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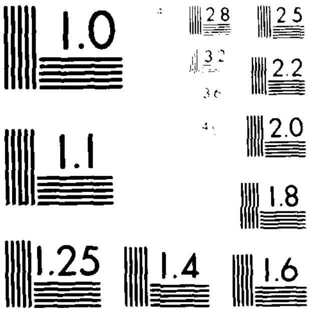

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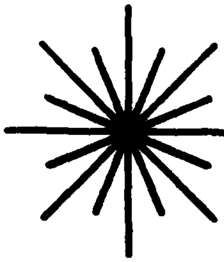

SEVENTH COLLOQUIUM

ON HIGH RESOLUTION MOLECULAR SPECTROSCOPY

14 TO 18 SEPTEMBER

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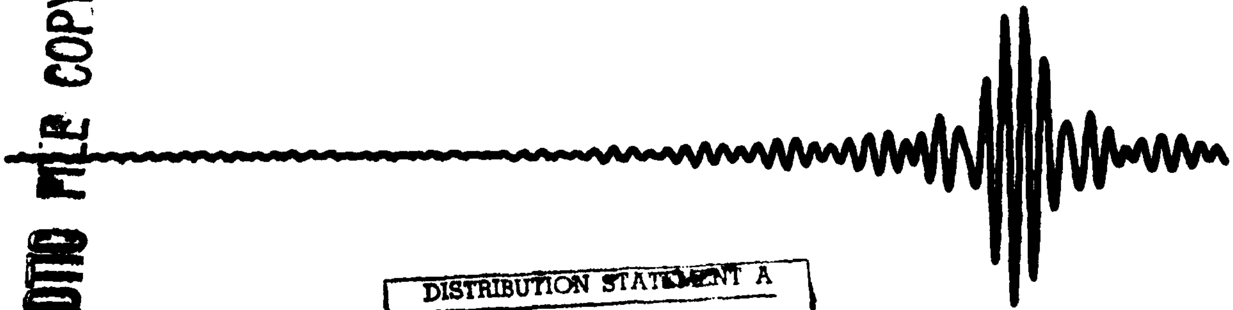
PROGRAMME AND ABSTRACTS

SEPTIEME COLLOQUE

SUR LA SPECTROSCOPIE MOLECULAIRE A HAUTE RESOLUTION

14 A 18 SEPTEMBRE



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Laser	Molecular Spectra	Laser Spectroscopy
Fourier Spectroscopy	Spectroscopy	High Resolution Spectra
Microwave	Infrared	Ultra Violet

20. Abstract

This conference addressed many aspects of high resolution molecular spectroscopy. Measurement techniques for remotely identifying trace gases in the atmosphere were discussed. Instrumentation for highly accurate and precise measurement of molecular emissions were described. The objective of the colloquium was to bring together molecular spectroscopists working in different regions of the electromagnetic spectrum from the ultraviolet to radio frequencies. These scientists shared a common interest in high resolution gas phase spectra and their analyses. The objective was met through the presentation of about 20 invited papers and many more contributed papers.

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This report has been reviewed by the EOARD Information Office and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

Peter Soliz

PETER SOLIZ
Major, USAF
Chief, Geophysics & Space

FOR THE COMMANDER

Winston K Pendleton

WINSTON K. PENDLETON
Lt Colonel, USAF
Chief Scientist

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SEVENTH COLLOQUIUM
ON
HIGH RESOLUTION
MOLECULAR SPECTROSCOPY

PROGRAMME
AND
ABSTRACTS

SEPTIEME COLLOQUE
SUR LA
SPECTROSCOPIE MOLECULAIRE
A HAUTE RESOLUTION

SEVENTH COLLOQUIUM ON HIGH RESOLUTION MOLECULAR SPECTROSCOPY

SEPTIÈME COLLOQUE SUR LA SPECTROSCOPIE MOLÉCULAIRE A HAUTE RESOLUTION

READING 1981

I. M. MILLS
Department of Chemistry
University of Reading
RG6 2AD
U.K.

G. AMAT
Laboratoire de Physique Moléculaire
et d'Optique Atmosphérique
Bâtiment 221 - Campus d'Orsay
91405 ORSAY CEDEX, France

Scientific Committee
Comité Scientifique

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J. BORDÉ
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I. KOVĀCS
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Nous exprimons notre gratitude aux Institutions et aux Sociétés qui, par leur aide financière, ont contribué a l'organisation matérielle du Colloque et ont rendu possible l'invitation de Conférenciers venant de loin:

We are grateful to the Institutions and Companies listed below, who have provided financial support to the Colloquium and, in particular, have made it possible to invite lecturers from abroad:

The University of Reading

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PROGRAMME

	Monday Lundi 14	Tuesday Mardi 15	Wednesday Mercredi 16	Thursday Jeudi 17	Friday Vendredi 18
Morning Matin	A Oka Sarre Marr Butcher	D Schawlow Barrow E Poster Session	G Owyoung Borde Takami H Poster Session	K Camy-Peyret,Flaud Rothman Daunt L Poster Session	N Lombardi Saykally O Poster Session
Afternoon Après-midi	B Poster Session C Poster Session	(free afternoon)	I Robiette Patterson J Poster Session	(free afternoon)	P Fuss Quack Q Poster Session
Evening Soir		F Saito Legon	(Special Buffet Supper)	M Gunthard Weltner	

PROGRAMME

Monday, 14 September	Lundi, 14 Septembre

A Invited Lectures - Conférences Invitées 9-30h to 12-40h Palmer G10

A1 The infrared spectrum of H_3^+ (35 min)

T. Oka (Ottawa, Canada and Chicago, U.S.A.)

A2 Laser Spectroscopy in ion beams (25 min)

P. Sarre (Nottingham, U.K.)

Coffee interval

A3 Molecular photoionisation phenomena using synchrotron radiation (35 min)

G. Marr (Aberdeen, U.K.)

A4 10 µm waveguide laser spectroscopy (25 min)

R.J. Butcher (Cambridge, U.K.)

B Poster Session 14-30h to 15-45h Palmer 101,102

B1 Experimental evidence for symmetry breaking and planarity relations in nitromethane

T. Pedersen and G.O. Sorensen (Copenhagen, Denmark)

B2 A new type of internal coordinate for XCH_3 deformations

F.M. Nicolaisen and J.S. Hansen (Copenhagen, Denmark)

B3 Absorption line profile parameters from frequency modulation

J.P.M. de Vreede, S.C. Mehrotra, A. Tal and H.A. Dijkerman (Utrecht, Netherlands)

B4 Rotational relaxation of BaO ($A\ \Sigma^+$) in Ar and N_2O

Th. G. Cats and H.A. Dijkerman (Utrecht, Netherlands)

B5 The microwave spectrum of trans-ethylamine

E. Fischer and I. Botskor (Ulm, W.Germany)

B6 Microwave spectrum of glycine methyl ester

W. Caminati and R. Cervellati (Bologna, Italy)

B7 Microwave studies of excited vibrational states of $PO^{35}C\ell_3$
R. Crane, J.H. Carpenter and J.G. Smith (Newcastle, U.K.)

B8 Microwave and millimeter wave spectrum of substituted fluoracetylene
M. Andolfatto and A. Guanieri (Kiel, W.Germany)

B9 Coriolis coupling in formamide
C.J. Nielsen (Oslo, Norway) and S.O. Sorensen (Copenhagen, Denmark)

B10 Offset-locked CO_2 waveguide laser study of HCOOH
B.M. Landsberg, D. Crocker and R.J. Butcher (Cambridge, U.K.)

B11 Infrared emission spectroscopy of internally excited H_3^+
U. Steinmetzger, A. Redpath and A. Ding (Berlin, W.Germany)

B12 The Fermi resonance between the $(\nu_1, 2\nu_5^0)$, $(\nu_1+\nu_6, 2\nu_5^0+\nu_6)$ and $(\nu_1+\nu_2, 2\nu_5^0+\nu_2)$ couples of infrared bands of methyl chloride
C. Alamichel and N. Bensaru-Zizi (Orsay, France)

B13 Detection of the infrared spectrum of HCCCCCN
K. Yamada and G. Winnewisser (Köln, W.Germany)

B14 LMR observation of ν_2 for HO_2 at 7.17 μm
F. Niebuhr, M.A. Gondal, A. Hinz, W. Rohrbeck, W. Urban
(Bonn, W.Germany) and J.M. Brown (Southampton, U.K.)

B15 Acoustic detection in laser Stark spectroscopy
A. Carrozzi, A. Di Lieto, M. Minguzzi and M. Tonelli (Pisa, Italy)

B16 Doppler free multiphoton spectroscopy with a CO_2 waveguide laser
F. Herlemont and J. Lemarie (Lille, France)

B17 The electronic spectrum of gaseous NaI
A.S. Ragone, D.H. Levy and R.S. Berry (Chicago, U.S.A.)

B18 Potential energy curve and dissociation energy of ScO
L.S. Gowda (Raichur, India) and V.N. Balaji (Bangalore, India)

B19 Lifetime measurements of excited states of PbSe, PbTe and SnTe
T. Ndikumana, M. Carleer and R. Colin (Bruxelles, Belgium)

B20 Fluorescence spectroscopy using supersonic jets
P.A. Freedman and A.M. Griffiths (Aberystwyth, U.K.)

Tea interval

C Poster Session 16-30h to 17-45h Palmer 101,102

C1 Collective and independent-particle behaviour in atoms and molecules
R.S. Berry, G.S. Ezra and H-J. Yuh (Chicago, U.S.A.)

C2 Analysis of the microwave spectrum of hydrazine
J.T. Hougen (Washington, U.S.A.)

C3 Use of Fourier transforms in computational handling of spectral data
J. Kauppinen (Oulu, Finland), D. Moffatt, H. Mantsch and D. Cameron (Ottawa, Canada)

C4 Homogenous and heterogeneous perturbations in excited singlet states of H_2, HD and D_2
P. Quadrelli, K. Dressler (Zurich, Switzerland) and L. Wolniewicz (Toruń, Poland)

C5 Microwave studies on the equilibrium configuration of molecules related to trithiapentalene
N.W. Larsen, L. Nygaard and T. Pedersen (Copenhagen, Denmark)

C6 Internal rotation spectrum in the ground state of cis-propionyl fluoride
F. Scappini and H. Dreizler (Kiel, W.Germany)

C7 Microwave spectra and structure of 1,1-dicyanoethane
H. Ruck and H.D. Rudolph (Ulm, W.Germany)

C8 Microwave Stark spectroscopy of continuous supersonic molecular beams
H. Zivi, A. Bauder and Hs H. Gunthard (Zurich, Switzerland)

C9 Resonances in the infrared spectrum of $CH_3C\ell$ between 2000 and 4500 cm^{-1}
C. Alamichel and N. Benzari-Zivi (Orsay, France)

C10 Spectroscopy of molecular ions by laser induced fluorescence
A. Richter and A. Ding (Berlin, W.Germany)

C11 The infrared bands ν_2 and ν_5 of CH_3Br with Coriolis interaction
R. Anttila (Oulu, Finland) and C. Betrencourt-Stirnemann (orsay, France)

C12 ℓ-resonance effects in some hot bands of acetylene
J. Hietanen (Oulu, Finland)

C13 Diode laser spectra of unstable molecules: $BC\ell$, SnO, $C\ell O$, etc.
A. Maki, F. Lovas, W.B. Olsen and R.D.Suenram (Washington DC, U.S.A.)

C14 High resolution infrared studies of $^{10}B_2H_6$ and $^{10}B_2D_6$

J.L. Duncan and E. Hamilton (Aberdeen, U.K.)

C15 FT infrared investigation of parallel bands of CF_3Cl, CF_3Br and CF_3I

H. Bürger, K. Burczyk, R. Grassow, P. Schulz (Wuppertal, W.Germany) and A. Ruoff (Ulm, W.Germany)

C16 Dissociation energy of LaO from true potential energy curves

L.S. Gowda, B.N.K. Setty (Raichur, India) and V.N. Balaji (Bangalore, India)

C17 Autoionisation effects in the theoretical study of the partial photoionisation cross section for the $b^4\Sigma_g^-$ state of O_2^+

A. Giusti, H. Lefebvre-Brion, H. Le Rouzo, G. Raseev and A.L. Roche (Orsay, France)

C18 High-resolution on the near ultraviolet A-X system of N_2O^+ by Doppler tuned laser predissociation

M. Larzilliere, M. Carre and M.L. Gaillard (Villeurbanne, France)

C19 Electronic transition moment of the blue-green band system of ScO

B. Narasimhamurthy and N. Sreedharamurthy (Mysore, India)

C20 Rotational analysis of the D-X and F-X transitions of SiCl

F. Melen, I. Dubois and H. Bredohl (Liege, Belgium)

Tuesday, 15 September Mardi, 15 Septembre

D Invited Lectures - Conférences Invitées 9-00h to 10-30h Palmer G10

D1 Some new methods in laser spectroscopy (40 min)

A. Schawlow (Stanford, U.S.A.)

D2 Problems in the spectroscopy of the group VI-VI molecules (30 min)

R.F. Barrow (Oxford, U.K.)

Coffee interval

E Poster Session 11-15h to 12-30h Palmer 101,102

E1 Second order vibration-rotation Hamiltonian for very strong Coriolis resonance

E. Willemot and J. Bellet (Lille, France)

E2 Non-adiabatic calculations of the emission spectrum of H_2^+

A.V. Bunge and C.F. Bunge (Iztapalapa, Mexico)

E3 Centrifugal distortion constants for diatomic molecules: an improved computational method

J.M. Hutson (Oxford, U.K.)

E4 Microwave Fourier transform spectroscopy and applications

G. Bestmann, E. Fliege and H. Dreizler (Kiel, W.Germany)

E5 Investigations on cyclobutylsilane by microwave spectroscopy

A. Wurstner and H.D. Rudolph (Ulm, W.Germany)

E6 Intramolecular hydrogen bonding in glycollic acid: microwave spectrum, dipole moment, molecular structure and quantum-chemical calculations

C.E. Blom and A. Bauder (Zurich, Switzerland)

E7 Propagation of a resonant / non-resonant electromagnetic step through an optically thick gas: experiments in the millimeter region

B. Segard, H. Deve, F. Rohart and B. Macke (Lille, France)

E8 A_0 and D_K for CD_3I from the ν_4 Raman and infrared bands

C. Poulsen and S. Brodersen (Aarhus, Denmark)

E9 Perturbations between an A_1 and E fundamental in a C_{3v} molecule

C.B. Mikkelsen and S. Brodersen (Aarhus, Denmark)

E10 The vibrational fundamentals of $^{12}CD_3F$ in the region 1040-1200 cm^{-1}

G.L. Caldow (Reading and Bristol, U.K.) and L.O. Halonen (Oxford, U.K.)

E11 High resolution infrared study of the a-Coriolis interacting band system $\nu_6, \nu_7, \nu_8, \nu_{10}$ in $H_2C{=}CD_2$

F. Hegelund (Aarhus, Denmark), A.R. Morrison and J.L. Duncan (Aberdeen, U.K.)

E12 Optoacoustic and classical infrared spectroscopy of C_2H_3D between 9 and 13 μm

Ph. Herbin, C.P. Courtoy (Namur, Belgium), A. Delplace and A. Fayt Louvain, Belgium)

E13 Rovibrational investigation of the ν_3 and ν_6 fundamentals of $H_3SiC\ell$, H_3SiBr and H_3SiI

H. Bürger, P. Schulz (Wuppertal, W.Germany) and A. Ruoff (Ulm,W.Germany)

E14 High resolution infrared spectra of ν_7, ν_8, ν_{10} and ν_6 bands of $H_2{}^{12}C{}^{13}CH_2$

M. De Vleeschouwer, Ch. Lambeau, A. Fayt (Louvain, Belgium) and C. Meyer (Orsay, France)

E15 Fourier transform spectra of $^{12}C_2H_4$, $H_2{}^{12}C^{13}CH_2$ and $^{13}C_2H_4$ from 1750 to 2380 cm^{-1}

M. De Vleeschouwer, Ch. Lambeau, A. Fayt (Louvain, Belgium) and G. Guelachvili (Orsay, France)

E16 Ultraviolet absorption spectrum of CaH

B. Kaving and B. Lindgren (Stockholm, Sweden)

E17 Rotational analysis of the $^3\Sigma_u^- - {}^3\Sigma_g^-$ transition of $^{11}B_2$ and $^{11}B^{10}B$

I. Dubois, H. Bredohl and P. Nzohabonayo (Liege, Belgium)

E18 The A $^1\Pi$ - X $^1\Sigma^+$ transition of the $CC\ell^+$ ion

H. Bredohl, I. Dubois and F. Melen (Liege, Belgium)

E19 Fourier transform absorption spectrum of $A0_u^+$-$X0_g^+$ system of $^{130}Te_2$

P. Luc (Orsay, France), J. Cariou and J. Lotrian (Brest, France)

E20 The dipole moments of ^{7}LiH and ^{7}LiD in the electronically excited A $^1\Sigma^+$ states

M. Brieger, A. Hese, A. Renn and A. Sodeik (Berlin, W.Germany)

F Invited Lectures - Conférences Invitées 20-00h to 21-30h Palmer G10

F1 Microwave spectroscopy and dye laser spectroscopy of transient molecules (35 min)

S. Saito (Okazaki, Japan)

F2 Hydrogen bonded complexes investigated with a pulsed nozzle Fourier transform microwave spectrometer (35 min)

A.C. Legon (London, U.K.)

Wednesday, 16 September Mercredi, 16 Septembre

G Invited Lectures - Conférences Invitées 9-00h to 10-55h Palmer G10

G1 Rotationally resolved studies in gases using stimulated Raman techniques (35 min)

A. Owyoung (Albuquerque, New Mexico, U.S.A.)

G2 Nuclear hyperfine and superfine structure (25 min)

J. Bordé (Orsay, France)

G3 Infrared-microwave double resonance using a tunable diode laser (25 min)

M. Takami (Tokyo, Japan)

Coffee interval

H Poster Session 11-20h to 12-35h Palmer 101,102

H1 Dynamic polarizabilities of H_2. Accuracy of theoretical determination

J. Rychlewski (Poznan, Poland)

H2 Microwave spectrum, dipole moment and substitution structure of peroxyformic acid

M. Oldani and A. Bauder (Zurich, Switzerland)

H3 Microwave photon echoes: influence of the transverse molecular motion and of the source bandwidth

F. Rohart, J.P. Prault and B. Macke (Lille, France)

H4 Etude des varietes isotopiques de SF_5Br en spectroscopie Hertzienne

P. Goulet, R. Jurek, and C. Verry (Dijon, France)

H5 The microwave spectra of SF_4NF and SF_4NCH_4

H. Günther (Tubingen, W.Germany)

H6 Spectrum of methane CD_4 at 10 μm: Assignment of ν_2 and ν_4, determination of six ground state rotational constants

A. Valentin and L. Henry (Paris, France) and M. Loete and J.C. Hilico (Dijon, France)

H7 The absorption bands of $^{12}C_2H_4$ in the 10 μm region: Fourier transform and saturation laser waveguide spectra

Ch. Lambeau, M. De Vleeschouwer and A. Fayt (Louvain-la-Neuve, France), J. Lemarie, F. Herlemont and M. Lyszyk (Lille, France)

H8 Low pressure photoacoustic spectroscopy of normal and ^{13}C isotopic species of ethylene at CO_2 laser frequencies

A. Delplace, P. Stouffs, J.G. Lahaye, Ch. Lambeau, M. De Vleeschouwer and A. Fayt (Louvain-la-Neuve, Belgium)

H9 Isotropic Raman spectra of CH_4

J-E. Lolck and S. Brodersen (Aarhus, Denmark) and A.G. Robiette (Reading, U.K.)

H10 Molecular constants of the interacting upper states of the $\nu_1,\nu_3,2\nu_2$, $\nu_2+\nu_4$ and $2\nu_4$ bands of $^{12}CH_4$

J-E. Lolck (Aarhus, Denmark), A.G. Robiette (Reading, U.K.) L.R. Brown (Pasadena, U.S.A.) and R.H. Hunt (Florida, U.S.A.)

H11 The pure rotation Raman spectrum of pyrazine and the pure rotation and vibration-rotation Raman spectra of some isotopically-substituted species of hydrogen and oxygen

D.A. Long, H.G.M. Edwards, N.J. Brassington, D.W. Farwell, A.C. Gorvin and K.A.B. Najim (Bradford, U.K.)

H12 Absorption of CD_3H at 905-1150 cm^{-1}: analysis of the ν_3 and ν_6 bands

J. Dupre-Maquaire, J. Dupre and G. Tarrago (Orsay, France)

H13 C W Raman amplification spectroscopy

J. Baran, A. Grofcsik and W.J. Jones (Aberystwyth, Wales)

H14 Hyperfine constants for v=1 in $^{15}N^{16}O$ determined from Fourier transform spectra

C. Amiot (Orsay, France) and P. Kristiansen (Oslo, Norway)

H15 C W stimulated Raman spectroscopy of the ν_1 fundamental band of GeH_4

S.Q. Mao, R. Saint-Loup, A. Aboumajd, P. Lepage and H. Berger (Dijon, France)

H16 Experimental and theoretical study of Rydberg states of SiF

Y. Houbrechts, I. Dubois and H. Bredohl (Liege, Belgium) and J.M. Robbe (Lille, France)

H17 On highly excited electronic states of the NO molecule reached by multiphoton spectroscopy

K. Dressler and E. Miescher (Zurich, Switzerland)

H18 Various investigations of the iodine B state with a supersonic beam

R. Bacis, S. Churassy, M.L. Gaillard, F. Hartmann, J.P. Pique and N. Sadeghi (Lyon and Grenoble, France)

H19 Hyperfine structure studies in the predissociating $B'0^+$ state of IBr

M. Siese, H. Knockel and E. Tiemann (Hannover, W.Germany)

H20 Magnetic rotation spectroscopy of free radicals with a colour centre laser

J. Pfeiffer, P. Kalkert, D. Kirsten and W. Urban (Bonn, W.Germany)

I Invited Lectures - Conférences Invitées 14-20h to 16-00h Palmer G10

I1 Recent results in the high-resolution spectroscopy of tetrahedral hydrides and deuterides (30 min)

A.G. Robiette (Reading, U.K.)

I2 High resolution spectroscopy of spherical top overtones with applications to multiple photon absorption (30 min)

C.W. Patterson (Los Alamos, New Mexico, U.S.A.)

Tea interval

J Poster Session 16-30h to 17-45h Palmer 101,102

J1 On the bending-internal rotation-rotation Hamiltonian of silyl isocyanate

M. Kreglewski (Poznan, Poland)

J2 A computer controlled microwave spectrometer system used for the study of equilibrium structures of fluoronitro benzenes and other molecules

N.W. Larsen and O.V. Nielsen (Copenhagen, Denmark)

J3 Measurement of the centrifugal distortion moment of CD_4

W.A. Kreiner, A.G. Robiette and H.D. Rudolph (Ulm, W.Germany and Reading, U.K.)

J4 Rotational spectrum of $F^{12}C^{15}N$ in excited vibrational states: Equilibrium structure of cyanogen fluoride

G. Cazzoli, G. Degli Esposti, P.G. Favero and S. Serenellini (Bologna, Italy)

J5 Theoretical line parameters versus experimental measurements in the 2250 to 3250 cm^{-1} region of $^{12}CH_4$

G. Poussigue, E. Pascard and G. Guelachvili (Orsay, France) and G. Pierre and J.P. Champion (Dijon, France)

J6 New Raman spectra for the fundamental bands of SiD_4

J-E. Lolck (Aarhus, Denmark)

J7 The Raman spectrum of CH_3CD_3

P. Jensen and S. Brodersen (Aarhus, Denmark)

J8 High resolution infrared analyses of Coriolis interacting vibrations in CH_3CD_3

J. Harper, A.R. Morrison, J.L. Duncan (Aberdeen, Scotland) and G.D. Nivellini and F. Tullini (Bologna, Italy)

J9 Rotational structure up to J=40 of the $v_2=v_4=1$ vibrational state of $^{12}CF_4$

G. Poussigue, G. Tarrago and A. Valentin (Orsay, France)

J10 Mid-infrared LMR using Faraday- and Voigt- effect for sensitive detection

A. Hinz, J. Pfeiffer, W. Bohle and W. Urban (Bonn, W.Germany)

J11 LMR with a CO laser between 6 and 8 µm

M.A. Gondal, A. Hinz, F. Niebuhr, W. Rohrbeck and W. Urban
(Bonn, W.Germany)

J12 Measurement of stratospheric trace gases by airborn infrared spectroscopy

W.G. Mankin and M.T. Coffey (Boulder, Colorado, U.S.A.)

J13 $^{12}C^{18}O_2$ and $^{13}C^{16}O_2$: wavenumbers and molecular parameters for $0V_2^{\ell}V_3 - 0V_2^{\ell}(V_3-1)$ transitions ($V_2=\ell$)

D. Bailly, R. Farrenq, G. Guelachvili and C. Rossetti (Orsay, France)

J14 Laboratory spectroscopy of planetary molecules

D.E. Jennings (Maryland, U.S.A.)

J15 Isotope field shift in the molecular transition A 0^+ - X $^1\Sigma^+$ of PbS

E. Tiemann and H. Knöckel (Hannover, W.Germany)

J16 A new double resonance technique: Microwave optical polarization spectroscopy (MOPS)

W.E. Ernst and T. Törring (Berlin, W.Germany)

J17 High resolution infrared studies on allene-d_4

F. Hegelund and P. Lund (Aarhus, Denmark) and R.Anttila, J. Kauppinen
and M. Koivusaari (Oulu, Finland)

J18 Optical-optical double resonance multiphoton ionisation spectroscopy of NO

D. Gauyacq, W.Y. Cheung, W.A. Chupka, S.D. Colsen and M. Seaver
(Connecticut, U.S.A.)

J19 Evidence for a 1g state amongst the E states of I_2

J.P. Perrot, J. Chevaleyre, S. Valignat, J.M. Chastan and M. Broyer
(Lyon, France)

J20 OODR excitation of autionising states of sodium dimers

M. Broyer, J. Chevaleyre, S. Martin, B. Caband, A. Hoareau, S. Valignat
and J.P. Perrot (Lyon, France)

Thursday, 17 September Jeudi, 17 Septembre

K Invited Lectures - Conférences Invitées 9-00h to 10-55h Palmer G10

K1 Title to be confirmed (35 min)
C. Camy-Peyret and J.M. Flaud (Besancon and Orsay, France)

K2 High resolution atmospheric spectra at the AFGL (25 min)
L.S. Rothman (Cambridge, Mass, U.S.A.)

K3 Title to be confirmed (25 min)
S.J. Daunt (Knoxville, Tennessee, U.S.A.)

Coffee interval

L Poster Session 11-15h to 12-30h Palmer 102,104,105

L1 Harmonic information from inertia defects in vibrationally excited C_{2v} molecules
D. Christen (Ulm, W.Germany)

L2 The intercomparison of force fields for triatomic molecules
M. Lacy and D.H. Whiffen (Newcastle, U.K.)

L3 Microwave spectrum of D_2CS and H_2CS
A.P. Cox, S.D. Hubbard and H. Kato (Bristol, U.K.)

L4 Collision induced rotational transitions of NH_3
D.B.M. Klaassen, J.J. ter Meulen, N. van Hulst and A. Dymanus (Nijmegen, Netherlands)

L5 Microwave and photoelectron detection of unstable species: Sulphido and selenido borons, XB=S and XB=Se
T.A. Cooper, M.A. King, H.W. Kroto and R.J. Suffolk (Sussex, U.K.)

L6 KCN: Isotopic substitution, structure and nuclear hyperfine effects
J.J. van Vaals, W. Leo Meerts and A. Dymanus (Nijmegen, Netherlands)

L7 Dipole moments of $^{15}NH_3$, ND_3 and PH_3 by laser stark saturation spectroscopy
G. Di Lonardo and A. Trombetti (Bologna, Italy)

L8 The $\nu_2, 2\nu_2, 3\nu_2, \nu_4$ and $\nu_2+\nu_4$ bands of $^{15}NH_3$
G. Di Lonardo, L. Fusina and A. Trombetti (Bologna, Italy)

L9 The vibration-rotation infrared emission spectrum of hydrogen isocyanide, HNC

W.J. Jones and M.J. Winter (Aberystwyth, Wales)

L10 Molecular beam electric resonance spectroscopy of the argon-nitric oxide van der Waals complex

C.M. Western, P.A. Mills and B.J. Howard (Oxford, U.K.)

L11 Laser spectroscopy of supersonic expansions of ICℓ

S.G. Hansen, J.D. Thompson and B.J. Howard (Oxford, U.K.)

L12 Infrared spectrum of CO_2 in the 5 μm region

Ph. Arcas, E. Arie, A. Henry and A. Valentin (Orsay and Paris, France)

L13 Infrared spectrum of CO_2 in the 2 μm region

Ph. Arcas, E. Arie, J. Chauville, M. Cuisenier and J.P. Maillard (Orsay and Paris, France)

L14 Infrared vibration-rotation spectrum of trans- and cis- HONO

C.M. Deeley and I.M. Mills (Reading, U.K.)

