES OF $^{85}$Rb$_2$, Ryan Coello, Edward E. Ely, Yoann Bruneau, Philipp Gould, W.C. Stwalley

TJ06 2:43 – 3:00
DOUBLE RESONANCE SPECTROSCOPY OF BaF AUTORIZATION RYDBERG STATES, Timothy J Barnum, David Grimes, Yan Zhou, Robert W Field

TJ07 3:00 – 3:17
MILLIMETER WAVE SPECTROSCOPY OF RYDBERG STATES OF MOLECULES IN THE REGION OF 260-295 GHz, David Grimes, Yan Zhou, Robert W Field, Bryan M. Wong

Intermission
3:17 – 3:36
3:36 – 3:51
3:51 – 3:55

TJ08 3:55 – 4:08
EFFECTIVE IN-ION-MOLECULE POTENTIALS FOR NON-PENETRATING RYDBERG STATES OF POLAR MOLECULES, Stephen Coy, David Grimes, Yan Zhou, Robert W Field, Bryan M. Wong

TJ09 4:08 – 4:25
ELECTRONIC STRUCTURE OF THE X $1 \Sigma^+$ ION CORE OF CaF RYDBERG STATES, Stephen Coy, Joshua H Baraban, David Grimes, Timothy J Barnum, Robert W Field, Bryan M. Wong

TJ10 4:25 – 4:42
SYSTEMATICS OF RYDBERG SERIES OF DIATOMIC MOLECULES AND CORRELATION DIAGRAMS, Chon-Woo Lee

TJ11 4:42 – 4:50
OBSERVATION OF CS TRILOBITE MOLECULES WITH KOLO-DEBYE MOLECULAR FRAME PERMANENT ELECTRIC DIPOLE MOMENTS, James P. Shaffer

TJ12 4:50 – 4:59
MOLECULE FORMATION AND STATE-CHANGING COLLISIONS OF SINGLE RYDBERG ATOMS IN A BIC, Kathrin Sophie Kleinbach, Michael Schlagmüller, Tara Cebul Leibisch, Karl Magnus Westphal, Fabian Böttcher, Robert Fröhlich, Sebastian Hofferberth, Tilman Pfau, Jesús Pfeifer-Ríos, C. H. Greene

TJ13 4:59 – 5:16
RYDBERG, VALENCE AND ION-PAIR QUINTESET STATES OF O$_3$, Gabriel J. Vaquez, Hans P. Liebermann, H. Lelebre-Brion

TJ14 5:16 – 5:33

Post-Deadline Abstract 5:01 – 5:16
RYDBERG, VALENCE AND ION-PAIR QUINTESET STATES OF O$_3$, Gabriel J. Vaquez, Hans P. Liebermann, H. Lelebre-Brion

Post-Deadline Abstract 5:18 – 5:33

Chair: Leslie Looney, University of Illinois, Urbana, IL, USA

WA. Plenary
Wednesday, June 24, 2015 – 8:30 AM
Room: Foellinger Auditorium

RAO AWARDS
8:30
Presentation of Awards by Yanjie Xu, University of Alberta

2014 Rao Award Winners

2014 Rao Award Winners
Grant Buckingham, University of Colorado
Kathryn Chew, Yale University
Yu-Hsuan Huang, National Chiao Tung University

MILLER PRIZE
8:40
Introduction by Mike Heaven, Emory University

WA01 8:45 – 9:00
INFRARED LASER STARK SPECTROSCOPY OF THE OH· CH·OH COMPLEX ISOLATED IN SUPERFLUID HELIUM DROPLETS, Christopher M. Leavitt, Joseph T. Brice, Gary E. Douberly, Federico J Hernandez, Gustavo A Pino

FLYGARE AWARDS
9:05
Introduction by Trevor Sears, Brookhaven National Laboratory

WA02 9:10 – 9:25
WHAT CAN WE EXPECT OF HIGH-RESOLUTION SPECTROSCOPES ON CARBOHYDRATES?, Emilio J. Cocinero, Patricia Erciga, Kiara Uriarte, Imanol Usabiaga, José A. Fernández, Francisco J. Basterretxea, Alberto Lesarri, Benjamin G. Davis

WA03 9:30 – 9:45
CONSTRUCTION OF POTENTIAL ENERGY SURFACES FOR THEORETICAL STUDIES OF SPECTROSCOPY AND DYNAMICS, Richard Dawes

Intermission
9:45 – 10:05
10:05 – 10:20
10:20 – 10:35

WA04 10:35 – 10:50
MILLIMETER AND SUBMILLIMETER STUDIES OF O(1D) INSERTION REACTIONS TO FORM MOLECULES OF ASTROPHYSICAL INTEREST, Brian Hays, Nadine Wehres, Bridget Allgood Deprince, Althea A. M. Roy, Jacob Laszlo, Susanna L. Wedeen-Mutter

WA05 10:55 – 11:10
TERAHertz AND INFRARED LABORATORY SPECTROSCOPY IN SUPPORT OF NASA MISSIONS, Shanshan Yu

Coblentz Award
11:15
Presentation of Award by Mark Dray, Coblentz Society

WA06 11:20 – 12:00
LASER SPECTROSCOPY OF RADICALS, CARBENES, AND IONS IN SUPERFLUID HELIUM DROPLETS, Gary E. Douberly
WF. Mini-symposium: High-Precision Spectroscopy
Wednesday, June 24, 2015 – 1:30 PM
Room: 116 Roger Adams Lab
Chair: Kevin Cossel, JILA - University of Colorado, Boulder, CO, USA

WF01
ULTRASENSITIVE, HIGH ACCURACY MEASUREMENTS OF TRACE GAS SPECIES, David A. Long, Adam J. Fleisher, David P. Plusquellic, Joseph Hodges
1:30 – 2:00

WF02
PROBING BUFFER-GAS COOLED MOLECULES WITH DIRECT FREQUENCY COMB SPECTROSCOPY IN THE MID-INFRARED, Ben Spaun, Bryan Changala, Bryce J Bjork, Oliver H Heckl, David Patterson, John M. Doyle, Jan Ye
2:05 – 2:20

WF03
FREQUENCY-AGILE DIFFERENTIAL CAVITY RING-DOWN SPECTROSCOPY, Zachary Reed, Joseph Hodges
2:22 – 2:37

WF04
QUANTUM-NOISE-LIMITED CAVITY RING-DOWN SPECTROSCOPY IN THE MID-INFRARED, Adam J. Fleisher, David A. Long, Qianjun Liu, Joseph Hodges
2:39 – 2:54

WF05
MOLECULAR LINE PARAMETERS PRECISELY DETERMINED BY A CAVITY RING-DOWN SPECTROMETER, Shui-Ming Hu
2:56 – 3:11

WF06
BROADBAND COMB-RESOLVED CAVITY ENHANCED SPECTROMETER WITH GRAPHENE MODULATOR, Kevin Lee, Christian Moehr, Jie Jiang, Martin Fermann, Chien-Chung Lee, Thomas R Schibli, Gregzorz Kowzan, Piotr Malowski
3:13 – 3:23

Intermission

WF07
ULTRASENSITIVE, HIGH ACCURACY MEASUREMENTS OF TRACE GAS SPECIES, David A. Long, Adam J. Fleisher, David P. Plusquellic, Joseph Hodges
3:42 – 4:12

WF08
LOCAL PERTURBATIONS IN THE (10108) AND (10109) LEVELS OF C2H2 FROM FREQUENCY COMB-COMBINED SPECTROSCOPY, Trevor Sears, Sylvester Tzyganayeva, Damien Forthomme, Gregory Hall, Matthew Cich
4:17 – 4:32

WF09
NOISE-IMMUNE CAVITY-ENHANCED OPTICAL HETERODYNE MOLECULAR SPECTROMETRY MEASURING SATURATED ABSORPTION, Patrick Dupuy
4:34 – 4:49

WF10
5:00 – 5:23

WF11
SPIN-ROTATION HYPERFINE SPLITTINGS AT MODERATE TO HIGH J VALUES IN METHANOL, LiHong Xu, Jin T. Hougen, Sergey Belov, G Yu GOLUMBATNIKOVA, Alexander Lapinov, V. Byushin, E. A. Aiken, A. A. MEDNICH
5:25 – 5:40

Intermission

WF01
INVITED TALK
ULTRASENSITIVE, HIGH ACCURACY MEASUREMENTS OF TRACE GAS SPECIES, David A. Long, Adam J. Fleisher, David P. Plusquellic, Joseph Hodges
1:30 – 2:00

WF02
INVITED TALK
PROBING BUFFER-GAS COOLED MOLECULES WITH DIRECT FREQUENCY COMB SPECTROSCOPY IN THE MID-INFRARED, Ben Spaun, Bryan Changala, Bryce J Bjork, Oliver H Heckl, David Patterson, John M. Doyle, Jan Ye
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WF03
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2:22 – 2:37

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2:56 – 3:11

WF06
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BROADBAND COMB-RESOLVED CAVITY ENHANCED SPECTROMETER WITH GRAPHENE MODULATOR, Kevin Lee, Christian Moehr, Jie Jiang, Martin Fermann, Chien-Chung Lee, Thomas R Schibli, Gregzorz Kowzan, Piotr Malowski
3:13 – 3:23

WG1
FINGERPRINTS OF INTRAMOLECULAR HYDROGEN BONDS: SYNCHROTRON-BASED FAR IR STUDY OF THE FORBIDDEN TRANSITIONS IN THE VUV SPECTRUM OF 2
5
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STATES OF THIIRANE, Corey Evans, Alan Heays
4:33 – 4:48

WG2
FAR-IR ACTION SPECTROSCOPY OF AMINOPHENOL AND ETHYLVANILLIN: EXPERIMENT AND THEORY, Vasyl Yatsyna, Raimund Felfel, Vitali Zhamenchykh, Daniel Bakker, Anouk Rijks
4:49 – 5:04

WG3
NONDOPED EFFECTS IN CHIRAL SYSTEMS MEASURED WITH LINEARLY POLARIZED LIGHT, K P Bowen, Timothy O’Hagan, Kevin P. Jones, Kevin P. Jones, Michael A MacDonald
5:05 – 5:20

WG4
MINI-SYMPOSIUM: Accelarator-Based Spectroscopy
Wednesday, June 24, 2015 – 1:30 PM
Room: 100 Noyes Laboratory
Chair: J. Oomens, Radboud University, Nijmegen, The Netherlands

WG01
INVITED TALK
INFRARED SPECTROSCOPY ON PEPTIDES AND PROTEINS AFTER ION MOBILITY SELECTION AND IN LIQUID HELIUM DROPLETS, Gert van der Velden
1:30 – 2:00

WG02
2:05 – 2:20

WG03
FAR-IR ACTION SPECTROSCOPY OF AMINOPHENOL AND ETHYLVANILLIN: EXPERIMENT AND THEORY, Vasyl Yatsyna, Raimund Felfel, Vitali Zhamenchykh, Daniel Bakker, Anouk Rijks
2:22 – 2:37

WG04
OPPORTUNITIES FOR GAS-PHASE MOLECULAR SPECTROSCOPY ON THE VLS-PGM BEAMLINE AT THE CANADIAN LIGHT SOURCE, Michael A MacDonald
2:39 – 2:54

WG05
THERMAL DECOMPOSITION OF C-HG RADICALS: BENZYL, TROPYL, AND NORBORNADIENYL, Grant Buckingham, Barney Ellison, John W Daily, Masahid Ahmed
2:56 – 3:11

Intermission

WG06
NONDOPED EFFECTS IN CHIRAL SYSTEMS MEASURED WITH LINEARLY POLARIZED LIGHT, K P Bowen, Timothy O’Hagan, Kevin P. Jones, Michael A MacDonald
3:30 – 3:40

WG07
APPLICATIONS OF THE VUV FOURIER TRANSFORM SPECTROMETER AT SYNCHROTRON SOLEIL, William T. Borden, Brenton R Lewis, Wim Uchachs, Ewine van Dishoeck
3:42 – 3:57

WG08
FOREIGN TRANSITIONS IN THE VUV SPECTRUM OF N5, Alan Hoyez, Ming Li Niu, Nelson de Oliveira, Edeki John Sulambredes, Brendon R Lewis, Wim Uchachs, Ewine van Dishoeck
3:59 – 4:14

WG09
SYNCHROTRON INFRARED SPECTROSCOPY OF ν1, ν2, ν3, AND ν4 STATES OF THIRANE, Corey Evans, Jason P Carter, Don McNaughton, Andy Wong, Dominique Appadoo
4:16 – 4:31

WG10
FINGERPRINTS OF INTRAMOLECULAR HYDROGEN BONDS: SYNCHROTRON-BASED FAR IR STUDY OF THE C IS AND TRANS CONFORMERS OF 2
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HOT BANDS IN THE ν
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STATES OF THIIRANE, Corey Evans, Alan Heays
4:33 – 4:48

WG11
INFRARED CROSS-SECTIONS OF NITRO-DERIVATIVE VAPORS: NEW SPECTROSCOPIC SIGNATURES OF EXPLSIVE EFFECTS IN CHIRAL SYSTEMS MEASURED WITH LINEARLY POLARIZED LIGHT, K P Bowen, Timothy O’Hagan, Kevin P. Jones, Michael A MacDonald
4:49 – 5:04

WG12
CHARACTERIZATION OF REACTION PATHWAYS IN LOW TEMPERATURE OXIDATION OF TETRAHYDROFURAN WITH MULTIPLEXED PHOTOFONIZATION MASS SPECTROMETRY TECHNIQUE, Ivan Antunov, Leonid Sheps
WH. Clusters/Complexes
Wednesday, June 24, 2015 – 1:30 PM
Room: B102 Chemical and Life Sciences

Chair: Elangannan Arunan, Indian Institute of Science, Bangalore, India

W101
A STRANGE COMBINATION BAND OF THE CROSS-SHAPED COMPLEX CO\(_3\)-CS\(_2\), Naser Mosazadeh-Abimadil, Bob McKellar
1:30 – 1:45

W102
RE-ANALYSIS OF THE DISPERSED FLUORESCENCE SPECTRA OF THE C\(_3\)-RARE GAS ATOM COMPLEXES, Yi-Jen Wang, Anthony Mero, Yin-Chin Hsu
1:47 – 2:02

W103
INFRARED SPECTROSCOPY OF Mn(CO\(_3\))\(_2\) CLUSTER ANIONS, Michael C Thompson, J Mathias Weber
2:04 – 2:19

W104
INFRARED SPECTROSCOPY OF (N\(_2\)O\(_3\))\(_2\) AND (N\(_2\)O\(_3\))O - CLUSTER ANIONS, Michael C Thompson, J Mathias Weber
2:21 – 2:36

W105
INFRARED SPECTROSCOPY OF PHENOL*-TETRAETHYLSILANE DIHYDROGEN-BONDED CLUSTER: INTRINSIC STRENGTH OF THE Si-H - H-O DIHYDROGEN BOND, Haruki Ishikawa, Takayuki Kawasaki, Risa Inomata
2:38 – 2:53

W106
INFRARED SPECTROSCOPY OF HYDROGEN-BONDED CLUSTERS OF PROTONATED HISTIDINE, Makato Kouda, Yasutoshi Kasahara, Haruki Ishikawa
2:55 – 3:10

W107
THEORETICAL INVESTIGATION OF THE UV/VIS PHOTODISSOCIATION DYNAMICS OF ICN\(^-\) (Ar)\(_m\), and BrCN (Ar)\(_m\), Hennie Opoku-Agyeman, Anne B McCoy
3:12 – 3:27

W108
DISPERSION-DOMINATED T-STACKED COMPLEXES CONSTRUCTED ON A DYNAMIC SCAFFOLD, Dragon Nephthys, Michael Cohen, Patrick Vaccaro
3:29 – 3:44

Intermission

W109
THE COMPETITION BETWEEN INSERTION AND SURFACE BINDING OF BENZENE TO THE WATER HEPTAMER, Patrick S. Walsh, Daniel P. Tabor, Edwin Silbert, Timothy S. Zivier
4:03 – 4:18

W110
VIBRATIONAL SPECTROSCOPY OF BENZENE-WATER\(_n\), CLUSTERS WITH N = 6, 7, Daniel P. Tabor, Edwin Silbert, Royji Kusaka, Patrick S. Walsh, Timothy S. Zivier
4:20 – 4:35

W111
THEORETICAL STUDY OF THE IR SPECTROSCOPY OF BENZENE-WATER\(_n\), CLUSTERS, Daniel P. Tabor, Edwin Silbert, Royji Kusaka, Patrick S. Walsh, Timothy S. Zivier
4:37 – 4:52

W112
SPECIFIC SPECTROSCOPIC INVESTIGATION OF TEMPERATURE EFFECTS ON THE HYDRATION STRUCTURE OF THE PHENOL CLUSTER CATION, Reona Yagi, Yasutoshi Kasahara, Haruki Ishikawa
4:54 – 5:09

W113
ULTRAVIOLET AND INFRARED PHOTOASSOCIATION SPECTROSCOPY OF HYDRATED ANILINUM ION, Ikuma Kasum, Reona Yagi, Yasutoshi Kasahara, Haruki Ishikawa
5:11 – 5:26

W114
WATER-NETWORK MEDIATED, ELECTRON INDUCED PROTON TRANSFER IN ANIONIC [C\(_2\)H\(_7\)N\((\text{H}_2\text{O})_n\)]\(^-\) CLUSTERS: SIZE-DEPENDENT FORMATION OF THE PYRIDINIUM RADICAL FOR n ≥ 3, Andrew F DeBlase, Gary H Weddle, Kaye A Archer, Kenneth D. Jordan, Mark Johnson
5:28 – 5:43
WJ. Non-covalent interactions
Wednesday, June 24, 2015 – 1:30 PM
Room: 217 Noyes Laboratory
Chair: Wolfgang Jager, University of Alberta, Edmonton, AB, Canada

1:30 – 1:45
WJ01 FORMATION OF COMPLEXES c-C₅H₆, MCl (M = Ag or Cu) AND THEIR CHARACTERIZATION BY BROADBAND ROTATIONAL SPECTROSCOPY, Daniel P. Zaleski, John Connor Mullane, Nick Walker, Anthony Legon

1:47 – 2:02
WJ02 ROTATIONAL SPECTROSCOPY OF MONOFLUORODETHANE, AGGREGATES WITH ITSELF AND WITH WATER, Jovis Thomas, Wenyuan Huang, Xunchen Liu, Wolfgang Jager, Yunjie Xu

2:04 – 2:19
WJ03 O-TOLUIC ACID MONOMER AND MONOHYDRATE: ROTATIONAL SPECTRA, STRUCTURES, AND ATMOSPHERIC IMPLICATIONS, Elijah O Schindler, Brandon L M Cox, JungSoo Kim, Peter Armentrout, Joshua Bartlett, Robert A. VanGundy, Michael Heaven

2:11 – 2:26

2:28 – 2:53
WJ05 THE MICROWAVE SPECTRUM AND UNEXPECTED STRUCTURE OF THE BIMOLECULAR COMPLEX FORMED BETWEEN ACETYLENE AND (Z)-1-CHLORO-2-FLUOROETHYLENE, Nazir D. Khan, Helen O. Leung, Mark D. Marshall

2:55 – 3:10
WJ06 CHLORINE NUCLEAR QUADRUPOLE HYPERFINE STRUCTURE IN THE VINYL CHLORIDE-HYDROGEN CHLORIDE COMPLEX, Helen O. Leung, Mark D. Marshall, Joseph P. Messinger

3:12 – 3:27
WJ07 ELECTRONIC COMMUNICATION IN COVALENTLY vs. NON-COVALENTLY BONDED POLYFLUORENE SYSTEMS: THE ROLE OF THE COVALENT LINKER, Brandon Ulrich, Neil J Reilly, Marat R Talipov, Maxim Ivanov, Qadir Timurghazin, Rajendra Rathore, Scott Reid

Intermission

3:46 – 4:01
WJ08 A GENERAL TRANSFORMATION TO CANONICAL FORM FOR POTENTIALS IN PARWISE INTERMOLECULAR INTERACTIONS, Jay R. Walton, Luis A. Rivera-Rivera, Robert R. Lucchese, John W. Breyan

4:03 – 4:18
WJ09 THREE-DIMENSIONAL WATER NETWORKS SOLVATING AN EXCESS POSITIVE CHARGE: NEW INSIGHTS INTO THE MOLECULAR PHYSICS OF ION HYDRATION, Conrad T. Wolfe, Joseph Foumière, Gary H. Weddell, Evangelos Milliordos, Sotiris Xanthas, Mark Johnson

4:20 – 4:35
WJ10 MATRIX ISOLATION INFRARED SPECTROSCOPY OF A SERIES OF 1:1 PHENOL-WATER COMPLEXES, Pujariini Banerjee, Tapas Chakraborty

4:37 – 4:52
WJ11 MATRIX ISOLATION IR SPECTROSCOPY AND QUANTUM CHEMISTRY STUDY OF 1:1 HYDROGEN BONDED COMPLEXES OF BENZENE WITH A SERIES OF FLUOROPHENOLS, Pujariini Banerjee, Tapas Chakraborty

4:54 – 5:09
WJ12 MATRIX ISOLATION IR SPECTROSCOPY OF 1:1 COMPLEXES OF ACETIC ACID AND TRIHALOACETIC ACIDS WITH WATER AND BENZENE, Pujariini Banerjee, Tapas Chakraborty

5:11 – 5:21
WJ13 SPECTROSCOPIC INVESTIGATION OF THE EFFECTS OF ENVIRONMENT ON NEWLY-DEVELOPED NEAR INFRARED EMITTING DYES, Laura E. McIntyre, Nikola Ljubanac, Jared Delcamp, Nathan J Hammert

5:23 – 5:38
WJ14 SPECTROSCOPIC SIGNATURES AND STRUCTURAL MOTIFS IN ISOLATED AND HYDRATED XANTHINE AND ITS METHYLATED DERIVATIVES, Vipin Bahadur Singh

2:21 – 2:36
WJ04

1.30 – 1.45
WJ01

2:28 – 2:53
WJ05

3:46 – 4:01
WJ08

4:20 – 4:35
WJ10

5:23 – 5:38
WJ14
RB. Mini-symposium: Accelerator-Based Spectroscopy
Thursday, June 25, 2015 – 8:30 AM
Room: 100 Noyes Laboratory
Chair: Gert von Helden, Fritz Haber Institute - MPG, Berlin, Germany

RB01
INVITED TALK
8:30 – 9:00
PROBING INTRA- AND INTER- MOLECULAR INTERACTIONS VIA BMRP EXPERIMENTS AND COMPUTATIONAL CHEMISTRY, Scott Hopkins, Terry McMahon

RB02
8:45 – 9:00
EXPLORING CONFORMATION SELECTIVE FAR INFRARED ACTION SPECTROSCOPY OF ISOLATED MOLECULES AND SOLVATED CLUSTERS, Daniel Bakker, Anouk Rijts, Jérôme Malé, Marie-Pierre Gaigett

RB03
9:05 – 9:20
FIRST INFRARED PredisSOCIATION SPECTRA OF Hz-TAGGED PROTONATED PRIMARY ALCOHOLS AT 4 K, Alexander Shokhiev, Britta Redlich, J. Oomens, Oskar Aviny, Sandra Brinken, Pavel Jusko, Sven Thörsen, Stephan Schlömann

RB04
9:25 – 9:40
METAL ION INDUCED PAIRING OF CYTOSINE BASES: FORMATION OF 4-MOTIF STRUCTURES IDENTIFIED BY IR ION SPECTROSCOPY, Juehan Gao, Giel Berden, J. Oomens

RB05
9:45 – 10:00
MOLECULAR PROPERTIES OF THE “ANTI-AROMATIC” SPECIES CYCLOPENTADIENONE, C, H,=0, Thomas Ormond, Barry Ellison, John W Daily, John F Stanton, Musahid Ahmed, Timothy S. Zwier, Patrick Hemberger

Intermission
10:25 – 10:40

RB06
HIGH-RESOLUTION SYNCHROTRON INFRARED SPECTROSCOPY OF THIOPHOSGENE: THE ν, 2ν, and ν bands, Bob McKellar, Brant E Billingshurst

RB07
10:45 – 10:57
THE SOLEIL VIEW ON SULFUR RICH OXIDES: THE S, O BENDING MODE ν2 AT 380 cm⁻¹ AND ITS ANALYSIS USING AN AUTOMATED SPECTRAL ASSIGNMENT PROCEDURE (ASAP), Marie-Aline Martin-Druilard, Christian Endres, Oliver Zingheim, T. Salomon, Jennifer van Wijngaarden, Olivier Pirlal, Sebastian Gruet, Frank Lewen, Stephan Schlemmer, Michael C McCarthy, Sven Thörsen

RB08
10:57 – 11:14
THE SOLEIL VIEW ON SULFUR RICH OXIDES: THE 2ν MODE OF S2O REVISITED, Sven Thörsen, Marie-Aline Martin-Druilard, Christian Endres, Oliver Zingheim, T. Salomon, Jennifer van Wijngaarden, Olivier Pirlal, Sebastian Gruet, Frank Lewen, Stephan Schlemmer, Michael C McCarthy

RB09
11:14 – 11:31
FT-IR MEASUREMENTS OF NH, LIVE INTENSITIES IN THE 60 – 550 CM⁻¹ USING SOLEIL/AILES BEAMLINE, Keryon Sung, Shanshan Yu, John Pearson, Laurent Manceron, F. Kwabia Tchana, Olivier Pirlal

RB10
Post-Deadline Abstract
11:33 – 11:48
NEW INSTRUMENTAL TOOLS FOR ADVANCED ASTROCHEMICAL APPLICATIONS
Amanda Stehr, Sabrina Zinn, Melanie Schnell, Anouk Rjis
8:30 – 8:40

DOPPLER AND SUB-DOPPLER MILLIMETER AND SUB-MILLIMETER WAVE SPECTROSCOPY OF KEY ASTROCHEMICAL MOLECULES
HNC AND CS, Oliver Zingsche, Thomas Schmitt, Frank Lewen, Stephan Schlemmer, Sven Thorwirth
8:42 – 8:57

MILLIMETRE-WAVE SPECTRUM OF ISOTOPOLOGUES OF ETHANOL FOR RADIO ASTRONOMY
Adam Walter, Mirko Schäfer, Matthias H. Ordu, Frank Lewen, Stephan Schlemmer, Helger S. P. Müller
8:59 – 9:14

TERRAHERTZ SPECTROSCOPY OF DEUTERATED METHYLENE BI-RADICAL, CD2
Hiroyuki Oshiki, Frédéric Studer, Marie-Aline Martin-Drumel, Sven Thorwirth
9:16 – 9:31

TERAHERTZ SPECTROSCOPY OF DEUTERATED METHYLENE BI-RADICAL, CD2
Mirko Schäfer, Matthias H. Ordu, Frank Lewen, Stephan Schlemmer, Holger S. P. Müller
9:33 – 9:48

THz SPECTROSCOPY OF D3H+, Shanshan Yu, John Pearson, Takayoshi Amano
9:50 – 10:05

THz SPECTROSCOPY OF 12CH3, 13CH3, AND 12CD3, Shanshan Yu, Brian Drouin, John Pearson, Takayoshi Amano
10:07 – 10:22

ROTATIONAL SPECTROSCOPY OF VIBRATIONALLY EXCITED N2H+ AND N2D+ UP TO 2 THz. Shanshan Yu, John Pearson, Brian Drouin, Timothy J Crawford, Adam M Daly, Ben Elliott, Takayoshi Amano
10:29 – 10:44

Intermission

NEW ACCURATE WAVE NUMBERS OF H12C1+ AND H13C1+ ROVIBRATIONAL TRANSITIONS IN THE v = 0 – 1 BAND OF THE II1 STATE. Jose Luis Domenech, Maite Cueno, Victor Jose Herrera, Isabel Tamaro, Jose Cernicharo
10:41 – 10:56

10:58 – 11:13

LINE STRENGTHS OF ROVIBRATIONAL AND ROTATIONAL TRANSITIONS IN THE X1Π GROUND STATE OF OH, James S.A. Brooke, Peter F. Bernard, Colin Western, Chris Sneed, Gan Li, Iouli E Gordon
11:15 – 11:30

Post-Deadline Abstract
CLASS I METHANOL MASER CONDITIONS NEAR SNRS, Bridget C. McEwen, Yvha M. Páldiömm, Lorán O. Szumem- erman
11:32 – 11:42

Post-Deadline Abstract
THE MISSING LINK: ROTATIONAL SPECTRUM AND GEOMETRICAL STRUCTURE OF DISILICON CARBIDE, Si2C, Michael C McCarthy, Joshua H Baraban, Bryan Changala, John F. Stanton, Marie-Aline Martin-Drumel, Sven Thorwirth, Neel J. Reilly, Carl A. Gottlieb
11:44 – 11:59

RE. Instrument/Technique Demonstration
Thursday, June 25, 2015 – 8:30 AM
Room: 217 Noyes Laboratory
Chair: Arthur Suits, Wayne State University, Detroit, MI, USA
8:30 – 8:45

OPTIMIZATION OF EXTREME ULTRAVIOLET LIGHT SOURCE FROM HIGH HARMONIC GENERATION FOR CONDENSED-PHASE CORE-LEVEL SPECTROSCOPY. Ming-Fu Liu, Max A. Verkamp, Elizabeth S Ryland, Kristin Bente, Kaif Zhang, Michaela Carlson, Josh Vura-Weis
8:47 – 9:02

DEVELOPMENT OF TWO-PHOTON PUMP POLARIZATION SPECTROSCOPY PROBE TECHNIQUE (TPP-PSP) FOR MEASUREMENTS OF ATOMIC HYDROGEN. Aman Saini, Robert P. Lucht
9:04 – 9:19

DEVELOPMENT OF COMBINED DUAL-PUMP VIBRATIONAL AND PURE-ROTATIONAL COHERENT ANTI-STOKES RAMAN SCATTERING TECHNIQUE. Aman Saini, Robert P. Lucht
9:21 – 9:36

VELOCITY MAP IMAGING STUDY OF THE PHOTONI TIZED CHARGE TRANSFER DISSOCIATION OF Cu+(C2H3+) AND Ag+(C3H5+), Jon Maner, Daniel Munney, Michael A Duncan
9:38 – 9:53

Intermission

MID-IR CAVITY RINGDOWN SPECTROSCOPY FOR ATMOSPHERIC ETHANE ABUNDANCE MEASUREMENTS, Lihua Shen, Thinh Quoc Bui, Lance Christiansen, Mitchio Okumura
9:55 – 10:10

STRONG THERMAL NONEQUILIBRIUM IN HYPERSONIC CO AND CH, PROBED BY CRDS, Maud Levasseur, Nicolas Suas-David, Vincent Bourdon, Robert Georges, Michael Key, Samir Kassi
10:12 – 10:27

IMPROVING SNR IN TIME-RESOLVED SPECTROSCOPES WITHOUT SACRIFICING TEMPORAL-RESOLUTION: APPLICATION TO THE UV PHOTOLYSIS OF METHYL CYANOFORMATE, Michael J. Wilhelm
10:29 – 10:44

ROVIBRATIONAL RESOLVED INFRARED SPECTROSCOPY OF THE 2ν3 BAND OF 1,3,5-TRIOXANE, Bradley M. Gibson, Nicole Koeppen, Jonathan M. Smith, Hai-Lung Dai
10:46 – 11:01

IMPROVING SNR IN TIME-RESOLVED SPECTROSCOPES WITHOUT SACRIFICING TEMPORAL-RESOLUTION: APPLICATION TO THE UV PHOTOLYSIS OF METHYL CYANOFORMATE. Michael J. Wilhelm, Jonathan M. Smith, Hai-Lung Dai
11:03 – 11:18

LASER-INDUCED PLASMAS IN AMBIENT AIR FOR INCOHERENT BROADBAND CAVITY-ENHANCED ABSORPTION SPECTROSCOPY, Albert A Ruth, Sophie Duxef, Johannes Orphal
11:20 – 11:35

Intermission

11:37 – 11:52

NEW ACCURATE NUMBERS OF 12H12C1+ AND 13H12C1+ ROVIBRATIONAL TRANSITIONS IN THE v = 0 – 1 BAND OF THE II1 STATE. Jose Luis Domenech, Maite Cueno, Victor Jose Herrera, Isabel Tamaro, Jose Cernicharo
11:54 – 12:09

NEW ACCURATE NUMBERS OF 12H12C1+ AND 13H12C1+ ROVIBRATIONAL TRANSITIONS IN THE v = 0 – 1 BAND OF THE II1 STATE. Jose Luis Domenech, Maite Cueno, Victor Jose Herrera, Isabel Tamaro, Jose Cernicharo
12:11 – 12:26

NEW ACCURATE NUMBERS OF 12H12C1+ AND 13H12C1+ ROVIBRATIONAL TRANSITIONS IN THE v = 0 – 1 BAND OF THE II1 STATE. Jose Luis Domenech, Maite Cueno, Victor Jose Herrera, Isabel Tamaro, Jose Cernicharo
12:28 – 12:43
RF. Atmospheric science
Thursday, June 25, 2015 – 1:30 PM
Room: 116 Roger Adams Lab
Chair: Joseph Hodges, National Institute of Standards and Technology, Gaithersburg, MD, USA

RF01 PHOTOACOUSTIC SPECTROSCOPY OF THE OXYGEN A-BAND, Elizabeth M Lunay, Thinh Quoc Bai, Caitlin Bray, Priyanka Rupasinghe, Mitchio Okumura
1:30 – 1:40

RF02 HIGH PRESSURE OXYGEN A-BAND SPECTRA, Brian Drouin, Kreyoon Sung, Shanshan Yu, Elizabeth M Lunay, Thinh Quoc Bai, Mitchio Okumura, Priyanka Rupasinghe, Caitlin Bray, David A. Long, Joseph Hodges, David Robichaud, D. Chris Benner, V. Malathy Devi, Tijuan Hoo
1:42 – 1:57

RF03 COLLISION-DEPENDENT LINE AREAS IN THE $a^1 \Delta_g \rightarrow X^3 \Sigma_g^+$ BAND OF MOLECULAR OXYGEN, Vincent Siron-areas, Adam J. Fleischauer, Joseph Hodges
1:59 – 2:14

RF04 ANOMALOUS CENTRIFUGAL DISTORTION IN HD$^+$ AND SPECTROSCOPIC DATA BASES, L. H. Coulter
2:16 – 2:31

RF05 SPEED-DEPENDENT BROADENING AND LINE-MIXING IN CH$^+$, PERTURBED BY AIR NEAR 1.64 $\mu$m FOR THE FRENCH/GERMAN CLIMATE MISSION MERLIN, Thiubali Delahaye, Thi Ngoc Ha Tran, Zachary Reed, Stephen E. Maxwell, Joseph Hodges
2:33 – 2:48

RF06 MID INFRARED DUAL FREQUENCY COMB SPECTROMETER FOR THE DETECTION OF METHANE IN AMBIENT AIR, Hans Schwenzer, Feng Zhu, Alexander Kolomenskii
2:50 – 3:05

RF07 IMPROVED OZONE AND CARBON MONOXIDE PROFILE RETRIEVALS USING MULTISPECTRAL MEASUREMENTS FROM NASA “A TRAIN”, NPP, AND TROPOMI SATELLITES, Dejina Fu
3:07 – 3:22

RF08 TEMPERATURE DEPENDENCES OF AIR-BROADENING AND SHIFT PARAMETERS IN THE $v_3$ BAND OF OZONE, Mary Ann H. Smith, V. Malathy Devi, D. Chris Benner
3:24 – 3:39

Intermission

RF09 MICROWAVE OPTICAL DOUBLE RESONANCE STUDIES OF PERTURBATIONS IN THE $\nu_3$ A$^1\Pi$ STATE, Andrew Richard Whitehill, Alexander W. Hull, Trevor J. Erickson, Jun Jiang, Carrie Womack, Barratt Park, Shuhei Ono, Mary Ann H. Smith
3:58 – 4:13

RF10 VALIDATION OF A NEW HNO$_3$ LINE PARAMETERS AT 7.6 $\mu$m USING LABORATORY INTENSITY MEASUREMENTS AND MIPS SATELLITE SPECTRA, Marco Ridolfi, Anna Perini, Jean-Marie Plass, Jean Vander Auwera, Massimo Carlo
4:15 – 4:30

RF11 ROTATIONAL SPECTROSCOPY OF NEWLY DETECTED ATMOSPHERIC OZONE DEPLETERS, CF$_3$-CH(Cl), CF$_3$CCl, and CF$_3$C(Cl,CH$_3$), Zbigniew Kisiel, Ewa Biedrowksa-Jaworska, Lech Puczkoowski, Iciar Uriarte, Patricia Eciuja, Francisco J. Basterretxea, Emilio J. Cocard
4:32 – 4:47

RF12 CHIRPED PULSE AND CAVITY FT MICROSCOPIC SPECTROSCOPY OF THE FORMIC ACID – TRIMETHYLAMINE WEAKLY BOUND COMPLEX, Becca Mackenzie, Chris Dewberry, Ken Leopold
4:49 – 5:04

RF13 FORMIC SULFURIC ANHYDRIDE: A NEW CHEMICAL SPECIES WITH POSSIBLE IMPLICATIONS FOR ATMOSPHERIC AEROSOLS, Becca Mackenzie, Chris Dewberry, Ken Leopold
5:06 – 5:21

RF14 ROTATIONAL SPECTROSCOPY OF METHYL VINYL KETONE, Olenna Zakharenko, R. A. Motiyenko, Juan-Ramon Aviles Moreno, T. R. Huet
5:23 – 5:38

RF15 THE MILLIMETER-WAVE SPECTRUM OF METHACROLEIN: TORSION-ROTATION-VIBRATION EFFECTS IN THE EXCITED STATES, Olenna Zakharenko, R. A. Motiyenko, Juan-Ramon Aviles Moreno, T. R. Huet
5:40 – 5:55
RH. Clusters/Complexes
Thursday, June 25, 2015 – 1:30 PM
Room: B102 Chemical and Life Sciences
Chair: Galen Sedo, University of Virginia’s College at Wise, VA, USA

RH01 1:30 – 1:45
CHIRPED PULSE AND CAVITY FT MICROWAVE SPECTROSCOPY OF THE HCH-2-6-DIFLUOROPYRIDINE WEAKLY BOUND COMPLEX, Chris Desbrey, Becca Mackenzie, Ken Leopold

RH02 1:47 – 1:57
MICROWAVE SPECTRUM, VAN DER WAALS BOND LENGTH, AND (1) Xe QUADRUPOLE COUPLING CONSTANT OF O-F-Se-O: Chris Desbrey, Anna Huff, Becca Mackenzie, Ken Leopold

RH03 1:59 – 2:14
DIMETHYL SULFIDE-ETHYL ETHER AND ETHYLENE OXIDE-ETHYLENE SULFIDE COMPLEXES INVESTIGATED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND AB INITIO CALCULATION, Yushoiku Kawahashi, Yoshiro Tatamitani, Takeyuki Masi, Eri Hirota

RH04 2:16 – 2:31
INTERNAL DYNAMICS IN SF6-NH3 OBSERVED BY BROADBAND ROTATIONAL SPECTROSCOPY, Dori M. Bitter, Daniel F. Zaleski, Susanna L. Stephens, Nick Walker, Anthony Legon

RH05 2:33 – 2:48
EVIDENCE FOR A COMPLEX BETWEEN THF AND ACETIC ACID FROM BROADBAND ROTATIONAL SPECTROSCOPY, Daniel P. Zaleski, Dori M. Bitter, John Connor Mullaney, Susanna L. Stephens, Adrian King, Matthew Hargood, Nick Walker

RH06 2:50 – 3:00
THE ROTATIONAL SPECTRUM OF PYRIDINE-FORMIC ACID. Lorenzo Spada, Qian Gou, Barbara Michela Giuliano, Walter Caminati

Intermission

RH07 3:19 – 3:34
FOURIER-TRANSFORM MICROWAVE AND MILLIMETERWAVE SPECTROSCOPY OF THE H3-6CN MOLECULAR COMPLEX, Keisuke Tanaka, Kensoke Harada, Yoshihiro Sumiyoshi, Masakazu Nakajima, Yanshi Endo

RH08 3:36 – 3:51
MICROWAVE SPECTROSCOPY OF THE CYCLOPENTANOL - WATER DIMER, Brandon Carroll, Jan A. Finnerin, Geoffrey Blake

RH09 3:53 – 4:08
HYDROGEN-BONDING AND HYDROPHOBIC INTERACTIONS IN THE ETHANOL-WATER DIMER, Jan A. Finnerin, Brandon Carroll, Marco A. Allodi, Geoffrey Blake

RH10 4:10 – 4:25
THE INFLUENCE OF FLUORINATION ON STRUCTURE OF THE TRIFLUOROACETONITRILE WATER COMPLEX, Wei Lin, Anan Wu, Xin Lu, Daniel A. Obenchain, Stewart E. Novick

RH11 4:27 – 4:42
THE POSITION OF DEUTERIUM IN THE HOD - N2O AS DETERMINED BY STRUCTURAL AND NUCLEAR QUADRUPOLE COUPLING CONSTANTS, Daniel A. Obenchain, Derek S. Frank, Stewart E. Novick, William Klemperer

RH12 4:44 – 4:59

RH13 5:01 – 5:16
HYDROGEN BONDING IN 4-MINOPYRROLIDINE ETHANOL A COMBINED BR-UV DOUBLE RESONANCE AND MICROWAVE STUDY, Caitlin Bray, Cara Rae Rivera, E. A. Arsenault, Daniel A. Obenchain, Stewart E. Novick, Joseph L. Knee

RH14 5:18 – 5:28
THEORETICAL STUDY OF THE EFFECT OF DOPING CLUSTERS (ZNO) 6 BY THE SELENIUM USING THE DFT, Noor E. Houda Bensiradj, Ourida Ouamerali

RH15 5:30 – 5:45
BORONYL IMIDE GOLD: A PHOTOELECTRON SPECTROSCOPY STUDY, Tom Jiao, Gary Lopez, Lu-Sheng Wang

Post-Deadline Abstract

RI. Astronomy
Thursday, June 25, 2015 – 1:30 PM
Room: 274 Medical Sciences Building
Chair: Harshal Gupta, California Institute of Technology, Pasadena, CA, USA

RI01 1:30 – 1:45
THE COMPLETE, TEMPERATURE RESOLVED SPECTRUM OF METHYL FORMATE BETWEEN 214 AND 265 GHz, James P. McMillan, Sarah Fortman, Christopher F. Reese, Frank C. De Lucia

RI02 1:47 – 2:02
ROTATIONAL SPECTROSCOPY OF 4-HYDROXY-2-BUTYNE-NITRILE, R. A. Motiyenko, L. Margulies, J.-C. Guillemin

RI03 2:04 – 2:19
TIME-DOMAIN TERAHERTZ SPECTROSCOPY OF ISOLATED PAHs, Brandon Carroll, Marco A. Allodi, Brett A. McGuire, Sergio Ioppolo, Geoffrey Blake

RI04 2:21 – 2:36
HIGH-RESOLUTION IR ABSORPTION SPECTROSCOPY OF POLYCYCLIC AROMATIC HYDROCARBONS: SHINING LIGHT ON THE INTERSTELLAR 3 MICRON EMISSION BANDS, Elena Maltseva, Alessandra Candian, Xavier Tielens, Annemieke Petrignani, J. Oomens, Wybren Jan Buma

RI05 2:38 – 2:53
EXPLORING MOLECULAR COMPLEXITY WITH ALMA (EMoCA): HIGH-ANGULAR-RESOLUTION OBSERVATIONS OF SAGITTARIUS B2(N) AT 3 mm, Holger S. P. Muller, Arnaud Belloche, Karl M. Menet, Robin T. Goyal

RI06 2:55 – 3:10
FIRST SPECTROSCOPIC STUDIES AND DETECTION IN SysB2 OF 13C-DOUBLY SUSTITUTED ETHYL CYANIDE, L. Margulies, R. A. Motiyenko, J.-C. Guillemin, Holger S. P. Muller, Arnaud Belloche

RI07 3:12 – 3:27
MILLIMETERWAVE SPECTROSCOPY OF ETHANOLINE AND PROPANINE AND THEIR SEARCH IN ORION, L. Margulies, R. A. Motiyenko, J.-C. Guillemin, Jose Cernicharo

Intermission

RI08 3:46 – 4:01
FURTHER STUDIES OF A 5797 Å DIFUSE INTERSTELLAR BAND, Takeshi Oka, L. M. Hobbs, Daniel E. Weitler, Donald N. Witt

RI09 4:03 – 4:18
LABORATORY OPTICAL SPECTROSCOPY OF THE PHENOXY RADICAL AS A DIFFUSE INTERSTELLAR BAND CANDIDATE, Missouri Arabi, Yuki Matsushita, Koichi Tsukiyama

RI10 4:20 – 4:35
INVESTIGATION OF CARBONACEOUS INTERSTELLAR DUST ANALOGUES BY INFRARED SPECTROSCOPY: EFFECTS OF ENERGETIC PROCESSING, Belén M. Mejía-Redondo, Isabel Tanarro, Victor Jose Herrero

RI11 4:37 – 4:52
REACTIONS OF GROUND STATE NITROGEN ATOMS N(3)(S) WITH ASTROCHEMICALLY-ReLEVANT MOLECULES ON INTERSTELLAR DUSTS, Laura Long, Sindersour

RI12 4:54 – 5:09
STABILITY OF GLYCINE TO ENERGETIC PROCESSING UNDER ASTROPHYSICAL CONDITIONS INVESTIGATED VIA INFRARED SPECTROSCOPY, Belén M. Mejía-Redondo, Victor Jose Herrero, Isabel Tanarro, Rafael Escobedo

RI13 5:11 – 5:21
MICROMETER AND SUBMICROMETER STUDIES OF INTERSTELLAR ICE ANALOGUES, Al Mejía-Redondo, Ian C. Wagner, Houston Hartwell Smith, Stefanie N. Milam, Susanna L. Walczak Weaver

RI14 5:23 – 5:38
UNTANGLED MOLECULAR SIGNALS OF ASTROCHEMICAL ICES IN THE Td: DISTINGUISHING AMORPHOUS, CRYSTALLINE, AND INTRAMOLECULAR MODES WITH BROADBAND THz SPECTROSCOPY, Brett A. McGuire, Sergio Ioppolo, Xander de Vries, Marco A. Allodi, Brandon Carroll, Geoffrey Blake

RI15 5:40 – 5:55
QUANTUM CHEMICAL STUDY OF THE REACTION OF C(4) WITH INTERSTELLAR ICE: PREDICTIONS OF VIBRATIONAL AND ELECTRONIC SPECTRA OF REACTION PRODUCTS, David E. Woon
RJ10 4:15 – 4:30
M. Broderick, Gary E. Douberly

RJ11 4:32 – 4:47
INFRARED SPECTRA OF THE CO2–H2O, CO2–H2O(2), and (CO2)2–H2O COMPLEXES ISOLATED IN SOLID NEON BETWEEN 90 AND 5000 cm⁻¹, Benoit Tremblay, Pascale Soulard

RJ12 4:49 – 4:59
MATRIX ISOLATION AND COMPUTATIONAL STUDY OF [2C, 2N, X] (X=S, SE) ISOMERS, Tamas Vonts, Gyorgy Taczay

RJ13 5:01 – 5:16
MATRIX ISOLATION SPECTROSCOPY AND PHOTOCHROMISTRY OF TRIPLETS 1,3-DIMETHYLPROPynyLIDENE (MeC=Me), Stephanie N. Knezz, Terese A Waltz, Benjamin C. Haenni, Nicola J. Burrmann, Robert J. McMahon

RJ14 5:18 – 5:33
EVIDENCE OF INTERNAL ROTATION IN THE O-H STRETCHING REGION OF THE 1:1 METHANOL–BENZENE COMPLEX IN AN ARGON MATRIX, Jay Amicangelo, Ian Campbell, Joshua Wilkins
FB. Spectroscopy as an analytical tool
Friday, June 26, 2015 – 8:30 AM
Room: 100 Noyes Laboratory

Chair: Christopher F. Neese, The Ohio State University, Columbus, OH, USA

FB01 8:30 – 8:45
CONTINUOUS MONITORING OF PHOTOLYSIS PRODUCTS BY THZ SPECTROSCOPY, Abdelaziz Omar, Arnaud Cuisset, Gael Mouret, Francis Hindle, Sophie Eliet, Robin Bocquet

FB02 8:47 – 9:02
MEDIUM RESOLUTION CAVITY SPECTROSCOPY FOR THE STUDY OF LARGE MOLECULES, Satyakumar Nagarajan, Christopher F. Neese, Frank C. De Lucia

FB03 9:04 – 9:19
SUBMILLIMETER/INFRARED DOUBLE RESONANCE: REGIMES FOR MOLECULAR SENSORS, See Sekantinith, Ivan Medvedev, Christopher F. Neese, Dane Phillips, Henry O. Everitt, Frank C. De Lucia

FB04 9:21 – 9:36
ROTATIONAL SPECTROSCOPY AS A TOOL TO INVESTIGATE INTERACTIONS BETWEEN VIBRATIONAL POLYADS IN SYMMETRIC TOP MOLECULES: LOW-LYING STATES v ≤ 2 OF METHYL CYANIDE, Holger S. P. Müller, Matthias H. Ordu, Frank Lewen, Linda Brown, Brian Drouin, John Pearson, Keryson Sung, Isabelle Kintner, Robert Sims

FB05 9:38 – 9:53
VIBRATIONAL SUM FREQUENCY STUDY OF THE INFLUENCE OF WATER-IONIC LIQUID MIXTURES IN THE CO2 ELECTROREDUCTION ON SILVER ELECTRODES, Natalia Garcia Rey, Dana Dlott

Intermission

FC. Comparing theory and experiment
Friday, June 26, 2015 – 8:30 AM
Room: B102 Chemical and Life Sciences

Chair: Edwin Sibert, The University of Wisconsin, Madison, WI, USA

FC01 8:30 – 8:45
VIBRATIONAL COUPLING IN SOLVATED FORM OF EIGEN PROTON, Jheng-Wei Li, Kaito Takahashi, Jer-Lai Kuo

FC02 8:47 – 9:02
BINDING BETWEEN NOBEL GAS ATOMS AND PROTONATED WATER MONOMER AND DIMER, Ying-Cheng Li, Jer-Lai Kuo

FC03 9:04 – 9:19
ANALYSIS OF HYDROGEN BONDING IN THE OH STRETCH REGION OF PROTONATED WATER CLUSTERS, Laura C. Dzugan, Anne B McCoy

FC04 9:21 – 9:36
SEMIEXPERIMENTAL STRUCTURE OF THE NON-RIGID BF2OH MOLECULE BY COMBINING HIGH RESOLUTION INFRARED SPECTROSCOPY AND AB INITIO CALCULATIONS, Natalja Vogt, Jean Demaison, Agnes Perrin, Hans Bürger

FC05 9:38 – 9:48
CONFORMATIONAL, VIBRATIONAL AND ELECTRONIC PROPERTIES OF C5H3XOS (X = H, F, Cl OR Br): HALOGEN AND SOLVENT EFFECTS, Mustafa Senyel, Gunes Esma, Cemal Parlak

FC06 9:50 – 10:05
COMBINED EXPERIMENTAL AND THEORETICAL STUDIES ON THE VIBRATIONAL AND ELECTRONIC SPECTRA OF 5-QUINOLINECARBONALDEHYDE, Mustafa Kümper, Mustafa Kocademir, Tüyabı Barakde

Intermission

FC07 10:24 – 10:39
COMBINED COMPUTATIONAL AND EXPERIMENTAL STUDIES OF THE DUAL FLUORESCENCE IN DIMETHYL-LAMINOBENZONITRILE (DMABN), Anastasia Edsell, Steven Shipman

FC08 10:41 – 10:56
MODELING SPIN-ORBIT COUPLING IN THE HALOCARBENES, Philagan Loura, Richard Dawes, Scott Reid, Silver Nyambu

FC09 10:58 – 11:13
GAS-PHASE CONFORMATIONS AND ENERGETICS OF PROTONATED 2-DEOXYADENOSINE-1'-MONOPHOSPHATE AND ADENOSINE-1'-MONOPHOSPHATE: REMPD ACTION SPECTROSCOPY AND THEORETICAL STUDIES, Pingan Wu, Y-W Nei, Chenchen He, Lucas Humlow, Giel Berden, J. Oomens, M T Rodgers
FD. Atmospheric science
Friday, June 26, 2015 – 8:30 AM
Room: 274 Medical Sciences Building
Chair: Kyle N Crabtree, University of California, Davis, Davis, CA, USA

FD01 9:21 – 9:36
HIGH-RESOLUTION SPECTRA OF CH₃COO : ASSIGNMENTS OF ν₁ AND 2ν₁ BANDS AND OVERLAPPED BANDS OF CH₃COO. Yu-Hee Chung, Li-Wei Chen, Yuan-Pern Lee

FD02 9:38 – 9:53
DIRECT INFRARED IDENTIFICATION OF THE CRIEGEE INTERMEDIATES ν⁺-CH₂COO AND THEIR DISTINCT CONFORMATION-DEPENDENT REACTIVITY. Hai-Yu Liu, Yu-Hee Chung, Xiaohong Wang, Joel Bowman, Yoshifumi Nishimura, Henry A Witte, Yuan-Pern Lee

FD03 9:55 – 10:10
THE-Å-Å ELECTRONIC TRANSITIONS OF THE CH₂BrOO AND CH₂COO RADICALS IN THE NEAR INFRARED REGION. Neal Kline, Meng Huang, Terry A. Miller

FD04 10:29 – 10:44
A THEORETICAL CHARACTERIZATION OF ELECTRONIC STATES OF CH₂OO AND CH₂OO RADICALS RELEVANT TO THE NEAR IR REGION. Richard Dawes, Phalgun Lohar, Meng Huang, Neal Kline, Terry A. Miller

FD05 10:46 – 11:01
JET-COOLLED LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF T-BUTOXY. Neil J Reilly, Lan Cheung, John F. Stanton, Terry A. Miller

FD06 11:03 – 11:18
DISPERSED FLUORESCENCE SPECTROSCOPY OF JET-COOLED ISOBUTOXY, 2-METHYL-1-BUTOXY, AND ISOPENTOXY RADICALS, Md Asmaul Reza, Neil J Reilly, Jahangir Alam, Amy Mason, Jinjun Liu

FD07 11:20 – 11:35
PHOTODISSOCIATION OF METHYL ISOTHIOCYANATE STUDIED USING CHIRPED PULSE UNIFORM FLOW SPECTROSCOPY. Nawand M Anysiangha, Lindsay N. Zuck, Chamara Abeysekera, Baptiste Joalland, Arthur Suits

FD08 11:37 – 11:52
DISPERSED FLUORESCENCE SPECTROSCOPY OF JET-COOLED METHYLCYCLOHEXOXY RADICALS. Jahangir Alam, Md Asmaul Reza, Amy Mason, Jinjun Liu

FD10 11:20 – 11:35
IMPACT OF COMPLEX-VALUED ENERGY FUNCTION SINGULARITIES ON THE BEHAVIOUR OF RAYLEIGH-SCHRÖDINGER PERTURBATION SERIES. H₂CO MOLECULE VIBRATIONAL ENERGY SPECTRUM. Andrey Bykov, Alexander Ikhov

FD11 11:38 – 11:53
THE LOWEST EIGHT VIBRATIONAL STATES OF HYDRAZOIC ACID (HN₃). Brent K. Amberger, Brian J. Esselman, Robert J. McMahon

FD12 11:54 – 12:10
MILLIMETER-WAVE SPECTROSCOPY AND GLOBAL ANALYSIS OF THE LOWEST EIGHT VIBRATIONAL STATES OF DEUTERATED HYDRAZOIC ACID (DN₃). Brent K. Amberger, Brian J. Esselman, Robert J. McMahon

FD13 12:11 – 12:26

FD14 12:27 – 12:42
OBSERVATION OF LEVEL-SPECIFIC PREDISSOCIATION RATES IN S₁ ACETYLENE. Jiang, Robert W Field, Michael C McCarthy

FD15 12:43 – 12:58
FULL DIMENSIONAL ROVIBRATIONAL VARIATIONAL CALCULATIONS OF THE S₁ STATE OF C₂H₂. Bryan Changala, Joshua H Barraban, John F. Stanton

Intermission

FE. Small molecules
Friday, June 26, 2015 – 8:30 AM
Room: 217 Noyes Laboratory
Chair: Robert W Field, MIT, Cambridge, MA, USA

FE01 9:21 – 9:36
TOWARDS A GLOBAL FIT OF THE COMBINED MILLIMETER-WAVE AND HIGH RESOLUTION FTIR DATA FOR THE LOWEST EIGHT VIBRATIONAL STATES OF HYDRAZOIC ACID (HN₃). Brent K. Amberger, Brian J. Esselman, Robert J. McMahon

FE02 9:38 – 9:53
MILLIMETER-WAVE SPECTROSCOPY AND GLOBAL ANALYSIS OF THE LOWEST EIGHT VIBRATIONAL STATES OF DEUTERATED HYDRAZOIC ACID (DN₃). Brent K. Amberger, Brian J. Esselman, Robert J. McMahon

FE03 9:54 – 10:09
SIMPLIFIED CARTESIAN BASIS MODEL FOR INTRAPOLYAD EMISSION INTENSITIES IN THE A-X TRANSITION OF ACETYLENE. Barrett Park, Adam H. Stevens, Joshua H Barraban, Robert W Field

FE04 10:10 – 10:25
OBSERVATION OF LEVEL-SPECIFIC PREDISSOCIATION RATES IN S₁ ACETYLENE. Catherine A. Saladrigas, Jun Jiang, Robert W Field

FE05 10:26 – 10:41
FULL DIMENSIONAL ROVIBRATIONAL VARIATIONAL CALCULATIONS OF THE S₁ STATE OF C₂H₂. Bryan Changala, Joshua H Barraban, John F. Stanton

Intermission
BREATHEING EASIER THROUGH SPECTROSCOPY: STUDYING FREE RADICAL REACTIONS IN AIR POLLUTION CHEMISTRY

MITCHIO OKUMURA, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA

Air pollution arises from the oxidation of volatile organic compounds emitted into the atmosphere from both anthropogenic and biogenic sources. Free radicals dominate the gas phase chemistry leading to the formation of tropospheric ozone, oxygenated organic molecules and organic aerosols, but this chemistry is complex. In this presentation, advances in our understanding of the spectroscopy and chemistry of atmospheric free radicals will be described that have come from exploiting the sensitivity and specificity of methods such as Cavity Ringdown Spectroscopy, Multiplied Photionization Mass Spectrometry and Cavity-Enhanced Frequency Comb Spectroscopy.

MOLECULAR ROTATION SIGNALS: MOLECULE CHEMISTRY AND PARTICLE PHYSICS

JENS UWE GRABOW, Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz Universität, Hannover, Germany.

Molecules - large or small - are attractive academic resources, with numerous questions on their chemical behaviour as well as problems in fundamental physics now (or still) waiting to be answered: Targeted by high-resolution spectroscopy, a rotating molecular top can turn into a laboratory for molecule chemistry or a laboratory for particle physics.

Once successfully entrained (many species - depending on size and chemical composition - have insufficient vapour pressures or are of transient nature, such that specifically designed pulsed-jet sources are required for their transfer into the gas phase or in-situ generation) into the collision-free environment of a supersonic-jet expansion, each molecular top comes with its own set of challenges, theoretically and experimentally: Multiple internal interactions are causing complicated energy level schemes and the resulting spectra will be rather difficult to predict theoretically. Experimentally, these spectra are difficult to assess and assign. With today’s broad-band chirp microwave techniques, finding and identifying such spectral features have lost their major drawback of being very time consuming for many molecules. For other molecules, the univallled resolution and sensitivity of the narrow-banded impulse microwave techniques provide a window to tackle - at the highest precision available to date - fundamental questions in physics, even particle physics – potentially beyond the standard model.

Molecular charge distribution, properties of the chemical bond, details on internal dynamics and intermolecular interaction, the (stereo-chemical) molecular structure (including the possibility of their spatial separation) as well as potential energy curves will be presented, as examples from Hannover, new directions, and an outlook at the future of molecular rotation spectroscopy.

CPUF: CHIRPED-PULSE MICROWAVE SPECTROSCOPY IN PULSED UNIFORM SUPERSONIC FLOWS

ARTHUR SUITS, CHAMARA ABYESSEKERA, LINDSAY N. ZACK, BAPTISTE JOALLAND, NUWANDI M ARYASINGHA, Department of Chemistry, Wayne State University, Detroit, MI, USA; BARRATT PARK, ROBERT W FIELD, Department of Chemistry, MIT, Cambridge, MA, USA; JAN SIMS, Institut de Physique de Rennes, Université de Rennes 1, Rennes, France.

Chirped-pulse Fourier-transform microwave spectroscopy has stimulated a resurgence of interest in rotational spectral spectroscopy owing to the dramatic reduction in spectral acquisition time it enjoys when compared to cavity-based instruments. This suggests that it might be possible to adapt the method to study chemical reaction dynamics and even chemical kinetics using rotational spectroscopy. The great advantage of this would be clear, quantifiable spectroscopic signatures for polyatomic products as well as the possibility to identify and characterize new radical reaction products and transient intermediates. To achieve this, however, several conditions must be met: 1) products must be thermalized at low temperature to maximise the population difference needed to achieve adequate signal levels and to permit product quantification based on the rotational line strength; 2) a large density and volume of reaction products is also needed to achieve adequate signal levels; and 3) for kinetics studies, a uniform density and temperature is needed throughout the course of the reaction. These conditions are all happily met by the uniform supersonic flow produced from a Laval nozzle expansion. In collaboration with the Field group at MIT we have developed a new instrument we term a CPUF (Chirped-pulseUniform Flow) spectrometer in which we can study reaction dynamics, photochemistry and kinetics using broadband microwave and millimeter wave spectroscopy as a product probe. We will illustrate the performance of the system with a few examples of photodissociation and reaction dynamics, and also discuss a number of challenges unique to the application of chirped-pulse microwave spectroscopy in the collisional environment of the flow. Future directions and opportunities for application of CPUF will also be explored.
The spectrum of molecular hydrogen can be measured in the laboratory to very high precision using advanced laser and molecular beam techniques, as well as frequency-comb based calibration [1]. The quantum level structure of this smallest neutral molecule can now be calculated to very high precision, based on a very accurate (10^{-13}) precision Born-Oppenheimer potential [3] and including subtle non-adiabatic, relativistic and quantum electrodynamic effects [4]. Comparison between theory and experiment yields a test of QED, and in fact of the Standard Model of Physics, since the weak, strong and gravitational forces have a negligible effect. Even fifth forces beyond the Standard Model can be searched for [5]. Astronomical observation of molecular hydrogen spectra, using the largest telescopes on Earth and in space, may reveal possible variations of fundamental constants on a cosmological time scale [6]. A study has been performed at a “look-back” time of 12.5 billion years [7]. In addition the possible dependence of a fundamental constant on a gravitational field has been investigated from observation of molecular hydrogen in the photospheres of white dwarfs [8]. The latter involves a test of the Einstein equivalence principle.

\[ E = mc^2 \]

The experimental and theoretical values are in excellent agreement with each other. The energy calculations, however, reduce in accuracy with the increase in rotational and vibrational excitation, limited by the accuracy of non-Born Oppenheimer corrections, as well as the higher-order QED effects. While on the experimental side, it remains difficult to sufficiently populate these excited levels in the ground electronic state.

We present here our high-resolution spectroscopic study on the X 1\textsc{A}^2\Sigma^+ electronic ground state levels with very high fundamental vibrational energy splitting [2], and rotational energy progression extending to J = 10 [3]. In general, the experimental and theoretical values are in excellent agreement with each other. The energy calculations, however, reduce in accuracy with the increase in rotational and vibrational excitation, limited by the accuracy of non-Born Oppenheimer corrections, as well as the higher-order QED effects. While on the experimental side, it remains difficult to sufficiently populate these excited levels in the ground electronic state.

CONTINUOUS SUPERSONIC EXPANSION DISCHARGE SOURCE FOR HIGH-PRECISION MID-INFRARED SPECTROSCOPY

MF04 2:30 – 2:54

EDCEL JOHN SALUMBIDES, Department of Physics and Astronomy, VU University, Amsterdam, Netherlands

The low temperatures and pressures of the interstellar medium provide an ideal environment for gas phase ion-neutral reactions that play an essential role in the chemistry of the universe. High-precision laboratory spectra of molecular ions are necessary to facilitate new astronomical discoveries and provide a deeper understanding of interstellar chemistry, but forming ions in measurable quantities in the laboratory has proved challenging. Even when cryogenically cooled, the high temperatures and pressures of typical discharge cells lead to dihedral and congested spectra from which extracting chemical information is difficult. Here we overcome this challenge by coupling an electric discharge to a continuous supersonic expansion source to form ions cooled to low temperatures. The ion production abilities of the source have been demonstrated previously as ion densities on the order of 10^{9} - 10^{10} cm^{-3} have been observed for H_{3}^{+}. With a smaller rotational constant and the expectation that it will be formed with comparable densities, H_{3}^{+} is used as a reliable measure of the cooling abilities of the source. Ions are probed through the use of a widely tunable mid-infrared (3-5 \mu m) spectrometer based on light formed by difference frequency generation and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS). To improve the sensitivity of the instrument the discharge is electrically modulated and the signal is fed into a lock-in amplifier before being recorded by a custom data acquisition program. Rotational transitions of H_{3}^{+} and H_{2}^{+} have been recorded, giving rotational temperatures of 80 - 120 K and 35 - 40 K, respectively. With verification of the source is producing rotationally cold ions, we move toward the study of primary ions of more astronomical significance, including H_{5}^{+}.