L15 The infrared vibration-rotation spectrum, equilibrium structure, and harmonic and anharmonic force field of HBS

P.H. Turner and I.M. Mills (Reading, U.K.)

L16 New set of Dunham coefficients for isotopically substituted carbon monoxide from high information Fourier transform spectroscopy

D. De Villenuve-Lefevre, R. Farrenq and G. Guelachvili (Orsay, France) and W. Urban (Bonn, W.Germany) and J. Verges (Orsay, France)

L17 Rotational analysis of the 7576 Å and 7463 Å bands of NO_2 by means of Fourier transform spectroscopy

A. Perrin, J.M. Flaud, C. Camy-Peyret and P. Luc (Orsay, France)

L18 The VUV absorption spectrum of CO_2 at high resolution: Assignment and rotational analysis of $A\ ^3\Sigma_u^- \leftarrow X\ ^1\Sigma_g^+$ Rydberg transition at 1106 Å.

C. Cossart-Magos, M. Eidelsberg, F. Launay, S. Leach and F. Rostas (Orsay and Meudon, France)

L19 Collisionally induced double resonance in iodine: Analysis of the D'(2g)-A'(2u) transition (340 nm iodine laser)

J. Koffend, A. Sibai and R. Bacis (Lyon, France)

L20 Fourier transform spectra of ν_5 and ν_6 of CH_2NH

G. Duxbury (Glasgow, Scotland) and M.L. Le Lerre (Bristol, U.K.)

L21 Rotational analysis of UV bands of benzene and sym-triazine
J.H. Callomon, J.E. Parkin and J. Sellors (London, U.K.)

L22 An infrared $^{2}\Sigma^{+}$ - X $^{2}\Pi_{i}$ electronic transition of CuO
Y. Lefebvre, B. Pinchamel, J.M. Delaval and J. Schamps (Lille, France)

L23 Observation and analysis of hyperfine structure in the yellow system of copper monofluoride, CuF
C.R. Brazier, J.M. Brown and T.C. Steimle (Southampton, U.K.)

L24 Analysis and interpretation of the spectrum of the CuF molecule
F. Ahmed, R.F. Barrow and A.H. Chojnicki (Oxford, U.K.) and C. Dufour and J. Schamps (Lille, France)

M Invited Lectures - Conférences Invitées 20-00h to 21-30h Palmer G10

M1 High-temperature and interstellar molecules in rare-gas matrices at 4K (35 min)
W. Weltner (Gainesville, Florida, U.S.A.)

M2 High resolution infrared matrix spectroscopy (35 min)
H.H. Günthard (Zurich, Switzerland)

Friday, 18 September Vendredi, 18 Septembre

N Invited Lectures - Conférences Invitées 9-00h to 10-30h Palmer G10

N1 Anticrossing and double resonance studies in glyoxal (35 min)
M. Lombardi (Grenoble, France)

N2 Infrared laser spectroscopy of transient species (35 min)
R.J. Saykally (Berkeley, California, U.S.A.)

Coffee interval

O Poster Session 11-15h to 12-30h Palmer 102,104,105

O1 The microwave spectrum of isotopic species of thietane
C. Castro and I.M. Mills (Reading, U.K.) and H. Wieser (Calgary, Canada)

O2 Microwave spectra of SiH_3CCH in excited states
A. Bauer and J. Carlier (Lille, France)

03 Millimeter wave spectrum of acetonitrile oxide CH_3CNO in the vibrational states $v_{10}=2$ and $v_{10}=3$

J. Galica, B.P. Winnewisser and M. Winnewisser (Giessen, W. Germany)

04 Rotation-inversion spectrum of isocyanamide NH_2NC and millimeter wave spectrum of diazomethane CH_2N_2

E. Schäfer and M. Winnewisser (Giessen, W.Germany)

05 Avoided-crossing molecular-beam study of the internal rotation in methyl silane

W. Leo Meerts (Nijmegen, Netherlands) and I. Ozier (Vancouver, Canada)

06 Infrared spectra of CF_3Br

A. Baldacci, A. Passerini and S. Ghersetti (Venice, Italy)

07 The ν_1 bands of $CH_3C\ell$ and applications to stratospheric problems

M. Morillon-Chapey and M. Dang-Nhu (Orsay, France)

08 Single vibronic level fluorescence and two-photon excitation spectra with a pulsed dye laser

J.M. Hollas, H. Musa and T. Ridley (Reading, U.K.)

09 Optically pumped CW FIR laser emissions from $H^{13}COOH$

D. Dangoise and P. Glorieux (Lille, France)

010 The infrared stretching fundamentals of SiF_2

G.L. Caldow, C.M. Deeley, P.H. Turner and I.M. Mills (Reading, U.K.)

011 Rotational energy transfer study of CO perturbed by H_2 and He: a test for *ab initio* calculations

A. Bersellini-Picard, R. Charneau and Ph Brechignac (Orsay, France)

012 A method for simultaneous measurements of strengths and collisional linewidths from Fourier transform spectra

N. Lacome and A. Levy (Orsay, France) and J.P. Houdeau and C. Boulet (Rennes, France)

013 The ν_3 and ν_4 infrared bands of SiH_3F

R. Escribano (Madrid, Spain), R.J. Butcher (Cambridge, U.K.) and I.M. Mills (Reading, U.K.)

014 Fourier transform analysis of the $^{129}I_2$ and $^{127-129}I_2$ X state

D. Cerny, R. Bacis and C. Effantin (Lyon, France) and J. Verges (Orsay, France)

015 Zeeman quantum beats in the NO_2 $^2B_2$ excited state

P.J. Brucat and R.N. Zare (Stanford, U.S.A.)

016 Laser excitation study of the CO_2^+ $\tilde{A}$ and $\tilde{B}$ interelectronic state mixing

M. Johnson (Stanford,U.S.A.), J. Rostas (Orsay, France) and R.N. Zare (Stanford, U.S.A.)

017 Interactions between the electronic sextet states of FeCℓ

J.M. Delaval and J. Schamps (Lille, France)

018 Spectroscopic study of MgO produced by chemical reaction

B. Bourguignon, J. Rostas and G. Taieb (Orsay, France)

019 Level crossing and anticrossing spectroscopy in NO_2

H.G. Weber (Heidelberg, W.Germany)

020 Deperturbation of the state B $^3\Sigma_u^-$ in S_2

P. Patino and R.F. Barrow (Oxford, U.K.)

021 Local mode overtone structure in some symmetric molecules

L. Halonen and M.S. Child (Oxford, U.K.)

022 Local and normal vibrational states

M.S. Child and R.T. Lawton (Oxford, U.K.)

023 Spin-orbit and Coriolis interactions in Rydberg states with $^2\Pi$ cores: the B $^3\Pi$ and C $^1\Pi$ states of DCℓ

K.P. Huber (Ottawa, Canada)

024 Analysis of the spectrum of PF_5 at 946 cm^{-1} with .014 cm^{-1} resolution

M.L. Palma and J. Bordé (Paris, France) and J. Dupré and C. Meyer (Orsay, France)

P Invited Lectures - Conférences Invitées 14-10h to 15-30h Palmer G10

P1 The importance of spectroscopy in infrared multiple photon excitation (30 min)

W. Fuss (München, W.Germany)

P2 Infrared photochemistry: dynamics and infrared spectroscopy (30 min)

M. Quack (Göttingen, W. Germany)

Tea interval

Q Poster Session 15-50h to 17-00h Palmer 102,104,105

Q1 Infrared spectroscopy with a microwave spectrometer: IR-MW double resonance of HCOF and ClO_2

H. Jones (Ulm, W.Germany)

Q2 The 923 cm^{-1} band of $CF_2C\ell_2$ by laser-microwave double resonance

H. Jones (Ulm, W.Germany) and M. Morillon-Chapey (Orsay, France)

Q3 Pressure - broadening in the millimeter wave spectrum of ozone

N. Monnanteuil and J.M. Colmont (Lille, France)

Q4 Laser-spectroscopic investigation of the van der Waals molecule sodium-argon

G. Aepfelbach, A. Nunnemann and D. Zimmerman (Berlin, W.Germany)

Q5 Measurements of intensities of some absorption lines of water vapour in atmosphere by intracavity laser spectroscopy

M. Chenevier, M-A. Melieres and F. Stoeckel (Grenoble, France)

Q6 Low temperature dielectric relaxation spectroscopy

J. Gilchrist (Grenoble, France)

Q7 The 325 nm electronic system of 1-pyrazoline

A.C.P. Alves and J.M. Hollas (Reading, U.K.)

Q8 The $2\nu_2,\nu_1$ and ν_3 bands of $D_2{}^{16}O$ and $2\nu_2$ and ν_1 bands of $HD^{16}O$

N. Papineau, C. Camy-Peyret and J.M. Flaud (Orsay, France)

Q9 Double resonance on the active medium of a FIR laser: dispersion effects

D. Dangoisse, P. Glorieux and M. Lefebvre (Lille, France)

Q10 Air-broadened N_2O linewidths: an improved calculation at different temperatures

N. Lacome, A. Levy and C. Boulet (Orsay, France)

Q11 High-order spectroscopic constants of ν_1, $2\nu_2$ and associated hot bands of N_2O isotopic species from high resolution F.T. spectroscopy

J.L. Teffo, A. Valentin, A. Henry (Paris, France)

Q12 Analysis of the diode laser spectrum of the ν_3 band of $^{14}N^{16}O_2$

P. Prastault, J. Laurent (Chatillion, France), V. Dana (Paris, France) and A. Goldman (Colorado, U.S.A.)

Q13 Sub-doppler Fourier transform spectroscopy: velocity changing collisions in the iodine B-state

J. Verges and P. Juncar (Orsay, France), P. Weiss and R.W. Field (Cambridge, Mass. U.S.A.) and C. Effantin, J. d'Incan and R. Bacis (Villeurbanne, France)

Q14 Microwave spectra of N-methyl pyrazole

N.K. Narain, S.L. Srivastava, Krishnaji (Allahabad, India)

Q15 2-12 μm ammonia bands recorded with the "Brault" Fourier transform spectrometer at Kitt Peak: a few highlights of the spectral characteristics

Jane Mills and K. Narahari Rao (Columbus, Ohio, U.S.A.)

Q16 Microwave spectra of CF_3CH_3

J. Baker and R.A. Creswell (Manchester, U.K.)

Q17 The LMR spectrum of CH_2 at 11 μm

P.R. Bunker, A.R.W. McKellar and T.J. Sears (Ottawa, Canada)

Q18 The pure rotational spectrum of PH_3 between 8 and 80 cm^{-1} with a resolution of 0.005 cm^{-1}

A. Bonetti, B. Carli and F. Mencaraglia (Firenze, Italy) and M. Carlotti, G. Di Lonardo and A. Trombetti (Bologna, Italy)

Q19 Analysis of the Isotope Subsitution effect on vibration-rotation molecular spectra in the case of heavy atom substitution

A.D. Bykov, Yu.S. Makushkin, O.N. Ulenikov (Tomsk, USSR)

Q20 Study of the methane absorption spectrum in the 1.08 μm region

A.E. Cheglokov, Yu.S. Makushkin, L.N. Sinitsa, O.N. Ulenikov, V.E. Zuev (Tomsk, USSR)

Q21 Analysis of heavy water vapor absorption spectrum in the 9161-9392 cm^{-1} region

A.D. Bykov, V.E. Zuev, V.P. Lopasov, Yu.S. Makushkin, L.N. Sinitsa, O.N. Ulenikov (Tomsk, USSR)

Q22 The theory of resonance vibration-rotation interactions in the methane molecule

V.I. Perevalov, Vl.G. Tyuterev, V.I. Zhelinski (Tomsk, USSR)

ABSTRACTS

A1

The Infrared Spectrum of H_3^+

Takeshi Oka

Herzberg Institute of Astrophysics
National Research Council of Canada
Ottawa, Canada K1A 0R6

and

Department of Chemistry and Astrophysics
University of Chicago
Chicago, Illinois 60637, U.S.A.

(no abstract)

A2

Laser Spectroscopy in ion beams

P J Sarre, C P Edwards and C S Maclean

Department of Chemistry, University of Nottingham,
University Park, Nottingham, UK NG7 2RD

Electronic spectra of molecular ions have been studied for many decades, but in recent years many new indirect experimental approaches to the spectroscopy of ions have been introduced with consequent exciting advances in our understanding of molecular ions. These indirect approaches have been necessary largely because of the difficulty in generating sufficient concentrations of ions to allow the more usual high resolution techniques to be employed.

In Nottingham we have obtained electronic absorption spectra of molecular ions in beams, and we usually study ions in which the upper electronic state is predissociated. This approach is indirect in that transitions are detected by monitoring the appearance of the fragment ion resulting from the predissociation. A spectrum is recorded by counting the number of fragment ions produced as a function of laser wavelength. A beam of molecular ions is generated by electron impact in a conventional mass spectrometer ion source, and the ions are accelerated to an energy variable between 500 and 5000 eV. A small electromagnet is used to select the ion of interest, and the ion beam is then irradiated coaxially over a 0.5m path length with either a fixed frequency Krypton ion laser (Coherent 3000K), or a tunable laser (Coherent 699 Ring Laser). A transition occurs when the laser is resonant with a rotational line in the electronic transition, and as the excited state levels are predissociated, this results in the production of daughter ions. These are then separated from the parent ion beam with a second small electromagnet, and are detected on an electron multiplier.

Transitions have been observed and identified in the 1-3 band of the $A^3\pi \leftarrow X^3\Sigma^-$ transition of SH^+ using the 406, 413 and 415 nm Krypton laser lines and the Doppler-tuning method. A particularly interesting feature of these spectra is the splitting of many of the rotational lines into doublets which is due to presence of the proton nuclear spin. The daughter S^+ ion is detected.

Rotational lines the $\tilde{A}^2A_1 \leftarrow \tilde{X}^2B_1$ transition of H_2S^+ have also been observed in the 400 nm region, and analysis of these results is in progress. The S^+ daughter ion is also detected in this work.

New lines in the spectrum of NH^+ have been recorded. The N^+ ion is detected, and as in SH^+, hyperfine splitting is observed.

A 3 Molecular Photoionisation Phenomena using Synchrotron Radiation

G. Marr

Department of Physics, University of Reading

and

Department of Physics, University of Aberdeen, U.K.

(no abstract)

A 4

10 μm Waveguide Laser Spectroscopy

R.J. Butcher

Cavendish Laboratory, Madingley Road, Cambridge, CB3 OHE, U.K.

In conventional infrared spectroscopy, resolution is generally limited by Doppler broadening while line measurements employ wavelength comparisons. In principle, several orders of magnitude improvement may be obtained by using laser saturation spectroscopy while, at the same time, frequency metrology can be employed. A system which exploits these laser advantages will be described. It employs two waveguide lasers. The first is locked to a Lamb dip in CO_2 fluorescent emission at 4.3 μm and provides a frequency standard. The second may be tuned over a pressure-broadened linewidth of a few hundred MHz. The frequency difference between the two lasers is counted continuously and used to control the operation of the second laser, which is them employed to obtain frequency calibrated saturation spectra. Examples of such spectra will be presented.

A principle requirement of any laser employed in high resolution spectroscopy is that it should provide a truly single frequency output, which is best obtained by operating the laser in a stable single mode of the optical cavity. Such operation can be achieved very easily for CO_2 lasers working at powers of a few watts, by using a simple waveguide design. This will be described briefly, together with some examples of its use.

B 1 Experimental Evidence for Symmetry Breaking and Planarity Relations in Nitromethane

T. Pedersen and G.O. Sørensen

H.C. Ørsted Institute
University of Copenhagen

A number of new excited state (m 0) transitions in nitromethane have been measured and a Δm = ±3 coupling previously postulated has been substantiated. In particular this coupling manifests itself in the states m = ±1 and m = ±2 which fulfill the Δm = 3 criterion.

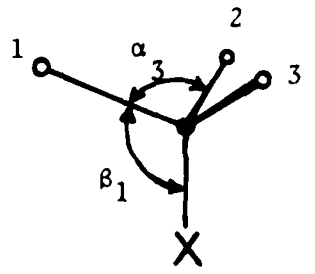
Similarly the relations between the centrifugal distortion constants, presented at the Sixth Colloquium at Tours, have been experimentally confirmed.

B 2 A New Type of Internal Coordinate, with ~~a~~ Simple Redundancy Condition, for the Description of Deformations of XCH_3 Groups and Related Systems

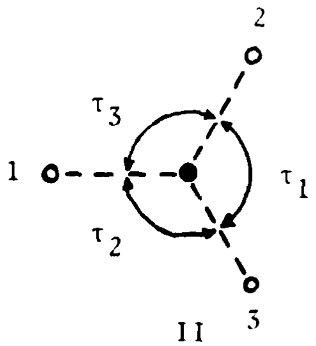
Flemming M. Nicolaisen and Jette Stokkebro Hansen

Chemical Laboratory V, University of Copenhagen
Universitetsparken 5, DK-2100 Copenhagen, Denmark

In addition to the internal bond stretching deformations, the deformation of methyl groups and related systems are conventionally described in the α,β system shown in I. The three α's and



I



II

the three β's are not independent, and for the general case of no symmetry the redundancy condition is very complicated.

If the α's are substituted by the dihedral angles d_{ij} between the H_iCX and the H_jCX planes (II), and $\tau_1 = d_{23}$, $\tau_2 = d_{31}$ and $\tau_3 = d_{12}$, the β's and τ's are independent and the redundancy condition for the general case is $\Delta\tau_1 + \Delta\tau_2 + \Delta\tau_3 = 0$. The τ-coordinates can in most computer programs be defined as torsions about the CX bond.

Examples of force fields in symmetry and internal coordinates, in the βτ system will be presented for XCH_3 molecules of C_{3v} symmetry and for methanol.

B 3 Absorption Line Profile Parameters determined by means of Frequency Modulation

J.P.M. de Vreede, S.C. Mehrotra*, A. Tal**, H.A. Dijkerman

Fysisch Laboratorium der Rijksuniversiteit Utrecht, Princetonplein 5,
3584 CC Utrecht, The Netherlands

We have extended the Karplus theory for frequency modulation in order to describe Voigt profiles while using an arbitrarily large modulation amplitude.

For first and second harmonic detection relations are found for the line profile parameters.

It appears that the detection limit for 1st and 2nd harmonic detection is equal within an factor of two.

Procedures can be given to determine the Lorentzian contribution from the apparent linewidth.

Information about linebroadening can be obtained from a single measurement at line centre using the second harmonic signal dependence on the modulation amplitude.

A number of experimental results for OCS and HCN will be presented.

* From Marathwada University, Aurangabad, India.

** Now at: University of Groningen, Groningen, The Netherlands.

B 4 Rotational Relaxation of BaO (A Σ^+) in Ar and N_2O by means of Laser Induced Fluorescence

Th.G. Cats, H.A. Dijkerman

Fysisch Laboratorium der Rijksuniversiteit Utrecht, Princetonplein 5,
3584 CC Utrecht, The Netherlands

In a Broida-type oven barium vapour is produced in a flowing argon carrier gas. N_2O is brought into the reaction volume to produce BaO. The 488.0 and 496.5 nm argon-ion laser lines coincide with rovibronic transitions in the BaO X←A spectrum. Depending on the working pressure rotational relaxation of the excited states can occur well before $BaO(A\Sigma^+)$ decays radiatively, the lifetime for this decay being about 300 ns. Therefore the fluorescence spectrum obtained with a high resolution 1 m monochromator reflects relaxation times, or equivalently, cross sections for the inelastic collisions:

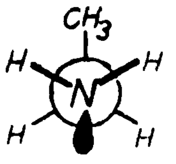
$$BaO(A\Sigma^+) + Ar \rightarrow BaO(A\Sigma^+) + Ar.$$

At the conference the experimental set-up will be outlined, and preliminary results will be given for rotational relaxation from the $v' = 8$, $J' = 49$ level.

B 5 THE MICROWAVE SPECTRUM OF TRANS-ETHYLAMINE

E. Fischer and I. Botskor
Dept. of Physical Chemistry
University of Ulm
D-7900 Ulm, W.Germany

The microwave spectrum of normal trans-ethylamine $CH_3CH_2NH_2$ and that of the -NHD and $-ND_2$ species have been measured and assigned. The obtained rotational constants for the ground state of the normal species are (in MHz): A = 31 758.33 ± 0.08, B = 8 749.157 ± 0.025 and C = 7 798.905 ± 0.025. The fitted dipole moment components are (in Debye): $|\mu_a| = 1.057 \pm 0.006$, $|\mu_b| = 0.764 \pm 0.009$, and $|\mu_t| = 1.304 \pm 0.011$. The quadrupole coupling constants were fitted as (in MHz): $\chi^+ = 1.62 \pm 0.035$ and $\chi^- = -1.89 \pm 0.08$. Analysis of the HFS of the deuterated species $-ND_2$ allowed the experimental determination of the principal quadrupole tensor values (in MHz): $\chi_{zz} = -4.68 \pm 0.20$, $\chi_{yy} = 1.75 \pm 0.06$ and $\chi_{xx} = 2.93 \pm 0.20$. The angle $CN\chi_{zz}$ was fitted as $108.9^\circ \pm 0.6^\circ$ and agreed with the expected general direction of the lone-electron-pair.



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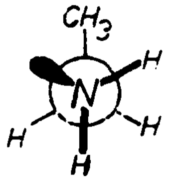

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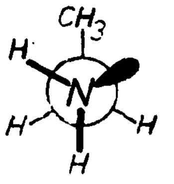

-gauche (II)

B 6 MICROWAVE SPECTRUM OF GLYCINE METHYL ESTER

W. Caminati and R. Cervellati

Istituto Chimico "G. Ciamician" - Università di Bologna (Italy)
and
Istituto di Spettroscopia Molecolare del C.N.R. - Bologna (Italy)

The microwave spectrum of glycine methyl ester has been analysed in the frequency range 26-40 GHz.

A conformer with the heavy atoms in a plane and with an internal bifurcated hydrogen bond has been detected. The rotational transitions of several torsional excited states have been measured. The barrier to the internal rotation of the methyl group has been determined to be $V_3 \simeq 1150$ cal/mole.

B 7 Millimeter-Wave Studies of the Excited Vibrational States of $PO^{35}Cl_3$

R. Crane, J.H. Carpenter and J.G. Smith

University of Newcastle upon Tyne, U.K.

The mm-wave spectra of $PO^{35}Cl_3$ have been recorded for the excited vibrational states $v_5=1$ and $v_6=1$. For the J values studied, J = 26 to 30 , quadrupole effects are small, and for low k lines any coupling was ignored. ℓ-resonance in the two states is pronounced and results in complex spectra. The analysis of the two states is presented and the Coriolis constants so derived are compared with the same parameters derived from infrared spectra.

The value of D_{JK} in the ground state is so small that this constant is not obtainable with certainty. It is however accurately determined in the excited states.

The distortion constants, Coriolis constants, and existing vibrational data have been used to obtain the harmonic force field.

B 8 Microwave and Millimeterwave Spectrum of substituted Fluoroacetylene ($X-C\equiv C-F$, $X=Cl,Br$)

M. Andolfatto and A. Guarnieri

Abteilung Chemische Physik, Institut für
Physikalische Chemie, Universität Kiel
Olshausenstr. 40-60, 2300 Kiel-G

Abstract

The microwave and millimeterwave spectra of Chlorofluoroacetylene $^{35}Cl-C\equiv C-F$, $^{37}-Cl-C\equiv C-F$ and of Bromofluoroacetylene $^{79}Br-C\equiv C-F$, $^{81}Br-C\equiv C-F$ have been investigated.

The rotational constants, centrifugal distortion constants and chlorine quadrupole coupling constants have been determined.

An approach to the r_o-structure has been performed assuming different values for the $C\equiv C$ distance.

B 9

CORIOLIS COUPLING IN FORMAMIDE STUDIED BY MICROWAVE SPECTROSCOPY.

C. J. Nielsen
Department of Chemistry, University of Oslo, Oslo 3, Norway
G. O. Sørensen
Chemical laboratory V, The H. C. Ørsted Institute, DK-2100,
Copenhagen, Denmark.

We have investigated the microwave spectrum of formamide in detail. Apart from the rotational transitions of the ground state, four excited states have been observed [1]. These have been assigned to the $v_{12}=1$ (NH_2 out-of-plane bending), the $v_9=1$ (NCO bending), the $v_{11}=1$ (NH_2 torsion) and the $v_{12}=2$ states. While the rotational spectra of the $v_{12}=1$ and $v_{12}=2$ states can be fitted using the normal rotation Hamiltonian, the $v_9=1$ and the $v_{11}=1$ states are strongly perturbed by a Coriolis coupling of a,b-type.

A program was written for solving the general eigenvalue problem of the "two state vib-rotor":

$$H_{red} = |i\rangle \{H_r^{(i)} + H_d^{(i)}\} \langle i| + |j\rangle \{H_r^{(j)} + H_d^{(j)} + W_{ij}\} \langle j| + |i\rangle H_c \langle j| + |j\rangle H_c \langle i|$$

$$H_r^{(i)} = X^{(i)} J_x^2 + Y^{(i)} J_y^2 + Z^{(i)} J_z^2$$

$$H_d^{(i)} = \{\text{Quartic and sextic distortion}\}^{(i)}$$

$$W_{ij} = \langle j| H_{vib}^{o} |j\rangle - \langle i| H_{vib}^{o} |i\rangle$$

$$H_c = \mu_{xy}(J_xJ_y+J_yJ_x) + \mu_{yz}(J_yJ_z+J_zJ_y) + \mu_{zx}(J_zJ_x+J_xJ_z) + L_xJ_x + L_yJ_y + L_zJ_z$$

From the analyses of 43 rotational transitions of the $v_9=1$ and $v_{11}=1$ states, the following vibration-rotation parameters were obtained:

$$W_{9,11} = 36.55(7)\ \mathrm{cm}^{-1}$$
$$|\xi^{a}_{9,11}| = 0.33(3)$$
$$|\xi^{b}_{9,11}| = 0.46(4)$$

1) E. Hirota, R. Sugisaki, C. J. Nielsen and G. O. Sørensen J. Mol. Spectrosc. 49 (1974) 251-267.

B 10 Offset-locked CO_2 Waveguide Laser Study of HCOOH: Reassement of FIR laser assignments

B.M. Landsberg, D. Crocker and R.J. Butcher

Cavendish Laboratory
University of Cambridge

A number of infrared transitions of formic acid have been measured to a precision of better than 100 kHz. In the light of these new data, far infrared laser measurements have been reassessed.
Available microwave data have also been incorporated in deriving new parameters for the ν_6 and ν_8 states, including the ν_6/ν_8 a-type Coriolis interaction.

B 11

INFRARED EMISSION SPECTROSCOPY OF INTERNALLY EXCITED H_3^+

by
U. Steinmetzger, A. Redpath and A. Ding
Hahn-Meitner-Institut f. Kernforschung
1 Berlin 39, Germany

Infrared emission from the products of the reaction

$$H_2^+ + H_2 -> H_3^+ + H + 1.7 \text{ eV}$$

has been observed. The reaction took place under very low pressure conditions (1 to 10.10^{-4} torr), the ionic reagents being produced by a high intensity electron beam (i_{el} 50 mA). A reaction vessel of large volume was used to ensure a large residence time of the ions. The emitted light was collected via a Welsh-cell arrangement and dispersed through a high throughput monochromator incorporating an echelle grating and a cooled circular variable filter (cf. fig. 1). Computer control allowed long time experiments (typically between 10 and 50 hours per spectrum) generating spectra with an improved signal to noise ratio. The InSb-detector employed allowed detection of the infrared radiation in te range between 1800 and 4000 cm^{-1}.

Fig. 2(top) shows a typical spectrum produced by the reaction of thermal H_2^+-ions. Possible sources for the emission are vibrationally and rotationally excited H_3^+, neutral electronically excited H_3 formed by electron capture of H_3^+ , and highly excited metastable H_2. The latter can be excluded because of the non linear pressure dependence of the observed emission and the lack of diatomic progressions.

A simulation of the rotational fine structure of the lower vibrational transitions [(01)->(00), (02)->(01), (11)->(10) and (21)->(20); ($v_s v_e$): v_s = symmetric stretch mode, v_e = degenerate asymmetric stretch mode] has been perfor-

med using a procedure given by Mills 1) and spectroscopic constants of Oka 2) and Porter et al. 3) which were suitably modified to take into account the influence of the higher vibrational excitation. This yielded the following results:
While there is very little excitation of the lower rotational levels of the (01)-state a significant intensity of the combination bands especially the (11)-level is observed (cf. bottom of fig. 2). The rotational constants for the optimum fit are very similar to those of the (01)-state:

(11):
A=B=43.551, C=19.189, DJ=0.047, DJK=-0.099, DK=0.040,
C =-19.027, q=-5.380, qJ=0.018, G=5572.0
(10):
A=B=42.068, C=19.708, DJ=0.047, DJK=-0.099, DK=0.040,
C =0, q=0, qJ=0, G=3196.0

This is in accordance with the expected dynamical behaviour of the reaction due to te large amount of internal energy available (2.2 to 2.5eV) and the change in equilibrium H-H-distance when forming H_3^+ from H_2, which favours a strong excitation of the symmetric stretch mode.

1) G.J. Cartwright, I.M. Mills, J.Mol.Spectr. 34,415(1970)
C. di Lauro, I.M. Mills, J.Mol.Spectr. 21,386(1966)
2) T. Oka Phys.Rev.Lett. 45,531(1980)
3) C.D.Carney, R.N. Porter Phys.Rev.Lett. 45,537(1980)

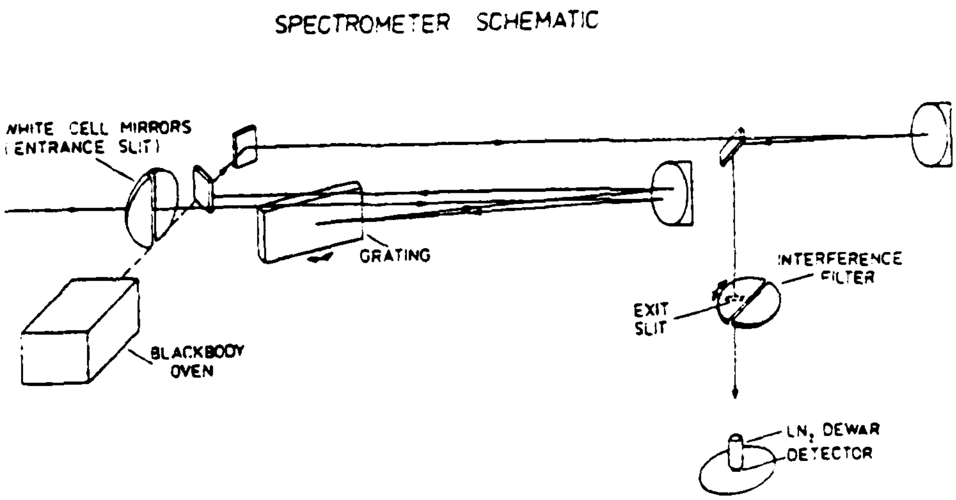

Fig.1: Schematic of the double monochromator

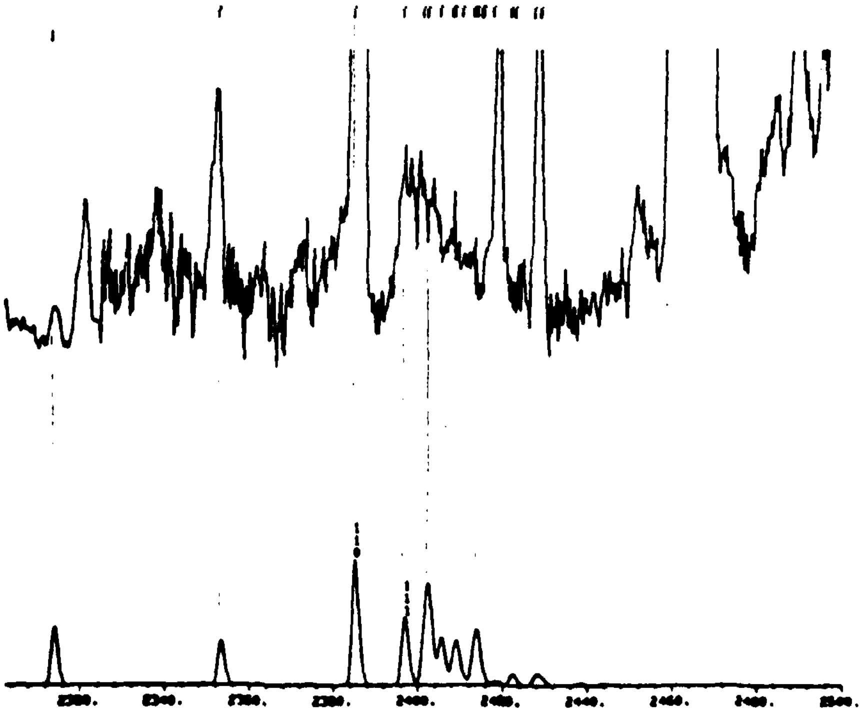

Fig.2: Experimental spektrum (top) and simulated rotational finestructure of the (11) -> (10) transition

B 12

THE FERMI RESONANCE BETWEEN THE $(\nu_1, 2\nu_5^0)$, $(\nu_1 + \nu_6, 2\nu_5^0 + \nu_6)$ AND $(\nu_1 + \nu_2, 2\nu_5^0 + \nu_2)$ COUPLES OF INFRARED BANDS OF METHYL CHLORIDE.

Claude ALAMICHEL and Najate BENSARI-ZIZI (**)
Laboratoire de Photophysique Moléculaire du C.N.R.S.(*)
Université de Paris-Sud, Bâtiment 213
91405 - ORSAY CEDEX France.

The existence of the Fermi resonance between ν_1 and $2\nu_5^0$ is an old subject of discussion : its supporters claim that it is the only explanation of the anomalous intensity of $2\nu_5^0$, and its opponents point our that the ν_1 band exhibits no rotational anomaly in spite of the strong perturbations of $2\nu_5^0$ caused by the Coriolis resonance with $\nu_2 + \nu_5$.

We have studied 3 couples of bands such as $\nu_1 + \nu_z$ and $2\nu_5^0 + \nu_z$ which are precisely linked by the same Fermi resonance as ν_1 and $2\nu_5^0$, if it exists : for z = 2, the $\nu_1 + \nu_2$ band only appears at a level crossing with $\nu_2 + \nu_4$, but for z = 3 and 6, the $\nu_1 + \nu_z$ bands look unperturbed exactly as ν_1. However, if no Fermi resonance is taken into account, it is impossible to explain the positions of the band centres, the shift between the experimental and calculated values reaching up to 4 cm^{-1}. On the contrary, if a Fermi resonance is assumed, we can write :

$$(\nu_1)^0_{\text{exp}} = \frac{1}{2}\left[(\nu_1)^0_{\text{true}} + (2\nu_5^0)^0_{\text{true}}\right] + \frac{1}{2}\sqrt{\left[(\nu_1)^0_{\text{true}} - (2\nu_5^0)^0_{\text{true}}\right]^2 + 4\,W_{155}^2}$$

$$(2\nu_5^0)^0_{\text{exp}} = \frac{1}{2}\left[(\nu_1)^0_{\text{true}} + (2\nu_5^0)^0_{\text{true}}\right] - \frac{1}{2}\sqrt{\left[(\nu_1)^0_{\text{true}} - (2\nu_5^0)^0_{\text{true}}\right]^2 + 4\,W_{155}^2}$$

(**) Present address : Faculté des Sciences, Université Mohammed V,
Charii Ibn Batouta, B.P. 1014, RABAT (Agdal) Maroc.

(*) Laboratoire associé à l'Université de Paris-Sud.

We have two informations, the experimental values of the band centres $(\nu_1)^0_{\text{exp}}$ and $(2\nu_5^0)^0_{\text{exp}}$, and three unknown parameters : $(\nu_1)^0_{\text{true}}$, $(2\nu_5^0)^0_{\text{true}}$ and the coupling W_{155}. For each couple $\nu_1 + \nu_z$ and $2\nu_5^0 + \nu_z$, we can write two similar equations connecting the experimental band centres $(\nu_1 + \nu_z)^0_{\text{exp}}$ and $(2\nu_5^0 + \nu_z)^0_{\text{exp}}$ to the true centres which are given by the following relationships :

$$(\nu_1 + \nu_z)^0_{\text{true}} = (\nu_1)^0_{\text{true}} + \nu_z^0 + x_{1z}$$

$$(2\nu_5^0 + \nu_z)^0_{\text{true}} = (2\nu_5^0)^0_{\text{true}} + \nu_2^0 + 2x_{5z}$$

As ν_z^0 is known, we can see that we have two new informations, $(\nu_1 + \nu_z)^0_{\text{exp}}$ and $(2\nu_5^0 + \nu_z)^0_{\text{exp}}$, but also two new unknown parameters . x_{1z} and x_{5z} . But, if we can measure x_{5z} by another method (with combination bands like $\nu_5 + \nu_z$ for instance), then we only have four unknown parameters ($(\nu_1)^0_{\text{true}}$, $(2\nu_5^0)^0_{\text{true}}$, W_{155} and x_{1z}) and the problem becomes solvable.

For z = 3 we did not succeed to measure x_{35} because $\nu_3 + \nu_5$ is not visible, but both cases z = 6 and 2 have been successful and have given approximately the same value of W_{155} :

for z = 6 we have obtained:

$$\left.\begin{aligned} x_{16} &= -\,4.66\ \text{cm}^{-1} \\ (\nu_1)^0_{\text{true}} &= 2950.20 \\ (2\nu_5^0)^0_{\text{true}} &= 2896.83 \\ W_{155} &= 35.30 \end{aligned}\right\} Z = 6$$

and for z = 2 :

$$\left.\begin{aligned} x_{12} &= 10.6\ \text{cm}^{-1} \\ W_{155} &= 38.0 \end{aligned}\right\} z = 2$$

We consider that the existence of the Fermi resonance is therefore unquestionable, and we can notice that the value obtained for W_{155} is quite close to the value that Duncan, Allan and MacKean have calculated, assuming that the whole intensity of $2\nu_5^0$ comes from ν_1.

B 13 Detection of the Infrared Spectrum of HCCCCCN

Koichi Yamada and Gisbert Winnewisser
I. Physikalisches Institut, Universität zu Köln,
D-5000 Köln 41

In our attempt to observe the high resolution infrared spectra of the astrophysically interesting cyanopolyyne molecules, we have recorded the infrared spectrum of cyanobutydiyne, HC_5N. By using a tunable diode laser we have scanned the wavelength region near 2260 cm^{-1}, which corresponds to the ν_2 fundamental, i.e. the $C{\equiv}N$ stretching vibration and found a dense spectrum with a conspicuous series of lines displaying a rotational spacing ($\sim$0.05 cm^{-1})expected for HC_5N. To our knowledge this constitutes the first detection of the infrared spectrum of HC_5N.

Among the observed dense spectrum we have assigned the rovibrational transitions of the fundamental ν_2 and the hot bands $\nu_2 + \nu_{11} - \nu_{11}$ and $\nu_2 + 2\nu_{11} - 2\nu_{11}$. The band origin of ν_2 was found to be located at 2256. 12417(16) cm^{-1}, which is slightly lower than the corresponding value of HCCCN at 2273.996 cm^{-1}. The HC_5N sample was prepared by reaction of acetylene, HCCH, with either hydrogen cyanide, HCN, or vinylcyanide, H_2C_2HCN, under the action of a rf-discharge according to the reaction schemes:

$$2HCCH + HCN \longrightarrow HCCCCCN + 2H_2$$
$$HCCH + H_2C_2HCN \longrightarrow HCCCCCN + 2H_2$$

Among the obtained discharge products HC_3N and HC_5N were purified by low-temperature vacuum distillation. The HC_5N spectra were recorded at a sample pressure of 1 Torr in a 60 cm long glass cell, sealed with NaCl windows.

B 14 LMR observation of ν_2 for HO_2 at 7.17 µm

F. Niebuhr, M.A. Gondal, A. Hinz,
W. Rohrbeck and W. Urban

Universitat Bonn, D-5300, Bonn
W. Germany

and

J.M. Brown,

Department of Chemistry
University of Southampton
U.K.

(no abstract)

B 15 Acoustic Detection in Laser-Stark Spectroscopy

A. Carrozzi, A. Di Lieto, M. Minguzzi and M. Tonelli

Istituto di Fisica, Universita di Pisa
P.za Torricelli, 2 - 56100 Pisa, Italy

The optoacoustic (OA) technique is based on the detection of an acoustic wave in the sample when a modulated radiation is absorbed. Recently this method has been successfully applied to high resolution laser spectroscopy(1). We present here an experiment where, for the first time, the OA method is applied to laser-Stark spectroscopy. We designed an acoustic cell that can be operated in the presence of strong electric fields; it features a high sensitivity with small Stark plates and without the need of multipass operation.

In our experimental apparatus the 9 µm radiation emitted by a cw CO_2 laser is mechanically chopped before entering the cell and the amplitude of the acoustic signal is recorded as a function of the electric field strength. The laser frequency is accurately stabilized by locking it to the saturated fluorescence at 4.3 µm in pure CO_2.

By an intermodulation technique(1) Doppler-free spectra can be studied as well: the gas is subjected to two counterpropagating laser beams modulated at different frequencies and the signal component at the frequency sum is detected. We have obtained Doppler-limited and Doppler-free spectra for some absorption lines of CH_3F and NH_3 with electric field strengths up to 32 KV/cm and pressures in the range 10-200 mTorr; the signal-to-noise ratio is comparable with that reported in conventional laser-Stark spectroscopy.

The absence of background and the high sensitivity in a small volume propose the OA cell as an interesting alternative for laser-Stark spectroscopy, particularly at sub-Doppler resolution.

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(1) A. Di Lieto, P. Minguzzi, M. Tonelli, Opt. Commun. 31,25 (1979)

B 16 Doppler-free multiphoton spectroscopy with a waveguide CO_2 laser

F. Herlemont and J. Lemaire

Laboratoire de Spectroscopie Hertzienne
Laboratoire associé au CNRS n° 249
Université de Lille I
59655 Villeneuve d'Ascq Cedex

Intracavity spectroscopy has been performed by placing the absorbing gas inside the cavity of a CO_2 waveguide laser.

Owing to the large laser intensity available, Doppler-free two-photon transitions are observed with strongly absorbing gases such as SF_6, CF_3Br.

Resolution is about 200 kHz for these 5 µm spectra. Further experimental details and some characteristics of the spectra will be given.

B 17

THE ELECTRONIC SPECTRUM OF GASEOUS NaI

Anthony S. Ragone, Donald H. Levy and R. Stephen Berry

Department of Chemistry and
the James Franck Institute
The University of Chicago
Chicago, Illinois 60637

Sodium iodide vapor, seeded in a hypersonic jet of helium, absorbs radiation from a pulsed, tunable dye laser in the region 316-380 nm, and fluoresces. We have studied with this fluorescence excitation spectrum and the fluorescence emission spectra from many of the (unresolved) rotational bands in the excitation spectrum. Many of these bands are due to triatomic or larger species: NaIHe and at least one other molecule, as yet unidentified, capable of fluorescing. However a v'-progression corresponding to v" = 0 and another progression corresponding to v" = 1 of diatomic NaI have been found and identified by a) the agreement between the intervals of NaI and b) the single "anti-Stokes" line of the v" + 1 progression due to emission from v' states to the ground level, v" = 0. The vibrational interval in the upper state in the Franck-Condon region is only about 50 cm^{-1}. The exact numbering of the v'-states is uncertain, but the observed states probably have v' $\gtrsim$ 50. The spacing of the upper states is so small and the Franck-Condon region spans so many of them that we observe intensity variations, especially in the v' = 1 progression, that we can attribute to the spatial distributions of the vibrational wavefunctions of the lower states. This work opens the way for a high-resolution study of the dependence of charge transfer curve-crossing on ro-vibrational state, i.e., a quantitative study of curve-crossing models at the level of individual quantum states.

B 18

True potential energy curves and dissociation energy of scandium oxide

L.S. Gowda and V.N. Balaji

Department of Physics
University of Agricultural Sciences
Agricultural Engineering Institute
Raichur - 584 101, India

Molecular Biophysics Unit
Indian Institute of Science
Bangalore - 560 012
India

The construction of potential energy curves is of considerable importance for the understanding of physical problems arising in astrophysics, gas kinetics and molecular spectra. Scandium monoxide bands of (B-X) system have been observed in the spectra of late type stars, of cool stars and of the stars of M-type. For the quantitative spectroscopic studies it is customary to employ a potential function which is mathematically simple and Morse is a very common choice. Since Morse potential is inadequate in representing a number of electronic states, it is necessary to compare it with true potential functions obtained by RKRV and modified-Rees methods. In this paper we report the potential energy curve of different methods using the vibrational and rotational constants. The true potential energy curve for the ground state of ScO has been used to estimate the dissociation energy by the method of curve fitting and adopting. The Lippincott and the H-H potential functions. The influence of vibration-rotation interaction is also studied for different rotational quantum numbers using the effective Morse potential. The calculations involved in the present investigation are carried out on DEC. 1090 computer at Indian Institute of Science, Bangalore.

B 19

Lifetime measurements of excited states of the PbSe, PbTe and SnTe molecules

T. Ndikumana, M. Carleer and R. Colin
Université Libre de Bruxelles
50 Ave. Franklin Roosevelt
B-1050 Bruxelles, Belgium

Samples of PbSe,PbTe,and SnTe molecules were evaporated from a Knudsen cell.The molecular beam was crossed with different Ar^+ laser lines and resonant fluorescence recorded on a 2m spectrograph.Due to the high number of isotopes for these molecules,only PbSe gave rise to a relatively simple spectrum when excited by the 4965 Å Ar^+line.The excitation takes place in the 9-0(J=50) and 10-0(J=132) bands of the $A0^+$-$X0^+$ transition.

22 vibrational levels of the lower state have been observed and more accurate constants derived.RKR potential and Franck-Condon factors have been calculated.

Using a pulsed N_2-pumped dye laser,lifetime measurements of A and B states in PbSe,B state in PbTe,B and C states in SnTe have been performed.The following lifetimes have been obtained:

molec. state,level		PbSe	PbTe	SnTe
A	$v'=9$:	4.04 ± 0.24 μsec.		
	10 :	3.92 ± 0.4 "		
B	1 :	3.86 ± 0.36 "		
	2 :			4.72 ± 0.08 μsec.
	3 :			
	4 :		6.6 ± 0.5 μsec.	3.70 ± 0.03 "
	5 :	4.49 ± 0.13 "	5.6 ± 0.4 "	
	6 :	4.04 ± 0.09 "	4.74 ± 0.3 "	3.34 ± 0.03 "
	7 :	4.17 ± 0.09 "		3.40 ± 0.03 "
	8 :	5.24 ± 0.14 "		3.51 ± 0.04 "
	9 :			3.47 ± 0.03 "
	10 :			3.92 ± 0.05 "

			SnTe	
C	5	:	4.65 ± 0.17	"
	6	:	3.91 ± 0.04	"
	7	:	5.86 ± 0.09	"

The electronic transition moments in the A-X and B-X systems of PbSe have been evaluated.The values 0.2 D^2 and 0.12 D^2 for $|Re|^2$ are respectively proposed.

As SnTe is considerably dissociated(~10%),we tried to observe and measure the lifetime of Te_2 molecule in the region where bands issuing from SnTe(B-X and C-X systems) and Te2($A0_u^+$-$X0_g^+$ and $B0_u^+$-$X0_g^+$)overlap, i.e.4400 Å-4700 Å.

Radiative lifetime of ten vibrational levels of Te2 in $A0_u^+$ and $B0_u^+$ states have been measured.The analysis is in progress and relaxation constants ranging from 85-110 nsec.,i.e.40 times smaller than in SnTe have been determined.

B 20 FLUORESCENCE SPECTROSCOPY USING A SUPERSONIC JET APPARATUS

By *Philip A. Freedman* and *A. M. Griffiths*

Edward Davies Chemical Laboratories,
University College of Wales,
Aberystwyth, Dyfed.

A number of resolved fluorescence studies of tetracene, pentacene and their Van der Waals complexes with inert gas atoms are described.

It is shown that for both the uncomplexed species, strong excitation to the out of plane B_{1g} (seesaw) vibrations occur in the visible excitation spectra. In the case of pentacene, the upper electronic state of this transition (B_{2u} symmetry) has a double minimum, although since the height of the well is under 1 cm^{-1}, the molecule remains quasi planar.

C1 COLLECTIVE AND INDEPENDENT-PARTICLE BEHAVIOR IN ATOMS AND MOLECULES

R. S. Berry, G.S. Ezra and H.-J. Yuh

The concept of collective motion of the electrons in atoms has been given precise, quantitative meaning and a highly plausible physical interpretation with the molecule-like description of Kellman and Herrick.[1] According to their model, many doubly-excited states of He form energy level patterns that correspond to rotational and vibrational states of a linear triatomic molecule. We have examined accurate wavefunctions for some key states of He** and find that the charge distributions indeed conform to a molecule-like system with collective rotation, bending vibrations and stretching vibrations. Computations with a model based on two particles confined to concentric spheres show that molecule-like collective motion may occur with a wide variety of interaction potentials. However the model also shows how energy level patterns and wavefunctions pass from a molecule-like limit to an independent-particle, shell model limit as the forces between the particles are weakened, the ratio of the radii of their spheres is changed from unity or their total energy is increased. The model suggests that the highly excited stretching-vibrational states of XY_n molecules, (in the region where local modes dominate the stretching) will have rovibrational energy level patterns exhibiting internal rotational motion replacing bending motion.

C 2 Analysis of the Microwave Spectrum of Hydrazine

J.T. Hougen and T. Kojima

Molecular Spectroscopy Division
National Bureau of Standards
Washington, D.C. 20234 U.S.A.

Physics Department
Toyama University
Toyama 930, Japan.

The hydrazine molecule H_2N-NH_2 exhibits three large amplitude vibrational motions: an internal rotation about the N-N bond, and an inversion motion in each NH_2 group. By making use of various group theoretical techniques described in the literature, a phenomenological rotational Hamiltonian has been derived, which is suitable for treating the microwave spectrum of the ground vibrational state, including all of the various tunneling splittings. A total of 368 lines with $J \leqslant 20$ have been fit with this Hamiltonian, yielding a standard deviation of 0.2 MHz. We believe that the correctness and usefulness of this model has been demonstrated, though some uncertainties, associated with choosing the centre frequency of the hyperfine patterns, still remain.

C 3 Use of Fourier Transforms in Computational Handling of Spectral Data

J. Kauppinen
Department of Physics, University of Oulu, SF-90570 Oulu 57, Finland

and

D. Moffatt, H. Mantsch, and D. Cameron
Division of Chemistry, National Research Council of Canada, Ottawa,
Ontario K1A 0R6

We have developed the use of fast Fourier transforms in spectral data handling such as Fourier self-deconvolution [1,2], derivation [3], smoothing [4], and complex self-deconvolution [5] for asymmetric lines. The use of fast Fourier transforms seems to be the most effective and accurate technique in these operations as compared with the other methods. All the operations mentioned above are based on the following formula

$$E'(\nu) = \mathcal{F}\left\{\frac{\mathcal{F}^{-1}\{W(\nu)\}\mathcal{F}^{-1}\{E(\nu)\}}{\mathcal{F}^{-1}\{E_0(\nu)\}}\right\},$$

where $\mathcal{F}\{\ \}$ and $\mathcal{F}^{-1}\{\ \}$ are the Fourier transform and the inverse Fourier transform, respectively, $E(\nu)$ is the original spectrum, $E'(\nu)$ is the resultant spectrum, $W(\nu)$ is a smoothing function, $E_0(\nu)$ is a symmetric (or asymmetric) lineshape function in the case of Fourier self-deconvolution (or complex self-deconvolution), $\mathcal{F}^{-1}\{E_0(\nu)\} = 1/(2\pi ix)^k$ for the k th derivative and $\mathcal{F}^{-1}\{E_0(\nu)\} = 1$ in the case of smoothing.

[1] Jyrki K. Kauppinen, Douglas J. Moffatt, Henry H. Mantsch, and David G. Cameron, Appl. Spectrosc. 35, 271 (1981).
[2] Jyrki K. Kauppinen, Douglas J. Moffatt, David G. Cameron, and Henry H. Mantsch, Appl. Opt. 20, 1866 (1981).
[3] Jyrki K. Kauppinen, Douglas J. Moffatt, Henry H. Mantsch, and David G. Cameron, Anal. Chem. (in press).
[4] Jyrki K. Kauppinen, Douglas J. Moffatt, and Henry H. Mantsch, to be published.
[5] Jyrki K. Kauppinen and Douglas J. Moffatt, to be published.

C 4

HOMOGENEOUS AND HETEROGENEOUS PERTURBATIONS IN EXCITED SINGLET STATES OF H_2 , HD AND D_2

P. Quadrelli and K. Dressler
Physical Chemistry Laboratory, ETH-Zentrum,
CH-8092 Zürich, Switzerland

L. Wolniewicz
Institute of Physics, N. Copernicus University,
Toruń, Poland

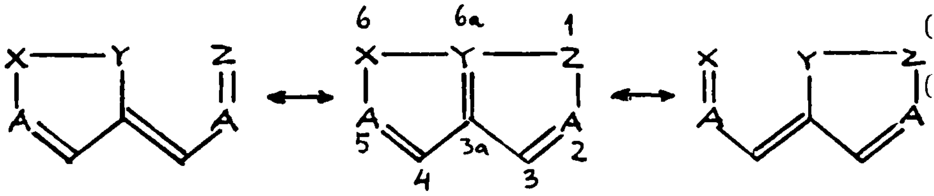
We present results of ab-initio calculations on the simultaneous homogeneous and heterogeneous interactions between the states EF $^1\Sigma_g^+$, GK $^1\Sigma_g^+$, H $^1\Sigma_g^+$, I $^1\Pi_g^+$, and J $^1\Delta_g^+$. Rovibronic energy levels derived from these states were computed with an interaction matrix based on bound and effective vibrational continuum states. The included interactions account for most of the perturbations observed below 118000 cm^{-1}.

The mass-dependence of the remaining deviations from observed energy levels in the three isotopes has been analyzed to get some information on the origin of these discrepancies.

C 5 ON THE EQILIBRIUM CONFIGURATION OF MOLECULES RELATED TO TRITHIAPENTALENE: DIOXADIAZATHIA-PENTALENE STUDIED BY MICROWAVE SPECTROSCOPY

N.W. Larsen
L. Nygaard and T. Pedersen
The H. C. Ørsted Institute
University of Copenhagen

Molecules related to 1,6,6aλ^4-trithiapentalene:



(A = CH or N)
(X,Y,Z = S,O)

have been studied with the aim of establishing whether such molecules actually correspond to the mesomerism above or rather exhibit valence tautomerism. In continuation of our study of 1,6-dioxa-6aλ^4thiapentalene [A = CH; X = Z = O; Y = S] we have now studied 1,6-dioxa-2,5-diaza-6aλ^4thiapentalene [A = N, X = Z = O, Y = S] by microwave spectroscopy* and have established that again the scheme above (mesomerism) is followed. The arguments are based on spinweights, inertial defect (indicating planarity) and excited state evidence.

A newly developed AC/DC technique is employed to determine the dipole moment.

*Pedersen, Skaarup and Pedersen, Acta Chem. Scand. B31, (1977) 711-18.

C 6 Internal Rotation Spectrum in the Ground State of cis- Propionyl Fluoride

F. Scappini and H. Dreizler
Institut fur Physikalische Chemie
Abteilung Chemische Physik
Olshausenstr. 40-60, D-2300 Kiel

Following a preceeding study [1], the ground state rotational spectrum has been further investigated. The new measurements involve low, intermediate, and high K transitions. The coupling of the internal rotation of the methyl top to the overall rotation produces splittings in most of the observed lines making a ground state barrier determination possible. For the intermediate and high K perpendicular transitions, lines have been observed which would be "forbidden" in the rigid rotor limit.

The measurements have been carried out using both Stark and Fourier transform microwave spectroscopy.

The analysis is still going on.

[1] O.L. Stiefvater and E.B. Wilson, J.Chem.Phys., 50, 5845 (1969).

C 7 Microwave Spectra and Structure of 1,1-Dicyanoethene

H. Rück and H.D. Rudolph
Department of Physical Chemistry
University of Ulm
D-7900 Ulm, W.Germany

The highly symmetric molecule 1,1-dicyanoethene, $H_2C=C(CN)_2$, shows a rotational b-type spectrum and presents a model case for a r_s-structure determination. All atoms excepting the central C have been isotopically substituted and the spectra carefully analyzed including the centrifugal distortion contributions. The substitution structure has been calculated making use of one 1st moment equation. The structure will be compared with that obtained by other methods (r_0; fitting to differences of moments of inertia) and discussed with respect to chemical bonding properties.

C 8

Microwave Stark Spectroscopy of Continuous Supersonic Molecular Beams: OCS in Pure and in Ar- and He-Seeded Beams.

H. Zivi, A. Bauder and Hs.H. Günthard,
Laboratory for Physical Chemistry, Swiss Federal Institute of
Technology, 8092 Zurich, Switzerland.

Rotational transitions of OCS in supersonic molecular beams have been observed. A newly developed spectrometer with a 1 m long groove guide was coupled to a supersonic beam source.

Highly resolved rotational spectra have been obtained. The resolution is limited mainly by the translational temperature of the supersonic beam. The measurements offer a convenient tool for molecular beam diagnostics yielding the translational temperature, the average beam velocity from the Doppler shifted transition frequency and relative beam intensity as a function of the beam source parameter settings.

Marked differences have been observed between pure, Ar- and He-seeded beams. The smallest linewidths obtained were 2.2 kHz (FWHM) for an Ar-seeded beam and 2.6 kHz for a He-seeded beam corresponding to translational temperatures of 4 K and 5 K, respectively.

From the phase of the signals detected and from the Doppler shifts measured it was concluded that the 0-1 rotational transition of OCS appears in emission rather than absorption.