MF03 2:22 – 2:37

BOUNDS ON THE NUMBER AND SIZE OF EXTRA DIMENSIONS FROM MOLECULAR SPECTROSCOPY

EDCEL JOHN SALUMBIDES, Department of Physics and Astronomy, VU University, Amsterdam, Netherlands

Modern string theories, which seek to produce a consistent description of physics beyond the Standard Model that also includes the gravitational interaction, appear to be most consistent if a large number of dimensions are postulated. For example the mysterious M-theory, which generalizes all consistent versions of superstring theories, requires 11 dimensions. We demonstrate that investigations of quantum level energies in simple molecular systems provide a testing ground to constrain the size of compactified extra dimensions, for example those proposed in the ADD [1] and RS scenarios [2]. This is made possible by the recent progress in precision metrology with ultrastable lasers on energy levels in neutral molecular hydrogen (H_{2}, HD and D_{2}) [3] and the molecular hydrogen ions (H_{3}^{+}, H_{2}^{+} and D_{2}^{+}) [4]. Comparisons between experiment and quantum electrodynamic calculations for these molecular systems can be interpreted in terms of probing large extra dimensions, under which conditions gravity will become much stronger. Molecules are a probe of space-time geometry at typical distances where chemical bonds are effective, i.e. at length scales of an Å.

MF01 1:30 – 2:00

PHYSICS BEYOND THE STANDARD MODEL FROM MOLECULAR HYDROGEN SPECTROSCOPY

WIM UBACHS, EDCEL JOHN SALUMBIDES, JULIA BAGDONAITE, Department of Physics and Astronomy, VU University, Amsterdam, Netherlands.

The spectrum of molecular hydrogen can be measured in the laboratory to very high precision using advanced laser and molecular beam techniques, as well as frequency-comb based calibration [1]. The quantum level structure of this smallest neutral molecule can now be calculated to very high precision, based on a very accurate (10^{-13}) precision Born-Oppenheimer potential [3] and including subtle non-adiabatic, relativistic and quantum electrodynamic effects [4]. Comparison between theory and experiment yields a test of QED, and in fact of the Standard Model of Physics, since the weak, strong and gravitational forces have a negligible effect. Even fifth forces beyond the Standard Model can be searched for [5]. Astronomical observation of molecular hydrogen spectra, using the largest telescopes on Earth and in space, may reveal possible variations of fundamental constants on a cosmological time scale [6]. A study has been performed at a “look-back” time of 12.5 billion years [7]. In addition the possible dependence of a fundamental constant on a gravitational field has been investigated from observation of molecular hydrogen in the photospheres of white dwarfs [8]. The latter involves a test of the Einstein equivalence principle.

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CONTINUOUS SUPERSONIC EXPANSION DISCHARGE SOURCE FOR HIGH-PRECISION MID-INFRARED SPECTROSCOPY

COURTNEY TALICKA, MICHAEL PORAMBIO, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA; BENJAMIN J. McCall, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL, USA.

The low temperatures and pressures of the interstellar medium provide an ideal environment for gas phase ion-neutral reactions that play an essential role in the chemistry of the universe. High-precision laboratory spectra of molecular ions are necessary to facilitate new astronomical discoveries and provide a deeper understanding of interstellar chemistry, but forming ions in measurable quantities in the laboratory has proved challenging. Even when cryogenically cooled, the high temperatures and pressures of typical discharge cells lead to dihedral and congested spectra from which extracting chemical information is difficult. Here we overcome this challenge by coupling an electric discharge to a continuous supersonic expansion source to form ions cooled to low temperatures. The ion production abilities of the source have been demonstrated previously as ion densities on the order of 10^{9} - 10^{10} cm^{-3} have been observed for H_{3}^{+}. With a smaller rotational constant and the expectation that it will be formed with comparable densities, H_{3}^{+} is used as a reliable measure of the cooling abilities of the source. Ions are probed through the use of a widely tunable mid-infrared (3-5 \mu m) spectrometer based on light formed by difference frequency generation and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS). To improve the sensitivity of the instrument the discharge is electrically modulated and the signal is fed into a lock-in amplifier before being recorded by a custom data acquisition program. Rotational transitions of H_{3}^{+} and H_{2}^{+} have been recorded, giving rotational temperatures of 80 - 120 K and 35 - 40 K, respectively. With verification of the source is producing rotationally cold ions, we move toward the study of primary ions of more astronomical significance, including H_{5}^{+}.


PROGRESS TOWARDS A HIGH-PRECISION INFRARED SPECTROSCOPIC SURVEY OF THE H$_3^+$ ION

ADAM J. PERRY, JAMES N. HODGES, CHARLES R. MARKUS, G. STEPHEN KOCHERIL, PAUL A. HENDRICKS*

Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL, USA; BEN-JAMIN J. MCCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL, USA.

The trihydrogen cation, H$_3^+$, represents one of the most important and fundamental molecular systems. Having only two electrons and three nuclei, H$_3^+$ is the simplest polyatomic system and is a key testing ground for the development of new techniques for calculating potential energy surfaces and predicting molecular spectra. Corrections that go beyond the Born-Oppenheimer approximation, including adiabatic, non-adiabatic, relativistic, and quantum electrodynamic corrections are becoming more feasible to calculate. As a result, experimental measurements performed on the H$_3^+$ ion serve as important benchmarks which are used to test the predictive power of new computational methods.

By measuring many infrared transitions with precision at the sub-MHz level it is possible to construct a list of the most highly precise experimental rovibrational energy levels for this molecule. Until recently, only a select handful of infrared transitions of this molecule have been measured with high precision (~1 MHz). Using the technique of Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy, we are aiming to produce the highest precision spectroscopic dataset for this molecule to date. Presented here are the current results from our survey along with a discussion of the combination differences analysis used to extract the experimentally determined rovibrational energy levels.

Collision-induced rotational energy transfer among rotational levels of ground state CN (N=2, v=0) radicals has been probed by saturation recovery experiments, using high-resolution, polarized transient FM spectroscopy to probe the recovery of population and the decay of alignment following ns pulsed laser depletion of selected CN rotational levels. Despite the lack of Doppler selection in the pulsed depletion and the thermal distribution of collision velocities, the recovery kinetics are found to depend on the probed Doppler shift of the depleted signal. The observed Doppler-shift-dependent recovery rates are a measure of the velocity dependence of the inelastic cross sections, combined with the moderating effects of velocity-changing elastic collisions. New experiments are underway, in which the pulsed saturation is performed with sub-Doppler velocity selection. The time evolution of the spectral hole bleached in the initially thermal CN absorption spectrum can characterize speed-dependent inelastic collisions along with competing elastic velocity-changing collisions, all as a function of the initially bleached velocity group and rotational state. The initial time evolution of the depletion recovery spectrum can be compared to a stochastic model, using differential cross sections for elastic scattering as well as speed-dependent total inelastic cross sections, derived from ab initio scattering calculations. Progress to date will be reported.

TOWARD TWO-COLOR SUB-DOPPLER SATURATION RECOVERY KINETICS IN CN (X, v = 0, J)

HONG XU, DAMIEN FORTHOMME, Department of Chemistry, Brookhaven National Laboratory, Upton, NY; USA; TREVOR SEARS*, GREGORY HALL, Chemistry Department, Brookhaven National Laboratory, Upton, NY, USA; PAUL DAGDIGIAN, Department of Chemistry, Johns Hopkins University, Baltimore, MD, USA.

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Interruption

HIGH PRECISION INFRARED SPECTROSCOPY OF OH$^+$

CHARLES R. MARKUS, ADAM J. PERRY, JAMES N. HODGES, G. STEPHEN KOCHERIL, PAUL A. HENDRICKS*

Departments of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA; BEN-JAMIN J. MCCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL, USA.

The molecular ion OH$^+$ is of significant importance to interstellar chemistry. OH$^+$ is a key intermediate in the formation of water, and the ratios of OH$^+$ to H$_2$O$^+$ and H$_2$O$^+$ have been used to calculate the cosmic ray ionization rates in diffuse molecular clouds. To improve on previous spectroscopic work, the sensitive technique Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy (NICE-OHVMS) has been used to record rovibrational transitions of OH$^+$. Previously this approach has been used to investigate HCO$^+$, H$_2$O$^+$, and HeH$^+$. Using an optical frequency comb for precise frequency calibration, the OH$^+$ line centers have been determined with high uncertainties. Here the most precise and accurate list of rovibrational transitions of OH$^+$ is presented. These values can then be used to empirically determine rotational transitions through combination difference analysis.

AN EMPIRICAL DIPOLE POLARIZABILITY FOR Hg FROM A FIT TO SPECTROSCOPIC DATA YIELDING ANALYSIS OF ELECTROSTATIC POTENTIALS FOR ALL ISOTOPOLOGUES OF HeH$^+$

YOUNG-SANG CHO, ROBERT J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada; NIKESH S. DATTANI*, Graduate School of Science, Department of Chemistry, Kyoto University, Kyoto, Japan.

All available spectroscopic data for all stable isotopologues of HeH$^+$ are analyzed with a direct-potential-fit (DPF) procedure that uses least-squares fits to experimental data in order to optimize the parameters defining an analytic potential. Since the coefficient of the leading (1/r^6) inverse-power term is C$_6$, it can be used to define the polarizability of the Hg atom. The fact that the present model for the long-range behavior includes accurate theoretical C$_6$, C$_7$, and C$_8$ coefficients (which are held fixed in the fits) should make it possible to obtain a good estimate of this quantity.

The Boltzmann constant k_B is a fundamental constant that can be defined temperature, is directly related to the dipole polarizability of a gas by the expression k_B = (α/ε_0)r_0$^2/2$, in which α is the permittivity of free space, and r_0 is the relative dielectric permittivity at pressure p and temperature T. If k_B can be determined with greater precision, it can be used to define temperature based on a fundamental constant, rather than based on the rather arbitrary triple point of water, which is only known to 5 digits of precision. α for Hg is known theoretically to 8 digits of precision, but an empirical variance exists. This work, examines the question of how precisely α$^{HeH^+}$ can be determined from a DPF to spectroscopic HeH$^+$ data, where the limiting long-range tail of the analytic potential has the correct form implied by Rydberg theory: α$^{HeH^+}$/2. Although the highest observed vibrational level is bound by 1000 cm$^{-1}$ (our current fit determined an upper level of C$_9$ = α$^{HeH^+}$/2 with an uncertainty of only 0.6%). It has been shown that with more precise spectroscopic data near the dissociation, α$^{HeH^+}$ can be determined with high enough precision to determine a more precise k_B and hence redefine temperature more accurately.

References:

ANALYTIC EMPIRICAL POTENTIALS FOR BeH+, BeD+, AND BeT+ INCLUDING UP TO 4TH ORDER QED IN THE LONG-RANGE AND PREDICTIONS FOR THE HALO NUCLEONIC MOLECULES 14BeH+ AND 14BeH+.

LENKA C. L. CHUEN FONG, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada; GREGORZ LACH, International Institute of Molecular and Cell Biology, Warsaw, Poland; ROBERT J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada; NIKHEX S. DATTANI, Graduate School of Science, Department of Chemistry, Kyoto University, Kyoto, Japan.

The 138(1/2)+ half-life of the halo nuclear atomic 1Be is orders of magnitude longer than those for any other halo nucleonic atom known, and makes Be-based diatomics the most promising candidates for the formation of the first halo nucleonic molecules. However, the 4e− species LiH and BeH+ are some of the first molecules for which the highest accuracy ab initio methods are not accessible, so empirical potential energy functions are important for making predictions and for benchmarking ab initio calculations break down at this transition from 3e− to 4e−. BeH+ is also very light, and has one of the most extensive data sets involving a tritium isotope, making it a very useful benchmark for studying Brunn-Oppenheimer breakdown. We therefore seek to determine an analytic empirical potential energy function for BeH+ that has as much precision as possible. To this end, all available spectroscopic data for all stable isotopologues of BeH+ are analyzed in a standard direct-potential-fit procedure that uses least-squares fits to optimize the parameters defining an analytic potential. The “MoreLong-range” (MLR) model used for the potential energy function incorporates the inverse-power long-range tail required by theory, and the calculation of the leading long-range coefficients C1, C2, C3, and C4 include non-adiabatic terms, and up to 4th order QED corrections. As a by-product, we have calculated some fundamental properties of Li+ systems with unprecedented precision, such as the dipole, quadrupole, octupole, non-adiabatic, and mixed higher order polarizabilities of hydrogen, deuterium, and tritium. We provide good first estimates for the transition energies for the halo nucleonic species 14BeH+ and 14BeH+. 

MF10
ANALYTIC EMPIRICAL POTENTIAL AND ITS COMPARISON TO STATE OF THE ART ab initio CALCULATIONS FOR THE 6+ EXCITED (1Σ1u)+ STATE OF Li2.

NIKHEX S. DATTANI, Graduate School of Science, Kyoto University, Kyoto, Japan; ROBERT J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada.

Despite only having 6+ as the most sophisticated Li2(1Σ1u)+ calculation5, there is an n, which disagrees with the empirical value by over 1500% of the latter’s uncertainty, and energy spacings that disagree with those of the empirical potential up to over 1.5 cm−1. The discrepancy here is far more than for the ground state of the 5+ system BeH+, for which the best ab initio calculation gives an n, which disagrees with the empirical value by less than 200% of the latter’s uncertainty6. In addition to this discrepancy, other reasons motivating the construction of an analytic empirical potential for Li2(1Σ1u)+ include (1) the fact that it is the most deeply bound Li2 state, (2) it is the only Li2 state out of the lowest five, for which an analytic empirical potential has yet been built, (3) the state it mixes with, the A1(3Σu+) state, is one of the most thoroughly characterized molecular states, but has a small gap of missing data in part of the region where it mixes with the 1Σu state, and (4) it is one of the states accessible by new ultra-high precision techniques based on photoassociation7. Finally (5) there is currently a discrepancy between the most sophisticated 5− ab initio calculation8, and the most current empirical value9, for the first Li2(1Σ1u)+(S−L)−(P−P) interaction term (C2), despite the latter being the most precisely experimentally determined oscillator strength for any system, by an order of magnitude. The lowest is one of the states that has this exact C2 interaction term.

MF11
PRECISION SPECTROSCOPY OF TRAPPED HF+ WITH A COHERENCE TIME OF 1 SECOND
KEVIN COSSEL, WILLIAM CABRINCROSS, MATT GRAU, DAN GRESH, YAN ZHOU, JUN YE, ERIC CORNELL, JILA, National Institute of Standards and Technology and Univ. of Colorado Department of Physics, University of Colorado, Boulder, Boulder, CO, USA.

Trapped molecular ions provide new systems for precision spectroscopy and tests of fundamental physics. For example, measurements of the permanent electric dipole moment of the electron (eEDM) test time-reversal symmetry10. Currently, we are using Ramsey spectroscopy between spin states of the metastable 3Σg− state in trapped HF+ for a measurement of the eEDM. We are regularly performing spectroscopy with a Ramsey time of 500 ms yielding what, to our knowledge, is the narrowest spectral line observed in a molecular system. Here, we will provide an overview of the experiment and the current eEDM results.

MF12
BROADBAND FREQUENCY COMB AND CW-LASER VELOCITY MODULATION SPECTROSCOPY OF ThF-
DAN GRESH, KEVIN COSSEL, JUN YE, ERIC CORNELL, JILA, National Institute of Standards and Technology and Univ. of Colorado Department of Physics, University of Colorado, Boulder, Boulder, CO, USA.

An experimental search for the permanent electric dipole moment of the electron (eEDM) is currently being performed using the metastable 3Σg− state in trapped HF+10. The use of ThF− could significantly increase the sensitivity due to the large effective electric field and longer 3Σg− state lifetime. Previous work by the Heaven group has identified several low-lying ThF− electronic states11, however, the ground state could not be conclusively assigned. In addition, transitions to intermediate electronic states have not been identified, but they are necessary for state detection, manipulation, and readout in an eEDM experiment. To date we have acquired 3700 ms−1 of densely-sampled ThF− spectra in the 695−1020 nm region with frequency comb and cw-laser velocity modulation spectroscopy12. With high resolution, we have accurately fit more than 29 ThF− vibronic transitions, including electronic states spaced by the known X−α energy separation13. We will report on the ThF− ground state assignment and its implications for an eEDM experiment.
At last year’s ISMS meeting, Zaleski et al. reported new broadband MW spectroscopy measurements of pure rotational transitions in the $v = 0 – 6$ levels of the $^2\text{H}_2\text{I}_2$ ground electronic state of PbI. The analysis presented at that time was a conventional $v$-level by $v$-level ‘band-constant’ analysis performed using the PGopher program. That level-by-level PGopher analysis yielded values of $B_1$, $B_2$, and five spin-splitting parameters for each vibrational level of each isotopologue. Ignoring the spin-splitting information, the $B_1$ and $B_2$ values were used to generate a set of synthetic pure $R(0)$ transitions for each level that were taken to represent the “mechanical” information about the molecule contained in these spectra. A standard direct-potential-fit (DPF) analysis was then used to fit these data to an “Expanded Morse Oscillator” (EMO) potential function form. The well-depth parameter $D_0$, was fixed at the literature value, while values of the equilibrium distance $r_e$ and three EMO exponent-coefficient expansion ‘potential shape’ parameters are determined from the fits. The best fits to the data yield potentials whose fundamental vibrational spacings are in excellent agreement with experiment together with reliable predictions for the first five overtone energies.


PGopher is a Computer Program for Simulating Rotational Structures, C. M. Western, University of Bristol, http://pgopher.chm.bris.ac.uk


2.04–2.19

MICROWAVE SPECTRA OF 1- AND 2-BROMOBUTANE

SOOHYUN KA, JIHYUN KIMa, HEESU JANG, JUNG JIN OH, Research Institute of Global Environment, Sookmyung Women’s University, Seoul, Korea.

The rotational spectrum of 1-bromobutane measured by the 480 MHz bandwidth chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy. In this paper, the ab initio calculation and the analysis of rotational spectrum were performed, and the properties of gas molecule are reported.

1-bromobutane have five conformers, aa, ag, ga, gg, gg'. The transitions were assigned to three different conformers which are most stable forms, aa, ag, ga. The spectra for the normal isotopic species and 14Br substitution were observed and assigned.

The rotational spectrum of 2-bromobutane has been observed in the frequency region 7–18 GHz. 2-bromobutane has the three possible conformers, Ga, A, G. The difference of their energy is very small, so the spectra of all conformers were found in the full range of our spectrum.

Consequently, the rotational constants, nuclear quadrupole constants, and centrifugal distortion constants were determined and the dipole moment of the aa conformer with 14Br were measured. All the experimental data is in good agreement with the calculated data.

2.21–2.36

ACCURATE EQUILIBRIUM STRUCTURES FOR trans-Hexatriene by the Mixed Estimation Method and for the Three Isomers of Octatetraene from Theory. Structural Consequences of Electron Delocalization

NORMAN C. CRAIG, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH, USA; JEAN DEMASION, Université Lille 1, Laboratoire PhLAM, Villeneuve d’Ascq, France; PETER GRONER, Depart- ment of Chemistry, University of Missouri - Kansas City, Kansas City, MO, USA; HEINZ DIETER RUDOLPH, Department of Chemistry, Universität Ulm, Ulm, Germany; NATALIA VOGT, Section of Chemical Information Systems, Universität Ulm, Ulm, Germany.

An accurate equilibrium structure of trans-hexatriene has been determined by the mixed estimation method with rotational constants from 8 deuterium and carbon isotopologues and high-level quantum chemical calculations. In the mixed estimation method bond parameter is fit concurrently to moments of inertia of various isotopologues and to theoretical bond parameters, each data set carrying appropriate uncertainties. The accuracy of this structure is 0.001 Å and 0.1 °.

Structures of similar accuracy have been computed for the cis,cis, trans,trans, and cis,cis isomers of octatetraene at the CCSD(T)/level with a basis set of wCVQZ(ae) quality adjusted in accord with the experience gained with trans-hexatriene. The structures are compared with butadiene and with cis-hexatriene to show how increasing the length of the chain in polyenes leads to increased blurring of the difference between single and double bonds in the carbon chain. In trans-hexatriene \( r^2(C_1-C_6) = 1.339 \text{ Å} \) and \( r(C_1-C_6) = 1.346 \text{ Å} \) compared to 1.338 Å for the “double” bond in butadiene; \( r(C_2-C_7) = 1.449 \text{ Å} \) compared to 1.454 Å for the “single” bond in butadiene. “Double” bonds increase in length, “single” bonds decrease in length.

2.53–3.10

CONFORMATIONAL TRANSFORMATION OF FIVE-MEMBERED RINGS: THE GAS PHASE STRUCTURE OF 2-METHYL-1,3,5-HEXATHIATRYTHIOPHENE

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2-Methylthiatrithiophene (2-MeTTFT) is a promising environmentally friendly solvent and biofuel component which is derived from renewable resources. Following the principles of Green Chemistry, 2-MeTTFT has been evaluated in various fields like organometallics, metathesis, and biosynthesis on the way to more eco-friendly syntheses.

Cyclopentane as the prototype of five-membered rings is well-known to exist as twist or envelope structures. However, the conformational analysis of its heterocyclic derivative 2-methyl-1,3,5-thiatrithiophene (MTTP) yielded two stable twist conformers and two envelope transition states. Here, we report on the heavy atom \( r_c \) structure of the oxygen-analog of MTTP. 2-MeTTFT, studied by a combination of molecular beam Fourier transform microwave spectroscopy and quantum chemistry. One conformer of 2-MeTTFT was observed and highly accurate molecular parameters were determined using the XIAM program. In addition, all \( 1^2 \)C isotopologues were assigned in natural abundance of 1%. A structural determination based on the \( r_c \) positions of all carbon atoms was achieved via Kraitchman’s equations. The methyl group in 2-MeTTFT undergoes internal rotation and causes A–E splittings of the rotational lines. The barrier was calculated to be 1142 cm\(^{-1}\) at the MP2/6-311++G(d,p) level of theory, which is rather high. Accordingly, narrow A–E splittings could be observed for only a few transitions. However, the barrier height could be fitted while the angles between the internal rotor axis and the principal axes of inertia were taken from the experimental geometry.
ASSIGNMENT OF THE MICROWAVE SPECTRUM OF 1,2-DIFLUOROBENZENE ··· HCCH: LESSONS LEARNED FROM ANALYSIS OF A DENSE BROADBAND SPECTRUM

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Dimers of aromatic molecules with weak proton donors such as acetylene are prototypical systems for investigating weak CH···π interactions. A logical progression from our recent rotational spectroscopic studies of benzene ··· HCCH and fluorobenzene ··· HCCH was to study 1,2-difluorobenzene ··· HCCH, so the effect of increasing the number of electronegative substituents could be investigated. In this talk, structures of benzene, fluorobenzene, and 1,2-difluorobenzene complexed with HCCH will be compared, and the challenges and pitfalls encountered during assignment of the very rich chirped-pulse Fourier-transform microwave (CP-FTMW) spectrum will be discussed.

The spectrum of a mixture of 1,2-dfbz and HCCH in a neon carrier was initially recorded using the CP-FTMW spectrometer at the University of Virginia. Transitions matching the patterns and approximate rotational constants predicted for 1,2-dfbz ··· HCCH were readily identified; however, efforts to fit the observed frequencies to an asymmetric top Hamiltonian were unsuccessful. A second CP-FTMW scan of only 1,2-dfbz monomer revealed that the transitions initially believed to be 1,2-dfbz ··· HCCH were actually present in both scans. Subtraction of lines common to both data sets revealed a previously unidentified pattern of transitions that have now been confirmed by isopic substitution with deuterium ··· HCCH. The originally identified transitions are likely 1,2-dfbz ··· Ne, which has a similar mass to the HCCH complex. Ab initio calculations for 1,2-dfbz ··· HCCH and 1,2-dfbz ··· Ne led to several possible orientations for each dimer with similar energies and rotational constants, and efforts to improve the computational methods and to reliably identify stationary points on the dimer potential energy surfaces are ongoing.

Transform Microwave Spectroscopy ··· Structure Determination and Chemical Interactions in H$_2$C-CHF: H$_2$C=CF$_2$ By Fourier-Transform Microwave Spectroscopy

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The weakly bound dimer involving fluorooethylene (FE) and 1,1-difluoroethylene (DFE) has been determined using a combination of chirped-pulse and resonant-cavity Fourier-transform microwave spectroscopy over a 7.5 to 19 GHz range. The rotational constants of the most abundant isotopeopmer were determined to be $A = 6601.14(35)$ MHz, $B = 833.35(65)$ MHz and $C = 744.02(175)$ MHz, and are in excellent agreement with ab initio predictions at the MP2/6-311+G(2d,2p) level. Observation of all four unique $^{13}$C isotopologues in natural abundance allowed for a full structure determination, showing that the dimer takes on a planar configuration with the H-C-F end of FE aligned with one of the F-C=C-H sides of DFE, forming two inequivalent CH···F contacts. The dipole moment components ($\mu_\parallel = 0.9002(18)$ D, $\mu_\perp = 0.0304(80)$ D) were determined using Stark effect measurements and confirmed the observed structure.

MILLIMETER WAVE SPECTROSCOPY AND EQUILIBRIUM STRUCTURE DETERMINATION OF PYRIMIDINE (m-Cl(H$_2$N)$_2$)

ZACHARY N. HEIM, BRENT K. AMBERGER, BRIAN J. ESSLERMAN, R. CLAUDE WOODS, ROBERT J. McMAHON, Department of Chemistry, The University of Wisconsin, Madison, WI, USA.

Pyrimidine, the meta substituted diazonium analog of benzene, has been studied in the mm-wave region from 260 – 360 GHz, expanding on previous studies up to 357 GHz. 14 The spectra of four of the singly-substituted $^{14}C$ and $^{15}N$ isotopologues were observed in natural abundance. Samples of deuterium enriched pyrimidine were synthesized, giving access to several deuterium-substituted isotopologues. The experimental rotational constants have been corrected for vibration-rotation coupling and electron mass. The vibration-rotation corrections were calculated with an anharmonic frequency calculation at the CCSD(T)/ANO1 level using CFOUR. An equilibrium structure determination has been performed using the corrected rotational constants with the xrefit module of CFOUR. Several vibrational satellites of pyrimidine have also been studied. Their rotational constants have been compared to those obtained computationally.

Phenyl isocyanate (PhNCO) has been studied in the frequency range of 250-360 GHz, improving on rotational and centrifugal distortion constants based on previous spectroscopic studies between 4.7 and 40 GHz. Using the rigid rotor/centrifugal distortion model, many transitions have been assigned for the ground state (approximately 2200 transitions) and the fundamental of the -NCO torsional vibration (approximately 1500 transitions) for J values ranging between 140 and 95 cm$^{-1}$.

MILLIMETER-WAVE SPECTROSCOPY OF PHENYL ISOCYANATE

CARA E. SCHWARZ, BRENT K. AMBERGER, BENJAMIN C. HAENNI, BRIAN J. ESSLERMAN, R. CLAUDE WOODS, ROBERT J. McMAHON, Department of Chemistry, University of Wisconsin, Madison, WI, USA.

Phenyl isocyanate (PhNCO) has been studied in the frequency range of 250-360 GHz, improving on rotational and centrifugal distortion constants based on previous spectroscopic studies between 4.7 and 40 GHz. Using the rigid rotor/centrifugal distortion model, many transitions have been assigned for the ground state (approximately 2200 transitions) and the fundamental of the -NCO torsional vibration (approximately 1500 transitions) for J values ranging between 140 and 95 cm$^{-1}$.

Broadband Microwave Spectroscopy as a Tool to Study the Structures of Odorant Molecules and Weakly Bound Complexes in the Gas Phase

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The rotational spectrum of trans-cinnamaldehyde (2E3-phenylprop-2-enal) has been obtained with chirped-pulse microwave spectroscopy in the frequency range of 2 - 8.5 GHz. The odorant molecule is the essential component in cinnamon oil and causes the characteristic smell. In the measured high-resolution spectrum, we were able to assign the rotational spectra of two conformers of trans-cinnamaldehyde as well as all singly $^{13}$C-substituted species of the lowest-energy conformer in natural abundance. Two different methods were used to determine the structure from the rotational constants, which will be compared within this contribution. In addition, the current progress of studying ether-alcohol complexes, aiming at an improved understanding of the interplay between hydrogen bonding and dispersion interaction, will be reported. Here, a special focus is placed on the complexes of diphenylether with small aliphatic alcohols.

The author thanks "The Hamburg Centre for Ultrafast Imaging" for financial support.
MICROWAVE SPECTRA OF 9-FLUORENONE AND BENZOPHENONE

Channing West, Galen Sedo, Department of Natural Sciences, University of Virginia’s College at Wise, Wise, VA, USA; Jennifer Van WingenArd, Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada.

The pure rotational spectra of 9-fluorenone (C\(_9\)H\(_8\)O) and benzophenone (C\(_8\)H\(_8\)O) were observed using chirped-pulse Fourier transform microwave spectroscopy (cp-FTMW). The 9-fluorenone spectrum was collected between 8 and 13 GHz, which allowed for the assignment of 124 rotational transitions. A separate spectrum spanning from 8 to 14 GHz was collected for benzophenone, allowing for the assignment of 133 rotational transitions. Both aromatic ketones exhibited strong b-type spectra with little to no centrifugal distortion, indicating highly rigid molecular structures. A comparison of the experimentally determined spectral constants of 9-fluorenone to those calculated using both ab initio and density functional theory strongly suggest the molecule conforms to a planar C\(_2\)v symmetric geometry as expected for its polycyclic structure. Whereas, a comparison of the experimental benzophenone constants to those predicted by theory suggests a molecule with a non-planar C\(_2\)v symmetry, where the two phenyl groups are rotated approximately 30° out-of-plane to form a paddlewheel-like geometry.

Assessing the Impact of Backbone Length and Capping on the Conformational Preferences of a Model Peptide: Conformation Specific IR and UV Spectroscopy of 2-Aminoisobutyric Acid

Joseph G. Gorden, Daniel M. Hewett, Department of Chemistry, Purdue University, West Lafayette, IN, USA; Matthew A. Kubaski, Department of Chemistry and Biochemistry, Fairfax University, Fairfax, CT, USA; Timothy S. Zwie, Department of Chemistry, Purdue University, West Lafayette, IN, USA.

2-Aminoisobutyric acid (Aib) is an achiral, α-amino acid having two equivalent methyl groups attached to C\(_2\). Extended Aib oligomers are known to have a strong preference for the adoption of a 3\(\alpha\)-helical structure in the condensed phase; here, we have taken a simplifying step and focused on the intrinsic folding propensities of Aib by looking at a series of capped Aib oligomers in the gas phase, free from the influence of solvent molecules and cooled in a supersonic expansion. Resonant two-photon ionization and BR-UV idfolumelengthening has been used to record single-conformation UV spectra using the Z-cap as the UV chromophore. Resonant anti-diab infrared (RADDIE) spectroscopy provides single-conformation IR spectra in the OH stretch and NH stretch regions. Data have been collected on a set of Z-Aib\(_n\)-X oligomers with n = 2, 4, 6 and X = OH and O-Methyl. The impacts of these capping groups and differences in backbone length have been found to dramatically influence the conformational preferences of these oligomers. Oligomers of n=4 have shown for the first time a complete turn of the 3\(\alpha\)-helix to be formed. Early interpretation of the data collected shows clear spectroscopic markers signaling the onset of helical structure as well as evidence of structures incorporating C\(_7\) and C\(_{14}\) hydrogen bonded rings.

This work has been supported by NASA Aura Science Team Grant NNX14AI55G and NASA Planetary Atmospheres Grant NNX13AI59G.
MH03 2:04 – 2:19
WORKING WITH HITRAN DATABASE USING HAPI: HITRAN APPLICATION PROGRAMMING INTERFACE
ROMAN V KOCHANOV, CHRISTIAN HILL, PIOTR WCISSLO, JOULI E GORDON, LAURENCE S. BOTH- MAN, XINCHU HUANG, and Astrophysics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA
JONAS WILZEWSKI, Department of Astronomy, Harvard University, Cambridge, MA, USA.
A HITRAN Application Programing Interface (HAPI) has been developed to allow users on their local machines more flexibility and power. HAPI is a programming interface for the main data-searching capabilities of the new “HITRAN-Online” web service (http://www.hitran.org). It provides the possibility to query spectroscopic data from the HITRAN database in a flexible manner using either functions or query language. Some of the prominent current features of HAPI are: a) downloading line-by-line data from the HITRAN online site to a local machine b) filtering and processing the data in SQL-like fashion c) conventional Python structures (lists, tuples, and dictionaries) for representing spectroscopic data. HAPI is designed to be used as a large set of third-party Python libraries to work with the data. HAPI is Python implementation of the HITRAN database, reduced to a substantial amount of work. Currently the API is a module written in Python and uses Numpy library providing fast array operations. It is designed to deal with data in multiple formats such as ASCII, CSV, HDF5 and XASIMS. This work has been supported by NASA Aura Science Team Grant NNX11AI59G and NASA Planetary Atmospheres Grant NNX11AI59G.

MH04 2:21 – 2:31
ACCELERATED INTENSITIES: A NEW METHOD OF COMPUTING EINSTEIN-A COEFFICIENTS
AHMED FARIS AL-REFAI, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom; SERGEI N. YURCHENKO, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom; JONATHAN TENNYSON, Department of Physics and Astronomy, University College London, London, UK, United Kingdom.

Abstract

The use of variational nuclear motion calculations to produce comprehensive molecular line lists is now becoming common. In order to produce high quality and complete line lists in particular applicable to high temperatures requires large amounts of computational resources. The more accuracy required, the larger the problem and the more computational resources needed. The two main bottlenecks in the production of these line lists are solving the eigenvalue problem and the computation of the Einstein-A coefficients. From the project’s recently released line lists, the number of transitions can reach up to 10 billion evaluated by the combination of millions of eigenvalues and eigenvectors corresponding to individual energy states. For line lists of this size, the evaluation of Einstein-A coefficients take up the vast majority of computational time compared to solving the eigenvalue problem. Recently, as part of the ExoMol [1] project, we have developed a new program called GPU Accelerated Intensities (GAIN) that utilises the highly parallel Graphics Processing Units (GPU) in order to accelerate the evaluation of the Einstein-A coefficients. Speed-ups of up to 700x can be achieved on a single GPU and can be further improved by utilising multiple GPUs. The GPU hardware, its limitations and how the problem was implemented to exploit parallelism will be discussed.

References


MH05 2:33 – 2:48
LINE SHAPE PARAMETERS FOR NEAR INFRARED CO2 BANDS IN THE 1.61 AND 2.06 MICRON SPECTRAL REGIONS
V. MALATHY DEVI, D. CHRIS BENNER, Department of Physics, College of William and Mary, Williamsburg, VA, USA; KEIYUOON SUNG, LINDA BROWN, TIMOTHY J CRAWFORD, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; MARY ANN H. SMITH, Science Directorate, NASA Langley Research Center, Hampton, VA, USA; ARLAN MANTZ. Department of Physics, Astronomy and Geophysics, Connecticut College, New London, CT, USA.

Accurate spectroscopic measurements of self- and air-broadened Lorentz half-width and pressure-shift coefficients and their temperature dependence exponents are crucial for the Orbiting Carbon Observatory (OCO-2) mission. Here we therefore analyzed 77 high-resolution high signal-to-noise spectra of CO2 and CO2-air mixtures and CO2 in OCO-2 channels at 1.61 and 2.06 μm. These spectra were recorded at various spectral resolutions (0.004-0.013 cm⁻¹) using two spectrometers: the Kist Peak PFT’s in Arizona and the Binkley 125HR PFT’s at the Jet Propulsion Laboratory in Pasadena, California. Different absorption cells with path lengths between 0.2 and 121 m were used with gas samples at a range of temperatures (170-297 K). The gas pressures ranged from 0.388 Torr for pure sample and 26-924 Torr for mixtures of CO2 and air with CO2 volume mixing ratios between 0.01 and 0.4. The cold sample spectra were acquired using a short 0.2038 m straight pass cell and a multipass Herriott cell having a 20.94 m total path A multiparameter fitting technique was employed to fit all the spectra simultaneously with a non-Voigt line shape profile including speed dependence and full line mixing. Examples of fitted spectra and retrieved parameters in both CO2 and CO2-air bands will be shown. Comparisons of some of the results with other published values will be provided.

MH06 2:50 – 3:05
RELIABLE IR LINE Lists FOR SO2 and CO2 ISOTOPOLOGUES COMPUTED FOR ATMOSPHERIC MODELLING ON VENUS and EXOPLANETS
XINCHU HUANG, Carl Sagan Center, SETI Institute, Mountain View, CA, USA; DAVID SCHWENKE, Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts, Lowell, MA, USA.

For SO2 atmospheric characterization in Venus and other Exoplanetary environments, recently we presented Ames-296K line lists for 626 upgraded) and other 4 symmetric isotopologues: 636, 646, 666 and 828. For CO2, we reported Ames-296K (1E−42 cm molK) and Ames-1008K (1E−38 cm molK) IR line lists up to E=18800 cm−1 for 13 CO2 isotopologues, including symmetric species 626, 636, 646, 666, 727, 827, 828, 838, and asymmetric species 627, 628, 637, 638, 728, 738. CO2 line shape parameters were also determined for different four temperature ranges: Mars, Earth, Venus, and higher temperatures. General line position prediction accuracy up to 5000 cm−1 (SO2) or 13000 cm−1 (CO2) is 0.01 – 0.02 cm−1. Most transition intensity deviations are less than 5−10%, when compared to experimental measured quantities. With such prediction accuracy, these SO2 and CO2 isotopologue lists are the best available alternative for those wide-spectra region missing from spectroscopic databases such as HITRAN and CDMS. For example, only very limited experimental data exist for SO2 046δ=3636 and no data at all for other minor isotopologues. They should greatly facilitate spectroscopic analyses in future laboratory or astronomical observations. Our line list work are based on “Best Theory + Reliable High-Resolution Experiment” strategy, i.e. using an ab inito potential energy surface refined with selected reliable high resolution experimental data, and high-quality CCS/DT’s from Kistiakowsky-Dipole moment surfaces. Note that we have solved a convergence defect on SO2 13C−12C. For further improvements the quality and completeness of the Ames-296K SO2 list by including most recent experimental data into the refinement. We will compare the Ames-296K SO2 and CO2 lists to latest experiments and HITRAN/CDMS models. We expect more interactions between experimental and theoretical efforts. Currently the Ames-296K lists are available at http://huang.seti.org/.
LASER SPECTROSCOPIC STUDY OF CaH IN THE B2Σ+ AND D2Σ+ STATES
KYOHEI WATANABE, KANAKO UCHIDA, KORI KOBAYASHI, FUSAKAZU MATSUMISHI, YOSHIKI NONAKAWA,
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Calcium hydride is one of the abundant molecules in the stellar environment, and is considered as a probe of stellar analysis. Ab initio calculations have shown that the electronic excited states of CaH have complex potential curves. It is suggested that the B2Σ+ state has an interesting double minimum potential due to the avoided crossing. Such a potential leads to drastic change of the rotational constants when the vibrational energy level goes across the potential barrier. Spectroscopic studies on CaH began in the 1920’s, and many studies have been carried out since then. Bell et al. extensively assigned the D2Σ+ → X2Σ+ bands in the UV region. Bernath’s group has observed transitions in the IR and visible regions and identified the upper states as the A2Π, B2Σ+, and B2Σ+ states. We have carried out a laser induced fluorescence (LIF) study in the UV region between 360 and 430 nm. We have produced CaH by using laser ablation of a calcium target in a hydrogen gas environment, then molecules have been excited by a second harmonic pulse of dye laser and the fluorescence from molecules have been detected by a photomultiplier. Determination of the D2Σ+ → X2Σ+ bands already identified by Bell et al. indicates the production of CaH. In addition, many other bands have been also found and a few bands have been assigned by using the combination differences, the lower state of these bands have been confirmed to the vibrational ground state of X2Σ+. We have tentatively assigned these bands as the B2Σ+ → X2Σ+ transition. We will discuss the assignment of these bands, together with the rotational constants comparing with those calculated from the ab initio potential.

EXPERIMENTAL LINE LISTS OF HOT METHANE
ROBERT J. HARGREAVES, PETER F. BERNATH, Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA.

Line lists of CH4 at high temperatures (up to 900 °C) have been produced between 2500 and 5000 cm−1. This spectral range contains the potential and overtone regions, and includes numerous fundamental, overtone and hot bands. Our method makes use of a quartz sample cell that is heated by a tube furnace. Four spectra are then recorded at each temperature using a Fourier transform infrared spectrometer at high resolution (0.02 cm−1). By combining these four spectra at each temperature, the emission and absorption from the cell and molecules are accounted for, and we obtain the true transmission spectrum of hot CH4. Analysis of this series of spectra enables the production of line lists that include positions, intensities and empirical lower state energies. We also compare our line lists to the best available theoretical line lists at high temperatures. Whilst our experimental line lists contain fewer lines than theoretical line lists, we are able to demonstrate the quality of our observed spectra by considering our observations as absorption cross sections. This is important at elevated temperatures, when numerous blended lines appear as a continuum.
CH$_3$D NEAR INFRARED CAVITY RING-DOWN SPECTRUM REANALYSIS AND IR-IR DOUBLE RESONANCE

SHAOYUE YANG, GEORGE SCHWARTZ, Department of Physics, The University of Virginia, Charlottesville, VA, USA; KEVIN LEHMANN, Departments of Chemistry and Physics, University of Virginia, Charlottesville, VA, USA.

As one of the most important hydrocarbon prototype molecules, CH$_3$D's overtone band in near infrared region has not been well studied. Various methods were used to help identifying transitions from previous cavity ring down spectrum of CH$_3$D in the near infrared region. Symmetric top molecules' Hamiltonian diagonal terms for the ground state, perpendicular state and parallel state were simulated by software PClopher. Combination differences were used to find possible pairs of transitions starting from adjacent ground state and ending in same excited states. Also we introduced our temperature controlled spectrum setup for ground state energy and rotational quanta prediction from temperature dependence, and proven to be working well for lower J levels for CH$_3$D. At last, we set up a double resonance system, using two lasers (3.3 and 1.65 μm, respectively) to excite transitions from the same ground state, to provide strong proof for the lower state quanta.

AYTY: A NEW LINE-LIST FOR HOT FORMALDEHYDE

AHMED FARIS AL-REFAIE, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom; SERGEI N. YURCHENKO, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom; JONATHAN TENNYSON, Department of Physics and Astronomy, University College London, London, IX, United Kingdom; ANDREY YACHMENEV, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom.

Abstract

The ExoMol [1] project aims at providing spectroscopic data for key molecules that can be used to characterize the atmospheres of exoplanets and cool stars. Formaldehyde (H$_2$CO) is of growing importance in studying and modelling terrestrial atmospheric chemistry and dynamics. It also has relevance in astrophysical phenomena that include interstellar medium abundance, proto-planetary and cometary ice chemistry and masers from extra-galactic sources. However there gaps in currently available absolute intensities and a lack of higher rotational excitations that makes it infeasible to accurately model high temperature systems such as hot Jupiters. Here we present AYTY [2], a new line list for formaldehyde applicable to temperatures up to 1500 K. AYTY contains almost 10 million states reaching rotational excitations up to $J = 70$ and over 10 billion transitions at up to 10 000 cm$^{-1}$. The line list was computed using the variational ro-vibrational solver TROVE with a refined ab-initio potential energy surface and dipole moment surface.

References


Helium atoms can attach to molecular cations via ternary collision processes forming weakly bound ($\approx 1$ kcal/mol) He–M$^+$ complexes. We developed a novel sensitive action spectroscopic scheme for molecular ions based on an observed rotational state dependency of the He attachment process [1]. A detailed account of the underlying kinetcs will be presented on the example of the CD$_3^+$ ion, where we study an induction of about 50% for the rotational state dependent ternary He–attachment rate coefficient of the $J = 1 \rightarrow 0$ level. Experiments are performed on mass-selected ions stored in a temperature-variable ($T \approx 3$ K) cryogenic rf 22-pole ion trap in the presence of a high number density of He ($\approx 10^{14}$). [2] Rotational spectra of the bare ions are recorded by measuring the change in the number of formed He$^+$ complexes after a certain storage time as a function of excitation wavelength. Here we will also present the first measurements of the rotational ground state transitions of CF$_3^+$ ($J = 1 \rightarrow 0$, unresolved) and NH$_2D^+$ ($J_a = 1 \rightarrow 0$, $h$-resolved), recorded in this way.


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**MI02 1:47 – 2:02**

**SYMMETRY BEYOND PERTURBATION THEORY: FLOPPY MOLECULES AND ROTATION-VIBRATION STATES**

**HANNÖ SCHMIEDT, STEPHAN SCHELMER, I. Physikalisches Institut, Universität zu Köln, Köln, Germany; HANSI JENSEN, Fachbereich C-Physikalische und Theoretische Chemie, Bergische Universität Wuppertal, D-42097 Wuppertal, Germany.

In the customary approach to the theoretical description of the nuclear motion in molecules, the molecule is seen as a near-static structure rotating in space. Vibrational motion causing small structural deformations induces a perturbative treatment of the rotation-vibration interaction, which fails in floppy molecules, where all rotational vibrations are large compared to the linear extension of the molecule. An example is protonated methane (CH$_4^+$). For this molecule, customary theory fails to simulate reliably even the low-energy spectrum. Within the traditional view of rotation and vibration being near-separable, rotational and vibrational wavefunctions can be symmetric classified separately in the molecular symmetry (MS) group. In the present contribution we discuss a fundamental group theoretical approach to the problem of determining the symmetries of molecular rotation-vibration states. We will show that all MS groups discussed so far are subgroups of the special orthogonal group in three dimensions SO(3). This leads to a group theoretical foundation of the technique of equivalent rotations. The MS group of protonated methane (CH$_4^+$) represents, to the best of our knowledge, the first example of an MS group which is not a subgroup of SO(3) (nor of SO(3) or SU(2)). Because of this, a separate symmetry classification of vibrational and rotational wavefunctions becomes impossible in this MS group, consistent with the fact that a decoupling of rotational and vibrational motion is impossible. We want to discuss the consequences of this. In conclusion, we show that the prototypical floppy molecule CH$_4^+$ represents a new class of molecules, where usual group theoretical methods for determining selection rules and spectral assignments fail so that new methods have to be developed.

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**MI03 2:04 – 2:19**

**STUDYING ROTATION/TORSION COUPLING IN H$_2^+$ USING DIFFUSION MONTO CARLO**

**MELANIE L. MARLETT, ZHOU LIN, ANNE B McCOY, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA.

H$_2^+$ is a highly flexible intermediate found in interstellar clouds. The rotational/bond coupling in this molecule are of great interest due to the unusually large coupling between these modes. However, theoretical studies of highly flexional molecules like H$_2^+$ are challenging due to the lack of a good zero-order model. In order to better understand the rotation/vibration interaction, a method has been developed to model the rotational/bonded motions. This method is based upon diffusion Monte Carlo (DMC). In this approach, the vibrational contribution to the wavefunction is modeled using standard DMC approaches, while the rotational/bond coupling is treated as a set of coefficients that are assigned to the various rotational/bonded state vectors. The potential portion of the Hamiltonian is expressed as a low-order expansion in terms of the torsion angle between the two outer H$_2$ units. The expansion coefficients are evaluated at each time step for each walker and depend on the $3N−7$ other internal coordinates. The transition frequencies obtained from this method for $J = 1$ agree well with results obtained using other methods such as fixed-node diffusion Monte Carlo. This new method is advantageous over the torsion angle approach because it allows for multiple state calculations at once which saves on computation time.

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**MI04 2:21 – 2:36**

**HIGH-ROTATIONAL LINES OF $^{13}$C ISOTOPOLOGUES OF HCO$^+$ MEASURED BY USING EVENSON-TYPE TUNABLE FIR SPECTROMETER**

**MARU SUZUKI, KYO DISHI, YOSHIKI MORIWA, FUKAOKAZU MATSUSHIMA, Department of Physics, University of Toyama, Toyama, Japan, TAKAYOSHI AMANO, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

Frequencies of high-rotational lines of HCO$^+$ and its isotopologues have been measured precisely by using an Evenson-type spectrometer in Toyama. The tunable far-infrared spectrometer (TuFIR in short) is based on synthesizing terahertz radiation from two mid-infrared CO$_2$ laser lines and one microwave source. Study of the isotopologues containing H or D, $^{13}$C, and $^{18}$O were reported last year. In the present work, isotopologues of H or D, $^{13}$C, and $^{18}$O have been studied. The HCO$^+$ ions are produced by discharging a $^{13}$CO$_2$ H$_2$ (or D$_2$), and Ar mixture in an extended negative glow discharge cell cooled with liquid nitrogen. Because the low-rotational lines have been investigated, our present study was focused mainly to the measurements of higher-J rotational lines. Currently we have observed the lines $J+1 \leftarrow J$ for HCO$^+$, and $J = 1 \leftarrow 0$ for $^{13}$CO$_2$ H$_2$. Molecular constants for these isotopologues (B, D, H, L) have been modified. From the analysis of the intensity of each rotational line, we estimate the rotational temperature to be as low as 140K. This low temperature makes it difficult to measure yet higher-J lines. Measurement of other isotopogues $H$, L) have been modified. From the analysis of the intensity of each rotational line, we estimate the rotational temperature to be as low as 140K. This low temperature makes it difficult to measure yet higher-J lines. Measurement of other isotopogues such as containing oxygen isotopes is now in preparation.

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**MI05 2:38 – 2:48**

**UV-UV HOLE-BURNING SPECTROSCOPY OF A PROTONATED ADENINE DIMER IN A COLD QUADRUPOLE ION TRAP**

**HYUK KANG, Department of Chemistry, Ajou University, Suwon, Korea.

A novel method for double-resonance photofragmentation spectroscopy in a cold quadrupole ion trap has been developed and utilized to differentiate the structures of a cold protonated adenine dimer. A burn laser generates a population pool of a certain conformer of the dimer stored in a cold quadrupole ion trap, and an auxiliary dipolar RF ejects the photofragments by the burn laser from the trap. A probe laser detects depletion of a certain conformer by the burn laser, and a conformer-specific UV or IR spectrum of a cold ion is obtained by scanning the wavelength of the burn or the probe laser. This simple and versatile method is applicable to any type of double-resonance photofragmentation spectroscopy in a cold quadrupole ion trap. To demonstrate its capability, it was applied to UV-UV hole-burning spectroscopy of a protonated adenine dimer. It is proved that a cold protonated adenine dimer has at least two hydrogen-bonding geometries and each has multiple electronically excited states with significantly different spectral bandwidths, possibly due to different excited state dynamics.
ERIN M. DEUFFY, BRETT MARSH, JONATHAN VOSS, ETIENNE GARAND, Department of Chemistry, University of Wisconsin, Madison, WI, USA.

The splitting of $\text{H}_2$O into $\text{H}_2$ and $\text{O}_2$ is an attractive option for alternative energy, but the oxygen evolution step poses a significant challenge. A decades-long effort to produce a suitable water oxidation catalyst (WOC) has made progress on this front, but the precise reaction mechanism of these catalysts is still not well understood. One of the most extensively studied WOCs is $\text{Ru(tpy)(bpy)(OH)}_2^{4+}$ (tpy = 2,2′,6,2′-terpyridine, bpy = 2,2′-bipyridine). Presented here are gas-phase infrared spectra of water clusters of $[\text{Ru(tpy)(bpy)}_2\text{OH}]^{n+}$ and the first intermediate of the catalytic cycle, $[\text{Ru(tpy)(bpy)}_2\text{OH}]^{n+}$. In particular, the O-H stretches are used as a probe of solvation strength, and trends in their spectral shifts are examined as a function of cluster size. With the aid of density functional theory (DFT) calculations, these spectra reveal structural changes induced by solvation that provide clear evidence for proton-coupled electron transfer (PCET), in support of proposed mechanisms.

M107
3:07 – 3:22
PRONING SOLVATION SHELLS OF Ni(H$_2$O)$_{n+}$ (n=4–10) AND Ni(OH)(H$_2$O)$_{n+}$ (n=2-5) WITH CRYOGENIC ION VIBRATIONAL SPECTROSCOPY.

JONATHAN VOSS, BRETT MARSH, JIA ZHOU, ETIENNE GARAND, Department of Chemistry, University of Wisconsin, Madison, WI, USA.

The solvation of metal cations, a process that dictates chemistry in both catalytic and biological systems, has been well studied using gas-phase spectroscopy. However, until recently the solvation of cation-anion pairs has been poorly explored. Here we present gas-phase spectra of $\text{Ni(H}_2\text{O)}_{n+}$ (n=4-10) and $\text{Ni(OH)(H}_2\text{O)}_{n+}$ (n=2-5) obtained via cryogenic ion vibrational spectroscopy (CIVS). Our results indicate that as cluster size decreases, the $\text{Ni(OH)(H}_2\text{O)}_{n+}$ moiety becomes more favorable over the $\text{Ni(H}_2\text{O)}_{n+}$ moiety. Analysis of the spectral data in conjunction with density functional theory calculations shows that both species have a 1$^+$ solvation shell consisting of six ligands. However, the $\text{Ni(OH)(H}_2\text{O)}_{n+}$ clusters show strong interactions between a first solvation shell water ligand and the OH$^-$ group of the metal, similar to the interactions previously observed in $\text{Cu(OH)}_{2n+}$ and $\text{Mg(OH)}_{2n+}$.5.

M108
3:24 – 3:39
MICROSOLVATION OF THE Mg$_2$SO$_4^{2+}$ CATION: CRYOGENIC VIBRATIONAL SPECTROSCOPY OF (Mg$^{2+})_n$SO$_4^{2-}$ (H$_2$O)$_{n-11}$.

PATRICK J. KELLISHER, JOSEPH W DePALMA, Department of Chemistry, Yale University, New Haven, CT.

EVA CHRISTOPHER JOHNSON, Department of Chemistry, Stony Brook University, Stony Brook, NY, USA.

JOSEPH FOURNIER, MARK JOHNSON, Department of Chemistry, Yale University, New Haven, CT, USA.

Cryogenic ion vibrational predissociation (CVP) spectroscopy was used to examine the onset of solvation upon the incremental addition of water molecules to the Mg$_2$SO$_4^{2+}$ (H$_2$O)$_n$ cation (n = 4 – 11). D$_2$ predissociation spectra are reported for each cluster over the range 1000-3800 cm$^{-1}$. Initially, the Mg$^{2+}$ atoms each interact with two oxygen atoms on the sulfate anion in a bifurcated arrangement. The breaking of this motif occurs upon addition of the eighth water molecule as evidenced by splitting of the water bend, and broad absorption in the 3000-3400 cm$^{-1}$ range indicative of hydrogen bonding between the water molecules and sulfate ion.

Intermission

M109
3:58 – 4:13
CAPTURE AND STRUCTURAL DETERMINATION OF ACTIVATED INTERMEDIATES IN NICKEL CATALYZED CO$_2$ REDUCTION.

STEPHANIE CRAIG, FABIAN MENGES, ABRON WOLK, JOSEPH FOURNIER, Department of Chemistry, Yale University, New Haven, CT, USA.

KNIKLA TOTSCH, Physikalische Chemie II, Ruhr University Bochum, Germany; MARK JOHNSON, Department of Chemistry, Yale University, New Haven, CT, USA.

The catalyzed reduction of CO$_2$ is an important step in the conversion of this small molecule into liquid fuels. Nickel 1,4,8,11-tetraazacyclotetradecane, (NHC), is a well-known catalyst for the reduction of CO$_2$ in solution. Cryogenic ion vibrational predissociation (CVP) spectroscopy of CO$_2$-messenger tagged ions cooled in a temperature controlled ion trap (PCET), in support of proposed mechanisms.

M110
4:15 – 4:30
THRESHOLD IONIZATION SPECTROSCOPIC CHARACTERIZATION OF La ATOM REACTION WITH ISOPRENE.

WENJIN CAO, DONG-SHENG YANG, Department of Chemistry, University of Kentucky, Lexington, KY, USA.

The reaction between La atom and isoprene (CH$_2$=CHC($\text{H})_3$=CH$_2$) was investigated in a supersonic molecular beam source and investigated by mass-analyzed threshold ionization spectroscopy (MATI) and theoretical calculations. Preliminary data analysis shows that La(CH$_2$=CHC($\text{H})_3$=CH$_2$) has a triangle structure (C$_3$v) with Ce binding to the two terminal carbon atoms of butadiene. The ground states of both species are triplets with a 4f$^6$La Ce-based electron configuration and those of the corresponding ions are doublets from the removal of the 6s$^2$ electron. The Ce(CH$_2$=CHC($\text{H})_3$=CH$_2$) complex is formed by ethylene dehydration, whereas Ce(CH$_2$=CHC($\text{H})_3$=CH$_2$) by ethylene dehydrogenation and carbon-carbon bond coupling. The MATI spectra of Ce(CH$_2$=CHC($\text{H})_3$=CH$_2$) and Ce(CH$_2$=CHC($\text{H})_3$=CH$_2$) are rather similar to those of the corresponding La complexes previously observed by our group, except that the spectra of the Ce complexes exhibit two electronic transitions with almost identical vibrational intervals. This observation suggests that the existence of a 4f electron results in an increased complexity of the electronic spectra and states of the lanthanide hydrides.
STRUCTURE DETERMINATION OF CISPLATIN-AMINO ACID ANALOGUES BY INFRARED MULTIPLE PHOTON DISSOCIATION ACTION SPECTROSCOPY

CHENCHEN HE, XUN BAO, YANLONG ZHUI, STEPHEN STROBEHEN, BEINT KI MUTCAL, Y-W YE, N-S CHOW, M-T RODGERS, Department of Chemistry, Wayne State University, Detroit, MI, USA; JUEHAN GAO, J. OOMENS, Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands.

To gain a better understanding of the binding mechanism and assist in the optimization of relevant drug and chemical probe design, both experimental and theoretical studies were performed on a series of amino acid-linked cisplatin derivatives, including glycine-, lysine-, and ornithine-linked cisplatin, Gplatin, Kleptin, and Oplatin, respectively. Cisplatin, the first FDA-approved platinum-based anticancer drug, has been widely used in cancer chemotherapy. Its pharmacological mechanism has been identified as its ability to coordinate to genomic DNA, and guanine is its major target. In previous reports, cisplatin was successfully utilized as a chemical probe to detect solvent accessible sites in ribosomal RNA (rRNA). Among the amino-acid-linked cisplatin derivatives, Oplatin exhibits preference for adenine over guanine. The mechanism behind its different selectivity compared to cisplatin may relate to its potential of forming a hydrogen bond between the carboxylate group in Pt(II) complex and the 6-amino moiety of adenine stabilizes A-Oplatin products. Tandem mass spectrometry analysis also indicates that different coordination sites of Oplatin on adenine affect glycosidic bond stability.

Infrared multiple photon dissociation (IRMPD) action spectroscopy experiments were performed on all three amino acid-linked cisplatin to characterize their structures. An extensive theoretical study has been performed on Gplatin to guide the selection of the most effective theory and basis set based on its geometric information. The results for Gplatin provide the foundation for characterization of the more complex amino acid-linked cisplatin derivatives, Oplatin and Kleptin. Structural and energetic information elucidated for these compounds, particularly Oplatin reveal the reason for its alternative selectivity compared to cisplatin.

UNRAVELING PROTON TRANSFER IN STEPWISE HYDRATED N-HETEROCYCLIC ANIONS

JOHN T. KELLY, NATHAN I HAMMER, Chemistry and Biochemistry, University of Mississippi, Oxford, MS, USA; KEF BOWEN, Department of Chemistry, Johns Hopkins University, Baltimore, MD, USA; GREGORY S. TSCHUMPER, Chemistry and Biochemistry, University of Mississippi, Oxford, MS, USA.

Depending upon the number and location of nitrogen atoms in a N-heterocyclic azabenzene, the addition of a single water molecule can result in a positive electron affinity. The transfer of a proton from a solvating water azine base can be induced by excess electron attachment. Here we explore this phenomenon through the use of photoelectron spectroscopy and electronic structure theory. Carefully calibrated density functional theory (DFT) computations indicate that the excess electron predominantly resides in a σ* orbital of the heterocycle.
Chair: Leah C O’Brien, Southern Illinois University, Edwardsville, IL, USA

MJ. Small molecules
Monday, June 22, 2015 – 1:30 PM
Room: 217 Noyes Laboratory

DEPERTURBATION ANALYSIS FOR THE a σ and c σ′: STATES OF C2
JAN TANG, WANG CHEN, KENTAROU KAWAGUCHI, Graduate School of Natural Science and Technology, Okayama University, Okayama, Japan.

In the last symposium and a recent paper, we reported a simultaneous analysis for the Phillips and Ballik-Ramsay band systems with a deperturbation treatment for the X σ+ and B σ−: states of C2 and also, for the first time, the observation of the forbidden transitions between the singlet and triplet states of C2. In the present study, we consider the interaction between the a σ: and c σ′: states to remove some anomalies in the higher order constants of the a σ: state presented in the previous work. The local interaction between the a σ: v=7 and c σ′: v=1 states was considered in a recent analysis for the perturbation of the spectrum. We consider the interaction between all the vibrational levels of the two electronic states with a set of Dunham-like constants. The progress and results will be presented.

MJ01 1:30 – 1:45

HIGH-RESOLUTION LASER SPECTROSCOPY OF THE A 3 Σ+ ← X 1 Σ+ SYSTEM OF ICl IN 0.7 μm REGION.
NORIO NISHIMIYA, TOKIO YUKIYA, MASAO SUZUKI, Faculty of Engineering, Tokyo Polytechnic University, Atsugi, Japan; ROBERT J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada.

Spectroscopic data for the A 3 Σ+ ← X 1 Σ+ states of ICl have been obtained by many researchers using grating spectrometers and Fourier-transform infrared spectrometers. In a previous paper we reported the measurement of doppler limited electronic v-r-rotational absorption lines of the A 3 Σ+ ← X 1 Σ+ system of ICl using a source modulation method, and new Mass-reduced Dunham coefficients were reported for the X-state. However, it is becoming increasingly common to analyse molecular spectroscopic data using the “direct-potential-fit” (DPF) method in which observed transition energies are fitted to simulated spectra generated from analytic models for the potential energy function(s). This method tends to require fewer fitting parameters than traditional Dunham analyses, as well as having more robust extrapolation properties in both the v and J domains. The present work combines all available previously reported data for the A 3 Σ+ ← X 1 Σ+ states with new measurements up to v’ = 10 in the 0 θ 1μm region obtained with a tune burst method using a Ti:Sapphire Ring Laser (M Squared Ltd SolTiS CW with Tera-scan) in the first DPF analysis reported for this system. The results of this study and our new fully analytic potential energy functions for the A 3 Σ+ ← X 1 Σ+ states of ICl will be presented.

MJ02 1:47 – 2:02

THE NEAR-INFRARED SPECTRUM OF NCl: ANALYSES OF THE (0,1), (1,0), & (2,1) BANDS OF SYSTEM G AND THE (1,0) BAND OF SYSTEM H.
JACK C HARRIS, COURTNEY N GIPSON, ETHAN M GRAMES, JAMES J O’BRIEN, Chemistry and Biochemistry, University of Missouri, St. Louis, MO, USA; LEAH C O’BRIEN, Department of Chemistry, Southern Illinois University, Edwardsville, IL, USA.

The near-infrared spectrum of nickel chloride, NCl, has been recorded at high resolution using intracavity laser absorption spectroscopy. The NCl molecules were produced in a plasma discharge of a nickel hollow cathode from a trace amount of CCl4 using Ar as the sputter gas. Spectra were collected from 12,490-12,660 cm−1 using 5 cm−1 scans. The (0,1), (1,0), and (2,1) bands of the [13.0] IΠ2→[12.9] IΠ3 transition, System G, were observed at 12,537 cm−1, 13,352 cm−1, and 13,318 cm−1, respectively. The (1,0) band of the [12.3] IΠ3→[12.2] IΠ4 transition, System H, was observed at 12,645 cm−1. Analyses of these bands will be presented.

MJ03 2:04 – 2:19

HIGH RESOLUTION LASER SPECTROSCOPY FOR ABSORPTION TO LEVELS LYING NEAR THE DISSOCIATION LIMIT OF THE A 3 Σ+ STATE OF IBr.
TOKIO YUKIYA, NORUO NISHIMIYA, MASAO SUZUKI, Faculty of Engineering, Tokyo Polytechnic University, Atsugi, Japan; ROBERT J. LE ROY, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada.

Spectroscopic data involving levels lying near the dissociation limit are very important for determining accurate molecular well depths and full potential energy curves. In previous work, we have reported the potential functions and values of parameters D and r1 for the A 3 Σ+ and B 1 Σ+ states of IBr.** That study used data extending to v′(A) = 29 and determined anomalous fluctuations in the ν-dependence of the first differences of ΔHν = Bν−1−Bν for levels v′ = 27–29 of the A 3 Σ+ state which, surprisingly, seems to have been smoothly accounted by a fitted potential energy function that shows no visually perceptible irregularities. In the present work, a Ti:Sapphire ring laser/M Squared LASERS Ltd. SolTiS CW with Tera-scan) has been introduced to probe the 0 θ 1μm region closer to the dissociation limit and examine whether the anomalous ΔHν behaviour expends further up the well. The results of this study will be presented.