C 9 Resonances in the Infrared Spectrum of Methyl Chloride between 2000 and 4500 cm^{-1}

Claude Alamichel and Najate Ben Sari-Zizi(xx)
Laboratoire de Photophysique moleculaire de CNRS(x)
Universite de Paris-Sud, Batiment 213
91405 Orsay cedex, France

The infrared spectrum of methyl chloride has been systematically studied between 2000 and 4500 cm^{-1} from recordings in high resolution (0.0050 – 0.0075 cm^{-1}) provided by G.Guelachvili . About 15000 lines , belonging to more than 20 vibrational bands , have been assigned . The unperturbed $\nu_1 - \nu_3$ hot band excepted , all this work has been focused on the study of three main interactions :

1°) The Fermi resonance in q_1q , involved between ν_1 and $2\nu_5^0$ or between any pair of bands like $\nu_1 + \nu_Z$ and $2\nu_5^0 + \nu_Z$: a more detailed outlook of this problem is given in another communication submitted to this colloquium .

2°) The Coriolis resonance between the ν_2 and ν_5 modes , which links the rovibrational levels of $2\nu_2$, $\nu_2 + \nu_5$, $2\nu_5^0$ and $2\nu_5^{\pm 2}$ six by six . Local resonances must be added to this six level scheme :

- a Coriolis-like resonance between $2\nu_5^0$ and $2\nu_3 + \nu_5$.
- an anharmonic resonance between $2\nu_5^0$ and $4\nu_3$.
- a ℓ (2,-1) resonance between both components of $2\nu_5$.
- the ℓ (2,2) resonance of the ν_5 mode .

We also must point out that the lines of two other bands are mixed with the previous ones : the $\nu_2 + 2\nu_3$ band , only coupled to $2\nu_3 + \nu_5$ by Coriolis resonance , and the $\nu_3 + 2\nu_6^0$ band, disconnected from the previous system of bands .

3°) The Darling-Dennison resonance in $q_4q_6^3$, which links ν_4 to $3\nu_6^1$, has been studied between three pairs of bands like $\nu_4 + \nu_Z$ and $3\nu_6 + \nu_Z$, with z = 2,3 and 6 . For z = 2 , the $\nu_2 + \nu_4$ band is also linked to $\nu_4 + \nu_5$ by Coriolis resonance of course , and for z = 6 the $\nu_4^{\pm 1} + \nu_6^{\mp 1}$ parallel band with perpendicular structure exhibits a ℓ vibrational resonance.

As a result of this systematic study , a great number of molecular parameters of methyl chloride have been measured , and more especially twenty anharmonicity constants .

(xx) Present address : Faculté des Sciences , Université Mohammed V , Charii Ibn Batouta , B.P. 1014 , Rabat (Agdal) , Morocco.

(x) Laboratoire associé à l'Université de Paris-Sud.

C 10

SPECTROSCOPY OF MOLECULAR IONS BY LASER INDUCED FLUORESCENCE

by K.Richter and A.Ding

Hahn-Meitner-Institut für Kernforschung Berlin GmbH
Glienicker Str. 100
1000 Berlin 39, Fed. Republic of Germany

The internal state distributions of N_2^+-molecular ions have been investigated by the method of laser induced fluorescence. Information about the dynamics of the ion forming process can be extracted from the measured rotation-vibrational distribution of the molecules. Two methods of generating the molecular ion have been employed:

1) plasma discharge of the parent molecule,
2) charge exchange in a beam of fast molecular ions.

The experimental configuration (Fig.1) consists of a plasma ion source, which produces a strong ion beam (typically 3×10^{-7}A) which is focussed into a collision chamber after passing through a magnetic mass analyser. The internal state distribution of the molecular ions is probed by a coaxial laser beam originating from a tunable dye laser and the fluorescence light emitted by the ions is then collected by a photomultiplier tube. Counting rates were in the order of one count per 20 laser pulses. Ion densities of 500 ions/cm in a particular state could be measured with this arrangement.

Without a target gas the original distribution of the ions caused by the collision process in the ion source could be determined. Filling the collision chamber with nitrogen, N_2^+-ions due to charge exchange processes could be measured. In the case of symmetric charge exchange the contribution from both (the primary ions and the product ions) could be separated because of the Doppler shift of their respective spectra (cf. Fig.2). While the rotational distribution of the charge exchanged molecules is well resembled by a room temperature distribution, significant rotational energy transfer occurs by inelastic collisions in the target chamber which results in a rotational temperature in excess of 1000 K (compared to 650 K of the primary beam).

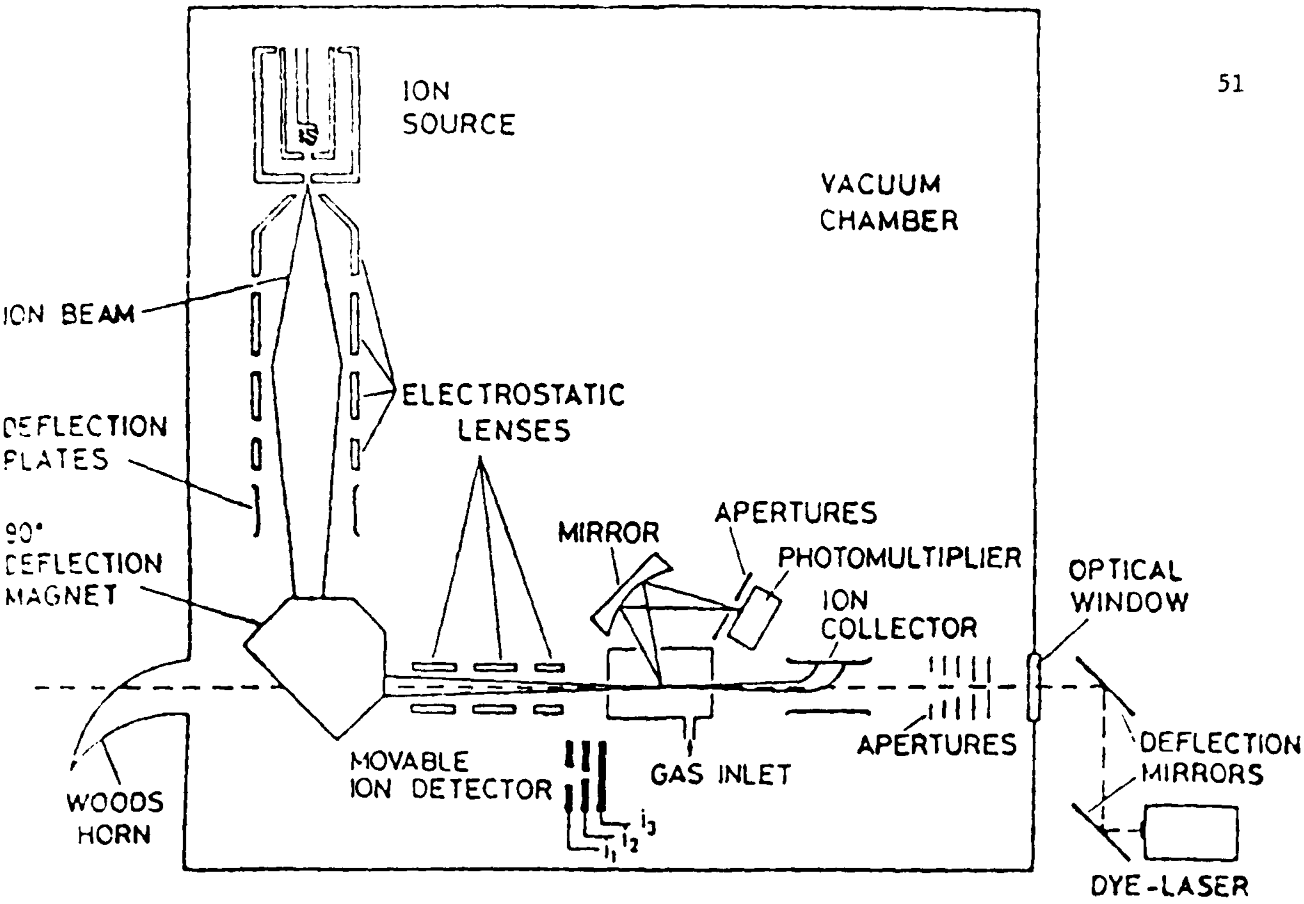


Fig.1: Experimental arrangement

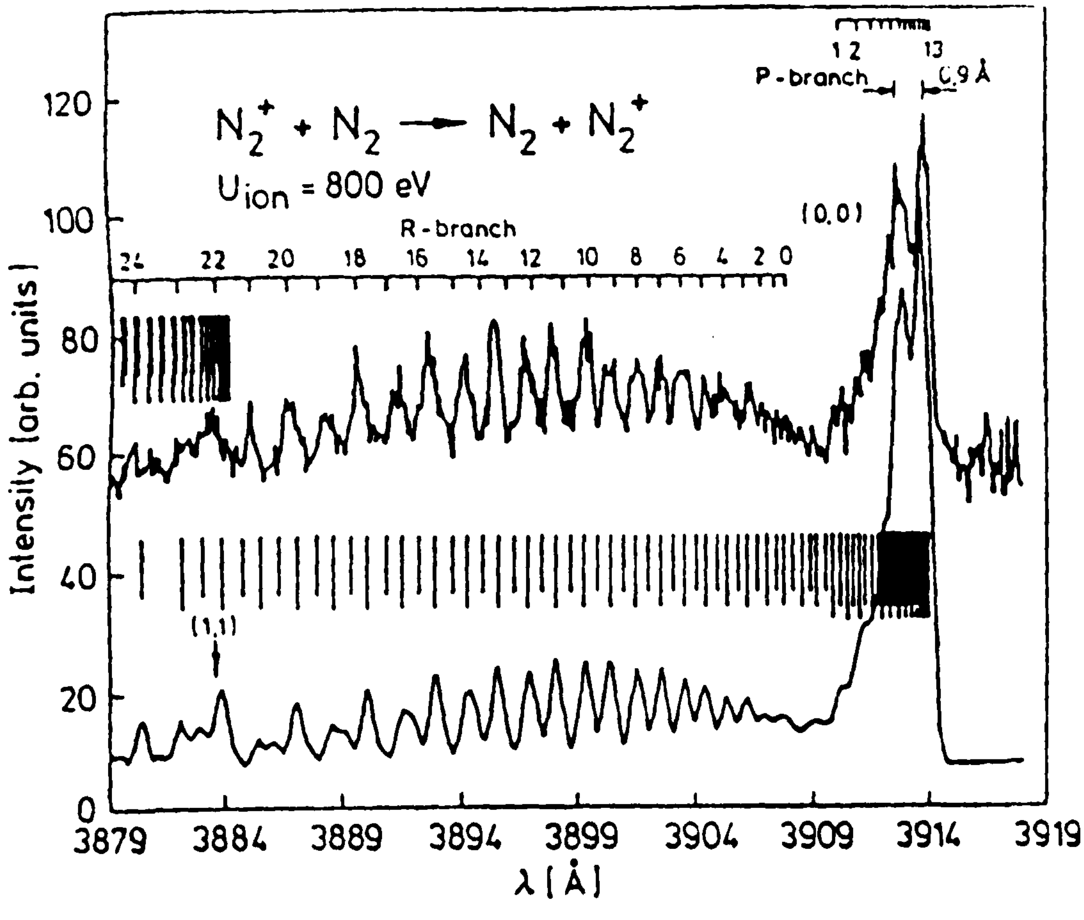


Fig.2: Experimental (top) and simulated (bottom) spectrum caused by inelastic and charge exchange collisions of N_2^+-ions with N_2

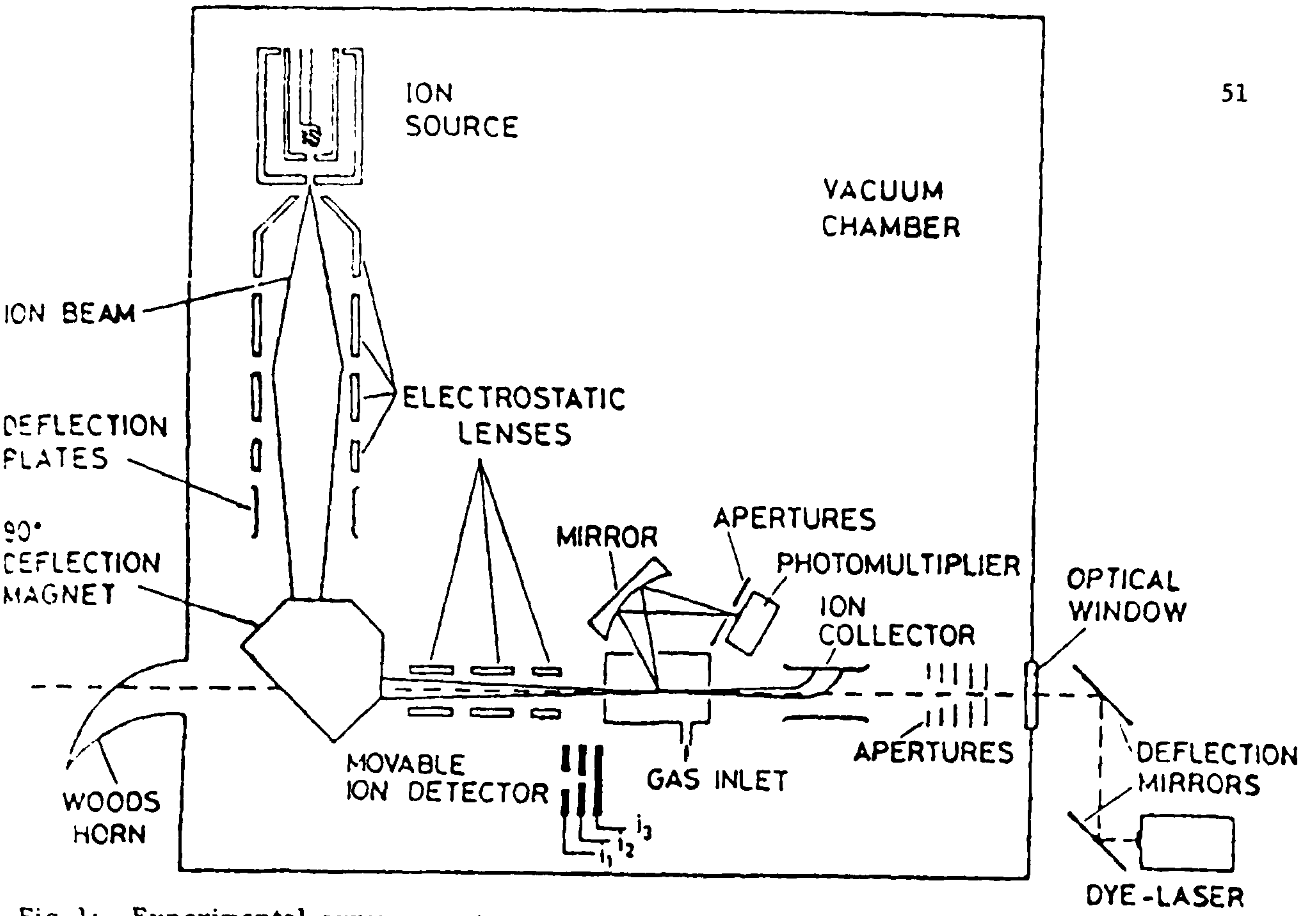


Fig.1: Experimental arrangement

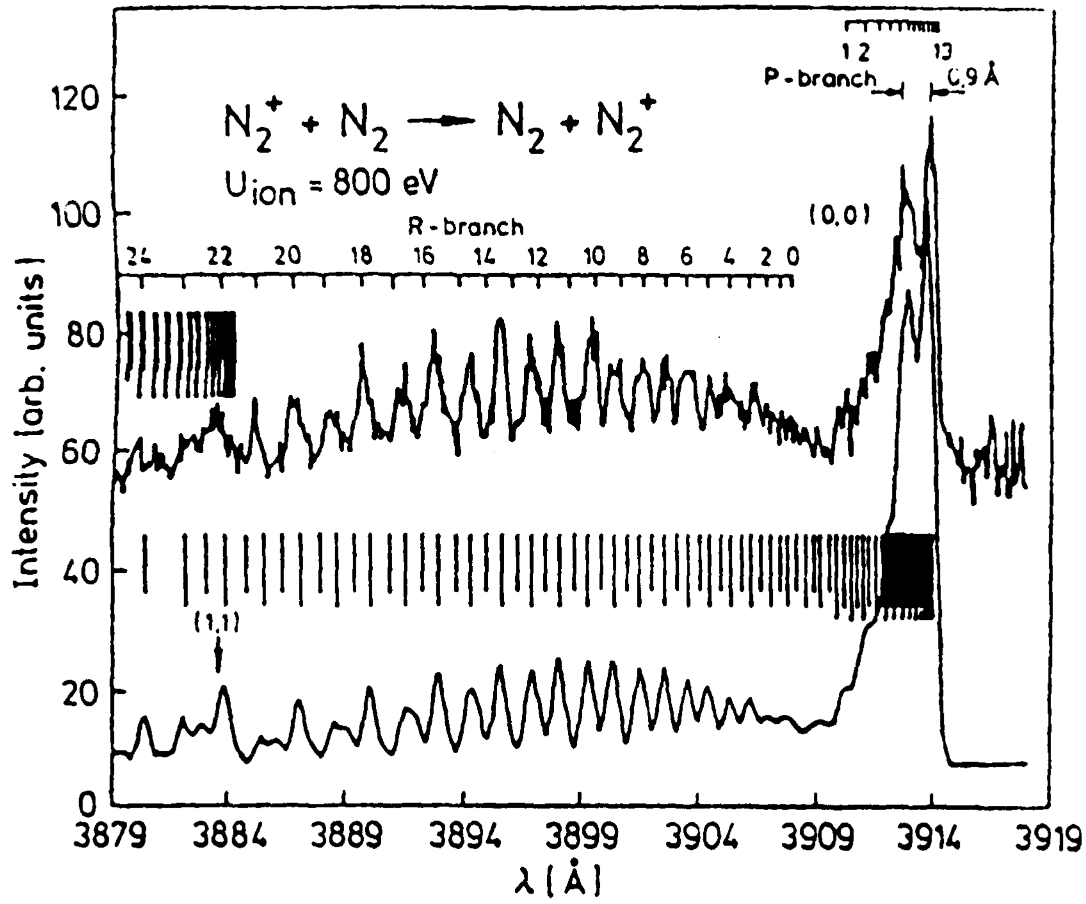


Fig.2: Experimental (top) and simulated (bottom) spectrum caused by inelastic and charge exchange collisions of N_2^+-ions with N_2

2A

C 11 THE INFRARED BANDS ν_2 AND ν_5 OF CH_3Br WITH CORIOLIS INTERACTION

R. Anttila
Department of Physics, University of Oulu, SF-90570 Oulu 57, Finland

and

C. Betrencourt-Stirnemann
Laboratoire d'Infrarouge, Université de Paris-Sud, Campus d'Orsay,
91405 Orsay Cedex, France

The infrared bands ν_2 and ν_5 of CH_3Br have been measured using a SISAM spectrometer [1]. The resolution attained was about 0.015 cm^{-1}. The absorption path length was 6 m for ν_2 and 15 m for ν_5, the sample pressures were slightly below 1 torr. The calibration was performed with the aid of CO_2 emission lines or H_2O absorption lines.

The lines due to the isotopic species $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ were resolved in general and altogether about 3 000 lines were assigned. In the parallel band ν_2 the highest K and J values were 10 and 57, respectively. In the perpendicular band ν_5 the measurement region covered the subbands from $K\Delta K = -6$ to $K\Delta K = 8$.

Between the rovibrational levels of the states $v_2 = 1$ and $v_5 = 1$ there exists a xy-Coriolis interaction. Accordingly both the bands were simultaneously analyzed by taking the resonance into account. Molecular constants at both the vibrational states were derived as well as the Coriolis coupling constant. The vibrational isotopic shifts proved to be small as the following ν_0 values [cm^{-1}] show:

	$CH_3{}^{79}Br$	$CH_3{}^{81}Br$
ν_2	1305.932	1305.903
ν_5	1442.936	1442.924.

The subband $K\Delta K = 6$ in ν_5 was clearly effected by a local perturbation, eg. the Q branch was composed of two separate parts. The resonance could be explained to be due to the interaction of $|v_2 = 1, K = 9\rangle$ with the upper state of the subband.

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C12 ℓ - RESONANCE EFFECTS IN THE HOT BANDS $3\nu_5 - 2\nu_5$, $(\nu_4+2\nu_5) - (\nu_4+\nu_5)$ AND $(2\nu_4+\nu_5) - 2\nu_4$ OF ACETYLENE

J. Hietanen

Department of Physics, University of Oulu, Linnanmaa
SF-90570 Oulu 57, Finland

Recently the infrared spectrum of acetylene around 700 cm^{-1} was published [1]. In this work the bending fundamental ν_5 as well as the accompanying hot bands starting from the levels $v_4 = 1$ and $v_5 = 1$ were analyzed. Using the same spectra the hot bands starting from the higher levels $v_4 = v_5 = 1$, $v_4 = 2$ and $v_5 = 2$ have now been studied.

Altogether 500 rotational lines were assigned to about 20 different vibrational transitions of the following types $3\nu_5 \leftarrow 2\nu_5$, $\nu_4 + 2\nu_5 \leftarrow \nu_4 + \nu_5$ and $2\nu_4 + \nu_5 \leftarrow 2\nu_4$. In these hot bands both the upper and the lower states are strongly perturbed by ℓ-type resonances.

The parameters characterizing the energy levels have been derived by using the basic theory worked out by Amat and Nielsen [2] and further developed by Pliva [3] and Winnewisser and Winnewisser [4].

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C 13

DIODE LASER SPECTRA OF UNSTABLE MOLECULES: BCl, SnO, ClO, etc.

Arthur Maki, Frank Lovas, Wm. Bruce Olson, and R. D. Suenram
Molecular Spectroscopy Division
National Bureau of Standards
Washington, D.C. 20234

Tunable infrared diode laser spectra have been measured on a number of molecules that are unstable (or short-lived) under normal laboratory conditions. Some of the molecules, such as SnO and LiF are produced in an oven at elevated temperatures. Some, such as BCl or ClO are produced by either a d.c. discharge or a 2450 MHz microwave discharge. In most cases, ClO is the only excpetion, transitions from vibrationally excited states have been measured. The most extensive set of hot bands to be observed was in the case of LiF where we have v = 1-0, 2-1, 3-2, 4-3, 5-4, 6-5, and 7-6 transitions.

Since the tunable diode laser that we are using only gives spectra over selected intervals within the wavenumber range from 827 cm^{-1} to 886 cm^{-1}, we have only been able to observe the v = 1-0, 2-1, and 3-2 transitions of AlF. For AlF, R-branch transitions have been measured from R(39) through the band head that occurs at R(98) and up to R(103) for v = 1-0, and v = 3-2, and R(109) for v = 2-1. All of the analyses include both infrared and microwave data, when available, in order to obtain the best set of Dunham coefficients.

With the exception of LiF, the transitions of different isotopic species of a given molecule have been fit to a single set of Dunham coefficients using the usual reduced mass relationships for the isotopic variation in the Dunham coefficients. Evidently a small break-down in the Born-Oppenheimer approximation causes small deviations from the usual reduced mass equations that prevents their application to the ^{6}LiF - ^{7}LiF isotopic shift. Measurements have been made on nine isotopic species of SnO and four isotopic species of BCL.

These infrared measurements have been calibrated with the aid of new frequency calibration tables that have been developed for OCS.[1] This calibration data has allowed us to determine many of the ClO absorption frequencies with an accuracy of ±15 MHz or better.

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[1] These tables are being prepared for the Journal of Physical Chemical Reference Data; see also J. S. Wells, F. R. Petersen, A. G. Maki, and D. J. Sukle, Appl. Opt. 20, 1676-1684 (1981).

C 14

HIGH RESOLUTION INFRARED STUDIES OF $^{10}B_2H_6$ AND $^{10}B_2D_6$. ROTATIONAL CONSTANTS, HARMONIC FORCE CONSTANTS AND AVERAGE STRUCTURE.

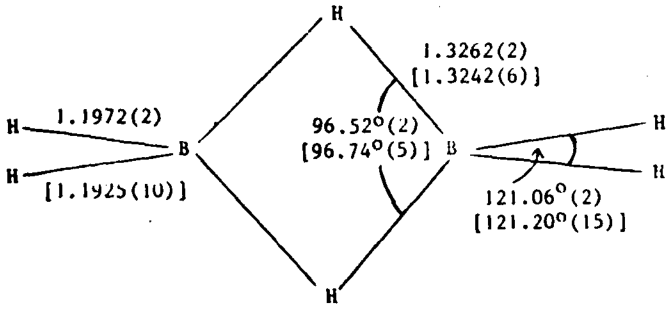
J.L. Duncan and E. Hamilton
Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland.

A number of essentially unperturbed bands in the infrared spectrum of $^{10}B_2H_6$ and $^{10}B_2D_6$ have been recorded at 0.05 cm^{-1} resolution. Assignments in 4 bands (3 type-A + 1 type-C) of $^{10}B_2H_6$ and 5 bands (3 type-A + 1 type-B + 1 type-C) of $^{10}B_2D_6$ have been made. These enable the ground state parameters A_o, B_o, C_o, Δ_J^o, Δ_{JK}^o, Δ_K^o to be determined, with δ_J^o and δ_K^o constrained to values predicted by the harmonic force field.

	$^{10}B_2H_6$	$^{10}B_2D_6$
A_o/cm^{-1}	2.655452(81)	1.334684(67)
B_o	0.642276(28)	0.459912(54)
C_o	0.587342(28)	0.406509(64)
Δ_J^o	1.29(4) × 10^{-6}	0.42(8) × 10^{-6}
Δ_{JK}^o	2.13(26) × 10^{-6}	1.12(29) × 10^{-6}
Δ_K^o	15.73(47) × 10^{-6}	3.16(38) × 10^{-6}
δ_J^o	[0.10 × 10^{-6}]	[0.08 × 10^{-6}]
δ_K^o	[2.00 × 10^{-6}]	[0.87 × 10^{-6}]

For $^{10}B_2H_6$, the results agree well with the previous results of Lafferty et al.(1), but are now more precisely defined.

A total of 80 input data (ω, $\Delta\omega$, ζ, Δ) for the six B_2H_6 and B_2D_6 isotopic species allows 27 of the 33 harmonic force constants to be determined unambiguously. The force field was used to correct the ground state inertial constants, I_α^o, to the ground state average, I_α^z, values, using also Lafferty et al.'s results for $^{11}B_2H_6$ (1). The nine available inertial constants, when used in conjunction with isotopic structural differences determined by electron diffraction (2), predict the ground state average structure parameters shown. Values in [ ] are for B_2D_6.



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C 15

FT infrared investigation of parallel bands of CF_3Cl, CF_3Br and CF_3I

H. Bürger, K. Burczyk, R. Grassow and P. Schulz
Anorganische Chemie, FB 9, Universität-Gesamthochschule,
D-5600 Wuppertal, F.R.G.

A. Ruoff
Sektion Schwingungsspektroskopie, Universität,
D-7900 Ulm, F.R.G.

The infrared parallel bands of CF_3Cl, CF_3Br and, in part, CF_3I have been examined in the gas phase with a resolution of 0.04 cm^{-1}, ^{35}Cl and ^{79}Br enriched isotopmers being employed. Rotational J structure was resolved, and all a_1 fundamentals and a great number of anharmonicity and rotation - vibration interaction constants have been measured. Strong Fermi resonance has been found in particular CF_3Br where the levels $(n+2)\nu_3/\nu_2 + n\nu_3/\nu_1 + (n-1)\nu_3/2\nu_5^0 + (n-1)\nu_3$ interact. This resonance causes a pronounced non - additivity of the α values. Hot bands, mainly with ν_6 and ν_3, play an important role at room temperature, and several of their rovibrational systems could be identified and analyzed both by polynomial and band contour simulation methods. J clusters are usually sharp, and no K structure could be resolved though one exception has been detected.

C 16 Dissociation energy of LaO from the true potential energy curve

L.S. Gowda and B.N.K. Setty
Department of Physics
University of Agricultural Sciences
Agricultural Engineering Institute
Raichur-584101 India

and

V.N. Balaji
Molecular Biophysics Unit
Indian Institute of Science
Bangalore-560012 India

The band systems of LaO are of considerable astrophysical and geophysical importance. LaO bands have been found in S-type stars extending in the wavelength region of 5015-6450 Å. The value for the dissociation energy De of LaO obtained from different methods have been reported by various investigators. It is found that these values differ from one another. Hence, in the present investigation, the Lippincott and the Hulburt-Hirschfelder (H-H) potential functions are chosen as the empirical potential functions. The turning points of the RKRV curve for the ground state of LaO are used in the empirical function and for a particular value of De. The energy values U(r) are obtained for various vibrational levels. These energy values can be compared with those obtained from experimental data G(v). The value of De for which the best fit of energy values is achieved is taken as the dissociation energy and the method is known as the curve fitting method. The influence of vibration-rotation interaction* on (B-X) system of Lanthanumoxide is also studied.