MJ04 2:21 – 2:36

ANALYSIS OF EMISSION SPECTRA OF YTTRIUM MONOIODIDE PRODUCED BY THE PHOTODISSOCIATION OF YI.
WEVERT WENDY CHEN, THOMAS C. GALVIN, THOMAS J. HOCHALAN, JR., J. GARY EDEN, Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, USA.

Emission spectra of yttrium monoxide (YI) spanning the 250 - 940 nm spectral region were generated by the photodissociation of yttrium tri-iodide under photoexcitation at 248 nm (KrF laser). Fluorescent spectra in the 13,000 - 19,000 cm−1 and 24,000 - 40,000 cm−1 regions will be first reported. New vibrational transitions of YI in the 20,000 - 25,000 cm−1 interval will be presented as well.
GESTATION OF VIBRATIONALLY EXCITED HCP FROM A STABLE SYNTHETIC PRECURSOR
ALEXANDER W. HULL, JUN... close to
the dissociation energy in agreement with the phase space theory predictions.

GENERATION OF VIBRATIONALLY EXCITED HCP FROM A STABLE SYNTHETIC PRECURSOR

ALEXANDER W. HULL, JUN... close to the dissociation energy in agreement with the phase space theory predictions.

INTERMISSION

DFF ANALYSES YIELD FULLY ANALYTIC POTENTIALS FOR THE B'1Π, "BARRIER" STATES OF Rb2 and L24 AND AN IMPROVED GROUND-STATE WELL DEPTH FOR H2
KAI LAUTHER, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada; NIKESH S. JATTAN, Graduate School of Science, Department of Chemistry, Kyoto University, Kyoto, Japan; CLAUDE E. AMIOT, Laboratoire Aimé Cotton, CNRS, Orsay, France; AMANDA J. ROSS, UMR 5306, IEM University Lyon 1 and CNRS, Villeurbanne, France; ROBERT J. LE ROY1, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada.

Determination of full model potential energy functions for molecular states that have a ‘natural’ rotationless barrier which protrudes above the potential asymptote, such as the B'1Π states of alkali dimers, is a challenging problem. The present work extends our previous Direct-Potential-Fit (DFF) analyses of data for the B'1Π state of Li2 by introducing a more sophisticated model for the long-range tail of the fully analytic ‘Double Exponential Long-Range’ (DELR) potential function form that takes account of the interstate coupling that occurs near the asymptotes of the sets of nS or nP alkali dimers. This type of analysis is then applied to data for the B'1Π state of Rb2, and a concurrent extension of the DFF analysis of Soto and Le Roy1 yields an improved fully analytic potential energy function for its ground X'1Σg+ state. The effect of taking account of the long-range inter-state coupling on the shapes of the outer walls of the B'1Π state potential functions for these two species will also be examined.

3M. Aubert-Frècon and G. Hadinger and S. Magnier and S. Rousseau, AMIOT, Waterloo, ON, Canada.

PHOTO-DISSIPATION RESONANCES OF JET-COOLLED NO2 AT THE DISSOCIATION THRESHOLD BY CW-CRDS, CHALLENGING RRKM THEORIES
PATRICK DUPRÉ, Laboratoire de Physico-Chimie de l’Atmosphère, Université du Littoral Côte d’Opale, Dunkerque, France.

Around 398 nm, the jet-cooled NO2 spectrum exhibits a well identified dissociation threshold (Dh). Combining LIF detection and continuous-wave absorption-based CRDS technique a frequency range of ~25 cm−1 is analyzed at high resolution around Dh. In addition to the usual rovibronic transitions of long-lived energy levels, ~115 wider resonances are observed. Over this energy range, the resonance widths spread from ~0.008 cm−1 (~450 μm) to ~0.7 cm−1 (~4 ps) with large fluctuations. At least two ranges of resonance width can be identified when increasing the excess energy. They are associated with the opening of the dissociation channels NO2 → NO (X'1Πg, ν = 0, J = 1/2) + O (3P1) and NO2 → NO (X'1Πg, ν = 0, J = 3/2) + O (3P2). Weighted mean unimolecular dissociation rate coefficients kb, are calculated. The density of reactants (following the RRKM predictions) is deduced, and it will be discussed versus the density of transitions, the density of resonances and the density of vibronic levels. The data are analyzed in the light of time-resolved data previously reported. This analysis corroborates the existence of loose transition states along the reaction path close to the dissociation energy in agreement with the phase space theory predictions.

SELF- AND CO2-BROADENED LINE SHAPE PARAMETERS FOR THE $\nu_2$ AND $\nu_3$ BANDS OF HDO

V. MALATHY


Knowledge of CO2-broadened line widths and their temperature dependence exponents are required to interpret atmospheric spectra of Mars and Venus. We therefore used nine high-resolution, high signal-to-noise spectra of HDO and HDO+CO2 mixtures to obtain broadening coefficients for transitions of the $\nu_2$ and $\nu_3$ vibrational bands located at 7.13 and 2.70 μm, respectively. The gas samples were prepared by mixing equal amounts of high-purity distilled H2O and a 99% enriched D2O sample. Spectra at different temperatures (255-296 K) were obtained using a 20.38 cm-long cold-atom cell installed in the sample compartment of the Bruker 125HR Fourier transform spectrometer at the Jet Propulsion Laboratory, Pasadena, CA, USA. The retrieved parameters included accurate line positions, intensities, self- and CO2-broadened half-width and pressure-shift coefficients and the temperature dependences of CO2 broadened HDO. The spectroscopic parameters for many transitions were obtained simultaneously by multitemperature fitting of all nine spectra in each band. A non-Voigt line shape with speed dependence was applied. Line mixing was also observed for several transition pairs. Preliminary results will be compared to other recent measurements reported in the literature.

The laser induced fluorescence (LIF) spectrum of $\Delta v=0$ to $\Delta v=4$ states of $S^1\nu_3$ SiCN was produced, as well as rotational information of both isotopologues. With known quantum assignments given for 45% of the features, over 4750 experimental line positions and 3300 line intensities were fitted with RMS standard deviations of 0.004 cm$^{-1}$ and 8.9%, respectively. The complete understanding of the $\tilde{C}_2$ state potential energy surface near the equilibrium geometry and it is relevant to the question of how vibronic coupling between $C^2\Pi$ state and higher lying $A^2\Pi$ state(s) give rise to unequal S-O bond lengths.

INTERNAL FORCE FIELD DETERMINATION OF $C^1\Pi_2$ STATE OF SO$_2$

LINDA BROWN, ARLAN MANTZ, TIMOTHY J. CRAWFORD, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; ANDREI V. NIKITIN, SERGEY TASHKUN, Atmospheric Spectroscopy Div., Institute of Atmospheric Optics, Tomsk, Russia; MICHAEL REY, VLADIMIR TYUTEREV, Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7351, Université de Reims, Reims Cedex 2, France; MARY ANN H. SMITH, Science Directorate, NASA Langley Research Center, Hampton, VA, USA; ROBERT R. GAMACHE, Department of Physics, Astronomy and Geophysics, Connecticut College, New London, CT, USA; ROBERT W. FIELD, Department of Chemistry, MIT, Cambridge, MA, USA.

A new study of 13CH$_3$ line positions and intensities in the Octad region between 3400 and 4800 cm$^{-1}$ will be reported. Nine spectra were recorded with two Fourier transform spectrometers (the McMath-Pierce FTS at Kitt Peak Observatory and the Bruker 125 HR FTS at the Jet Propulsion Laboratory) using 13C-enriched samples at temperatures from 299 K to 80 K. Line positions and intensities were determined by non-linear least squares curve-fitting procedures and analyzed using the effective Hamiltonian and the effective Dipole moment expressed in terms of irreducible tensor operators adapted to spherical top molecules. Quantum assignments were found for all the 24 sub-vibrational states of the Octad (some as high as J=10). Over 4750 experimental line positions and 3300 line intensities were fitted with RMS standard deviations of 0.004 cm$^{-1}$ and 6.9%, respectively. A new list of over 9680 measured positions and intensities from 3600 to 4735 cm$^{-1}$ was produced, with known quantum assignments given for 45% of the features.

Part of the research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, NASA Langley Research Center, and Connecticut College, under contracts and cooperative agreements with the National Aeronautics and Space Administration. The support of the Groupement de Recherche International SAMIA between CNRS (France) and RFFR (Russia) is acknowledged.
BONDING AT THE EXTREME: DETECTION AND CHARACTERIZATION OF THORIUM DIMER, Th₂

TIMOTHY STEMLE, SETH MUSCARELLA, DAMIAN L. KOKKIN, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, USA.

Due to the difficulty of working with actinides (radioactive, short lifetimes) and the number of electrons in these systems our chemical understanding either experimentally or theoretically on these systems is very limited. The electronic spectrum of thorium dimer, Th₂, is expected to be heavily congested due to the predicted twelve electronic states within an energy less than 1 eV of the calculated Σg ground state. The chemical bond is predicted to be a quadruple bond in both the ground state and low lying Σu+ ground state (ΔT=+400 cm⁻¹). Experimentally Th₂ was detected in the gas phase by mass spectrometry.

Here we report on the detection of the gas fluorescence spectrum of Th₂ in the 495-560 nm range via application of 2D LIF spectroscopy and attempts to record high resolution field free and Zeeman spectra.

TA02
8:47 – 9:02
THE QUINTESSENTIAL BOND OF MODERN SCIENCE. THE DETECTION AND CHARACTERIZATION OF DIATOMIC GOLD SULFIDE, AuS.

DAMIAN L. KOKKIN, RUCHAN ZHANG, TIMOTHY STEMLE, Department of Chemistry, Biochemistry, Arizona State University, Tempe, AZ, USA; BRADLEY W. PEARLMAN, IAN A. WYSE, THOMAS D. VAR, HERG, Chemistry Department, Macalester College, Saint Paul, Minnesota, USA.

The gold sulfur bond is becoming ever more important to a vast range of scientific endeavors. We have recorded the electronic spectrum of gas-phase AuS, at vibrational resolution, over the 440-740 nm wavelength range. By application of a symmetric production technique, but hollow-cathode spattering source and cold laser ablation molecular beam source, excitation from both spin components of the inverted ¹Σ⁺ ground state is possible. Excitation into four different excited electronic states involving approximately 100 red-degraded bands has been observed. The four excited states have been characterized as Σʊ, Π_1, Π_2, Π_3, and Σ_2. The observed red-degraded vibronic bands where then globally analyzed to determine an accurate set of term energies and vibrational constants for the excited and ground electronic states. The electronic configurations from which these states arise will be discussed.

TA03
9:04 – 9:19
LASER SPECTROSCOPY OF RUTHERFORD CONTAINING DIATOMIC MOLECULES: RuH₂ and RuP.

ALLAN G. ADAM, RICARDA M. KONDER, NICOLE M. NICKERSON, Department of Chemistry, University of New Brunswick, Fredericton, NB, Canada; COLAN LINTON, D. W. TOKARYK, Department of Physics, University of New Brunswick, Fredericton, NB, Canada.

In the last few years, the Cheung group in Hong Kong and the Steimle group in Arizona have successfully studied several ruthenium containing diatomic molecules, RuX (X = C, O, N, B, P), using the laser-ablation molecular jet technique. Based on this success, the UNB spectroscopy group decided to try and find the optical signatures of other RuX molecules. Using CH₃[¹H] and PH₃ as reactant gases, the RuH₂ and RuP diatomic molecules have been detected in surveys of the 420-675 nm spectral region. RuH₂ has also been made using fully deuterated methanol as a reactant. Dispersed fluorescence experiments have been performed to determine ground state vibrational frequencies and the presence of any low-lying electronic states. Rotationally resolved spectra for these molecules have also been taken and the analysis is proceeding. The most recent results will be presented.

TA04
9:21 – 9:36
OPTICAL ZEEMAN SPECTROSCOPY OF CALCIUM FLUORIDE, CaF.

TIMOTHY STEMLE, DAMIAN L. KOKKIN, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, USA; JACK DEWIS, MICHAEL TARBUTT, Centre for Cold Matter, Blackett Laboratory, Imperial College London, London, United Kingdom.

Recently laser cooling has been demonstrated for the diatomic radical calcium fluoride, CaF. The mechanism of magneto-optical trapping for diatomic molecules has been elucidated recently by Tarbutt where a rate model was used to model the interaction of molecules with multiple frequencies of laser light. It was shown that the correct choice of laser polarization depends on the sign of the upper state magnetic g-factor. The magnetic tuning of the low rotational levels in the XΣ¹, AΠ₁ and ΣΠ₂ electronic states of CaF have been experimentally investigated using high resolution optical Zeeman spectroscopy of a cold molecular beam sample. The observed Zeeman-induced shifts and splittings were successfully modeled using a traditional effective Hamiltonian approach to account for the interaction between the (g=0) AΠ₁ and (g=0) ΣΠ₂ states. The determined magnetic g-factors for the XΣ¹, AΠ₁ and ΣΠ₂ states are compared to those predicted by perturbation theory.

TA05
9:38 – 9:53
ELECTRONIC TRANSITIONS OF YTRRIUM MONOPHOSPHIDE.

ALLAN S.C. CHEUNG, Department of Chemistry, The University of Hong Kong, Hong Kong, Hong Kong; BIU WA LI, Department of Chemistry, The Chinese University of Hong Kong, Hong Kong, Hong Kong; CHEN CHAO CHAN, Department of Chemistry, The Chinese University of Hong Kong, Hong Kong, Hong Kong, China.

Electronic transition spectrum of the ytrrium monophosphide (YP) molecule in the visible region between 715 nm and 880 nm has been recorded using laser ablation/excitation free jet expansion and laser induced fluorescence spectroscopy. The YP molecule was produced by reacting laser - ablated yttrium atoms with PH₃ seeded in argon. Thirteen vibrational bands were analyzed and five electronic transition systems have identified, namely the [12.2] 1 → 3 - XΠ₁ transition, [13.3] 1 → 3 - XΠ₁ transition, [13.4] 1 → 3 - XΠ₁ transition, [13.5] 1 → 3 - XΠ₁ transition, and [13.4] 2 → 2 - XΠ₁ transition. Least squares fits of the measured rotational lines yielded molecular constants for the ground and excited states. The ground state symmetry and the bond length of the YP molecule have been determined to be a XΠ₁ state and 2.4413 Å respectively in this work. A molecular orbital energy level diagram has been used to help the assignment of the observed electronic states. This work represents the first experimental investigation of the spectrum of the YP molecule.

TA06
9:55 – 10:10
ROTATIONALLY RESOLVED SPECTROSCOPY OF THE BΠ₁ ← XΣ⁺ and CΣ⁺ ← XΣ⁺ TRANSITIONS OF C₂O.

MICHAEL SULLIVAN, JACOB STEWART, MICHAEL HEAVEN, Department of Chemistry, Emory University, Atlanta, GA, USA.

The BΠ₁ ← XΣ⁺ and CΣ⁺ ← XΣ⁺ transitions of C₂O, at energies below 30 000 cm⁻¹, were previously investigated by Loguerino. The arc source used in that work yielded spectra at energies above 30 000 cm⁻¹ that were too congested for analysis. In the present study we have used jet-cooling of C₂O to extend the characterization of the B ← X and C ← X band systems up to 35 000 cm⁻¹. Analyses of these data and spectroscopic constants will be reported. This work is being carried out in support of two-color photionization studies of the cation, where the higher energy vibrionic levels of the B and C states are used as the first excitation step.

A. Loguerino, Atoms For Peace 5, 83, 1954
TA07 10:29–10:44
HIGH RESOLUTION LASER SPECTROSCOPY OF NICKEL MONOBORIDE, NiB

E.S.GOUDREAU, COLAN LINTON, Department of Physics, University of New Brunswick, Fredericton, NB, Canada

Diatomic nickel boride, NiB, has been produced in the UNB laser ablation molecular jet source. Survey spectra, taken at medium resolution with a pulsed dye laser in the 415 – 510 nm region, showed an intense band system which had previously been observed and assigned as a $\Sigma^+_g - \Sigma^+_u$ transition by Zhen et al. Using a single frequency ring dye laser, we have obtained high resolution spectra of the 0-0, 2-0 and 3-0 bands of the most abundant isotope, $^{60}\text{Ni}^{10}\text{B}$, and the 2-0 band of $^{60}\text{Ni}^{11}\text{B}$. The rotational analysis showed that the transition was from an $\Omega = 0.5$ upper state to the ground $\Sigma^+_2$ state. The data were found to fit equally well as $\Sigma^+_2 - \Sigma^+_3$ or $\Sigma^+_2 - \Sigma^+_2$. The fine structure of $\Omega$ parity splitting was examined for each of the two options in an attempt to determine the identity of the upper state. Partially resolved hyperfine structure due to the $^6\text{Ni}$ nuclear spin, I = 3/2, was observed and analyzed to try and determine the nature of the $\text{boron atom contribution to the state configuration.}$ The results of the rotational and hyperfine structure analysis will be discussed.

TA08 10:46–11:01
MOLECULAR LINE LISTS FOR SCANDIUM AND TITANIUM HYDRIDE USING THE DUO PROGRAM

LORENZO LOGLI, Department of Physics and Astronomy, University College London, London, IX, United Kingdom

Transition-metal-containing (TMC) molecules often have very complex electronic spectra because of their large number of low-lying, interacting electronic states, of the large multi-reference character of the electronic states and of the large magnitude of spin-orbit and relativistic effects. As a result, fully ab initio calculations of line positions and intensities of TMC molecules have an accuracy which is considerably worse than the one usually achievable for molecules made up by main-group atoms only. In this presentation we report on new theoretical line lists for scandium hydride ScH and titanium hydride TiH. Scandium and titanium are the lightest transition metal atoms and by virtue of their small number of valence electrons are amenable to high-level electronic-structure treatments and serve as ideal benchmark systems. We report for both systems energy curves, dipole curves and various coupling curves (including spin-orbit) characterising their electronic spectra up to about 20 000 cm$^{-1}$. Curves were obtained using Internally-Contracted Multi Reference Configuration Interaction (IC-MRCI) as implemented in the quantum chemistry package MOLPRO. The curves where used for the solution of the coupled-surface ro-vibronic problem using the in-house program DUO. DUO is a newly-developed, general program for the spectroscopy of diatomic molecules and its main functionality will be described. The resulting line lists for ScH and TiH are made available as part of the Exomol project.\(^a\)

TA09 11:03–11:18
UV SPECTROSCOPY ON GAS PHASE Cu(I)-BIPYRIDYL COMPLEXES

SHUANG XU, JILA and Department of Physics, University of Colorado at Boulder, Boulder, CO, USA, CASEY CHRISTOPHER, J. MATHIAS WEBER, JILA and the Department of Chemistry and Biochemistry, University of Colorado-Boulder, Boulder, CO, USA

Transition metal complexes with bipyridine ligands are of great interest in metal-organic chemistry, since they are prototypes for many applications in photochemistry and homogenous catalysis. Under-coordinated bipyridyl complexes are elusive species in the condensed phase, and the ligand-induced changes in electronic structure are of fundamental interest. We present 1V photodissociation spectra of mass-selected monocationic copper(I)-bipyridyl complexes $[^{57}\text{Cu}^+\text{Cu-L}]^{1+}$ with different ligands ($L = \text{H}_2\text{O}, \text{D}_2\text{O}, \text{N}_2\text{O}, \text{MeOH}, \text{Cl}$). Complexes were prepared via electrospray ionization of copper/bipyridine solutions followed by accumulation and buffer gas cooling in a cryogenic Paul trap. In addition, we show spectra of similar species based on copper oxide. ($[^{57}\text{Cu}^+\text{Cu-L}]^{1+}$)

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TB01
JET-COOLLED SPECTROSCOPY ON THE AILES INFRARED BEAMLINE OF THE SYNCHROTRON RADIATION FACILITY SOLEIL
ROBERT GEORGES, DIP UMB521, CNRS - Université Rennes 1, Rennes, France.

The Advanced Infrared Line Exploited for Spectroscopy (AILES) extracts the bright far infrared (FIR) synchrotron continuum of the third generation radiation facility SOLEIL. This beamline is equipped with a high resolution (10^{-10} cm^{-1}) Bruker IFS125 Fourier transform spectrometer which can be operated in the FIR but also in the mid and near infrared by using its internal conventional sources. The jet-AILES consortium (IPR, PALM, MONARIS, SOLEIL) has implemented a superersonic-jet apparatus on the beamline to record absorption spectra at very low temperature (5-50 K) and in highly supersaturated gaseous conditions. Heatable slit-nozzles of various lengths and widths are used to set properly the stagnation conditions. A mechanical pumping (roots pumps) was preferred for its ability to evacuate important mass flow rates and therefore to boost the experimental sensitivity of the set-up, the counterpart being a non-negligible consumption of both carrier (argon, helium or nitrogen) and spectroscopic gases. Various molecular systems were investigated up to now using the Jet-AILES apparatus. The very low temperature achieved in the gas expansion was either used to simplify the rotation-vibration structure of monomers, such as SF₆, CF₄ or naphthalene, or to stabilize the formation of weakly bonded molecular complexes such as the trimers of HP₃ or the dimer of acetic acid. The nucleation of water vapor and the nuclear spin conversion of water were also investigated under free-jet conditions in the mid infrared.

TB02
LOWEST VIBRATIONAL STATES OF ACETYLONITRILE
ZBIGNIEW KISIEL, ON2, Institute of Physics, Polish Academy of Sciences, Warszawa, Poland; MAREE-ALINE MARTIN-DRUMEL, Spectroscopy Lab, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; OLIVIER PIRAILL, AILES beamline, Synchrotron SOLEIL, Saint Aubin, France.

Recent studies of the broadband rotational spectrum of acetonitrile, CH₃CN, revealed the presence of multiple resonances between rotational levels in different vibrational states. The resonances affect even the ground state transitions and their analysis allowed determination of vibrational term values for the first three excited states above the ground state and of vibrational energy differences in several polys of above these states. At that time there was no infrared data of sufficient resolution to assess the reliability of the resonance based vibrational energy determinations.

We presently report results based on a 40-700 cm⁻¹ high-resolution spectrum of acetonitrile recorded at the AILES beamline of the SOLEIL synchrotron. This spectrum was reduced by using the AABS package and allowed assignment of vibration-rotation transitions in four fundamentals, five hot bands, and one overtone band. The infrared data and previous measurements made with microwave techniques have been combined into a single global fit encompassing over 31000 measured transitions. Precise vibrational term values have been determined for the eight lowest excited vibrational states.

The new results validate the previous estimates from rotational perturbations and are also compared with results of ab initio anharmonic force field calculations.

TB03
FIR SYNCHROTRON SPECTROSCOPY OF HIGH TORSIONAL LEVELS OF CD₃OH: THE TAU OF METHANOL
RONALD M. LEES, 11-HONG XU, Department of Physics, University of New Brunswick, Saint John, NB, Canada; BRANT E BILINGHURST, LED, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada.

Malonaldehyde (C₂H₃O₂) is a prototype molecule for the study of intramolecular tunnelling proton transfer. In the case of malonaldehyde, this transfer occurs between the two terminal oxygen atoms in its open-ring structure. Although the ground state tunnelling splitting of 21 cm⁻¹ has been accurately determined from microwave studies, the splitting has never been obtained with high resolution in any excited vibrational state. The τ₁ vibrational band was investigated in a diode laser jet experiment in 2004, but the researchers were not able to identify the τ₂ parity tunnelling component and so could not determine the splitting. We have collected high-resolution far-IR Fourier transform spectra from a number of fundamental vibrational bands of malonaldehyde at the CLS (Canadian Light Source) synchrotron in Saskatoon, Saskatchewan, exploiting the considerable gain in signal-to-noise ratio at the highest resolution available afforded by the intense and well-collimated beam. We will report on our tunnelling-rotation analysis of the anti-symmetric out-of-plane bend near 384 cm⁻¹ and present its tunnelling splitting value.
The discrete nature of the coherent synchrotron radiation

Stefano Tammaro, Ailes beam line, Synchrotron SoLEIL, Saint Aubin, France; Jean Francois Lampin, Gaelle Ducourneau, Institut d’Electronique de Microelectronique et de Nanotechnologie, Université de Lille I, Villeneuve d’Ascq, France; Arnaud Cussenet, Francis Hindle, Ailes beamline, Laboratoire de Physico-Chimie de l’Atmosphère, Université du Littoral Côte d’Opale, Dunkerque, France.

Frequency Comb (FC) have radically changed the landscape of frequency metrology and high-resolution spectroscopy investigations extending tremendously the achievable resolution while increasing signal to noise ratio. Initially developed in the visible and near-IR spectral regions, the use of FC has been expanded to mid-IR, extreme ultra-violet and X-ray. Significant effort is presently dedicated to the generation of FC at THz frequencies. One solution based on converting a stabilized optical frequency comb using a photoconductive terahertz emitter, remains hampered by the low available THz power. Another approach is based on active mode locked THz quantum-cascade lasers providing intense FC over a relatively limited spectral extension. Alternatively, we show that dense powerful FCs are generated over one decade of frequency by coherent synchrotron radiation (CSR). In this mode, the entire ring behaves in a similar fashion to a THz resonator wherein electronic bunches emit powerful THz pulses quasi-synchronously. The observed FC has been fully characterized and is demonstrated to be offset free. Based on these recorded specifications and a complete review of existing THz frequency comb, a special attention will be paid on similarities and differences between them.

We used a 93 m total optical path length. Five pure methane pressures (from 10 to 100 mbar) and four CH4/N2 mixtures (20 % of methane with a total pressure from 100 to 800 mbar) were used. These measurements allow us to obtain data for physical conditions approaching those of Titan’s atmosphere and to estimate temperature exponents.

TB07 Hydrogen and nitrogen broadened ethane and propane absorption cross sections

Robert J. Harderaves, Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA; CMA Dominique Appadoo, 800 Blackburn Road, Australian Synchrotron, Melbourne, Victoria, Australia; Brant E. Billinghurst, EFD, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada; Peter F. Bernath, Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA.

High-resolution infrared absorption cross sections are presented for the v3 band of ethane (CH3H2) at 823 cm⁻¹. These cross sections make use of spectra recorded at the Australian Synchrotron using a Fourier transform infrared spectrometer with maximum resolution of 0.00096 cm⁻¹. The spectra have been recorded at 150, 120 and 90 K for hydrogen and nitrogen broadened CH3H2. They cover appropriate temperatures, pressures and broadening gases associated with the atmospheres of the outer planets and Titan, and will improve atmospheric retrievals. The THz/Far-IR beamline at the Australian Synchrotron is unique in combining a high-resolution Fourier transform spectrometer with an ‘enclosure flow cooling’ (EFC) cell designed to study molecules at low temperatures. The EFC cell is advantageous at temperatures for which the vapor pressure is very low, such as CH3H2 at 90 K. Hydrogen broadened absorption cross sections of propane between 700 and 1200 cm⁻¹ will also be presented based on spectra obtained at the Canadian Light Source.
TC. Mini-symposium: Spectroscopy in the Classroom

Tuesday, June 23, 2015 – 8:30 AM
Room: B102 Chemical and Life Sciences

Chair: S. A. Cooke, Purchase College SUNY, Purchase, NY, USA

PGOPHER IN THE CLASSROOM AND THE LABORATORY

COLIN WESTERN, School of Chemistry, University of Bristol, Bristol, United Kingdom.

PGOPHER is a general purpose program for simulating and fitting rotational, vibrational and electronic spectra. As it uses a graphical user interface the basic operation is sufficiently straightforward to make it suitable for use in undergraduate practicals and computer based classes. This talk will present two experiments that have been in regular use by Bristol undergraduates for some years based on the analysis of infra-red spectra of cigarette smoke and, for more advanced students, visible and near ultra-violet spectra of a nitrogen discharge and a hydrocarbon flame. For all of these the rotational structure is analysed and used to explore ideas of bonding. The talk will discuss the requirements for the apparatus and the support required. Other ideas for other possible experiments and computer based exercises will also be presented, including a group exercise.

The PGOPHER program is open source, and is available for Microsoft Windows, Apple Mac and Linux. It can be freely downloaded from the supporting website http://pgopher.chm.bris.ac.uk. The program does not require any installation process, so can be run on student’s own machines or easily setup on classroom or laboratory computers.

To address this problem, for over 20 years our department has been teaching a popular Introductory Spectroscopy course that assumes as background only a one-term introductory chemistry course containing a unit on atomic theory, and a familiarity with rudimentary calculus. This survey course provides an introduction to microwave, infrared, Raman, electronic, photoelectron and NMR spectroscopy in a manner that allows students to understand many of these phenomena as intuitive generalizations of the problem of a particle in a 1-D box or a particle-on-a-ring, and does not require any high level mathematics.

RESEARCH AT A LIBERAL ARTS COLLEGE: MAKE SURE YOU HAVE A NET FOR YOUR HIGH WIRE ACT

MARK D. MARSHALL, HELEN O. LEUNG, Chemistry Department, Amherst College, Amherst, MA, USA

A career as a spectroscopist at a primarily (or exclusively) undergraduate institution presents both great rewards and significant challenges. Strategies that we have found helpful in meeting some of the challenges are presented along with some of the work we have been able to accomplish with undergraduate students. The most important resource is a network of colleagues who can provide mentoring and collaboration, and the role of the International Symposium on Molecular Spectroscopy in facilitating this support is highlighted.
A SPECTROSCOPIC BASED P-CHEM LAB, INCLUDING A DETAILED TEXT AND LAB MANUAL

JOHN MUENTER, Department of Chemistry, University of Rochester, Rochester, NY, USA.

Rochester’s second semester physical chemistry lab course is based on spectroscopy experiments and follows a full semester of quantum mechanics lectures. The laboratory course is fully separate from the traditional physical chemistry course and has its own lectures. The lab course is constructed to achieve three major goals: provide a detailed knowledge of the instrumentation that acquires data, establish a good understanding of how that data is analyzed, and give students a familiarity with spectroscopic techniques and quantum mechanical models. Instrumentation is emphasized by using common components to construct different experiments. Microwave, modulation and detection components are used for both OCS pure rotation and ESR experiments. Optical components, a monochromator, and PMT detectors are used in a HeNe laser induced fluorescence experiment on I$_2$ (J. Chem. Ed. 73, 576 (1996)) and a photoluminescence experiment on pyrene (J. Chem. Ed. 73, 580 (1996)). OCS is studied in both the microwave and infrared regions, and the C=O stretching vibration is identified through microwave intensity measurements. Lecture notes and laboratory instructions are combined in an exhaustive text of more than 400 pages, containing 325 figures, 285 equations and numerous Matlab data analysis programs. This text can be downloaded as a 10 Mbyte pdf file at chem.rochester.edu/~muenter/CHEM232Manual.

Intermission

HOW WE KNOW: SPECTROSCOPY IN THE FIRST YEAR AND BEYOND

KRISTOPHER J OOMS, Chemistry, The King’s University, Edmonton, Alberta, Canada.

Chemical educators face the never ending challenge of showing students that the content written in their textbook arises from a rich interplay of experimentation, imagination and a desire to understand and impact the world. We have found that asking three simple questions — What do we know, How do we know it, Why do we care — is an effective strategy to guide the content and pedagogy within our chemistry classes. Of these three questions What do we know is the most thoroughly covered and with the growing use of rich context teaching, the Why we care is becoming more central to our chemistry teaching. How are we doing on telling students How we know?

Spectroscopy is at the core of our ability to answer questions about how we know things about the molecular world. Yet the teaching of spectroscopy is not a central part of student’s early chemistry learning, often being left to the later stages of degrees and courses. For example, a brief look at common North American general chemistry text books reveals almost no discussion of spectroscopic techniques and their centrality to understanding chemistry.

In this talk I will discuss efforts to bring spectroscopy into the first year course and some of the repercussions this has for the whole chemistry undergraduate curriculum. The goal is to make students better aware of where the ideas in chemistry arise from, the strengths and weaknesses of spectroscopic experiments, and how our models of the molecular world are built on rigorous experimentation.

EXPANDED CHOICES FOR VIBRATION-ROTATION SPECTROSCOPY IN THE PHYSICAL CHEMISTRY TEACHING LABORATORY

JOEL R SCHMITZ, DAVID A DOLSON, Department of Chemistry, Wright State University, Dayton, OH, USA.

Many third-year physical chemistry laboratory students in the US analyze the vibration-rotation spectrum of HCl in support of lecture concepts in quantum theory and molecular spectroscopy. Contemporary students in physical chemistry teaching laboratories increasingly have access to FTIR spectrometers with 1/8th cm$^{-1}$ resolution, which allows for expanded choices of molecules for vibration-rotation spectroscopy. Here we present the case for choosing HBr/Br$_2$ for such a study, where the 1/8th cm$^{-1}$ resolution enables the bromine isotopic lines to be resolved. Vibration-rotation lines from the fundamental and first-overtones bands of four hydrogen bromide isotopomers are combined in a global analysis to determine molecular spectroscopic constants. Sample production, spectral appearance, analysis and results will be presented for various resolutions commonly available in teaching laboratories.

SPECTROSCOPIC CASE-BASED STUDIES IN A FLIPPED QUANTUM MECHANICS COURSE

STEVEN SHIPMAN, Department of Chemistry, New College of Florida, Sarasota, FL, USA.

Students in a flipped Quantum Mechanics course were expected to apply their knowledge of spectroscopy to a variety of case studies involving complex mixtures of chemicals. They used simulated data, prepared in advance by the instructor, to determine the major chemical constituents of complex mixtures. Students were required to request the appropriate data in order to ultimately make plausible guesses about the composition of the mixtures, allowing them ownership over the discovery process. This talk will describe how these activities worked in practice, give caveats for instructors who wish to adopt them in the future, and discuss how the results of these exercises can be used for both formative and summative assessment.

THE H-ATOM SPECTRUM: NOT A CLASSROOM DEMONSTRATION …

WOLFGANG JÄGER, Department of Chemistry, University of Alberta, Edmonton, AB, Canada.

The spectrum of the hydrogen atom is topic of every freshmen chemistry course and at the same time a first brush with quantum mechanics for many students. A picture of the four possible emission lines of the Balmer series is shown in probably every introductory Chemistry textbook, but only few students have likely seen those lines with their own eyes.

I will tell you about a simple in-class activity that allows the students to see those lines and can be done in large classes (I have done it in classes with up to 500 students) at low cost.

RAMAN INVESTIGATION OF TEMPERATURE PROFILES OF PHOSPHOLIPID DISPERSIONS IN THE BIOCHEMISTRY LABORATORY

NORMAN C. CRAIG, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH, USA.

The temperature dependence of self-assembled, cell-like dispersions of phospholipids is investigated with Raman spectroscopy in the biochemistry laboratory. Vibrational modes in the hydrocarbon interiors of phospholipid bilayers are strongly Raman active, whereas the vibrations of the polar head groups and the water matrix have little Raman activity. From Raman spectra increases in fluidity of the hydrocarbon chains can be monitored with intensity changes as a function of temperature in the CH-stretching region. The experiment uses detection of scattered 1064-nm laser light (Nicolet NXR module) by a Fourier transform infrared spectrometer (Nicolet 6700). A thermoelectric heater-cooler device (Melcor) gives convenient temperature control from 5 to 95$^\circ$C for samples in melting point capillaries. Use of deuterium oxide instead of water as the matrix avoids some absorption of the exciting laser light and interference with intensity observations in the CH-stretching region. Phospholipids studied range from dimyristoylphosphatidylcholine (C$_{14}$) (transition T = 24°C) to dibehenoylphosphatidylcholine (C$_{22}$) (transition T = 75°C).
Online education tools and flipped (reverse) class models for teaching and learning have become quite mature in the last few years because of the revolution in video, interactive software and social learning tools. Open Educational resources of dependable quality and variety are also becoming available throughout the world making the current era truly a renaissance period for higher education using Internet. In my presentation, I shall highlight structured course content preparation online in several areas of spectroscopy and also the design and development of virtual lab tools and kits for studying optical spectroscopy.

Both elementary and advanced courses on molecular spectroscopy are currently under development jointly with researchers in other institutions in India. I would like to explore participation from teachers throughout the world in the teaching-learning process using flipped class methods for topics such as experimental and theoretical microwave spectroscopy of semi-rigid and non-rigid molecules, molecular complexes and aggregates. In addition, courses in Raman, Infrared spectroscopy experimentation and advanced electronic spectroscopy courses are also envisaged for free, online access. The National Programme on Technology Enhanced Learning (NPTEL) and the National Mission on Education through Information and Communication Technology (NMEICT) are two large Government of India funded initiatives for producing certified and proctored and certified examination processes for large numbers in some of the above courses.

I would like to present a summary of developments in these areas to help focus classroom (online and offline) learning of Molecular spectroscopy.

TD01
8:30 – 8:45
A JOINT THEORETICAL AND EXPERIMENTAL STUDY OF THE SiH₂O₂ ISOMERIC SYSTEM
MICHAEL C. MCCARTHY, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA
URGEN GAUSS, CoCoMol, Max-Planck-Institut für Physikalische Chemie, Universität Mainz, Mainz, Germany

In contrast to the CH₂O isomers, those of SiH₂O₂ have received relatively little attention, either theoretically or experimentally. High-level coupled cluster calculations predict a much different energy ordering in comparison to that found for CH₂O, with the three conformers of Si-dihydroxycarbene, HOSiOH, most stable, followed by the Si-analogues of cis and trans formic acid, and then a cyclic isomer with C₃ᵥ symmetry, c-SiH₂O₂. Guided by these theoretical predictions, rotational lines of the cis, trans isomer of HOSiOH, as well as c-SiH₂O₂, have been detected by Fourier transform microwave spectroscopy. The lines of the cyclic form are sufficiently strong that several rare isotopic species have also been found, enabling, in combination with calculated vibrational corrections, a precise semi-experimental structure to be derived. This talk will provide a status report on our joint study of this unusual isomeric system, and an update on searches for still other isomers.

TD02
8:47 – 9:02
A MINTY MICROWAVE MENAGERIE: THE ROTATIONAL SPECTRA OF MENTHOLE, MENTHOL, CARVACROL, AND THYMOL
DAVID SCHMITZ, V. ALVIN SHUBERT, THOMAS BETZ, CoCoMol, Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany
MELANIE SCHNELLE, CoCoMol, Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany
BARRABARA MICHELA GIULIANO, Department of Chemistry, University of Bologna, Bologna, Italy

Terpenes represent one of the largest classes of secondary metabolites in nature and are derived from adding substituents to their core building block, isoprene. They exhibit a huge assortment of structures and thus a variety of chemical and biological activities. We recently investigated a number of monoterpeneoids using broadband rotational spectroscopy in the 2-8.5 GHz frequency range.

We present a comparative study of the aromatic monoterpeneoids thymol and carvacrol and aliphatic menthol and menthone. The differences in their electronic and steric structures significantly influence molecular properties such as internal rotation barriers and conformational flexibility. These influences are revealed in the rotational spectra. We report the rotational spectra and the experimentally determined molecular parameters. Results from extensive quantum chemical calculations of the conformational spaces of these molecules are compared with the experimentally determined molecular parameters.
ROTATIONAL SPECTRUM AND CONFORMATIONAL STRUCTURES OF METHYL VALERATE

HA VINH LAM NGUYEN, CNRS, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Université Paris Dauphine, CNRS, Université Paris 1 Panthéon-Sorbonne, UMR 7588; WOLFGANG STAHL, Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany.

Methyl valerate, C₆H₄COOCH₃, belongs to the class of fruit esters, which play an important role in nature as odorants of different fruits, flowers, and wines. A sufficient explanation for the structure–odor relation of esters is not available. It is known that predicting the odor of a substance is not possible by knowing only its chemical formula. A typical example is the blueberry- or pear-like odor of ethyl isovalerate while its isomer ethyl valerate and isoinonyl acetate smell like green apple and banana, respectively. Obviously, not only the composition but also the molecular size and the number of carbon atoms are not negligible by determining the odor of a substance. Gas phase structures of fruit esters are thus important for a first step towards the determination of structure–odor relation since the sense of smell starts from gas phase molecules.

For this purpose, a combination of microwave spectroscopy and quantum chemical calculations (QC) is an excellent tool. Small esters often have sufficient vapor pressure to be transferred easily in the gas phase for a rotational study but already contain a large number of atoms which makes them too big for classical structure determination by isotopic substitution and requires nowadays a comparison with the structures optimized by QC. On the other hand, the results from QC have to be validated by the experimental values.

The methyl salicylate-water complex was first studied using fluorescence-detected infrared spectroscopy; only one monomeric conformer was found in that work. In the present study, we employed both broadband chirped and cavity based Fourier transform microwave spectroscopy to examine the competition between intra- and intermolecular hydrogen-bonding interactions and possible large amplitude motions associated with the methyl group and the water subunit. In contrast to the previous infrared study, two monohydrate conformers were identified, with carbonyl O or hydroxyl O as the hydrogen bond acceptors. Detailed analyses of the observed hyperfine structures will be presented, as well as our efforts to extend the study to larger methyl salicylate hydration clusters.

CONFORMATIONALLY RESOLVED STRUCTURES OF JET-COOLED PHENACETIN AND ITS HYDRATED CLUSTERS

CHEOL JOO MOON, AHREUM AHN, MYONG YONG CHOI, Department of Chemistry, Gyeongnam National University, Jinju, GyeongnamNamDo, Korea. 4

Phenacetin (PA) is one of the typical synthetic fever reducers as similar to acetaminophen (AAP), a major ingredient of Tylenol®. PA and AAP are both derivatives of acetanilide (AA), substituted by ethyl group and hydroxyl group in the para position of AA, respectively. In this work, we present the conformational investigations and photophysics of jet-cooled PA and its 1:1 hydrate using resonance enhanced multiphoton ionization (REMPI), UV-UV hole-burning and IR-dip spectroscopy. Moreover, we calculated the optimized structures of PA and its 1:1 hydrates by density functional theory. Here, we report the structural information of PA and its 1:1 hydrate with an aid of the experimental data and the ab initio calculations.
**THE INHERENT CONFORMATIONAL PREFERENCES OF GLUTAMINE-CONTAINING PEPTIDES: THE ROLE FOR SIDE-CHAIN BACKBONE HYDROGEN BONDS**

**PATRICK S. WALSH**
Department of Chemistry, Purdue University, West Lafayette, IN, USA; CARL MCBURNEY, SAMUEL H. GELLMAN
Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA; TIMOTHY S. ZWIER
Department of Chemistry, Purdue University, West Lafayette, IN, USA.

Glutamine is widely known to be found in critical regions of peptides which readily fold into amyloid fibrils, the structures commonly associated with Alzheimer’s disease and glutamine repeat diseases such as Huntington’s disease. Building on previous single-conformation data on Gln-containing peptides containing an aromatic cap on the N-terminus (Z-Gln-OH and Z-Gln-SHBn), we present here single-conformation UV and IR spectra of Ac-Gln-SHBn and Ac-Ala-Gln-SHBn, with its C-terminal benzyl cap. These results point towards side-chain to backbone hydrogen bonds dominating the structures observed in the cold, isolated environment of a molecular beam. We have identified and assigned three main conformers for Ac-Gln-SHBn all involving primary side-chain to backbone interactions. Ac-Ala-Gln-SHBn extends the peptide chain by one amino acid, but affords an improvement in the conformational flexibility. Despite this increase in the flexibility, only a single conformation is observed in the gas-phase: a structure which makes use of both side-chain-to-backbone and backbone-to-backbone hydrogen bonds.

**APPLICATIONS OF STRUCTURAL MASS SPECTROMETRY TO METABOLOMICS: CLARIFYING BOND SPECIFIC SPECTRAL SIGNATURES WITH ISOTOPE EDITED SPECTROSCOPY**

**OLGA GORLOVA, CONRAD T. WOLKE, JOSEPH FOURNIER, SEAN COLVIN, MARK JOHNSON, SCOTT MILLER**
Department of Chemistry, Yale University, New Haven, CT, USA.

Comprehensive FTIR, MS/MS and NMR of pharmaceuticals are generally readily available but characterization of their metabolites has been an obstacle. Atorvastatin is a statin drug responsible for the maintenance of cholesterol in the body. The efficient extraction of cellulose from biomass and its subsequent conversion to glucose derivatives is an attractive goal in the field of energy science. However, current industrial methods require high ionic strength and harsh conditions. The efficient extraction of cellulose from biomass and its subsequent conversion to glucose derivatives is an attractive goal in the field of energy science. However, current industrial methods require high ionic strength and harsh conditions. Ionic liquids (ILs) are a class of “green” compounds that have been shown to dissolve cellulose in concentrations of up to 25 wt%. In order to understand ILs’ extraordinary cellulose dissolving power, a molecular level understanding of the IL-cellulose interaction is needed. Toward that end, we have acquired infrared pre-dissociation spectra of $M^+$-glucose, where $M^+$=Li$^+$, Na$^+$, or K$^+$. Through comparisons with density functional theory calculations, we have determined the relative abundances of various $M^+$-glucose binding motifs in both the thermodynamic and kinetic limits. These results provide insight on the hydrogen bonding dynamics of glucose and are a step towards a fuller understanding of cellulose interactions with ionic liquids.
TE. Instrument/Technique Demonstration
Tuesday, June 23, 2015 – 8:30 A.M
Room: 217 Noyes Laboratory
Chair: Ken Leopold, University of Minnesota, Minneapolis, MN, USA

TE01 8:30 – 8:45
ELIMINATION OF THE VACUUM PUMP REQUIREMENT FOR HIGH-RESOLUTION ROTATIONAL SPECTROSCOPY

JENNIFER HOLT, Department of Physics, The Ohio State University, Columbus, OH, USA; RYAN W DALY, Battelle Memorial Institute, Columbus, Ohio, USA; CHRISTOPHER F. NIESE, FRANK C. DE LUCIA, Department of Physics, The Ohio State University, Columbus, OH, USA.

It has been observed that with the advances being driven by the wireless communications industry, the microwave components for submillimeter wave spectrometers and sensors will become almost “free”. Moreover, these electronic components will require little power. However, neither of these attributes applies to the vacuum requirements for high-resolution rotational spectroscopy. We will report on the design, construction, and operation of a simple spectrometric cell that overcomes these problems.

Intermission

TE02 8:47 – 8:57
3-D PRINTED SLIT NOZZLES FOR FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

CHRIS DEWBERRY, BECCA MACKENZIE, Chemistry Department, University of Minnesota, Minneapolis, MN, USA; SUSAN GREEN, Chemistry Department, Macalester College, Saint Paul, Minnesota, USA; KEN LEOPOLD, Chemistry Department, University of Minnesota, Minneapolis, MN, USA.

3-D printing is a new technology whose applications are only beginning to be explored. In this report, we describe the application of 3-D printing to the facile design and construction of supersonic nozzles. The efficacy of a variety of designs is assessed by examining rotational spectra OCS and As-OCS using a Fourier transform microwave spectrometer with tandem cavity and chirped-pulse capabilities. This work focuses primarily on the use of slit nozzles but other designs have been tested as well. New nozzles can be created for $0.50 or less each, and the ease and low cost should facilitate the optimization of nozzle performance (e.g., jet temperature or cluster size distribution) for the needs of any particular experiment.

TE03 8:59 – 9:14
IMPLEMENTATION OF CMOS MILLIMETER-WAVE DEVICES FOR ROTATIONAL SPECTROSCOPY

BRIAN DROUIN, ADRIAN TANG, ERICH T SCHLECHT, ADAM M DALY, EMILY BRAGEOT, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; QUN JANE GU, YU YE, RAN SHU, Department of Electrical and Computer Engineering, University of California - Davis, Davis, CA, USA; M.-C. FRANK CHANG, ROD M. KIM, Electrical Engineering, University of California - Los Angeles, Los Angeles, CA, USA.

The extension of radio-frequency CMOS circuitry into millimeter wavelengths promises the extension of spectrometric techniques in compact, power-efficient systems. We are now exploiting the use of CMOS millimeter devices for low-mass, low-power instrumentation capable of remote or in-situ detection of gas composition during space missions. This effort focuses on the development of a semi-confocal Fabry-Perot cavity with mm-wavelength CMOS transmitter and receiver attached directly to a cavity coupler. Placement of the devices within the cavity structure bypasses problems encountered with signal injection and extraction in traditional cavity designs and simultaneously takes full advantage of the miniaturized form of the CMOS hardware. The presentation will provide an overview of the project and details of the accomplishments thus far, including the development and testing of a pulse modulated 83-98 GHz transmitter.

TE04 9:16 – 9:31
FAST SWEEPING DIRECT ABSORPTION (SUB)MILLIMETER SPECTROSCOPY BASED ON CHIRPED-PULSE TECHNOLOGY

BRIAN HAYS, Department of Chemistry, Emory University, Atlanta, GA, USA; STEVEN SHIPMAN, Department of Chemistry, New College of Florida, Sarasota, FL, USA; SUSANNA L. WIDICUS WEaver, Department of Chemistry, Emory University, Atlanta, GA, USA.

Chirped-pulse Fourier Transform Microwave (CP-FTMW) technology has transformed traditional microwave spectroscopy into a rapid-acquisition, broadband spectral technique. The CP-FT technique has recently been expanded to the millimeter-wave region, but this approach requires costly equipment that is not readily available in most spectroscopy labs. To overcome this challenge, a new experiment has been designed that combines the broadband aspects of CP-FTMW with the high sensitivity of (sub) millimeter absorption spectroscopy. Using the arbitrary waveform generator from a CP-FTMW experiment, and the frequency multipliers and hot electron bolometer detector from a (sub) millimeter wave experiment, we have designed and benchmarked a highly sensitive spectrometer that offers broad spectral coverage and rapid spectral acquisition speeds. This technique is comparable in performance to other rapid-acquisition techniques currently used in the (sub) millimeter range, but offers more sensitivity after averaging. The design of this instrument and the benchmarking results will be presented.

TE05 9:33 – 9:48
FAST SWEEPING DOUBLE RESONANCE MICROWAVE-(SUB)MILLIMETER SPECTROSCOPY BASED ON CHIRPED-PULSE TECHNOLOGY

BRIAN HAYS, SUSANNA L. WIDICUS WEaver, Department of Chemistry, Emory University, Atlanta, GA, USA; STEVEN SHIPMAN, Department of Chemistry, New College of Florida, Sarasota, FL, USA.

Microwave-millimeter double resonance spectroscopy has been commonly applied by driving absorption with the millimeter light and then probing the resonance using a Fourier Transform Microwave (FTMW) spectrometer. We will present data from an inverse scheme, in which millimeter light is used to probe a transition whose intensity is modulated by the application of microwave radiation. This detection scheme is effective in adding the assignment of millimeter-wave transitions by revealing which energy levels are associated with particular spectral lines. To increase the speed of this detection technique, we incorporated an arbitrary waveform generator into the microwave source to rapidly sweep the microwave radiation through a broad frequency range. We will discuss this approach as applied to pulsed valve experiments and in combination with a laser-induced chemistry experiment. Potential applications to other experimental designs will also be discussed.

Intermission
ON THE PHASE DEPENDENCE OF DOUBLE-RESONANCE EXPERIMENTS IN ROTATIONAL SPECTROSCOPY
DAVID SCHMITZ, V. ALVIN SHUBERT, ANNA KRIN, CoCoMoL, Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany; DAVID PATTERSON, Department of Physics, Harvard University, Cambridge, MA, USA; MELANIE SCHNELL, CoCoMoL, Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany.

We report double-resonance experiments using broadband chirped-pulse Fourier transform microwave spectroscopy that facilitate spectral assignment and yield information about weak transitions with high resolution and sensitivity. Using the diastereomers menthone and isomenthone as examples, we investigate both the amplitude and the phase dependence of the free-induction decay of the molecular signal transition from pumping a radio frequency transition sharing a common level.

We observe a strong phase change when scanning the radio frequency through molecular resonance. The direction of the phase change depends on the energy level arrangement, i.e., if it is progressive or regressive. The experimental results can be simulated using the density-matrix formalism using the three-level Bloch equations and are best described with the AC Stark effect within the dressed-state picture, resulting in an Autler-Townes splitting.

The characteristic phase inversion allows for the precise frequency determination of the typically weak radio frequency transitions exploiting the high sensitivity of the connected strong microwave signal transition and provide definitive information about the connectivity of the energy levels involved, i.e., progressive or regressive arrangements.

MICROWAVE THREE-WAVE MIXING EXPERIMENTS FOR CHIRALITY DETERMINATION: CURRENT STATUS
CRISTOBAL PEREZ, V. ALVIN SHUBERT, DAVID SCHMITZ, CHRIS MECRAFT, ANNA KRIN, MELANIE SCHNELL, CoCoMoL, Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany.

Microwave three-wave mixing experiments have been shown to provide a novel and sensitive way to generate and measure enantiomer-specific molecular signatures. The handedness of the sample can be obtained from the phase of the molecular free induction decay whereas the enantiomeric excess can be determined by the amplitude of the chiral signal. After the introduction of this technique by Patterson et al., remarkable improvements have been realized and experimental strategies for both absolute phase determination and enantiomeric excess have been presented. This technique has been also successfully implemented at higher microwave frequencies. Here we present the current status of this technique as well future directions and perspectives. This will be illustrated through our systematic study of chiral terpenes as well as preliminary results in molecular clusters.

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10:07 – 10:22

A SEMI-AUTOMATED COMBINATION OF CHIRPED-PULSE AND CAVITY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY
KYLEN CRAFTREE, Department of Chemistry, The University of California, Davis, CA, USA; MARIE-ALINE MARTIN-DUMEL, Spectroscopy Lab, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; MICHAEL C. MCCARTHY, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; SYDNEY A. GASTER, TAYLOR M. HALL, DEONDRE L. PARKS, GORDON G. BROWN, Department of Science and Mathematics, Coker College, Hartsville, SC, USA.

A combination of chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy and cavity Fourier transform microwave (c-FTMW) spectroscopy has been used to analyze the spectra of 3,4-dihydrobenzaldehyde and two distinct fluoropyridines — carbon dioxide complexes. In all cases, the 8–18 GHz CP-FTMW spectrum was measured, and the most intense transitions were chosen for further analysis. The intensities of the identified transitions were measured at multiple polarization powers using the c-FTMW spectrometer. Subsequently, a series of double-resonance experiments were performed on these transitions, again using the c-FTMW spectrometer, in order to discover which transitions shared a common quantum state.

Following the double-resonance experiments, the assignments of the spectra were trivial. The results of the spectroscopic analysis, as well as the semi-automated method, will be presented.

SUBMILLIMETER ABSORPTION SPECTROSCOPY IN SEMICONDUCTOR MANUFACTURING PLASMAS AND COMPARISON TO THEORETICAL MODELS
YASER H. HELAL, CHRISTOPHER F. NEESE, FRANK C. DE LUCIA, Department of Physics, The Ohio State University, Columbus, OH, USA; PAUL R. EWING, Applied Materials, Austin, TX, USA; ANKUR AGARWAL, BARRY CRAVER, PHILLIP J. STOUT, MICHAEL D. ARMACOST, Applied Materials, Sunnyvale, CA, USA.

Plasmas used in the semiconductor manufacturing industry are of a similar nature to the environments often created for submillimeter spectroscopic study of astrophysical species. At the low operating pressures of these plasmas, submillimeter absorption spectroscopy is a method capable of measuring the abundances and temperatures of molecules, radicals, and ions without disturbing any of the properties of the plasma. These measurements provide details and insight into the interactions and reactions occurring within the plasma and their implications for semiconductor manufacturing processes. A continuous wave, 500 to 750 GHz, absorption spectrometer was designed and used to make measurements of species in semiconductor processing plasmas. Comparisons with expectations from theoretical plasma models provide a basis for validating and improving these models, which is a complex and difficult science itself. Furthermore, these comparisons are an evaluation for the use of submillimeter spectroscopy as a diagnostic tool in manufacturing processes.

CLOUD COMPUTING FOR THE AUTOMATED ASSIGNMENT OF BROADBAND ROTATIONAL SPECTRA: PORTING AUTOFIT TO AMAZON EC2
AARON COLINCER, STEVEN SHIPMAN, Department of Chemistry, New College of Florida, Sarasota, FL, USA.

Recent developments in instrumentation have made it possible to collect broadband rotational spectra far faster than those spectra can be assigned. As such, we have been working to develop automated assignment algorithms so that the analysis can catch up with the data acquisition. The AUTOFIT project has made strides in this direction, but it is still quite slow on spectra with high line densities, such as those collected near room temperature. Given that the AUTOFIT algorithm is highly parallelizable, we have used Amazon’s EC2 web service to run a modified version of AUTOFIT simultaneously across a large number of cores, allowing us to obtain results in a fraction of the time normally required by a typical desktop computer. In this talk, we will describe how AUTOFIT was modified to run on EC2 and present some benchmark results.
We have developed a sub-Doppler resolution spectrometer. A difference frequency generation source, which consists of a pump source of a Nd:YAG laser, a signal source of an extended-cavity laser diode, and a waveguide-type PPLN, covers from 87 to 93 THz (2900 to 3100 cm⁻¹). An enhanced-cavity absorption cell remarkably improves the sensitivity of Lamb dips. An optical frequency comb controls the central frequency of the source with an uncertainty of a few kilohertz. Because the idler frequency is swept based on absolute frequency through the comb, recorded spectra can be repeatedly accumulated without any frequency drift. We have applied the spectrometer to resolve the hyperfine structure of the fundamental band of HCl with a spectral resolution of about 250 kHz.

To reduce the transit-time broadening, a novel enhanced-cavity absorption cell coupled with an idler wave of 1.9-mm beam radius at the beam waist has been introduced. The A₁-A₂ splitting of the ν₁ and ν₂ bands of HClD is resolved for a few tens low-J transitions with the Lamb-dip linewidth of 60 to 100 kHz. Very recently, the source linewidth has reduced to 3 kHz using a linewidth transfer technique from the Nd:YAG laser to the extended-cavity laser diode through a novel optical frequency comb with a fast servo control. When methane sample is cooled with liquid-nitrogen, and the beam radius is expanded to 3 mm, the observed Lamb dip is 20 kHz wide without any enhanced-absorption cell absorption.

Sub-Doppler resolution spectrometry of the fundamental bands of HCl and HClD has been carried out for the ν₁ and ν₂ fundamental bands using a comb-referenced difference-frequency generation spectrometer. Thirty transitions from the low-J=0 and K′=1 levels are observed with a resolution of 60 to 100 kHz, and the A₁-A₂ splitting is resolved for twenty-three of the thirty transitions. Most of them are overlapped in Doppler broadening and resolved for the first time, as far as we know. The absolute transition frequencies are determined with a typical uncertainty of 4 kHz. The A₁-A₂ splitting constant of the K′=1 levels is yielded as 2ν₁,A₁-2 = (1.5641 ± 0.0026) Hz for the ground vibrational state. Those of the K′=2 levels for the ν₁ = 1 states and of the (K′=2, J=1, l=1) and (K′=4, J=1, l=1) levels for the ν₂ = 1 state are also determined including the J-dependence terms.

In high-resolution molecular spectroscopy, the precise measure of the optical frequency is crucial to evaluate minute frequency characteristics of scanning laser. To satisfy these contradictory requirements, we have developed two types of high-resolution spectroscopic systems employing an optical frequency comb. One of the systems employs RF band-pass filters to generate equally spaced frequency markers for optical frequency calibration, and is appropriate for wide wavelength-range measurement with relatively high scanning rate. In the other system, the beat frequency between the optical frequency comb and the scanning laser is controlled by an acousto-optic frequency shifter. This system is suitable for more precise measurement, and enables detailed analyses of frequency characteristics of scanning laser.

In the present study, we observe Doppler-free two-photon absorption spectra of A′₁B₂(ν₁ = 0) → X′₁A₂(ν = 0) transition of naphthalene around 298 nm. The spectral lines are rotationally resolved and the resolution is about 100 kHz.
Fourier transform spectrometers (FTS) based on optical frequency combs (OFC) allow detection of broadband molecular spectra with high signal-to-noise ratios within acquisition times orders of magnitude shorter than traditional FTIRs based on thermal sources. Due to the pulsed nature of OFCs the interferogram consists of a series of bursts rather than a single burst at zero optical path difference (OPD). The comb mode structure can be resolved by acquiring multiple bursts, in both-mechanical FTS systems and dual-comb spectroscopy. However, in all existing demonstrations the resolution was ultimately limited either by the maximum available OPD between the interferometer arms or by the total acquisition time enabled by the storage memory. We present a method that provides spectral resolution exceeding the limit set by the maximum OPD using an interferogram containing only a single burst. The method allows measurements of absorption lines narrower than the OPD-limited resolution without any influence of the instrumental lineshape function. We demonstrate this by measuring undistorted CO and CO absorption lines with linewidth narrower than the OPD-limited resolution using OFC-based mechanical FTS in the near- and mid-infrared wavelength ranges. The near-infrared system is based on an Er:fiber femtosecond laser locked to a high finesse cavity and phase-modulated at a frequency precisely equal to (a multiple of) the cavity free spectral range. Residual frequency noise on the OFC relative to the cavity affects each component in an identical manner. The transmitted intensity contains a beat signal at the modulation frequency that is immune to frequency-to-amplitude noise conversion by the OFC. The OPD-limited resolution is eventually recovered by the spectral interference pattern. The comb structure is resolved by acquiring multiple bursts, in both-mechanical FTS systems and dual-comb spectroscopy. However, in all existing demonstrations the resolution was ultimately limited by the maximum available OPD between the interferometer arms or by the total acquisition time enabled by the storage memory. We present a method that provides spectral resolution exceeding the limit set by the maximum OPD using an interferogram containing only a single burst. The method allows measurements of absorption lines narrower than the OPD-limited resolution without any influence of the instrumental lineshape function. We demonstrate this by measuring undistorted CO and CO absorption lines with linewidth narrower than the OPD-limited resolution using OFC-based mechanical FTS in the near- and mid-infrared wavelength ranges. The near-infrared system is based on an Er:fiber femtosecond laser locked to a high finesse cavity, while the mid-infrared system is based on a Tm:fiber-laser-pumped optical parametric oscillator coupled to a multi-pass cell. We show that the method allows acquisition of high-resolution molecular spectra with interferometer length orders of magnitude shorter than traditional FTS.

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**Post-Deadline Abstract**

**METROLOGY WITH AN OPTICAL FEEDBACK FREQUENCY STABILIZED CRDS**

SAMIR KASS, JOHANNES BURKART, UMRS5558 LIPhy, Universite Grenoble 1/CNRS, Saint Martin de V Haven, France.

We will present a metrological application of our recently developed Optical Feedback Frequency Stabilized - Cavity Ring Down Spectrometer (OFFS-CRDS). This instrument, which ideally fits with an optical frequency comb for absolute frequency calibration, relies on the robust lock of a steady cavity ring down resonator against a highly stable, radiofrequency tunable optical source. At 1.6 μm, over 7 mm, we demonstrate Lamb dip spectroscopy of CO2 with line frequency retrieval at the kHz level, a dynamic in excess of 700,000 on the absorption scale and a detectivity of 4x10^13 cm/Hz^1/2. Such an instrument nicely meets the requirements for the most demanding spectroscopy spanning from accurate isotopic ratio determination and very precise lineshape recordings to Boltzmann constant redefinition.

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**NOISE-IMMUNE CAVITY-ENHANCED OPTICAL FREQUENCY COMB SPECTROSCOPY**

LUCILE RUTKOWSKI, AMIR KHODABAKSH, ALEXANDRA C JOHANSSON, ALEKSANDRA POLYNYOWICZ, Department of Physics, Umea University, Umea, Sweden.

We present noise-immune cavity-enhanced optical frequency comb spectroscopy (NICE-OFCS), a recently developed technique for sensitive, broadband, and high resolution spectroscopy. In NICE-OFCS an optical frequency comb (OFC) is locked to a high finesse cavity and phase-modulated at a frequency precisely equal to (a multiple of) the cavity free spectral range. Since each comb line and sideband is transmitted through a separate cavity mode in exactly the same way, any residual frequency noise on the OFC relative to the cavity affects each component in an identical manner. The transmitted intensity contains a beat signal at the modulation frequency that is immune to frequency-to-amplitude noise conversion by the OFC. The light transmitted through the cavity is detected with a fast-scanning Fourier-transform spectrometer (FTS) and the NICE-OFCS signal is obtained by fast Fourier transform of the synchronously demodulated interferogram. Our NICE-OFCS system is based on an Er fiber femtosecond laser locked to a cavity with a finesse of ~9000 and a fast-scanning FTS equipped with a high-bandwidth commercial detector. We measured NICE-OFCS signals from the 3υ_3 υ_2 overtone band of CO2 around 1.57 μm and achieved absorption sensitivity 6.4x10^13 cm^-1 Hz^-1/2 per spectral element, corresponding to a minimum detectable CO2 concentration of 25 ppb after 330 s integration time. We will describe the principles of the technique and its technical implementation, and discuss the spectral lineshapes of the NICE-OFCS signals.
A NEW BROADBAND CAVITY ENHANCED FREQUENCY COMB SPECTROSCOPY TECHNIQUE USING GHz VERNIER FILTERING

JÉRÔME MORVILLE, UMR 5006, ILM University Lyon 1 and CNRS, Villeurbanne, France; LUCILE RUTKOWSKI, Department of Physics, Umeå University, Umeå, Sweden; GEORGI DOBREVA*; Department of Physics, Sofia University, Sofia, Bulgaria; PATRICK CROIZET, UMR 5006, ILM University Lyon 1 and CNRS, Villeurbanne, France.

We present a new approach to Cavity Enhanced - Direct Frequency Comb Spectroscopy where the full emission bandwidth of a Titanium:Sapphire laser is exploited at GHz resolution. The technique is based on a low-resolution Vernier filtering obtained with an appreciable –actively stabilized– mismatch between the cavity Free Spectral Range and the laser repetition rate, using a diffraction grating and a split-photodiode 5. This particular approach provides an immunity to frequency-amplitude noise conversion, reaching an absorption baseline noise in the 10^−10 cm^−1 range with a cavity finesse of only 3000. Spectra covering 1800 cm^−1 (1−5 THz) are acquired in recording times of about 1 second, providing an absorption figure of merit of a few 10^−31 cm^−1/s/√Hz. Initially tested with ambient air, we report progress in using the Vernier frequency comb method with a discharge source of small radicals.

A DECADE-SPANNING HIGH-RESOLUTION ASYNCHRONOUS OPTICAL SAMPLING BASED TERAHERTZ TIME-DOMAIN SPECTROMETER

JACOB T GOOD, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA; DANIEL HOLLAND, Translational Imaging Center, University of Southern California, Los Angeles, CA, USA; IAN AFINNERAN, BRANDON CARROLL, MARCO A. ALLODI, GEOFFREY BLAKE, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA.

High-resolution ASynchronous OPtical Sampling (ASOPS) is a technique that substantially improves the combined frequency resolution and bandwidth of ASOPS based Ti:sapphire OSCillators with repetition frequencies of 80 MHz operating at a fixed repetition frequency offset of 100 Hz. This offset lock is maintained by a Phase-Locked Loop (PLL) operating at the 60th harmonic of the repetition rate of the Ti:Sapphire oscillators. Their respective time delay is scanned across 12.5 ms requiring a scan time of 10 ms, supporting a time delay resolution of up to 15.6 fs. ASOPS-THz-TDS enables high-resolution spectroscopy that is impossible for a THz-TDS system employing a mechanical delay stage. We measure a timing jitter of 1.36 fs for the system using an air-gap etalon and an optical cross-correlator. We report a Root-Mean-Square deviation of 20.7 kHz and a mean deviation of 14.4 MHz for water absorption lines from 0.5 to 2.7-THz. High-resolution ASOPS-THz-TDS enables high-resolution spectroscopy of both gas-phase and condensed-phase samples across a decade of THz bandwidth.
TG. Large amplitude motions, internal rotation

Tuesday, June 23, 2015 – 1:30 PM
Room: 100 Noyes Laboratory
Chair: Kaori Kobayashi, University of Toyama, Toyama, Japan

The high-resolution infrared spectrum of gaseous ethane-1d, at 130 K shows transitions that are split into A and E components due to the interaction of overall rotation with the internal rotation of the CH3 group. An analysis of the spectrum from 600 to 900 cm⁻¹ with an expanded version of the program ERHAM has been successful in assigning the bands at 1501(1) = 805 cm⁻¹ and 1512(1) = 715 cm⁻¹. A discussion of the interactions among the fundamental levels of ν5 and ν2 with overtone levels of ν5 and the CH3 torsion will be given. ERHAM has been, and continues to be, very successful in the analysis of pure rotational spectra of molecules containing internal rotation and the vibrational spectrum of C2H6D serves as an excellent system to test the extension of the program.


ADAM M DALLY, BRIAN DROUIN, JOHN PEARSON, ADAM M DALY, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA. Methanol is the simplest molecule with a three-fold internal rotation and the observation of its ν3 band served the primary catalyst for the development of internal rotation theory. The 75 subsequent years of investigation into the ν3 band region have yielded a large number assignments, numerous high precision energy levels and a great deal of insight into the coupling of ν8 and ν3 with ν2 and ν1 and other nearby states. In spite of this progress numerous assignment mysteries persist. The origin of almost all the far infrared laser lines remain unknown and all attempts to model the region quantum mechanically have had very limited success. The C2H5 internal rotation Hamiltonian has successfully modeled the ν8=0,1 & 2 states of methanol and other internal rotors. However, successful modeling of the coupling between torsional bath states and excited small amplitude motion remains problematic and coupling of multiple interacting excited small amplitudes vibrations featuring large amplitudes remains almost completely unexplored. Before such modeling can be attempted, identifying the remaining low lying levels of ν8 and ν3 is necessary. We present an analysis to interpret the microwave spectrum of ν8 and ν3 along with the underlying torsional band in ν8≈3 and ν8≈4.


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TG01 1:30 – 1:45

THE BAND OF C2H5CH3D FROM 770-880 cm⁻¹

ADAM M DALLY, BRIAN DROUIN, JOHN PEARSON, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA. PETER GREENER, Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO, USA; KEEYOUNG SUNG, LINDA BROWN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; ARLAN MANTZ, Department of Physics, Astronomy and Geophysics, Con- necticut College, New London, CT, USA; MARY ANN H. SMITH, Science Directorate, NASA Langley Research Center, Hampton, VA, USA.

To extend the ethane database we recorded a 0.0028 cm⁻¹ resolution spectrum of C2H5CH3D from 650 to 1500 cm⁻¹ using a Bruker IFS-125HR at the Jet Propulsion Laboratory. The 98% deuterium-enriched sample was contained in the 2039 cm absorption cell; one scan was taken with the sample cryogenically cooled to 130 K and another at room temperature. From the cold data, we retrieved line positions and intensities of 8704 individual absorption features from 770 – 880 cm⁻¹ using a least squares fitting algorithm. From this set of measurements, we assigned 5041 transitions to the ν5=0,1 and 2 states of methanol. The positions were modeled using a 22 term torsional Hamiltonian using SPFIT producing the A and E energy splittings of 5-909(25)x10⁻¹⁷ cm⁻¹ (220 MHz) with a standard deviation of 7x10⁻¹⁷ cm⁻¹ (121 MHz). The calculated line intensities at 130 K agree very well with retrieved intensities. To predict line intensities at different temperatures, the partition function value was determined at eight temperatures between 9.8 and 300 K by summing individual energy levels up to J = 100. The positions were modeled using a 22 term torsional Hamiltonian using SPFIT producing the A and E energy splittings of 5-909(25)x10⁻¹⁷ cm⁻¹ (220 MHz) with a standard deviation of 7x10⁻¹⁷ cm⁻¹ (121 MHz). The calculated line intensities at 130 K agree very well with retrieved intensities. To predict line intensities at different temperatures, the partition function value was determined at eight temperatures between 9.8 and 300 K by summing individual energy levels up to J = 100. The resulting prediction of singly-deuterated ethane absorption at 12.5 μm enables its detection in planetary atmospheres, including those of Titan and exoplanets.


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TG04 2:21 – 2:36

FIRST HIGH RESOLUTION ANALYSIS OF THE ν13 BAND OF PROPANE AT 921.4 cm⁻¹: EVIDENCE OF LARGE-AMPLITUDE-MOTION TUNNELING EFFECTS

AGNES PERRIN, F. KWABIA TCHANIA, JEAN-MARIE FLAUD, LISA, CNRS, Université Paris Est Créteil et Paris Didorrot, Créteil, France; LAURENT MAINCERON, Synchrotron SOLEIL, CNRS-MONARIS UMR 8233 and Beamline AILES, Saint Aubin, France; JEAN DEMADISON, NADALIA VOGT, Section of Chemical Information Systems, Université Ulm, Ulm, Germany; PETER GREENER, Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO, USA; WALTER LAFFERTY, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD, USA. A high resolution (0.0015 cm⁻¹) IR spectrum of propane, C3H8, has been recorded with synchrotron radiation at the French light source facility at SOLEIL coupled to a Bruker IFS-125 Fourier transform spectrometer. A preliminary analysis of the ν13 fundamental band (ν13, CH3 rock) near 921.4 cm⁻¹ reveals that the rotational energy levels of 21 are split by interactions with the internal rotations of the methyl groups. Conventional analysis of this A-type band yielded band centers at 921.372(38), 921.382(31) and 921.397(44) cm⁻¹ for the A, E, E and E A and E tunneling splitting components, respectively. These tunneling splittings most probably are due to anharmonic and/or Coriolis resonance coupling with nearby highly excited states of both internal rotations of the methyl group. In addition, several vibrational-rotational transitions and resonances were observed that affect the torsional components in different ways. The analysis of the E-type band near 870 cm⁻¹ (ν8, sym. C=C stretch) which also contains split rovibrational transitions due to internal rotation is in progress. It is performed by using the effective rotational Hamiltonian method ERHAM with a code that allows prediction and least-squares fitting of such vibration-rotation spectra.

Large amplitude motions in methyl rotor systems have been well studied, especially the coupling between the CH$_3$ torsion and the CH stretches. The CH$_3$OO radical is a example of a system where this coupling is relatively small, but its effects still can be observed in the infrared spectrum taken by the Lee group.\(^3\) Rotational contour simulations based on an asymmetric rotor model show good agreement with the experimental spectrum except for an unexplained broadening of the Q-branch of one of the CH stretch features. The broadening is likely caused by low frequency torsional modes populated at room temperature resulting in sequence band transitions that are slightly shifted from the origin. A reduced dimension model involving the three CH stretches and the CH$_3$ torsion is applied to CH$_3$OO to simulate the observed spectrum. The CH stretches are described by a harmonically coupled anharmonic oscillator model in which the parameters depend on the CH$_3$ torsion angle. Based on these calculations, the observed broadening of the Q-branch can be qualitatively explained by coupling between two CH stretch/CH torsion combination bands which differ by one quantum in torsional excitation. The A-X electronic transitions of halogenated methyl peroxy radicals, CH$_3$XOO (X-Cl, Br, I), show a complementary structure. At room temperature multiple peaks have been observed in the region of the origin and OX stretch vibrionic bands in all three radicals. A report for CH$_3$OO, being by far the most complex, will be presented later. This work is supported by the National Science Foundation.


The torsion-vibration-rotation analysis of nearly degenerate vibrational states involving both small and large amplitude motions has acquired significant quantum mechanical description. Unfortunately the intermediate medium is filled with many prevalent molecules that feature internal rotation that couples strongly with torsional bath states. Many excited states are prevalent molecules that feature internal rotation that couples strongly with torsional bath states. Many excited states are highly populated by the hot bands originated from excited torsional states. Several theoretical models have been investigated to calculate the Franck-Condon factors that govern the structure. A calculation that models the I-C-O torsion using curvilinear internal coordinates and molecular geometry and harmonic torsion frequencies predicted by electronic structure calculations shows the best agreement with the CH$_3$OO experimental and simulated spectra. The multiple peak structure results from the change in X-C-O-O torsion dihedral between the X state and A states. Interestingly, a similar calculation with Cartesian coordinates fails to explain the torsional structure. This study shows the importance of coordinate system choice if a significant displacement in the torsional coordinate occurs upon electronic excitation.


The methylidyne molecule, CH$_3$CN, is of interest as a potential astrophysical species and as a model system for the study of quasiasymmetric behavior. The rotational spectrum is very complex by the presence in CH$_3$CN of two large-amplitude motions: an almost free internal rotation and a low barrier skeletal bending motion. This challenging spectrum has, nevertheless, been assigned at 8-38 GHz by Stark spectroscopy\(^4\) and has been measured at 117-376 GHz with the broadband FASSST technique.\(^5\)

\(^4\) J. Kral, J. Mol. Spectrosc. 151, 131 (1994)

\(^5\) J. Kral et al., J. Opt. Spectrosc. and Molecular Spectroscopy, The Ohio State University (Ohio 2010) RC-13

\(3\) Intermission

\(3\) YUEYUE ZHAO, Institute for Physical Chemistry, RWTH Aachen University, Aachen, Germany; HA VINH LAM NGUYEN, CNRS et Université Paris Est Créteil, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Créteil, France; WOLFGANG STAHL, Institute for Physical Chemistry, RWTH Aachen University, Aachen, Germany; EDN J. T. JAGGER, Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD, USA.

The molecular-beam Fourier-transform microwave spectrum of pinacolone (methyl tert-butyl ketone) has been measured in several regions between 2 and 40 GHz. Assignments of a large number of A and E transitions were confirmed by combination assignments, but fits of the assigned spectrum using several torsion-rotation computer programs based on different models led to the unexpected conclusion that no existing program correctly captures the internal dynamics of this molecule. A second puzzle arose when it become clear that roughly half of the spectrum remained unsigned even after all predicted transitions were added to the assignment list. Quantum chemical calculations carried out at the MP2/6-311+G(d,p) level indicate that this molecule does not have a plane of symmetry at equilibrium, and that internal rotation of the light methyl group induces a large oscillatory motion of the heavy tert-butyl group from one side of the C$_3$ saddle point to the other. The effect of this non-C$_3$ equilibrium structure was modeled for $J = 0$ levels by a simple two-top Hamiltonian, where magnitudes of the strong top-top coupling terms were determined directly from the ab initio two-dimensional potential surface. A plot of the resultant torsional levels on the same scale as a one-dimensional potential curve along the zig-zag path connecting the six (unequally spaced) minima bears a striking resemblance to the 1:2:1 splitting pattern of levels in an internal rotation problem with a six-fold barrier. A plot of the six minima closely resembles the potential surface for methylamine. This talk will focus on implications of these resemblances for future work.

\(4\) KRAL, J. MOL. SPECTROSC., 131 (1994)

\(5\) KRAL et al., J. OPT. SPECTROSC. AND MOLECULAR SPECTROSCOPY, THE OHIO STATE UNIVERSITY (OHIO 2010) RC-13
GAS PHASE CONFORMATIONS AND METHYL INTERNAL ROTATION FOR 2-PHENYLETHYL METHYL ETHER
AND ITS ARGON VAN DER WAALS COMPLEX FROM FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

RANIL M. GURUSINGHE, MICHAEL TUBERGHN, Department of Chemistry and Biochemistry, Kent State University, Kent, OH, USA.

A mini-cavity microwave spectrometer was used to record the rotational spectra arising from 2-phenylethyl methyl ether and its weakly bonded argon complex in the frequency range of 10.5 – 22 GHz. Rotational spectra were found for two stable conformations of the monomer: anti-anti and gauche-anti, which are 1.4 kJ·mol⁻¹ apart in energy at wB97XD6-311++G(d,p) level. Doubled rotational transitions, arising from internal motion of the methyl group, were observed for both conformers. The program XIAM was used to fit the rotational constants, centrifugal distortion constants, and barrier to internal rotation to the measured transition frequencies of the A and E internal rotation states. The best global fits of the rotational constants for the anti-anti conformer are A= 3799.066(3) MHz, B= 577.95180(17) MHz, C= 544.7532(5) MHz and the A state rotational constants of the gauche-anti conformer are A= 2676.1202(7) MHz, B= 760.77250(2) MHz, C= 684.78901(2) MHz. The rotational spectrum of 2-phenylethyl methyl ether – argon complex is consistent with the geometry where argon atom lies above the plane of the benzene moiety of gauche-anti conformer. Tunneling splittings were too small to resolve within experimental accuracy, likely due to an increase in three fold potential barrier when the argon complex is formed. Fitted rotational constants are A= 1061.2337(6) MHz, B= 499.81754(7) MHz, C= 518.33553(7) MHz. The lowest energy solvated ether – water complex with strong intermolecular hydrogen bonding has been identified theoretically. Progress on the assignment of the water complex will also be presented.

MICROWAVE SPECTRA AND AB INITIO STUDIES OF THE NE-ACETONE COMPLEX

RANIL M. GURUSINGHE, MICHAEL TUBERGHN, Department of Chemistry and Biochemistry, Kent State University, Kent, OH, USA.

Rotational spectra of α-Methylstyrene, cis-β-Methylstyrene, and trans-β-Methylstyrene were previously fit (essentially to experimental measurement error) using an all-tunneling Hamiltonian formalism. Theoretical calculations at wB97XD6-311+G(d,p) level predict only one stable conformer for each molecular system. Spectra were recorded in the frequency range of 10.5 – 22 GHz using a cavity based Fourier transform microwave spectrometer. A related potential scan for the methyl torsion at wB97XD6-311+G(d,p) level of theory was used to estimate the associated barrier for the hindered internal rotation. The program XIAM was used to fit the rotational constants, distortion constants and barrier to methyl internal rotation to the measured transition frequencies of the A and E internal rotation states.

MICROVE SPECTRA AND AB INITIO STUDIES OF THE NE-ACETONE COMPLEX

RADGAZ JAVIN THOMAS, YUNJIE XU, WOLFGANG JÄGER, Department of Chemistry, University of Alberta, Edmonton, AB, Canada.

Microwave spectra of the neon-acetone van der Waals complex were measured using a cavity-based molecular beam Fourier-transform microwave spectrometer in the region from 5 to 18 GHz. Both 20Ne and 22Ne containing isotopologues were studied and both e- and weaker a-type rotational transitions were observed. The transitions are split into multiplets due to the interaction between methyl groups in acetone. Electronic state calculations were done at the MP2 level of theory with the 6-31+G* basis set for all atoms and the internal rotation barrier height of the methyl groups was determined to be about 2.8 kJ·mol⁻¹. The ab initio rotational constants were the basis for our spectroscopic searches, but the multiplet structure and fleggness of the complex made the quantum number assignment very difficult. The assignment was finally achieved with the aid of constructing closed frequency loops and predicting internal rotation splittings using the XIAM code. Analyses of the spectra yielded rotational and centrifugal distortion constants, as well as internal rotation parameters, which were interpreted in terms of structure and internal dynamics of the complex.
The ground state rotational spectrum of itaconic acid (methylenesuccinic acid) and N-acetylethanolamine (AEA) have been collected and analyzed over the frequency range of 7-17.5 GHz. Both molecules displayed an unexpected tunneling splitting pattern caused by a V2 and V3 barriers, respectively. AEA’s methyl rotor is directly connected to a carbonyl and is expected to have too high of a barrier to internal motion. Itaconic acid contains no methyl groups or any symmetry, yet a torsional splitting was observed. The origin of this motion as well their barrier heights and lowest energy conformations will be discussed.

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A theoretical simulation of the photoelectron spectrum for the ground state of methoxy radical is reported based on the quasidibatic model Hamiltonian originally proposed by Köppel, Domcke, and Cederbaum. The parameters in the model Hamiltonian have been obtained from ab initio coupled-cluster calculations. The linear and quadratic force constants have been calculated using equation-of-motion coupled-cluster ionization potential method with the singles, doubles, and triples (EOM-CCSDT) truncation scheme together with atomic natural orbital basis sets of triple-zeta quality (ANO1). The cubic and quartic force constants have been obtained from EOM-CCSD calculations with ANO basis sets of double-zeta quality (ANO0), and the spin-orbit coupling constant has been computed at the EOM-CCSD/pcVQZ level. The nuclear Schrödinger equation has been solved using the Lanczos algorithm to obtain vibronic energy levels as well as the corresponding intensities. The simulated spectrum compares favorably with the recent high-resolution slow electron velocity-map imaging experiment for vibronic levels up to 2000 cm$^{-1}$.

Using the potential energy force field and calculated spectra of the methoxy radical by Nagesh and Sibert and the potential energy surface of methoxy radical from the potential energy minimum, we are able to use an expanded version of the linear Jahn-Teller Hamiltonian to assign the states. The spectrum is further complicated due to spin-orbit and Fermi couplings. The standard diabatic normal mode quantum numbers are poor labels due to this vibronic mixing.

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RE-EVALUATION OF HO₃ STRUCTURE USING MILLIMETER-SUBMILLIMETER SPECTROSCOPY

LUYAO ZOU, BRIAN HAYS, SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA, USA.

The HO₃ radical is of great interest in both atmospheric and astrophysical chemistry. However, its molecular structure has not been fully characterized by previous spectral studies. Microwave spectroscopy on the trans-HO₃ conformer did not access higher $K_a$ levels due to their limited frequency range. As a result, several centrifugal distortion constants could not be determined. We have therefore conducted spectroscopy of HO₃ in the millimeter and submillimeter ranges, from 70 to 450 GHz, under the guidance of a new fast sweep technique we developed for line searching. Large frequency shifts, primarily due to a large $\Delta K_a$ centrifugal distortion constant, are observed compared to the spectral extrapolation from previous microwave studies. In addition, new spectral branches have been detected. The measured lines and preliminary spectral analysis will be presented, and the implications of these results will be discussed.

ON THE STARK EFFECT IN OPEN SHELL COMPLEXES EXHIBITING PARTIALLY QUENCHED ELECTRONIC ANGULAR MOMENTUM

GARY E. DOUBERLY, CHRISTOPHER P. MORADI, Department of Chemistry, University of Georgia, Athens, GA, USA.

The Stark effect is considered for polyatomic open shell complexes that exhibit partially quenched electronic angular momentum. Specifically, a zero-field model Hamiltonian is employed that accounts for the partial quenching of electronic orbital angular momentum in hydroxyl radical containing molecular complexes. Spherical tensor operator formalism is employed to derive matrix elements of the Stark Hamiltonian in a parity conserving. Hund’s case (a) basis for the most general case, in which the permanent dipole moment has projections on all three inertial axes of the system. Ro-vibrational transition intensities are derived, again for the most general case; namely, the laser polarization is projected onto axes parallel and perpendicular to the Stark electric field, and the transition dipole moment vector is projected onto all three inertial axes in the molecular frame. The model discussed here is compared to experimental spectra of OH-(C₂H₅) and OH-(CH₂CH₃), and OH-(H₂O) complexes formed in He nanodroplets.

INFRARED LASER SPECTROSCOPY AND AB INITIO COMPUTATIONS OF OH-(D₃O)₂ COMPLEXES IN HELIUM NANODROPLETS

DEEPIK J. BRICE, CHRISTOPHER M. LEAVITT, CHRISTOPHER P. MORADI, GARY E. DOUBERLY, Department of Chemistry, University of Georgia, Athens, GA, USA; FEDERICO J. HERNANDEZ, GUSTAVO A. PINO, INFTQC (CONICET – Universidad Nacional de Córdoba) and Facultad de Ciencias Químicas Universidad Nacional de Córdoba, Ciudad Universitaria, Córdoba, Argentina.

OH-(D₃O)₂ complexes are assembled in He droplets via the sequential pickup of D₂O molecules and the hydroxyl radical, which is formed via the pyrolytic decomposition of tert-butyl hydroperoxide. Bands due to clusters as large as N=4 are observed. Ro-vibrational spectroscopy of the binary complex reveals a vibrationally averaged C₆₀ structure. The effect of partial quenching of the electronic angular momentum in the complex is partially resolved in the rotational fine structure associated with the νOH stretch. Stark spectroscopy of this band reveals a permanent electronic dipole moment for the binary complex equal to 3.7(5) D. OH stretch bands in larger clusters do not exhibit rotational fine structure; however, polarization spectroscopy of the OH-(D₃O)₂ complex, when compared to predictions from ab initio computations, reveals two nearly isoenergetic isomers, both of which resemble the cyclic water trimer. Lower frequency OH stretch bands are assigned to cyclic tetramer and cyclic pentamer clusters on the basis of D₂O pressure dependence and ab initio frequency computations.

VIBRATIONAL-TORSIONAL COUPLING REVEALED IN THE INFRARED SPECTRUM OF HE-SOLVATED n-PROPYL RADICAL

CHRISTOPHER P. MORADI, BERNADETTE M. BRODERICK, JAY AGARWAL, HENRY F. SCHAEFER III, GARY E. DOUBERLY, Department of Chemistry, University of Georgia, Athens, GA, USA.

The n-propyl and i-propyl radicals were generated in the gas phase via pyrolysis of n-butyli nitrite (CH₃C(ONO)₂) and i-butyli nitrate (CH₃C(CH₃)CH(ONO)₂) precursors, respectively. Nascent radicals were promptly solvented by a beam of He nanodroplets, and the infrared spectra of the radicals were recorded in the C-H stretching region. In addition to the three vibrations of n-propyl previously measured in an Ar matrix, we observe many unreported bands between 2800 and 3150 cm⁻¹, which we attribute to propyl radicals. The C-H stretching modes observed above 2900 cm⁻¹ for both radicals are in excellent agreement with anharmonic frequencies computed using VPT2. Between 2800 and 2960 cm⁻¹, however, the spectra of n-propyl and i-propyl radicals become quite congested and difficult to assign due to the presence of multiple anharmonic resonances. Computations reveal the likely origin of the spectral congestion to be strong coupling between the high frequency C-H stretching modes and a lower frequency torsional motion, which modulates quite substantially a through-space hyperconjugation interaction.

VIBRONIC SPECTROSCOPY OF HETERO DIHALO-BENZYL RADICALS GENERATED BY CORONA DISCHARGE – JET COOLED CHLOROFLUOROBENZYL RADICALS

YOUNG YOON, SANG LEE, Department of Chemistry, Pusan National University, Pusan, Korea.

The technique of corona excited supersonic jet expansion coupled with a pinhole-type glass nozzle was applied to vi- bronic spectroscopy of jet-cooled chlorofluorobenzyl radicals for the vibronic assignments and measurements of electronic energies of the D₁ → D₂ transition. The vibronic emission spectra were recorded with a long-path monochromator in the visible region. The 2.3-, 2.4-, and 2.5-Chlorofluorobenzyl radicals were generated by corona discharge of corresponding precursor molecules, chlorofluorobenzyls seeded in a large amount of helium carrier gas. The emission spectra show the vibronic bands originating from benzyl-type radicals, chlorofluorobenzyl and fluorobenzyl benzyl radicals, in which fluorobenzyl radicals were obtained by displacement of CI by H atom produced by the dissociation of methyl-C-H bond. From an analysis of the spectra observed, we could determine the electronic energies in the D₁ → D₂ transition and vibrational mode frequencies at the D₂ state of chlorofluorobenzyl radicals which show the origin band of the electronic transition to be shifted to red region, with the parent benzyl radical. The red-shift is highly sensitive to the number, position, and kind of substituents in chlorofluorobenzyl radicals. From the quantitative analysis of the red-shift, it has been found that the ad- ditivity rule, discovered recently by Lee group predicts the observation very well. In addition, the negligible contribution of the substituent at the 4-position, the nodal point of the Hückel’s molecular orbital theory, can be well described by the discon- nection of substitution from molecular plane of the benzene ring available for delocalized e electrons. In this presentation, I will discuss the spectroscopic observation of new chlorofluorobenzyl radicals and substituent effect on electronic transition energy which is useful for identification of isomeric substituted benzyl radicals.
GROWING UP RADICAL: INVESTIGATION OF BENZYL-LIKE RADICALS WITH INCREASING CHAIN LENGTHS

Joseph A. Korn, Khadda M. Jawad, Daniel M. Hewett, Timothy S. Zwie, Department of Chemistry, Purdue University, West Lafayette, IN, USA.

Combustion processes involve complex chemistry including pathways leading to polyaromatic hydrocarbons (PAHs) from small molecule precursors. Resonance stabilized radicals (RSRs) likely play an important role in the pathways to PAHs due to their unusual stability. Benzyl radical is a prototypical RSR that is stabilized by conjugation with the phenyl ring. Earlier work on α-methyl benzyl radical showed perturbations to the spectroscopy due to a hindered methyl rotor. If the alkyl chain is lengthened then multiple conformations become possible. This talk will discuss the jet-cooled spectroscopy of α-ethyl benzyl radical and α-propyl benzyl radical produced from the discharge of 1-phenyl propanol and 1-phenyl butanol respectively. Electronic spectra were obtained via resonant two-photon ionization, and IR spectra were obtained by resonant ion-dip infrared spectroscopy.


ANALYSIS OF ROTATIONALLY RESOLVED SPECTRA TO NON-DEGENERATE (α) UPPER-STATE VIBRONIC LEVELS IN THE 2A′′0 − 2A′′1 ELECTRONIC TRANSITION OF NO3

Mourad Roudiane, Terrance Joseph Codd, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA; Ming-Wei Chen, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA; Henry Tran, Dmitry G. Melnik, Terrry A. Miller, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA; John F. Stanton, Department of Chemistry, The University of Texas, Austin, TX, USA.

The vibronic structure of the \( \tilde{A} \rightarrow \tilde{X} \) electronic spectrum of NO3 has been observed using both room-temperature and jet-cooled samples. A recent analysis of this structure is consistent with the Jahn-Teller effect (JTE) in the \( \tilde{c}v_2 \) vibrational mode (N-O stretch) being quite strong while the JTE in the \( \tilde{c}v_4 \) mode (O-N-O bend) is rather weak. Electronic structure calculations quantitatively predict these results but the calculated magnitude of the JTE is quantitatively inconsistent with the spectral analysis.

Rotationally resolved spectra have been obtained for over a dozen vibronic bands of the \( \tilde{A} \rightarrow \tilde{X} \) electronic transition in NO3. An analysis of these spectra should provide considerably more experimental information about the JTE in the \( \tilde{A} \) state of NO3 as the rotational structure should be quite sensitive to the geometric distortion of the molecule due to the JTE. This talk will focus upon the parallel bands, which terminate on \( \tilde{A} \) state levels of \( \tilde{c}v_2 \) vibronic symmetry, which were the subject of a preliminary analysis reported at this meeting in 2014. We have now recorded the rotational structure of over a half-dozen parallel bands and have completed analysis on the \( \tilde{c}\lambda_{01}^1 \) and \( \tilde{c}\lambda_{01}^2 \) transitions with several other bands being reasonably well understood. Two general conclusions emerge from this work. (i) All the spectral bands show evidence of perturbations which can reasonably be assumed to result from interactions of the observed \( \tilde{A} \) state levels with high vibrational levels of the \( \tilde{X} \) state. The perturbations range from severe in some bands to quite modest in others. (ii) Analyses of observed spectra, insofar as the perturbations permit, have all been performed with an oblate symmetric top model including only additional spin-rotation effects. This result is, of course, consistent with an effective, undistorted geometry for NO3 of D\( \infty \) symmetry on the rotational timescale.

Rovibronic variational calculations of the nitrate radical

Bryan Changala, JILA, National Institute of Standards and Technology and Univ. of Colorado Department of Physics, University of Colorado, Boulder, CO, USA; Joshua H Baraban, Department of Chemistry, University of Colorado, Boulder, CO, USA; John F. Stanton, Department of Chemistry, The University of Texas, Austin, TX, USA.

In recent years, sophisticated diabatic Hamiltonians have been developed in order to understand the low-energy vibronic level structure of the nitrate radical (NO3), which exhibits strong coupling between the \( \tilde{X} \) and doubly degenerate \( \tilde{B} \) states. Previous studies have reproduced the observed vibronic level positions up to 2000 \( \text{cm}^{-1} \) above the zero-point level, yet the rotational structure has remained uninvestigated with ab initio methods. In this talk, we present calculations of the \( N \geq 0 \) rovibronic structure of low-lying vibronic states of NO3, in which complicated rovibrational and Coriolis interactions have been observed. Our results include calculations using both adiabatic and diabatic Hamiltonians, enabling a direct comparison between the two. We discuss extensions of our treatment to include spin-orbit and spin-rotation effects.
VIBRONIC STRUCTURE OF THE $\tilde{X}^{2}A'$ STATE OF NO$_3$

MASARU FUKUSHIMA$^a$, Information Sciences, Hiroshima City University, Hiroshima, Japan.

We have measured dispersed fluorescence (DF) spectra from the single vibronic levels (SVL's) of the $\tilde{B}^{2}E'$ state of jet-cooled $^{15}$NO$_3$ and $^{15}$NO$_3$, and found a new vibronic band around the $v_4$ fundamental. This new band has two characteristics; (1) intense isotope shift, and (2) unexpectedly strong intensity, i.e. comparable with that of the $v_4$ fundamental. We concluded on the basis of the isotope effect that the terminated (lower) vibrational level of the new vibronic band should have vibrationally $\Delta v_4$ symmetry, and assigned to the third over-tone of the $v_4$ asymmetric ($v'$) mode, $3v_4$ ($v_4'$). We also assigned a weaker band at about 160 cm$^{-1}$ above the new band to one terminating to $3v_4$ ($v_4'$). The $3v_4$ ($v_4'$) and ($v_4'$) levels are ones with $\ell = \pm 3$. Hirota proposed new vibronic coupling mechanism which suggests that degenerate vibrational modes can induce electronic orbital angular momentum ($L$) even in non-degenerate electronic states. We interpret this as a sort of break-down of the Born-Oppenheimer approximation, and think that $\pm \ell$ induces $\pm \tilde{L}$, where $\tilde{L}$ expresses the pseudo-$L$ for the present system, one of the components of the third over-tone level, $[\tilde{L} = 0; v = 3, \ell = \pm 3]$, can have contributions of $[\tilde{L} = 1; v = 3, \ell = \pm 2]$ and $[-2; \ell = \pm 1]$. Under this interpretation, it is expected that there is sixth-order vibronic coupling, $\langle \nu \tilde{Q}_1^2 + \tilde{Q}_1^2 \tilde{Q}_3 \rangle$, between $[0; 3, \ell = \pm 3]$ and $[3; 3, \ell = \pm 3]$. The sixth-order coupling is weaker than the Renner-Teller term (the fourth-order term, $\langle \nu \tilde{Q}_1^2 + \tilde{Q}_1^2 \tilde{Q}_3 \rangle$, but stronger than the eighth-order term, $\langle \nu \tilde{Q}_1^2 + \tilde{Q}_1^2 \tilde{Q}_3 \rangle$. It is well known in linear molecules that the former shows huge separation, comparable with vibrational frequency, among the vibronic levels of II electronic states, and the latter shows considerable splitting, $\sim 10$ cm$^{-1}$, at $\Delta$ electronic states. Consequently, the $\sim 160$ cm$^{-1}$ splitting at $v_4 = 3$ is attributed to the sixth-order interaction. The relatively strong intensity for the band to $3v_4$ ($v_4'$) can be interpreted as a part of the huge 0-0 band intensity, because the $3v_4$ ($v_4'$) level, $[0; 3, \ell = \pm 3]$, can connect with the vibrationless level, $[0; 0, 0]$. $3v_4$ ($v_4'$) has two-fold intensity because of the vibrational wavefunction, $[0; 3, \ell = \pm 3]$ and $[3; 3, \ell = \pm 3]$, while negligible intensity is expected for $3v_4$ ($v_4'$) with $[0; 3, \ell = \mp 3]$ and $[3; 3, \ell = \mp 3]$ due to the cancellation. To confirm these interpretations, experiments on rotationally resolved spectra are underway.

$^a$Author thanks T. Hirota and E. Hirota for their valuable discussion and support.
$^b$E. Hirota and T. Hirota, pages 9591, 20062011, and pages 9507, 20062014.
Chair: Patrick Vaccaro, Yale University, New Haven, CT, USA

**TI01**

**MULTISCALE SPECTROSCOPY OF DIFFUSING MOLECULES IN CROWDED ENVIRONMENTS**

**AHMED A. HUIKAL**

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Living cells are known to be crowded with organelles, biomembranes, and macromolecules such as proteins, DNA, RNA, and actin filaments. It is believed that such macromolecular crowding affect biomolecular diffusion, protein–protein and protein–substrate interaction, and protein folding. In this contribution, I will discuss our recent results on rotational and translational diffusion of small and large molecules in crowded environments using time-resolved anisotropy and fluorescence correlation spectroscopy methods. In these studies, rhodamine green and enhanced green fluorescent proteins are used as fluorescent probes diffusing in buffers enriched with biomimetic crowding agents such as Ficol70, bovine serum albumin (HSA), and ovalbumin. Controlled experiments on pure and glycerol-rich buffers were carried out in environments with variable, homogeneous viscosity. Our results indicate that the microviscosity differs from the corresponding bulk viscosity, depending on the nature of crowding agents (i.e., proteins versus polymers), the concentration of crowding agents and spatiotemporal scaling of our experimental approach. Our findings provide a foundation for fluorescence-based studies of diffusion and binding of biomolecules in the crowded milieu of living cells.

**TI02**

**INVESTIGATING THE ROLE OF HUMAN SERUM ALBUMIN ON THE EXCITED STATE DYNAMICS OF INDOCYANINE GREEN USING SHAPED FEMTOSECOND LASER PULSES**

**MUATH NAIRAT**, ARKAPRABHA KONAR, MARIE KANIECKI, VAIDIM Y. LOZIOVY, MARCOS DANUS.

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In this talk, I will present recent developments aimed at investigating the role of human serum albumin (HSA) on the excited state dynamics of indocyanine green (ICG). ICG is a near-infrared dye and photosensitizer approved by the Food and Drug Administration (FDA) for the treatment of superficial vein and vascular malformations. HSA is a large globular protein that plays a crucial role in many biological processes. Our results indicate that HSA hinders torsional motion and also mitigates the triplet state formation in ICG. Low frequency vibrational motion of ICG is observed more clearly when it is bound to the HSA protein.

**TI03**

**ULTRAFAST SPECTROSCOPIC AND AB INITIO COMPUTATIONAL INVESTIGATIONS ON SOLVATION DYNAMICS OF NEUTRAL AND DEPROTONATED TYROSINE**

**TAKASHI FUTAWARA**, Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH, USA; MAAREM Z. ZOTERISKI, Statice Laboratory, National Research Council of Canada, Ottawa, ON, Canada.

We have studied one of the aromatic amino acids, tyrosine, regarding its photophysical properties in various solvent conditions by using a femtosecond fluorescence up-conversion technique and high-level TD-DFT and CC2 computations. In this talk, I will present our recent results on electrophysical properties of neutral tyrosine in various solvents, also on the excited-state dynamics for a single- (or double)-deprotonated tyrosine under various pH solutions will be presented. In high basicity, tyrosine shows different absorption/emission spectra, and a total spectrum consists of a combination of these individual spectra that depend on the pH of the solution. The time scale of acid-base equilibrium is essential in solvation dynamics; whereas the protonation is simply controlled by diffusion, the deprotonation is considered to be a slow process depending on the solution. The ultrafast dynamics of nucleic acids have been under scrutiny for the past couple of decades because of the role that the high-energy electronic states play in photodynamics and carcinogenesis. Kinetic models have been proposed, based on both experimental and theoretical discoveries. Direct experimental evidence of the intersystem crossing rate and population of the triplet state for most nucleic acid bases has yet to be reported, even though the triplet state is thought to be the most reactive species. Utilizing ultrafast femtosecond transient absorption spectroscopy, we reveal that triplet population transfer occurs in several nucleic acid derivatives in the condensed phase. The implication of these results to the current understanding of the DNA and RNA photostability will be discussed. The authors acknowledge the CAREER program of the National Science Foundation (Grant No. CHE-1255084) for financial support.

**TI04**

**WHICH ELECTRONIC AND STRUCTURAL FACTORS CONTROL THE PHOTOSTABILITY OF DNA AND RNA PURINE NUCLEOBASES?**

**MARVIN POLLUM, CHRISTIAN RECHARDT, CARLOS E. CRESPO-HERNÁNDEZ**, Chemistry, Case Western Reserve, Cleveland, OH, USA; LARA MARTÍNEZ-FERNÁNDEZ, INÉS CORRAL, Departamento de Química, Universidad Autónoma de Madrid, Madrid, Spain; CLEMENS RAUER, SEBASTIAN MAL, PHILIP MARQUETAND, LETICIA GONZALEZ, Instituto de Theoretical Chemistry, University of Vienna, Vienna, Austria.

Following ultraviolet excitation, the canonical purine nucleobases, guanine and adenine, are able to efficiently dissipate the absorbed energy within hundreds of femtoseconds. This property allows these nucleobases with great photostability. Conversely, non-canonical purine nucleobases exhibit high fluorescence quantum yields or efficiently populate long-lived triplet excited states from which they can be used for photovoltaic applications. This hypothesis is supported by preliminary power conversion efficiency results in devices.
MOLECULE-LIKE CdSe NANOCLUSTERS PASSIVATED WITH STRONGLY INTERACTING LIGANDS: ENERGY LEVEL ALIGNMENT AND PHOTONINDUCED ULTRAFAST CHARGE TRANSFER PROCESSES

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Semiconductor nanoclusters (SCNCs) are promising electronic materials for use in solid-state device fabrication, where device efficiency is strongly controlled by charge generation and transfer from SCNCs to their surroundings. In this paper we report the excited-state dynamics of molecule-like 1.6 nm diameter CdSe SCNCs, which are passivated with the highly conjugated ligand phenylthiodiisocarbamate (PDTC) or para-substituted PDTCs. Femtosecond transient absorption studies reveal sub-picosecond hole transfer ($\tau = 0.9$ ps) from a SCNC to its ligand shell based on strong electronic interaction and hole delocalization, and electron transfer ($\tau = 0.2$ ps) to interfacial states created by charge separation. A series of control experiments were performed by varying SCNC size (1.6 nm v.s. 2.9 nm) and photon energy of the pump laser ($388$ nm v.s. $490$ nm), as well as addition of electron quencher (benzoquinone) and hole quencher (pyridine), which rules out alternative mechanisms and confirms the critical role of energy level alignment between the SCNC and its passivating ligands.

TOWARD THE ACCURATE SIMULATION OF TWO-DIMENSIONAL ELECTRONIC SPECTRA

ANGELO GIUSSANI, ARTUR NENOV, JAVIER SEGARRA-MARTÍ, VISHAL K. JAIWAL, Departamento di Chimica G. Ciamician, Università di Bologna, Bologna, Italy; IVAN RIVALTA, ELISE DUMONT, Laboratoire de Chimie, École Normale Supérieure de Lyon, Lyon, FR; SHAUL MUKAMEL, Department of Chemistry, University of California, Irvine, Irvine, CA, USA; MARCO GARAVELLI, Dipartimento di Chimica G. Ciamician, Università di Bologna, Bologna, Italy.

Two-dimensional pump-probe electronic spectroscopy is a powerful technique able to provide both high spectral and temporal resolution, allowing the analysis of ultrfast complex reactions occurring via complementary pathways by the identification of decay-specific fingerprints. [1-2] The understanding of the origin of the experimentally recorded signals in a two-dimensional electronic spectrum requires the characterization of the electronic states involved in the electronic transitions photinduced by the pump/probe pulses in the experiment. Such a goal constitutes a considerable computational challenge, since up to 100 states need to be described, for which state-of-the-art methods as RASSCF and RASPT2 have to be wisely employed. [3] With the present contribution, the main features and potentialities of two-dimensional electronic spectroscopy are presented, together with the machinery in continuous development in our groups in order to compute two-dimensional electronic spectra. The results obtained using different level of theory and simulations are shown, bringing as examples the computed two-dimensional electronic spectra for some specific cases studied. [2-4]


ULTRAFAST TERAHERTZ KERR EFFECT SPECTROSCOPY OF LIQUIDS AND BINARY MIXTURES

MARCO A. ALLODI, IAN A. FENNERAN, GEOFFREY BLAKE, Division of Chemistry and Chemical Engi- neering, California Institute of Technology, Pasadena, CA, USA.

The ultrafast TeraHertz Kerr effect (TKE) has recently been demonstrated as a nonlinear spectroscopic technique capable of measuring the dielectric relaxation of liquids. The true power of this technique lies in its ability to provide complementary information to measurements taken using heterodyne-detected optical Kerr effect (OKE) spectroscopy. The optical pulses in OKE measurements interact with the sample via the molecular polarizability, a rank-two tensor, in contrast with TKE pulses that interact with the molecules via the dipole moment, a rank-one tensor. Given the different light-matter interactions in the two techniques, TKE measurements help complete the physical picture of intermolecular interactions at short timescales.

We report here our implementation of heterodyne-detected TKE spectroscopy, along with measurements of pure liquids, and binary mixtures. Some of the liquids presented here were previously believed to be TKE inactive, thus showing that we have achieved a greater sensitivity than the previous implementation in the literature. In addition, we will discuss a variety of binary mixtures and show how the TKE data can be compared with OKE data to deepen our physical understanding of intermolecular interactions in liquids.

ULTRAFAST TERAHERTZ KERR EFFECT SPECTROSCOPY OF AROMATIC LIQUIDS

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Ultrafast TeraHertz Kerr Effect (TKE) spectroscopy is a relatively new nonlinear THz technique that is sensitive to the orientational dynamics of anisotropic, condensed-phase samples. The sample is excited by a single high field strength (~1 psecosecond THz pulse, and the resulting transient birefringence is measured by a ~40 femtosecond 800 nm probe pulse. We have measured the TKE response of several aromatic liquids at room temperature, including benzene, benzene-d6, hexafluoro- benzene, pyridine, and toluene. The measured decay constants range from ~1-10 ps, and, along with previous optical Kerr effect results in the literature, give insights into intermolecular interactions in these liquids.

VIBRATIONALLY-RESOLVED KINETIC ISOTOPE EFFECTS IN THE PROTON-TRANSFER DYNAMICS OF GROUND-STATE TROPOLONE

KATHRYN CHEW, ZACHARY VEALY, PATRICK VACCARO, Department of Chemistry, Yale University, New Haven, CT, USA.

The vibrational and isotope dependence of the hindered (tunneling-mediated) proton-transfer reaction taking place in the ground electronic state ($^1A_1$) of monodeuterated tropolone (TDG) has been explored under ambient (bulk-gas) conditions by applying two-color variants of resonant four-wave mixing (RFWM) spectroscopy in conjunction with polarization-resolved detection schemes designed to alleviate spectral complexity and facilitate rovibrational assignments. Full rotation-tunneling analyses of high-resolution spectral profiles acquired for the fundamental and first-overton bands of a reaction-promoting O−D•O deformation/ring-breathing mode, $v_{\text{OH}}(a_1)$, were performed, thereby extracting refined structural and dynamical information that affords benchmarks for the quantitative interpretation of tunneling-induced signatures found in long-range scans of $^1A_1$ vibrational levels residing below $E_{\text{rot}} = 1700$ cm$^{-1}$. Observed kinetic isotope effects, which reflect changes in both reaction kinematics and vibrational displacements, will be discussed, with high-level quantum-chemical calculations serving to elucidate state-resolved propensities for proton transfer in TOH and TDD.

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CHARACTERIZATION OF CHBrCl2 PHOTOLYSIS BY VELOCITY MAP IMAGING

W G MERRILL, AMANDA CASE, Department of Chemistry, The University of Wisconsin, Madison, WI, USA; BENJAMIN C. HAIÑNI, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; ROBERT J. McMATHON, FLEMING CRIM, Department of Chemistry, The University of Wisconsin, Madison, WI, USA.

Halomethanes have attracted extensive research efforts of considerable variety, owing to their relative simplicity and ubiquitous presence in synthetic and environmental settings as well as their amenability to benchmark problems in physical chemistry. Their role in atmospheric processes is well known, most famously as the source of atomic halogens which catalyze the depletion of stratospheric ozone. Indeed, the photolytic cleavage of the carbon-halogen bond is the primary fate of halomethanes in the atmosphere. We utilize laser-induced photolysis to study the C-Br bond cleavage in CHBrCl2 in a molecular beam. Atomic bromine fragments are probed with resonance enhanced multiphoton ionization (REMPI), which allows ground state and spin-excited products to be independently detected. Action spectroscopy in conjunction with velocity map imaging is used to determine the internal energy of the CHCl2 partner fragment. Product state distributions as a function of photolysis energy may be discerned with these techniques. Current results will be presented.

EFFICIENT SUPER ENERGY TRANSFER COLLISIONS THROUGH REACTIVE-COMPLEX FORMATION: H + SO2

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Translational-to-vibrational energy transfer (ET) from a hyperthermal H atom to ambient SO2 was characterized using time-resolved Fourier transform infrared emission spectroscopy. Vibrational excitation of SO2 following collisions with H atoms containing 59 kcal/mol of kinetic energy, generated from the 193 nm photolysis of HBr, is detected in two distinct energy distributions: one with excitation predominantly at the fundamental vibrational levels is attributable to classical impulsive collisions, while the other, accounting for 80% of the excited SO2 with vibrational energy as high as 14,000 cm⁻¹, is proposed to arise from the formation of a transient reactive-complex during the collision. The cross-section for this super ET collision is determined to be 0.53±0.05 Å², or roughly 2% of all hard sphere collisions. This observation reveals that in collisions between a hyperthermal atom and an ambient molecule, for which a reactive-complex exists on the potential energy surface, a large quantity of translational energy can be transferred to the molecule with high efficiency.

FOURTH-ORDER VIBRATIONAL TRANSITION STATE THEORY AND CHEMICAL KINETICS

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Second-order vibrational perturbation theory (VPT2) is an enormously successful and well-established theory for treating anharmonic effects on the vibrational levels of semi-rigid molecules. Partially as a consequence of the fact that the theory is exact for the Morse potential (which provides an appropriate qualitative model for stretching anharmonicity), VPT2 calculations for such systems with appropriate ab initio potential functions tend to give fundamental and overtone levels that fall within a handful of wavenumbers of experimentally measured positions. As a consequence, the next non-vanishing level of perturbation theory – VPT4 – offers only slight improvements over VPT2 and is not practical for most calculations since it requires information about force constants up through sextic. As a consequence, the next non-vanishing level of perturbation theory – VPT4 – offers only slight improvements over VPT2 and is not practical for most calculations since it requires information about force constants up through sextic. However, VPT4 (as well as VPT2) can be used for other applications such as the next vibrational correction to rotational constants (the “gammas”) and other spectroscopic parameters. In addition, the marriage of VPT with the semi-classical transition state theory of Miller (SCST) has recently proven to be a powerful and accurate treatment for chemical kinetics. In this talk, VPT4-based SCTST tunneling probabilities and cumulative reaction probabilities are given for the first time for selected low-dimensional model systems. The prospects for VPT4, both practical and intrinsic, will also be discussed.

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Precise spectroscopy in cold molecules: The first rotational intervals of He\textsuperscript{4} by high-resolution spectroscopy and Rydberg-series extrapolation

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Having only three electrons, He\textsuperscript{4} represents a system for which highly accurate \textit{ab initio} calculations are possible. The latest calculation of vibrational energies in He\textsuperscript{4} do not include relativistic or QED corrections but claim an accuracy of about 120 MHz\textsuperscript{2}. The available experimental data on He\textsuperscript{4}, though accurate to 300 MHz, are not precise enough to rigorously test these calculations or reveal the magnitude of the relativistic and QED corrections. We have performed high-resolution Rydberg spectroscopy of metastable He\textsuperscript{4} molecules and employed multichannel-quatum-defect-theory extrapolation techniques to determine the rotational energy-level structure in the He\textsuperscript{4} ion. To this end we have produced samples of helium molecules in the \textit{1}Σ\textsuperscript{+} state in supersonic beams with velocities tunable down to 100 m/s by combining a cryogenic supersonic-beam source with a multistage Zeeman decelerator\textsuperscript{2}. The metastable He\textsuperscript{4} molecules are excited to no Rydberg states using the frequency-doubled output of a pulse-amplified ring dye laser. Although the bandwidth of the laser systems is too large to observe the reduction of the Doppler width resulting from deceleration, the deceleration greatly simplifies the spectral assignments because of its spin-rotational state selectivity. Our approach enabled us to determine the rotational structure of He\textsuperscript{4} with unprecedented accuracy, to determine the size of the relativistic and QED corrections by comparison with the results of Ref. \textit{a} and to precisely measure the rotational structure of the metastable state for comparison with the results of Foca et al.\textsuperscript{3}.

\textsuperscript{5}F. Foca, F. F. Brunet, and R. Celio, J. Mol. Spectrosc. 100, 208 (1985).

1. PRECISION SPECTROSCOPY IN COLD MOLECULES: THE FIRST ROTATIONAL INTERVALS OF He\textsuperscript{4} BY HIGH-RESOLUTION SPECTROSCOPY AND RYDBERG-SERIES EXTRAPOLATION

2. MICROWAVE SPECTROSCOPY OF THE CALCIUM \textit{4s}\textit{f} \rightarrow \textit{4}\textit{s}(\textit{n} + 1)\textit{d}, \textit{4}\textit{f}\textit{g}, \textit{4}\textit{n}\textit{f}, AND \textit{4}\textit{m}\textit{h} TRANSITIONS

Jirakan Nunkaw, Tom Gallagher, Department of Physics, The University of Virginia, Charlottesville, VA, USA

We use a delayed field ionization technique to observe the microwave transitions of calcium Rydberg states, from the \textit{4s}\textit{f} states to the \textit{4}(\textit{n} + 1)\textit{d}, \textit{4}\textit{f}\textit{g}, \textit{4}\textit{n}\textit{f}, and \textit{4}\textit{m}\textit{h} states for 18 \textless \textit{n} \textless 23. We analyze the observed intervals between the \textit{f} and \textit{f}' states of the same \textit{n} to determine the Ca\textsuperscript{+} \textit{4s} dipole and quadrupole polarizabilities. We show that the adiabatic core polarization model is not adequate to extract the Ca\textsuperscript{+} \textit{4s} dipole and quadrupole polarizabilities and a non adiabatic treatment is required. We use the non adiabatic core polarization model to determine the ionic dipole and quadrupole polarizabilities to be \textit{α}_d = 76(9) a_0 and \textit{α}_q = 206(9) a_0, respectively.

Figure 1: Electrons gaining or losing energy during the first microwave cycle depending on the initial launching direction. Here the phase of the microwave field is adjusted to provide a maximum energy transfer. The oscillations in energy are synchronized with the 14GHz microwave field.
HIGH-RESOLUTION SPECTROSCOPY OF LONG-RANGE MOLECULAR STATES OF $^{85}\text{Rb}_2$

RYAN CAROLLO, EDWARD E. EYLER, YOANN BRUNEAU, PHILLIP GOULD, W.C. STWALLEY, Department of Physics, University of Connecticut, Storrs, CT, USA.

We present analysis of low-$n$ long-range molecular Rydberg states in $^{85}\text{Rb}_2$, based on high-resolution spectra. The weakly bound states are accessed by bound-bound transitions from high-$n$ levels of the $^{3} \Sigma^+_u$ state, which are prepared by photooassociation of laser-cooled atoms. Single-photon transitions to target states near the $5\alpha + 7\gamma$ asymptote are excited by a frequency-doubled pulse-amplified CW laser with a narrow linewidth, under 200 MHz. The long-range portion of the binding potential is dominated by the elastic scattering interaction of the Rydberg electron of a perturbed $\gamma\text{p}$ atom and a nearby ground-state atom, in much the same manner as trilobite states. We use time of flight to selectively measure molecular ions, which are formed via autodetachment. This technique gives two orders-of-magnitude improvement in linewidth over our previous work, reported in Ref. [1]. We also present calculations of a proposed scheme for STRAP transfer from the current $v^0 = 35$ level of the $^{3} \Sigma^+_u$ state to the $v^0 = 39$ level. The long-range states accessible to us are defined in large part by the Franck-Condon factors, which are dominated by the outer lobe of the wavefunction. Thus, choosing a $v^0$ sets R, and determines the Franck-Condon window. The proposed $v^0 = 39$ level has a classical outer turning point at $\sim 72\text{ \mu m}$, and will provide access to higher-$n$ states with longer-range wells. This work is supported by the NSF and AFOSR.


DOUBLE RESONANCE SPECTROSCOPY OF BaF$^+$ AUTODIONIZING RYDBERG STATES

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We have studied the $\lambda$=1 Rydberg states of BaF in the energy region $E$=38000-39100 cm$^{-1}$ ($n^V$(n=15,25) via optical-optical double resonance spectroscopy. Rydberg states excited above the first ionization potential spontaneously autoionize and $1^{13}\text{Ba}^+\text{F}^-$ ions are detected by TOF-MS. In addition, BaF possesses a particularly low ionization potential, which allows for the study of autoionization dynamics in the absence of predissociative decay. This work extends the assignments of core-penetrating Rydberg states of BaF (Jakubek and Field, 2000) for applications to state-selective ion production schemes. Polarization and Stark spectroscopy techniques will be discussed in the context of accurate and efficient assignment of spectra.

MILLIMETER WAVE SPECTROSCOPY OF RYDBERG STATES OF MOLECULES IN THE REGION OF 260-295 GHz

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Free induction decay detected chirped pulse millimeter wave spectroscopy of Rydberg-Rydberg transitions in atoms and molecules is a powerful and flexible method for characterizing the electronic structure of Rydberg states and determining the structure and dynamics of the ion-core. Complicating the use of this technique are the difficulties in reliably and repeatedly accessing not just the most information rich core-penetrating states, but also the low-$\ell$ core-penetrating Rydberg states in the area of principal quantum number $n^\ast > 35$. Small transition moments and narrow linewidths for transitions between valence electronic states and high Rydberg states are the primary limiting factor. We demonstrate a simple method to avoid the problem entirely by using chirped pulse technology operating in the frequency range of 260-295 GHz, which allows us to sample a lower range of $n^\ast$ values than before with comparable frequency resolution and accuracy as our previous W-band experiments. Further improvements to our experiment in order to accurately capture details of Stark demotion, a technique that provides rapid differentiation between core-penetrating and core-nonpenetrating states, will also be discussed.

SYSTEMATICS OF RYDBERG SERIES OF DIATOMIC MOLECULES AND CORRELATION DIAGRAMS

CHUN-WOO LEE, Chemistry, Ajou University, Suwon, Republic of Korea.

Rydberg states are studied for $^{2}H$, $^{2}Li$, $^{2}He$, $^{2}LiH$ and $^{2}BeH$ using the multi-reference configuration interaction (MRCI) method. The systematics and regularities of the physical properties such as potential energies curves (PECs), quantum defect curves, permanent dipole moment and transition dipole moment curves of the Rydberg series are studied. They are explained using united atom perturbation theory by Binnig and Byers-Brown, Fermi model, Stark theory, and Mulliken’s theory. Interesting mirror relationships of the dipole moments are observed between l-mixed Rydberg series, indicating that the members of the l-mixed Rydberg series have dipole moments with opposite directions, which are related to the reversal of the polarity of a dipole moment at the avoided crossing points. The assignment of highly excited states is difficult because of the usual absence of the knowledge on the behaviors of potential energy curves at small internuclear separation whereby the correlation between the united atom limit and separated atoms limit cannot be given. All electron MRCI calculations of PECs are performed to obtain the correlation diagrams between Rydberg orbitals at the united-atom and separated atoms limits.
We present results on Cs ultracold Rydberg atom experiments involving trilobite and butterfly molecules. Trilobite molecules are predicted to have giant, body-fixed permanent dipole moments, on the order of 1000 Debye. In addition, we have also recently observed states whose spectra show characteristics of p-wave dominated butterfly states. The work on what we believe to be the butterfly states will be compared and contrasted to the measurements of the trilobite states.

A single Rydberg excitation in the high-density and low-temperature environment of a Bose-Einstein condensate (BEC) leads to a fascinating testbed of low-energy electron-neutral and ion-neutral scattering. In particular the small interparticle spacing in a BEC makes it possible to study the role of ion-neutral interactions in l-changing collisions on time scales much shorter than the Rydberg lifetime. We take advantage of the mean field density shift, caused by elastic electron-neutral collisions, to probe density dependent shells of the Rydberg electron that matches well with the energy gap to the next-lowest manifold. We measure a change in kinetic energy of the Rydberg atoms that matches well with the energy gap to the next-lowest manifold. We measure Rb BEC and thereby measure the l-changing collision time versus density and principal quantum number. We report on l-changing collisions due to inelastic scattering of the Rydberg electron with a neutral atom located near the Rydberg ion core. We measure timescales of both the l-changing collision and the Rb\textsubscript{87} molecule formation of less than one nanosecond for n < 100 at the highest BEC densities. We extract a change in kinetic energy of the Rydberg atoms that matches well with the energy gap to the next-lowest manifold. We measure Rb\textsubscript{87} signal that decreases with increasing principal quantum number. The mechanism and timescales of the l-changing collision are compared with simulations including the motion of the ion core and neutral atoms, as well as the Rydberg electron.

We carried out a relatively comprehensive ab-initio study of the electronic structure of O\textsubscript{2} and O\textsubscript{2}\textsuperscript{+}. We employed the MRCI-CI package together with the cc-pVQZ basis set augmented with seven diffuse functions of s, p, d character on each atom. In this contribution we focus on the quintet states. Potential energy curves of about 50 quintet states were computed. The spectroscopic constants of the six valence quintet states (\text{^2}\Sigma\text{^g}, \text{^2}\Sigma\text{^u}, \text{^2}\Pi\text{^g}, \text{^2}\Pi\text{^u}, \text{^2}\Delta\text{^g}, \text{^2}\Delta\text{^u}) dissociating to the first dissociation limit O\textsuperscript{2+}(\text{^2}\Pi\text{^u}(P)) are reported. The four ion-pair quintet states (\text{^2}\Sigma\text{^g}, \text{^2}\Sigma\text{^u}, \text{^2}\Pi\text{^g}, \text{^2}\Pi\text{^u}) dissociating to O\textsuperscript{2+}(\text{^2}\Sigma\text{^g}(P)) at 17.28 eV were also computed and their spectroscopic constants will be presented. A number of bound quintet Rydberg states belonging to series converging to the \text{^2}\Pi\text{^u}(P) and \text{^2}\Pi\text{^g}(P) states of O\textsuperscript{2+} were identified and attributed. Long-range interactions involving the ion-pair states as they slowly approach their dissociation limit will be shown.

In this presentation we report progress in the computation of superexcited states of O\textsubscript{2}, namely, of bound \text{^2}\Pi\text{^u}, Rydberg states of the neutral molecule converging to the \text{^2}\Pi\text{^u} state of O\textsuperscript{2+}. Up to twenty \text{^2}\Pi\text{^u} potential energy curves were computed. The MRCI-CI package together with the cc-pVQZ basis set augmented with seven diffuse functions of s, p, d type on each atom were employed. This study was prompted by the demand of potential curves to try to understand the mechanism of the neutral dissociation of O\textsubscript{2} above the first ionization limit (IP\textsuperscript{+} = 12.07 eV) where there exists a competition between autoionization and predissociation. This undertaking focuses on the computation of the \text{^2}\Pi\text{^u} and \text{^2}\Pi\text{^g} states that have been postulated as involved in the neutral dissociation of O\textsubscript{2} in the 865–790 \textdegree A (14.33–15.69 eV) energy region.
WHAT CAN WE EXPECT OF HIGH-RESOLUTION SPECTROSCOPES ON CARBOHYDRATES?

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Carbohydrates are one of the most multifaceted building blocks, performing numerous roles in living organisms. We present several structural investigations on carbohydrates exploiting an experimental strategy which combines microwave (MW) and laser spectroscopies in high-resolution. Laser spectroscopy offers high sensitivity coupled to mass and conformer selectivity, making it ideal for polysaccharides studies. On the other hand, microwave spectroscopy provides much higher resolution and direct access to molecular structure of monosaccharides. This combined approach provides not only accurate chemical insight on conformation, structure and molecular properties, but also benchmarking standards guiding the development of theoretical calculations.

In order to illustrate the possibilities of a combined MW-laser approach we present results on the conformational landscape and structural properties of several monosaccharides and oligosaccharides including microsolvation and molecular recognition processes of carbohydrates.1, 4

MILLIMETER AND SUBMILLIMETER STUDIES OF O(1D) INSERTION REACTIONS TO FORM MOLECULES OF ASTROPHYSICAL INTEREST

BRIAN HAYS, NADINE WEHRES, BRIDGET ALLGOOD DEPRINCE, ALTHEA A. M. ROY, JACOB LAAS, SUSANNA L. WIDUCUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA, USA.

While both the number of detected interstellar molecules and their chemical complexity continue to increase, understanding of the processes leading to their formation is lacking. Our research group combines laboratory spectroscopy, observational astronomy, and astrochemical modeling for an interdisciplinary examination of the chemistry of star and planet formation. This talk will focus on our laboratory studies of O(1D) insertion reactions with organic molecules to produce molecules of astrophysical interest. By employing these reactions in a supersonic expansion, we are able to produce interstellar organic reaction intermediates that are unstable under terrestrial conditions; we then probe the products using millimeter and submillimeter spectroscopy. We benchmarked this setup using the well-studied O(1D) + methane reaction to form methanol. After optimizing methanol production, we moved on to study the O(1D) + ethylene reaction to form vinyl alcohol (CH₃CHOH), and O(1D) + methyl amine reaction to form aminomethanold (NH₂CH₂OH). Vinyl alcohol measurements have now been extended up to 450 GHz, and the associated spectral analysis is complete. A possible detection of aminomethanol has also been made, and continued spectral studies and analysis are underway. We will present the results from these experiments and discuss future applications of these molecular and spectroscopic techniques.

TERAHERTZ AND INFRARED LABORATORY SPECTROSCOPY IN SUPPORT OF NASA MISSIONS

SHANSHAN YU, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

The JPL molecular spectroscopy group supports NASA programs encompassing Astrophysics, Atmospheric Science, and Planetary Science. Ongoing activities include measurement and analysis of molecular spectra in the terahertz and infrared regions under conditions akin to the remote environments under study in NASA missions. This presentation will show the implementation of state-of-the-art spectroscopic techniques to fulfill spectroscopic demands of the Herschel Space Observatory and the Orbiting Carbon Observatory re-flight (OCO-2). A demonstrative example of the significantly improved frequency predictions for the H₂O¹ ground state high J transitions will be given. This work was critical to Herschel’s successful identification of highly excited metastable H₂O¹ Terahertz lines with J = K up to 11, one of the Herschel mission’s many surprising observational results. The observation and subsequent laboratory work revealed that (1) these highly excited H₂O¹ lines had already been observed by European Southern Observatory’s Atacama Pathfinder Telescope a few years before but had been classified as U lines; (2) the H₂O¹ number density was previously underestimated by an order of magnitude, due to ignorance of the population in the metastable states. A second example focuses on O₃, an important absorber from the microwave through the drop U.V. This work is motivated by the challenge of developing an accurate and complete spectroscopic characterization of molecular oxygen across a wide frequency range for current and planned Earth atmospheric observations. Especially, OCO-2 utilizes the O₃ A-band for air mass calibration; extremely accurate O₃ molecular data, i.e., line positions with uncertainty on the order of MHz for the A-band around 15000 cm⁻¹, are required to fulfill the demand of the proposed 0.25% precision for the carbon dioxide concentration retrievals.