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C 17

AUTOIONIZATION EFFECTS IN THE THEORETICAL STUDY OF THE PARTIAL PHOTOIONIZATION CROSS SECTION FOR THE $b^4\Sigma_g^-$ STATE OF O_2^+

A. GIUSTI, H. LEFEBVRE-BRION, H. LE ROUZO, G. RASEEV
and A.L. ROCHE

Laboratoire de Photophysique Moléculaire, Bâtiment 213,
Université de Paris-Sud 91405 Orsay, France.

An interpretation of the partial photoionization cross sections in the region 610-660 Å leading O_2^+ in the $b^4\Sigma_g^-$ state[1] is proposed. The direct ionization process is calculated by an ab-initio method based on the static exchange (or Hartree-Fock) approximation[2]. The multichannel Quantum Defect Theory (M.Q.D.T.) is used for calculating the effect of the electronic autoionization[3] due to the Rydberg states of the "strong" and "weak" series converging to the $B^2\Sigma_g^-$ state of O_2^+[4]. The interaction parameters used in the MQDT are compared to ab-initio calculations. This interpretation is supported by the vibrationally resolved partial photoionization cross sections observed in this region[5].

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C 18

HIGH RESOLUTION ON THE NEAR ULTRAVIOLET A --- X SYSTEM OF N_2O^+ BY DOPPLER-TUNED LASER PREDISSOCIATION.*

M.LARZILLIERE, M.CARRE and M.L.GAILLARD

Laboratoire de Spectrométrie *Ionique* et *Moléculaire* (associé au CNRS)
Université Claude Bernard - Lyon 1
Campus de la Doua, 69622 - VILLEURBANNE, France.

With a Kr^+ laser as a light source, we applied the fast ion beam laser spectroscopy method (1) to the near ultraviolet system of N_2O^+ whose upper state is partially predissociated into NO^+ and N.

Through electrical detection of the photofragments NO^+, we obtained a rotationally resolved predissociation spectrum which is quite similar to the emission spectrum previously analysed by Callomon and Creutzberg (2).

Further improvement in the laser line width was obtained by use of an intracavity Fabry Perot etalon which leads to a width of few MHz on the 337.5 nm laser line, well below The Doppler line width due to the velocity spread of the ion beam (80 - 100 MHz).

A Doppler scan for ion beam energies between 15 and 150 KV corresponds to the recording of the predissociation spectrum from 29550 to 29600 wavenumbers with a resolution which exceeds 10^7. Under those conditions, we observed the rotational band identified by Callomon as the $A^2\Sigma^+$ (100) --- $X^2\Pi$(000) transition.

The resolution improvement reveals however that the fine structure of the observed transition does not confirm earlier identifications and that one should rather invoke a $^2\Delta$ - $^2\Pi_{3/2}$ transition in order to explain the details of the rotational structure. The implications of such a change for the analysis of the N_2O^+ spectrum and predissociation mechanism will be discussed.

Detailed observation of each rotational line, also provides the first experimental evidence of the hyperfine structure due to the nuclear spin of the nitrogen atoms.

* This work was supported in part by DRET contract n°79/386

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C 19

ELECTRONIC TRANSITION MOMENT OF THE BLUE-GREEN BAND SYSTEM OF SCANDIUM MONOXIDE

B.NARASIMHAMURTHY and N.SREEDHARAMURTHY
Department of Physics, University of Mysore, Mysore 570 006
India

Astrophysically important molecule scandium monoxide is studied in its ($B^2\Sigma - X^2\Sigma$) band system. In an arc source fed with scandium oxide, bands are excited. Integrated intensities for seventeen bands are measured by the technique of heterochromatic photographic photometry. Morse potential is found adequate to represent the electronic states of $B^2\Sigma$ and $X^2\Sigma$ of ScO for the v-values encountered in the present study. Appropriate to this potential the Franck-Condon factors and the r-centroids are calculated by numerical integration. The r-centroid approach is followed to extract the form of electronic transition moment. It is a linear function of the internuclear separation. An array of band strengths for the system is provided. Effective vibrational temperature of the source is calculated.

C 20 Rotational Analysis of the D-X and F-X transition of SiCl

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F. MELEN, I. DUBOIS, and H. BREDOHL
Institut d'Astrophysique
Université de Liège
B-4200 Cointe-Ougrée, BELGIQUE

Three electronic transitions of SiCl (D-X, E-X and F-X) have been reported in absorption under low resolution by Oldershaw and Robinson (J. Mol. Spectr. 38, 306, 1971).

High resolution emission and absorption spectra have been obtained in the 2350-2000 Å region. Rotational analysis has been done for six bands of the $D^2\Sigma^+ - X^2\Pi_r$ transition (0-0, 0-1, 0-2, 0-3, 1-0 and 2-0) as well as for two bands of the $F^2\Sigma^+ - X^2\Pi_r$ transition (0-0 and 0-1).

For the E-X system, only the 0-0 band at 45375, 45169 cm^{-1} is observed in absorption at high resolution and show a very heavy predissociation.

D 1 Some Recent Techniques in Laser Spectroscopy

Arthur L. Schawlow

Stanford University,
California 94305, U.S.A.

We have used two-step polarization labeling to identify even-parity excited electronic states in Na_2. Constants have thus been obtained for more than twenty states, including several Rydberg series which can be extrapolated to give values for the ground state of the molecular ion. We have also observed and identified many strong c.w. two-photon transitions in Na_2, enhanced by very near (less than 0.1 cm^{-1}) coincidence with allowed lines in the A-X band. Doppler free spectra in atoms have been detected by an extremely simple radiofrequency electrodeless discharge method, using the reaction on the oscillator which excites the discharge. The POLINEX method of T.W. Hänsch (modulated polarization) has been used to eliminate the Doppler-broadened background from velocity-changing collisions. Multiple wedge interferometers are being developed to measure wavelengths of pulsed lasers.

D 2 Problems in the Spectroscopy of the Group VI-VI Molecules

R.F. Barrow

Physical Chemistry Laboratory
Oxford University
South Parks Road
Oxford OX1 3QZ, U.K.

(no abstract)

E 1 Second order vibration - rotation Hamiltonian for Very strong Coriolis resonance : Microwave Spectra of $H^{12}COOH$ and $D^{12}COOH$

E. WILLEMOT, J. BELLET
Laboratoire de Spectroscopie Hertzienne de Lille - L.A. N° 249
59655 VILLENEUVE D'ASCQ CEDEX - FRANCE

For $H^{12}COOH$ and $D^{12}COOH$, the importance of the Coriolis perturbation strength needs a complete development of the coupling part of the vibration - rotation Hamiltonian up to the second order. The new molecular model proposed consists of two asymmetric WATSON's rotators linked by 10 vibration - rotation coupling terms.

For the $H^{12}COOH$ molecule, a complete investigation of the 8 → 280 GHz region allowed the assignment of 260 pure rotational transitions to the $v_7 = 1$ and $v_9 = 1$ vibrational states strongly coupled by a Coriolis resonance. The quality of the 31 fitted molecular parameters allowed the assignment of 14 intervibrational states transitions induced by the very strong resonance. Consequently, it is possible to give the energy difference between the ν_7 and ν_9 band centers with a precision of 0.5 MHz. For the $D^{12}COOH$ molecule, 92 pure rotational transitions have been assigned to the $v_7 = 1$ and $v_9 = 1$ resonant vibrational states, and 2 microwave intervibrational transitions have just been assigned. At this time, 24 parameters are well determined.

E 2

Nonadiabatic calculations of the emission spectrum of H_2^+

Annik Vivier Bunge and Carlos F. Bunge

Departamento de Química, Universidad Autónoma Metropolitana,
Iztapalapa, México 13, D.F., MEXICO

We treat H_2^+ as a two-proton system with the coordinate frame centered at the electron. Atomic-like L-S symmetry applies, there being an approximate correspondence between these and adiabatic Born-Oppenheimer states. Extensive configuration interaction calculations using $r^{n-1}\exp(-\alpha r)\cos(\beta r)$ radial funcations are carried out in an effort to identify the most likely emission spectrum. Oscillator strengths and wavelengths for $2p\pi_u$(discrete) → $1s\sigma_g$(continuum), $3d\sigma_g$(resonance) → $2p\sigma_u$(continuum) and $2p\pi_u$(discrete) → $3d\sigma_g$(resonance) transitions will be presented.

E 3 Centrifugal distortion constants for diatomic molecules: an improved computational method

JEREMY M. HUTSON

Physical Chemistry Laboratory, Oxford University,
South Parks Road, Oxford OX1 3QZ, England.

Centrifugal distortion constants are important when fitting molecular parameters to spectroscopic data, but it is often difficult to separate the effects of centrifugal distortion from those of other parameters on experimental grounds alone. However, if an accurate potential energy curve is available, centrifugal distortion constants may be calculated theoretically. Several methods have been proposed for this [1-4], and work well for low vibrational levels, but all are either inaccurate or computationally difficult for highly excited vibrational states. We have developed an alternative approach which eliminates this problem.

In the present method, the perturbation theory approach of Albritton et al. [1] is reformulated to eliminate summations over excited vibrational states. In the usual formulation of Rayleigh-Schrödinger perturbation theory, these summations appear when the solution of an inhomogeneous differential equation is expressed as a sum over the eigenfunctions of the unperturbed Hamiltonian. In the present method, this differential equation is solved numerically, eliminating the summations and giving an exact solution using much less computer time than in the original perturbation theory method. The centrifugal distortion constants are then calculated by a straightforward numerical integration. The effects of continuum levels are included exactly, so that the results remain valid for vibrational levels near dissociation.

The method is very accurate and computationally inexpensive, and centrifugal distortion constants of high order may be calculated at very little additional expense. A fully documented FORTRAN program is available for calculating the centrifugal distortion constants D_v, H_v, L_v and M_v from a potential curve.

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E 4

Microwave Fouriertransform Spectroscopy and Applications

G. Bestmann, E. Fliege and H. Dreizler

Abteilung Chemische Physik, Institut für Physikalische Chemie, Universität Kiel, Olshausenstr.
4o - 6o, D-23oo Kiel.

The construction of a Microwave-Fouriertransform Spectrometer in X- and Ku-band (8-18 GHz) will be presented. This spectrometer is built for gas phase rotational spectroscopy at low pressures down to 10^{-4} mT. It seems to be more sensitive than usual Starkspectrometers. Also the resolution is superior for different reasons. A range of 50 MHz may be observed during a single measurement.

Up to now the spectrometer has been tested with more than 2o molecules.

Presently the HFS structure of nitrogen and the torsion fine structure of high barrier molecules are under investigation, which could not be investigated hitherto.

Examples bill be given.

E5

INVESTIGATIONS ON CYCLOBUTYLSILANE BY MICROWAVE SPECTROSCOPY

A. Wurstner and H.D. Rudolph
Dept. of Physical Chemistry
University of Ulm
D-7900 Ulm, W.Germany

The microwave spectra of cyclobutylsilane in the ground state and in a first excited state have been investigated in the region 13.0 - 39.0 GHz. Sixty-eight a- and c-type transitions of the ground vibrational state were analyzed. The rotational and centrifugal distortion constants were fitted. As a monoderivative of cyclobutane cyclobutylsilane could exist in two possible conformations with the silylgroup in either the axial or equatorial position with respect to the puckered cyclobutane ring. The rotational constants of cyclobutylsilane were predicted using structural parameters of cyclopropylsilane and cyclobutylchloride. The experimentally obtained values are in considerably better agreement with the equatorial structure. The dipole moment components were determined from Stark effect measurements and agree with the equatorial structure of the compound.

E 6

Intramolecular Hydrogen Bonding in Glycolic Acid: Microwave Spectrum, Dipole Moment, Molecular Structure and Quantum-Chemical Calculations.

C.E. Blom and A. Bauder,
Laboratory for Physical Chemistry, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland.

The microwave spectrum of glycolic acid ($CH_2OHCOOH$) has been investigated in the frequency range from 18 GHz to 40 GHz . Rotational constants and centrifugal distortion constants for ground state and two vibrationally excited states have been adjusted to the measured transition frequencies. Only one conformer was found. From observed Stark splittings the electric dipole moment has been determined: $\mu_a = 1.913(5)$ D, $\mu_b = 0.995(14)$ D and $\mu_{total} = 2.156(9)$ D .

From the rotational constants of the parent molecule and nine isotopic species (all eight single and one double substitution) the molecular structure of glycolic acid has been determined. The hydroxyl group points towards the carbonyl oxygen of the carboxylic group with an intramolecular O$\cdots$H distance of 2.11 Å .

The substitution structure is compared with results from neutron diffraction and with the quantum-chemical calculations. The centrifugal distortion constants agree with those computed from a General Valence Force Field based on infrared matrix spectra.

E7 Propagation of a resonant / non resonant electromagnetic step through an optically thick gas : experiments in the millimetre region

B. SEGARD, H. DEVE, F. ROHART and B. MACKE

Laboratoire de Spectroscopie Hertzienne de LILLE, Associé au CNRS
Bât. P5 Université de LILLE I
59655 Villeneuve d'Ascq Cedex, FRANCE

We have examined the propagation of an electromagnetic step at $\lambda = 1.6$ mm through a $\ell = 17$ m - long cell filled with OCS gas at low pressure. Its frequency was equal or nearly equal to that of the OCS rotational line $J = 14 \rightarrow J = 15$. This line has a large linear absorption coefficient ($\alpha = 1.84\ \mathrm{m}^{-1}$) leading to a cell optical thickness $\alpha\ell \simeq 31$ at resonance. The 1.6 mm - wave power was low enough to avoid any saturation effect.

(1) when the incident 1.6 mm - wave is exactly resonant, only a short pulse is transmitted by the cell in the collisional limit. Its rise time is only limited by that of the step ($\simeq 7$ ns) for it is clear that there cannot be any absorption of the front edge : there has not been time to create the necessary gas polarization. Surprisingly enough, the pulse fall time is much shorter than the collisional relaxation time T_2, namely a few $T_2/\alpha\ell$, a result in agreement with a previous theoretical calculation.

(2) when the incident 1.6 mm - wave is detuned from resonance (so as the gas is transparent and weakly dispersive in steady state), the signal delivered by the quadratic detector consists of a transient beat at the detuning frequency superimposed on the main step. This beat is simply interpreted as resulting from the mixing of the incident wave and of a resonant pulse reemitted by the molecules at their eigenfrequency (SIRF pulse, SIRF = Stimulated Inelastic Resonance Fluorescence). In the collisional limit, a theoretical calculation taking account of the SIRF reabsorption shows that the SIRF pulse is strongly modulated. Its amplitude and its duration are respectively proportional and in inverse ratio to the optical thickness $\alpha\ell$, its area being $\alpha\ell$ independent. All the theoretical predictions are well supported by the experiments.

Let us note that the phenomena discussed in this communication are closely related to two problems encountered in laser spectroscopy : the interest of the experiments in the millimetre region is to benefit from a favourable time scale facilitating the observation.

E 8 A_0 and D_K for CD_3I from the ν_4 Raman and IR bands

Carsten Poulsen and Svend Brodersen

Dept. of Chemistry, Aarhus University

8000 Aarhus C, Denmark.

Accurate experimental values for A_0 and D_K have been known for some time for all the methyl halides of species CH_3X, except for CD_3I.

The ν_4 vibration-rotational Raman band of CD_3I has been recorded at a resolution of 0.28 cm^{-1}. The prominent features in the spectrum are the two series of unresolved Q-branches of the two components $\Delta K = +1$ and $\Delta K = -2$. The J assignment of each Q-branch was found iteratively by assigning to each peak the J value of the individual line being nearest to the peak. The weighted least squares fit included data from the ν_4 infrared band [1]. The residuals show no systematic trend, in contrast to the simultaneous analysis by Peterson and Edwards [1] of the ν_4 and $2\nu_4$ infrared bands.

$A_0 = 2.59607(10)$ cm^{-1} and $D_K = 2.05(8) \times 10^{-5}$ cm^{-1} are obtained, in addition to values for ν_o, $(A\zeta)_4$, ΔA and ΔB. The A_0 value fits excellently with the known values for the other seven methyl halides species, and the D_K value agrees with the theoretical value of 2.1×10^{-5} cm^{-1} calculated by Duncan [2].

[1] R.W. Peterson and T.H. Edwards: J. Mol. Spectrosc. 38, 1 (1971).

[2] J.L. Duncan: J. Mol. Spectrosc. 60, 225 (1976).

E 9

Perturbations between an A_1 and an E fundamental state in a C_{3v} molecule

Claus Bo Mikkelsen and Svend Brodersen
Department of Chemistry
Aarhus University
DK-8000 Aarhus C
Denmark

The blocking of the Hamiltonian matrix is shown graphically for the two possible cases:

1. Symmetry blocking only. Dimensions of blocks are J-depended.
2. Off-diagonal elements are selected to obtain blocks of J-independent dimensions (max. 3×3).

The identity of blocks, energies and intensities is discussed.

The second case is examplified by means of an energy level diagram for the $\nu_2(A_1)$ and $\nu_5(E)$ vibrational states of CD_3F.

E 10

The Vibrational Fundamentals of $^{12}CD_3F$ in the region 1040-1200 cm^{-1}

G.L. Caldow *

Department of Chemistry
University of Reading
Reading RG6 2AD, U.K.

L.O. Halonen

Department of Theoretical Chemistry
South Parks Road, Oxford, U.K.

Preliminary work (1) on the laser Stark spectra of $^{12}CD_3F$ has led to a reliable estimate of the ν_5 band origin and to an interpretation of the Q branch structure of ν_5 in the FTIR spectrum. However the perturbation model used in that study is insufficiently accurate to allow a complete interpretation of all the laser Stark data in this region or to predict the microwave data to experimental accuracy. Nevertheless the model is sufficiently accurate to assign the low J transitions of the K=0 and 1 Q branches as measured using laser diode techniques (2).

We have now written a computer program which diagonalises the complete interaction Hamiltonian matrix for the ν_2 and ν_5 ro-vibrational energy levels. This has allowed us to fit simultaneously the microwave, laser Stark and diode spectra and over 800 transitions in the Nicolet FTIR spectrum for the region 1040-1200 cm^{-1}. A comparison of the calculated and observed infrared spectra shows the phases of the dipole moment derivatives to be of opposite sign. Some of the transitions which would be forbidden in the absence of the interaction are of comparable intensity to the allowed ν_5 transitions.

In our previous study (1) we noted that some of the unassigned Stark spectra were observed to have Lamb dips. These are now shown to arise from ν_5 transitions where there is significant mixing with ν_2. These results suggest that care must be taken in assigning Stark spectra where strong interactions are likely to occur.

(1) G.L. Caldow and G. Duxbury, J.Mol.Spectro., in press.
(2) J. Sattler and L. Worchesky, private communication.

* on study leave from the Department of Theoretical Chemistry, University of Bristol, U.K.

E 11

HIGH RESOLUTION INFRARED STUDY OF THE A-CORIOLIS INTERACTING BAND SYSTEM $\nu_6, \nu_7, \nu_8, \nu_{10}$ IN H_2CCD_2.

F. Hegelund*, A.R. Morrisson and J.L. Duncan,
Department of Chemistry, University of Aberdeen,
Old Aberdeen, AB9 2UE, Scotland.

The intense ν_7 and ν_8 c-type and the weaker ν_6 and ν_{10} b-type fundamentals of as-ethylene-d_2 have been studied at a resolution of ca 0.05 cm^{-1} using spectra obtained on a Nicolet FTIR spectrometer.

From the ν_7 and ν_8 bands the following ground state rotational and distortion constants have been determined in terms of the full asymmetric rotor model (cm^{-1}):

$A_o = 3.25196(16)$, $B_o = 0.85648(10)$, $C_o = 0.67622(15)$

$\overset{o}{\Delta}_J = 1.03(15) \times 10^{-6}$, $\overset{o}{\Delta}_{JK} = 6.6(7) \times 10^{-6}$, $\overset{o}{\Delta}_K = 39.3(8) \times 10^{-6}$

$\overset{o}{\delta}_J = 0.19(10) \times 10^{-6}$, $\overset{o}{\delta}_K = 11(3) \times 10^{-6}$.

The uncertainties which are given in units of the last digit(s) quoted are 2.5 standard deviations.

a-Coriolis interactions between the b- and c- type bands result in global perturbations of all four bands. Taking into account these resonances, unperturbed upper state rotation and vibrational parameters are obtained from sub-band origins. In addition, full asymmetric rotor analyses of ν_7 and ν_8 yield B,C and distortion constants for these levels.

Localized higher order Coriolis resonances between the inactive ν_4 level and ν_8, as well as between ν_7 and ν_{10} are discussed in some detail.

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* Permanent address: Department of Chemistry;
Aarhus University,
DK-8000 AARHUS C,
Denmark.

E 12 Optoacoustic and Classical Infrared Spectroscopy of C_2H_3D between 9 and 13 μm.

Ph. Herbin, C.P. Courtoy
Laboratoire de Spectroscopie Moléculaire
Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles, 61
B-5000-Namur, BELGIQUE.

A. Delplace , A. Fayt
Laboratoire de Spectroscopie Moléculaire
Université Catholique de Louvain, Chemin du Cyclotron, 2
B-1348-Louvain-La-Neuve, BELGIQUE.

We have undertaken the study of the absorption of C_2H_3D between 9 and 13 μm to determine the contribution of this isotopic species in the optical pumping of ethylene by CO_2 lasers.

We have recorded the absorption spectrum of C_2H_3D from 720 to 920 cm^{-1} with our "dual-grill" spectrometer. The absorption is due to the ν_7 band (C-type band near 807 cm^{-1}) and to the ν_8 band (C-type band near 943 cm^{-1}). The ν_7 and ν_8 levels are coupled through a-and b-type Coriolis interactions with the ν_{10} level near 730 cm^{-1}. We have performed a simultaneous analysis of those three levels taking into account the a-type Coriolis interaction between them.

On the other hand, some coïncidence between C_2H_3D absorption lines and CO_2 laser lines have been detected by using a quite sensitive optoacoustic cell. The analysis of those results will be discussed.

E 13

Rovibrational investigation of the ν_3 and ν_6 fundamentals of H_3SiCl, H_3SiBr and H_3SiI

H. Bürger and P. Schulz
Anorganische Chemie, FB 9, Universität-Gesamthochschule,
D-5600 Wuppertal, F.R.G.

A. Ruoff
Sektion Schwingungsspektroskopie, Universität,
D-7900 Ulm, F.R.G.

The rovibrational spectra of $H_3Si^{35}Cl$, $H_3Si^{79}Br$, $H_3Si^{81}Br$, H_3SiI and of natural material have been investigated with a resolution of 0.04 in the region of the fundamentals and several overtones. Spectra and their evaluation will be presented for the fundamentals ν_3 (a_1) and ν_6 (e), the overtones $2\nu_3$ (H_3SiCl), $2\nu_6^{\pm 2}$ and $2\nu_6^{0}$ and hot bands $2\nu_3-\nu_3$, $\nu_3+\nu_6-\nu_6$, $\nu_6+\nu_3-\nu_3$ and $2\nu_6^{\pm 2,0}-\nu_6$. While ν_3 (and $2\nu_3$) appear as typical parallel bands possessing P and R branches with sharp J clusters and no resolvable K structure, the perpendicular bands ν_6 and $2\nu_6^{\pm 2}$, for $\Delta J = \pm 1$, are resolved into J lines belonging to different $K \Delta K$ values.

Typically 800 - 2000 lines could be measured, assigned and fitted, σ (J,K) being in the order of 5×10^{-3} cm^{-1}. The strongly perturbed $\nu_3+\nu_6$ state of H_3SiI has been identified, and a second order Coriolis resonance is likely to occur in this molecule between ν_6 and $2\nu_3$.

E 14

HIGH RESOLUTION INFRARED SPECTRA OF ν_7, ν_8, ν_4, ν_{10} AND ν_6 BANDS OF $H_2{}^{12}C^{13}CH_2$.

M. De Vleeschouwer, Ch. Lambeau and A. Fayt.
Department of molecular spectroscopy,
University of Louvain
Chemin du Cyclotron, 2, 1348 Louvain-La-Neuve, Belgium.

C. Meyer
Laboratoire d'Infrarouge, Université de Paris-Sud,
Bâtiment 350, 91405 ORSAY Cédex, France.

The study of optical pumping of ethylene in the 10μm region has brought our attention on the $H_2{}^{12}C^{13}CH_2$ *molecule which is by far the most abundant isotopic impurity (~2.2 %) in normal samples.*

The infrared spectrum of $H_2{}^{12}C^{13}CH_2$ *has been recorded from 836 to 991* cm^{-1} *using the double pass SISAM spectrometer of Laboratoire d'Infrarouge at Orsay, with a 0.015* cm^{-1} *resolution.*

Five levels ν_6, ν_7, ν_8, ν_{10} *and* ν_4 *are strongly coupled by a-type and b-type Coriolis interactions. The* ν_6 *and* ν_8 *levels, only Raman active for* $H_2{}^{12}C^{12}CH_2$ *are infrared active for* $H_2{}^{12}C^{13}CH_2$ *because of the lack of symmetry for that molecule. The* ν_8 *band appears to be about five times weaker than the* ν_7 *one. The infrared activity of* ν_8 *will substantially increase the possibilities of optical pumping for* $H_2{}^{12}C^{13}CH_2$ *which enhance the interest of studying that molecule.*

The analysis has been applied to the five levels simultaneously to take into account the interactions mixing them.

The final set of parameters gives a calculated spectrum in perfect agreement with the experimental data. Predictions about coincidences between $H_2{}^{12}C^{13}CH_2$ *lines and* N_2O *and* CO_2 *isotopics lasers have been calculated like for* $H_2{}^{12}C^{12}CH_2$.★

★ *Ch. Lambeau, A. Fayt, J.L. Duncan and T. Nakagawa, J. Mol. Spectrosc., 81, 227-247 (1980).*

E 15

FOURIER TRANSFORM SPECTRA OF $^{12}C_2H_4$, $^{12}C^{13}CH_4$ AND $^{13}C_2H_4$ FROM 1750 TO 2380 CM^{-1}.

M. De Vleeschouwer, Ch. Lambeau and A. Fayt
Department of molecular spectroscopy,
University of Louvain,
Chemin du Cyclotron, 2, 1348 Louvain-La-Neuve, Belgium.

G. Guelachvili
Laboratoire d'Infrarouge
Université de Paris-Sud
Bâtiment 350, 91405 ORSAY Cédex, France.

The low and high pressure spectra of $^{12}C_2H_4$, $^{12}C^{13}CH_4$ and $^{12}C_2H_4$ have been recorded from 1750 to 2380 cm^{-1} using the Fourier Transform spectrometer of Laboratoire d'Infrarouge at Orsay with a 0.005 cm^{-1} resolution and an absolute precision of a few 10^{-4} cm^{-1}.

The great quality of the spectra yields to the determination of ground state combination differences up to high values of J and K_a and consequently to the first determination of the ground state energy levels of $^{13}C_2H_4$.

The analysis of $^{12}C_2H_4$ and $^{13}C_2H_4$ has been performed by treating simultaneously $\nu_7 + \nu_8$, $\nu_4 + \nu_8$ and $\nu_8 + \nu_{10}$ to take into account the strong interactions mixing them.

For $^{12}C^{13}CH_4$, the $2\nu_8$, $2\nu_7$, $\nu_7 + \nu_{10}$ and $\nu_4 + \nu_{10}$ bands, only Raman active for $^{12}C_2H_4$ and $^{13}C_2H_4$, are also infrared active because of the lack of symmetry. They are strongly coupled with $\nu_7 + \nu_8$, $\nu_4 + \nu_8$ and $\nu_8 + \nu_{10}$ so that they must be introduced in the analysis.

The study of this region leads to the determination of the upper states of the hot bands transitions appearing in optical pumping processes in ethylene.

E 16

Ultraviolet Absorption Spectrum of the CaH Molecule

B. Kaving and B. Lindgren

Institute of Physics, University of Stockholm
Vanadisvägen 9, S-113 46 Stockholm, Sweden

The spectra of CaH and Cad have been studied between 2450 and 3600 Å. Metallic calcium has been heated in a hydrogen (deuterium) atmosphere in a King type furnace. Temperatures of 1200 and 1400°C gave sufficient absorption.

Apart from the well-known C-X and F-X transitions this region of the spectrum is dominated by strong features around 3060, 2850, 2611 and 2530 Å. The first two features are identified as transitions between the 5p and 4d complexes and the ground state. This identification leads to an ionization energy of 47 250±750 cm^{-1}. Deuteride studies have confirmed these results.

The 6p and 5d complexes are then estimated to lie around 2535 Å and 2475 Å respectively. The long wavelength part of the feature around 2530 Å has the expected intensity distribution of a transition involving the $p\sigma$ part of the complex.

The band at 2611 Å is identified as the (2,1) band of the F-X transition. This band shows a marked perturbation. The perturbing state has a higher B-value than the $v=2$ level of the F state has. Neighter the (2,0) nor the (2,2) band show any marked intensity but at the wavelength where the (2,0) band is expected transitions from the $6p\pi$ state to the ground state are found.

The identification of the 5d complex is rather uncertain. A band at 2493 Å with single P, Q and R branches might be a transition to the $5d\pi$ state.