LASER SPECTROSCOPY OF RADICALS, CARBENES, AND IONS IN SUPERFLUID HELIUM DROPLETS

GARY E. DOUBERLY, Department of Chemistry, University of Georgia, Athens, GA, USA.

The first beam of helium droplets was reported in the 1961 paper “Strahlen aus kondensiertem Helium im Hochvakuum” by von E. W. Becker and co-workers. However, molecular spectroscopy of helium-solvated dopants wasn’t realized until 30 years later in the laboratories of Scoles and Torrie. It has now been two decades since this early, seminal work on doped helium droplets, yet the field of helium droplet spectroscopy is still fresh with vast potential. Analogous in many ways to cryogenic matrix isolation spectroscopy, the helium droplet is an ideal environment to spectroscopically probe difficult to prepare molecular species, such as radicals, carbenes and ions. The quantum nature of helium at 0.35 K often results in molecular spectra that are sufficiently resolved to resolve an evolution of line shapes and fine-structure that is worthy of the International Symposium on Molecular Spectroscopy. The present talk will focus on our recent successful attempts to efficiently dope the title molecular species into helium droplets and probe their properties with infrared laser Stark and Zeeman spectroscopies.

COBLENTZ AWARD

Presentation of Award by Mark Druy, Coblenz Society
WF. Mini-symposium: High-Precision Spectroscopy
Wednesday, June 24, 2015 – 1:30 PM
Room: 116 Roger Adams Lab

Chair: Kevin Cossel, JILA - University of Colorado, Boulder, CO, USA

WF01
INVITED TALK
1:30 – 2:00
ULTRASENSITIVE, HIGH ACCURACY MEASUREMENTS OF TRACE GAS SPECIES
DAVID A. LONG, ADAM J. FLEISHER, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA;
DAVID F. PLUSQUELLIC, Physical Measurement Laboratory, National Institute of Standards and Technology, Boulder, CO, USA;
JOSEPH HODGES, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA.

Our laboratory seeks to apply novel cavity-enhanced spectroscopic techniques to present problems in atmospheric and physical chemistry. Primarily we use cavity ring-down spectroscopy in which the passive decay of optical power within a Fabry-Perot resonator is utilized to extract an absorption signal. With this technique we have demonstrated quantum (shot) noise limited sensitivities in both the near-infrared and mid-infrared spectral regions. Both commercial and home-built optical frequency combs are employed either to serve as absolute frequency references for molecular spectra or in a multiheterodyne approach for multiplexed sensing. I will discuss this novel instrumentation as well as measurements we have made of atmospherically relevant species such as CO₂, H₂O, O₃, CH₄, and CO with implications for in situ and remote (i.e. satellite-based) sensing. I will conclude by discussing future directions and plans for challenging measurements in the mid-infrared.

WF02
2:05 – 2:20
PROBING BUFFER-GAS COOLED MOLECULES WITH DIRECT FREQUENCY COMB SPECTROSCOPY IN THE MID-INFRARED
JUN YE, JILA, National Institute of Standards and Technology and Univ. of Colorado Department of Physics, University of Colorado, Boulder, CO, USA;
CREDITS: ADAM J. FLEISHER, DAVID A. LONG, QIANGQING LIU, JOSEPH HODGES.

We present the first demonstration of cavity-enhanced direct frequency comb spectroscopy on buffer-gas cooled molecules by coupling a mid-infrared frequency comb to a high- finesse cavity surrounding a helium buffer-gas chamber, we can gather rotationally resolved absorption spectra with high sensitivity over a broad wavelength region. The measured ~10 K rotational and translational temperatures of buffer-gas cooled molecules drastically simplify the observed spectra, compared to those of room temperature molecules, and allow for high spectral resolution limited only by Doppler broadening (10-100 MHz). Our system allows for the extension of high-resolution spectroscopy to larger molecules, enabling detailed analysis of molecular structure and dynamics, while taking full advantage of the powerful optical properties of frequency combs.

WF03
2:22 – 2:37
FREQUENCY-AGILE DIFFERENTIAL CAVITY RING-DOWN SPECTROSCOPY
ZACHARY REED, JOSEPH HODGES, Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD, USA.

The ultimate precision of highly sensitive cavity-enhanced spectroscopic measurements is often limited by interferences (etalons) caused by weak coupled-cavity effects. Differential measurements of ring-down decay constants have previously been demonstrated to largely cancel these effects, but the measurement acquisition rates were relatively low [1,2]. We have previously demonstrated the use of frequency agile rapid scanning cavity ring-down spectroscopy (FARS-CRDS) for acquisition of absorption spectra [3]. Here, the method of rapidly scanned, frequency-agile differential cavity ring-down spectroscopy (FADS-CRDS) is presented for reducing the effect of these interferences and other shot-to-shot statistical variations in measured decay times. To this end, an electro-optic phase modulator (EOM) with a bandwidth of 20 GHz is driven by a microwave source, generating pairs of sidebands on the probe laser. The optical resonator acts as a highly selective optical filter to all laser frequencies except for one tunable sideband. This sideband may be stepped arbitrarily from mode-to-mode of the ring-down cavity, at a rate limited only by the cavity build-up/decay time. The ability to probe any cavity mode across the EOM bandwidth enables a variety of methods for generating differential spectra. The differential mode spacing may be changed, and the effect of this method on suppressing the various coupled-cavity interactions present in the system is discussed. Alternatively, each mode may also be differentially referenced to a single point, providing immunity to temporal variations in the base losses of the cavity while allowing for conventional spectral fitting approaches. Differential measurements of absorption are acquired at 3.3 kHz and a minimum detectable absorption coefficient of 5 x 10⁻¹² cm⁻¹ s⁻¹ averaging time is achieved.


WF04
2:39 – 2:54
QUANTUM-NOISE-LIMITED CAVITY RING-DOWN SPECTROSCOPY IN THE MID-INFRARED
ADAM J. FLEISHER, DAVID A. LONG, QIANGQING LIU, JOSEPH HODGES, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA.

We report a highly sensitive mid-infrared spectrometer capable of recording cavity ring-down events in the quantum (shot) noise limit. A linear optical cavity of finesse 31,000 was pumped by a distributed feedback quantum cascade laser (DFB-QCL) operating at 4.5 μm until a cavity transmission threshold was reached. A fast optical switch then extinguished optical pumping and initiated a cavity decay which exhibited root-mean-square noise proportional to the square root of optical power (quantum noise) for several cavity time constants until a detector noise floor was reached. This spectrometer has achieved a noise-equivalent absorption of NEA ≈ 2.6 x 10⁻¹¹ cm⁻¹ Hz⁻¹/2 and a minimum absorption coefficient of α ≈ 2.3 x 10⁻¹³ cm⁻¹ in 5 seconds. Applications for such a highly sensitive spectrometer operating in the mid-infrared region, including ultra-trace molecular spectroscopy of CO₂ isotopologues and the direct interrogation of weak mirror birefringence and polarization-dependent losses, will be discussed.
MOLECULAR LINE PARAMETERS PRECISELY DETERMINED BY A CAVITY RING-DOWN SPECTROMETER

SHUI-MING HU, YAN TAN, JIN WANG, YAN LIU, CUN-FENG CHENG, YU ROBERT SUN, AN-WEN LIU, 
Hebei National Laboratory for Physical Science at Microscale, University of Science and Technology of China, Hefei, China.

A cavity ring-down spectrometer calibrated with a set of precise atomic lines was built to retrieve precise line parameters in the near infrared.[1,2] The spectrometer allows us to detect absorptions with a sensitivity of $10^{-11}$ cm$^{-1}$ and a spectral precision up to $10^{-6}$ cm$^{-1}$. Re-resolved laser lines in the second overtone of H$_2$ have been observed, including the extremely weak S(5) line with a line intensity less than $1 \times 10^{-12}$ cm$^{-1}$ molecule$^{-1}$, which is among the weakest molecular lines detected by absorption in the gas phase. The absolute line positions of H$_2$ agree well with the high-level quantum chemical calculations including relativistic and QED corrections, with the deviation being less than $5 \times 10^{-6}$ cm$^{-1}$. [3,4] A quantitative study has also been carried out on the ν$_2 + ν_3$ band of CO.[5] It was the first CO band observed 80 years ago in the spectrum of Venus. We determined the line positions with an accuracy of $1 \times 10^{-12}$ cm$^{-1}$, two orders of magnitude better than previous studies. Similar studies have been carried out to determine the line parameters of H$_2$O[6,7] and CO[8] in the spectral regions near 0.8 μm. The spectroscopic parameters can be used in various studies, from the atmospheres of the earth-like planets to the test of fundamental physics.

References
LOCAL PERTURBATIONS IN THE (10110) AND (10101) LEVELS OF C2H2 FROM FREQUENCY COMB-REFERENCED SPECTROSCOPY

TREVOR SEARS*, Chemistry Department, Brookhaven National Laboratory, Upton, NY, USA; SYLVESTRE TWIGRAZEU, DAMIEN FORTHOMME, Department of Chemistry, Brookhaven National Laboratory, Upton, NY, USA; GREGORY HALL, Chemistry Department, Stony Brook University, Stony Brook, NY, USA.

In work reported by Twigravez et al. at this meeting, the rest frequencies of more than 100 lines in the v3 and v5 hot bands in the C2H2 molecule have been measured by saturation dip spectroscopy using an extended cavity diode laser locked to a frequency comb. This work was originally directed towards providing a set of accurate frequencies for the hot band line positions to aid in modeling the transitions of the main lines in the band. In analyzing the results, we find that many of the upper levels in the hot band transitions suffer small, and in some cases not so small, local perturbations. These arise because of J-dependent near degeneracies between the title levels and background levels of the same symmetry, mostly derived from zero order states involving multiple quanta of bending excitation. The vibration-rotation levels at the energies in question have previously been modeled using a polyad-based Hamiltonian and the present data can be interpreted on the basis of this model, but they also provide information which can be used to refine the model, and point to terms that may have previously been neglected. The most important result is that the high precision of the measurements gives the ability to compare the effects of background levels associated with high bending quantum numbers and angular momentum states that are otherwise very difficult to access.

Acknowledgments: We are most grateful to D. S. Perry (U. Akron) and M. Herman (U. Libre de Bruxelles) for helpful discussions. Work at Brookhaven National Laboratory is funded by the Division of Chemical Sciences, Geosciences and Biosciences within the Offices of Basic Energy Sciences, Office of Sciences, U.S. Department of Energy under Contract Nos. DE-AC02-98CH10886 and DE-SC0012704.

MAGNETIC SPIN-TORSION COUPLING IN METHANOL

L. H. COUDERT, C. OUTLE, EDA, CNRS, Université Paris Est Créteil et Paris Diderot, Créteil, France; T. H. HEUET, Laboratoire P3dAM, UMR 8325 CNRS - Université de Lille I, Villeneuve d'Ascq, France; JENS-UWE GRABOW, Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz-Universität, Hannover, Germany.

The hyperfine structure of non-rigid molecules in which hyperfine coupling arises from equivalent nuclei can be exchanged by large amplitude motions is of great interest and lead to unexpected results. In the non-rigid (C2H2) and (D2H2) dimers, the hyperfine structure arising for nondegenerate tunneling sublevels can be accounted for using an effective quadrupole coupling Hamiltonian with the same coupling constant for all four deuterium atoms. In the non-rigid species CD, COH and HCOOCOH, the large amplitude torsional motion leads to hyperfine patterns which are qualitatively dependent on the torsional symmetry of the levels. The interaction between a large amplitude torsional motion and the hyperfine coupling may also lead to a less known hyperfine effect, the so-called magnetic spin-torsion coupling, which was first studied by Heuvel and Dymanus and which has not yet been conclusively evidenced. In this talk, the magnetic hyperfine structure of the non-rigid methanol molecule will be investigated experimentally and theoretically. 13 hyperfine patterns were recorded using two molecular beam microwave spectrometers and spin-pulse spectrometers, along with previously recorded ones, were analyzed in an attempt to evidence the effects of the magnetic spin-torsion coupling. The theoretical approach setup to analyze the observed data accounts for the spin-torsion coupling, in addition to the molecular dipole moment and spin-spin couplings, and relies on symmetry arguments to restrict the hyperfine coupling Hamiltonian and a spin-rotation-torsion wavefunction compatible with the Pauli exclusion principle.

In this talk, the results of the analysis will be presented. The hyperfine coupling parameters retrieved will be discussed and we hope to be able to conclusively evidence the effects of the magnetic spin-torsion.

NOISE-IMMUNE CAVITY-ENHANCED OPTICAL HETERODYNE MOLECULAR SPECTROMETRY MODELLING UNDER SATURATED ABSORPTION

PATRICK DUPRE, Laboratoire de Physico-Chimie de l’Atmosphère, Université du Littoral Côte d’Opale, Dunkerque, France.

The Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectrometry (NICE-OHMS) is a modern technique renowned for its ultimate sensitivity, because it combines long equivalent absorption length provided by a high finesse cavity, and very high resolution, achieved by optical resonant enhancement (ORE) of the Doppler shifts and by paying attention to the molecular Zeeman sublevels and to the EMF polarization. The theoretical approach setup to analyze the observed data accounts for the spin-torsion coupling, in addition to atomic dipole moment and spin-spin couplings, and relies on symmetry arguments to restrict the hyperfine coupling Hamiltonian and a spin-rotation-torsion wavefunction compatible with the Pauli exclusion principle.

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Post-Deadline Abstract

NOISE-IMMUNE CAVITY-ENHANCED OPTICAL HETERODYNE MOLECULAR SPECTROMETRY MODELLING UNDER SATURATED ABSORPTION

PATRICK DUPRE, Laboratoire de Physico-Chimie de l’Atmosphère, Université du Littoral Côte d’Opale, Dunkerque, France.

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In this talk, the results of the analysis will be presented. The hyperfine coupling parameters retrieved will be discussed and we hope to be able to conclusively evidence the effects of the magnetic spin-torsion.

SPIN-ROTATION HYPERFINE SPLITTING AT MODERATE TO HIGH J VALUES IN METHANOL

L-HONG XIU, Department of Physics, University of New Brunswick, Saint John, NB, Canada; JON T. BIRGEN, Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD, USA; SERGEY BELOV, G Y GOLUBIATNIKOV, ALEXANDER LAPINOV, Microwave Spectroscopy, Institute of Applied Physics, Novosibirsk, Russia; V. ILYUSHIN, E. A. ALEKSEEV, A. A. MIESCHYAROV, Radiospectroscopy Department, Institute of Radio Astronomy of NASU, Kharkov, Ukraine.

In this talk we present a possible explanation, based on torsionally mediated proton-spin-overall-rotation interaction, for the surprising observation in Novosibirsk several years ago of doublets in some Lamb dip sub-natural-line-width transitions between torsion-rotation states of the symmetry in methanol. These observed doublet splittings, some as large as 70 kHz, were later confirmed by independent Lamb dip measurements in Kharkov. In this talk we first show the observed J-dependence of the doublet splittings for two b-type Q branches (one from each laboratory), and then focus on our theoretical explanation. The latter involves three topics: (i) group theoretically allowed terms in the spin-rotation Hamiltonian; (ii) matrix elements of these terms between the degermate components of torsion-rotation E states, calculated using wavefunctions from an earlier global fit of torsion-rotation transitions of methanol in the ν3 = 1, 2 and 3 states, and (iii) least-squares fits of coefficients of these terms to about 35 experimentally resolved doublet splittings in the quantum number ranges of K = +2 to +2, J + 13 to 34, and ν3 = 0. Rather pleasing results are obtained for these doublet splittings, and a number of narrow transitions, in which no doublet splitting could be detected, are also in agreement with predictions from the theory. Some remaining disagreements between the experiment and the present theoretical explanation will be mentioned.

References:

IR SPECTROSCOPY ON PEPTIDES AND PROTEINS AFTER ION MOBILITY SELECTION AND IN LIQUID HELIUM DROPLETS

CORNELIS VAN HELDEN, Department of Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany.

IR spectroscopy has become a frequently used tool to characterize gas-phase peptides and proteins. In many experiments, ions are m/z selected, irradiated by intense and tunable IR light and fragmentation is monitored as a function of IR wavelength. The presence of some of these ions, however, complicate the interpretation, as the resulting spectra represent the sum of the spectra of the individual components. We constructed a setup, in which ion mobility methods are used to obtain m/z selected ions of defined shape on which are then further investigated by IR spectroscopy. First results on peptide aggregates are presented and some of these ions, the IR spectra show a transition from helical or random coil to beta sheet structures. In a different experiment, peptide or protein ions are captured in liquid helium droplets prior to IR spectroscopic investigation. The complexes inside the helium droplets are isothermal at 0.35 K, hence the interaction between the helium matrix and the molecules are weak so that only small perturbations on the molecule are expected. IR spectra for m/z selected peptides with up to 10 amino acids and proteins containing more than 100 amino acids have been measured. The spectra of the smaller species show resolved bands of individual oscillators, which can be used for structure assignment. For the larger species, band envelopes are obtained and for the case of highly charged proteins, a transition form helical to extended structures is observed.

COMBINING THE POWER OF RMPD WITH ION-MOLECULE REACTIONS: THE STRUCTURE AND REACTIVITY OF RADICAL IONS OF CYSTEINE AND ITS DERIVATIVES

MICHAEL LEISSLE, Department of Chemistry and Biochemistry, Northern Illinois University, Dekalb, IL, USA; SANDRA OSSBURN, Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA, USA; GILBERT J. OOMENS, Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, The Netherlands, VICTOR RYZHOV, Department of Chemistry and Biochemistry, Northern Illinois University, Dekalb, IL, USA.

Most of the work on peptide radical cations has involved protons as the source of charge. Nonetheless, using metal ions as charge sources often offers advantages like stabilization of the structure via multidentate coordination and the elimination of the “mobile proton.” Moreover, characterization of metal-bound amino acids is of general interest as the interaction of peptide side chains with metal ions in biological systems is known to occur extensively. In the current study, we generate thyl radicals of cysteine and homocysteine in the gas phase complexed to alkali metal ions. Subsequently, we utilize infrared multiple-photon dissociation (IRMPD) and ion-molecule reactions (IRM) to characterize the structure and reactivity of these radical ions.

Our group has worked extensively with the cysteine-based radical cations and anions, characterizing the gas-phase reactivity and rearrangement of the amino acid and several of its derivatives. In a continuation of this work, we are pursuing the effects of metal ions as the charge bearing species on the reactivity of the sulfur radical. Our S-nitroso chemistry can easily be used in conjunction with metal ion coordination to produce initial S-based radicals in peptide radical-metal ion complexes. In all cases we have been able to achieve radical formation with significant yield to study reactivity. Ion-molecule reactions of metallated radicals with allyl iodide, dimethyl disulfide, and allyl bromide have all shown decreasing reactivity going down group 1A.

Recently, we determined the experimental IR spectra for the homocysteine radical cation with Li+, Na+, and K+ as the charge bearing species at the FELIX facility. For comparison, the predicted IR spectrum of homocysteine has previously been obtained by our group. A preliminary match of the IR spectra has been confirmed. Finally, calculations are underway to determine the bond distances of all the metal adduct structures.

OPPORTUNITIES FOR GAS-PHAS MOLECULAR SPECTROSCOPY ON THE VLS-PGM BEAMLINE AT THE CANADIAN LIGHT SOURCE

MICHAEL A. MACDONALD, EFD, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada.

The VLS-PGM beamline at the Canadian Light Source cover the energy range from 12eV to 250eV with a resolving power better than 10^6 throughout this range. Associated with this beamline are two endstations designed for gas phase spectroscopy.

The first is a dual toroid electrostatic particle energy analyser. Each toroid can (independently) measure the energy and angular distribution of charged particles emitted from the interaction region and can be set for either positive or negative. This allows both photoelectron and ion kinetic energy spectra to be recorded. Recent results from this instrument will be presented including both high resolution photoelectron spectra and photoelectron asymmetry parameter (β) spectra.

Coincidence crosstalk exists to avoid, in favourable circumstances, the measurement of molecular frame photoelectron angular distributions (MPADs) where the detection of an ion fragment allows orientation of the parent molecule to be deduced.

The second is a Wiley-McLaren Time-of-Flight mass spectrometer equipped with multihit electronics. This allows partial ion yield (P2Y) spectra to be recorded as well as multi ion coincidence spectra (P2YPCICO). Again recent results will be presented looking at double ionisation in benzene like molecules.

FAR-IR ACTION SPECTROSCOPY OF AMINOPHENOL AND ETHYL Vanillin: EXPERIMENT AND THEORY

VASYL YATSYN, RADMUND FEIFEI, VITALI ZHAUNERCHYK, Department of Physics, Faculty of Science, University of Gothenburg, Gothenburg, Sweden; DANIEL BAKKER, ANOUK RIJS, FELIX Laboratory, Radboud University Nijmegen, Nijmegen, The Netherlands.

Investigations of molecular structure and conformational isomerism are at the forefront of today’s biophysics and biochemistry. In particular, vibrations excited by far-IR radiation can be highly sensitive to the molecular 3D structure as they are delocalized over large parts of the molecule. Current theoretical predictions of vibrational frequencies in the far-IR range are not accurate enough because of the non-local character and anharmonicity of these vibrations. Therefore experimental studies in the far-IR are vital to guide theory towards improved methodology.

In this work we present the conformer-specific far-IR spectra of aminophenol and ethylvanillin molecules in the range of 220-800 cm^-1 utilizing ion-dip action spectroscopy carried out at the free electron laser FELIX in Nijmegen, Netherlands. The systems studied are aromatic molecules with important functional groups such as the hydroxyl (OH) and amine (NH2) groups in aminophenol, and the hydroxyl, ethoxy (OCH2CH3) and formyl (CHO) groups in ethylvanillin. The experimental spectra show well resolved conformer-specific vibrational bands. In the case of ethylvanillin only two planar conformers have been observed under supersonic jet expansion conditions. Despite the fact that these conformers differ only in the position of the formyl group with respect to ethoxy group, they are well distinguishable in far-IR spectra.

The capability of numerical methods based on density functional theory (DFT) for predicting vibrational frequencies in this spectral region within the harmonic approximation has been investigated by using several hybrid-functionals such as B3LYP, PBE0, B2PLYP and CAM-B3LYP. An anharmonic correction based on vibrational second order perturbation theory approach was also applied. We have found that the methods we considered are well suited for the assignment of far-IR vibrational features except the modes which are strongly anharmonic, like the NH wagging mode in aminophenol which is likely to be due to double well potential governing this motion.
THERMAL DECOMPOSITION OF C$_7$H$_7$ RADICALS; BENZYL, TROPYL, AND NORBORNADIENYL

**G rant B uckingham, B arney E llison, J ohn W. D aily**, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA; M usahid A hmed, U SK, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA.

Benzyl radical (C$_7$H$_7$CH$_3$) and other C$_7$H$_7$ radicals are commonly encountered in the combustion of substituted aromatic compounds found in biofuels and gasoline. High temperature pyrolysis of benzyl radical requires isomerization to other C$_7$H$_7$ radicals that may include cycloheptatrienyl (tropyl) radical (C$_7$H$_7$CH$_3$) and norbornadienyl radical. The thermal decomposition of all three radicals has now been investigated using a micro-reactor that heats dilute gas-phase samples up to 1600 K and has a residence time of about 100 $\mu$s. The pyrolysis products exit the reactor into a superionic expansion and are detected using synchrotron-based photoionization mass spectrometry and matrix-isolation IR spectroscopy. The products of the pyrolysis of benzyl radical (C$_7$H$_7$CH$_3$) along with three isotopomers (C$_7$H$_7$H$_2$CH$_3$, C$_7$D$_3$H$_7$CH$_3$, and C$_7$H$_7$CD$_3$) were detected and identified. The distribution of $^{12}$C atoms and D atoms indicate that multiple different decomposition pathways are active.

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**N elson De Oliveira, D enis J oyieux, DESIRS Beamline, Synchrotron SOLEIL, Saint Aubin, France; K e nji T to, DESIRS Beamline, Synchrotron SOLEIL, Saint Aubin, France; B ernard G ane, D ESIRS Beamline, Synchrotron SOLEIL, Orsay, 94105, France; L aurent Nahon, D ESIRS Beamline, Synchrotron SOLEIL, Saint Aubin, France.**

Fourier transform spectrometers (FTS) are usually based upon amplitude division interferometers through beamsplitters (BS) as in the Michelson interferometer geometry. However, the manufacture of broadband BS is difficult and even impossible in the far VUV (below $\lambda = 140$ nm). We therefore conceived an instrument based upon an original design involving only reflective plane surfaces, giving access to the whole VUV range without the restrictions associated with BS. The VUV–FTS is a permanent endstation connected to one of the three experimental branches of the DESIRS beamline and devoted to high resolution photoabsorption in the UV-VUV spectral range, typically between $\lambda = 300$ and 40 nm. Since 2008, a large international community of users interested in laboratory measurements with applications in astrophysics, molecular physics or planetary atmospheres has been attracted by the VUV–FTS capabilities including its efficiency in terms of signal to noise ratio, even when high spectral resolution was not an issue. A large number of dedicated gas phase sample environments have been developed including a windowless cell that can be cooled down, a heated windowless cell, a free molecular jet set-up and various windowed cells. Besides, a new discharge gas phase cell for production and study of transient species gave recently its first results. As an illustration, the VUV absorption spectrum of the CH$_2$ radical down to 140 nm will be shown in this presentation.

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**E. P. B owen, O. H emmers, Chemistry, University of Nevada Las Vegas, Las Vegas, NV, USA; R. G uillemin, Laboratoire de Chimie Physique – Matière et Rayonnement, Université Pierre et Marie Curie, Paris, France; W. C. Stolte, National Security Technologies, LLC, Livermore, CA, USA; M. N. Piancastelli, Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden; D. W. Lindle, Chemistry, University of Nevada Las Vegas, Las Vegas, NV, USA.**

With the advent of third-generation synchrotron light sources, it has been demonstrated that higher-order corrections to the dipole approximation are necessary for the description of light-matter interactions in the soft x-ray range. These effects, known as ‘non-dipole effects’, present themselves as asymmetries in the angular distributions of photoelectrons. Chiral molecules, known to have asymmetries in photoelectron angular distributions when exposed to circularly polarized light, have been proposed to demonstrate a chiral-specific non-dipole effect when exposed to linearly polarized light. We present the first ever measurement of non-dipole chiral angular distributions for the case of each enantiomer of camphor in the photon energy range 206-343 eV.

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**A. L. H eays, Leiden Observatory, University of Leiden, Leiden, Netherlands; M. G. Thew, laserLab Amsterdam, Vrije Universiteit Amsterdam, Amsterdam, Netherlands; N. De Oliveira, DESIRS Beamline, Synchrotron SOLEIL, Saint Aubin, France; E. DeCie, J. H. Almbek, Department of Physics and Astronomy, Vrije Universiteit, Amsterdam, Netherlands; B. R. Lewis, Research School of Physics and Engineering, Australian National University, Canberra, ACT, Australia; W. M. Ubachs, Department of Physics and Astronomy, Université d’Amsterdam, Amsterdam, Netherlands; E. W. D. H. D. F. E. Weis, Leiden Observatory, University of Leiden, Leiden, Netherlands.**

The predissociation of N$_2$ excited levels is enabled by the presence of optically-inaccessible triplet states. We have recorded vacuum ultraviolet (VUV) spectra at the SOLEIL synchrotron which reveal these states through their perturbation of allowed transitions or their direct appearance due to intensity borrowing. Some of these measurements were recorded at 900 K in order to access high rotational levels, other measurements investigated weak forbidden transitions at high column density. Following careful analysis, significant new information has been obtained elucidating the states responsible for the astrophysically and atmospherically significant N$_2$ predissociation mechanism, and allowing for improvements in its quantitative modelling.

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**C orey Evans, Jason P. Carter, Department of Chemistry, University of Leicester, Leicester United Kingdom; D on McNaughton, Andy Wong, School of Chemistry, Monash University, Melbourne, Victoria, Australia; Dominique Appadoo, 800 Blackburn Road, Australian Synchrotron, Melbourne, Victoria, Australia.**

The high-resolution (0.001 cm$^{-1}$) spectrum of thirane has been recorded using the infrared beamline at the Australian synchrotron facility. Spectra have been recorded between 750 cm$^{-1}$ to 1120 cm$^{-1}$ and re-vibrational transitions associated with four bands have been observed and assigned. Coriolis coupling was observed between the $v_3$ (1024 cm$^{-1}$) and the $v_4$ (1050 cm$^{-1}$) fundamentals as well as between $v_3$ (825 cm$^{-1}$) and the $v_5$ (895 cm$^{-1}$) fundamentals. The $v_6$ (945 cm$^{-1}$) fundamental was also observed and was found to have no significant perturbations associated with it. For each of the observed bands rotational, centrifugal distortion and Coriolis interaction parameters have been determined. The ground state constants have also been further refined.

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**Nelson De Oliveira, Denis Joyieux, DESIRS Beamline, Synchrotron SOLEIL, Saint Aubin, France; K enji T to, DESIRS Beamline, Synchrotron SOLEIL, Saint Aubin, France.**
FINGERPRINTS OF INTRAMOLECULAR HYDROGEN BONDS: SYNCHROTRON-BASED FAR IR STUDY OF THE CIS AND TRANS CONFORMERS OF 2-FLUOROPHENOL

AIMEE BELL, JAMES SINGER, JENNIFER VAN WINGAARDEN. Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada.

Rotational–resolved vibrational spectra of two planar conformers of 2-fluorophenol have been collected from 100–1000 cm−1 using the Bruker IFS125HR FTIR spectrometer at the Canadian Light Source with a resolution of 0.000959 cm−1. The cis conformer is lower in energy by 2.9 kcal/mol (MP2/6-31G(d,p)-B3LYP) and is thought to be stabilized by an intramolecular hydrogen bond between the hydroxyl group and neighbouring fluorine atom on the ring. The OH out-of-plane torsion bands below 400 cm−1 provide the best fingerprint to distinguish between the two conformers in the gas phase spectrum—the γ-type conformer origin of the cis conformer is blue-shifted by 36 cm−1 from that of the trans conformer as result of the intramolecular interaction. In this talk, we will discuss the progress of the analysis of this complex far infrared spectrum of 2-fluorophenol.

Infrared Cross-sections of Nitro-derivative Vapors: New Spectroscopic Signatures of Explosive Tags and Degradation Products

ARNAUD CUISSET, GAEI MOURET, Laboratoire de Physico-Chimie de l’Atmosphère, Université de Littoral Côte d’Opale, Dunkerque, France, OLIVIER PIRIOL, SÉBASTIEN GRUET, AILÉES beamline, Synchrotron SOLEIL, Saint-Aubin, France, GERARD PASCAUD PIAU, GILLES FOURNIER, Airbus Group Innovations, Airbus, Saures, France.

Classical explosives such as RDX or TNT exhibit a very low vapor pressure at room temperature and their detection in air requires very sensitive techniques with levels usually better than 1 ppb. To overcome this difficulty, it is not the explosive itself that is detected, but another compound more volatile present in the explosive. This volatile compound can exist naturally in the explosive due to the manufacturing process. For example, in the case of DinitroToluene (DNT), the molecule is a degradation product of TNT and is required for its manufacture. Ortho-Mononitrotoluene (2-NT) and para-mononitrotoluene (4-NT) can be also used as detection tags for explosive detection.

In this study, using the exceptional properties of the SOLEIL synchrotron source, and adapted multipass-cells, gas phase Far-IR vibrational spectra of different isomers of mononitrotoluene and diisotoluene have been investigated. Room temperature Far-IR cross-sections of the 3 isomer forms of mononitrotoluene have been determined for the lowest frequency vibrational bands located below 700 cm−1. Cross sections and their temperature dependences have been also measured in the mid-IR using conventional PTR spectroscopy probing the nitro-derivatives vapors in a heated multipass-cell.

Post-Deadline Abstract

CHARACTERIZATION OF REACTION PATHWAYS IN LOW TEMPERATURE OXIDATION OF TETRAHYDROFURAN WITH MULTIPLEXED PHOTOIONIZATION MASS SPECTROMETRY TECHNIQUE

IVAN ANTONOV, LEONID SHEPS. Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA.

Tetrahydrofuran (THF) is a prototype biofuel and a common intermediate in combustion of alkanes and alkenes. Photo-lysic C1 atom-initiated oxidation of THF was studied with multiplexed photoionization mass spectrometry (MPMS) technique. Time-of-flight mass spectra and kinetic time traces were recorded simultaneously for all mass channels. Photoionization spectra, recorded with tunable VUV synchrotron radiation, were used to separate and identify isotopes with the same nominal molecular formula, providing mechanistic insight into the underlying kinetics. Our study suggests that formation of aldehydes/radicals and their subsequent isomerization to hydroperoxyalkyl radicals plays an important role in low temperature oxidation of THF, while ring opening of THF...γ reactant (which dominates THF oxidation at T>300 K) is less important at our conditions.

Infrared Spectroscopy of Mn(CO)2(ν) Cluster Anions

MICHAEL C. THOMPSON. JILIAN MATHIAS WEBER, JILA and the Department of Chemistry and Biochemistry, University of Colorado-Boulder. Boulder, CO, USA.

We present infrared photoassociation spectra of Mn(CO)2(ν) (n = 2 − 10) cluster ions. The spectra are interpreted in the framework of density functional theory and compared to other first-row transition metals in anionic clusters with CO2, allowing to draw conclusions to the structure and spin state of the charge carrier.
INFRARED SPECTROSCOPY OF (N$_2$O)$^-$

MICHAEL C THOMPSON, J. MATHIAS

We report infrared photoabsorption spectra of nitrous oxide cluster anions, $(N_2O)^-$ [($n = 7$–$11$) and $(N_2O)_mO^- $ ($m = 1$–$11$)]. Structural changes of the charge carrier in the clusters are driven by increasing levels of solutions. The spectra are interpreted with comparison with quantum chemical calculations.

INFRARED SPECTROSCOPY OF PHENOL$^-$

TREETHYL SILANIDE DIHYDROGEN-BONDED CLUSTER: INTRINSIC STRENGTH OF THE Si-H O-DYHYDROGEN BOND

HARUKI ISHIKAWA, TAKAYUKI KAWASAKI, RISA INOMATA

Dihydrogen bond is known to be one of the unconventional hydrogen bonds. When a hydrogen atom is bonded to an electronegative atom, such as B, F, or O, the hydrogen atom has a partial negative charge. Then, a hydrogen-bond type interaction are formed between the oppositely charged two hydrogen atoms. This interaction is called a dihydrogen bond. In the previous study, we reported the infrared spectroscopy of neutral phenol (PhOH)-triethylsilane (TES) cluster. It was suggested that the Si-H···O-H dihydrogen bond should be as strong as the Si-O hydrogen bond. In the present study, we investigate the intrinsic strength of the Si-H···O-H dihydrogen bond, infrared photoabsorption spectroscopy on the PhOH-TES and PhOH···(dihithylmethylsilane) (DMS) cationic clusters was carried out. The clusters exhibit a very broad and intense band centered at about 2860 cm$^{-1}$. This band is assigned as the OH stretching band of the PhOH mure. Based on the amount of the red-shift of the OH stretching band and the results of the theoretical calculations, the intrinsic strength of the Si-H···O-H dihydrogen bond is evaluated to be stronger than that of the n-type hydrogen bond. The proton affinities of TES and DMS estimated by the theoretical calculation are larger than those of benzene and ethylene. These results are consistent with our experimental observations. 

INFRARED SPECTROSCOPY OF HYDROGEN-BONDED CLUSTERS OF PROTONATED HISTIDINE

MAKOTO KENKEI, YASUTOSHI KASAHARA, HARUKI ISHIKAWA

Histidine(His), one of the essential amino acids, is involved in active sites in many enzyme proteins, and known to play fundamental roles in human body. Thus, to gain detailed information about intermolecular interactions of His as well as its structure is very important. In the present study, we have recorded IR spectra of hydrogen-bonded clusters of protonated His(His$^+$) in the gas phase to discuss the relation between the molecular structure and intermolecular interaction of His$^+$. Clusters of His$^+$····(MeOH)$_n$ ($n = 1$, 2) were generated by an electrospray ionization of the MeOH solution of L-His hydrochloride monohydrate. IR photoabsorption spectra of His$^+$····(MeOH)$_n$ were recorded. By comparing the results of the DFT calculations, we determined the structures of these clusters. In the case of $n = 1$ cluster, MeOH is bonded to the imidazole ring as a proton acceptor. The most of vibrational bands observed were well explained by this isomer. However, a free NH stretch band of the imidazole ring was also observed in the spectrum. This indicates an existence of an isomer in which MeOH is bounded to the carboxyl group of His$^+$. Furthermore, it is found that a protonated position of His is influenced by a hydrogen bonding position of MeOH. In the case of $n = 2$ cluster, one MeOH molecule is bonded to the amino group, while the other MeOH molecule is separately bonded to the carboxyl group in the most stable isomer. However, there is a possibility that other conformers also exist in our experimental condition. The details of the experimental and theoretical results will be presented in the paper.
WH09 4:03 – 4:18
THE COMPETITION BETWEEN INSERTION AND SURFACE BINDING OF BENZENE TO THE WATER HEPTAMER
PATRICK S. WALSH, Department of Chemistry, Purdue University, West Lafayette, IN, USA; DANIEL P. TA- 
BOR, EDWIN SIBERT, Department of Chemistry, The University of Wisconsin, Madison, WI, USA; TIMOTHY 
S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN, USA.

Previous work on the benzene-(water)_{7} clusters with n=7 have focused attention on the main conformer, whose S_{6}S_{5} 
6', R_{2}P_{1} transition appears ~118 cm^{-1} above the benzene monomer. Using resonant ion-dip infrared spectroscopy with a 
higher resolution IR source, we have recently returned to this cluster to record improved OH stretch infrared spectra and 
more thoroughly consider the possible Bz-(H_{2}O)_{7} structures that might give rise to it. Analysis of that spectrum led to its 
assignment as an inserted cube structure with pseudo-S_{3} symmetry. This talk will consider the spectrum and structure of a 
minor conformer of Bz-(H_{2}O)_{6} with R_{2}P_{1} transition ~65 cm^{-1} to the blue of the monomer. This spectrum, recorded for the 
first time, shows a distinctive OH stretch infrared spectrum that is best matched with an expanded prism structure in which 
the seventh water molecule inserts into one edge of the hexamer prism. In this case, benzene acts as acceptor for an OH \rightarrow H-
bond, sitting on the surface of a preformed water heptamer structure. The infrared spectra of the two Bz-(H_{2}O)_{7} structures are 
compared, and the results of a local mode Hamiltonian model are applied to make an assignment for the observed structure. 
The monomer Hamiltonians resulting from this model shed light on the unique two- and three-coordinate water molecules 
found in this structure.

WH10 4:20 – 4:35
VIBRATIONAL SPECTROSCOPY OF BENZENE-(WATER)_{N} CLUSTERS WITH N = 6, 7
DANIEL P. TABOR, EDWIN SIBERT, Department of Chemistry, The University of Wisconsin, Madison, WI, 
USA; RVOSH KUSAKA, Chemistry, Hiroshima University, Higashi-Hiroshima, Japan; PATRICK S. WALSH, 
TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN, USA.
The investigation of benzene-water clusters (Bz-(H_{2}O)_{n}) provides insight into the relative importance of hydrogen bond 
interactions in cluster formation. Taking advantage of the higher resolution of current IR sources, isomer-specific resonant 
ion-dip infrared (RIDIR) spectra were recorded in the OH stretch region (3000-3750 cm^{-1}). A local mode Hamiltonian for 
describing the OH stretch vibrations of water clusters is applied to Bz-(H_{2}O)_{6} and Bz-(H_{2}O)_{7} and compared with the 
RIDIR spectra. These clusters are the smallest water clusters in which three-dimensional H-bonded networks containing 
three-coordinate water molecules begin to be formed, and are therefore particularly susceptible to re-ordering or re-shaping 
in response to the presence of a benzene molecule. The spectrum of Bz-(H_{2}O)_{6} is assigned to an inverted book structure while 
the major conformer of Bz-(H_{2}O)_{7} is assigned to an S_{5} derived inserted cubic structure in which the benzene occupies one 
corner of the cube. The local mode model is used to extract monomer Hamiltonians for individual water molecules, including 
stretch-bend Fermi resonance and intra-monomer couplings. The monomer Hamiltonians divide into sub-groups based on 
their local H-bonding architecture (DA, DDA, DAA) and the nature of their interaction with benzene.

WH11 4:37 – 4:52
THEORETICAL STUDY OF THE IR SPECTROSCOPY OF BENZENE-(WATER)_{7} CLUSTERS
DANIEL P. TABOR, EDWIN SIBERT, Department of Chemistry, The University of Wisconsin, Madison, WI, 
USA; RVOSH KUSAKA, Chemistry, Hiroshima University, Higashi-Hiroshima, Japan; PATRICK S. WALSH, 
TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN, USA.
The local mode Hamiltonian that assigns RIDIR spectra for Bz-(H_{2}O)_{6} and Bz-(H_{2}O)_{7} is explored in detail for Bz-
(H_{2}O)_{n} with n = 3 – 7. In addition to contributions from OH stretches, the Hamiltonian includes the anharmonic coupling 
of each water monomer’s bend overtone and its OH stretch fundamentals, which is necessary for accurately modeling 3150-
3300 cm^{-1} region of the spectra. The parameters of the Hamiltonian can be calculated using either MP2 or density functional 
theory. The relative strengths and weaknesses of these two electronic structure approaches are examined to gain further 
physical understanding. Initial assignments of Bz-(H_{2}O)_{6} and Bz-(H_{2}O)_{7} were based on a linear scaling of M06-2X harmonic 
frequencies. In most cases, counterpoise-corrected MP2 calculations obtain similar frequencies (across all cluster sizes) if 
stretch anharmonicity is taken into account. Individual “monomer Hamiltonians” are constructed via the application of fourth 
order Van Vleck perturbation theory to MP2 potential energy surfaces. These calculations elucidate the sensitivity of intra-
monomer couplings to chemical environment. The presence of benzene has particularly important consequences for the 
spectra of the Bz-(H_{2}O)_{6} clusters, in which the symmetry of the water cycles is broken by H-bonding to benzene. 
The nature of these perturbations is discussed.

WH12 4:54 – 5:09
SPECTROSCOPIC INVESTIGATION OF TEMPERATURE EFFECTS ON THE HYDRATION STRUCTURE OF THE PHENOL CLUSTER CATION
KEFENA YAGE, YASUTOSHI KASAHARA, HARUKI ISHIKAWA, Department of Chemistry, School of Sci-
ence, Kansai University, Suita, Japan.

Owing to recent technical developments of various spectroscopies, microscopic hydration structures of various clusters 
in the gas phase have been determined so far. The next step for further understanding of the microscopic hydration is to 
reveal the temperature effect, such as a fluctuation of the hydration structure. Thus, we are carrying out photodissociation 
spectroscopy on the hydrated phenol cation clusters, [PhOH(H_{2}O)]^{n+}. Since electronic spectra of [PhOH(H_{2}O)]^{n+} have 
been reported already, this system is suitable for our purpose.

In the present study, we use our temperature-variable 22-pole ion trap apparatus. The ions in the trap become thermal 
equilibrium condition by multiple collisions with temperature-controlled He buffer gas. By this way, the temperature of the 
ions can be controlled.

In the electronic spectrum of the n = 5 cluster measured at 30 K, a sharp band is observed. It shows that the temperature 
of ions is well-controlled. Contrary to the n = 5 cluster, the n = 6 cluster exhibits a wider band shape. The temperature 
dependence of the band shape indicates the existence of several, at least two, isomers in the present experimental condition.

ULTRAVIOLET AND INFRARED PHOTODISSOCIATION SPECTROSCOPY OF HYDRATED ANILINIUM ION

ITARU KURUSU, REONA YAGI, YASUTOshi KASAHARA, HARUKI ISHIKAWA, Department of Chemistry, School of Science, Kitasato University, Sagamihara, Japan.

To understand the temperature effect on the microscopic hydration, we have been carrying out the laser spectroscopy of temperature-controlled hydrated phenol cation clusters using our temperature-variable ion trap apparatus. In the present study, we have chosen an anilinium ion (AnH$^+$) as a solute. Since the phenol cation has (1+1)$^\text{a}$ configuration, the phenyl ring does not play as a proton acceptor. On the contrary, the $\pi$-orbitals in the AnH$^+$ are fulfilled and both the NH$^+$ and phenyl groups can behave as hydrogen-bonding sites. Thus, hydration structures around the AnH$^+$ are expected to be different from those of the phenol cation. Since there is no spectroscopic report on the hydrated AnH$^+$ clusters, we have carried out the UV and IR photodissociation spectroscopy of AnH$^+$ (H_2O) clusters.

In the present study, the AnH$^+$ (H_2O) is produced by an electrospray ionization method. As the first step, spectroscopic measurements are carried out without temperature control. In the UV photodissociation spectrum, the 0-0 band appears at 36351 cm$^{-1}$ which is red-shifted by 1863 cm$^{-1}$ from that of the AnH$^+$ monomer. The band pattern is similar to that of the AnH$^+$ monomer. This indicates that the structure of the AnH$^+$ is not so affected by the single hydration. In the IR photodissociation spectrum, OH stretching band of the H_2O moiety and free NH stretching band of AnH$^+$ moiety are observed. Comparison with the results of the DFT calculation at M05-2X/6-31++G(d,p) level, we determined the structure of the AnH$^+$ (H_2O) cluster.


W1H4
WATER-NETWORK MEDIATED, ELECTRON INDUCED PROTON TRANSFER IN ANIONIC [C$_2$H$_4$N(H$_2$O)$_3$]$^-$ CLUSTERS: SIZE DEPENDENT FORMATION OF THE PYRIDINIUM RADICAL FOR $n \geq 3$

ANDREW F DEBLASE, Department of Chemistry, Purdue University, West Lafayette, IN, USA; GARY H WEIDENBRUN, Department of Chemistry and Biochemistry, Fairfield University, Fairfield, CT, USA; KAYE A ARCHER, KENNETH D. JORDAN, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, USA; MARK JOHNSON, Department of Chemistry, Yale University, New Haven, CT, USA.

As an isolated species, the radical anion of pyridine (Py$^-$) exists as an unstable transient negative ion, while in aqueous environments it is known to undergo rapid protonation to form the neutral pyridinium radical (PyH$^+$) along with hydroxide. Furthermore, the negative abdatic anodic affinity (AEA) of Py$^-$ can become diminished by the solvation energy associated with cluster formation. In this work, we focus on the hydrates [Py(H$_2$O)$_n$]$^-$ with $n = 3$-5 and elucidate the structures of these water clusters using a combination of vibrational predissociation and photoelectron spectroscopies. We show that H-transfer to form PyH$^+$ occurs in these clusters by the infrared signature of the nascent hydroxide ion and by the sharp bending vibrations of aromatic ring CH bending.

First scientific observations with the new 12 m antenna of the Atacama Large Millimeter Array (ALMA) from the European Southern Observatory (ESO). The antenna was located at the Very Large Array (VLA) site near Socorro, New Mexico. During the summer of 2013, the antenna was prepared for the move to the ARO Kitt Peak site in Arizona, and in November 2013, the actual transport began. The 97 ton antenna was transported to Arizona in two major parts: the 40 ft. reflector and the base/receiver cabin, which were reassembled in the dome at Kitt Peak in December 2013. Recommissioning began in January 2014, and “first light” observations occurred in September 2014 at 115 GHz. Scientific observations began in December 2014.

As an isolated species, the radical anion of pyridine (Py$^-$) exists as an unstable transient negative ion, while in aqueous environments it is known to undergo rapid protonation to form the neutral pyridinium radical (PyH$^+$) along with hydroxide. Furthermore, the negative abdatic anodic affinity (AEA) of Py$^-$ can become diminished by the solvation energy associated with cluster formation. In this work, we focus on the hydrates [Py(H$_2$O)$_n$]$^-$ with $n = 3$-5 and elucidate the structures of these water clusters using a combination of vibrational predissociation and photoelectron spectroscopies. We show that H-transfer to form PyH$^+$ occurs in these clusters by the infrared signature of the nascent hydroxide ion and by the sharp bending vibrations of aromatic ring CH bending.
MAPPING THE SPATIAL DISTRIBUTION OF METAL-BEARING OXIDES IN VY CANIS MAJORIS
ANDREW BURKHARDT, S. TOM BOOTH, Department of Astronomy, The University of Virginia, Charlo-
tsville, VA, USA; BRADY J. COOPER, Department of Astronomy, The University of Arizona, Tucson, AZ, USA;
BRANDON CARROLL, Division of Chemistry and Chemical Engineering, California Institute of
Technology, Pasadena, CA, USA; LUCY ZIURYS, Department of Astronomy, University of Arizona, Tucson, AZ, USA.

The formation of silicate-based dust grains is not well constrained. Despite this, grain surface chemistry is essential to
modern astronomical formation models. In carbon-poor stellar envelopes, such as the red hypergiant VY Canis Majoris (VY
CMA), metal-bearing oxides, the building blocks of silicate grains, dominate the grain formation, and thus a key location to
study dust chemistry. TiO$_2$, which was only first detected in the radio recently (Kaminski et al. 2003), has been proposed to
be a critical molecule for silicate grain formation, and not oxides containing more abundant metals (e.g. Si, Fe, and Mg)
(Gail and Sedlmayr, 1998). In addition, other molecules, such as SiO$_2$, have been found to trace shells produced by numerous
outflows pushing through the expanding envelope, resulting in a complex velocity structure (Zurowsi et al., 2007). With the
advanced capabilities of ALMA, it is now possible to individually resolve the velocity structure of each of these outflows and
constrain the underlying chemistry in the region. Here, we present high resolution maps of rotational transitions of several
metal-bearing oxides in VY CMA from the ALMA Band 7 and Band 9 Science Verification observations. With these maps,
the physical parameters of the region and the formation chemistry of metal-bearing oxides will be studied.

C$^+$ AND THE CONNECTION BETWEEN DIFFERENT TRACERS OF THE DIFFUSE INTERSTELLAR MEDIUM
STEVEN FEDERMAN, JOHNATHAN S. RICE, Physics and Astronomy, University of Toledo, Toledo, OH, USA;
JORG-E. PIENZA, WILLIAM D. LANGER, PAUL F. GOLDSMITH, J.L. (NICK) INDRIOLO, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA;
LUCY ZIURYS, Department of Astronomy, University of Arizona, Tucson, AZ, USA;
NICK INDRIOLO, Physics and Astronomy, The Ohio State University, Columbus, OH, USA;
LUCY ZIURYS, Department of Astronomy, University of Arizona, Tucson, AZ, USA.

Observations of carbon chain molecules are useful in determining the number densities and temperatures of diffuse
interstellar clouds. In 2003, C$_2$ was observed towards ten different sightlines and the rotational distributions were determined
using the oscillator strengths available at that time.$^1$ The population of each rotational level was adjusted individually in order to
obtain the best fit for all of the P, Q, and R branch lines. This past year, the effect of perturbing states on the C$_2$
spectra was elucidated, and improved oscillator strengths determined.$^2$ With these new values, we have redetermined
the rotational distribution of C$_2$ in these ten sightlines, and used a rotational excitation model analogous to that of Rosell et al.$^3$
and collisional cross sections from Smith et al.$^4$ to infer the kinetic temperatures and number densities.

CO SPECTRAL LINE ENERGY DISTRIBUTIONS IN ORION SOURCES: TEMPLATES FOR EXTRAGALACTIC OBSER-
VATIONS
NICK INDRIOLO, EDWIN BERGIN, Department of Astronomy, University of Michigan, Ann Arbor, MI, USA.

The Herschel Space Observatory has enabled the observation of CO emission lines originating in the J = 5 through J = 7 rotational levels. Surveys of active galaxies (e.g., starbursts, Seyfert, ULBrgs) detect emission from levels as high as J = 30, but the precise excitation mechanisms responsible for producing the observed CO SLEDs (Spectral Line Energy Distributions) remain ambiguous. To better constrain the possible excitation mechanisms in extragalactic sources, we investigate the CO SLEDs arising from sources with known characteristics in the nearby Orion region. Targets include
Orion-KL (high-mass star forming region containing a hot core, embedded protostars, outflows, and shocks), Orion South (high-mass star forming region containing embedded protostars, outflows, and a photodissociation region), Orion H$_2$, Peak 1 (molecular shock), and the Orion Bar (a photodissociation region). Emission lines from complex sources are decomposed using velocity information from high spectral resolution observations made with Herschel-HIFI (Heterodyne Instrument for the Far Infrared). Each source and/or component is taken as a template for a particular excitation mechanism, and then applied to interpret excitation in more distant regions within the Galaxy, as well as external galaxies.

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$^1$Schilke et al. (2006a, 2006b) (2004)

$^2$Rosell et al. (2006a, 2006b) (2002)

THE DISTRIBUTION, EXCITATION, AND ABUNDANCE OF C+, CH+, AND CH IN ORION KL

HARSHAL GUPTA, PATRICK MORRIS, Infrared Processing and Analysis Center, California Institute of Technology, Pasadena, CA, USA; ZOFIA NAGY, Department of Physics and Astronomy, University of Toledo, Toledo, OH, USA; JOHN PEARSON, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; VOLKER OSSENKOPF, I. Physikalisches Institut, Universität zu Köln, Köln, Germany.

The CH+ ion was one of the first molecules identified in the interstellar gas over 75 years ago, and is postulated to be a key species in the initial steps of interstellar carbon chemistry. The high observed abundances of CH+ in the interstellar gas remain a puzzle, because the main production pathway of CH+, i.e., C+ + H2 → CH+ + H, is so endothermic (4460 K), that it is unlikely to proceed at the typical temperatures of molecular clouds. One way in which the high endothermicity may be overcome is if a significant fraction of the H2 is vibrationally excited, as is the case in molecular gas exposed to intense far-ultraviolet radiation fields. Elicidating the formation of CH+ in molecular clouds requires characterization of its spatial distribution, as well as that of the key participants in the chemical pathways yielding CH+. Here we present high-resolution spectral maps of the two lowest rotational transitions of CH+, the fine structure transition of C+ and the hyperfine-split fine structure transitions of CH+ in a ∼3′ × 3′ region around the Orion Kleinmann-Low (KL) nebula, obtained with the Herschel Space Observatory's Heterodyne Instrument for the Far-Infrared (HIFI). We compare these maps to those of CH3+ and C2H+ in the Orion Bar photodissociation region (PDR), and discuss the excitation and abundance of CH+ toward Orion KL in the context of chemical and radiative transfer models, which have recently been successfully applied to the Orion Bar PDR.1

1These observations were done as part of the Herschel observatories of Extraordinary courses: the Orion and Sagittarius star-forming regions (HExoKey) Key Programmes, led by E. A. Bergin at the University of Michigan, Ann Arbor, MI.2

THE DISTRIBUTION OF SH− AROUND ORION KL

HARSHAL GUPTA, Infrared Processing and Analysis Center, California Institute of Technology, Pasadena, CA, USA; KARL M. MENTEN, Millimeter- and Submillimeter-Astronomie, Max-Planck-Institut für Radioastronomie, Bonn, NRW, Germany; ZOFIA NAGY, Department of Physics and Astronomy, University of Toledo, Toledo, OH, USA; PATRICK MORRIS, Infrared Processing and Analysis Center, California Institute of Technology, Pasadena, CA, USA; JOHN PEARSON, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

The SH− ion is thought to probe energetic processes such as shocks, turbulence, and intense UV fields in interstellar clouds, because its principal formation route is endothermic by a temperature equivalent of 1017 K—more than twice as endothermic as that of the well-known ion CH+. Here we present spectral maps of the lowest fine-structure transitions of SH− obtained with the Atacama Pathfinder EXperiment (APEX) telescope over a small (∼1′ × 1′) region in the vicinity of the Orion Kleinmann-Low (KL) nebula, the closest chemically rich star-forming region known to contain hot young stars and shocked gas. Observations of SH− provide complementary information to those of CH− (see, e.g., abstract P130), and may help assess the role of UV irradiation vs shocks in the production of SH− and CH+, as well as the molecular fraction and electron density in the regions traced by SH− and CH+. We also present chemical and radiative transfer models to help elucidate the production of SH− and CH+, and assess the utility of these ions as probes of processes that regulate the thermal balance of the interstellar gas and influence star formation in molecular clouds.

CHEMICAL COMPLEXITY IN THE SHOCKED OUTFLOW L1157-B REVEALED BY CARMA

NIKLAUS M. DOLLHOFF, Department of Astronomy, The University of Virginia, Charlottesville, VA, USA; BRETT A. McGUIRE, NAOCS, National Radio Astronomy Observatory, Charlottesville, VA, USA; BRANDON CARROLL, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA; ANTHONY REMIJAN, ALMA, National Radio Astronomy Observatory, Charlottesville, VA, USA.

We present results from a targeted chemical search toward the prototypical shocked outflow L1157. L1157-B0, -B1, and -B2 are shocked regions within the outflow from the Class 0 low-mass protostar L1157-mm. We have mapped a variety of molecular tracers in the region with typical spatial resolutions of ∼3 arcsec using CARMA, and find differences in the chemical makeups between shocked regions within the same precursor outflow material. We present observations of CH3(OH), HCO+3, HCN, and CH3CN and compare to 3mm results, from several species including, dimethyl ether [CH3(OH)], ethyl cyanide [C2H5CN], acetone [CH3CO2], SO, and SO2.

THE CURIOUS CASE OF NH2OH: HUNTING A DIRECT AMINO ACID PRECURSOR SPECIES IN THE INTERSTELLAR MEDIUM

BRETT A. McGUIRE, NAOCS, National Radio Astronomy Observatory, Charlottesville, VA, USA; BRANDON CARROLL, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA; KARL M. MENTEN, Max-Planck-Institut für Radioastronomie, Bonn, NRW, Germany; ZOFIIA NAGY, Department of Physics and Astronomy, University of Toledo, Toledo, OH, USA; GEORFFREY BLAKE, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA; ANTHONY REMIJAN, ALMA, National Radio Astronomy Observatory, Charlottesville, VA, USA.

Despite the detection of amino acids, the building blocks of the proteins that support life, in cometary and meteoritic samples, we do not yet understand the conditions under which these life-essential species have formed. Hydroxylamine (NH2OH) is potentially a direct precursor to the formation of the amino acids glycine and alanine in the ISM, through reaction with acetic and propionic acids. Recent laboratory and modeling work has shown that there are a variety of pathways to the formation of NH2OH in interstellar ices both efficiently and in high abundance. Here, we present the result of a deep, multi-telescope search for NH2OH in the shocked, complex molecular source L1157. We find no evidence suggesting the presence of this important precursor, and discuss the implications of this non-detection on the reactivity of NH2OH both within the ices, and in the gas-phase ISM. We will also discuss how these observations should inform the direction of future studies, both in the laboratory and with state-of-the-art telescopes such as ALMA.
NEW RESULTS FROM THE CARMA LARGE AREA STAR FORMATION SURVEY (CLASSY)

ROBERT J HARRIS, LESLIE LOONEY, DOMINIQUE M. SEGURA-COX, Department of Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL, USA; MANUEL FERNANDEZ-LOPEZ, Instituto Argentino de Radioastronomía, Centro Científico Tecnológico La Plata, Villa Elisa, Argentina; LEE MUNDY, SHAYE STORM, MAXIME RIZZO, Department of Astronomy, University of Maryland, College Park, MD, USA; KATHERINE LEE, Radio and Geoastronomy Division, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; HECTOR ARCE, Astronomy Department, University of New Haven, New Haven, CT, USA.

Interferometric imaging spectroscopy of molecular clouds permits the physical and thermalodynamic structure, kinematics, and chemistry of molecular clouds to be probed over a wide range of spatial scales, from entire clouds to the individual cores where stars are born. As such, it allows the study of what fundamental physical processes are at play in star formation. The CARMA Large Area Star formation Survey (CLASSY) is a key project that has surveyed dense gas tracers (HCN, HCO\(^+\)) and dust continuum emission over 

WJ15 5:45 – 6:00
ADMIT: ALMA DATA MINING TOOLKIT

DOUGLAS FREIDEL, LESLIE LOONEY, Department of Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL, USA; LISA XU, NCSA, University of Illinois at Urbana-Champaign, Urbana, IL, USA; MARC W. POUND, PETER J. TEUBEN, KEVIN P. RAUCH, LEE MUNDY, Department of Astronomy, University of Maryland, College Park, MD, USA; JEFFREY S. KERN, NAOJ, Socorro, NM, USA.

ADMIT (ALMA Data Mining Toolkit) is a toolkit for the creation and analysis of new science products from ALMA data. ADMIT is an ALMA Development Project written purely in Python. While specifically targeted for ALMA science and production use after the ALMA pipeline, it is designed to be generally applicable to radio-astronomical data. ADMIT quickly provides users with a detailed overview of their science products: line identifications, line ‘cutout’ cubes, moment maps, and production use after the ALMA pipeline, it is designed to be generally applicable to radio-astronomical data. ADMIT is an ALMA Development Project written purely in Python. While specifically targeted for ALMA science and production needs. Future implementations of ADMIT may include EVLA and other instruments.
Clusters of carboxylic acids with water, sulfonic acid, and other atmospheric species potentially increase the rate of new particle formation in the troposphere.\(^{1,2}\) Here, we present high-resolution pure rotational spectra of o-toluc acid and its complex with water in the range of 5.1–8.19 GHz, measured with a cavity-based molecular beam Fourier-transform microwave spectrometer. In both the monomer and the complex, the carboxylic acid functional group adopts a sym-conformation, with the acidic proton oriented away from the aromatic ring. In the complex, water participates in two hydrogen bonds, forming a six-membered intermolecular ring. Despite its large calculated $c$-dipole moment, no $c$-type transitions were observed for the complex, because of a large amplitude “wagging” motion of the unbound hydrogen of water, similar to the case of the benzoic acid-water complex.\(^{3}\) No methyl internal rotation splittings were observed, consistent with a high barrier (7 kJ mol$^{-1}$) calculated for the monomer at the B3LYP/6-311++G(d,p) level of theory. Using thermodynamic and rotational constants were combined with a theoretical frequency analysis and binding energy to give an estimate of the percentage of hydrated acid in the atmosphere under various conditions.

**References**

A GENERAL TRANSFORMATION TO CANONICAL FORM FOR POTENTIALS IN PAIRWISE INTERMOLECULAR INTERACTIONS

JAY A. WALTON, Department of Mathematics, Texas A & M University, College Station, TX, USA; LUIS A. RIVERA-RIVERA, ROBERT R. LUCHESSE, JOHN W. BEVAN, Department of Chemistry, Texas A & M University, College Station, TX, USA.

A generalized formulation of explicit transformations is introduced to investigate the concept of a canonical potential in both fundamental chemical and intermolecular bonding. Different classes of representative ground electronic state pairwise interatomic interactions are referenced to a single canonical potential illustrating application of explicit transformations. Specifically, accurately determined potentials of the diatomic molecules H2, H2+, HF, LiH, argon dimer, and one-dimensional dissociative coordinates in Ar-HBr, OC-HF, and OC-Cl2 are investigated throughout their bound potentials. The advantages of the current formulation for accurately evaluating equilibrium dissociation energies and a fundamentally different unified perspective on nature of intermolecular interactions will be emphasized. In particular, this canonical approach has relevance to previous assertions that there is no very fundamental distinction between van der Waals bonding and covalent bonding at that matter hydrogen and halogen bonds.

THREE-DIMENSIONAL WATER NETWORKS SOLVATING AN EXCESS POSITIVE CHARGE: NEW INSIGHTS INTO THE MOLECULAR PHYSICS OF ION HYDRATION

CONRAD T. WOLKE, JOSEPH FOURNIER, Department of Chemistry, Yale University, New Haven, CT, USA; GARY H. WEIDLE, Department of Chemistry and Biochemistry, Fairfield University, Fairfield, CT, USA; EVANGELOS MILIORDOS, SOTIRIS XANTHEAS, Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA; MARK JOHNSON, Department of Chemistry, Yale University, New Haven, CT, USA.

In a recent effort our group investigated the vibrational mechanics of water using the cage of 20 water molecules surrounding an alkali ion as a paradigm system. The M+ (H2O)19 clusters are well-known “magic number” species (for the larger alkali metals) and are thought to form a pentagonal dodecahedral web encapsulating the ion. We are attracted to these systems because they are sufficiently large to display broad OH fundamental envelopes in a manner similar to that found in bulk water, but do so with a relatively small number of structurally distinct, three coordinated sites in a finite assembly that, although challenging, can be analyzed with electronic structure calculations in the context of a “supermolecule.” We show how this arrangement can provide an ideal platform on which to unambiguously identify the spectral signatures of particular binding sites, information that is invoked to explain the bulk (and interface) spectrum of water but cannot be directly measured in bulk water.

Although this behavior is most relevant to simulations of interfacial water, a future direction of this study will be gaining site-specific information for water in an extended two dimensional structure, and the elucidation of the paths of spectral diffusion associated with this arrangement. This unprecedented work will clarify a number of open questions regarding the site specificity of ground and vibrationally excited state dynamics.

MATRIX ISOLATION INFRARED SPECTROSCOPY OF A SERIES OF 1:1 PHENOL-WATER COMPLEXES

PUJARINI BANERJEE, TAPAS CHAKRABORTY, Physical Chemistry, Indian Association for the Cultivation of Science, Kolkata, India.

We report here the FTIR spectra of 1:1 complexes of eight fluorophenol derivatives with water measured under matrix isolation condition. In all the complexes, oxygen of water is the hydrogen bond acceptor and phenolic O-H the hydrogen bond donor. The attributes of the O-H-O linkage in the complexes are tuned remotely by fluorescence substitutions at different aromatic sites of phenol. The goal of the study is to find the intermolecular interactions that correlate best with the sequence of spectral shifts of the donor O-H stretching (νO-H) frequencies. Measurements reveal that the probe phenolic νO-H shifts vary by nearly 90% from unsubstituted phenol to pentfluorophenol. Interestingly, this large variation correlates poorly with the predicted binding energies of the complexes. Secondly, although electrostatic interaction is considered to dominate the overall stabilization of such classical hydrogen bonds, we see that the shifts do not display any correlation with this interaction at the hydrogen bonding site. On the other hand, the purely quantum mechanical charge-transfer interaction energies, as obtained from Natural Bond Orbital analysis are found to display good correspondence with the spectral shifts. Thus, we propose that such local charge-transfer type interactions are better descriptors of weakening of the hydrogen bond donor than electrostatic energy parameters.

MATRIX ISOLATION IR SPECTROSCOPY AND QUANTUM CHEMISTRY STUDY OF 1:1 HYDROGEN BONDED COMPLEXES OF BENZENE WITH A SERIES OF FLUOROPHENOLS

PUJARINI BANERJEE, TAPAS CHAKRABORTY, Physical Chemistry, Indian Association for the Cultivation of Science, Kolkata, India.

O-H stretching infrared fundamentals (νO-H) of phenol and a series of fluorophenol monomers and their 1:1 complexes with benzene have been measured under a matrix isolation condition (KBr). For the phenol-benzene complex the measured shift of νO-H is 78 cm⁻¹ and for 3, 4, 5-trifluorophenol it is 98 cm⁻¹. Although the cold matrix isolation environment is very different from an aqueous medium, the measured spectral shifts display an interesting linear correlation with the aqueous phase acid dissociation constants (pK a) of the phenols. The spectral shifts predicted by quantum chemistry calculations at several levels of theory are consistent with the observed values. Correlations of the shifts are also found with respect to energetic, geometric and several other electronic structure parameters of the complexes. Partitioning of bonding energies of the complexes into components following the Morokuma-Kitaura scheme shows that dispersion is the predominant component of attractive interaction, and electrostatics, polarization and charge-transfer terms also have contributions to overall binding stability. NBO analysis reveals that hyperconjugative charge-transfers from the filled π-Orbitals of the hydrogen bond acceptor (benzene) to the anti-bonding σ*(O-H) orbital of the donors (phenols) display correlations which are fully consistent with the observed variations of spectral shifts. The analysis also shows that the O-H bond dipole moments of all the phenolic species are nearly the same, implying that local electrostatics has only a little effect at the site of hydrogen bonding.
A comparative study of infrared spectral effects for 1:1 complex formation of acetic acid (AA), trifluoroacetic acid (TFAA) and trichloroacetic acid (TCAA) with water and benzene has been carried out under a matrix isolation environment. Despite the large difference in aqueous phase acidities of the three acids, the measured νC=O stretching frequencies of the monomers of the three molecules are found to be almost same, and in agreement with gas phase electronic structure calculations. Intrinsic acidities are expressed only in the presence of the proton acceptors, water or benzene: although electronic structure calculations predict distinct νC=O red-shifts for all three acids, the measured spectral features for TCAA and TFAA in this range do not allow unambiguous assignments for the 1:1 complex. On the other hand, the spectral changes in the νOC=O region are more systematic, and the observed changes are consistent with predictions of theory. Components of overall binding energy of each complex have been obtained from energy decomposition analysis, which allows determination of the relative contributions of various physical forces towards overall stability of the complexes, and the details will be discussed in the talk.

The effects of environment on the photophysical properties of a series of newly-developed near infrared emitting dyes was studied spectroscopically. Properties of interest include fluorescence emission, fluorescence lifetime, and quantum yield. Tracking how the photophysics of these compounds are affected in the solid phase, in thin films, in solution, and at the single molecule level with changing environment will provide a deeper insight into how dye structure affects their function.

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RA01
8:30 – 8:45
HYPERFINE RESOLVED PURE ROTATIONAL SPECTROSCOPY OF SrN, YN, AND BaH(N)/C(13)N**: INSIGHT INTO METAL-METAL BONDING
LINDSAY N. ZACK, Department of Chemistry, Wayne State University, Detroit, MI, USA; MATTHEW BUCCHINO, Department of Chemistry and Astronomy, University of Arizona, Tucson, AZ, USA; JUSTIN YOUNG, MARSHALL BINNS, PHILLIP M. SHERIDAN, Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY, USA; LUCY ZIURYS, Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA.

Fourier transform microwave spectroscopy coupled with a discharge-assisted laser ablation source (DALAS) has been used to record the J = 1−0 pure rotational transitions of SrN, Sr(N)/C(13)N, YN, Y(N)/C(13)N, and BaH(N)/C(13)N. Each species was synthesized by the reaction of the ablated metal with either NH3 or 13NH3 in the presence of a DC discharge. For each species hyperfine structure was resolved. In the case of SrN and YN hyperfine parameters (quadrupole and nuclear spin-rotation) for the metal and nitrogen were determined and for BaH(N) the nitrogen quadrupole coupling constant was measured. These hyperfine constants are interpreted to gain insight into the metal-nitrogen bonding in each species. In addition, DFT calculations were performed to assist with the assignment of each spectrum and the characterization of the metal-nitrogen bond.

RA02
8:47 – 9:02
THE SUBMILLIMETER/THz SPECTRUM OF AlH (Xσ+), C(13)H, and SH (Xσ−)
DEWAYNE HALFEN, Department of Chemistry and Astronomy, University of Arizona, Tucson, AZ, USA; LUCY ZIURYS, Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA.

The N = 2 − 1 transition of the C(13)H radical near 730–734 GHz and the J = 2 − 1 line of AlH (Xσ+), near 755 GHz have been measured using submillimeter/Terahertz direct absorption spectroscopy. C(13)H was created in an AC discharge of Cr(O)3 vapor and H2 in the presence of argon. AlH was produced from Al(CH3)3 vapor and H2 in argon with an AC discharge. In addition, three fine structure components of the N = 1 − 0 transition of the SH (Xσ−) cation from 345–683 GHz were recorded. SH− was generated from H2S and argon in an AC discharge. The data have been analyzed, and spectroscopic constants for these species have been refined. These parameters are in excellent agreement with past millimeter, infrared, and optical data. SH− is a known interstellar molecule, and these measurements confirm recent observations of this species. The new data for CH3 and AlH could facilitate the detection of these species in interstellar/circumstellar gas.

RA03
9:04 – 9:19
FORMATION OF M+C≡C-C (M = Ag or Cu) AND CHARACTERIZATION BY ROTATIONAL SPECTROSCOPY
DANIEL P. ZALESKI, School of Chemistry, Newcastle University, Newcastle-upon-Tyne, United Kingdom; DAVID PETER TEW, School of Chemistry, University of Bristol, Bristol, United Kingdom; NICK WALKER, School of Chemistry, Newcastle University, Newcastle-upon-Tyne, United Kingdom; ANTHONY LEGON, School of Chemistry, University of Bristol, Bristol, United Kingdom.

The new linear molecule AgCu:C≡C-C has been detected and characterized by means of rotational spectroscopy. It was synthesized by laser ablation of a silver rod in the presence of a gaseous sample containing a low concentration of CCl4 in argon, cooled to a rotational temperature approaching 2 K through supersonic expansion and analyzed by chipped pulse Fourier transform microwave spectroscopy. Substitution coordinates are available for the silver and chlorine positions and will be compared to ab initio calculations at the CCSD(T)/aug-cc-pVQZ level of theory. The Ag-C≡C-C=C-C(C13)Cu isomeric was also observed using a similar gas mixture containing 13CCl4. The Cu analogue Cu-C≡C-C=C-C(C13)Cu was similarly identified and characterized.

RA04
9:21 – 9:36
(CH3)3N···AgI AND H3N···AgI STUDIED BY BROADBAND ROTATIONAL SPECTROSCOPY AND AB INITIO CALCULATIONS
DROR M. BITTNER, DANIEL P. ZALESKI, SUSANNA L. STEPHENS, NICK WALKER, School of Chemistry, Newcastle University, Newcastle-upon-Tyne, United Kingdom; ANTHONY LEGON, School of Chemistry, University of Bristol, Bristol, United Kingdom.

The pure rotational spectra of 8 isotopologues of H3N···AgI and 8 isotopologues of (CH3)3N···AgI were measured in a chiped pulse Fourier-transform microwave spectrometer. The complexes were synthesized in a molecular beam from a gas sample containing H3N or (CH3)3N and CF3I precursors diluted in argon. Laser ablation was used to introduce silver atoms to the gas phase. The rotational constant B0, centrifugal distortion constants D2 and D4, and the nuclear quadrupole coupling constant h0(Ag) have been determined for (CH3)3N···AgI, C13H3N···AgI, H3N···AgI, C13H3N···AgI and D2N···AgI by fitting the measured transitions to a symmetric top Hamiltonian. The spectroscopic constants (h0(Ag), D2 and D4) have been determined for D2HN···AgI through fits that employed a Hamiltonian appropriate for a very near prolate asymmetric rotor. Partial effective (h0) and substitution (T2) structures have been determined.

RA05
9:38 – 9:53
MICROWAVE SPECTRA AND GEOMETRIES OF C2H2···AgI and C2H4···AgI
SUSANNA L. STEPHENS, Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada; DAVID PETER TEW, School of Chemistry, University of Bristol, Bristol, United Kingdom; NICK WALKER, School of Chemistry, Newcastle University, Newcastle-upon-Tyne, United Kingdom; ANTHONY LEGON, School of Chemistry, University of Bristol, Bristol, United Kingdom.

A chiped-pulse Fourier transform microwave spectrometer has been used to measure the microwave spectra of both C2H2···AgI and C2H4···AgI. These complexes are generated via laser ablation at 532 nm of a silver surface in the presence of argon. AlH was produced from Al(CH3)3 vapor and H2 in argon with an AC discharge. The data have been analyzed, and spectroscopic constants for these species have been refined. These parameters are in excellent agreement with past millimeter, infrared, and optical data. SH− is a known interstellar molecule, and these measurements confirm recent observations of this species. The new data for CH3 and AlH could facilitate the detection of these species in interstellar/circumstellar gas.

Intermission
EVALUATION OF THE EXOTHERMICITY OF THE CHEMI-IONIZATION REACTION Sm + O → SmO+ + e−
RICHARD M COX, JUNGSOO KIM, PETER ARMENTROUT, Department of Chemistry, University of Utah, Salt Lake City, UT, USA; JONATHA BARTLETT, ROBERT A. VANGUNDY, MICHAEL C. HEAVEN, Department of Chemistry, Emory University, Atlanta, GA, USA; JOSUA J. MIELKO, Department of Chemistry, University of North Florida, Jacksonville, FL, USA; SHAUN ARD, NICHOLAS S. SHUMAN, ALBERT VIGGIANO, Space Vehicles Directorate, Air Force Research Lab, Kirtland AFB, NM, USA.

The chemi-ionization reaction Sm + O → SmO+ + e− has been used for chemical release experiments in the thermolysis. This reaction was chosen, in part, because the best available data indicated that it is exothermic by 0.35 ± 0.12 eV. Low ion yields in the initial atmospheric release experiments raised questions concerning the accuracy of the ionization energy (IE) for SmO and the bond dissociation energy (BDE) of SmO+. New measurements of these values, obtained using a selected ion flow tube and guided ion beam techniques, yielded a more precise value of 5.73 ± 0.07 eV. The ionization energy of SmO was reexamined using pulsed-field ionization zero kinetic energy (ZEKE) photoelectron spectroscopy. The value obtained, 5.74 ± 0.006 eV, was significantly higher than the literature value. Combined with literature bond energies of SmO, this result indicates an exothermicity for Sm + O → SmO+ + e− of 0.14 ± 0.17 eV independent from and in agreement with the value deduced from the guided ion beam measurements. The implications of these results for consideration of chemical release experiments are considered.

RA07 10:29 – 10:44
THE PERMANENT ELECTRIC DIPOLE MOMENT AND HYPERFINE INTERACTION IN GOLD SULFIDE, AuS
RUOHAN ZHANG, DAMIAN L. KOKKIN, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, USA; THOMAS D. VARGHER, Chemistry Department, Macaulay College, Saint Paul, Minnesota, USA; TIMOTHY STEIMLE, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, USA.

The bonding and electronic properties of gold containing molecules are highly influenced by the large relativistic and electron correlation effects. Here we report on the electric permanent dipole moment measurement and hyperfine interaction analysis of the \( ^1\Delta_1 \rightarrow ^1\Sigma_1^+ \) and \( ^1\Delta_2 \rightarrow ^1\Pi_2 \) bands of AuS. A cold molecular beam sample of gold sulfide was generated using a supersonic expansion source. The electronic bands were recorded at high resolution (55 MHz PPM) using laser excitation spectroscopy both field-free and in the presence of a static electric field. The observed hyperfine spectral features were assigned and a set of spectroscopic parameters for the \( ^1\Delta \) and \( ^1\Sigma \) states were obtained. The Stark shifts induced of selected low-rotational features were analysed to determine the permanent electric dipole moments in both the ground and excited states.

RA08 10:46 – 11:01
HIGH-ACCURACY CALCULATION OF Cu ELECTRIC-FIELD GRADIENTS: A REVISION OF THE Cu NUCLEAR QUADRUPOLE MOMENT VALUE
LAN CHENG, Department of Chemistry, The University of Texas, Austin, TX, USA; DEVIN A. MATTHEWS, Department of Chemistry and Biochemistry, The University of Texas, Austin, TX, USA; JURGEN GAUSS, Institut für Physikalische Chemie, Universität Mainz, Mainz, Germany; JOHN F. STANTON, Department of Chemistry, The University of Texas, Austin, TX, USA.

A revision of the value for the Cu nuclear quadrupole moment (NQM) is reported based on high-accuracy ab initio calculations on the Cu electric field gradients in the CuF and CuCl molecules. Electron-correlation effects have systematically been taken into account using a hierarchy of coupled-cluster methods including up to quadruple excitations. It is shown that the full CCSD(T) method provides a more reliable treatment of triple correlations for Cu-electric-field gradients than the ubiquitously applied CCSD(T) method, which is tentatively attributed to the importance of the wavefunction relaxation in the calculations of a core property. Augmenting large-basis-set CCSD(T) results with the remaining corrections obtained using additive schemes, including full triples contributions, quadruples contributions, zero-point vibrational corrections, spin-orbit corrections, as well as the correction from the Gaunt term, a new value of 209(7)(50) mBarn for the Cu NQM has been obtained. The new value substantially reduces the uncertainty of this parameter in comparison to the standard value of 220(15) mBarn obtained from a previous inorganic experiment.

RA09 11:03 – 11:18
CATION-π AND CH-π INTERACTIONS IN THE COORDINATION AND SOLVATION OF Cu+ (ACETYLENE)n (n=1-6) COMPLEXES INVESTIGATED VIA INFRARED PHOTODISSOCIATION SPECTROSCOPY
ANTONIO DAVID BRATHWAITE, College of Science and Mathematics, University of the Virgin Islands, St. Thomas, EUSV; RICHARD S. WALTERS, TIMOTHY B WARD, MICHAEL A DUNCAN, Department of Chemistry, University of Athens, Georgia, GA, USA.

Mass-selected copper cation complexes of the form \( \text{CuC}_n \) (n = 1-6) are produced by laser ablation and studied via infrared laser photodissociation spectroscopy in the C-H stretching region (3000-3500 cm\(^{-1}\)). Spectra for larger species are measured via ligand elimination, whereas argon tagging is employed to enhance dissociation yields in smaller complexes. The number of formed nuclei, their fragment positions and their relative intensities provide insight into the structure and bonding of these ions. Density functional theory calculations are carried out in support of this work. The combined data show that cation-π bonds are formed for the n=1-3 species, resulting in red-shifted C-H stretches on the acetylene ligands. Three acetylene ligands complete the coordination of the copper cation. Additional ligands (n=4-6) solve the n=3 core by forming cation-π bonds. Distinctive vibrational patterns are exhibited for coordinated vs. solvent ligands. Theory reproduces these results.

RA10 11:20 – 11:35
ANION PHOTOELECTRON SPECTROSCOPIC STUDIES OF NbCr(CO)\(_3\) (n=2) HETEROBIMETALLIC CARBONYL COMPLEXES
MELISSA A. BAUDHUIN, PRAVEENKUMAR HOOPALACHANDRAN, DOREEN LEOPOLD, Chemistry Department, University of Minnesota, Minneapolis, MN, USA.

Anion photoelectron spectra and density functional calculations are reported for NbCr(CO)\(_3\) and NbCr(CO)\(_3\) complexes prepared by addition of CO\(_2\). Tropos to a flow tube equipped with a niobium cathode discharge source. Electron affinities (± 0.007 eV) are measured to be 1.668 eV for NbCr(CO)\(_3\) and 1.62 eV for NbCr(CO)\(_3\), which exceed the 0.793 eV electron affinity previously measured for ligand-free NbCr. The vibrationally-resolved 488 nm photoelectron spectra are compared with Franck-Condon spectra predicted for various possible isomers and spin states of the atomic and neutral metal carbonyl complexes. Results are also compared with photoelectron spectra of the corresponding chromium carbonyl complexes and of NbCr and NbCr\(_2\) - which have formal bond orders of 5.5 \((\Delta g=6\text{ and } b=12^2)\), respectively. These comparisons help to elucidate the effects of sequential carbonylation on this multiple-metal bond, and of the formation of this bond on the chromium-carbonyl interactions.

RA11 11:37 – 11:52
MASS-ANALYZED THRESHOLD IONIZATION SPECTROSCOPY OF CYCLIC La(\(\text{C}_2\)H\(_2\)) FORMED BY LA ATOM ACTIVATION OF PENTANE AND PENTADIENE
WENJIN CAO, YUCHEN ZHANG, DONG-SHENG YANG, Department of Chemistry, University of Kentucky, Lexington, KY, USA.

La atom reactions with 1-pentene (C\(_5\)H\(_{10}\)) and 1,4-pentadiene (C\(_8\)H\(_{12}\)) in a jet expansion were measured by mass-analyzed threshold ionization spectroscopy. The most stable isomer of La(C\(_5\)H\(_{12}\)) was identified as a six-membered metallacycle, La(\(\text{C}_2\)H\(_2\))\(_n\) (n=1-3) with three vibrational modes of the ion measured to be 318, 407, and 538 cm\(^{-1}\), which correspond to the La-π stretching, carbon skeleton bending with \(\text{C}_2\)H\(_2\) rocking, and carbon skeleton bending with \(\text{C}_2\)H\(_2\) twisting, respectively. In addition, two hot bands were observed at 276 and 367 cm\(^{-1}\) below the origin band and identified to be the vibrational frequencies of the La-π stretching and carbon-skeleton bending with \(\text{C}_2\)H\(_2\) rocking modes of the neutral complex.
**Chair:** Gert von Helden, Fritz Haber Institute - MPG, Berlin, Germany

**Room:** 100 Noyes Laboratory

**Thursday, June 25, 2015 – 8:30 AM**

**RB01**
**8:30 – 9:00**

**INVITED TALK**

**PROBING INTRA- AND INTER- MOLECULAR INTERACTIONS VIA IRMPD EXPERIMENTS AND COMPUTATIONAL CHEMISTRY**

**SCOTT HOPKINS, TERRY McMAHON, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada.**

Experiments carried out at the CLID Free Electron Facility have been used to probe a range of novel bonding motifs and dissociation dynamics in a variety of chemical systems. Among these are species which exhibit anion-π interactions in complexes of halide ions with aromatic ring systems with electron withdrawing substituents, charge solvated and twotronic clusters of protonated melamylamines with phenylalanines; hydrogen bonded dimers of nucleic acid analogues and Pd complexes potentially involving apotic hydrogen bond interactions. Accompanying DFT computational work is used to assist in identifying the most probable structure(s) present in the IRMPD experiments.

**RB02**
**9:05 – 9:20**

**EXPLORING CONFORMATION SELECTIVE FAR INFRARED ACTION SPECTROSCOPY OF ISOLATED MOLECULES AND SOLVATED CLUSTERS**

**DANIEL BAKKER, ANDRÖS RUS, FELIX Laboratory, Radboud University Nijmegen, Nijmegen, The Netherlands; JÉRÔME MAHE, MARIE-PIERRE GAIGEOT, Laboratoire Analyse et Modélisation pour la Biologie et l’Environnement, Université d’Evry val d’Essonne, Evry, France.**

Far-Infrared (IR) spectroscopy has been labeled as a promising method for identifying structural motifs in large molecules. However, several hurdles have kept this promising spectral region from breaking through to widespread use for gas phase experiments. Normal modes in the far-IR mostly have weak intensities, and high brightness sources of far-IR radiation are rare. Moreover, standard density functional theory - applied to identify the specific molecular structure responsible for the measured IR spectra - does not reproduce features in the far-IR well. This mismatch can be attributed to the high degree of anharmonicity of many of the normal modes present in the far-IR. We have overcome these hurdles by combining an advanced laser source with novel experiments and high-level dynamical calculations.

We present far-IR spectra of a family of phenolic molecules and solvated clusters, obtained using the free electron laser FELIX. By employing IR-UV ion-dip spectroscopy in the gas phase, we are able to obtain conformer specific far-IR spectra of isolated molecules or solvated clusters. The studied systems display both intra- and intermolecular hydrogen bonding, enabling us to study the merits of far-IR action spectroscopy for direct probing of these weak interactions. Moreover, the combination of far-IR experiments with quantum chemical calculations allows us to test the limits of the harmonic approximations in DFT calculations, and to test the possibilities of employing a more sophisticated technique, namely Born-Oppenheimer molecular dynamics.

**RB03**
**9:22 – 9:37**

**FIRST INFRARED PREDISSOCIATION SPECTRA OF He-TAGGED PROTONATED PRIMARY ALCOHOLS AT 4 K**

**ALEXANDER STOFFELS, BRITTIA REDLICH, JO DÖMEN, Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands; OSKAR ASVANY, SANDRA BRÜNKEN, PAVOL JUSKO, SVEN THORWIRTH, STEPHAN SCHLIEMMER, I. Physikalisches Institut, Universität zu Köln, Köln, Germany.**

Cryogenic multipole ion traps have become popular devices in the development of sensitive action-spectroscopic techniques. The low ion temperature leads to enhanced spectral resolution, and less congested spectra. In the early 2000s, a 22-plate ion trap was coupled to the Free-Electron Laser for Infrared Experiments (FELIX), yielding infrared Laser Induced Reaction (LIR) spectra of the molecular ions C2H5OH and C3H7OH. This pioneering work showed the great opportunities combining cold mass-selected molecular ions with widely tunable broadband IR radiation.

In the past a year cryogenic (T>3.9 K) 22-plate ion trap designed and built in Cologne (FELIX) has been successfully coupled to FELIX, which in its current configuration provides continuously tunable infrared radiation from 5 µm to 150 µm, hence allowing to probe characteristic vibrational spectra in the so-called “fingerprint region” with a sufficient spectral energy density also allowing for multiple photon processes (IR-MPD). Here we present the first infrared predissociation spectra of He-tagged protonated methanol and ethanol (C2H5OH, C3H7OH) stored at 4 K. These vibrational spectra were recorded with both a commercial OPO and FELIX, covering a total spectral range from 3700 cm⁻¹ to 550 cm⁻¹ at a spectral resolution of a few cm⁻¹. The O-H-H stretching and bending modes clearly distinguish the protonated alcohols from their neutral analogs. For C2H5OH also IR-MPD spectra of the bare ion could be recorded. The symmetric and antisymmetric O-H-O stretching bands at around 3 µm show no significant shift within the given spectral resolution in comparison to those recorded with He predissociation, indicating a rather small perturbation caused by the attached He. The vibrational bands were assigned using quantum-chemical calculations on different levels of theory. The computed frequencies correspond favorably to the experimental spectra. Subsequent high resolution measurements could lead to a better structural characterization of these protonated alcohols.

**RB04**
**9:39 – 9:49**

**METAL ION INDUCED PAIRING OF CYTOSINE BASES: FORMATION OF I-MOTIF STRUCTURES IDENTIFIED BY IR ION SPECTROSCOPY**

**JUHAN GAO, GIEL BERDEN, J. DÖMEN, Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands.**

While the Watson-Crick structure of DNA is among the most well-known molecular structures of our time, alternative base-pairing motifs are also known to occur, often depending on base sequence, pH, or presence of cations. Pairing of two cytosine (C) bases induced by the sharing of a single proton (C-H=C) gives rise to the so-called i-motif, occurring particularly in the telomeric region of DNA, and particularly at low pH. At physiological pH, silver cations were recently suggested to induce a clearly different dimer structure, in which the two cytosine units are parallelly displaced. In addition to coordination complexes potentially involving agnostic hydrogen bond interactions. Accompanying DFT computational work is used to assist in identifying the specific molecular structure responsible for the measured IR spectra - does not reproduce features in the far-IR well. This mismatch can be attributed to the high degree of anharmonicity of many of the normal modes present in the far-IR. We have overcome these hurdles by combining an advanced laser source with novel experiments and high-level dynamical calculations.

We present far-IR spectra of a family of phenolic molecules and solvated clusters, obtained using the free electron laser FELIX. By employing IR-UV ion-dip spectroscopy in the gas phase, we are able to obtain conformer specific far-IR spectra of isolated molecules or solvated clusters. The studied systems display both intra- and intermolecular hydrogen bonding, enabling us to study the merits of far-IR action spectroscopy for direct probing of these weak interactions. Moreover, the combination of far-IR experiments with quantum chemical calculations allows us to test the limits of the harmonic approximations in DFT calculations, and to test the possibilities of employing a more sophisticated technique, namely Born-Oppenheimer molecular dynamics.

**References:**
2. J. Physikalisches Institut, Universität zu Köln, Köln, Germany

Molecular Properties of the “Anti-Aromatic” Species Cyclopentadienone, C5H4O

THOMAS ORMUND, BARNEY ELLISON, JOHN W. DAILY, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA; JOHN F. STANTON, Department of Chemistry, The University of Texas, Austin, TX, USA; MUSAHID AHMED, USXL, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA; TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN, USA; PATRICK HEMBERGER, General Energy, Paul Scherrer Institute, Villigen, Switzerland.

A common intermediate in the high temperature combustion of benzene is cyclopentadienone, C5H4O. Cyclopentadienone is considered to be an “anti-aromatic” molecule. It is certainly a metastable species; samples persist at LN2 temperatures but dimerize upon warming to -80°C. It is of great interest to physically characterize this “anti-aromatic” species. The microwave spectrum, the infrared spectrum, the ionization energy, and the electron affinity of cyclopentadienone have been measured. Plash pyrolysis of o-phenylene sulfide (C12H8S0) provides molecular beams of C5H4O entrained in a rare gas carrier. The beams are interrogated with time-of-flight photoionization mass spectrometry, confirming the clean, intense production of C5H4O as well as the associated hot band (795 cm−1). The electron affinity, EA(C5H4O), to be 1.06 ± 0.01 eV.

High-Resolution Synchrotron Infrared Spectroscopy of Thioephene: The ν2 at 380 cm−1 and Its Analysis Using an Automated Spectral Assignment Procedure (ASAP)

MARIE-ALINE MARTIN-DRUMEL, Spectroscopy Lab, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; CHRISTIAN ENDRES, OLIVER ZINGSHEIM, T. SALOMON, I. Physikalisches Institut, Universität zu Köln, Köln, Germany; JENNIFER VAN WEINGAARDEN, Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada; OLIVER PIALI, SEBASTIEN GRUET, AILES beamline, Synchrotron SOLEIL, Saint Aubin, France; FRANK LEWEN, STEPHAN SCHLIEEMER, I. Physikalisches Institut, Universität zu Köln, Köln, Germany; MICHAEL C. McCARTHY, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; SVEN THORWIRTH, J. Physikalisches Institut, Universität zu Köln, Köln, Germany.

The fundamental vibrational bending mode ν2 of disulfur monoxide, S2O, and the associated hot band 2ν2−ν2 have been observed at high spectral resolution for the first time at the SOLEIL synchrotron facility using Fourier-transform far-infrared spectroscopy. This transient species has been produced using a radio-frequency discharge by flowing SO2 over elemental sulfur. The spectroscopic analysis has been performed using an Automated Spectral Assignment Procedure (ASAP) which has enabled the accurate determination of more than 3500 energy levels of the ν2 = 1 and ν2 = 2 vibrational states. In addition, the high-resolution synchrotron study, pure rotational spectra of S2O in the ν2 = 1 and 2 vibrational states were observed in the frequency range 250 – 500 GHz in a long-path absorption cell.

The Soleil View on Sulfur Rich Oxides: The ν3 Mode of S2O Visited

SVEN THORWIRTH, I. Physikalisches Institut, Universität zu Köln, Köln, Germany; MARIE-ALINE MARTIN-DRUMEL, Spectroscopy Lab, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; CHRISTIAN ENDRES, OLIVER ZINGSHEIM, T. SALOMON, I. Physikalisches Institut, Universität zu Köln, Köln, Germany; JENNIFER VAN WEINGAARDEN, Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada; OLIVER PIALI, SEBASTIEN GRUET, AILES beamline, Synchrotron SOLEIL, Saint Aubin, France; FRANK LEWEN, STEPHAN SCHLIEEMER, I. Physikalisches Institut, Universität zu Köln, Köln, Germany; MICHAEL C. McCARTHY, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA.

In the course of our recent study of the bending mode of S2O (Martin-Drumel et al.; see Talk P1190), the S-S stretching mode ν2 located at 679 cm−1 and first studied by Lindenmayer et al. in 1986 (J. Mol. Spectrosc. 119, 56) has been re-investigated at the French national synchrotron facility SOLEIL using Fourier-transform far-infrared spectroscopy. In addition to the vibrational fundamental, evidence for at least one more hot band, most likely ν2 + ν2, was found. Complementary submillimeter wave measurements of the pure rotational spectrum in the ν2 = 1 state were also performed.
Ammonia ($\text{NH}_3$) has been found ubiquitous, e.g., in the interstellar medium, low-mass stars, jovian planets of our solar system, and possibly in the low temperature exoplanets. Their spectroscopic line parameters are essential in the accurate interpretation of the planetary and astrophysical spectra observed with Herschel, SOFIA, ALMA, and JWST.

In our previous paper\cite{1}, the $\text{NH}_3$ line positions in the far-IR region were studied for the ground state and $\nu_3$ in an unprecedented accuracy, which revealed significant deficiencies in the $\text{NH}_3$ intensities, for instance, some weak $\Delta K = \pm 3$ lines were predicted to be 100 times stronger. Measurement of line intensity for these lines in a consistent manner is demanded because the $\Delta K = \pm 3$ forbidden lines are only way other than collisions and $J$-doubled states to excite $\text{NH}_3$ to $K > 0$ levels. Regularly, that $\text{NH}_3$ transition lines in the high $J$ and $K$ up to 18 were detected toward the star in the galactic center in the far infrared region of $\text{Sgr B}_2$, their accurate intensity measurements are critical in explaining the observed high $K$ excitation, which will provide insights into radiative-transfer $\nu_3$, collision excitation mechanisms of interstellar $\text{NH}_3$.

For this, we obtained a series of spectra of $\text{NH}_3$, in the 50 – 550 cm$^{-1}$ using a Fourier-transform spectrometer, Bruker 125HR, and AILES beam line at Synchrotron SOLEIL, France. Line positions, intensities, and pressure-broadened half-widths have been measured using non-linear least squares spectrum fitting algorithm. In this paper we report and discuss preliminary results of $\nu_3$ and the vibration-rotation transitions of $\nu_2$, $\nu_2$, $\nu_1$, $\nu_1$ for the $\nu_3$ and $\nu_2$ in this region. Comparison of the new measurements with the current databases and ab initio calculations will be discussed.

\textit{Invited Talk}


$\nu_3$ and $\nu_2$ of $\text{NH}_3$ have been measured in the region $\nu_2$ = 3000 – 4000 cm$^{-1}$ and $\nu_3$ = 3000 – 5000 cm$^{-1}$ using FTIR with SOLEIL/AILES beamline, Synchrotron SOLEIL, Saint-Aubin, France, F. Kwabia Tchana, J.S. CNRS, Université Paris Est Créteil et Paris Diderot, Créteil, France; Olivier Pirali AILES beamline, Synchrotron SOLEIL, Saint-Aubin, France.

$\text{NH}_3$ has been measured using the SOLEIL/AILES beamline, Synchrotron SOLEIL, Saint-Aubin, France, P. Roy, P. J. Phys. Chem. A. 2011, 115, 2523

$\text{NH}_3$ has been measured using the SOLEIL/AILES beamline, Synchrotron SOLEIL, Saint-Aubin, France, S. Kassi, D. Petitprez, G. Wlodarczak, J. Mol. Struct. 2000, 517–518, 375

The new measurements with the current databases and interpretation of the planetary and astrophysical spectra observed with Herschel, SOFIA, ALMA, and JWST.

Discuss preliminary results of line position and intensity measurements for the inversion transitions in the ground state, $\nu_3$, $\nu_2$, $\nu_1$ and for the vibration-rotation transitions of $\nu_2$, $\nu_2$, $\nu_1$, $\nu_1$ and $\nu_2$ and $\nu_2$ in this region. Comparison of the new measurements with the current databases and ab initio calculations will be discussed.

The $\text{H}_2\text{O}-\text{CH}_3\text{F}$ complex could have two geometries, one with a hydrogen bond and one with the newly proposed bond. While in general carbon bonds are weaker than hydrogen bonds, this complex appears to have comparable energies for the two structures. Infrared (IR) and microwave (MW) spectroscopic measurements using, respectively, the Jet-AILES apparatus\cite{2} and the FTMMW spectrometer at the PhILAM laboratory\cite{3}, have been carried out to determine the structure of the deuterated. The IR spectrum shows the formation of the $\text{CH}_3\text{F}^-\text{H}_2\text{O}$ hydrogen bonded complex and small red-shifts in OH frequency most probably due to ($\text{CH}_3\text{F}^-\text{H}_2\text{O}$)$_2$ clusters. Noticeably, addition of CH$_3$F in the mixture promotes the formation of small water clusters. Preliminary MW spectroscopic measurements indicate the formation of the hydrogen bonded complex. So far, we have no experimental evidence for the carbon bonded structure. However, calculations of the $\text{As}-\text{CH}_3\text{F}$ complexes show three energetically equivalent structures: a T-shape, a fluorine bond and a carbon bond. The MW spectrum of the $\text{As}-\text{CH}_3\text{F}$ complexes is currently under analysis.

**References**


**Post-Deadline Abstract**

THE $\text{H}_2\text{O}$-$\text{CH}_3\text{F}$ COMPLEX: A COMBINED MICROWAVE AND INFRARED SPECTROSCOPIC STUDY SUPPORTED BY STRUCTURE CALCULATIONS

SHARON PRIYA GNANASEKAR, Department of Inorganic and Physical Chemistry, Indian Institute of Sci.

ence, Bangalore, India

MANUEL GOUBERT, Laboratoire PhILAM, Université Lille 1, Villeneuve d’Ascq, France

ELANGANAN ARUNAN, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

ROBERT GEORGIES, IFPUM6251, CNRS - Université Rennes 1, Rennes, France

PIERRE SOULARD, Université Rennes 1, Rennes, France; MONARZU UM213, CNRS - Université Paris 6 ECPMC, Paris, France; T. R. HUET, Laboratoire PhILAM, UMB8523 CNRS - Université Lille 1, Villeneuve d’Ascq, France; Olivier Pirali AILES beamline, Synchrotron SOLEIL, Saint-Aubin, France.

The $\text{H}_2\text{O}$-$\text{CH}_3\text{F}$ complex could have two geometries, one with a hydrogen bond and one with the newly proposed bond. While in general carbon bonds are weaker than hydrogen bonds, this complex appears to have comparable energies for the two structures. Infrared (IR) and microwave (MW) spectroscopic measurements using, respectively, the Jet-AILES apparatus\cite{2} and the FTMMW spectrometer at the PhILAM laboratory\cite{3}, have been carried out to determine the structure of the deuterated. The IR spectrum shows the formation of the $\text{CH}_3\text{F}^-\text{H}_2\text{O}$ hydrogen bonded complex and small red-shifts in OH frequency most probably due to ($\text{CH}_3\text{F}^-\text{H}_2\text{O}$)$_2$ clusters. Noticeably, addition of CH$_3$F in the mixture promotes the formation of small water clusters. Preliminary MW spectroscopic measurements indicate the formation of the hydrogen bonded complex. So far, we have no experimental evidence for the carbon bonded structure. However, calculations of the $\text{As}-\text{CH}_3\text{F}$ complexes show three energetically equivalent structures: a T-shape, a fluorine bond and a carbon bond. The MW spectrum of the $\text{As}-\text{CH}_3\text{F}$ complexes is currently under analysis.

**References**


**Mini-symposium: Spectroscopy in the Classroom**

THURSDAY, JUNE 25, 2015

**Room:** B102 Chemical and Life Sciences

**Chair:** Kristopher J Ooms, The King’s University, Edmonton, Alberta, Canada

**Invited Talk**

DIRECT DIGITAL SYNTHESIS CHIRPED PULSE MICROWAVE SPECTROMETERS FOR THE CLASSROOM AND RESEARCH

GEORGE BLAKE, BRANDON CARROLL, IAN A FINNERAN, Division of Chemistry and Chemical Engineering, Caltech Institute of Technology, Pasadena, CA, USA.

Michael Storry-Lombardi, Department of Physics, Harvey Mudd College and Kino Institute, Claremont, CA, USA; Melanie R. Mombille, Department of Biological Sciences, Missouri University of Science and Technology, Rolla, MO, USA; G. S. Grubis, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA.

Research, design, construction, and operation of a portable mixed Raman and Fluorescence type spectrometer implemented by the Missouri University of Science and Technology’s Mars Rover Design Team will be presented. This spectrometer has been built for the team’s annual competition. The spectrometer, completely built by undergraduates, is designed to use a 50 mW 532 nm laser to probe a sample of soil to find bacteria or bio-markers. However, initial tests of the spectrometer were carried out in a laboratory environment making the spectrometer also suitable for simple undergraduate physical chemistry or chemical physics laboratory experiments. The final cost of the device is roughly $2100, weighs 1.4 kg, and is 22.9 cm x 22.6 cm in size. Integrating the spectrometer with a computer database, results from the competition, complications of fitting mixed Raman-Fluorescence spectra, and future ideas/improvements will also be discussed.

**Invited Talk**

LIF AND RAMAN SPECTROSCOPY IN UNDERGRADUATE LABS USING GREEN DIODE-PUMPED SOLID-STATE LASERS

JEFFREY A. GRAY, Department of Chemistry, Ohio Northern University, Ada, OH, USA.

Electronic spectroscopy of molecular iodine vapor has long been studied in undergraduate physical chemistry teaching laboratories, but the effectiveness of emission work has typically been limited by availability of instrumentation. This talk shows how to make inexpensive green diode-pumped solid-state (DPSS) lasers easily tunable for efficient, selective excitation of I$_2$. Miniature fiber-optic spectrometers then enable rotationally resolved fluorescence spectroscopy up to $\nu_3 = 42$ near 900 nm with acquisition times of less than one minute. DPSS lasers are also versatile excitation sources for vibrational Raman spectroscopy, which is another common exercise that has been limited by lack of proper instrumentation in the teaching laboratory. This talk shows how to construct a simple accessory for commercial fluorimeters to record vibrational Raman spectra and depolarization ratios for CCl$_4$ and C$_4$H$_3$C, as part of a lab exercise featuring molecular symmetry.
A windows based, mouse-event driven software program that acts as a graphical user interface to Pickett's fitting programs has been created and improved. The program, SpecFitter, is aimed at walking users through the process of assigning pure rotational spectra. Rotational spectra, in XY format, may be viewed and inspected and the user is provided with tools for observing and recording repeating, similar patterns of transitions. The structure of these patterns is interpreted into “guesses” at rotational constants which the user may then use to predict a spectrum. Observed transition frequencies may then be assigned quantum number transitions and appended to the .lin file through mouse clicks. Although the thrust of this project is to develop a users ability to assign spectra without knowing the molecule producing the spectra the program can also read in and display calculated structures of target molecules produced by the Gaussian03 software, or alternatively the user can draw their own structures. Structures can be edited allowing users to observe the relationship between molecular structure and (i) the direction of dipole moment components and (ii) the relationships between structure and rotational constants. Users may also easily predict spectra from the molecules structure and further relate rotational constants to observed spectra. Students in CHEM 3510 at Purchase College have been vital in developing the software.

A study of the vibrational spectra of cis- and trans-1,2-dichloroethylene provides an excellent way for undergraduates to gain experience with the application of group theory in the physical chemistry laboratory. Although the group vibrations are similar for these two molecules, the selection rules for infrared (IR) and Raman spectra differ significantly. Most of the transitions for the fundamentals of the cis isomer of C\(_2\)H\(_2\)Cl\(_2\) symmetry are both IR and Raman active. Mutual exclusion for the IR-active and Raman-active selection rules for the trans isomer is IR active and half are Raman active. The two isomers are volatile enough that gas-phase IR spectra can be recorded at room temperature. Band shapes in gas-phase IR spectra provide additional evidence for assignments of fundamentals. The two isomers are small enough that good quality quantum chemical calculations of harmonic frequencies can be done by students with commercial software.
VIBRATION-ROTATION ANALYSIS OF THE $^{13}$CO$_2$ ASYMMETRIC STRETCH FUNDAMENTAL BAND IN AMBIENT AIR FOR THE PHYSICAL CHEMISTRY TEACHING LABORATORY

DAVID A. DOLSON, CATHERINE B. ANDERS*, Department of Chemistry, Wright State University, Dayton, OH, USA.

The CO$_2$ asymmetric stretch fundamental band near 4.3 $\mu$m is one of the strongest infrared absorption transitions of all small molecules. This band is an undesired interference in most infrared spectra, but it also serves as a potential choice for a vibration-rotation analysis experiment in the physical chemistry teaching laboratory. Due to the strength of this band and the 1.1% natural abundance of carbon-13, the asymmetric stretch fundamental band of $^{13}$CO$_2$ is readily observable in a typical ambient air background spectrum and is shifted sufficiently from the stronger CO$_2$ fundamental such that the $^{13}$CO$_2$ P-branch lines are almost completely free of interferences and are easily assigned. All of the $^{13}$CO$_2$ R-branch lines appear within the $^{12}$CO$_2$ P-branch, which creates assignment challenges. Students in our program have analyzed the $^{13}$CO$_2$ fundamental asymmetric stretch band over a two-year period. Analyses of the P-branch line positions enabled the prediction of additional R-branch line positions, which guided line identification and measurements in the $^{13}$CO$_2$ R-branch. C=O bond lengths determined from analyses of the $^{13}$CO$_2$ spectra improved when R-branch lines were added to the initial P-branch data sets. Spectral appearance, analyses and results will be presented for spectra obtained at 0.5 cm$^{-1}$ resolution and at 0.125 cm$^{-1}$ resolution. The challenge of predicting and finding the $^{13}$CO$_2$ R-branch lines among other interfering lines adds an element of realism to this experiment that is not found in many student experiments of this type.

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UTILIZING SPECTROSCOPIC RESEARCH TOOLS AND SOFTWARE IN THE CLASSROOM

G. S. GRUBBS II, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA.

Given today’s technological age, it has become crucial to be able to reach the student in a more “tech-savvy” way than traditional classroom methods afford. Given this, there are already a vast range of software packages available to the molecular spectroscopist that can easily be introduced to the classroom with success. This talk will highlight taking a few of these tools (Gaussian09, SPFIT/SPCAT, the AABS Package, LabViewTM, etc.) and implementing them in the classroom to teach subjects such as Quantum Mechanics and Thermodynamics as well as to aid in the linkage between these subjects. Examples of project implementation on both undergraduate and graduate level students will be presented with a discussion on the successes and failures of such attempts.

NEW INSTRUMENTAL TOOLS FOR ADVANCED ASTROCHEMICAL APPLICATIONS

AMANDA STIERI, The Centre for Ultrahigh Imaging (CUI), Universität Hamburg, Hamburg, Germany, SABRINA ZENN, MELANIE SCHNELL, CoCoMol, Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany, ANOUK RISS, Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands.

Astrochemistry has been a growing field over the past several years. As the data from the Atacama Large Millimeter Array (ALMA) becomes publicly available, new and fast techniques for the analysis of the data will need to be developed, as well as fast, sensitive laboratory techniques. This lab is in the process of building up instrumentation that will be dedicated to the measurement of astrochemically relevant species, both in the microwave and the millimeter wave regimes. Discharge experiments, laser ablation experiments, as well as time of flight measurements will be possible with this instrumentation. Coupled with instrumentation capabilities will be new software aimed at a speeding up the analysis. The laboratory data will be used to search for new molecular signatures in the interstellar medium (ISM), and help to elucidate molecular reaction pathways occurring in the ISM.

DOPPLER AND SUB-DOPPLER MILLIMETER AND SUB-MILLIMETER WAVE SPECTROSCOPY OF KEY ASTRONOMICAL MOLECULES: HNC AND CS

OLIVER ZINGHEIM, THOMAS SCHMITT, FRANK LEWEN, STEPHAN SCHLEMMER, SVEN THORWIRTH, I. Physikalisches Institut, Universität zu Köln, Köln, Germany.

In the course of ongoing efforts to determine accurate pure rotational transition frequencies for the astronomical community, the millimeter- and submillimeter-wave spectra of HNC and selected isotopic species have been investigated using a radio-frequency discharge of (isotopically enriched) methyl cyanide. Besides the ground vibrational state, vibrational satellites from the first excited bending mode were targeted. In part, rotational transitions were observed employing the Lamb-Dip technique to obtain sub-Doppler resolution. The Lamb-dip technique has also been applied to other short-lived molecules such as carbon monosulfide, CS.
MILLIMETRE-WAVE SPECTRUM OF ISOTOPOLOGUES OF ETHANOL FOR RADIO ASTRONOMY
ADAM WALTERS, IRAP, Université de Toulouse 3 - CNRS - OMP, Toulouse, France; MIKRO SCHÄFER, MATTHIAS-H. ORDU, FRANK LYLEN, STEPHAN SCHLEMMER, HÖLGER S. P. MULLER, J. Physikalisches Institut, Universität zu Köln, Köln, Germany.

Complex molecules have been identified in star-forming regions and their formation is linked to the specific physical and chemical conditions there. They are suspected to form a role in the origins of life. Amongst these, ethanol is a fairly abundant molecule in warmer regions.

For this reason, we have recently carried out laboratory measurements and analyses of the rotational spectra of the three mono-substituted deuteron isotoptopes of ethanol (one of which, CHDCHDH, exists as two distinct conformers according to the position of the deuteron atom with respect to the molecular skeleton). Measurements were taken between 35-500 GHz, allowing accurate predictions in the range of radio telescopes. We have concentrated on the lowest energy anti conformation. The dataset was constrained for fitting with a standard Watson-S reduction Hamiltonian by rejecting transitions from high-lying states, which appear to be perturbed by the gauche states, and by averaging some small methyl torsional splittings. This treatment is compatible with the needs for a first search in the interstellar medium, in particular in spectra taken by ALMA. For this purpose an appropriate set of predictions will be included on the Cologne Database for Molecular Spectroscopy.

Previous results on the three mono-substituted 13CO isotoptopes* which led to a tentative detection in Sgr B2(N)* will be briefly summarized and compared with the latest measurements.

The usefulness of studying different isotoptopes in the interstellar medium will also be rapidly addressed.

*Chelicki et al. JQUM 113:10, 1119-1124, 2012

CH

A known interstellar molecule that has been detected towards hot cores in dense interstellar clouds. CH is also thought to be present in cosmic meteors. In the gas-phase chemical models of both dense and diffuse molecular clouds, CH is a key intermediate in interstellar carbon chemistry which is produced primarily by dissociative recombination of the methyl ion, CH3. Recently tentative detection of the mono-deuterated methyl ion, CH3D* has been reported toward an infrared source in the vicinity of Orion.* Deuterated methylene CHD and CD2 can be produced from this ion or its counterpart CHD2 by dissociative recombination with an electron:

CH3D+ + e− → CHD + H or CHD + D; (1)

CHD2+ + e− → CHD + D or CD2 + H. (2)

Thus, both CHD and CD2 can be observed in warm interstellar clouds, where the deuteration fractionation process is important. Precise laboratory reference data are desirable for radioastronomical observation of these molecules.

Here we report on our high-resolution spectroscopic investigation on the deuterated methylene radical, CD2 (13C=H) up to 1.45 THz. At present time, eleven out of the twelve fine-structure components of four pure rotational transitions have been newly recorded, and these measurements double the number of previously observed transitions. CD2 was generated in a discharge in CD3CO which was obtained from the flash pyrolysis of acetic anhydride-d8 (CD3CO2D). Effort is currently made to measure the astronomically important J=1−0 transition whose fine-structure components are predicted to occur at 1.224-1.228 and 1.234 THz.


Precise laboratory reference data are desirable for radioastronomical observation of these molecules.

The usefulness of studying different isotopoalogues in the interstellar medium will also be rapidly addressed.

This presentation, we extended the measurements up to 2 THz by using the JPL frequency multiplier chains, and observed three new THz lines and re-measured the three known transitions. D2H+ was generated in an extended negative glow discharge cell cooled to liquid nitrogen temperature. Six rotational transition frequencies together with the combination bands, have been investigated extensively. On the other hand, the pure rotational transitions have not been studied so extensively. Only the lowest rotational transition, J = 1−0, was observed in the laboratory for the normal species, 12CD2−. Based on the laboratory frequency, CH3+ was detected in star forming regions with the Herschel space observatory. Cer- nicharo et al. identified pure rotational transitions from J = 2−1 to J = 6−5 in the far-infrared region in the ISO spectrum of the planetary nebula NGC 7027. The ISO spectra, however, were of low-resolution, so high-resolution spectroscopic observation is highly desirable.

In this presentation, we have extended the measurements to higher J lines up to 2 THz. For production of CH3+ an extended negative glow discharge in a gas mixture of CH4 (~0.5 mtorr) diluted in He (~60 mtorr) was used. The optimum discharge current was about 15 mA and the axial magnetic filed to 160 Gauss was applied up. The discharge cell was cooled (716, L1 (2010)
ROTATIONAL SPECTROSCOPY OF VIBRATIONALLY EXCITED N$_2$H$^+$ and N$_2$D$^+$ UP TO 2 THz

SHANSHAN YU, JOHN PEARSON, BRIAN DROUN, TIMOTHY J CRAWFORD, ADAM M DALY, BEN ELLIOTT, TAKUSHI AMANO, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

Terahertz absorption spectroscopy was employed to extend the measurements on the pure rotational transitions of N$_2$H$^+$, N$_2$D$^+$ and their $^{15}$N-containing isotopologues in the ground state and first excited vibrational states for the three fundamental vibrational modes. In total 88 new pure rotational transitions were observed in the range of 0.7–2.0 THz. The observed transition frequencies were fit to experimental accuracy, and the impure molecular parameters were obtained. The new measurements and predictions will support the analysis of high-resolution astronomical observations made with facilities such as SOFIA and ALMA where laboratory rest frequencies with uncertainties of 1 MHz or smaller are required for proper analysis of velocity resolved astrophysical components.

Intermission

NEW ACCURATE WAVENUMBERS OF H$^{13}$Cl and H$^{37}$Cl ROVIBRATIONAL TRANSITIONS IN THE $\nu = 0 \rightarrow 1$ BAND OF THE $^2$II STATE

JOSE LUIS DOMENECH, MAITE CUETO, VICTOR JOSE HERRERO, ISABEL TANARO, Molecular Physics, Instituto de Estructura de la Materia (IEM-CSIC), Madrid, Spain; ROSE CERNICHARO, Molecular Astrophysics, ICMM, Madrid, Spain.

HCl$^\prime$ is a key intermediate in the interstellar chemistry of chlorine. It has been recently identified in space from Herschel's spectrUM and it has also been detected in the laboratory through its optical emission$^4$, infrared$^5$ and mm-wave spectra$^6$. Now that Herschel's decommissioned, further astrophysical studies on this radical ion will likely rely on ground-based observations in the mid-infrared. We have used a difference frequency laser spectrometer coupled to a hollow cathode discharge Iodine-stabilized Argon laser to measure the absorption spectrum of H$^{13}$Cl and H$^{37}$Cl in the $\nu = 0 \rightarrow 1$ band of the $^2$II state with Doppler limited resolution. The accuracy of the individual measurements ($\sim 10$ MHz) relies on a solid state wave meter referenced to an iodine-stabilized Ar' laser.

LINE STRENGTHS OF ROVIBRATIONAL AND ROTATIONAL TRANSITIONS IN THE X$^2\Pi$ GROUND STATE OF OH

JAMES S.A. BRIDGITT, MLA, P. PAPAYANNAKOS, Physics and Astronomy, The University of New Mexico, Albuquerque, NM, USA; BRIAN B. KOETKE, James Madison University, Harrisonburg, VA, USA; JAMES S. BROOK, Department of Chemistry, University of York, York, United Kingdom; ALBERTO CAMPISAN, Department of Physics, University of Padua, Padova, Italy.

We present results from calculations of the physical conditions necessary for the occurrence of 36.169 (4, − 4σ), 44.070 (3, − 5π), 84.521 (5, − 4σ), and 95.169 (7, − 4σ) GHz methanol (CH$_3$OH) maser emission lines near supernova remnants (SNRs), using the MOLPOP-CEP program. The calculations show that given a sufficient methanol abundance, methanol maser emission arises over a wide range of densities and temperatures, with optimal conditions at $n \sim 10^4$–$10^5$ cm$^{-3}$ and $T \sim 60$ K. The 36 GHz and 44 GHz transitions display more significant maser optical depths compared to the 84 GHz and 95 GHz transitions over the majority of physical conditions. It is also shown that line ratios are an important and applicable probe of the gas conditions. The line ratio changes are largely a result of the $^2$II→$^2$II transition, and it has been recently identified in space from Herschel's spectrUM and it has also been detected in the laboratory through its optical emission$^4$, infrared$^5$ and mm-wave spectra$^6$. Now that Herschel's decommissioned, further astrophysical studies on this radical ion will likely rely on ground-based observations in the mid-infrared. We have used a difference frequency laser spectrometer coupled to a hollow cathode discharge Iodine-stabilized Argon laser to measure the absorption spectrum of H$^{13}$Cl and H$^{37}$Cl in the $\nu = 0 \rightarrow 1$ band of the $^2$II state with Doppler limited resolution. The accuracy of the individual measurements ($\sim 10$ MHz) relies on a solid state wave meter referenced to an iodine-stabilized Ar' laser.

CLASSES I METHANOL MASER CONDITIONS NEAR SNRS

BRIDGET C. ORR, YLVA M. PHILSTROM, Physics and Astronomy, The University of New Mexico, Albuquerque, NM, USA; DOUGLAS L. JOHNSON, Department of Chemistry, University of California, Santa Cruz, CA, USA; ANDREW N. SMITH, Department of Chemistry, University of California, Santa Cruz, CA, USA.

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THE MISSING LINK: ROTATIONAL SPECTRUM AND GEOMETRICAL STRUCTURE OF DISILICON CARBIDE, Si₂C

MICHAEL C. MCCARTHY, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; JOSHUA H BARABAN, Department of Chemistry, University of Colorado, Boulder, CO, USA; YURAYA CHANGALA, JILA, National Institute of Standards and Technology and Univ. of Colorado Department of Physics, University of Colorado, Boulder, CO, USA; JOHN F. STANTON, Department of Chemistry, The University of Texas, Austin, TX, USA; MARIE-ALINE MARTIN-DRUMEL, Spectroscopy Lab, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; SVEN THOHWIRTH, J. Physikalisches Institute, Universität zu Köln, Köln, Germany; NEIL J REILLY, Department of Chemistry, Maquette University, Milwaukee, WI, USA; CARL A GOTTLEIB, Radio and Geoastronomy Division, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA.

Disilicon carbide Si₂C is one of the most fascinating small molecules for both fundamental and applied reasons. Like C₂, it has a shallow bending angle, and may therefore also serve as a classic example of a quasilinear species. Si₂C is also thought to be quite stable. Mass spectrometric studies conclude that it is one of the most common gas-phase fragments in the evaporation of silicon carbide at high temperature. For these same reasons, it may be abundant in certain evolved carbon stars such as IRC+10216. Its electronic spectrum was recently studied by several of us, but its ground state geometry and rotational spectrum remain unknown until now. Using sensitive microwave techniques and high-level coupled cluster calculations, Si₂C has been detected in the radio band, and is found to be highly abundant. Its more common rare isotopic species have also been observed either in natural abundance or using isotopically-enriched samples, from which a highly precise semi-experimental mass spectrometric study has been derived. This talk will summarize recent work, and discuss the prospects for astronomical detection. Now observed either in natural abundance or using isotopically-enriched samples, from which a highly precise semi-experimental structure has been derived. This talk will summarize recent work, and discuss the prospects for astronomical detection. Now observed either in natural abundance or using isotopically-enriched samples, from which a highly precise semi-experimental structure has been derived. This talk will summarize recent work, and discuss the prospects for astronomical detection. Now observed either in natural abundance or using isotopically-enriched samples, from which a highly precise semi-experimental structure has been derived. This talk will summarize recent work, and discuss the prospects for astronomical detection. Now observed either in natural abundance or using isotopically-enriched samples, from which a highly precise semi-experimental structure has been derived. This talk will summarize recent work, and discuss the prospects for astronomical detection. Now observed either in natural abundance or using isotopically-enriched samples, from which a highly precise semi-experimental structure has been derived. This talk will summarize recent work, and discuss the prospects for astronomical detection. Now observed either in natural abundance or using isotopically-enriched samples, from which a highly precise semi-experimental structure has been derived. This talk will summarize recent work, and discuss the prospects for astronomical detection.
DEVELOPMENT OF COMBINED DUAL-PUMP VIBRATIONAL AND PURE-ROTATIONAL COHERENT ANTI-STOKES RAMAN SCATTERING TECHNIQUE.

AMAN SATHI, ROBERT P. LUCHT, Mechanical Engineering, Purdue University, West Lafayette, IN, USA.

Coherent anti-Stokes Raman scattering is a parametric, four-wave mixing process. CARS, as a diagnostic technique, has been used extensively for obtaining accurate temperature and species concentration information in non-reacting and reacting flows. Dual-pump vibrational CARS (DPVCARS) can provide quantitative temperature and concentration information on multiple species in the probe volume. Mole-fraction information on molecules such as N₂, O₂, H₂, and CO₂ have been obtained in flames with peak temperature in excess of 2000 K. Although DPVCARS provides high accuracy at higher temperatures it has low sensitivity at lower temperatures (below 800 K). Typically, pure-rotational CARS (PRCARS) provides excellent sensitivity and precision at lower temperatures. We have combined DPVCARS and two-beam PRCARS into a single system which employs three laser beams at different wavelengths. The accuracy and precision of the new combined CARS system has been characterized in laminar flames. The system’s single-shot precision is better than 5.5% between 295-2200 K, indicating its suitability for diagnostics in turbulent flames. The new system has been applied towards understanding flame structure of CH₃OH-air laminar flames, stabilized in a counter-flow burner. Here, we present results detailing the development and application of the new combined CARS technique.

VELOcity MAP imaging STUDY OF THE PHOTONITECTED CHARGE-TRANSFER DISSOCIATION OF Cu⁺(C₂H₆) AND Ag⁺(C₂H₆)

ION MANER, DANIEL MAUNEY, MICHAEL A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA, USA.

M⁺(C₂H₆) (M = Cu, Ag) complexes are generated in the gas phase by laser vaporization and detected in a reflection time-of-flight mass spectrometer. Excitation of M⁺(C₂H₆) at 355 nm results exclusively in dissociative charge transfer, leading to neutral M and C₂H₄⁺ products for both Cu and Ag complexes. Kinetic energy release in translationally hot C₂H₄⁺ fragments is detected using a new apparatus designed for photoshod fighter imaging of mass-selected ion beams. Velocity mapping and slice imaging techniques are employed. Analysis of the data provide new information on the bonding energrs of Cu⁺(C₂H₆) and Ag⁺(C₂H₆).

INTERmission

STRONG THERMAL NONEQUILIBRIUM IN HYPERSONIC CO AND CH₄ PROBED BY CRDS

MAUD LOUVIOT, Laboratoire ICB, CNRS/Université de Bourgogne, DIJON, France; NICOLAS SUAS-DAVID, IFR UMR6251, CNRS - Université Rennes 1, Rennes, France; VINCENT BOUDON, Laboratoire ICB, CNRS/Université de Bourgogne, DIJON, France; ROBERT GEORGES, IFR UMR6251, CNRS - Université Rennes 1, Rennes, France; MICHAEL REY, Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, Université de Reims, Reims Cedex 2, France; SAMIR KASSI, UMR5585 LIPhy, Université Grenoble I/CNRS, Saint Martin d’Hères, France.

A new experimental set-up coupling a High Enthalpy Source (HES) tracking 2000 K to a cw Cavity Ring-Down Spectrometer has been developed to investigate rotationally cold hot bands of polyatomic molecules in the [3.5, 1.7] μm region. The rotational and vibrational molecular degrees of freedom are strongly decoupled in the hypersonic expansion produced by the HES and probed by Cavity Ring-Down Spectroscopy. Carbon monoxide has been used as a first test molecule to validate the experimental approach. Its expansion in argon led to rotational and vibrational temperatures of 6±0.8 K and 2006±476 K, respectively. The Tetradecad polyad of methane (1.67 μm) was investigated under similar conditions. Leading to rotational and vibrational temperatures of 13±5 K and 750±100 K, respectively. The rotationally cold structure of the spectra reveals many hot bands involving highly excited vibrational states of methane.

INTERmission

ROTATIONALLY-RESOLVED INFRARED SPECTROSCOPY OF THE ν₁ ν₃ ν₅ COMBINATION BAND OF 1,3,5-TRIOXANE

BRADLEY M. GIBSON, NICOLE KORPEN, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA; BENJAMIN J. MCCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL, USA.

1,3,5-trioxane is the simplest cyclic form of polyoxymethylene (POM), a class of formaldehyde polymers that has been proposed as the origin of distributed formaldehyde formation in comet comae and a potential source of formaldehyde in prebiotic chemistry. Although claimed POM detections have since been proven to be inconclusive, laboratory simulations of cometary conditions have yielded trioxane and other POMs. While the microwave spectrum of 1,3,5-trioxane has been studied extensively, to date only one rotationally-resolved infrared vibrational spectrum has been published. Here, we present our studies of the ν₁ band of gas-phase trioxane centered at 1177 cm⁻¹. Trioxane was entrained in a supersonic expansion of argon and characterized by continuous-wave cavity ringdown spectroscopy using an etalon-stabilized external-cavity quantum cascade laser. Rotationally resolved spectra were obtained with less than 15 MHz resolution.

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RF01 10:46 – 11:01
IMPROVING SNR IN TIME-RESOLVED SPECTROSCOPIES WITHOUT SACRIFICING TEMPORAL-RESOLUTION: APPLICATION TO THE UV PHOTOYSISIS OF METHYL CYANOFORMATE

MICHAEL J. WILHELM, JONATHAN M. SMITH, HAI-LUNGI DAL. Department of Chemistry, Temple University, Philadelphia, PA, USA.

We demonstrate a new analysis for the enhancement of the signal-to-noise ratio (SNR) in time-resolved spectroscopies, termed spectral reconstruction analysis (SRA). As distinct from a simple linear average which produces only a single representative spectrum with enhanced SNR, SRA produces a comparable enhancement, but fully preserves the measured time-dependence. Specifically, given a series of (n) time-resolved spectra, SRA yields an approximate (n) SNR enhancement for each of the original n-spectra. SRA operates by eliminating noise in the temporal domain, thereby significantly attenuating noise in the spectral domain, as follows (see Figure). Temporal profiles of each measured frequency are fit to capture the representative temporal evolutions, then time-resolved spectra are reconstructed by replacing the signal at each point with its profile.

In addition to simulated control data sets, we demonstrate SRA with experimentally measured time-resolved IR emission spectra, collected following the 193 nm photolysis of methyl cyanofomate (CH₃OC(O)CN). Of significance, we now show the appearance of resonances assignable to hydrogen cyanide (HCN), which were previously obscured in the noise of the measured spectra. The presence of HCN suggests the occurrence of a previously uncharacterized dissociation channel, likely involving a cyclic 5-center transition state.

RE09 11:03 – 11:18
LASER-INDUCED PLASMAS IN AMBIENT AIR FOR INCOHERENT BROADBAND CAVITY-ENHANCED ABSORPTION SPECTROSCOPY

ALBERT A RUTHE; SOPHIE DIXNEUF. Physics Department and Environmental Research Institute, University College Cork, Cork, Ireland; JOHANNES ORPHAL, Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology, 76144 Eggenstein-Leopoldshafen, Germany.