E 17 Rotational analysis of the $^3\Sigma_u^- - {}^3\Sigma_g^-$ transition of $^{11}B_2$ and $^{11}B^{10}B$

I. DUBOIS, H. BREDOHL and P. NZOHABONAYO
Institut d'Astrophysique
Université de Liège
B-4200 Cointe-Ougrée, BELGIQUE

The emission spectrum of B_2, first observed by Douglas and Herzberg (Can. J. Research 18, 165, 1940) in the near UV region, has been reinvestigated under high resolution.

Rotational analysis has been performed for 6 bands of the $^{11}B_2$ species (0-0, 1-1, 1-0, 2-1, 3-2 and 0-1) as well as for 4 bands of the isotopic $^{11}B^{10}B$ species (0-0, 1-0, 2-1, 3-2).

Accurate molecular constants have been obtained for the two isotopic molecules.

On the other hand, evidence of the triplet nature of the electronic states ($^3\Sigma_u^- - {}^3\Sigma_g^-$) has been found in the strongest 0-0 band.

E 18 The $A^1\Pi$ - $X^1\Sigma^+$ transition of the CCl^+ ion

H. BREDOHL, I. DUBOIS and F. MELEN
Institut d'Astrophysique
Université de Liège
B-4200 Cointe-Ougrée, BELGIQUE

An emission spectrum in the 2300-2400 Å region has been tentatively attributed to CCl^+ by Barrow et al. (Proc. Phys. Soc. 67, 186, 1954).

This spectrum has been observed under high resolution in a HF discharge through Helium and CCl_4. It has been rotationaly analysed as effectively due to a $^1\Pi$ - $^1\Sigma^+$ transition of CCl^+. The analogy with the corresponding transition of CF^+ (Verna, Can. J. Phys. 39, 1377, 1961) is stricking.

E 19

Fourier transform absorption spectrum of the $AO_u^+ - XO_g^+$ system of $^{130}Te_2$

New results

P. LUC, Laboratoire Aimé Cotton, CNRS II, Bât. 505, 91405 ORSAY, France

J. CARIOU, J. LOTRIAN, Laboratoire de Spectroscopie Quantitative,
Faculté des Sciences et Techniques, 6 Avenue Le Gorgeu
29200 BREST, France

As we achieved the identification of the $AO_u^+ - XO_g^+$ band system of $^{130}Te_2$ (about 20.000 lines), recorded at different temperatures (from 510°C to 900°C) between 15.900 cm^{-1} and 23.700 cm^{-1} we present the global results of this investigation :

- differences between measured and calculated wavenumbers for different values of the rotational number J ;

- the expansion parameters for the molecular constants $G_{v''}$, $B_{v''}$, $D_{v''}$ for the XO_g^+ fundamental state (v" = 0 to 14) and $G_{v'}$, $B_{v'}$, $D_{v'}$, $H_{v'}$ for the lower excited state AO_u^+ (v' = 0 to 35).

Some of these results are compared to those calculated by previous authors.

To assign all the lines in the vicinity of, for example, argon ion and krypton ion laser lines, we show it is necessary to study (what we are doing now) the $BO_u^+ - XO_g^+$ system, which is much more perturbated than the A - X system.

All the results we present will be important for the users of the Tellurium Atlas edited by Aimé Cotton Laboratory.

E 20 The Dipole Moment of ^{7}LiH and ^{7}LiD in the Excited A^{1+} State

M. Brieger, A. Hese, A. Renn and A. Sodeik
Institut fur Strahlungs- und Kernphysik, T.U. Berlin
Rondellstrasse 5, D-1000 Berlin 37, BRD

Alkalihydrides show some remarkable features that made them object to many investigations, both theoretical and experimental. One of these features originating from avoided curve crossings is the strongly distorted potential energy curve of the first excited electronic state $A^1\Sigma^+$. An outstanding property of LiH in the A^1 $^+$ state is the pronounced dependence of the electric dipole moment on the vibrational quantum number which was recently established by experimental results (1,2). By means of the accurately known $A^1\Sigma^+$ potential curve of LiD and the dipole moment function of LiH (3), which should be the same for LiD within the Born-Oppenheimer approximation, dipole moments for LiD were calculated.

The experimental technique applied, was laser induced Stark Quantum Beat Spectroscopy (SQBS) which allows an exact determination of electric dipole moments. LiD molecules were excited by short pulses of a nitrogen laser pumped dye laser with an output bandwidth of less than 0.01 nm. Fig.1 shows a part of the excitation spectrum in the vicinity of the 6-0 band head in the A-X system. A decay curve of the $A^1\Sigma^+$ v'=6, J'=1 level which exhibits a modulation frequency of 87.3 MHz corresponding to a dipole moment of μ_6=.44 D is presented in fig.2. This value is 14% larger than the theoretical result $\mu_{6\ th}$=.38 D indicating that the dipole moment functions of LiH and LiD are different.

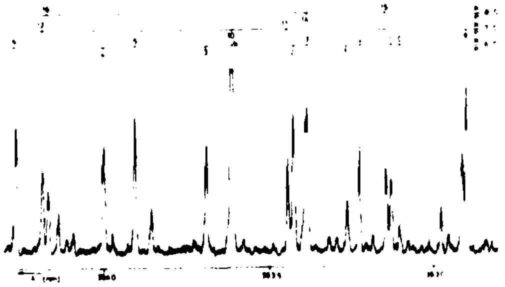

Fig.1

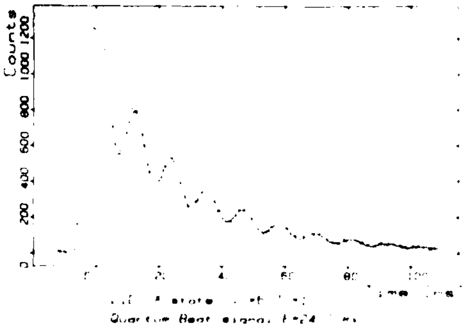

Fig.2

References: 1. P. Dagdigian, J. Chem. Phys. 73 (1980) 2049

2. M. Brieger, A. Hese, A. Renn and A. Sodeik
Chem. Phys. Lett. 76 (1980) 465

3. H. Partridge, S.R. Langhoff and W.C. Stwalley
to be published in J. Chem. Phys.

F1

Microwave spectroscopy and dye laser spectroscopy of transient molecules

S. Saito

Institute for Molecular Science
Myodaiji
Okazaki 444
JAPAN

(no abstract)

F 2

Hydrogen-bonded complexes investigated with a Fourier-transform microwave spectrometer incorporating a Fabry-Perot cavity fed with a pulsed-nozzle source of dimers.

P D Aldrich, W H Flygare and P D Soper, Noyes Laboratory, University of Illinois, Urbana, Illinois 61801

and

A C Legon, Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ.

Rotational spectroscopy is a rich source of information about the intermolecular potential energy function (e.g. equilibrium geometry, H-bond stretching force constant k_σ, dissociation energy D_e) and the electric charge distribution (e.g. electric dipole moment μ and the electric field gradients $\partial^2 V/\partial z^2$ at certain nuclei) for isolated hydrogen-bonded dimers B···HA. Conventional Stark modulation spectroscopy has been successfully applied to dimers such as HCN···HF, H_2O···HF and $(HCN)_2$ by using low pressure gas mixtures at equilibrium at ∿200K but is less well-suited to the investigation of more weakly bound species for which much lower temperatures are required to give a sufficient number density of dimers. Unfortunately, lower temperatures are difficult to sustain and, moreover, the dimer vapour pressures then become too low.

Recently, W H Flygare and his group have developed a new type of microwave spectrometer that has the desirable characteristics of a very high sensitivity for molecular dimers coupled with a high resolution. The spectrometer is of the Fourier-transform type in which the molecule-radiation interactions occur in a Fabry-Perot cavity that is fed with an appropriate gas mixture in the form of a pulse produced by supersonic expansion from a solenoid valve. Since the gas pulse thereby obtained has a very low effective temperature and carries a high number density of dimers, the technique is particularly suitable for the investigation of weakly bound dimer species.

The principles of operation of the new spectrometer will be outlined, with emphasis on its advantages and disadvantages compared with conventional Stark modulation spectroscopy. The results that can be obtained with such a spectrometer will be illustrated by references to a number of weakly hydrogen-bonded species, including (CO,HF), (RCN,HF) where R=CH_3 and NC, and (B,HCl) where B=ethyne, ethene and cyclopropane. Some details of intermolecular potential energy functions and electric charge distributions that have been obtained from the rotational spectra of these dimers will be discussed.

G1 ROTATIONALLY RESOLVED STUDIES IN GASES USING STIMULATED RAMAN TECHNIQUES*

Adelbert Owyoung and Peter Esherick
Sandia National Laboratories
Albuquerque, NM 87185

ABSTRACT

The development of high resolution stimulated Raman spectroscopy (SRS) has enabled a variety of gas phase spectroscopic studies with unprecedented sensitivity and spectral resolution (~ 0.002 cm^{-1}). Investigations of Q-branch spectra, particularly in spherical top molecules, illustrate the attractiveness of SRS in ultra-high-resolution studies which are beyond the reach of spontaneous methods.

New areas of application for SRS techniques over the past year include spatially resolved probing of molecules in supersonic free-expansion jets and time resolved investigations of photo-excited molecules. In the former case, the jet has provided a unique environment which offers advantages of (1) spectral simplification, (2) reduced spectral broadening, and (3) high sample densities. In the time resolved investigations, we are seeking to demonstrate the unique capabilities

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*Supported by the United States Department of Energy.

of SRS in probing dynamic photophysical processes, whether in a static cell or a free expansion jet. Preliminary experiments which illustrate this potential are currently being conducted on CO_2-laser-excited SF_6 molecules. These studies will serve as a first step toward the eventual goal of using SRS techniques to study molecular photofragments or other transient species.

G2 Nuclear hyperfine and superfine structure

J. Bordé

Laboratoire de Spectroscopie Moleculaire
Universite Pierre et Marie Curie
4 Place Jussieu
75230 Paris cedex 05
FRANCE

(no abstract)

G3

IR-MW Double Resonance Spectroscopy of CF_4 Using a Tunable Diode Laser

Michio Takami
The Institute of Physical and Chemical Research
Wako, Saitama 351, Japan.

Pure rotational spectra of CF_4 were investigated by infrared-microwave double resonance. A frequency tunable semiconductor diode laser was used for the pumping radiation source. Many microwave and radiofrequency transitions were observed in the ν_3 and $\nu_2 + \nu_3$ states of $^{12}CF_4$ and the ν_3 state of $^{13}CF_4$. The double resonance measurement allowed detailed analysis of the badly congested ν_3 Q-branch spectra. Tentative molecular constants were determined for the ν_3 states of $^{12}CF_4$ and $^{13}CF_4$.

H 1 Dynamic Polarizabilities of H_2. Accuracy of Theoretical Determination.

Jacek Rychlewski

Institute of Chemistry, A.Mickiewicz University,Poznan,Poland.

A variation-perturbation method has been used to calculate the dynamic dipole polarizability $\alpha(\omega)$ and the polarizability anisotropy $\gamma(\omega)$ of the hydrogen molecule over the bond length range $0.6 \leqslant R \leqslant 10.0\ a_o$ and for a wide range of frequencies ω . The unperturbed wavefunction consisted of an expansion of 80 terms and the first order perturbed function consisted of an expansion of 65 terms.These functions take explicit account of electron correlation.The results were averaged over the nuclear motion to give the polarizability and its anisotropy in a number of vibration-rotation states for the H_2,HD and D_2 molecules.The results are in excellent agreement with the experimental values obtained from refractive index data. It is found that the values obtained by averaging $\alpha(\omega,R)$ over vibration-rotation wavefunctions are not significantly different from those obtained by the method based on the Kramers-Heisenberg dispersion formula (J.Chem.Phys., 72,5125 (1980)) .

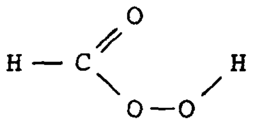
Discussion of the accuracy of the theoretical values of polarizability obtained from different methods will be given .

H 2

Microwave Spectrum, Dipole Moment and Substitution Structure of Peroxyformic Acid

M. Oldani and A. Bauder
Laboratory for Physical Chemistry, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland.

The microwave spectrum of peroxyformic acid



has been investigated between 12.4 and 40 GHz. Rotational transitions of the ground vibrational state have been assigned up to $J = 50$. Rotational constants and all quartic centrifugal distortion constants have been adjusted from the measured transition frequencies. The electric dipole moment has been determined from Stark splittings of three transitions.

From the magnitude of the inertia defect and from the absence of a μ_c dipole component it was concluded that the molecule is planar. No other rotamer of peroxyformic acid has been found so far in the microwave spectrum.

Isotopically substituted species with D, ^{13}C and ^{18}O have been prepared. Their microwave spectra have been analyzed in the same frequency range as for the parent molecule. The substitution structure has been determined from the moments of inertia of the singly substituted isotopic species. The planar structure of peroxyformic acid is stabilized by an intramolecular hydrogen bond.

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SEVENTH COLLOQUIUM ON HIGH RESOLUTION MOLECULAR SPECTROSCOPY 14--ETC(U)
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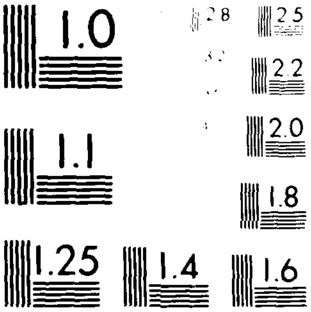

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

H 3

Microwave photon echoes : influence of the transverse molecular motion and of the source bandwidth

F. Rohart, J.P. Prault and B. Macke
Laboratoire de Spectroscopie Hertzienne
Associé au C.N.R.S.
Université de Lille I
59655 Villeneuve d'Ascq Cedex, FRANCE

The photon echo technique is a non linear method of high resolution spectroscopy in which the coherence relaxation of a gas of two-level systems is probed by the aid of two (or more) optical pulses. Contrary to many theoretical calculations, one may wonder about influences of the actual structure of the optical beam and of the source banwidth : these two points are considered in this paper.

i) in a realistic experiment, the optical beam is no longer a plane wave, and one has to take account of molecular locations and motions through the inhomogeneous optical field. The detected signal is calculated by projecting the induced polarization on the propagation mode of the optical field. This allows to determine the role of the field inhomogeneity on the absolute signal amplitude and to point out the residual Doppler effect related to transverse molecular motions.

ii) in the case of a c.w. source, the frequency fluctuations of the optical field generaly prevail over amplitude ones : they are responsible of an extra damping of the transients observed in experiments involving many shots and an averaging of the detected signals. Assuming a phase diffusing model, two asymptotic behaviours are pointed out according to the relative values of the sequence duration and of the frequency correlation time. In particular, photon echo technique reveals usefull when the frequency exhibits slow drifts (1).

Some experiments at 3 mm - wavelengths illustrate these results.

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(1) F. Rohart and B. Macke, Appl. Phys. (1981) in press.

H 4

ETUDE DES VARIETES ISOTOPIQUES DE SF_5B_r EN SPECTROSCOPIE HERTZIENNE.

GOULET P., JUREK R. , VERRY C.
Laboratoire de Spectronomie Moléculaire - Groupe de Radioélectricité
Faculté des Sciences MIPC, 6 Bd Gabriel - 21100 DIJON (France)

La mesure des spectres de rotation pure de la molécule SF_5B_r effectuée pour des transitions allant de $J = 28 \rightarrow 29$ jusqu'à $J = 92 \rightarrow 93$ a permis de déterminer :

- la valeur précise de B_o D_J D_{JK} eq Q et R_6 dans le cas des deux variétés isotopiques les plus abondantes $^{32}SF_5\,^{79}B_r$ (48%) et $^{32}SF_5\,^{81}B_r$ (47%)

- la valeur probable de B_o pour $^{34}SF_5\,^{79}B_r$ (2,02%) et $^{34}SF_5\,^{81}B_r$ (1,98%) compte tenu de la faible intensité des spectres.(intensité comparable à celles des états excités également observés).

On donne :

	$^{32}SF_5\,^{79}B_r$	$^{32}SF_5\,^{81}B_r$	$^{34}SF_5\,^{79}B_r$	$^{34}SF_5\,^{81}B_r$
B_o (MHz)	1172.154	1159.772	1170.1	1157.76
D_J (Hz)	69.5	68.4	-	-
D_{JK} (Hz)	165	163.3	-	-
eq Q (MHz)	708	585	-	-
R_6 (Hz)	0.3	0.26	-	-

Les déterminations des distances

$$z_S = 0,618\ \mathring{A} \quad \text{et} \quad z_{B_r} = 1,5244\ \mathring{A}$$

par la méthode de Kraitchmann sont cohérentes entre elles. A partir de la valeur de R_6 on déduit la géométrie de cette molécule.

H 5 The Microwave Spectra of SF_4NF and SF_4NCH_3

Horst Günther

Institut für Physikalische und Theoretische Chemie
Universität TÜBINGEN
FRG

The spectra of SF_4NF and SF_4NCH_3 were measured with a conventional Stark-spectrometer.

Centrifugal Distortion Analysis and torsional calculations have been carried out.

The Quadrupole coupling constants of the N nuclei were determined.

The dipole moment components are calculated from stark hyperfine splittings.

Combination of the rotational constants with the results of an Electron Diffraction investigation yielded structural data for the molecules. For this combination, a Normal coordinate analysis was carried out.

H 6

SPECTRUM OF METHANE CD_4 AT 10µ ASSIGNMENTS FOR ν_2 AND ν_4 DETERMINATION OF SIX GROUND-STATE ROTATIONAL CONSTANTS.

A. VALENTIN and L. HENRY
Laboratoire de Spectronomie Moléculaire
Université Pierre et Marie Curie - 75230 PARIS CEDEX 05

M. LOETE and J.C. HILICO
Laboratoire de Spectronomie Moléculaire
Université de DIJON - B.P. 138 - 21004 - DIJON CEDEX

The ν_2 and ν_4 bands of methane-d_4 have been recorded between 930 cm^{-1} and 1180 cm^{-1} on the new Fourier spectrometer at the University of Paris. The resolution attained was 0.004 cm^{-1}.

Up to now, only 3 rotational constants were known :

i) B_o and D_o from Raman spectroscopy [1] , ii) D_t from theory (isotopic relations) [2]

The resolution and the accuracy of the spectrum allow a ground-state combination difference analysis which yields the following constants :(in cm^{-1})

Scalar constants	Tensorial constants
B_o = 2.6327274 (34)	D_t = 1.0932 (36) 10^{-6}
D_o = 2.7648 (27) 10^{-5}	H_{4t} = -1.14 (26) 10^{-10}
H_o = 1.00 (9) 10^{-9}	H_{6t} = 4.48 (67) 10^{-11}

These constants were obtained from a least squares fit of 180 differences with a standard deviation of 0.00022 cm^{-1}.

Vibrational v_2 = 1 and v_4 = 1 states are strongly linked by a Coriolis resonance. Using the full third order hamiltonian of this diade [3], a set of 16 upper state constants was obtained, namely : 7 for ν_4, 4 for ν_2 and 5 for the interaction. These 16 parameters, together with the fixed 6 above ground-state constants allow the assignment of more than 1200 lines with a standard deviation better than 0.012 cm^{-1}.

[1] S. BRODERSEN, D.L. GRAY and A.G. ROBIETTE
Mol. Phys. 34, (1977) 617-628

[2] G. POUSSIGUE
Thesis, Paris, (1968) C.N.R.S. AO 2822)

[3] C. PIERRE, G.PIERRE, J.P. CHAMPION and B.L. LUTZ
J. Physique (lettres) 41, (1980), L 319 - L 323

H 7

THE ABSORPTION BANDS OF $^{12}C_2H_4$ IN THE 10 μM REGION : FOURIER-TRANSFORM SPECTRA AND SATURATION WAVEGUIDE LASER MEASUREMENTS

Ch. Lambeau, M. De Vleeschouwer and A. Fayt
Department of Molecular Spectroscopy, University of Louvain
Chemin du Cyclotron, 2 B - 1348 LOUVAIN-LA-NEUVE, BELGIUM

A. Valentin and L.Henry
Laboratoire de Spectronomie Moléculaire
Université Pierre et Marie Curie
F - 75230 PARIS Cedex 05, FRANCE

J. Lemaire, F. Herlemont and M. Lyszyk
Laboratoire de Spectroscopie Hertzienne
Université des Sciences Techniques de Lille I
BP 36, F - 59650 VILLENEUVE D'ASQ, FRANCE

Fourier -Transform spectra of ethylene have been recorded between 797 and 1091 cm^{-1}. They cover the ν_4, ν_7 and ν_{10} absorption bands with an apparatus function of 3.10^{-3} cm^{-1}.

On the other hand saturation spectroscopy of C_2H_4 has been performed with a CO_2 waveguide laser on the basis of previous linear measurements*. Seventeen lines have been measured with a precision of the order of 100 kHz.

These data have been used to obtain an absolute precision of 2.10^{-4} cm^{-1} on the whole Fourier-Transform spectra. On the basis of our previous work ** we have performed a complete analysis of the 1000 cm^{-1} region by treating simultaneously ν_4, ν_7 and ν_{10} strongly coupled by Coriolis interactions.

The results yield to the assignments of the coincidences between laser emission lines and C_2H_4 absorption lines with an accuracy better than 10 MHz.

* F. Herlemont, M. Lyszyk, J. Lemaire, Ch. Lambeau and A. Fayt
J. Mol. Spectrosc. 74, 400-408 (1979)

** Ch. Lambeau, A. Fayt, J.L. Duncan and T. Nakagawa
J. Mol. Spectrosc. 81, 227-247 (1980)

H8

LOW PRESSURE PHOTOACOUSTIC SPECTROSCOPY OF NORMAL AND ^{13}C ISOTOPIC SPECIES OF ETHYLENE AT CO_2 LASER FREQUENCIES.

A. Delplace, P. Stouffs, J.G. Lahaye, Ch. Lambeau, M. De Vleeschouwer and A. Fayt.
University of Louvain, Department of Molecular Spectroscopy
Chemin du Cyclotron, 2
B - 1348 LOUVAIN-LA-NEUVE - BELGIUM

Photoacoustic spectroscopy of ethylene has been performed with a resonant optoacoustic cell as proposed by E. Kritchaman et al. [1]. With pressures less than 0.5 torr, absorption lines are Doppler broadened (FWHM = 60 MHz) and photoacoustic signals are detected for coincidences within about 100 MHz. In such conditions, we can select all laser lines which can give rise to some optical pumping effect even in low pressure conditions. Systematic measurements have been performed on $^{12}C_2H_4$, $^{12}C^{13}CH_4$ and $^{13}C_2H_4$ with a classical CO_2 laser. According to the laser line, quite different signal amplitudes have been obtained, with a 10^5 factor between the strongest and the weakest ones. On the basis of our analysis of ethylene spectra in the 10 μm region, we have assigned most transitions involved in the pumping processes. For example, the strongest OA signal observed for $^{12}C_2H_4$ is due to a $\Delta K_a = +3$ forbidden transition from the GS to the ν_{10} level.

[1] E. Kritchman, S. Shtrikman and M. Slatkine, J. Opt. Soc. Am., 68, 9 Sept 1978.

H 9 Isotropic Raman Spectra of CH_4

Jens-Erik Lolck and Svend Brodersen
Department of Chemistry
Aarhus University
DK-8000 Aarhus C
Denmark

Alan G. Robiette
Department of Chemistry
Reading University
Reading RG6 2AD
England

The Raman spectrum of CH_4 in the 2400 cm^{-1} to 3400 cm^{-1} range has been recorded at 0.30 cm^{-1} resolution with the linearly polarised exciting light parallel to and perpendicular to the direction of observation in order to obtain purely anisotropic and mixed isotropic and anisotropic spectra, respectively. By "subtraction" of the former spectrum from the latter a purely isotropic experimental spectrum is obtained.

Isotropic Raman transitions occur between the vibrational ground state and upper vibrational states of species A_1. They obey the selection rule $\Delta J=0$. In the spectral range in question the following vibrational states are found: $v_1=1(A_1)$, $v_3=1(F_2)$, $v_2=2(A_1+E)$, $v_4=2(A_1+E+F_2)$, $v_2=v_4=1$ (F_1+F_2), and so we should only expect three isotropic Raman Q-branches. However, the five vibrational states are linked by a number of interactions and isotropic intensity is mixed into otherwise forbidden bands. Thus we observe a great number of isotropic transitions to the "$v_2=v_4=1$ states" and a small number of weak transitions to the "$v_4=2(E+F_2)$ states".

The structure of these spectra has been interpreted in terms of a theoretical model (1,2) which treats all five states simultaneously and which takes explicitly into account the interactions. The experimental and computed spectra and details of the interpretation will be presented.

1. J.-E. Lolck and A.G. Robiette,
   J. Mol. Spectrosc. in press and poster at this conference.
2. J.-E. Lolck, S. Brodersen, and A.G. Robiette,
   J. Raman Spectrosc. in press.

H 10 Molecular Constants for the Interacting Upper States of the ν_1, ν_3, $2\nu_2$, $\nu_2+\nu_4$, and $2\nu_4$ Bands in $^{12}CH_4$

Jens-Erik Lolck
Department of Chemistry
Aarhus University
DK-8000 Aarhus C
Denmark

Alan G. Robiette
Department of Chemistry
Reading University
Reading RG6 2AD
England

Linda R. Brown
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91103
U. S. A.

Robert H. Hunt
Departmentment of Physics
Florida State University
Tallahassee, Florida 32306
U. S. A.

In the 2400 cm^{-1} to 3200 cm^{-1} range a number of infrared and Raman bands of methane are found: these are the fundamentals ν_1 and ν_3, the overtones $2\nu_2$ and $2\nu_4$, and the combination $\nu_2+\nu_4$. These bands have been recorded at 0.01 cm^{-1} resolution in IR (1), and at 0.3 cm^{-1} resolution in Raman (2,3). The ν_3 infrared band has also been studied at Doppler-limited resolution (4) and so has the ν_1 isotropic Raman Q-branch (5). The upper states of these bands are linked by interactions of Fermi type, *Darling-Dennison type, and Coriolis type.*

We have developed a computer program for the analysis of these bands based on a theoretical model which incorporates the fourth order (Amat-Nielsen scheme) effective Hamiltonians for the five vibrational states and the model gives an explicit treatment of the interaction terms (6). Using this program we have succeeded in fitting more than 1200 (90% of all) upper state energy levels through $J'=12$ with a standard deviation of 0.017 cm^{-1}, and we have obtained estimates of nearly 100 constants appearing in the effective Hamiltonians and in the interaction terms. A detailed account of our results will be presented.

1. R.A. Toth, L.R. Brown, R.H. Hunt, and L.S. Rothman, Applied Optics 20, 932 (1981).
2. J.-E. Lolck, S. Brodersen, and A.G. Robiette, J. Raman Spectrosc., in press.
3. J.-E. Lolck, S. Brodersen, and A.G. Robiette, in preparation and poster at this conference.
4. D.L. Gray, A.G. Robiette, and A.S. Pine, J. Mol. Spectrosc. 77, 440 (1979).
5. A. Owyoung, C.W. Pattersen, and R.S. McDowell, Chem.Phys. Lett. 59, 156 (1978); Eratum 61, 636 (1979).
6. J.-E. Lolck and A.G. Robiette, J. Mol. Spectrosc., in press.

H 11

THE PURE ROTATION RAMAN SPECTRUM OF PYRAZINE AND THE PURE ROTATION AND VIBRATION-ROTATION RAMAN SPECTRA OF SOME ISOTOPICALLY-SUBSTITUTED SPECIES OF HYDROGEN AND OXYGEN.

D.A. LONG, H.G.M. EDWARDS, N.J. BRASSINGTON, D.W. FARWELL,
A.C. GORVIN AND K.A.B. NAJM.

School of Chemistry, University of Bradford, Bradford, West
Yorkshire, England. BD7 1DP.

ABSTRACT

This paper gives an account of experimental studies of the pure rotation Raman spectrum of pyrazine, $C_4H_4N_2$, and the pure rotation and vibration-rotation Raman spectra of ${}^{17}O^{18}O$, ${}^{17}O_2$, ${}^{18}O_2$, ${}^{1}H_2$, ${}^{1}H^{2}H$ and ${}^{2}H_2$.

The following results have been obtained for pyrazine and the oxygen species:

$\underline{C_4H_4N_2}$: $\tilde{B} = 0.20478 \pm 0.00001\ cm^{-1}$; $(C-\tilde{B}) = -0.10238 \pm 0.00003\ cm^{-1}$;
$10^8 D_J = 9 \pm 1\ cm^{-1}$; $10^8 D_K = 5.6 \pm 0.4\ cm^{-1}$;
$C = 0.10240 \pm 0.00004\ cm^{-1}$.

$\underline{{}^{17}O_2}$: $B_o = 1.35314 \pm 0.00004\ cm^{-1}$; $10^6 D_o = 4.6 \pm 0.2\ cm^{-1}$;
$\alpha = 0.01449 \pm 0.00002\ cm^{-1}$; $B_e = 1.36041 \pm 0.00003\ cm^{-1}$;
$r_e = 120.754 \pm 0.002$ pm.

$\underline{{}^{17}O^{18}O}$: $B_o = 1.31553 \pm 0.00005\ cm^{-1}$; $10^6 D_o = 3.8 \pm 0.3\ cm^{-1}$;
$\alpha = 0.01388 \pm 0.00004\ cm^{-1}$; $B_e = 1.32270 \pm 0.00003\ cm^{-1}$;
$r_e = 120.754 \pm 0.002$ pm.

$\underline{{}^{18}O_2}$: $B_o = 1.27796 \pm 0.00004\ cm^{-1}$; $10^6 D_o = 3.9 \pm 0.1\ cm^{-1}$;
$\alpha = 0.01319 \pm 0.00001\ cm^{-1}$; $B_e = 1.28458 \pm 0.00003\ cm^{-1}$;
$r_e = 120.756 \pm 0.003$ pm.

The spectra of the hydrogen species are presently being analysed and the results will be presented at the meeting.

H 12

ABSORPTION OF TRIDEUTEROMETHANE AT 905 - 1150 cm^{-1}

ANALYSIS OF ν_3 AND ν_6 BANDS

J. DUPRE-MAQUAIRE, J. DUPRE, G. TARRAGO

Laboratoire d'Infrarouge,
Associé au C.N.R.S.
Université de Paris-Sud,
Bâtiment 305

91405 ORSAY CEDEX, FRANCE

The absorption spectrum of $^{12}CD_3H$ was recorded using a symmetric double pass interferometer (SISAM). The gas pressure was 15 torr, the absorption path length 30 cm and the effective line width about 0.025 cm^{-1}. The spectrum was recorded in the 4 - 5th orders of the gratings using a Pb Sn Te detector cooled at 77 K. CO_2 superradiant lines observed in the 4 - 5th orders and H_2O absorption lines observed in the 6 - 7th orders are used as reference lines. The CD_3H wavenumbers are attained by interpolation from fringes produced by a Michelson interferometer illuminated by a He-Ne Laser. About 1200 experimental lines belonging to ν_3 and ν_6 of $^{12}CD_3H$ were assigned including J values up to 21. The analysis of the data led to a set of vibration rotation constants available for the two vivrational states $v_3=1$ and $v_6=1$ and reproducing the experimental data with an overall standard deviation equal to 0.008 cm^{-1}. The vicinity of the two bands ν_3 and ν_6, at 1004.554 and 1035.917 cm^{-1} respectively, is responsible for a strong Coriolis interaction treated rigorously in the analysis.

The value $$\rho = \left|\frac{d\mu}{dq_3} \Big/ \frac{d\mu}{dq_6}\right| = 1.25 \pm 0,05 \qquad (1)$$ was deduced for the ratio between dipole moment derivatives responsible for ν_3 and ν_6. Using $S_3+S_6 = 62 \pm 5\ cm^{-2}\ atm^{-1}$ given by Hiller & Straley J. Mol. Spect. 5, 24-34 (1960), Eq.(1) leads for the two band strengths to: $S_3 = 27 \pm 4\ cm^{-2}\ atm^{-1}$ and $S_6 = 35 \pm 4\ cm^{-2}\ atm^{-1}$.

New absolute intensity measurements are now desirable for an improvement of this first estimation of S_3 and S_6 separately.

H 13 CW Raman Amplification Spectroscopy

Jan Baran, Andras Grofcsik and W.J. Jones

Edward Davies Chemical Laboratories, University College
of Wales, Aberystwyth, Dyfed, SY23 1NE.

The newly developed techniques of Raman Amplification Spectroscopy, variously called Inverse Raman, Raman Gain, Raman Loss, etc., are serving to revolutionise the study of the Raman spectra of solids, liquids and gases. The Raman amplification techniques are employed when two beams of monochromatic laser radiation, one of which is tunable, interact in a Raman medium. When the frequency difference between the two lasers coincides with a Raman active transition in the molecules, amplification of one of the components occurs at the expense of the other, depending on the population difference between the two states involved in the Raman transition. Recent results obtained in the investigation of Raman spectra using low power cw lasers will be presented, including the rather unusual $2\nu_2$ band of carbon dioxide.

H 14 Hyperfine Constants for v=1 in $^{15}N^{16}O$ Determined from Fourier Transform Spectra

C. AMIOT, Laboratoire de Physique Moleculaire et d'Optique Atmospherique,
Bat. 221, Campus d'Orsay, 91405 Orsay Cedex FRANCE

P.KRISTIANSEN, Institute of physics, University of Oslo,
Box 1048 , Blindern, Oslo 3, NORWAY.

The Infrared Spectrum of $^{15}N^{16}O$ has been obtained with Fourier Transform Spectrometer (1), with an overall uncertainty of 5 Mhz. In the Q-branch of the (1 - 0) transition there is clear doublet structure, due to the two strong hyperfine transitions with $\Delta F=\Delta J=0$ ($I=\frac{1}{2}$).

These doublets have been studied in order to find the hyperfine constants for v= 1. The splitting which is probably correct to within 1 Mhz, is determined by the hyperfine splitting in both the v=0 and v=1 state. Measurements of hyperfine splitting in the v=0 state has therefore been included in a simultaneous linear least square fit to determine hyperfine constants for both v=0 and v=1. (2,3)

The fitted values for the v=1 state is in good agreement with the corresponding parameters for v=0

1) C.Amiot and G.Guelachvili, J.Mol.Spectrosc. 76, 86 (1979)

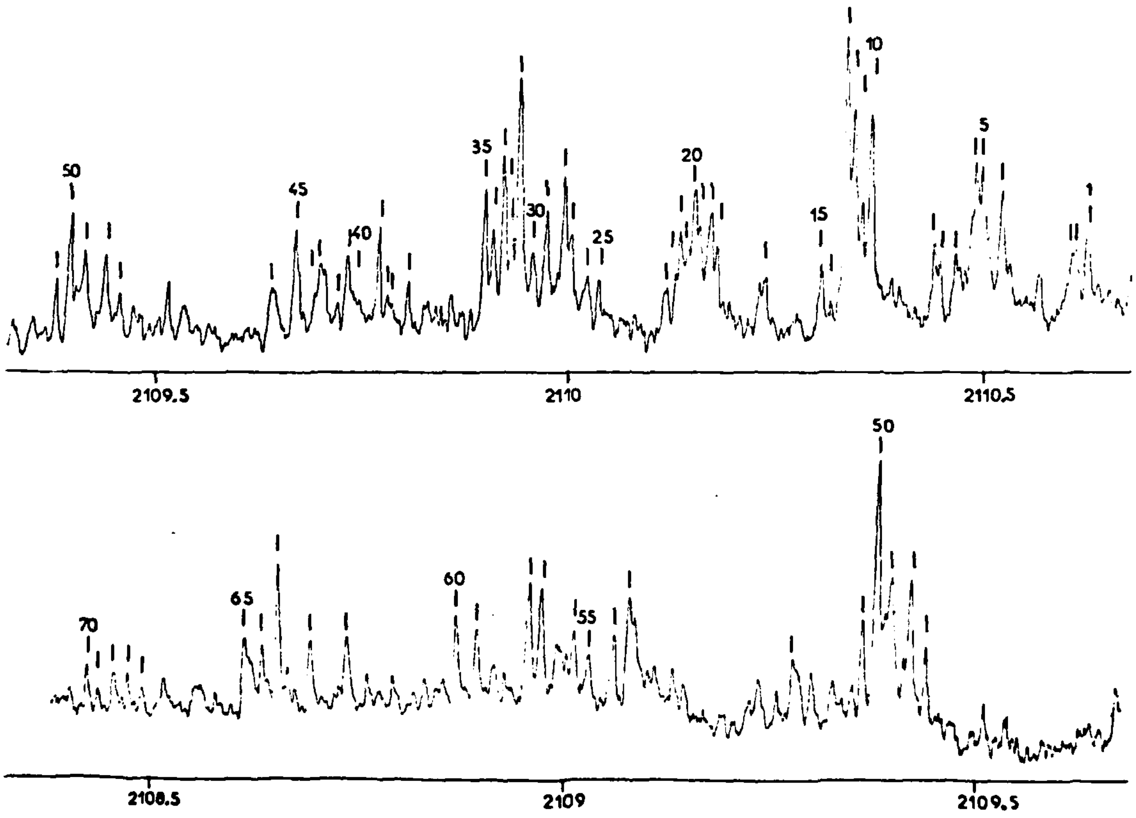
2) W.L.Meerts and A.Dymanus, J.Mol.Spectrosc. 44, 320 (1972)

3) P.G.Favero, A.M.Mirri and W.Gordy, Phys. Rev. 114, 1534 (1959)

H 15 C.W. Stimulated Raman Spectroscopy of the ν_1 Fundamental Band of GeH_4

S.Q. MAO, R. SAINT-LOUP, A. ABOUMAJD, P. LEPAGE and H. BERGER
Laboratoire de Spectronomie Moléculaire
Faculté des Sciences , 6 Bd Gabriel - 21100 DIJON - France

We present the preliminary results of our stimulated Raman experiment. The ν_1 band of natural germane has been recorded with a resolution of about 0.004 cm^{-1} . These data should allow an improved determination of the parameters of the upper level.



Stimulated Raman spectrum of the ν_1 band of natural germane.

H 16 Experimental and Theoretical Study of Rydberg States of SiF

Y. HOUBRECHTS, I. DUBOIS, H. BREDOHL
Université de Liège
Institut d'Astrophysique
B-4200 Cointe-Ougrée (BELGIQUE)

and J.M. ROBBE
Université des Sciences et Techniques de Lille
UER de Physique Fondamentale
59655 Villeneuve d'Ascq (FRANCE)

Nineteen Rydberg states (ten of them never reported before) have been observed and analysed for SiF. Seven of them have been unambiguously arranged into five Rydberg series corresponding to the excitation of the (v π) outer electron to nsσ, npσ npπ, ndσ and ndπ, therefore converging to the ground state $^1\Sigma^+$ of the SiF^+ ion.

The ionisation potential is found to be 60500 cm^{-1}, or 7.5 ev, in perfect agreement with mass-spectrometry measurements (Ehbert and Margrave, J. Chem. Phys., 41, 1066, 1965).

Ab initio CI calculations have been made using a basis set formed of valence orbitals for Si and F atoms and Rydberg orbitals of Si. These calculations confirm the proposed identifications of the observed states.

H 17

On highly excited electronic states of the NO molecule reached by multiphoton spectroscopy

K. Dressler, ETH-Zentrum, CH-8092-Zürich, Switzerland
E. Miescher, Institute of Physics, University of Basel, Switzerland

A recent multiphoton experiment by Wallace and Innes[1] involves an energy level of the NO molecule that belongs to a very interesting sequence of rovibronic states in which a $3p\pi,\sigma$ Rydberg complex (C $^2\Pi$ + D $^2\Sigma^+$) and a regular and an inverted valence state (B $^2\Pi_r$ and L $^2\Pi_i$) are strongly mixed with each other.[2] This multistate interaction, which is typical for highly excited molecular states reached in multiphoton spectroscopy, can be regarded as an unique example of a non-trivial case of Mulliken's Rydbergization of valence states.[3] We have used Gallusser's vibronic coupling calculation[4] and new interpretations of local perturbations in three different isotopes to establish the absolute vibrational numbering and the deperturbed rovibronic and spin-orbit constants of the L $^2\Pi_i$ state which had been very poorly known previously.

A slight improvement in the line width of the multiphoton resonance (0.8 cm^{-1} in Ref. 1) would enable an experimental parity assignment within the Λ-doublet (splitting of 1.0 cm^{-1})[2] of the mixed state L $^2\Pi_{1/2}$, v=5 + C $^2\Pi$, v=6, J = 9/2 to be compared with theoretical expectations.

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[1] S.C. Wallace and K.K. Innes, J.Chem.Phys. 72, 4805 (1980).

[2] A. Lagerqvist and E. Miescher, Can.J.Phys. 44, 1525 (1966).

[3] R.S. Mulliken, Chem.Phys.Letters 46, 197 (1977).

[4] R. Gallusser and K. Dressler, to be published.

H 18

VARIOUS INVESTIGATIONS OF THE IODINE B STATE WITH A SUPERSONIC BEAM

R. BACIS[†], S. CHURASSY[†], M. GAILLARD[†], F. HARTMANN[††], J.P. PIQUE[††],
N. SADEGHI[††]

[†]Laboratoire de Spectrométrie Ionique et Moléculaire, Université
Lyon I, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

[††]Laboratoire de Spectrométrie Physique, Université Scientifique et
Médicale de Grenoble, B.P. 53X, 38041 Grenoble Cedex, France

The iodine supersonic molecular beam used in our experiments is a powerful tool for high resolution spectroscopy. Very weak $BO_u^+ - X^1\Sigma_g^+$ transitions with BO_u^+ levels close to the dissociation limit may be detected since the flux of molecules along the axis of the beam is high. Thus it has been possible to measure the hyperfine structure of I_2 BO_u^+ levels very close to the dissociation limit. The evolution of hyperfine structure constants in the B state is in good agreement with theoretical predictions.

We have also measured radiative lifetimes for single hyperfine levels in the BO_u^+ state for v'=43 J'=12 and 16. The variation of lifetimes for different hyperfine levels is due to an interaction of the BO_u^+ state with a repulsive 1u state. Our results are in excellent agreement with the theory of iodine hyperfine predissociation as established by Vigué et al.(1).

(1) J. VIGUE, M. BROYER and J.C. LEHMANN, Journal de Physique 42, 937 (1981).

H 19

Hyperfine structure studies in the predissociating $B' 0^+$ state of IBr.

M. Siese, H. Knöckel, E. Tiemann, Institut A für Experimentalphysik, Universität Hannover, Appelstrasse 2, 3 Hannover, Germany.

From line profile studies of the molecular transition $B' 0^+ - X\, ^1\Sigma^+$ including the strongly predissociating state B' it is known, that some rotational levels of the state B' have natural widths of less than about 15 MHz [1], so that hyperfine structure studies on these levels should be possible. Using molecular beam laser spectroscopy the appropriate rovibronic transitions were investigated. The obtained spectra will be presented and compared. This enables us to discuss the perturbation of the hyperfine structure in highly predissociating states.

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H 20

MAGNETIC ROTATION SPECTROSCOPY OF FREE RADICALS WITH A COLOUR CENTRE LASER

J.Pfeiffer, P.Kalkert, D.Kirsten, W.Urban
Institut für Angewandte Physik, Universität Bonn, D-5300 Bonn, FRG

Mid-infrared LMR can give very high sensitivity for free radical spectroscopy [1], however the interpretation can be difficult due to the randon distribution of near coincidences with molecular gas-lasers. This problem can be overcome if a continuously tunable IR-laser is used in connection with Zeeman modulation (ZM) [2] or Faraday rotation (FR) [3,4]. The latter has considerable advantages if laser noise is the limiting factor rather than detector noise. In the ZM configuration circularly polarized light is applied to the sample and the modulation signal corresponds to the derivative of the absorption coefficient. The laser power is fully applied to the detector. At the FR configuration the sample is between nearly crossed polarizers, the FR signal is determined by the first derivative of the disperion. Only a small fraction of the laser power reaches the detector.
We use a colour centre laser as tunable IR source [3] and can cover the range between 3030 and 4100 cm^{-1}. The minimum detectable absorption coefficient for ZM has been determined to be 10^{-5} cm^{-1}, with FR the corresponding figure is 10^{-7} cm^{-1} which corresponds to a minimum detectable concentration of free radicals of 10^{11} cm^{-3}. Spectra of free radicals in the gasphase will be discussed.

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I 1 Recent Results in the High-Resolution Spectroscopy of Tetrahedral Molecules

A.G. Robiette

Department of Chemistry
University of Reading
Reading RG6 2AD, U.K.

(no abstract)

I 2 High Resolution Spectroscopy of Spherical Top Overtones with Application to Multiple Photon Absorption

C.W. Patterson

Los Alamos National Laboratory
P.O.Box 1663 Los Alamos, NM 87545
U.S.A.

(no abstract)

J1 On the Bending - Internal Rotation - Rotation Hamiltonian of Silylisocyanate

Marek Kreglewski

Institute of Chemistry, A. Mickiewicz University, Poznan, Poland.

A new bending - internal rotation - rotation Hamiltonian for silylisocyanate, SiH_3NCO, has been developed in which the bending and internal rotation motions are considered simultaneously with the overall rotation. The approach, based on the ideas of Hougen, Bunker and Johns[1], leads to a Hamiltonian which has a non-essential singularity at the linear configuration of the skeleton (i.e. when the Si-N-C angle is 180°). The form of the singularity $[(k+l)^2 - 0.25]/\rho^2$, where k and l are the quantum numbers of the z component of overall and internal rotation angular momenta respectively, indicates the strong coupling between overall and internal rotations. It is also shown that if one neglects the internal rotation in the derivation of the Hamiltonian (i.e. if the internal rotation angle is fixed) then the singularity vanishes, leading to incorrect results.

The above explains why the simple quasilinear model, which has a singularity at the linear configuration, could be successfully applied by Durig et al.[2] for the study of the low frequency bending mode of silylisocyanate.

The new Hamiltonian is used to determine the barrier for linearity and the effective equilibrium angle for silylisocyanate.

1. Hougen, Bunker and Johns, J. Mol. Spectrosc. 34, 136 (1970)
2. Durig, Kalasinsky and Kalasinsky, J. Chem. Phys. 69, 918 (1978)

J 2

A COMPUTER CONTROLLED MICROWAVE SPECTROMETER SYSTEM USED FOR THE STUDY OF EQULIBRIUM STRUCTURE OF FLUORONITROBENZENES, AND OTHER MOLECULES.

Niels W. Larsen and Ole V. Nielsen
The H. C. Ørsted Institute
University of Copenhagen.

A computer system have been developed for the control of a Hewlett-Packard 8460 microwave spectrometer by a microcomputer, based on a Motorola M 6800 microprocessor.

Frequency and Stark voltage are controlled from the microcomputer and the microwave spectra are stored and accumulated in the memory of the microcomputer. However, the microcomputer is controlled from a larger computer (RC 4000) which is used for further treatment and permanent storage of the spectra.

A technique of adding spectra obtained at different Stark voltages has proved useful in many respects. An example is the assignment of separate torsional states in non-planar fluoronitrobenzenes. In 2,4-difluoronitrobenzene it has thereby been possible to determine both constants in a torsional potential function of the form

$$V(\tau) = \tfrac{1}{2}v_2(1-\cos 2\tau) + \tfrac{1}{2}\tau_4(1-\cos 4\tau)$$

where τ is the internal rotation angle. The values obtained are $V_2 = 932\ \mathrm{cm}^{-1}$, $V_4 = -407\ \mathrm{cm}^{-1}$.

J 3

Measurement of the Centrifugal Distortion Moment of CD_4

W.A. KREINER Dept. of Physical Chemistry
University of ULM, West Germany

A.G. ROBIETTE Dept. of Chemistry
The University of READING

H.D. RUDOLPH Dept. of Physical Chemistry
University of ULM, West Germany

The near coincidence of the $C^{18}O_2$ 9P(36) laser line with a ν_4 transition of CD_4 has been used to investigate the Stark effect in the vibrational ground state by RF-IR double resonance. The J=21 $F_1^{(6)} \leftarrow F_2^{(6)}$ rotational transition shows second order Stark effect. Although single m components could not be resolved, the asymmetric shift of their envelope was used to determine θ_z^{xy} by comparison with a computer simulated shape. The result agrees well with the value predicted from the regular species of methane.

J 4

ROTATIONAL SPECTRUM OF $F^{12}C^{15}N$ IN EXCITED VIBRATIONAL STATES. EQUILIBRIUM STRUCTURE OF CYANOGEN FLUORIDE.

G.Cazzoli,C.Degli Esposti,P.Favero and S.Serenellini

Laboratorio di Spettroscopia Molecolare del C.N.R. and
Istituto chimico "G.Ciamician" dell'Università di Bologna
- Bologna (Italy)

The rotational spectrum of $F^{12}C^{15}N$ has been observed in the ground state and in the $(0\ 1^1\ 0)$,$(0\ 2^0\ 0)$,$(1\ 0^0\ 0)$, $(2\ 0^0\ 0)$,$(0\ 0^0\ 1)$ excited vibrational states.
The technique of vibrational energy transfer from active nitrogen has been used to observe the rotational transitions in the $(0\ 0^0\ 1)$ level.
The vibrational energy levels and the rotational constants actually available for $F^{12}C^{14}N$, $F^{12}C^{15}N$ and $F^{13}C^{14}N$ have been analysed taking into account the Fermi resonance coupling the states $|v_1,v_2,l_2,v_3\rangle$ with $|v_1-1,v_2+2,l_2,v_3\rangle$ $|v_1,v_2+2,l_2,v_3-1\rangle$ and $|v_1+2,v_2,l_2,v_3-1\rangle$ throgh the normal coordinates cubic force constants K_{221},K_{223} and K_{113} respectively. The rotational dependence of the Fermi resonance matrix elements has also been considered.
This kind of analysis has allowed to obtain the values of the equilibrium rotational constants of $F^{12}C^{14}N$, $F^{12}C^{15}N$ and $F^{13}C^{14}N$, from which the equilibrium structure of cyanogen fluoride has been evaluated.

J 5

THEORETICAL LINE PARAMETERS VERSUS EXPERIMENTAL MEASUREMENTS IN THE 2250 TO 3250 CM^{-1} REGION OF $^{12}CH_4$.

G. POUSSIGUE, E. PASCAUD, G. GUELACHVILI
Laboratoire d'Infrarouge Bâtiment 350 91405 ORSAY FRANCE

G. PIERRE and J.P. CHAMPION
Laboratoire de Spectronomie Moléculaire 6 Bd Gabriel 21100 DIJON FRANCE

The spectrum of $^{12}CH_4$ in the region from 2250 to 3250 cm^{-1} has been analysed using a rovibrational hamiltonian developed to the third order (according to Amat Nielsen classification) for both diagonal and off-diagonal terms.

The experimental data included in the final fit are IR F.T.S. data from the Laboratoire d'Infrarouge d'Orsay and coherent Raman data of ν_1 (1).

A single set of numerical values is given for the hamiltonian parameters of the ground state, the diade (ν_2 and ν_4) and the pentade (ν_1,ν_3,$2\nu_2$,$\nu_2+\nu_4$ and $2\nu_4$). The 6 ground state parameters and the 16 diade parameters have been fixed to values determined from previous works. We have determined 63 new parameters on the pentade data.

Detailled quantitative results (J' = 0 to 18)

Band	Nb of fitted levels	Nb of transitions	Standard deviation
$2\nu_4$	500	924	0.017 cm^{-1}
$\nu_2+\nu_4$	658	1482	0.026
ν_1	82	53 IR + 36 Raman	0.018
ν_3	444	1027	0.015
$2\nu_2$	226	418	0.032
Pentade	1910	3904 IR + 36 Raman	0.022

The following computer outputs will be presented:

- Calculated infrared spectrum from 2250 to 3250 cm^{-1}: 5919 transitions (3904 already assigned) with relative intensities in the range 8 - 550 000.

- Calculated isotropic Raman spectrum.

- Calculated energy levels (J' = 0 to 18) with vibrational assignments based on eigenvectors.

(1) A.Owyoung, C.W.Patterson and R.S.McDowell, Chem. Phys. Lett. 59, 156 (1978)

J 6 New Raman Spectra of the Fundamental Bands of SiD_4

Jens-Erik Lolck
Department of Chemistry
Aarhus University
DK-8000 Aarhus C
Denmark

Silane-d_4 has four normal vibrations: two stretching modes $\nu_1(A_1)$ and $\nu_3(F_2)$ located at 1563 cm^{-1} and 1598 cm^{-1}, respectively, and two bending modes $\nu_2(E)$ and $\nu_4(F_2)$ located at 685 cm^{-1} and 674 cm^{-1}, respectively. The Raman spectra of all four bands have been studied by Kattenberg and Oskam at 0.6 cm^{-1} resolution (1), while Willetts et al. (2) recorded and analysed the ν_3 Raman band at a significantly higher resolution.

In this work the Raman spectra of the fundamentals have been recorded at 0.3 cm^{-1} resolution and with a much better signal-to-noise ratio than the previous spectra. Further, the masking of anisotropic O and P ν_3 lines by the strong ν_1 isotropic Q-branch around 1560 cm^{-1} has been reduced substantially using an experimental setup which allows only about 1% of the isotropic scattered radiation to be transmitted along with the anisotropic scattered radiation into the spectrograph.

Infrared spectra at 0.06 cm^{-1} resolution of the ν_3 and of the interacting ν_2 and ν_4 fundamentals have been recorded in Reading (3), and a combined analysis of the IR and Raman spectra is in progress. The Raman spectra and preliminary results of the analysis will be presented.

1. H.W. Kattenberg and A. Oskam,
   J. Mol. Spectrosc. 49, 52 (1974).
2. D.W. Willetts, W.J. Jones, and A.G. Robiette,
   J. Mol. Spectrosc. 55, 200 (1975).
3. A.G. Robiette and P.H. Turner,
   Private Communication.

J 7

The Raman Spectrum of CH_3CD_3

Per Jensen and Svend Brodersen
Dept. of Chemistry, Aarhus University
8000 Aarhus C, Denmark.

Raman spectra of the ethane isotopic species CH_3CD_3 have been recorded in the regions 800-1200 cm^{-1} (ν_5, ν_4, ν_{10}, ν_{11}), 1300-1500 cm^{-1} (ν_3, ν_5), 1900-2300 cm^{-1} (ν_2, ν_8, $2\nu_4$, $2\nu_{10}$), and 2600-3100 cm^{-1} ($2\nu_3$, $2\nu_9$, ν_1, ν_7). These spectra will be presented.

In order to estimate the effect on the spectra of the hindered internal rotation of CH_3CD_3, an exact Hamiltonian for a symmetric top molecule with two non-identical coaxial rotors has been derived. Approximate calculations seem to indicate that the effect of the torsion on transitions not involving excited torsional states is too small to be observed in our spectra. This means that the usual rigid molecule model may be used as a basis for the analysis of transitions between states which have the torsional quantum number equal to zero.

Analyses of the ν_7 and ν_5 bands are presently being carried out, and preliminary results may be presented.

J 8

HIGH RESOLUTION INFRARED ANALYSES OF CORIOLIS INTERACTING VIBRATIONS IN CH_3CD_3

J. Harper, A.R. Morrisson, J.L. Duncan, G.D. Nivellini[1], and F. Tullini[2]
Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland.

In the first high resolution infrared study of CH_3CD_3 in the region below 2000 cm^{-1}, analyses have been made of the CH_3 deformation (ν_3, ν_9) and CD_3 deformation, CH_3 rocking (ν_4, ν_{10}, ν_{11}) interacting rovibration systems from FTIR spectra recorded with a resolution of 0.05 cm^{-1}.

The effects of the x,y-Coriolis interaction between ν_3 (a_1, 1386 cm^{-1}) and ν_9 (e, 1471 cm^{-1}) can be followed through the observed changes in the subband α^B values in ν_9. ν_3 is so weak that its Q branch can only barely be observed. Analysis of the spectrum, with the effects of the Coriolis interaction explicitly allowed for, yields a full set of vibration and rotation parameters for ν_9, and limited information for ν_3.

In the ν_4, ν_{10}, ν_{11} system, ν_{11} (e, 1067 cm^{-1}, CD_3 deformation) is observed strongly. ν_4 (a_1, 1120 cm^{-1}, CD_3 deformation) and ν_{10} (e, 1114 cm^{-1}, CH_3 rocking) lie higher, are almost accidentally degenerate, but are both very weak. Coriolis interaction between ν_{10} and ν_{11} through $\zeta^a_{10,11}$ is negligible, but the x,y-Coriolis interactions between ν_4 and ν_{11}, and ν_{10} and ν_{11} are both significant. Because of the differing selection rules for Coriolis interaction between a_1 and e, and e and e fundamentals, ν_4 affects the R branch of ν_{11} but ν_{10} affects the P branch. This accounts for the unusual behaviour of the subband α^B values, which decrease and then increase again through the band. Analysis of ν_{11}, taking both Coriolis interactions into account, yields a full set of parameters for ν_{11} and limited information for ν_4 and ν_{10}.

ν_9^o	1470.948(6)	ν_{11}^o	1066.680(6)
$A_o - (A\zeta_9^a)$	2.3422(2)	$A_o - (A\zeta_{11}^a)$	2.4384(2)
α_9^B	-0.00033(3)	α_{11}^B	0.00023(5)
α_9^A	0.00502(4)	α_{11}^A	0.00723(6)
D_K	$6.0(6) \times 10^{-6}$	D_K	$6.4(8) \times 10^{-6}$
$(B\zeta_{3,9}^b)$	0.311(3)	$(B\zeta_{4,11}^b)$	0.242(6)
ν_3^o	1386.5(1)	ν_4^o	1120.(1)
α_3^B	0.008(3)	ν_{10}^o	1114 [illegible]
		$(B\zeta_{10,11}^b)$	0.144(4)

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[1] **Permanent address:** Istituto di Spettroscopia Molecolare del C.N.R., Via Castagnoli 1, Bologna, Italy.

[2] **Permanent address:** Istituto di Chimica Fisica e Spettroscopi, Università degli Studi, Viale del Resorgimento 4, Bologna, Italy.

J 9

ROTATIONAL STRUCTURE UP TO J=40 OF THE $V_2=V_4=1$ VIBRATIONAL STATE OF $^{12}CF_4$.