The emission from a laser-induced plasma in ambient air, generated by a high power femtosecond laser, was utilized as pulsed incoherent broadband light source in the center of a quasi-confocal high finesse cavity. The time dependent spectra of the light leaking from the cavity was compared with those of the laser-induced plasma emission without the cavity. It was found that the light emission was sustained by the cavity despite the initially large optical losses of the laser-induced plasma in the cavity. The light sustained by the cavity was used to measure part of the S₁ – S₀ absorption spectrum of gaseous azomethane at vapour pressure at room temperature in ambient air as well as the strongly forbidden ν₁ – ν₅ band in molecular oxygen. 1/2ν₂^2 (ν₁^2 – 2) – Xν₂ν₅/ν₂^3 = 0

RF02 1:00 – 1:15
PHOTOACOUSTIC SPECTROSCOPY OF THE OXYGEN A-BAND

ELIZABETH M LUNNY, THINH QUOC BUI. Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA; CAITLIN BRAY, National Institute of Standards and Technology, Gaithersburg, MD, USA; MITCHIO OKUMURA, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA.

The oxygen A-band (760 nm) is used in a number of remote sensing applications due to the precisely known, uniform distribution of molecular oxygen throughout the atmosphere and the spectral isolation of the band. The A-band is used to determine the pathlength of solar radiation for OCO-2, a current NASA mission which seeks to measure the global sources and sinks of carbon dioxide at unprecedented spatial and temporal resolution. The goal of measuring atmospheric carbon dioxide concentrations with a precision of 0.25% requires a precise knowledge of line shape parameters. Currently, the most significant uncertainties in A-band spectroscopy result from line mixing and collision induced absorption, which become more prominent at elevated pressures. Photoacoustic spectroscopy is ideal to observe these phenomena due to the large dynamic range and zero-background advantages of the technique. Photoacoustic spectra of the oxygen A-band over a range of pressures will be presented in addition to line shape parameters extracted from multiplex beam fits of the data.

RF. Atmospheric science
Thursday, June 25, 2015 – 1:30 PM
Room: 116 Roger Adams Lab
Chair: Joseph Hodges, National Institute of Standards and Technology, Gaithersburg, MD, USA

RF01 1:30 – 1:40
PHOTOACOUSTIC SPECTROSCOPY OF THE OXYGEN A-BAND

ELIZABETH M LUNNY, THINH QUOC BUI, MITCHIO OKUMURA, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA; CAITLIN BRAY, National Institute of Standards and Technology, Gaithersburg, MD, USA; DAVID A. LONG, JOSEPH HODGES, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA; SHANSHAN YU, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

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COLLISION-DEPENDENT LINE AREAS IN THE \( \Delta \alpha \rightarrow X^3\Sigma^− \) BAND OF MOLECULAR OXYGEN

VINCENT SIRONNEAU, ADAM J. FLEISHER, JOSEPH HODGES, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA.

We report precise line areas for individual rotationally resolved transitions within the \( \Delta \alpha \rightarrow X^3\Sigma^− \) electronic band of molecular oxygen recorded as a function of pressure for both neat samples of \( \text{O}_2 \) as well as samples of \( \text{O}_2 \) diluted with a variety of collisional partners. Using optical frequency comb referenced frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) near 1.27 \( \mu \text{m} \) we measure line areas with a quality-of-fit QF \( \leq 50 \), using a partially correlated quadrature-speed-dependent Näräk-Ghatak profile. This spectrometer has achieved this high QF by both suppressing coupled cavity effects and by preserving a high-fidelity frequency axis with absolute frequency accuracy approaching 1 part in \( 10^8 \). With this instrument we are also currently exploiting collision-induced absorption (CIA) and perturbative line mixing effects in \( \text{O}_2 \) over the entire 7800-7940 cm\(^{-1}\) spectral range.

FRENCH/GERMAN CLIMATE MISSION MERLIN

THIBAULT DELAHAYE, THI NGOC HA TRAN, CNRS et Université Paris Est et Paris Diderot, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Créteil, France; ZACHARY REED, STEPHEN E MAXWELL, JOSEPH HODGES, Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD, USA.

Climate change is one of the greatest challenges presently facing mankind, and methane is one of the most powerful anthropogenic greenhouse gases. For a better understanding of future climate trends, a satellite dedicated to the measurements of atmospheric methane is under joint development by the French and German space research centers (CNES and DLR). The so-called MERLIN mission (Methane Remote Sensing Lidar Mission, 2019) aims at providing global information on atmospheric methane concentration with a relative uncertainty less than 2% and with a spatial resolution of 50 km\(^2\). Such spectroscopic monitoring of gases in the atmosphere of the Earth requires a precise description of absorption lines shapes that goes beyond the usual Voigt profile (VP). In the case of methane, the differences between the measured profiles and those given by the VP can be very important, making the VP completely incompatible with the reliable detection of sources and sinks from space. In this work, we present the first results on the modeling of methane lines broadened by air in the 1.64 \( \mu \text{m} \) region and the associated spectroscopic parameters, taking into account various collisional effects between molecules that are neglected by the VP: collisional interference between the lines (line-mixing), collision-induced velocity changes (Dicke narrowing effect) and speed dependence of the collisional broadening and shifting. These results were obtained by simultaneously fitting the model parameters to high sensitivity and high-resolution cavity ring-down spectroscopy (CRDS) spectra recorded at the National Institute of Standards and Technology (NIST) over a wide pressure range (5 to 100 kPa). These spectroscopic data and the associated model to calculate the spectrum absorption coefficient will be then used to analyze ground-based atmospheric spectra at the TCCON facility in Park Falls, Wisconsin.

ANOMALOUS CENTRIFUGAL DISTORTION IN HD AND SPECTROSCOPIC DATA BASES

L. H. COUDERT, CNRS et Universités Paris Est et Paris Diderot, LISA, Créteil, France.

The HD molecule is important from the atmospheric point of view as it can be used to study the water cycle in the earth atmosphere. It is also interesting from the spectroscopic point of view as it displays an anomalous centrifugal distortion similar to that of the normal species H\( _2 \)O. A model developed to treat the anomalous distortion in HD should account for the fact that it lacks a two-fold axis of symmetry.

A new treatment aimed at the calculation of the vibrational energy of the HD molecule and allowing for anomalous centrifugal distortion effects has been developed. It is based on an effective Hamiltonian in which the large amplitude bending \( \nu_2 \) mode and the overall rotation of the molecule are treated simultaneously. Due to the lack of a two-fold axis of symmetry, this effective Hamiltonian contains terms arising from the non-diagonal component of the inertia tensor and from the Coriolis-coupling between the large amplitude bending \( \nu_2 \) mode and the overall rotation of the molecule.

This new treatment has been used to perform a line position analysis of a large body of infrared data: microwave and hot water vapor data involving the ground and (010) state up to \( J = 22 \). For these 4413 data, a unitless standard deviation of the strength of 1.1 was achieved. A line intensity analysis was also carried out and allowed us to reproduce the strength of 1316 transitions with a unitless standard deviation of 1.1.

In the talk, the new theoretical approach will be presented. The results of both analyses will be discussed and compared with those of a previous investigation. The new spectroscopic data base built will be compared with HITRAN 2012.

MID INFRARED DUAL FREQUENCY COMB SPECTROMETER FOR THE DETECTION OF METHANE IN AMBIENT AIR

HANS SCHUESSLER, FENG ZHU, Department of Physics and Astronomy, Texas A&M University, College Station, TX, USA; ALEXANDER KOLOMENSEK, Department of Physics and Astronomy, Texas A&M University, college station, TX, USA.

We demonstrate using mid infrared dual frequency comb spectroscopy for the detection of methane in ambient air. The mid infrared frequency comb sources based on femtosecond Er fiber oscillators are produced through difference frequency generation with periodically poled MgO doped lithium niobate crystals and stabilized at slightly different repetition rates at about 250 MHz. We performed dual frequency comb spectroscopy in the spectral range between 2900 cm\(^{-1}\) and 3150 cm\(^{-1}\) with 0.07 cm\(^{-1}\) resolution using a multipass cell of about 580 meter path length, and achieved the sensitivity about 7.6e-7 cm\(^{-1}\) with 80 ms data acquisition time. We determined the methane concentration as about 1.5 ppbv in the ambient air of the laboratory, and the minimum detection limit as about 60 ppbv for the current setup.

This work was funded by the Robert A. Welch Foundation, Grant No. A1546 and the Qatar Foundation under Grant No. NPRP 6-465-1-091.
IMPROVED OZONE AND CARBON MONOXIDE PROFILE RETRIEVALS USING MULTISPECTRAL MEASUREMENTS FROM NASA “A TRAIN”, NPP, AND TROPOMI SATELLITES

DEJIAN FU, Jet Propulsion Laboratory, California Institute of Technology, PASADENA, CA, USA

Tropospheric ozone is at the juncture of air quality and climate. Ozone directly impacts human health, is a phytotoxin that undermines crop uptake, and directly forces the climate system through absorption of solar radiation. Carbon monoxide is a chemical precursor of greenhouse gases CO2 and tropospheric O3, and is also an ideal tracer of transport processes due to its medium life times (weeks to months). The Aura-AIRS and Aura-OMI instruments in the NASA “A-Train”, CRIS and OMPS instruments on the NOAA Suomi-NPP, and GOME-2 on METOP-TROPOMI aboard the Sentinel 5 Precursor (S5P) have the potential to provide the synoptic chemical and dynamical context for ozone necessary to quantify long-range transport at global scales and as an anchor to the near-term constellation of generation sounding satellites. NASA TEMPO, ESA Sentinel 4, and the Korean GEMS. We introduce the JPL Multi-Spectral, Multi-Species, Multi-Satellite (MS3) retrieval algorithm, which ingests panspectral observations across multiple platforms in an non-linear optimal estimation framework. It incorporates the advances in remote sensing science developed during EOS era including rigorous error analysis diagnostics and observation operators needed for trend analysis, climate model evaluation, and data assimilation. Its performances have been demonstrated through prototype studies for multi-satellite missions (AIRS, CRIS, TROPOMI, TES, OMI, and OMPS). We present the preliminary joint tropospheric ozone retrievals from AIRS/OMI and CRIS/OMPS, and demonstrate the potential of joint carbon monoxide profiles from TROPOMI/CRIS. These results indicate that ozone can be retrieved at close to 1 degree of freedom (dof). The joint ozone retrievals are the first ozone retrievals from the NASA Tropospheric Emission Spectrometer than any single instruments retrievals. Joint CO profiles have a dof similar to the MS3Tropospheric multiregional retrieval. Consequently, multispectral retrievals show promise in providing continuity with NASA EOS observations and paving the way towards a new advanced atmospheric composition constellation. To further improve the quality of measurements using multiple spectral regions, next generation of ozone and carbon monoxide spectroscopic parameters should mitigate the existing discrepancies among different spectral regions (microwave, thermal infrared, visible and ultraviolet).

TEMPERATURE DEPENDENCIES OF AIR-BROADENING AND SHIFT PARAMETERS IN THE ν3 BAND OF OZONE

MARY ANN H. SMITH, Science Directorate, NASA Langley Research Center, Hampton, VA, USA; V. MARIAKIS, PIERI, D. CHRIS BENNER, Department of Physics, College of William and Mary, Williamsburg, VA, USA.

Line parameter errors can contribute significantly to the total errors in retrievals of terrestial atmospheric ozone concentration profiles using the strong 9.6-μm band, particularly for nadir-viewing experiments. Detailed knowledge of the interfering ozone signal is also needed for retrievals of other atmospheric species in this spectral region. We have determined Lorentz air-broadening and pressure-induced shift coefficients along with their temperature dependences for a number of transitions in the ν3 fundamental band of O3. These results were obtained by applying the multispectrum nonlinear least-squares fitting technique to a set of 31 high-resolution infrared absorption spectra of O3 recorded at temperatures between 160 and 300 K with several different room-temperature and coolable sample cells at the McMath-Pierce Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. We compare our results with other available measurements and with retrieved with 2 degrees of freedom (dof).

Microwave Optical Double Resonance Studies of Perturbations in the SO A3Π State and Tropospheric Ozone

ANDREW RICHARD WHITEHILL, Earth, Atmospheric, and Planetary Sciences, MIT, Cambridge, MA, USA; ALEXANDER W. HULL, TREVOR J. ERICKSON, JUN HANG, CARRE WOMACK, BARRATT PASK, Department of Chemistry, MIT, Cambridge, MA, USA; SHUHEI ONO, Earth, Atmospheric, and Planetary Sciences, MIT, Cambridge, MA, USA; ROBERT W. YIELD, Department of Chemistry, MIT, Cambridge, MA, USA.

There is a possibility that perturbations of the SO A′′ state provide a mechanism for photodissociation of SO by a 1 - 1’ two-color solar radiation process. The resultant S atom photofragments could depart from the isotopologue natural abundance ratios. The SO A′′-A states transition is very weak and the radiative lifetimes of c < 4 levels of the A′′ state are > 10 μs. The lowest vibrational levels of the A′′ state are perturbed by high vibrational levels of three metastable states: c, A, and A′′. Some upper atmospheric photophysical process were to populate the SO c, A, and A′′ states, emission from these states would escape detection. A - (c, A, A′′) perturbations by the various isotopologues will culminate at widely separated values of J with the result that, for some isotopologues, the perturbations are located outside of the region of thermally populated rotational levels. These perturbations are exceptionally difficult to characterize by Laser Induced Fluorescence. In addition to Chirped Pulse millimeter-Wave (CPmmW) spectroscopy in the A′′ state, we are using Coherence Converged Population Transfer (CCPT) in the X3Σ− state, an especially sensitive form of microwave-detected Microwave Optical Double Resonance, in order to characterize the A′′ state and its perturbations.

Validation of a New HNO3 Line Parameter at 7.6 μm Using Laboratory Intensity Measurements and MIPAS satellite spectra

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A new set of line parameters (positions, intensities and line widths) for nitric acid has been generated in the 7.6 μm region using the results of recent high quality experimental laboratory studies and of theoretical calculations. The validation of this new database was performed thanks to limb emission radiances measured in 2002-2012 by the “Michelson Interferometer for Passive Atmospheric Sounding” (MIPAS) instrument on board the ENVISAT satellite. This study will help to improve HNO3 satellite retrievals by allowing measurements to be performed using simultaneously 11 μm and 7.6 μm microinfrared. Hopefully this will be the case for the forthcoming Infrared Atmospheric Sounding Interferometer New Generation (IASI-N) instrument developed by CNES. IASI-NG will be the key payload element of the future METOP Second Generation (METOP-SG) series of EUMETSAT meteorological polar-orbit satellites.
RF11

ROTATIONAL SPECTROSCOPY OF NEWLY DETECTED ATMOSPHERIC OZONE DEPLETERS: CF₃CH₂Cl, CF₃CCl₃, AND CF₃CCl(CF₂)Cl

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In recent study of unpolluted air samples from Tasmania and of deep firn snow in Greenland four previously overlooked ozone-depleting substances have been identified.² These compounds started to emerge in the atmosphere in the 1960s, and two: CF₃CCl(CF₂)Cl (CFC-113a) and CF₃CH₂CH₂Cl (HCCHF-133a) continue to accumulate in the atmosphere.

Three of the four compounds have non-zero dipole moments and are amenable to study by rotational spectroscopy, establishing the basis for analytic applications. Relatively limited studies have been reported for CF₃CH₂Cl² and CF₃CCl₃,² while CF₃CCl(CF₂)Cl has not yet been studied by this technique. We presently report extensive results obtained for all three compounds, resulting from concerted application of supercomputational expansion FTMW spectroscopy in chirped pulse and cavity modes, and room-temperature MMW spectroscopy. Among the plentiful results, we have been able to resolve and fit the complex nuclear quadrupole hyperfine splitting.

RG01
ALKYL CH STRETCH VIBRATIONS AS A PROBE OF LOCAL ENVIRONMENT AND STRUCTURE
EDWIN SIBERT, DANIEL P. TALAR, Department of Chemistry, The University of Wisconsin, Madison, WI.
TOM NATHANIEL KIDWELL, JACOB C. DEAN, TIMOTHY S. ZWER, Department of Chemistry, Purdue University, West Lafayette, IN, USA.

The CH stretch region is a good candidate as a probe of structure and local environment. The functional groups are ubiquitous and their vibration spectra exhibit a surprising sensitivity to molecular structure. In this talk we briefly review our theoretical model Hamiltonian [J. Chem. Phys. 138 064308 (2013)] for describing vibrational spectra associated with the CH stretch of CH2 groups and then describe an extension of it to molecules containing methyl and methoxy groups. Results are compared to the infrared spectroscopy of four molecules studied under supersonic expansion cooling in gas phase conditions. The molecules include 1,1-diphenylethylene, 1,1-diphenylpropane, 2-methoxyphenol (guaiacol), and 1,3-dimethoxy-2-hydroxybenzene (syringol). The curvilinear local-mode Hamiltonian predicts most of the major spectral features considered in this study and provides insights into mode mixing. We conclude by returning to CH2 groups and explain both why the CH stretch spectrum of cyclohexane is substantially modified when it forms a complex with an alkali metal and what these spectra tell us about the structure of the complex.

RG02
COMPUTING THE VIBRATIONAL ENERGIES OF CH3O AND CH3CN WITH PHASE-SPACED LOCALIZED FUNCTIONAL BASIS AND AN ITERATIVE EIGENSOLVER
JAMES BROWN, TUCKER CARRINGTON, Department of Chemistry, Queen’s University, Kingston, ON, Canada.

For decades scientists have attempted to use ideas of classical mechanics to choose basis functions for calculating spectra. The hope is that a classically-motivated basis set will be small because it covers only the dynamically important part of phase space. One popular idea is to use phase-space localized (PSL) basis functions. Because the overlap matrix, in the matrix eigenvalue problem obtained by using PSL functions with the variational method, is not an identity, it is costly to use iterative methods to solve the matrix eigenvalue problem. Iterative methods are imperative if one wishes to avoid storing matrices which is important for large molecules. Recently we showed it was possible to circumvent the orthogonality (overlap) problem and use iterative eigensolvers. Here, we present calculated vibrational energies of CH3O and CH3CN using the iterative Ansöltz algorithm and PSL functions, and show that our PSL basis is competitive with other previously used basis sets for these molecules.

RG03
A MULTILAYER SUM-OF-PRODUCTS METHOD FOR COMPUTING VIBRATIONAL SPECTRA WITHOUT STORING FULL-DIMENSIONAL VECTORS OR MATRICES
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By optimizing sum-of-products (SOP) basis functions, it is possible to compute vibrational spectra, using a direct product basis, without storing vectors with as many components as there are product basis functions. These ideas are presented in a recent paper [Leclerc and Carrington, J. Chem. Phys. 140 174111 (2014)]. In that paper, the SOP basis functions are products of factors that depend on a single coordinate. When using factors that depend on one coordinate the number of terms (rank) in the SOP basis functions increases with the size of the molecule and the coupling strength. Using multi-dimensional factors makes it possible to incorporate some of the coupling into the factors and to calculate spectra of molecules with more than a dozen atoms. We use multi-dimensional factors that are eigenfunctions of reduced-dimension Hamiltonians. These can be constructed, in different ways, by organizing the factors into a multiple layer tree. Each node in a layer two represents eigenfunctions of a reduced-dimension Hamiltonian for a group of coordinates. We have done calculations with tensor-train and binary tree structures. Efficiency is significantly enhanced by representing the potential with the same tree structure. The ideas are tested by computing energy levels of a 64-D model coupled oscillator Hamiltonian and of CH3CN (12 dimensions) with a realistic potential.
VIBRATIONAL JAHN-TELLER EFFECT IN NON-DEGENERATE ELECTRONIC STATES

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The Jahn-Teller theorem 2 states that “All non-linear nuclear configurations are therefore unstable for an orbitally degenerate electronic state.” In 1982, Kellman 3 realized that the Jahn-Teller theorem also applies to nonlinear molecular species in non-degenerate electronic states when there are high-frequency vibrations that are degenerate at a symmetric reference geometry. When these high frequencies can be considered as adiabatic functions of degenerate low-frequency coordinates, there is a spontaneous Jahn-Teller distortion that lifts the degeneracy of the high-frequency vibrations. Kellman applied the vibrational Jahn-Teller (vJT) concept to the Van der Waals dimer (SF6).

In this talk, the vJT concept is applied to E ⊗ e systems that are small bound molecules in non-degenerate electronic states. The first case considered in systems for which the global minimum of the electronic potential has C2v symmetry. For such systems, including (CH3)2CO and CH3CN, the vJT effect leads to a significant splitting of the degenerate high-frequency vibrations (CH or CO stretches), but the spontaneous vJT distortion is exceptionally small. The second case in the second case systems, where the global minimum of the electronic potential is substantially distorted from the C2v reference geometry. For the second case systems, including CH3OH and CH3SH, the vJT splitting of the degenerate CH stretches is much larger, on the order of several 100s of cm–1. For both cases, there is the symmetry-required vibrational conical intersection at the C2v reference geometry. For the second case systems, there are additional symmetry-allowed vibrational conical intersections, far from the C2v geometry but energetically accessible to the molecule at thermal energies. For both cases, the vibrational adiabatic surfaces, including the multiple conical intersections, are well described by modest extensions to a high-order Hamiltonian that was developed for the electronic Jahn-Teller problem.

ANALOG OF DUSCHINSKY MATRIX AND CO-ASSIGNMENT OF FREQUENCIES IN DIFFERENT ELECTRONIC STATES

YURI PANCHENKO, ALEXANDER ABRAMENKO
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The analog of the Duschinsky matrix, D, is defined as $D = \{L_1, L_2\}$, where $L_1$ and $L_2$ are the matrices of the vibrational modes of the molecule under investigation. They are obtained by solving the vibrational problems in the I and II electronic states, respectively. Choosing the dominant elements in columns of the D matrix and permuting these columns to arrange these elements along the diagonal of the transformed matrix $D^*$ makes it possible to establish the correct co-assignment of the calculated frequencies in the I and II electronic states. The rows of $D^*$ are for the vibrational modes in the II electronic state, whereas the columns are for vibrations in the I electronic state. The results obtained may be tested by analogous calculations of $D^{**}$ for isopropylamines.

HIGH RESOLUTION INFRARED SPECTRA OF TRIACETYLENE

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Triacetylene, H3C=CH=CH2, is the longest polyacetylene chain found in space, and is believed to be involved in the formation of longer chain molecules and polycyclic aromatic hydrocarbons (PAHs). However, abundances are expected to be low, and observational confirmation requires knowledge of the gas-phase spectra, which up to now has been incomplete with only the weak, low lying bending modes being known. We present new infrared (IR) spectra in the C-H stretch region obtained using a tunable infrared laser spectrometer. The talk reviews the accurate determination of the rotational constants of the asymmetric fundamental mode, $\omega_{1}$, including discussion on the perturber state, and associated hot bands $\omega_{2}$, including discussion on the perturber state, and associated hot bands $\omega_{3}$. The determined molecular parameters are accurate enough to aid astronomical searches with such facilities as ALMA (Atacama Large Millimeter Array) or the upcoming JWST (James Webb Space Telescope), which can now probe even trace molecules (abundances of $\sim 10^{-10}$ to $10^{-11}$ with respect to H).
GROUND AND EXCITED STATE ALKYL CH STRETCH IR SPECTRA OF STRAIGHT-CHAIN ALKYLBENZENES

DANIEL M. HEWETT, JOSEPH A. KORN, TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN, USA.

Vibrational spectra of alkanes in the CH stretch region are often complicated by Fermi resonance with the overtone of the CH bend. This complication has made the CH stretch region difficult to use as a spectroscopic tool for assigning structures to experimental infrared spectra. A first-principles model accounting for Fermi resonance has been developed by Sibert and co-workers, and has been successfully implemented to predict the CH stretch region of alkyl groups as a variety of settings (both -CH3- and -CH2-). We have recorded jet-cooled, single-conformation infrared spectra of a series of straight chain alkylbenzenes having chain lengths of two carbons and longer, serving as a foundation for further tests and refinement of the theoretical model. Ground and excited state IR spectra of these alkylbenzenes were acquired using fluorescence dip infrared spectroscopy. A novel approach for taking the excited state spectra that utilizes the gain of a second, infrared-induced fluorescence peak will be discussed and compared to the typical depletion spectra, using ethylbenzene as a prototypical system.

ASYMMETRY OF M+(H2O)RG COMPLEXES, (M=V, Nb) REVEALED WITH INFRARED SPECTROSCOPY

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M+(H2O)Ar and M+(H2O)Ne clusters (M=V, Nb) were produced in a laser vaporization/pulsed nozzle source. The clusters were then mass selected in a time-of-flight mass spectrometer and studied with infrared photoassociation spectroscopy in the CH stretching region. Spectra showed two bands, with the asymmetric band showing k-type rotational structure. Previous work has shown that most metal-water rare gas-tagged systems adopt C3v geometry and exhibit the well-known 3:1 ortho:para ratio in the k-type rotational structure in asymmetric stretch band. However these two metals display a pattern that indicates a breaking of the C3v symmetry. Computational work confirms the breaking of C3v symmetry giving an Ar M+-O angle of 163.7 degrees for V and 172.1 degrees for Nb. In the ground state we obtain rotational constants that match up well with obtained spectra using 166 degrees for V and 175 degrees for Nb.

INFRARED SPECTROSCOPY OF PROTONATED ACETYLACETONE AND MIXED ACETYLACETONE/WATER CLUSTERS

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Acetilacetone (acac) is the simplest of the beta-diketones, which have both keto and enol tautomers with multiple protonation sites. We readily produce the protonated forms in the gas phase and the current investigation uses vibrational spectroscopy coupled with argon tagging to determine which protonated isomers are present in clusters of acac and the effects of solvation on the isomers observed.
CHIRPED PULSE AND CAVITY FT MICROWAVE SPECTROSCOPY OF THE HCCH-2,6-DIFLUOROPYRIDINE WEAKLY BOUND COMPLEX

CHRIS DEWHERRERY, BECCA MACKENZIE, KEN LEOPOLD, Chemistry Department, University of Minnesota, Minneapolis, MN, USA

The microwave spectrum of the HCCH-2,6-difluoropyridine complex has been observed using a chirped pulse and conventional cavity-type Fourier transform microwave spectroscopy. The acetylene moiety forms a hydrogen bond to the nitrogen of the 2,6-difluoropyridine, and this structure is contrasted with several systems involving HCCH or CO2 bound to pyridine or 2,6-difluoropyridine. The results of DFT calculations support the experimental observations and are reported as well. The chirped pulse spectrometer is new in our laboratory and is built in tandem with our cavity-type spectrometer with a design that allows for switching between the two modes of operation without having to break vacuum. Pertinent details of the spectrometer will also be given.

MICROWAVE SPECTRUM, VAN DER WAALS BOND LENGTH, AND 133Xe QUADRUPOLE COUPLING CONSTANT OF XE-SO

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Nine isotopologues of Xe-SO3 have been observed by pulsed-nozzle Fourier transform microwave spectroscopy. The complex is a symmetric top with a Xe-S van der Waals distance of 3.577(2) Å. The increase in rare gas distance relative to that in Kr-SO3 is equal to the difference in van der Waals radii between Xe and Kr. The 133Xe nuclear quadrupole coupling constant indicates that the electric field gradient at the xenon nucleus is 78% larger than that at the Kr nucleus in Kr-SO3.

DIMETHYL SULFIDE-DIMETHYL ETHER AND ETHYLENE OXIDE-ETHYLENE SULFIDE COMPLEXES INVESTIGATED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND AB INITIO CALCULATION


The ground-state rotational spectra of the dimethyl sulfide-dimethyl ether (DMS-DME) and the ethylene oxide and ethylene sulfide (EO-ES) complexes were observed by Fourier transform microwave spectroscopy, and a-type and c-type transitions were assigned for the normal, \(^3\Sigma^+\), and three \(^1\Sigma^+\) states of the DMS-DME. The observed transitions were analyzed by using an S-reduced asymmetric-top rotational Hamiltonian. The rotational parameters thus derived for the DMS-DME were consistent with a structure of \(\Sigma^+\) symmetry with the DMS bond to the DME by two C1(H(DMS))-O and one S-H(CDME) hydrogen bonds. The barrier height \(V_b\) to internal rotation of the "free" methyl group in the DME was determined to be 915.4 (23) cm\(^{-1}\), which is smaller than that of the DME monomer, 951.72 (70) cm\(^{-1}\), and larger than that of the DME dimer, 785.4 (32) cm\(^{-1}\). For the ES-DME complex, the observed data were interpreted in the terms of an antisymmetric \(\Sigma^+\) geometry with the ES bound to the DME by two C-H(ES)---O and two S-H(ESO) hydrogen bonds. We have applied a natural bond orbital (NBO) analysis to the DMS-DME and ES-DME to calculate the stabilization energy \(\Delta E\) (\(\Delta E_{\text{ES-DME}}\)), which were closely correlated with the binding energy \(E_B\), as found for other related complexes.

\(^{196}\)Rh04 2:16 – 2:31

INTERNAL DYNAMICS IN SF6···NH3 OBSERVED BY BROADBAND ROTATIONAL SPECTROSCOPY

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The rotational spectra of SF6···NH3 isotopologues have been observed in a pulsed nozzle chirped pulse Fourier-transform microwave spectrometer in the frequency range 6.5-18.5 GHz. The spectrum of SF6\(^{13}\)N\(^{15}\)H has been fitted to a Hamiltonian describing a symmetric top complex in which two symmetric top subunits undergo free internal rotation about a common symmetry axis. The distance between the centers of mass of the two monomers was found to be 4.15787(6) Å. Challenges associated with fitting \(m=1\) transitions (correlating with K of free NH3) for SF6···\(^{13}\)N\(^{15}\)D\(^{14}\) imply complexed internal dynamics occurs within the complex.

Evidence for a complex between THF and acetic acid from broadband rotational spectroscopy was presented. Transitions believed to belong to the complex were first identified in a gas mixture containing small amounts of THF, triethyl borane, and acetic acid balanced in argon. Ab initio calculations suggest a complex between THF and acetic acid is more likely to form compared to the analogous acetic acid complex with triethyl borane, the initial target. The observed rotational constants are also more similar to those predicted for a complex formed between THF and acetic acid, than for those of a complex formed between triethyl borane and acetic acid. Subsequently, multiple isotopologues of acetic acid have been measured, confirming its presence in the structure. No information has yet been obtained through isotopic substitution within the THF sub-unit. Ab initio calculations predict the most likely structure is one where the acetic acid subunit coordinates over the ring creating a "bridge" between the THF oxygen, the carbonyl O-H, and the carbonyl oxygen to a hydrogen atom on the back of the ring.

EVIDENCE FOR A COMPLEX BETWEEN THF AND ACETIC ACID FROM BROADBAND ROTATIONAL SPECTROSCOPY

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Evidence for a complex between tetrahydrofuran (THF) and acetic acid from broadband rotational spectroscopy was presented. Transitions believed to belong to the complex were first identified in a gas mixture containing small amounts of THF, triethyl borane, and acetic acid balanced in argon. Ab initio calculations suggest a complex between THF and acetic acid is more likely to form compared to the analogous acetic acid complex with triethyl borane, the initial target. The observed rotational constants are also more similar to those predicted for a complex formed between THF and acetic acid, than for those of a complex formed between triethyl borane and acetic acid. Subsequently, multiple isotopologues of acetic acid have been measured, confirming its presence in the structure. No information has yet been obtained through isotopic substitution within the THF sub-unit. Ab initio calculations predict the most likely structure is one where the acetic acid subunit coordinates over the ring creating a "bridge" between the THF oxygen, the carbonyl O-H, and the carbonyl oxygen to a hydrogen atom on the back of the ring.

THE ROTATIONAL SPECTRUM OF PYRIDINE-FORMIC ACID

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The rotational spectrum of three 1:1 complexes of pyridine with formic acid has been observed and assigned using pulsed jet Fourier transform microwave technique. The two subunits are held together through one O-H···N hydrogen bond and one C-H···O weak hydrogen bond, forming a seven-membering cyclic structure. The rotational spectrum of the pyridine-CHOH is considerably shifted towards lower frequencies, with respect to the "rigid" model, suggesting a considerable Ubbelohde effect, similar in nature to that observed in the bi-molecules of carboxylic acids.

Intermission
FOURIER-TRANSFORM MICROWAVE AND MILLIMETERWAVE SPECTROSCOPY OF THE H2-HCN MOLECULAR COMPLEX

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Fourier-Transform microwave (FTMW) spectroscopy has been applied to observe the J = 1 - 0 rotational transitions of the H2-HCN/DCN complexes containing both the para-H2 (Ia=0) and para-H2 (Ib=0) molecules. Rotational spectra of the H2-HCN/DCN up to J = 5 - 4 were also observed in the millimeter-wave (MMW) region below 180 GHz. Observed FTMW lines for the H2-HCN/DCN split into hyperfine components due to the nuclear quadrupole interaction of N and D nucl. For the ortho-H2 species, the hyperfine splitting due to the magnetic interaction between the hydrogen nuclear spin and ortho-H2 partner (Ia=1, Ia=0) was also observed, but not for the para-H2 species (Ia=0, Ib=0). From the observed nuclear spin-singlet coupling constants of ortho-H2 species, d = 21.9(47) and 24.66(68) kHz for HCN and DCN complexes, respectively, the average values of < J2a(2a) > = 0.380(8) and 0.439(10) were derived indicating the nearly free rotation of H2 in the complex with J2a(2a) = 1 and J2a(2a) = 0.

The nuclear quadrupole interaction constants due to N and D nuclei show that the HCN/DCN part executes a floppy motion with a large mean square amplitude of about 29/25 and 33/30 degree in the para species, respectively. From the observed rotational constants, the center-of-mass distances of H2 and HCN/DCN were derived to be 3.96(7)/3.96(36) Å for the ortho species and 4.159(5)/4.159(36) Å for the para species. The isotropic effect on rotational constants confirmed the totally different configurations in the ortho and para species: H2 is attached to the H/D end of HCN/DCN for the para species, while to the N end for the ortho species, as suggested by IR spectroscopy and theoretical study.

MICROWAVE SPECTROSCOPY OF THE CYCLOPENTANOL - WATER DIMER

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Observations of gas-phase dimers are one of the simplest methods for studying bimolecular interactions. These dimers are an excellent tool for developing models for the interactions, providing a model for theoretical studies, and for understanding complex molecular interactions. Of particular interest are studies of strong (O—H) and weak (C—H) long-range interactions of water. We have recently recorded the pure rotational spectrum of the cyclopentanol-water dimer with chirped-pulse Fourier transform microwave spectroscopy (CP-FTMW). We will present the understanding and modeling more complex interactions. Of particular interest are studies of strong (O—H) and weak (C—H) long-range interactions of water.

HYDROGEN-BONDING AND HYDROPHOBIC INTERACTIONS IN THE ETHANOL-WATER DIMER

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The conformational energy landscape of the ethanol-water dimer is determined by the relative hydrogen-bond donor and acceptor strengths of the two molecules, as well as weaker hydrophobic interactions between the water and the ethyl group. Using a combination of ab initio calculations and chirped-pulse Fourier transform microwave spectroscopy, we have recorded the first rotationally-resolved, jet-cooled spectrum of the ethanol-water dimer between 8-18.5 GHz and identified two water-donor ethanol-acceptor conformers. The lowest energy conformer is chiral, has ethanol in the gauche configuration, and is consistent with previous x-ray and infrared results. The second conformer corresponds to the trans-ethanol configuration, and exhibits a significant splitting.

THE INFLUENCE OF FLUORINATION ON STRUCTURE OF THE TRIFLUOROACETONITRILE WATER COMPLEX

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Acetonitrile, CH3CN, and trifluoroacetonitrile, CF3CN, are symmetric tops. In a recent study of the rotational spectrum of the acetonitrile and water complex, it was observed that the structure was also an effective symmetric top, with the external hydrogen freely rotating about the O—H bond aligned towards the nitrogen of the cyanide of CH3CN. Unlike the CH3CN – H2O complex, the CH3CN – Ar and CF3CN – Ar complexes were observed to be asymmetric tops. Having a series of symmetric and asymmetric top complexes of acetonitrile and trifluoroacetonitrile for comparison, we report the rotational spectrum of the weakly bound complex between trifluoroacetonitrile and water. Rotational constants and quadrupole coupling constants will be presented, and the structure of CF3CN – H2O will be revealed.

THE POSITION OF DEUTERIUM IN THE HOD – N2O AS DETERMINED BY STRUCTURAL AND NUCLEAR QUADRUPOLE COUPLING CONSTANTS

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A recent investigation of the HOD – N2O complex measuring the OH + OD excited band in the near-IR was completed by Fodors et al. During this study, one of us (WAK) was contacted about the position of deuterium in the HOD – N2O complex, as his group completed the original microwave study of H2O – N2O and its deuterated isotopologues in 1992. The results of this microwave study did not give the orientation of HOD in the complex, however, we present here a supplementary study to the original microwave work using a Balle-Flygare cavity instrument, attempting to determine the orientation of HOD relative to the N2O. In addition to a Kraitchman and a least-squares inertial structure fit of the molecule, we present the nuclear quadrupole coupling tensor of deuterium to determine the position of HOD in the complex.


THE CP-FTMW SPECTROSCOPY AND ASSIGNMENT OF THE MONO- AND DIHYDRATE COMPLEXES OF PERFLUOROPROPIONIC ACID

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While searching for the chirped pulse spectra of allyl phenyl ether, the authors used current rotational spectroscopic fitting tools to assign multiple sets of spectra of unknown origin. Previous chirped pulse experiments searching for hydrate complexes of perfluoropropionic acid had not been successful but, through theoretical agreement, it was determined that at least one of the sets of unknown spectra belonged to the perfluoropropionic acid-water complex. Further determination showed that the dihydrate had also been observed. The determination process and spectral assignment will be discussed. Structural determinations of the complexes will also be discussed.

THEORETICAL STUDY OF THE EFFECT OF DOPING CLUSTERS (ZNO) 6 BY THE SELENIUM USING THE DFT

NOUR EL HOUDA BENSIRADJ, OURIDA OUAMERALI, Laboratory lctcp, University USTHB, Algiers, Algeria.

Nano structures (ZnO) 6 have a great interest in the creation of new materials used in energy technologies. We have used the technique of doping to introduce impurities at the geometry of these clusters; replacing each time by an oxygen atom a selenium atom. This implies a change in the electronic and energetic properties. Clusters obtained (containing selenium) have interesting characteristics in the development of solar energy systems and the field of radiology in medicine. The clusters studied are shown in a 3D geometry (crystal form b). The geometric parameters of these systems are calculated using the theory of density functional (DFT). The optimisation the first excited state is performed at the Hartree-Fock method, Single Configuration interaction (HF / CIS), the transmission-absorption spectra are given by the TDDFT method. The results for the excited states have a good process for materials for application in solar cells. The emission spectra of these clusters are located in the tera-hertz region (between the far infrared and microwave), which is less than the ionizing X-ray spectral region and could soon replace for applications medicine.

BORONYL MEMICS GOLD: A PHOTOELECTRON SPECTROSCOPY STUDY

TIAN RAN, GARY LOPÉZ, LALI-SHENG WANG, Department of Chemistry, Brown University, Providence, RI, USA.

Previous studies have found that gold atom and boronyl bear similarities in bonding in many gas phase clusters. B\(_{2}\)(BO), B\(_{3}\)(BO), B\(_{4}\)(BO), (n=1, 2) were found to possess similar bonding and structures to Bi\(_{2}\)Au, Bi\(_{3}\)Au, Bi\(_{4}\)Au, (n=1, 2), respectively. During the recent photoelectron spectroscopy experiments, the spectra of BBO\(^{−}\) and BiAu\(^{−}\) clusters are found to exhibit similar patterns, hinting that they possess similar geometric structures. While BiAu\(^{−}\) is a linear molecule, BBO\(^{−}\) is also linear. The similarity in bonding between BBO\(^{−}\) and BiAu\(^{−}\) is owing to the fact that Au and BO are monovalent σ ligands. The electron affinities are measured to be 1.79±0.04eV for BBO\(^{−}\) and 1.36±0.02eV for BiAu\(^{−}\). The current results provide new examples for the BO/Au isolobal analogy and enrich the chemistry of boronyl and gold.

H2N

OH

Both amine and hydroxyl functional groups are present in 4-aminophenyl ethanol (4-AE), and each functional group can form hydrogen bonds with carboxylic acids, such as formic acid and acetic acid. Predicting the structures of such complexes involving 4-AE is rather complex, given the many possible conformations and their similarities (and method and basis-dependent) energies. In particular, the carboxyl group, COOH, can act as both a hydrogen bond donor or acceptor, or both at once.

In this study we report the formic acid – 4-AE hydrogen bonded complex. An infrared-ultraviolet double resonance spectrometer is used to examine the shifts in IR frequencies of 4-AE from the monomer to the complex. Fourier transform microwave spectroscopy is used to determine structures of the species. Results from both experiments are compared to DFT and ab initio results. Time permitting, results of the water complex with 4-AE will also be presented.
We have studied methyl formate, one of the so-called ‘astronomical weeds’, in the 214–265 GHz band. We have experimentally gathered a set of intensity calibrated, complete, and temperature resolved spectra from across the astronomically significant temperature range of 248–406 K. Using our previously reported method of analysis, the point by point method, we are capable of generating the complete spectrum at an arbitrary temperature. Thousands of lines, of nontrivial intensity, which were previously not included in the available astrophysical catalogs have been found. The sensitivity of the point by point analysis is such that we are able to identify lines which would not have manifest in a single scan across the band. The consequence has been to reveal not only a number of new methyl formate lines, but also trace amounts of contaminants. We show how the intensities from the contaminants can be removed with indiscernible impact on the signal from methyl formate. To do this we use the point by point results from our previous studies of these contaminants. The efficacy of this process serves as strong proof of concept for usage of our point by point results on the problem of the weeds. The success of this approach for dealing with the weeds has also previously been reported.5


Recently we studied the rotational spectrum of hydroxycetone (HOC\(\text{CH}_2\text{CN}\), HAN) in order to provide a firm basis for its possible detection in the interstellar medium.7 Different plausible pathways of the formation of HAN in the interstellar conditions were proposed; however, up to now, the searches for this molecule were unsuccessful. To continue the study of nitriles that represent an astrophysical interest we present in this talk the analysis of the rotational spectrum of 4-hydroxy-2-butytnitrile (HOC\(\text{CH}_2\text{CC-CN}\), HBN), the next molecule in the series of hydroxymethyl nitriles. Using the Lille spectrometer the spectrum of HBN was measured in the frequency range 50 – 500 GHz. From the spectroscopic point of view HBN molecule is rather similar to HAN, because of -OH group tunnelling in gauche conformation. As it was previously observed for HAN, due to this large amplitude motion, the splittings in the rotational spectra of HBN are easily resolved making the spectral analysis more direct. Additional difficulties arise from the near symmetrical top character of HBN (\(a = -0.996\)), and very dense spectrum because of relatively small values of rotational constants and a number of low-lying excited vibrational states. The analysis carried out in the frame of reduced axis system approach of Pickard’s allows to fit within experimental accuracy all the rotational transitions in the ground vibrational state. Thus, the results of the present study provide a reliable catalog of frequency predictions for HBN.

The support of the Action sur Projets de l’ODIS/ PCMI, and ANR-13-RS05-0008-02 IMOLABS is gratefully acknowledged.


RI01 1:30–1:45
THE COMPLETE, TEMPERATURE RESOLVED SPECTRUM OF METHYL FORMATE BETWEEN 214 AND 265 GHz
JAMES P. McMILLAN, SARAH FORTMAN, CHRISTOPHER F. NEES, FRANK C. DE LUCIA, Department of Physics, The Ohio State University, Columbus, OH, USA

RI02 1:47–2:02
ROTATIONAL SPECTROSCOPY OF 4-HYDROXY-2-BUTYTNITRILE
R. A. MOTTIVIENKO, 1 MARQUIES, Laboratoire PhlAM, UMR 8523 CNRS - Université Lille 1, Villeneuve d’Ascq, France, T.-E. GUILLAUMIN, Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes 1, Rennes, France.

RI03 2:04–2:19
TIME-DOMAIN TERAHERTZ SPECTROSCOPY OF ISOLATED PAHS
BRANDON CARROLL, MARCO A. ALLODI, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA; BRET A. McCABE; NAAC, National Radio Astronomy Observatory, Charlottesville, VA, USA; SERGIO IOPPOLO. Department of Physical Sciences, The Open University; Milton Keynes, UK; GEOFFREY BLAKE, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA.

RI04 2:21–2:36
HIGH-RESOLUTION IR ABSORPTION SPECTROSCOPY OF POLYCYCLIC AROMATIC HYDROCARBONS: SHINING LIGHT ON THE INTERSTELLAR 3 MICRON EMISSION BANDS
ELENA MAITSEVA, Van ’t Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, Netherlands; ALESSANDRA CANDIAN, XANDER TIELENS, Leiden Observatory, University of Leiden, Leiden, Netherlands; ANNEEMIKE PETRIGNANI, J. OMSENS, Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands; WYBREN JAN BUMA, Van ’t Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, Netherlands.

Various astronomical objects show distinctive series of IR emission bands indicated as unidentified infrared emission bands. These features are nowadays mainly attributed to the IR fluorescence of Polycyclic Aromatic Hydrocarbons (PAHs) even though an unambiguous identification of which PAHs are involved has not been possible yet. We present here a high-resolution IR absorption study of a number of jet-cooled polycyclic aromatic hydrocarbons in the 3.3 μm region obtained by IR-UV ion depletion techniques. The experimental spectra display many more bands than expected, and lead to the conclusion that the appearance of the spectrum is dominated by fourth-order vibrational coupling terms. This has far-reaching consequences since up till now the assignment of infrared emission features observed in different types of space objects in this wavelength region -and the conclusions drawn from these assignments on the evolution of interstellar gas- has relied heavily on harmonic quantum chemical calculations. We also observe that the presence of hydrogen sites in a PAH leads to a shift of the overall spectrum to the high-energy side and to a broadening of the 3 μm band. This observation provides an appealing explanation for previous speculations that the emission of 3 μm band consists of two components. Moreover, it paves for using this structure to derive the composition of different objects.
EXPLORING MOLECULAR COMPLEXITY WITH ALMA (EMoCA): HIGH-ANGULAR-RESOLUTION OBSERVATIONS OF SAGITTARIUS B2(N) AT 3 mm

HOLGER S. MÜLLER, J Physisches Institut, Universität zu Köln, Köln, Germany; ARNAUD BELLOCHÉ, KARL M. MINTEN, Millimeter- und Submillimeter-Astromie, Max-Planck-Institut für Radioastronomie, Bonn, NRW, Germany; ROBERT T. GARROD, Departments of Chemistry and Astronomy, The University of Virginia, Charlottesville, VA, USA.

Sagittarius B2 (Sgr for short) B2 is the most massive and luminous star-forming region in our Galaxy, located close to the Galactic Center. We have carried out a molecular line survey with the IRAM 30 m telescope toward its two major sites of star-formation, Sgr B2(M) and (N). Toward the latter source, which is particularly rich in Complex Organic Molecules (COMs), we detected three molecules for the first time in space, aminoacetinicetole, ethyl formate, and n-propyl cyanide.

We have recently obtained ALMA data of Sgr B2(N) between ~84 and ~111 GHz within Cycle 1. At angular resolutions of 1.8″ and 1.4″, respectively, the two main hot cores, the prolific Sgr B2(N-LMH) and the likely less evolved Sgr B2(N-SMA1) are well separated, and line confusion is reduced greatly for the latter. As a consequence, we have been able to identify the first branched alkyl molecule in space, iso-propyl cyanide, toward Sgr B2(N-SMA1). Our ongoing analyses include investigations of cyanides and isocyanides, alkyls and thioalkyls, and deuterated molecules among others. We will present some of our results.

Belloche et al. 2014, Science, 345, 1584

FIRST SPECTROSCOPIC STUDIES AND DETECTION IN SgrB2 OF 13C-DOUBLY SUBSTITUTED ETHYL CYANIDE

L. MARQUELÉS, R. A. MOTIYENKO, Laboratoire PhilAM, UMR 8523 CNRS - Université Lille 1, Villeneuve d’Ascq, France; J.-C. GIULLEMIN, Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes 1, Rennes, France; JOSE CERNICHARO, Departamento de Astrofísica, Centro de Astrobiología CAB, CSIC-INTA, Madrid, Spain.

The aldimines are important to understand amino acid formation process as they appear in reaction scheme of Strecker-type synthesis. Following the detection in the ISM of methanimine (CH$_2$NH) in 1979 and the more recent one of ethanimine (CH$_3$C=NH), we decided to investigate the next molecule in the series: propanimine (CH$_3$C=NH$_2$). For this molecule no spectroscopic information was available up to now. We measured the rotational spectrum of propanimine in the frequency range up to 500 GHz. Since the spectroscopic studies of ethanimine were limited to 150 GHz, we also extended the measurements up to 300 GHz. The spectra of both E- and Z-isomers are analyzed for the two molecules. Usually aldimines, which are unstable molecules, are obtained by discharge or pyrolysis methods, here pure sample were obtained by synthesis process.

For ethanimine, the methyl top internal rotation should be taken into account, therefore the analysis is performed using a new version of RAM36 code which includes the treatment of the nuclear quadrupole hyperfine structure.

The spectroscopic results and their searches in Orion will be presented.

This work was supported by the CNES and the Action sur Projets de l’DPSU, PCMI. This work was also done under ANR-13-BS05-0008-02 IMOLARS.

MILLIMETERWAVE SPECTROSCOPY OF ETHANIMINE AND PROPANIMINE AND THEIR SEARCH IN ORION

L. MARGUL`ES, R. A. M OTIYENKO, Laboratoire PhilAM, UMR 8523 CNRS - Université Lille 1, Villeneuve d’Ascq, France; J.-C. GIULLEMIN, Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes 1, Rennes, France; JOSE CERNICHARO, Departamento de Astrofísica, Centro de Astrobiología CAB, CSIC-INTA, Madrid, Spain.

We have recently obtained ALMA data of Sgr B2(N) between 3 mm and 850 μm. The vibrationally excited states are enough populated under ISM conditions and could be detected. As part of the deuterated ones, all mono-substituted isomers of ethyl cyanide ($^{13}$C and $^{15}$N) have been detected in the ISM. The detection of isomers in the ISM is important: it can give information about the formation process of complex organic molecules, and it is essential to clean the ISM spectra from the lines of known carriers. Toward Her 36 was ascribed to the lengthening of bonds upon the electronic excitation, vibronic satellites involving stretch vibrations are expected. Among the 73 DBs observed toward HD 183143 to the blue of 5797.1 MHz, two DBs, $\lambda 5545.1$ and $\lambda 5492.2$ stand out as highly correlated with $\lambda 5797.1$ DB. Their correlation coefficients 0.941 and 0.943, respectively, are not sufficiently high to establish the vibronic relation by themselves but can be explained as due to high uncertainties due to their weakens and their stellar blends. They are above the $\lambda 5797.1$ DB by 784.0 cm$^{-1}$ and 951.2 cm$^{-1}$, respectively, approximately expected for stretching vibrations.

Another observations which may possibly be explained by our hypothesis is the emission at 5800 Å from the Red Rectangle Nebula called RR 5800. Our analysis suggests that $\lambda 5797.1$ DB and RR 5800 are consistently explained as caused by the same molecule.

Reference:
Belloche et al. 2014, Science, 345, 1584

Futher studies:
TAKESHI OKA, L. M. HOBBS, D. WELTY, D. G. YORK, Department of Astronomy and Astrophysics, University of Chicago, Chicago, IL, USA; JULIE DAHLSTROM, Department of Physics and Astronomy, Carthage College, Kenosha, WI, USA; ADOLF N. WITT, Department of Physics and Astronomy, University of Toledo, Toledo, OH, USA.

The $\lambda 5797.1$ DB is unique with its sharp central feature. We simulated the spectrum based on three premises: (1) its carrier molecule is polar as concluded from the anomalous spectrum toward the star Herchel 54. (2) The central feature is Q-branch of a parallel band of a probe tetra. (3) The radiative temperature of the environment is $T = 273 K$. A comparison with observed spectrum indicated that the carrier contains 5-7 heavy atoms.

To further strengthen this hypothesis, we have looked for vibrionic satellites of the $\lambda 5797.1$ DB. Since its anomaly toward Her 36 was ascribed to the lengthening of bonds upon the electronic excitation, vibrionic satellites involving stretch vibrations are expected. Among the 73 DBs observed toward HD 183143 to the blue of 5797.1 MHz, two DBs, $\lambda 5545.1$ and $\lambda 5492.2$ stand out as highly correlated with $\lambda 5797.1$ DB. Their correlation coefficients 0.941 and 0.943, respectively, are not sufficiently high to establish the vibronic relation by themselves but can be explained as due to high uncertainties due to their weakens and their stellar blends. They are above the $\lambda 5797.1$ DB by 784.0 cm$^{-1}$ and 951.2 cm$^{-1}$, respectively, approximately expected for stretching vibrations.

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TAKESHI OKA, L. M. HOBBS, D. WELTY, D. G. YORK, Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL, USA; JULIE DAHLSTROM, Department of Physics and Astronomy, Carthage College, Kenosha, WI, USA; ADOLF N. WITT, Department of Physics and Astronomy, University of Toledo, Toledo, OH, USA.
MITSUNORI ARAKI, YUKI MATSUSHITA, Faculty of Science Division I, Tokyo University of Science, Musashino-ku, Tokyo, Japan; KOICHI TSUKIYAMA, Faculty of Science Division I, Tokyo University of Science, Musashino-ku, Tokyo, Japan.

Diffuse Interstellar Bands (DIBs) are optical absorption lines observed in diffuse clouds in interstellar space. They still remain the longest standing unsolved problem in spectroscopy and astrochemistry, although several hundreds of DIBs have been already detected. Aromatic radicals in a gas phase are potential DIB candidate molecules. The electronic transitions of aromatic radicals result in optical absorption. Last year we reported the gas-phase optical absorption spectrum of the $^2A_2 \rightarrow ^2B_1$ transition of the thiophenoxyl radical $\text{C}_4\text{H}_3\text{O}$ using a cavity ringdown spectrometer. As the next step, we observed the $^2A_2 \rightarrow ^2B_1$ transition of the phenoxyl radical $\text{C}_6\text{H}_5\text{O}$ in the discharge of anisole. The four broad and asymmetric peaks making a progression of 500 cm$^{-1}$ were detected in the 5700–6450 Å region. The progression was assigned to the $^6\text{a}_1$ mode, and the broad and asymmetric peak profiles were accounted for by the origins of the $^6\text{b}_2$ mode. Each vibrational component has a broad structure of 23 Å, which can be explained by lifetime broadening. Based on the assignment of the progression and the sequences, the vibronic components from $v=0$ in the $^2 \Sigma^+$ ground state can be extracted from the broad and asymmetric peak profiles to compare the laboratory bands with DIBs. Although the components did not agree with the reported DIBs, the upper limit of the column density for the phenoxyl radical in the diffuse clouds toward HD 204827 was evaluated to be $4 \times 10^{13}$ cm$^{-2}$. Therefore, the most fundamental aromatic radicals, the phenoxyl and phenoxy radicals, could not explain DIBs observed at present.

INVESTIGATION OF CARBONACEOUS INTERSTELLAR DUST ANALOGUES BY INFRARED SPECTROSCOPY: EFFECTS OF ENERGETIC PROCESSING

BELÉN MATE, MIGUEL JIMÉNEZ-REDONDO, ISABEL TANARRO, VICTOR JOSE HERRERO, Molecular Physics, Instituto de Estructura de la Materia (IEM-CSIC), Madrid, Spain.

Carbonaceous compounds, both solids and gas-phase molecules, are found in very diverse astronomical media. A significant amount of the elemental carbon is found in small dust grains. This carbonaceous dust, mostly formed in the last stages of evolution of C-rich stars, is the carrier of characteristic IR absorption bands revealing the presence of aliphatic, aromatic and olefinic functional groups in variable proportions. Among the various candidate materials investigated as possible carriers of these bands, hydroxylated aromospheric carbon ($\text{C}_6\text{H}_5\text{OH}$) has led to the best agreement with the observations. Carbonaceous grains are processed by H atoms, UV radiation, cosmic rays and interstellar shocks in their passage from asymptotic giant branch stars to planetary nebulae and to the diffuse interstellar medium. The mechanisms of a-C:H production and evolution of the interstellar environment, the samples have been subjected to electron bombardment, UV irradiation, and both He and H$_2$ plasma processing. IR spectroscopy is employed to monitor the changes in the structure and composition of the carbonaceous films.

REATIONS OF GROUND STATE NITROGEN ATOMS $\text{N}(^4\text{S})$ WITH ASTROCHEMICALLY-RELEVANT MOLECULES ON INTERSTELLAR DUSTS

LAHOUI ARIMI, SÉNDRIES NOURRY, Department of Chemistry, MONAIS, CNRS, UMR 8233, Sorbonne Université, UPMC Univ Paris 06, Paris, France.

In the last few years, ambitious programs were launched to probe the interstellar medium always more accurately. One of the major challenges of these missions remains the detection of prebiotic compounds and the understanding of reaction pathways leading to their formation. These complex heterogeneous reactions mainly occur on icy dust grains, and their studies require the coupling of laboratory experiments mimicking the extreme conditions of extreme cold and dilute media. For that purpose, we have developed an original experimental approach that combine the study of heterogeneous reactions (by exposing neutral molecules adsorbed on ice to non-energetic radicals $\text{H}_2$, $\text{OH}$, N$_2$) and a neon matrix isolation study at very low temperatures, which is of paramount importance to isolate and characterize highly reactive reaction intermediates. Such experimental approach has already provided answers to many questions raised about some astrochemically-relevant reactions occurring in the ground state on the surface of dust grain ices in dense molecular clouds. The aim of this new present work is to show the implication of ground state atomic nitrogen on hydrogen atom abstraction reactions from some astrochemically-relevant species, at very low temperatures (3K–20K), without providing any external energy. Under cryogenic temperatures and with high barrier heights, such reactions involving $\text{N}(^4\text{S})$ nitrogen atoms should not occur spontaneously and require an initiating energy. However, the detection of some radicals species as byproducts, in our solid samples left in the dark for hours at 10K, proves that hydrogen abstraction reactions involving ground state $\text{N}(^2\text{P})$ nitrogen atoms may occur in solid phase at cryogenic temperatures. Our results show the efficiency of radical species formation stemming from non-energetic N-atoms and astrochemically-relevant molecules. We will then discuss how such reactions, involving nitrogen atoms in their ground states, might be the first key step towards complex organic molecules production in the interstellar medium.
MILLIMETER AND SUBMILLIMETER STUDIES OF INTERSTELLAR ICE ANALOGUES
AJ MESKO, JAN C WAGNER, HOUSTON HARTWELL SMITH, Department of Chemistry, Emory University, Atlanta, GA, USA; STEPHANE N MILAM, Astrochemistry, NASA Goddard Space Flight Center, Greenbelt, MD, USA; SUSANNA L. WIDICUS WEAVER, Department of Chemistry, Emory University, Atlanta, GA, USA.

The chemistry of interstellar ice analogues has been a topic of great interest to astrochemists over the last 20 years. Currently, the models of interstellar chemistry feature icy-grain reactions as a primary mechanism for the formation of many astrochemical species as well as potentially astrobiologically-relevant complex organic molecules. This talk presents new results collected by a millimeter and submillimeter spectrometer coupled to a vacuum chamber designed to study the sublimation or sputtered products of icy-grain reactions initiated by thermal-processing or photo-processing of interstellar ice analogues. Initial results from thermal desorption and UV photoprocessing experiments of pure water ice and processed water + methanol ice mixtures will be presented.

UNTANGLING MOLECULAR SIGNALS OF ASTROCHEMICAL ICES IN THE THz: DISTINGUISHING AMORPHOUS, CRYSTALLINE, AND INTRAMOLECULAR MODES WITH BROADBAND THz SPECTROSCOPY
BRETT A. McGUIRE, NASA, National Radio Astronomy Observatory, Charlottesville, VA, USA; SERGIO IOPPOLO, Department of Physical Sciences, The Open University, Milton Keynes, UK; XANDER DE VRIES, Theoretical Chemistry, University of Nijmegen, Nijmegen, Netherlands; MARCO A. ALLODI, BRANDON CARROLL, GEOFFREY BLAKE, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA.

We have previously reported at this meeting on the initial construction of a broadband (0.3 – 7.5 THz) TerraThz time-domain spectrometer to study condensed-phase samples of astrophysically-relevant species. Here, we present the latest results from this instrument, focusing on the interaction of theory with experiment in the interpretation of our spectra. We will present both simple (CO₂) and more complex (CH₃OH and beyond) species, in their purely-crystalline and purely-amythous states, at varying levels of matrix isolation, and as mixtures of these species. We will discuss the relative contributions of individual molecular motions (i.e. torsional modes) and bulk motions within the ice to the observed laboratory spectra. We will also touch upon the feasibility of direct interstellar detection of species from these spectra, and the results of proof-of-concept observations with the FIFI-LS instrument on the SOFIA telescope, currently scheduled for Spring 2015.

QUANTUM CHEMICAL STUDY OF THE REACTION OF C⁺ WITH INTERSTELLAR ICE: PREDICTIONS OF VIBRATIONAL AND ELECTRONIC SPECTRA OF REACTION PRODUCTS
DAVID E. WOON, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA.

The C⁺ cation (CH⁺) is the dominant form of carbon in diffuse clouds and an important tracer for star formation in molecular clouds. We studied the low energy deposition of C⁺ on ice using density functional theory calculations on water clusters as large as 18 H₂O. Barrierless reactions occur with water to form two dominant sets of products: HOC + H²O and CO + H₂O. In order to provide testable predictions, we have computed both vibrational and electronic spectra for pure ice and processed ice clusters. While vibrational spectroscopy is expected to be able to discern that C⁺ has reacted with ice by the addition of H₂O⁺ features not present in pure ice, it does not provided characteristic bands that would discern between HOC and CO. On the other hand, predictions of electronic spectra suggest that low energy absorptions may occur for CO⁺ and not HOC, making it possible to distinguish one product from the other.
THE OPTICAL BICHROMATIC FORCE IN MOLECULAR SYSTEMS

LELAND M. ALDRIDGE, SCOTT E. GALICA, EDWARD E. FYLER, Department of Physics, University of Connecticut, Storrs, CT, USA

The bichromatic optical force (BCF), which can greatly exceed radiative forces, seems ideal for laser slowing and cooling of molecules because it minimizes the effects of radiative decay. However, it relies on sustained coherences between optically coupled states, and molecules, with their many sublevels and decay pathways, present new challenges in maintaining these coherences compared with simple atoms. We have conducted extensive numerical simulations of BCF in model molecular systems based on the $B \rightarrow X$ transition in CaF and have begun experimental tests in a molecular beam.

In our modeling, the effects of fine and hyperfine structure are examined using a simplified level scheme that is sufficiently complete to include the major pathways leading to loss or decoherence. To circumvent optical pumping into coherent dark states we explore two possible schemes: (1) a skewed dc magnetic field, and (2) rapid optical polarization switching. The effects of repumping to compensate for out-of-system radiative decay are also examined. Our results verify that the BCF is a promising method for creating large forces in molecular beams while minimizing out-of-system radiative losses, and provide detailed guidance for experimental designs. Compared to a two-level atom, the peak force is reduced by about an order of magnitude, but there is little reduction in the velocity range over which the force is effective. Our experiments on deflection and slowing using the CaF $B \rightarrow X$, (0,0) transition, still at an early stage, include studies of both the $P_j(1)/Q_j(1)$ and $Q_j(0)/Q_j(1)$ branch, a quasi-cycling configuration with extensive hfs, and the $R_j(0)/Q_j(0)$ branch, which has a much simpler hfs but requires rotational repumping.

Intermission

A NEW EQUATION OF STATE FOR SOLID ortho-HYDROGEN

TIECHENG WANG, ROBERT J. LE ROY, PIERRE-NICHOLAS ROY, Center for Graduate Work in Chemistry and Biophysics, University of Waterloo, Waterloo, Ontario, Canada.

Solid para-H$_2$O is a popular accommodating host for impurity spectroscopy due to its unique softness and the spherically symmetric of para-H$_2$O in its J=0 rotational level. To simulate the properties of impurity-doped solid para-H$_2$O, a reliable model for the "soft" pure solid para-H$_2$O at different pressures is highly desirable. While a couple of experimental and theoretical studies aimed at elucidating the equation of state (EOS) of solid para-H$_2$O have been reported, the calculated EOS is shown to be highly dependent on the potential energy surface (PES) between two para-H$_2$O that was used in the simulations. The current study also demonstrates that different choices of the parameters governing the Monte Carlo simulation could produce different EOS curves.

To obtain a reliable model for solid pure para-H$_2$O, we used a new 1-D para-H$_2$O PES reported by Faruk et al. that was obtained by averaging over Hinde's highly accurate 6-D H$_2$O PES. The EOS of pure solid para-H$_2$O was calculated using the PIMC algorithm with periodic boundary conditions (PBC). To precisely determine the equilibrium density of solid para-H$_2$O, both of the PIMC time step $\epsilon$ and the number of particles in the PBC cell were extrapolated to convergence. The resulting EOS agreed well with experimental observations, and the hsp structured solid para-H$_2$O was found to be more stable than the fcc one at 4.2K, in agreement with experiment. The vibrational frequency shift of para-H$_2$O as a function of the density of the pure solid was also calculated, and the value of the shift at the equilibrium density is found to agree well with experiment.
**REACTIVE INTERMEDIATES IN He NANODROPLETS: INFRARED LASER STARK SPECTROSCOPY OF DHYDROXYCARBENE**

BERNADETTE M. BRODERICK, CHRISTOPHER P. MORADI, GARY E. DOUBERLY, Department of Chemistry, University of Georgia, Athens, GA, USA; LAURA MCCASLIN, JOHN F. STANTON, Department of Chemistry, The University of Texas, Austin, TX, USA.

Singlet dihydroxyacarbene (HOOC) is produced via pyrolytic decomposition of oxalic acid, captured by helium nanodroplets, and probed with infrared laser Stark spectroscopy. Vibrational bands in the OH stretch region are assigned to either trans- or cis-trans- rotamers on the basis of symmetry type. Nuclear spin statistical weights, and comparisons to electronic structure theory calculations. Stark spectroscopy provides the inertial components of the permanent dipole moments for these rotamers. The dipole components for trans-trans- and trans-cis- rotamers are $\mu_{zz} = 0.00$, $1.60(6)$, and $(1.63(3), 1.50(5))$ respectively. The infrared spectra lack evidence for the higher energy cis-cis- rotamer, which is consistent with a previously proposed pyrolytic decomposition mechanism of oxalic acid and computations of HOOC torsional interconversion and tautomerization barriers.

**INFRARED LASER STARK SPECTROSCOPY OF THE PRE-REACTIVE Cl−HCI COMPLEX FORMED IN SUPERFLUID He DROPLETS**

CHRISTOPHER P. MORADI, GARY E. DOUBERLY, Department of Chemistry, University of Georgia, Athens, GA, USA.

Chlorine atoms, generated through the thermal decomposition of Cl₂, are solvated in superfluid helium nanodroplets and characterized with ClH₂ molecules. The Cl-H stretch modes of these clusters are probed via infrared laser spectroscopy. A broad band centered at $2880.9 \text{ cm}^{-1}$ is assigned to the binary Cl−HCI complex. The band center is red shifted by only 74 cm$^{-1}$ from the "free" HCl stretch (v₁) of (HCl)₂ and, as such, is consistent with an assignment to a similarly "free" HCl stretch. Also, the breadth of the band ($\sim 22 \text{ cm}^{-1}$ FWHM) is consistent with a assignment to a modestly b-type component of the H-Cl stretch; the band is lifetime broadened to the extent that it is predominantly b-type v₁ stretch of (HCl)₂, due to fast rotational relaxation facilitated by the helium droplet environment. Despite the lack of rotational structure, which would verify our assignment, the spectrum is consistent with stabilization of a weakly-bound complex having an L-shaped geometry. Computations reveal that the projection of the transition dipole moment onto the a-axis results in a dramatic decrease ($\sim 700$ times) in the intensity of the a-type band relative to the b-type band intensity, indeed, the signal-to-noise ratio in our experiment implies that the a-type band is not observed. No bands were observed that could derive from a strongly H-bonded Cl−HCI complex. Additionally, we located two bands at 2764.0 and 2798.5 cm$^{-1}$ that are consistent with the pick-up of two HCl molecules and are therefore assigned to vibrations of the Cl−(HCl)₂ complex.

**HELIUM NANODROPLET INFRARED SPECTROSCOPY OF THE TROPYL RADICAL**

MATIN KAUFMANN, Physicalische Chemie II, Ruhr University Bochum, Bochum, Germany; BERNADETTE M. BRODERICK, GARY E. DOUBERLY, Department of Chemistry, University of Georgia, Athens, GA, USA.

Helium nanodroplet spectroscopy is a well-established experimental technique to study weakly bound complexed and reactive species. The superfluid helium interacts weakly with the embedded species, leading to only small matrix-induced shifts in vibrational spectra. This technique has been applied for the spectroscopic study of the resonance-stabilized allyl radical and its reactions and complexes.¹ ² The tropyl radical is another example of a π-accepting radical, being of a reaction intermediate in organic chemistry. Having an electron in a pair of degenerate orbitals, its geometry is subject to the Jahn-Teller effect.¹ The Jahn-Teller distortion of the ground electronic state is probed with IR laser spectroscopy.


**MICROSOLVATION STUDIES IN HELIUM NANODROPLETS**

GERHARD SCHWAAB, MATIN KAUFMANN, DANIEL LEICHT, RAFFAEL SCHWAN, THEO FISCHER, DEVENDRA MANI, MARTINA HAVENITH, Physikalische Chemie II, Ruhr University Bochum, Bochum, Germany.

In bulk aqueous solutions the interactions between solute and solvent are still not fully understood. We apply spectroscopy in Helium nanodroplets to investigate solvation processes step by step (bottom up approach). Recently, the Bochum helium nanodroplet spectrometer has been equipped with a quantum cascade laser spanning the frequency range from 1000–1400, 1600–1700, and 2500–2600 cm$^{-1}$. First results with the extended setup will be presented.

**MICROSOLVATION STUDIES IN HELIUM NANODROPLETS**

GERHARD SCHWAAB, MATIN KAUFMANN, DANIEL LEICHT, RAFFAEL SCHWAN, THEO FISCHER, DEVENDRA MANI, MARTINA HAVENITH, Physikalische Chemie II, Ruhr University Bochum, Bochum, Germany.

The van der Waals complex of H₂O with Cl₂ has attracted considerable theoretical interest since it is a typical example of a weak binding complex (less than 5 kcal/mol), but a very few IR data are available in gas. For these reasons, we have studied in solid neon hydrogen bonded complexes involving carbon dioxide and water molecules. Evidence for the existence of at least three (Cl₂O)₅, (HCl)₂O, or m:n complexes has been obtained from the appearance of many new absorptions near the well-known monomers fundamental transitions. Concentration effects and detailed vibrational analysis allowed identification of fifteen, eleven and four transitions for the 1:1, 1:2, and 2:1 complexes, respectively. Careful examination of the far infrared allows the assignment of several 1:1 and 1:2 intermolecular modes, confirmed by the observation of combinations of intra-intermolecular transitions. All of these results significantly increase the number of one and, especially, two quanta vibrational transitions observed for these complexes, and anharmonic coupling constants have been derived. This study shows the high sensitivity of the solid neon isolation for the spectroscopy of the hydrogen-bonded complexes since two quanta transitions can’t be easily observed in gas phase.

**MATRIX ISOLATION AND COMPUTATIONAL STUDY OF [2C₂N. X] (X=S, SE) ISOMERS**

TAMAS VOROS, GYORGY TARCZAY, Institute of Chemistry, Eotvos University, Budapest, Hungary.

The [2C₂N. S] and the [2C₂N. Se] systems were investigated by quantum chemical computations and matrix isolation IR spectroscopy. For both systems nine isomers were computationally investigated, for which harmonic and anharmonic vibrational wavenumbers and infrared (IR) intensities were calculated using the CSCD/cc-pVTZ level of theory. The results show that each of the isomers has two or more detectable bands in the mid IR region, which have one or two orders of magnitude larger intensity compared to the IR intensity of the most intense bands of the most stable NCSCN and NCS(Se)CN isomers. It follows that if the most stable isomer can be detected, then the other previously unobserved isomers generated from NCSCN or NCS-SeCN should also be detectable with IR spectroscopy. UV spectra were also computed for each isomer at the TD-DFT B3LYP/cc-pVTZ level of theory. These computations showed that the most stable isomers (NCSCN and NCS(Se)CN) can absorb the UV radiation around 250 nm, and the irradiation may promote photoisomerization. This means that if the initial isomers are irradiated by near-band UV radiation, new isomers may be generated, which likely decompose by irradiating broad-band UV radiation.

The two most stable isomers, sulphur dicyanide (NCSCN) and selenium dicyanide (NCS(Se)CN), were prepared following literature methods. The matrix isolation IR spectra of these molecules in Ar and Kr were measured for the first time. As a result of a selective 254 nm-irradiation of the deposited matrices some new bands appeared in the IR spectra, while the intensity of the bands of NCSCN or NCS(Se)CN were decreased at the same time. Irradiation of the matrices with broad-band UV light decreased the intensity of the bands corresponding to the deposited isomers and some of the bands appeared on the 254 nm-irradiation. On the basis of the analysis of the formation rates of the different bands upon 254 nm photoisomerisation and by comparison with the results of the quantum chemical calculations these bands could be assigned to new isomers. In the case of sulphur analogue NCSSC and NCSNCS were unambiguously identified, and for selenium analogue the formation of NCS(Se)SC and NCS(Se)NCSC isomers were observed.
MATRIX ISOLATION SPECTROSCOPY AND PHOTOCHEMISTRY OF TRIPLET 1,3-DIMETHYLPROPYNILIDENE (MeCMe)

STEPHANIE N. KNEZ, Department of Chemistry, The University of Wisconsin, Madison, WI, USA; TERESE A. WALTZ, Department of Geoscience, and Physics, Edgewood College, Madison, WI, USA; BEN-JAMES C. HAENN, Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA; NICOLO J. BURRMANN, Department of Chemistry, Heartland Community College, Normal, IL, USA; ROBERT J. McMAHON, Department of Chemistry, The University of Wisconsin, Madison, WI, USA.

Acetylenic carbones and conjugated carbon chain molecules of the HC\_H family are relevant to the study of combustion and chemistry in the interstellar medium (ISM). Propynilidene (HC\_H) has been thoroughly studied and its structure and photochemistry determined. Here, we produce triplet diradical 1,3-dimethylpropynilidene (MeCMe) photochemically from a precursor diazo compound in a cryogenic matrix (N\_2 or Ar) at 10 K, and spectroscopic analysis is carried out. The infrared, electronic absorption, and electron paramagnetic resonance spectra were examined in light of the parent (HC\_H) system to ascertain the effect of alkyl substituents on delocalized carbon chains of this type. Computational analysis, EPR, and infrared analysis indicate a triplet ground state with a quasilinear structure. Further experimental and computational results pertaining to the structure and photochemistry will be presented.

EVIDENCE OF INTERNAL ROTATION IN THE O-H STRETCHING REGION OF THE 1:1 METHANOL–BENZENE COMPLEX IN AN ARGON MATRIX

JAY AMICANGELO, VAN CAMPBELL, JOSHUA WILKINS, School of Science (Chemistry), Penn State Erie, Erie, PA, USA.

Co-depositions of methanol (CH\_3OH) and benzene (C\_6H\_6) in an argon matrix at 20 K result in the formation of a 1:1 methanol-benzene complex (CH\_3OH\_2C\_6H\_6) as evidenced by the observation of distinct infrared bands attributable to the complex near the O-H and C-O stretching fundamentals of C\_6H\_6 and the hydrogen out-of-plane bending fundamental vibration of CH\_3OH. Co-deposition experiments were also performed using isotopically labeled methanol (CH\_3\_2D\_2) and benzene (C\_6H\_6\_2D) and the corresponding deuterated complexes were also observed. Based on an initial density functional theory calculations, the structure of the complex is thought to be an H\_2O complex in which the CH\_3OH is above the C\_6H\_6 ring with the OH hydrogen atom interacting with the x y cloud of the ring. Close inspection of the O-H and O-D stretching peaks of the complexes reveals small, distinct satellite peaks that are approximately 3 – 4 cm\(^{-1}\) lower than the primary peak. A series of experiments have been performed to ascertain the nature of the satellite peaks. These consist of co-depositions in which the concentrations of both monomers were varied over a large range (1:200 to 1:1600 S:R/M ratios), annealing experiments (20 K to 35 K), and lower temperature cycling experiments (20 K to 8 K). Based on the results of these experiments, it is concluded that the satellite peaks are due to rotational structure and not due to matrix site effects, higher aggregation or distinct complex geometries. Given the rigidity of a low temperature argon matrix, it is proposed that the rotational motion responsible for the satellite peaks is internal rotation within the methanol subunit of the complex rather than overall molecular rotation of the complex.

SIGN CHANGE IN THE ELECTRIC DIPOLE MOMENT OF EXCITED STATES IN RUBIDIUM–ALKALINE EARTH DIATOMIC MOLECULES

JANNA M. D. WITTMANN, Institute of Physical Chemistry, ETH Zürich, Zurich, Switzerland; PETR HAJEK, Institute of Atomic and Molecular Physics, National Research Centre, Prague, Czech Republic; ANTOINE BERNARD, Department of Chemistry, University of California, Los Angeles, CA, USA; ANDREAS W. HAUSER, WOLFGANG E. ERNST, Institute of Physical Chemistry, Göttingen University, Göttingen, Germany; ANDREAS W. HAUSER, WOLFGANG E. ERNST, Institute of Physical Chemistry, Göttingen University, Göttingen, Germany.

In a recent series of combined experimental and theoretical studies we investigated the ground state and several excited states of the Rb\_2Ca molecule using a variety of electronic and vibrionic spectroscopic techniques. The group of alkali-alkaline-earth (AK-AKE) molecules has drawn attention for applications in ultracold molecular physics and the measurement of fundamental constants due to their large permanent electric and magnetic dipole moments in the ground state. These properties should allow for an easy manipulation of the molecules and simulations of spin models in optical lattices. In our studies we found that the permanent electric dipole moment points in different directions for certain electronically excited states, and changes the sign in some cases as a function of bond length. We summarize our results, give possible causes for the measured trends in terms of molecular orbital theory and extrapolate the tendencies to other combinations of AK and AKE - elements.
HIGH RESOLUTION VELOCITY MAP IMAGING PHOTOELECTRON SPECTROSCOPY OF THE BERYLLIUM OXIDE ANION, BeO-

AMANDA REED, KYLE MASCARITOTO, MICHAEL HEAVEN, Department of Chemistry, Emory University, Atlanta, GA, USA.

The photodetachment spectrum of BeO+ has been studied for the first time using high resolution velocity map imaging photoelectron spectroscopy. Vibrational contours were imaged and compared with Franck-Condon simulations for the ground and excited states of the neutral. The first measured electron affinity of BeO+ and anisotropies of several transitions were also measured. Experimental findings are compared to high level ab initio calculations.

INTERMISSION

ELECTRONIC AUTODETACHMENT SPECTROSCOPY AND IMAGING OF THE ALUMINUM MONOXIDE ANION, AlO-

AMANDA REED, KYLE MASCARITOTO, ADRIAN GARDNER, MICHAEL HEAVEN, Department of Chemistry, Emory University, Atlanta, GA, USA.

The Σ+ − Σ+ ground state to dipole bound state electronic transition of AlO+ has been studied with both rotationally resolved autoionization spectroscopy and high resolution velocity map imaging photoelectron spectroscopy in a newly constructed apparatus. Vibrational and rotational molecular constants have been determined for both the ground state (ν = 0) and excited dipole bound state (ν = 0.1) of the aluminum monoxide anion. The spectra yield the electron binding energy of the dipole bound state, and a more accurate electron affinity for AlO. The photoelectron anisotropies of several transitions were measured. Experimental findings are compared to high level ab initio calculations. Additionally, high resolution photodetachment imaging of AlO+ Σ+ − Σ+ within energy ranges well above the detachment threshold were measured and compared to previous, low resolution photodetachment results.

SPECTROSCOPY OF THE LOW-ENERGY STATES OF BaO+

JOSHUA BARTLETT, ROBERT A. VANGUNDY, MICHAEL HEAVEN, Department of Chemistry, Emory University, Atlanta, GA, USA.

The BaO+ cation is a promising candidate for studies conducted at ultra-cold temperatures. It is known that the ion can be formed by the reaction of laser-cooled Ba+ with N2O or O2. Spectroscopic data are now needed for the BaO+ cation, for both characterization of the internal state population distributions and the design of population transfer schemes. We have obtained the first spectroscopic data for BaO+ using the pulsed-field ionization, zero kinetic energy (PFI-ZEKE) photoelectron technique. Two-color ionization was carried out via the A′Σ+ − XΣ+ transition of BaO. Vibrionic levels of the XΣ+ and A′Σ+ states of BaO+ have been characterized. The results are compared with the predictions of high-level electronic structure calculations.
Hydrocarbons such as ethylene (C\(_2\)H\(_4\)) and methane (CH\(_4\)) are of considerable interest for the modeling of planetary atmospheres and other astrophysical applications. Knowledge of rovibrational transitions of hydrocarbons is of primary importance in many fields but remains a formidable challenge for the theory and spectral analysis. Essentially two theoretical approaches for the computation and prediction of spectra exist. The first one is based on empirically-fitted effective spectroscopic models. Several databases aim at collecting the corresponding data but the information about C\(_2\)H\(_4\) is limited, only some spectral ranges around 1000, 3000 and 6000 cm\(^{-1}\) are available. Another way for computing energies, line positions and intensities is based on global variational calculations using \(\text{ab initio}\) surfaces. Although they do not yet reach the spectroscopic accuracy, they can provide reliable predictions which could be quantitatively accurate with respect to the precision of available observations and as complete as possible. All this thus requires extensive first-principles quantum mechanical calculations essentially based on two necessary ingredients: (i) accurate intramolecular potential energy surface and dipole moment surface components and (ii) efficient computational methods to achieve a good numerical convergence. We report predictions of vibrational and rovibrational energy levels of C\(_2\)H\(_4\) using our new ground state potential energy surface obtained from extended \(\text{ab initio}\) calculations\(^6\). Additionally we will introduce line positions and line intensities predictions based on a new dipole moment surface for ethylene. These results will be compared with previous works on ethylene and its isotopologues.


Naphthalene is one of the simple polycyclic aromatic molecule, and it is interesting that the excited state dynamics take place. To understand the excited state dynamics, rotationally resolved fluorescence excitation spectra of several vibrionic bands were measured\(^4\). In this work, we have measured high-resolution fluorescence excitation spectra across a single mode laser and molecular beam at light angle. Vibrionic bands, which lies 2866 cm\(^{-1}\) and 3068 cm\(^{-1}\) above the 0-0 band (0\(^0\)\(\rightarrow\) 0\(^0\) + 2866 cm\(^{-1}\) band and 0\(^0\)\(\rightarrow\) 0\(^0\) + 3068 cm\(^{-1}\) band), were measured. Absolute wavenumber was calibrated with accuracy 0.0002 cm\(^{-1}\) by the measurement of Doppler-free absorption spectrum of I\(_2\) molecule and transmitting light intensity of the stabilized etalon. Rotational lines of the 0\(^0\)\(\rightarrow\) 0\(^0\) + 2866 cm\(^{-1}\) band were almost resolved. A part of the rotational lines were assigned, and several energy shifts were found. On the other hand, rotational lines were not completely resolved for the 0\(^0\)\(\rightarrow\) 0\(^0\) + 3068 cm\(^{-1}\) band.


We demonstrate the potential of THz spectroscopy to monitor the real time evolution of the gas phase concentration of photolysis products and determine the kinetic reaction rate constant. In the primary work, we have chosen to examine the photolysis of formaldehyde (HCHO) in a jet. Exposure of HCHO to a UVB light (250 to 360 nm) in a single pass of 135 cm length cell leads to decomposition via two mechanisms: the radical channel with production of HOCO and the molecular channel with production of CO. A commercial THz source (frequency multiplication chain) operating in the range 600-900 GHz was used to detect and quantify the various chemical species as a function of time. Monitoring the concentrations of CO and HOCO via rotational transitions, allowed the kinetic rate of HOCO consumption to be obtained, and an estimation of the rate constants for both the molecular and radical photolysis mechanisms.

We have modified our experimental setup to increase the sensitivity of the spectrometer and changed sample preparation protocol specifically to quantify the HCO concentration. Acetaldehyde was used as the precursor for photolysis by UVC resulting in the decomposition mechanism can be described by:

\[ CH_3CHO \rightarrow CH_3 + HOCO \rightarrow CH_4 + CO + CO_2 \]

Frequency modulation of the source and Zeeman modulation is used to achieve the high sensitivity required. Particular attention has been paid to the mercury photosensitization effect that allowed us to increase the HOCO production enabling high-resolution rotational identification of the monitored radical. We quantify the HCO radical and start a spectroscopic study of the line positions.

It is well known that as molecules become larger the spectral lines of their high-resolution rotational spectra begin to merge, first into modest blends, then into clusters of many lines, and finally into continua. In addition to impacting specificity, the usual signal processing strategies used to separate spectral information from background become ineffective. Medium resolution Cavity Spectroscopy trades the usual excess of specificity of rotational spectroscopy for a means of obtaining spectra of large molecules with congested or semi-continua spectra. The chief scientific question to be answered is how to develop strategies to approach white noise sensitivity limits. Experimental details and results, and theoretical results will be presented.
Understand the molecular dynamics on buried electrodes under electrochemical transformations of is significant interest. There is a big gap of knowledge in the CO2 electroreduction mechanism due to the limitations to access and probe the liquid-metal interfaces [1, 2]. Vibrational Sum Frequency Spectroscopy (VSFS) is a non-invasive and surface sensitive technique, with molecular level detection that can be used to probe electrochemical reactions occurring on the electrolyte-electrode interface [2]. We observed the CO2 electroreduction to CO in ionic liquids (ILs) on poly Ag using VSFS synchronized with cyclic voltammetry. In order to follow the CO2 reduction on the ionic liquid-Ag interface, the CO2, CO, and imidazolium vibrational modes (resonant SFS) were monitored as a function of potential. We identified at which potential the CO was produced and how the EMIM-BF4 played an important role in the electron transfer to the CO2, lowering the CO2 energy barrier. A new approach to reveal the double layer dynamics to the electrostatic environment is presented by the study of the nonresonant sum frequency intensity as a function of the applied potential. By this method, we studied the influence of water-ionic liquid mixtures in the CO2 electroreduction on Ag electrode. We observed a shift to lower potentials in the CO2 electroreduction in water-ILs electrolyte. Previous studies in gas diffusion cells have shown the CO2 electroreduction in a water-imidazolium-based ILs on Ag nanoparticles at lower overpotential [3]. Our VSFS study helps to understand the fundamental electrochemical mechanism, showing how the ILs structural transition influences the CO2 electroreduction.


Intermission

ELUCIDATING THE COMPLEX LINESHAPES RESULTING FROM THE HIGHLY SENSITIVE, ION SELECTIVE, TECHNIQUE NIC-EHVMS

JAMES N. HODGES, BRIAN SILLER. Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA; BENJAMIN J. MCCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL, USA.

The technique Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy, or NIC-EHVMS, has been used to great effect to precisely and accurately measure a variety of molecular ion transitions from species such as H2, CH2, H2O, and H2O2, achieving MHz or in some cases sub-MHz uncertainty.6,7 It is a powerful technique, but a complete theoretical understanding of the complex NIC-EHVMS lineshape is needed to fully unlock its potential. NIC-EHVMS is the direct result of the combination of the highly sensitive spectroscopic technique Noise Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NIC-OHMS) with Velocity Modulation Spectroscopy (VMS), applying the most sensitive optical detection method with ion species selectivity.6 The theoretical underpinnings of NIC-EHVMS lineshapes are well established,6,7 as are those of VMS.6 This presentation is the logical extension of those two preceding bodies of work. Simulations of NIC-EHVMS lineshapes under a variety of conditions and fits of experimental data to the model are presented. The significance and accuracy of the various inferred parameters, along with the prospect of using them to extract additional information from observed transitions, are discussed.

FC. Comparing theory and experiment

Friday, June 26, 2015 – 8:30 AM
Room: B102 Chemical and Life Sciences
Chair: Edwin Sibert, The University of Wisconsin, Madison, WI, USA

FC01
8:30 – 8:45
VIBRATIONAL COUPLING IN SOLVATED FORM OF EIGEN PROTON
JHENG-WEI LI, KAITO TAKAHASHI, JER-LAI KUO
Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

The most simple solvated proton, the hydronium ion H₃O⁺ has been studied experimentally in its bare case as well as with the messenger techniques. Recent studies have shown that features in the vibrational spectra can be modulated not only by the different messengers, but also by the number of messengers. Theoretical molecular dynamics simulations have shed light on the H₂O (H₂O₃) clusters, but understanding on the effect of microsolvation by the messenger toward the spectra is still far from complete. We compare the experimental H₃O⁺ Arn, n=1-3 spectra with accurate theoretical simulations and obtain the peak position and absorption intensity by solving the quantum vibrational Schrödinger equation using the potential and dipole moment obtained from DFT methods. One of the main goals of the study is to glean into the vibrational couplings induced by the microsolvation by the argon on the spectra region of 1500-3800 cm⁻¹, and to provide assignment on the peaks observed in these regions.

FC02
8:47 – 9:02
BINDING BETWEEN NOBEL GAS ATOMS AND PROTONATED WATER MONOMER AND DIMER
YING-CHENG LI, JER-LAI KUO
Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

H₂O and H₂O⁺, Eigen and Zundel forms of the excess proton, are the basic moieties of hydrated proton in aqueous media. Using vibrational pre-disortion spectra, vibrational spectra of messenger-tagged species are often measured; however, only neat species have been studied in detail by theoretical and computational means. To bridge this gap, we carry out extensive CSE/SCT-angle-space-pTZ calculations to investigate the binding between commonly used noble gas (NG) messengers (He, Ne or Ar) with H₂O and H₂O⁺ to get an accurate estimate on the binding energy which yields the upper limits of vibrational temperature of NG-tagged clusters. The binding sites of NG and low-lying transition states have also been searched to give a better description on the energy landscape. In addition, a few exchange/correlation functionals have been tested to access the accuracy of these methods for future and more sophisticated theoretical studies.

FC03
9:04 – 9:19
ANALYSIS OF HYDROGEN BONDING IN THE OH STRETCH REGION OF PROTONATED WATER CLUSTERS
LAURA C. DZUGAN, ANNE B. MCCOY
Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA.

There are two types of bands in the OH stretch region of the vibrational spectra of hydrogen-bonded complexes; narrow peaks due to isolated OH stretches and a broadened feature reflecting the OH stretches involved in strong hydrogen bonding. This second region can be as wide as several hundred wavenumbers and is shifted to the red of the narrow peaks. In this work we focus on Hₙ(OH)₂, n = 3 or 4. Both of these systems exhibit a very intense, broad-band bond. This breadth arises from coupling between the OH stretches and the low frequency modes. To understand the broadening observed in the spectra, we have developed a computational scheme in which we sample displacement geometries from the equilibrium structure based on the ground state harmonic wavefunction. Then we combine the harmonic spectra in the OH stretch region for each computed geometry to generate the spectrum for each protonated water structure. Based on the large anharmonicities at play in these modes, we extend the approach using second-order perturbation theory to solve the reduced-dimensional Hamiltonian that involves only the HOH bends and the OH stretches. This is done by expressing the normal modes used to expand the Hamiltonian as linear combinations of internal coordinates. In this talk we will describe the approach used for these anharmonic calculations and report preliminary results for these protonated water clusters.

FC04
9:21 – 9:36
SEMIXPERIMENTAL STRUCTURE OF THE NON-RIGID BF₂OH MOLECULE BY COMBINING HIGH RESOLUTION INFRARED SPECTROSCOPY AND AB INITIO CALCULATIONS.
NATALIA VOKT, JEAN DEMAISON, Section of Chemical Information Systems, Universität Ulm, Ulm, Germany; AGNES PERRIG, LISA, CNRS, Universités Paris Est Créteil et Paris Diderot, Créteil, France; HANS BURGER, Anorganische Chemie, Bergische Universität Wuppertal, Wuppertal, Germany.

In BF₂OH, difluorosilicic acid, the OH group is subject of a large amplitude torsion motion which induces a splitting in the rotational spectrum as well as in the high-resolution infrared spectrum. It is interesting to check whether it is still possible to determine a semiexperimental equilibrium structure for such a molecule. For this goal, the rotation-vibration interactions constants have been experimentally determined by analyzing all the fundamental bands. They have also been computed ab initio using two different levels of theory. The results of the analysis as well as the determination of the structure will be reported.

FC05
9:38 – 9:48
CONFORMATIONAL, VIBRATIONAL AND ELECTRONIC PROPERTIES OF CHS₄XOH (X = H, F, Cl or Br): HALOGEN AND SOLVENT EFFECTS
MUSTAFA SENYEL, Department of Physics, Anadolu University, Eskisehir, Turkey; GUNES ESMA, Physics, Anadolu University, Eskisehir, TURKEY; CEMAL PARLAK, Physics, Dumlupınar University, Kütahya, TURKEY.

The effects of halogen and solvent on the conformer, vibrational and electronic properties of thiophene-2-carbalddehyde (CSH₄OH) and thiophene-2-carboxyl-halogenates (CS₄XOH; X = F, Cl or Br) were investigated employing the DFT and TD-DFT methods. The B3LYP functional was used with the 6-31+G(d,p) basis set. Computations were focused on the two conformational isomers of the compounds in the gas phase and both in a non-polar solvent and in a polar solvent. The present work explores the effects of both the halogen and the medium on the conformational preference, geometrical parameter, dipole moment, vibrational spectra, UV spectrum and HOMO-LUMO orbital. The findings of this work can be useful to those systems involving changes in the conformations analogous to the compounds studied.

FC06
9:50 – 10:05
COMBINED EXPERIMENTAL AND THEORETICAL STUDIES ON THE VIBRATIONAL AND ELECTRONIC SPECTRA OF 5-QUINOLINECARBOXALDEHYDE
MUSTAFA KUMRU, MUSTAFA KOCADEMIR, TAYYIBE BARDAKCI, Department of Physics, Fatih University, Istanbul, Turkey.

Theoretical and experimental investigations have been performed on the structure, vibrational and electronic spectra of 5-quinolinocarboxaldehyde (5QC). The 4000-5000 cm⁻¹ region was studied by FT-IR and FT-Raman and the 1900-1100 nm region UV-Vis spectra of 5QC were recorded at the room temperature. Structural and spectroscopic properties of the cis and trans conformers of 5QC were calculated by Hartree-Fock (HF) and B3LYP density functional methods using the 6-31+G(d,p) basis set. Although calculated B3LYP frequencies are found to be closer to the experimental frequencies than the HF calculation results, scaled frequencies of both HF and B3LYP levels are in good agreement with the experimental data. The time-dependent density functional theory (TDDFT) is also used to find excitation energies, absorption wavelength, oscillator strengths and HOMO and LUMO energies of the title molecule.

Keywords: FT-IR, FT-Raman, and UV-vis spectra, HF, DFT, HOMO-LUMO.

Intermission

FC07 10:24 – 10:39
COMBINED COMPUTATIONAL AND EXPERIMENTAL STUDIES OF THE DUAL FLUORESCENCE IN DIMETHYLAMINOBENZONITRILE (DMABN)

ANASTASIA EDESELL, STEVEN SHIPMAN, Department of Chemistry, New College of Florida, Sarasota, FL, USA

The dual fluorescence of dimethylaminobenzonitrile (DMABN) has been investigated since the 1960s. Despite more than 50 years of previous research, the spatial configuration of the excited state causing the dual fluorescence is still controversial. We have performed excited state calculations of DMABN in a variety of solvents of varying hydrogen-bonding affinity and polarity using implicit solvation (COSMO-PCM) at the M06-HF level of theory, and we have also collected steady-state absorption and fluorescence spectra of DMABN in these solvents. Our experimental spectra are broadly consistent with previous work, and the computational results show a significant solvent dependence.

FC08 10:41 – 10:56
MODELING SPIN-ORBIT COUPLING IN THE HALOCARBENES

PHALGUN LOLUR, RICHARD DAWES, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA; SCOTT REID, SILVER NYAMBO, Department of Chemistry, Marquette University, Milwaukee, WI, USA

Halocarbenes are organic reactive intermediates with a neutral divalent carbon atom that is covalently bonded with a halogen and another substituent. Being the smallest carbenes that exhibit closed shell ground states, they have contributed greatly to our understanding of the reactivity of singlet carbene species and the factors that contribute to singlet-triplet energy gaps. We report an analysis of spin-orbit coupling in the mono-halocarbenes, CHBrX, where X = Cl, Br, I; Single Vibronic Level (SVL) emission spectroscopy and Stimulated Emission Pumping (SEP) spectroscopy have been used to probe the ground vibrational level structures in these carbene which have indicated the presence of perturbations involving the low-lying triplet state. In this talk, we present two approaches to model these interactions. Anharmonic constants, singlet-triplet gaps and geometry-dependent spin-orbit (SO) coupling surfaces were computed using high-level explicitly correlated methods such as CCSD(T)-F12b and MRCCF12. These were used to evaluate SO coupling matrix elements and hence predict the mixed-perturbed singlet-triplet experimental levels. Results are also compared to those from a simpler model using a geometry-independent SO-constant.

FC09 10:58 – 11:13
GAS-PHASE CONFORMATIONS AND ENERGETICS OF PROTONATED 2′-DEOXYADENOSINE-5′-MONOPHOSPHATE AND ADENOSINE-5′-MONOPHOSPHATE: IRMPD ACTION SPECTROSCOPY AND THEORETICAL STUDIES

RANRAN WU, Y-W NEI, CHENCHEN HE, LUCAS HAMLow, Department of Chemistry, Wayne State University, Detroit, MI, USA; GIEL BERDEN, J. OOMEN, Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands; M T RODGERS, Department of Chemistry, Wayne State University, Detroit, MI, USA

Nature uses protonation to alter the structures and reactivities of molecules to facilitate various biological functions and chemical transformations. For example, in nucleobase repair and salvage processes, protonation facilitates nucleobase removal by lowering the activation barrier for glycosidic bond cleavage. Systematic studies of the structures of protonated 2′-deoxyribonucleotides and ribonucleotides may provide insight into the roles protonation plays in altering the nucleobase orientation relative to the glycosidic bond and sugar puckering. In this study, infrared multiple photon dissociation (IRMPD) action spectroscopy experiments in conjunction with electronic structure calculations are performed to probe the effects of protonation on the structures and stabilities of 2′-deoxyadenosine-5′-monophosphate (pdAdo) and adenosine-5′-monophosphate (pdA). Photodissociation as a function of IR wavelength is measured to generate the IRMPD action spectra. Geometry optimizations and frequency analyses performed at the B3LYP/6-311+G(d,p) level of theory are used to characterize the stable low-energy structures and to generate their linear IR spectra. Single point energy calculations performed at the B3LYP/6-311+G(3d,2p) and MP2(full)/6-311+G(3d,2p) levels of theory provide relative stabilities of the optimized conformations. The structures accessed in the experiments are determined by comparing the calculated linear IR spectra for the stable low-energy conformers computed to the measured IRMPD action spectra. The effects of the 2′-hydroxyl moiety are elucidated by comparing the structures and IRMPD spectra of [pdAdo+H] 2+ to those of its DNA analogue. Comparisons are also made to the deprotonated forms of these nucleotides and the protonated forms of the analogous nucleosides to elucidate the effects of protonation and the phosphate group on the structures.
FD01
Observation of the simplest Criegee Intermediate CH$_3$OO in the Gas-Phase Ozonolysis of Ethylene

CARRIE WOSNACK, Department of Chemistry, MIT, Cambridge, MA, USA; MARIE-ALINE MARTIN-DRUMEL, Spectroscopy Lab, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; GORDON G BROWN, Department of Science and Mathematics, Coker College, Hartsville, SC, USA; ROBERT W FIELD, Department of Chemistry, MIT, Cambridge, MA, USA; MICHAEL C McCARTHY, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA.

Criegee intermediates (H$_2$R$_2$OO) are understood to be critical intermediates in the ozonolysis of alkenes, but their high reactivity has traditionally made them very difficult to study directly. Although the smallest Criegee intermediates have now been generated in the laboratory using a diiodomethane photolysis scheme, numerous questions still remain about the product branching ratios of Criegee intermediates formed directly from ozonolysis. This talk will discuss our recent detection of the simplest Criegee intermediate, CH$_3$OO, in the ozonolysis of ethylene, using Fourier transform microwave spectroscopy and a modified pulse nozzle. Nine other product species of the reaction were also detected, in abundances that qualitatively support the published mechanisms and rate constants.

FD02
High-Resolution Spectra of CH$_3$OO: Assignments of ν$_3$ and 2ν$_2$ Bands and Overlapped Bands of IClOO

YU-HUAN HUANG, LI-WEI CHEN, YUAN-PERN LEE, Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan.

The simplest Criegee intermediate CH$_3$OO, important in atmospheric chemistry, has recently been detected with infrared (IR) absorption in the reaction of CH$_3$I + O$_3$. We have recorded high-resolution infrared spectrum of CH$_3$OO with rotational lines partially resolved. In addition to deriving some critical spectral parameters to confirm the previous assignments of ν$_3$ at 1234.1 cm$^{-1}$, ν$_2$ at 1285.7 cm$^{-1}$, ν$_3$ at 999.2 cm$^{-1}$, and ν$_3$ at 847.4 cm$^{-1}$, the high-resolution spectra enable us to assign with confidence the 2ν$_2$ at 1233.5 cm$^{-1}$ and ν$_2$ at 1233.0 cm$^{-1}$. Observed vibrational wavenumbers, relative intensities, and rotational structures agree well with those predicted by high-level quantum calculations. Some hot bands and combination bands are also observed. We also recorded the IR spectrum of IClOO under high-pressure conditions. Observed IR intensities and vibrational wavenumbers of 1233.8 (ν$_3$), 1221 (ν$_3$), 1087 (ν$_3$), and 923 (2ν$_3$) cm$^{-1}$ agree with those simulated according to theoretical predictions and those observed in solid-p-HF. The ν$_2$ band of IClOO interferes with the 2ν$_2$ band of CH$_3$OO even at pressure as low as 100 Torr. With direct detection of both CH$_3$OO and IClOO, we determined the pressure dependence of the yield of CH$_3$OO. The yield of CH$_3$OO near one atmosphere is greater than previous reports.

FD03
Direct Infrared Identification of the Criegee Intermediates syn- and anti-CH$_3$CHO and Their Distinct Conformation-Dependent Reactivity

HUI-YULIN, YU-HSUAN HUANG, Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan; XI-AOHONG WANG, JOEL BOWMAN, Department of Chemistry, Emory University, Atlanta, GA, USA; YOSHI-FUMI NISHIMURA, HENRY A WITEK, YUAN-PERN LEE, Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan.

The Criegee intermediates are carbonyl oxides that play critical roles in ozonolysis of alkenes in the atmosphere. Su et al. reported the mid-infrared spectrum of the simplest Criegee intermediate CH$_3$CHO$_2$. Methyl substitution of CH$_3$OO produces two conformers of CH$_3$CHO and consequently complicates the infrared spectrum. We report the transient infrared spectrum of both syn- and anti-CH$_3$CHO$_2$ produced from CH$_3$CH + O$_3$ in a flow reactor, using a step-scan Fourier-transform spectrometer. Guided and supported by high-level full-dimensional quantum calculations, rotational contours of the four observed bands are simulated successfully and provide definitive identification of both conformers. Although nearly all observed bands of anti-CH$_3$CHO$_2$ overlapped with syn-CH$_3$CHO$_2$, the Q-branch of ν$_3$ near 1090.6 cm$^{-1}$ is contributed solely by syn-CH$_3$CHO$_2$, and that of ν$_2$ near 1280.8 cm$^{-1}$ is also dominated by syn-CH$_3$CHO$_2$. Furthermore, anti-CH$_3$CHO$_2$ shows a reactivity greater than syn-CH$_3$CHO$_2$ toward NO/NO$_2$ at the later period of reaction, the spectrum can be simulated with only syn-CH$_3$CHO$_2$. Without NO/NO$_2$, anti-CH$_3$CHO$_2$ also decays much faster than syn-CH$_3$CHO$_2$. The direct infrared detection of syn- and anti-CH$_3$CHO$_2$ should prove useful for field measurements and laboratory investigations of the Criegee mechanism.

FD04
The $\Lambda$ Electronic Transitions of the CH$_3$BrOO and CH$_3$CIOO Radicals in the Near Infrared Region

NEAL KLINE, MING HUANG, TERRY A MILLER, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA.

Moderate resolution cavity ring-down spectroscopy (CRDS) is used to obtain the $\Lambda$-electronic transition of the CH$_3$BrOO and CH$_3$CIOO radicals in the near-infrared region at room temperature. The CH$_3$BrOO radical was generated by 248nm excimer laser photolysis of a gas mixture of CH$_3$Br$_2$, O$_2$, and inert gas. The CH$_3$CIOO radical was generated similarly except for using CH$_3$Cl as the precursor. In both spectra, the first strong transition is located near 6800 cm$^{-1}$, and is assigned as the origin band. Several transitions are observed in the region between the origin and 9900 cm$^{-1}$. A strong vibrational transition is observed around 800 cm$^{-1}$ to the blue of the origin and attributed to the OOO stretch which is characteristic of the peroxy radical spectra. Our analysis of the vibrational structure is conducted using frequencies and Franck-Condon factors based on electronic structure calculations. Rotational structure analyses with ab-initio calculated rotational constants and dipole moments show good agreement with the contour of the origin band. Numerous transitions around the origin band in the CH$_3$BrOO radical spectrum can be explained by excitation from low-lying torsional levels in the $\Lambda$ state that are populated at room temperature.
THE A-X ELECTRONIC TRANSITION OF CH2IOO RADICAL IN THE NEAR INFRARED REGION

NEAL KLINE, MENG HUANG, TERRY A. MILLER, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA; PHALGUN LOULUR, RICHARD DAWES, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA.

In the past few years, the photolysis of CH3I in the presence of O2 has received much attention. It has been shown to be an attractive method for producing the Criegee intermediate, CH2O2. Under certain conditions the reaction is also expected to produce the iodomethyl peroxy radical, CH2IOO. Interestingly both species are expected to have electronic transitions in the near infrared (NIR). The transition in CH2O2 would be analogous to the A-X singlet-triplet transition in O2 and a NIR A-X transition in well-known to be characteristic of peroxo radicals. Notwithstanding the above, NIR spectra have not been reported for either CH2O2 or CH2IOO.

Based upon these considerations, we have performed the CH3I2 photolysis with O2 in the optical cavity of our room temperature cavity ringdown spectrometer and have discovered a spectrum in the NIR. Our recorded spectrum consists from a complex origin structure at ~6000 cm−1 to beyond 9000 cm−1. Aside from the origin its strongest feature is a similar, complex band at 870 cm−1 to the blue of it, which is likely an O-O stretch vibrational transition, which is present in peroxo radicals but might also be expected for CH2O2. With the aid of high-level ab initio calculations (described in detail in the subsequent talk) we have undertaken the analysis of the spectrum. We find that a spectral analysis, including a number of hot bands arising from populated torsional levels, is consistent with the electronic structure calculations for the A and X states of CH2IOO.

Intermission

JET-COOLED LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF T-BUTOXY

NEIL J. REILLY a, *, Department of Chemistry, University of Louisville, Louisville, KY, USA; LAN CHENG, JOHN F. STANTON, Department of Chemistry, The University of Texas, Austin, TX, USA; TERRY A. MILLER, Department of Chemistry, The Ohio State University, Columbus, OH, USA; MENG HUANG, NEAL KLINE, TERRY A. MILLER, Department of Chemistry, University of Louisville, Louisville, KY, USA.

The vibrational structures of the A-X and X-X states of t-butoxy were obtained in jet-cooled laser-induced fluorescence (LIF) and dispersive fluorescence (DF) spectroscopic measurements. The observed transitions are assigned based on vibrational frequencies calculated using Complete Active Space Self-Consistent Field (CASSCF) method and the predicted Franck-Condon factors. The spin-orbit (SO) splitting was measured to be 35(5) cm−1 for the lowest vibrational level of the ground (X-X) state and increases with increasing vibrational quantum number of the CO stretch mode. Vibronic analysis of the DF spectra suggests that Jahn-Teller (JT)-active modes of the ground-state t-butoxy radical are similar to those of methoxy and would be the same if methyl groups were replaced by hydrogen atoms. Coupled-cluster calculations show that electron delocalization, introduced by the substitution of hydrogens with methyl groups, reduces the electronic contribution of the SO splittings by only around ten percent, and a calculation on the vibronic levels based on quasidiabatic model Hamiltonian clearly attributes the relatively small SO splitting of the X-X state of t-butoxy mainly to stronger reduction of orbital angular momentum by the JT-active modes when compared to methoxy. The rotational and fine structure of the LIF transition to the first CO stretch overtone level of the A-X state has been simulated using a spectroscopic model first proposed for methoxy, yielding an accurate determination of the rotational constants of both A and X states.

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A THEORETICAL CHARACTERIZATION OF ELECTRONIC STATES OF CH2IOO AND CH2OO RADICALS RELEVANT TO THE NEAR IR REGION

RICHARD DAWES, PHALGUN LOULUR, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA; NEAL KLINE, TERRY A. MILLER, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA.

Criegee intermediates (R=RCO or Cl) arise from ozonolysis of biogenic and anthropogenic alkenes, which is an important process in the atmosphere. Recent breakthroughs in producing them in the gas phase have resulted in a flurry of experimental and theoretical studies. Producing the simplest CI (CH3I2O) in the lab via photolysis of CH2O2 in the presence of O2 yields both CH2OO and CH2IOO with pressure-dependent branching.

As discussed in the preceding talk, both species might be expected to have electronic transitions in the near IR (NIR). Here we discuss electronic structure calculations used to characterize the electronic states of both systems in the relevant energy range. Using explicitly correlated multireference configuration interaction (MRCl-F12) and coupled-cluster (CCSD(T)-F12b) calculations we were first able to exclude CH2OO as the carrier of the observed NIR spectrum. Next, by computing frequencies and relaxed full torsional scans for the A and X states, we were able to aid in analysis and assignment of the NIR spectrum attributed to CH2IOO.

Intermission

FD07 10:29 – 10:44

NITROSYL IODIDE, INO: MILLIMETER-WAVE SPECTROSCOPY GUIDED BY AB INITIO QUANTUM CHEMICAL COMPUTATION

STEPHANE BAILLEUX, DENIS DUFLLOT, Laboratoire PhLAM, Université de Lille - Sciences et Technologies, Villeneuve d’Ascq, France; SHOHEI AIBA, HIROYUKI OZEKI, Department of Environmental Science, Tokyo University, Funabashi, Japan.

In the series of the nitrosyl halides, XNO (where X = F, Cl, Br) have been well studied, both theoretically and experimentally. However, relatively little is known about the iodine-containing analogues, although they also are of potential importance in tropospheric chemistry. In 1991, the INO has received much attention. It has been shown to be an important process in the atmosphere, especially halogen and nitrogen oxides chemistry that adversely impacts ozone levels. In the family of the nitrogen oxyhalides such as nitrosyl (XNO), nitryl (NO), nitrite (ONO), and nitrate (ONO2), halides, those with X = F, Cl, Br have been well studied, both theoretically and experimentally. However, relatively little is known about the iodine-containing analogues, although they also are of potential importance in tropospheric chemistry. In 1991, the Fourier-transform IR spectroscopic detection of IND, INO2 and INO3NO in the gas phase has been reported t.

The INO molecule was generated by co-solvent mixing continuously I2 and NO in a 50-cm long reaction glass tube whose outlet was connected to the absorption cell using a tubin tube. At the time of writing this abstract, 68 μs-type transitions (ΔJ = 0 → 0 → -1), all weak, have been successfully assigned. The hyperfine structures due to both I and N nuclei will also be presented.

S.B. and D.D. acknowledge support from the Laboratoire d’Excellence CaPPA (Chemical and Physical Properties of the Atmosphere) through contract ANR-10-LABX-005 of the Programme d’Investissement d’Avenir.

It is well known that rate constants of certain reactions of alkoxyl radicals, e.g., unimolecular dissociation (decomposition by C-C bond fission) and isomerization via 1,5 H-shift, are highly sensitive to the molecular structure. In the present and the next talks, we report dispersed fluorescence (DF) spectra of various alkoxyl radicals obtained under supersonic jet-cooled conditions by pumping different vibrionic bands of their $\tilde{B} \rightarrow \tilde{X}$ laser induced fluorescence (LIF) excitation spectra.\textsuperscript{a-d} This talk focuses on the DF spectra of 2-methyl-1-propoxy (isobutoxy), 2-methyl-1-butoxy, and 3-methyl-1-butoxy (isopentoxy). In all cases, strong CO-stretch progressions were observed, as well as transitions to other vibrational levels, including low-frequency ones. Quantum chemical calculations were carried out to aid the assignment of the DF spectra. Franck-Condon factors were calculated using the ezSpectrum program.\textsuperscript{e}

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\textsuperscript{c}W. Q. Li; L. G.; Z. L.; Fang, W. J. Phys. Chem. A 2002, 106, 1065-1067


\textsuperscript{f}V. V. N. V. Mohle and J. A. Keysler, http://openshell.usc.edu/

Vibrational structures of the nearly degenerate $X$ and $\tilde{A}$ states of all four positional isomers of the methycyclohexoxy (MCHO) radicals were studied by jet-cooled dispersed fluorescence (DF) spectroscopy, which unravels the effect of methyl substitution at different positions on the six-membered ring. Experimentally observed vibrionic transitions in the DF spectra were assigned based upon vibrational frequencies from quantum chemical calculations and predicted Franck-Condon factors that take into account the Duschinsky rotation. DF spectra of $2\nu_3$, $3\nu_3$, and $4\nu_3$-MCHO radicals are dominated by CO-stretch progressions or the progressions of CO-stretch modes in combination with the excited vibrational modes. DF spectra of two lowest-energy conformers of the tertiary 1-MCHO radical, chair-axial and chair equatorial, are significantly different from each other and from those of the other three positional isomers. Strong C-CH\textsubscript{3} stretch progressions as well as progressions of its combination bands with the CO stretch modes or the excited modes were observed. Such differences between the isomers and the conformers can be explained by variation of geometry and symmetry of the electronic states of cyclohexoxy upon methyl substitution at different positions. DF study of MCHO provides direct measurement of the energy separation between the $\tilde{A}$ and $X$ states that are subject to the pseudo-Jahn-Teller effect.

FD10  11:20 – 11:35
PHOTODISSOCIATION OF METHYL ISOTHIOCYANATE STUDIED USING CHIRPED PULSE UNIFORM FLOW SPECTROSCOPY

NITUWANDRA ARTIYASINGHA, LINDSAY N. ZACK, CHAMARA ABEYSEKERA, BAPTISTE JOALLAND, ARTHUR SUITS, Department of Chemistry, Wayne State University, Detroit, MI, USA.

Chirped-Pulse Fourier-transform microwave spectroscopy has been applied in a uniform supersonic flow (Chirped-pulse/Uniform flow, CPUF) to study the 193 nm photodissociation of methyl isothiocyanate (MITC). Several products (CH\textsubscript{3}N\textsubscript{C} = N\textsubscript{C}S, H\textsubscript{2}CS, HCN, and HNC) were identified via their pure rotational spectra. Observation of CH\textsubscript{3}NC and NCS are consistent with previous studies of this system, however it is the first detection of H\textsubscript{2}CS and HCNS/HCNC. Branching ratios were obtained from these data and will be discussed.

FD11  11:37 – 11:52
DISPERSED FLUORESCENCE SPECTROSCOPY OF JET-COOLED METHYLCYCLOHEXYLOXY RADICALS

JAHANGIR ALAM, MD ASMAUL REZA, AMY MASON, JINJUN LIU, Department of Chemistry, University of Louisville, Louisville, KY, USA.

Hydroacetic acid (H\textsubscript{2}NCH\textsubscript{2}CHO) is a near-prolate asymmetric top molecule which we have extensively studied in the millimeter-wave region. Having completed an $K$ structure determination based on 14 isotopeologues of H\textsubscript{2}NCH\textsubscript{2}CHO, we have moved on to analyze the very complex rotational spectra for the first 7 vibrationally excited states, as well as the higher $K$ levels of the ground vibrational state. The excited states include the 4 lowest (out of 6) fundamental modes $\nu_4$, $\nu_6$, $\nu_7$, and $\nu_8$) and the 3 lowest combination and overtone states (2$\nu_4$, 2$\nu_6$, and $\nu_4+\nu_6$). All of these states are totally symmetric ($A'$) except for $\nu_7$ and $\nu_8$, which are antisymmetric ($A''$). The $\nu_4$-vibrational states are substantially more intermingled than in most molecules due to unusually wide rotational spacing in H\textsubscript{2}NCH\textsubscript{2}CHO. This intermingling leads to a tangled web of perturbations connecting the various $\nu_4$-vibrational states: a-type and b-type Coriolis interactions between $\nu_4$ and $\nu_6$, between $\nu_4$ and $\nu_8$, and between $\nu_4$, $\nu_5$, and $\nu_7$, local Fermi resonance between $\nu_4$ and $\nu_6$, and a strong centrifugal distortion interaction between the ground state and $\nu_6$. Fortunately, we have been able to make extensive use (in both assignment of spectra and fitting of spectroscopic parameters) of previously published high resolution FTIR data for the $\nu_4$, $\nu_5$, $\nu_6$, and $\nu_7$ bands and the pure rotational spectrum of the ground vibrational state.\textsuperscript{a-b} The $\nu_4$-vibrational states are substantially more intermingled than in most molecules due to unusually wide rotational spacing in H\textsubscript{2}NCH\textsubscript{2}CHO. This intermingling leads to a tangled web of perturbations connecting the various $\nu_4$-vibrational states: a-type and b-type Coriolis interactions between $\nu_4$ and $\nu_6$, between $\nu_4$ and $\nu_8$, and between $\nu_4$, $\nu_5$, and $\nu_7$, local Fermi resonance between $\nu_4$ and $\nu_6$, and a strong centrifugal distortion interaction between the ground state and $\nu_6$. Fortunately, we have been able to make extensive use (in both assignment of spectra and fitting of spectroscopic parameters) of previously published high resolution FTIR data for the $\nu_4$, $\nu_5$, $\nu_6$, and $\nu_7$ bands and the pure rotational spectrum of the ground vibrational state.\textsuperscript{a-b}
MILLIMETER-WAVE SPECTROSCOPY AND GLOBAL ANALYSIS OF THE LOWEST EIGHT VIBRATIONAL STATES OF DEUTERATED HYDRAZIC ACID (DN$_3$)

BRENT K. AMBERGER, R. CLAUDE WOODS, BRIAN J. ESSLERMAN, ROBERT J. MCMAHON, Department of Chemistry, University of Wisconsin, Madison, WI, USA.

Hydroscopic acid (HN$_3$) and DN$_3$ have qualitatively different rotational spectra, owing in large part to a substantial difference in their A rotational constants (345 GHz for DN$_3$, vs 611 GHz for HN$_3$). Like HN$_3$, DN$_3$ has six fundamental vibrational modes, of which four are visible in our millimeter-wave spectra at room temperature. Between 240 and 450 GHz, many pure rotational transitions for the ground vibrational state, $v_5$ (496 cm$^{-1}$), $v_6$ (586 cm$^{-1}$), $v_8$ (955 cm$^{-1}$), the first overtones of $v_5$ and $v_6$, and the combination $v_5v_6$ have been observed and assigned. Because DN$_3$ is a light molecule, the rotational energy levels are widely spaced, leading to numerous interactions between rotational states of different vibrational modes. We have drawn on a wealth of previously published rotational data from high resolution FTIR spectra$^{1,2,3}$, in our efforts to understand these perturbations. The centrifugal distortion interaction between $v_5$ and the ground state of DN$_3$ is less dramatic than in HN$_3$, but still significant. DN$_3$ shows the set of Coriolis interactions as does HN$_3$, but again, their magnitude is generally smaller. In DN$_3$, the $v_5$ state is at slightly lower energy than $v_6$, instead of being nearly degenerate with $v_5$, as is the case for HN$_3$. Therefore, there are strong local interactions between $v_6$ and $v_8$, as well as between $v_5$ and $v_6$. A notable advantage in solving the DN$_3$ problem compared to HN$_3$ is the substantial increase in the number and diversity of observable b-type lines in our frequency region. Furthermore, the smaller A value permits higher K states to be observed due to a more gradual decrease in state populations. Ground state observations have been extended through K = 11 and through J = 50. Picket’s SPFIT has been employed to carry out multi-state fits using combined datasets of our millimeter-wave data and the published FTIR data.


SIMPLIFIED CARTESIAN BASIS MODEL FOR INTRAPOLYAD EMISSION INTENSITIES IN THE Σ A → $\tilde{X}$ BENT-TO-LINEAR TRANSITION OF ACETYLENE

BARRATT PARK, Department of Chemistry, MIT, Cambridge, MA, USA; ADAM H. STEEVES, Chemistry, Duke University, Dukea, NY, USA; JOSHUA H BARABAN, Department of Chemistry, University of Colorado, Boulder, CO, USA; ROBERT W FIELD, Department of Chemistry, MIT, Cambridge, MA, USA.

The acetylene emission spectrum from the trans-bent electronically excited $\tilde{A}$ state to the linear ground electronic $\tilde{X}$ state is of considerable interest because it grants Franck-Condon access to local bending vibrational levels of the $\tilde{X}$ state with large-amplitude motion along the acetylene $=\equiv$ vinylidine isomerization coordinate. For emission from the ground vibrational level of the $\tilde{X}$ state, there is a simplifying set of Franck-Condon propensity rules that give rise to only one zero-order bright state per conserved vibrational polyad of the $\tilde{X}$ state. Unfortunately, when the upper level involves excitation in the highly admixed $\tilde{A}$ ground state with $\tilde{X}$ bending motion to the acetylene vinylidene = $\equiv$ vinylidine isomerization coordinate. For emission from the ground vibrational level of the $\tilde{X}$ state, there is a simplifying set of Franck-Condon propensity rules that give rise to only one zero-order bright state per conserved vibrational polyad of the $\tilde{X}$ state. Unfortunately, when the upper level involves excitation in the highly admixed $\tilde{A}$ ground state with $\tilde{X}$ bending motion to the acetylene vinylidene = $\equiv$ vinylidine isomerization coordinate. For emission from the ground vibrational level of the $\tilde{X}$ state, there is a simplifying set of Franck-Condon propensity rules that give rise to only one zero-order bright state per conserved vibrational polyad of the $\tilde{X}$ state. Unfortunately, when the upper level involves excitation in the highly admixed $\tilde{A}$ ground state with $\tilde{X}$ bending motion to the acetylene vinylidene = $\equiv$ vinylidine isomerization coordinate.
MILLIMETER-WAVE SPECTROSCOPY OF FORMYL AZIDE (HC(O)N₃)

NICHOLAS A. WALTERS, BRENT K. AMBERGER, BRIAN J. ESSELMAN, R. CLAUDE WOODS, ROBERT T. MACMANUS. Department of Chemistry, University of Wisconsin, Madison, WI, USA.

Formyl azide (HC(O)N₃) is a highly unstable molecule (t₁/₂ < 2 hours at room temperature as a gas) that has only recently been studied spectroscopically by UV, IR, Raman and NMR methods. We have synthesized formyl azide and obtained its absorption spectrum at room temperature over the range 250-360 GHz. As in the case of carbonyl diazide, two conformers are expected for HC(O)N₃, with the syn-isomer 2.8 kcal/mol lower in energy than the anti-isomer (CCSD(T)/ANO). Calculations at the same level of theory and the same basis set predict the dipole moments for the syn-isomer (μ = 1.56 D) and anti-isomer (μ = 2.56 D). These calculations also indicate that b-type transitions should dominate the syn-isomer spectrum, while a-type transitions become more significant in the case of the anti-isomer. Despite the anti-isomer having a larger dipole moment, the syn-isomer still gives rise to all the dominant features of the spectrum. Thus far, five vibrational states (υ₁, υ₂, 2υ₃, υ₄ + υ₅, υ₆) have been studied for the syn-isomer, with the highest energy state υ₅ = 582.6 cm⁻¹. Searches for the spectra of the anti-isomer are ongoing.

References:
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Sponsor of the Women’s Lunch – Wednesday June 24th

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ABB Bomem-Michelson Award: ABB sponsors the Bomem-Michelson Award to honor scientists who have advanced the technique(s) of vibrational, molecular, Raman, or electronic spectroscopy. Contributions may be theoretical, experimental, or both. The recipient must be actively working and at least 37 years of age. The nomination should include a resume of the candidate’s career as well as a synopsis of the candidate’s research. A nomination must include a resume of the candidate as well as a synopsis of the special research achievements that make the candidate an eligible nominee for the ABB sponsored Bomem-Michelson Award. Nominations for the award are open between February 1st and May 1st each year. Further information regarding the ABB Bomem-Michelson Award can be found at [www.coblentz.org/awards/the-bomem-michelson-award](http://www.coblentz.org/awards/the-bomem-michelson-award).

Coblentz Award: The Coblentz Award is presented annually to an outstanding young molecular spectroscopist under the age of 40. The candidate must be under the age of 40 on January 1st of the year of the award. Nominations should include a detailed description of the nominee’s accomplishments, a curriculum vitae, and as many supporting letters as possible. Annual updates of files of nominated candidates are encouraged. Nominations for the Coblentz Award are open between January 1st and July 15th each year. Further information regarding the Coblentz Award is available at [www.coblentz.org/awards/the-coblentz-award](http://www.coblentz.org/awards/the-coblentz-award).

Craver Award: The Craver Award is presented annually to an outstanding young molecular spectroscopist whose efforts are in the area of applied analytical vibrational spectroscopy. The candidate must be under the age of 45 on January 1st of the year of the award. The work may include any aspect of (near-, mid-, or far-infrared) IR, THz, or Raman spectroscopy in applied analytical vibrational spectroscopy. Nominations are welcome from academic, government, or industrial research. Nominations must include a detailed description of the nominee’s accomplishments, curriculum vitae or resume, and a minimum of three supporting letters. Nominations for the Craver Award are open between March 30th and August 30th each year. Further information about the Craver Award is available at [www.coblentz.org/awards/the-craver-award](http://www.coblentz.org/awards/the-craver-award).

Ellis R. Lippincott Award: The Ellis R. Lippincott Award is presented annually in recognition of significant contributions and notable achievements in the field of vibrational spectroscopy. The medal is jointly sponsored by the Coblentz Society, the Optical Society of America and the Society for Applied Spectroscopy. Recipients must have made significant contributions to vibrational spectroscopy as judged by their influence on other scientists. Because innovation was a hallmark of the work of Ellis R. Lippincott, the quality of the contributions of candidates will be carefully appraised. Nominations for the award are open between January 1st and October 1st each year. Nominations should be submitted to Lippincott Award Chairperson, ellipawards@osa.org. Further information regarding the Ellis R. Lippincott Award is available at [www.coblentz.org/awards/the-lippincott-award](http://www.coblentz.org/awards/the-lippincott-award).

Honorary Membership: The Coblentz Society awards honorary memberships in the Society to people who have made outstanding contributions to the field of vibrational spectroscopy or any other field related to the purposes of the Society. Nominations close on February 1st each year. Call for nominations and details may be found at the Annual Membership Meeting at Pittcon and presented at F4CSN. Send your nomination for 2015 to Dr. Mark Druy, Coblentz Society President at mark.druy@gmail.com.

ISMS MEETING VENUE INFORMATION

All contributed talks will be held in the Chemistry complex (and immediately adjoining buildings). The plenary talks will be held across the quad (about 60’th) in Foellinger Auditorium.
ACCESSIBLE ENTRANCES

NOYES LABORATORY (NL)

Noyes Laboratory houses our Registration and Exhibitor/Refreshment Rooms (163/165), the Computer Lab (151), two lecture halls (NL 100 and NL 217), and the Chemistry Library.
**ROGER ADAMS LABORATORY (RAL)**

Roger Adams Laboratory is across the street to the east of Chemistry Annex. It has one lecture hall (RAL 116). Please note that in Roger Adams Lab, the ground level is called “Ground” and the First Floor is equivalent to the Second Floor in the other buildings.

![RAL First Floor diagram](image)

**CHEMICAL AND LIFE SCIENCES (CLSL)**

CLSL is a multi-wing building located across the street to the east of Noyes Laboratory. The lecture hall (CLSL B102) is in the B wing across the pedestrian walkway to the northeast of Roger Adams.

![CLSL diagram](image)

**MEDICAL SCIENCES BUILDING (MSB)**

Medical Sciences is across the pedestrian walkway to the north of Roger Adams. It has one lecture hall (MSB 274).

![MSB diagram](image)
Foellinger Auditorium (Plenary and Intermission)

Foellinger Auditorium is located at the South end of Quad. The main doors on the North (quad) side will open at 8:10 AM (the side ADA/wheelchair door will be open around 8:00 AM). There is seating on the main level and the upper balcony. There is no elevator in the building.

PARKING (E14) TO BOUSFIELD DORM

If you purchase a parking permit and are staying at the dorm, you will park in lot E14 (any spot). E14 is nearly due south of Bousfield Hall Dorm.

Parking enforcement begins at 6:00 AM on Monday, so you will need to have your car in lot E14 with your permit displayed before then. There are many parking meters on E. Peabody Drive (and in the lot across from Bousfield) if you wish to park closer for short periods (25 cents/15 minutes - generally between 6 AM and 6 PM, but check the meter because some go until 9 PM).
BOUSFIELD/NUGENT DORM to MEETING VENUE (walking)

Bousfield & Nugent Halls are just under a mile (15-20 minute walk) from the main symposium buildings.

BOUSFIELD/NUGENT DORM to MEETING VENUE (bus)

There is convenient and free bus service between Bousfield/Nugent Dorms and 1 block from the meeting venue. The Yellow Line picks up on the corner of First and Peabody (Bousfield), and also on Gregory Drive (Nugent) in front of Kenberry Commons, and drops off at the Wright Street Terminal (just outside of the Henry Administration Building). Return locations are the same but across the street. The Yellow Line will also take you to downtown Champaign, but you will need to pay for your return (only iStops are free). Approximately every 10 minutes during the day.
The Gold Line picks up on the corner of First and Peabody, and also on Gregory Drive in front of Ikenberry Commons and drops off at the Krannert Center (across the street from CSLI-B). Return locations are across the street. Runs every ~10 minutes during the day (offset from the Yellow Line by 5 minutes).

Bus Stops (Yellow Line = Left Arrow, Gold Line = Right Arrow, Foellinger Auditorium (Plenary) and Noyes Lab = Stars)