POUSSIGUE Gérard, TARRAGO Ginette
Laboratoire d'Infrarouge, Orsay, FRANCE
VALENTIN Alain
Laboratoire de Spectronomie Moléculaire, Paris, FRANCE

The analysis of the $\nu_2+\nu_4$ band of $^{12}CF_4$ has been extended to J=40, using a very high resolution spectrum recorded on a F.T. interferometer (Laboratoire de Spectronomie Moléculaire de Paris).

The main features observed in the rotational structure for higher and higher J values can be summarized as follows :

a- For each J value in the upper state $v_2=v_4=1$, the first order Coriolis term is responsible for the main splitting according to R= J-1, J, J+1 (upper, middle, lower component). The second order terms lead to a finer structure, which can be understood as :

1º) a splitting in two parts of each Coriolis component R, according to two values of a pseudo angular momentum quantum number S_α, $S_\alpha = (R+2)_u$ and $(R-2)_g$ in our symmetry conventions.*

2º) a tetrahedral splitting of each S_α component according to the $\mathcal{D}^{S_\alpha} \Downarrow T_d$ decomposition rule, where the usual clustering of the rotational levels is well observed (especially F_1F_2, $A_1E\ F_1$ $A_2E\ F_2$ clusters).

b- The observed intensities of the individual lines are also well understood using this coupling scheme.

For numerical convenience, the fit of the experimental data is performed on the basis of Champion formalism for computation of energies and transition moments. Presently about 1300 transitions are fitted within the third order approximation with an overall standard deviation equal to 0.004 cm^{-1}.

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*such a coupling scheme is described in Michelot Thesis.

J 10

MID-INFRARED LMR USING FARADAY- AND VOIGT-EFFECT FOR SENSITIVE DETECTION.

A.Hinz, J.Pfeiffer, W.Bohle, W.Urban
Institut für Angewandte Physik, Universität Bonn, D-5300 Bonn, FRG

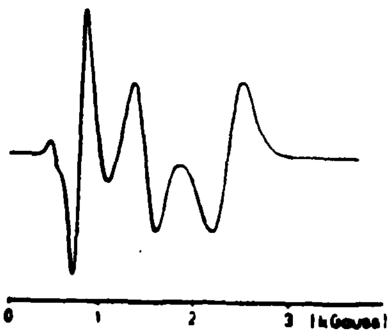
In LMR-spectroscopy high sensitivity is achieved by the intracavity configuration, thus increasing the effective pathlength through the sample. The optimization of this has recently been investigated by Radford et al.[1]. In the mid-IR very powerful lasers are available and in most experiments the limiting factor is the laser noise, which can be several orders of magnitude higher than detector noise. Our recent approach to increase the sensitivity in LMR experiments is based on this observation. We make use of the fact that in experimental configurations where the sample is placed between almost crossed polarizers, the radiation power at the detector is very low [2].
For the detection of paramagnetic species two configurations correspond to this requirement:

(a) Faraday configuration: magnetic field parallel to laser beam the signal shows the first derivative of the dispersion[2,3].

(b) Voigt configuration: magnetic field perpendicular to laser beam, the signal is given by the first derivative of the absorption (Fig.1).

We have investigated both possibilities and will present quantitative results obtained with our CO-laser system.

[1] H.E.Radford, W.Rohrbeck, K.M.Evenson, A.R.W.McKellar, A.Hinz, 15th International Symposium on Free Radicals, A4 (1981)
[2] J.Pfeiffer, D.Kirsten, P.Kalkert, W.Urban, Appl.Phys.(subm.)1981
[3] J.Pfeiffer, P.Kalkert, D.Kirsten, W.Urban, Magnetic Rotation Spectroscopy of Free Radicals with a Colour Centre Laser, Reading 1981



Voigt-Signal of
NO $X^2\Pi_{3/2}$ R(1.5) by
CO $P(13)_{9-8}$ laser line

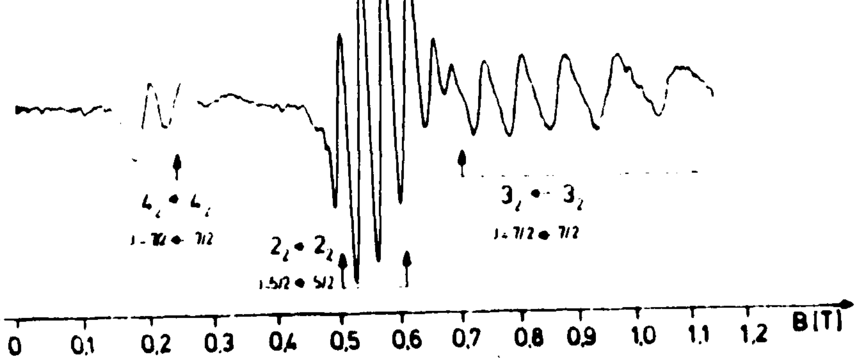
J 11

LMR WITH A CO-LASER BETWEEN 6 AND 8 μm

M.A.Gondal*, A.Hinz, F.Niebuhr, W.Rohrbeck, W.Urban
Institut für Angewandte Physik, Universität Bonn, D-5300 Bonn, FRG
*On leave from Pakistan Inst.of Nucl.Sc.and Techn., Islamabad

We have slightly modified the CO-laser system described in [1], in order to use it for LMR-investigations between 6 and 8 μm. In a first experiment we have investigated the ν_2-bending mode of HO_2 near 7.2 μm. At six different laser lines LMR signals could be observed, five different reactions were used. For this experiment we had chosen an intracavity configuration. The sensitivity limiting factors will be discussed. The results are in good agreement with recent observations by Nagai et al.[2].
In the region near 6 μm, where the laser power is fairly high, we have chosen the Voigt-effect configuration [3] in order to increase the sensitivity to study transitions in electronic excited molecules. Our first candidate is the a $^3\Pi$ CO*, which is created by different methods. The production rate of CO* is monitored by the UV-fluorescence in the Cameron-band.
A comparison between Voigt-effect-LMR and conventional intracavity-LMR will be given.

[1] T.X.Lin, W.Rohrbeck, W.Urban, Appl.Phys. in press (1981)
[2] K.Nagai, Y.Endo, E.Hirota, J.Chem.Phys. in press (1981)
[3] A.Hinz, J.Pfeiffer, W.Bohle, W.Urban
Mid.IR LMR Using Faraday- and Voigt-Effect for Sensitive Detection
Reading 1981



J 12

Measurement of Stratospheric Trace Gases
by Airborne Infrared Spectroscopy

by

William G. Mankin and M. T. Coffey

National Center for Atmospheric Research*
P. O. Box 3000
Boulder, Colorado 80307 USA

An airborne Fourier transform spectrometer with 0.06 cm^{-1} resolution will be described; the spectrometer has been used to record spectra of the rising or setting sun from an aircraft altitude of 12 km, covering the latitude range 23°S to 70°N. Spectra have been recorded in both winter and summer. From analysis of the spectra, the total stratospheric column amount of a number of minor molecular species has been determined. Results will be presented for N_2O, NO, NO_2, HNO_3, OCS, HCN, CO, HCl, and HF. For some molecules variations with latitude and season will be shown.

*The National Center for Atmospheric Research is sponsored by the National Science Foundation.

J 13

$^{12}C^{18}O_2$, $^{13}C^{16}O_2$: WAVENUMBERS AND MOLECULAR PARAMETERS FOR $0V_2^{\ell}V_3$ — $0V_2^{\ell}(V_3-1)$ TRANSITIONS $(V_2=\ell)$

BAILLY D. , FARRENQ R. , GUELACHVILI G. , ROSSETTI C.

Laboratoire d'Infrarouge, Associé au CNRS,
Université Paris - Sud,
Bât. 350, 91405 ORSAY CEDEX, FRANCE.

As a part of a more extensive work on CO_2 *isotopic species in emission studied by Fourier Transform Spectroscopy (Resolution 5.4* $10^{-3}cm^{-1}$*), spectroscopic constants and molecular parameters are given for vibrational transitions type:* $0V_2^{\ell}V_3$ — $0V_2^{\ell}(V_3-1)$ *with* $\ell=V_2$ *of* $^{12}C^{18}O_2$ *and* $^{13}C^{16}O_2$ *respectively located in the spectral ranges : 2354 - 2023* cm^{-1} *and 2323 - 1977* cm^{-1}*.*

The set of molecular parameters allows to reproduce the 1500 experimental wavenumbers for each isotopic species with a R.M.S. of $10^{-4}cm^{-1}$ *on the whole.*

Following a recent paper to be published in Journal of Molecular Spectroscopy *, *we present also for* $^{12}C^{16}O_2$ *some spectroscopic constants concerning levels in Fermi resonance. These levels are involved in sequential laser transitions.*

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* $^{12}C^{16}O_2$ — *Analysis of emission FOURIER spectra in the 4.5µm region : rovibrational transitions* $0V_2^{\ell}V_3$ — $0V_2^{\ell}(V_3-1)$, $V_2=\ell$.
BAILLY D. , FARRENQ R. , GUELACHVILI G. , ROSSETTI C.

J 14

Abstract for Seventh Colloquium on High Resolution Molecular Spectroscopy,
Reading 1981

LABORATORY SPECTROSCOPY OF PLANETARY MOLECULES

D.E. Jennings
Infrared and Radio Astronomy Branch
NASA Goddard Space Flight Center
Greenbelt, Maryland 20771, U.S.A.

As the number of species contributing to infrared spectra of planetary atmospheres increases, so does the importance of characterizing the vibration-rotation structure of known and possible component molecules. The Voyager infrared spectra of the outer planets, and particularly Titan, have added several new species to the already large list. Ground-based planetary observations which resolve the rotational structure of molecular bands can yield atmospheric temperature and abundance profiles if strength and broadening parameters have been determined from high resolution laboratory studies. In addition, minor constituents can be identified from line detections when measured transition frequencies are available.

By combining diode laser spectroscopy at ultra-high resolution and Fourier transform spectroscopy at various resolutions it is possible to derive most molecular parameters relevant to planetary atmospheres. Low and moderate resolution FTS laboratory spectra have recently led to the identifications of C_3H_4, C_3H_8, C_4H_2, HC_3N, and C_2N_2 in Voyager 1 spectra of Titan[1]. Diode laser line strength measurements in ν_4 of $^{12}CH_4$ have yielded a precise band strength and Herman-Wallis factor.[2] Diode laser and FTS spectra of ν_6 of H_2O_2 (a possible participant in the oxygen chemistry on Mars) have produced the first vibration-rotation analysis of that fundamental.[3] For the species C_2H_6 (ν_9) and H_2, diode laser spectra used in conjunction with 0.005 cm^{-1} FTS spectra have produced both Doppler-limited precision and high absolute accuracy. FTS spectra of $3\nu_3$ of methane[4] have shown that line strengths in the R-branch of that band are significantly greater for $^{12}CH_4$ than for $^{13}CH_4$, contrary to the assumption used in deriving ^{12}C:^{13}C abundance ratios for Jupiter and Saturn[5].

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[5] M. Combes, J.P. Maillard, and C. deBergh, Astron. Astrophys. <u>61</u>, 531, (1977).

J 15

Isotope field shift in the molecular transition $A\,0^+ - X\,^1\Sigma^+$ of Pb S

E. Tiemann, H. Knöckel, Institut A für Experimentalphysik,
Universität Hannover, Appelstrasse 2, 3 Hannover, Germany.

The isotopic field shift due to the finite nuclear size is well-known in atomic spectra. From observations of the isotopic hyperfine structure in atomic lines one can derive the change of the quadratic nuclear charge radius from one isotope to the other.

In molecular spectra such isotope effect was never observed and is expected to be small compared to mass shifts from the nuclear motion in the molecule and therefore should be inseparable from the much larger ones.

We used laser excitation spectroscopy of a molecular beam of PbS to observe the band heads of the system $A\,0^+ - X\,^1\Sigma^+$ for the three isotopic species ^{208}PbS, ^{207}PbS, and ^{206}PbS. The absolute line positions were measured with the help of the well-known I_2-spectrum and precise vibrational frequencies could be derived. Using the frequency markers from a well calibrated Fabry-Perot the rotational finestructure and the energy separations of the different isotopes were determined. From all these results the pure electronic isotope shift could be deduced. This will be compared with similar results on atomic spectra of Pb and contains new information about the electron density change at the nucleus Pb.

Also this first detection of an isotopic field shift in molecular spectra will change the interpretation of higher order isotope shifts for the rotational constant in the case of heavy molecules as measured by microwave spectroscopy.

J 16 A New Double Resonance Technique: Microwave Optical Polarization Spectroscopy (MOPS)

W. E. Ernst and T. Törring
Institut für Molekülphysik, Freie Universität Berlin,
Boltzmannstr. 20, D 1000 Berlin 33

A new type of microwave optical double resonance experiment has been performed on BaO showing the feasibility of a new sensitive optical detection scheme for rotational ground state transitions. Linearly polarized microwaves introduced via a horn radiator pump a rotational transition whose upper state is optically pumped by a laser beam the polarization plane of which is turned by 45° with respect to the microwave polarization. Absorption of microwaves causes an alignment of the upper rotational state of the ground state which is detected via the change of the polarization of the laser beam. In analogy to laser polarization spectroscopy the laser beam is passed through crossed polarizers such as to detect polarization changes on a nearly zero background.

About 10^{-4} torr BaO was produced by reacting barium metal vapor with N_2O in an argon carrier-gas stream the total pressure in the cell being 0.05 torr. A stabilized cw dye laser of 1 MHz bandwidth was tuned to 580.7 nm to coincide with the P(3) line of the $A^1\Sigma - X^1\Sigma$ (1,0) band of BaO to pump molecules out of the $J'' = 3$ level. Microwave radiation of 56105.3 MHz is resonant with the $J'' = 2 \rightarrow 3$ transition. While the laser frequency was kept fixed on the P(3) line center the microwave frequency was swept. The signal was obtained by phase sensitive detection the microwave power being amplitude modulated at 1kHz. Total microwave power coupled into the cell was only about 3 mW. Using a beam diameter of 7 mm an optimum signal was observed at a laser power of 17 mW. The recorded line width was only about 1,5 MHz mainly due to pressure broadening.

Comparing these first results with previous microwave optical double resonance (MODR) experiments |1| we find that with the new MOPS technique the same sensitivity can be obtained at a considerably lower laser power density (factor 100). This will be of great advantage especially for double resonance experiments in the shorter optical wavelength region. As a consequence of the low power densities the line shape is not influenced by saturation and other nonlinear effects as in the previous experiments.

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J 17 HIGH RESOLUTION INFRARED STUDIES ON ALLENE-d_4: ν_7 BAND AND THE HOT BANDS ACCOMPANYING ν_9 AND ν_{10}

F. Hegelund and P. Lund
Department of Chemistry, University of Aarhus, DK-8000 Aarhus, Denmark

and

R. Anttila, J. Kauppinen, and M. Koivusaari
Department of Physics, University of Oulu, SF-90570 Oulu 57, Finland

Recently the ν_9 and ν_{10} fundamentals of allene-d_4 were studied [1]. The spectra were recorded with the Fourier spectrometer at the University of Oulu. The resolution attained was about 0.01 cm^{-1}. Using the same interferograms we have now investigated the parallel fundamental band ν_7 and also the hot bands $\nu_9+\nu_{11}-\nu_{11}$ and $\nu_{10}+\nu_{11}-\nu_{11}$.

The ν_7 band around 1030 cm^{-1} could be analyzed using an unperturbed model although several resonances proved to have effects on the constants at the level $v_7=1$. The band gave a lot of ground state combination differences. They were analyzed together with those from ν_{10} [1] and from ν_{11} [2]. The resulting ground state constants were: $B_0 = 0.232153(15)$ cm^{-1}, $D_0^J = 5.82(39) \times 10^{-8}$ cm^{-1}, $D_0^{JK} = 2.59(45) \times 10^{-6}$ cm^{-1} and $H_0^{JJK} = -3.5(27) \times 10^{-9}$ cm^{-1}. (Error limits 3 x std. dev.).

The hot bands $\nu_9+\nu_{11}-\nu_{11}$ and $\nu_{10}+\nu_{11}-\nu_{11}$ both consist of two components: $A_1,A_2 \leftarrow E$ and $B_1,B_2 \leftarrow E$. In them altogether 1 500 lines were assigned. In the analysis the global z-Coriolis resonance between the levels $\nu_9+\nu_{11}$ and $\nu_{10}+\nu_{11}$ as well as the vibrational ℓ-type resonances within these levels were taken into account. In $\nu_{10}+\nu_{11}-\nu_{11}$ the rotational and vibrational ℓ-type doublings occuring in the $K\Delta K = -1$ sub-bands were investigated in detail. A localized (x,y)-Coriolis resonance between $\nu_{10}+\nu_{11}$ and $\nu_4+\nu_{11}$ was observed and the interaction parameter was deduced.

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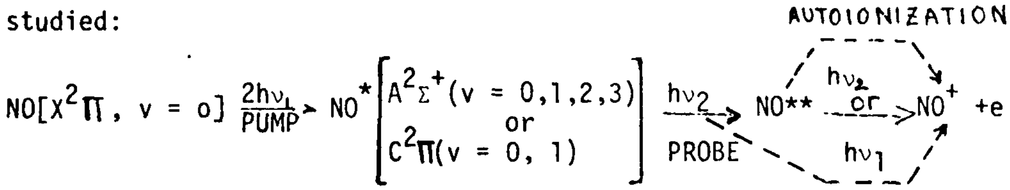
J 18

OPTICAL-OPTICAL DOUBLE RESONANCE MULTIPHOTON IONIZATION SPECTROSCOPY OF NO

M. Seaver, W.Y. Cheung, D. Gauyacq,* W.A. Chupka, S.D. Colson
Department of Chemistry, Yale University, New Haven, Connecticut 06520
U.S.A.

Resonantly enhanced multiphoton ionization of NO has been investigated using two tunable dye laser beams oppositely directed and having a common focus. The focus lies between two electrodes in a cell containing 4-15 torr of NO. The following processes are studied:



$$\mathrm{NO}[X^2\Pi,\ v = o] \xrightarrow[\text{PUMP}]{2h\nu_1} \mathrm{NO}^*\begin{bmatrix} A^2\Sigma^+(v = 0,1,2,3) \\ \text{or} \\ C^2\Pi(v = 0,\ 1) \end{bmatrix} \xrightarrow[\text{PROBE}]{h\nu_2} \mathrm{NO}^{**} \overset{\text{AUTOIONIZATION}}{\xrightarrow[h\nu_1]{h\nu_2 \text{ or}}} \mathrm{NO}^+ + e$$

The first laser beam pumps an intermediate rovibronic state. The second laser beam is scanned over a blue dye spectral region leading to ionization by one or two photon excitation from the intermediate state. The total amplified ion current is detected.

The rotational selection of the pump transition and the Rydberg character of the intermediate state lead to spectra which are greatly simplified compared to the usual single photon absorption or photoionization spectra. This technics has provided high resolution data on the high lying Rydberg and non-Rydberg states below and above the ionization limit with special attention to the Rydberg-non Rydberg perturbations and dynamic processes (autoionization, predissociation) occuring in this energy range.

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* On leave from the Laboratoire de Photophysique Moleculaire du CNRS, Bat 213, Universite de Paris-Sud, 91405 ORSAY (FRANCE)

J 19

EVIDENCE FOR A 1g STATE AMONGST THE E STATES OF I_2

J.P. Perrot, J. Chevaleyre, S. Valignat, J.M. Chastan and M. Broyer

Laboratoire de Spectrométrie Ionique et Moléculaire (associé au
C.N.R.S.) L.A. n°171, Université de Lyon I, 69622 Villeurbanne Cedex
France.

We have studied the E states of I_2 by Optical Optical Double Resonance (O.O.D.R.). The pump laser is a continuous wave argon ion laser operating at 5017 Å and 5145 Å. The probe laser is a 3 GHz bandwith pulsed dye laser which excites the E states from well defined v, J levels of the $B(^3\Pi_{0_u^+})$ state. By this technique two states are observed :

- one of them is the already studied 0^+g state,
- the other is a state of 1g symmetry identified by the observation of Q lines.

For these two states spectroscopic constants and RKR potential curves have been determined.

Moreover the lifetimes of these 0^+g and 1g states have been measured as a function of vibrational quantum numbers. No evidence for a v-dependence of this lifetime has been observed. The results are $\tau = 27.7 \pm 1.3$ ns for the 0^+g and $\tau = 11.9 \pm 1.2$ ns for the 1g state.

J 20

OODR EXCITATION OF AUTOIONIZING STATES OF SODIUM DIMERS

M. Broyer, J. Chevaleyre, S. Martin, B. Cabaud, A. Hoareau, S. Valignat, J.P. Perrot

Laboratoire de Spectrométrie Ionique et Moléculaire (associé au C.N.R.S.)
L.A. n°171, Université de Lyon I, 69622 Villeurbanne Cedex, France.

We present here some results concerning the study under high resolution of the autoionizing states of the Na_2 molecule. A beam of sodium dimers, produced by the supersonic expansion of sodium vapour through a nozzle, is crossed at right angle by two superimposed laser beams from two dye lasers pumped simultaneously by the same nitrogen laser. Laser wavelengths were tuned in order to perform optical-optical double resonances in Na_2 molecules via a fixed $(B\ ^1\Pi_u, v, J)$ intermediate level. By scanning the wavelength of the second laser, energy levels beyond the ionization limit have been explored.

Ion current spectra have been recorded. They show from a single $(B\ ^1\Pi_u, v, J)$ intermediate level about 300 excitation lines newly observed in this experiment. They are distributed among several Rydberg progressions. The most extended one is spreading over 15 different principal quantum numbers. It allows estimated values of rotational and vibrational constants to be deduced :

$$B_e = 0.113\ \text{cm}^{-1} \quad \text{and} \quad \omega_e = 118\ \text{cm}^{-1}$$

They are in good agreement with constants obtained by two-step polarization labeling experiment.[1]

The n-dependence of energy levels as a function of quadrupole moment and polarizability of the core is now in progress.

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K1

C. Camy-Peyret and J-M. Flaud

Laboratoire de Physique Moléculaire
et d'Optique Atmosphérique, C.N.R.S.
Bat.221 - Campus d'Orsay - 91405
FRANCE

(no abstract)

K2

High Resolution Atmospheric Transmission/Emission at the Air Force Geophysics Laboratory

Laurence S. Rothman

Air Force Geophysics Laboratory
Optical Physics Division
Hanscom AFB, MA 01731
U.S.A.

The program, direction, and status of the AFGL absorption line parameter compilations[1] will be discussed. There has recently been significant improvement in the high resolution data obtained and analyzed for the main infrared atmospheric absorbers as well as the addition of numerous neutral species discovered in the terrestrial atmosphere. Examples of the application of the atmospheric transmission/emission code[2] developed at AFGL using the molecular data base will be shown.

Recent results obtained at AFGL with the 2-meter interferometer and hot gas cell on carbon dioxide will be presented. Preliminary results from the cryogenically cooled balloon-borne interferometer for detection of stratospheric emission[3] will also be presented

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K3

S.J. Daunt

Department of Physics & Astronomy
University of Tennessee
Knoxville, Tennessee 37916
U.S.A.

(no abstract)

L 1

Harmonic Information from Inertial Defects in Vibrationally excited C_{2v} molecules

Dines Christen

Institut für Physikalische und Theoretische Chemie
Universität TÜBINGEN
FRG

Since it seems impossible to extract separate harmonic and anharmonic contributions from the vibration-rotation interaction constants ε (α), the next best thing, namely inertial defects ($I_\gamma - I_\alpha - I_\beta$) were investigated.

It will be shown that for molecules of orthorhombic symmetry in general, and for C_{2v} molecules in particular, certain differences in inertial defects between non totally symmetric fundamental states and the ground state are purely harmonic - at least in the same approximation (linear in (v+1/2)) where inertial defects of planar molecules are purely harmonic.

Calculations have been carried out on CH_2F_2 [1] as well as on SF_4 and SeF_4.
These new pieces of information seem to be quite sensitive to changes in the force field, and thus seem very relevant for the determination of harmonic force fields.

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L 2

THE INTERCOMPARISON OF FORCE FIELDS FOR TRIATOMIC MOLECULES

M. Lacy and D.H. Whiffen
Dept. Physical Chemistry, University of Newcastle-upon-Tyne, U.K.

A simple method is presented for comparing force fields by focussing on the potential surface they describe, rather than examining the individual coefficients of the analytical function. Advantages of this approach are discussed, and the different perspective it gives to the appreciation of force fields is illustrated by its application to N_2O, H_2O and OCS.

L3

Microwave Spectrum of D_2CS and H_2CS

by A.P. Cox, S.D. Hubbard and H. Kato

School of Chemistry, University of Bristol
Cantock's Close, Bristol BS8 1TS

Microwave transitions up to J= 53 in the ground vibrational state of deuterothioformaldehyde, CD_2S, have been studied between 8-40 GHz. A detailed centrifugal distortion analysis yields accurate constants for comparison with force field values. The isotopic species $^{13}CH_2S$, $CH_2{}^{34}S$, $CH_2{}^{33}S$, $^{13}CD_2S$, $CD_2{}^{34}S$ and $CD_2{}^{33}S$ have been studied in natural abundance. Accurate average zero-point structures have been determined for both CD_2S and CH_2S:

CH_2S CS = 1.6136(4) CH = 1.0965(6)Å ∠HCH = 116° 13(6)'

CD_2S CS = 1.6134(4) CD = 1.0933(4)Å ∠DCD = 116° 23(5)'

Changes in the zero-point geometry for deuterium substitution have been established.

Quadrupole fine structure arising from the ^{33}S nucleus has been measured in $CH_2{}^{33}S$ and $CD_2{}^{33}S$. Analysis gives the following coupling constants (for both molecules) as $\chi_{aa} = -11.7$ and $\chi_{bb} - \chi_{cc} = 88.1$ MHz. The dipole moment of CD_2S has been measured to be 1.6588(8)D and an accurate comparison with CH_2S has been made; the ratio of dipole moments CD_2S/CH_2S was found to be 1.0062(4). The spectroscopic and bonding properties of CH_2S will be compared with formaldehyde and other molecules.

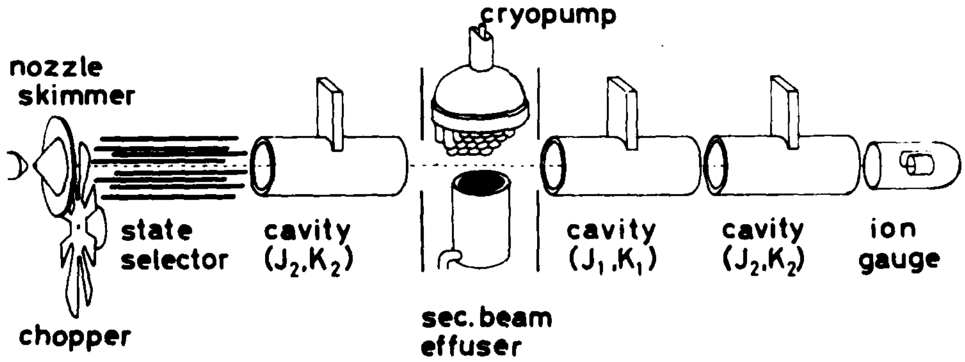
L 4

COLLISION INDUCED ROTATIONAL TRANSITIONS OF NH_3

D.B.M. Klaassen, J.J. ter Meulen, N. van Hulst and A. Dymanus
Fysisch Laboratorium, Katholieke Universiteit
6525 ED Nijmegen, The Netherlands

Rotational transitions of NH_3 induced by collisions with polar and non-polar molecules have been investigated in a molecular beam maser. Hereto the NH_3 molecules cross a secondary beam between two microwave cavities tuned at the frequencies of two inversion transitions (J_2,K_2) and (J_1,K_1). The relative population distribution over the two (J_2,K_2) doublet states determined by the power density in the first cavity is measured by a third microwave cavity. Only when collisions take place changes in the (J_2,K_2) population distribution cause effects on the (J_1,K_1) microwave signal due to rotational transitions $(J_2,K_2) \rightleftarrows (J_1,K_1)$. By measuring these effects as a function of the secundary beam density (apparatus) cross sections for collision induced rotational transitions are determined.

Measurements were done with NH_3, CH_3F, CF_3H, CO_2, N_2 and H_2 as scattering gases. In all cases transitions were observed of the type $\Delta K=0$, $\Delta J=\pm 1$, whereas for NH_3-NH_3 also $\Delta K=0$, $\Delta J=2$ could be detected. Cross sections are of the order of 10 $Å^2$ for polar gases and 0.1 $Å^2$ for H_2. Accuracies are about 10% or better.



L 5

Microwave and Photoelectron detection of unstable species: Sulphido and Selenido borons; XB=S and XB=Se.

T.A. Cooper, M.A. King
H.W. Kroto and R.J. Suffolk

School of Chemistry and Molecular Sciences, University of Sussex,
Brighton BN1 9QJ

Using fast flow pyrolysis techniques several monomeric sulphido and selenido boron molecules have been identified. These species are produced by the high temperature reaction between an appropriately substituted disulphide X_2S_2 and crystalline boron at temperatures in excess of 1000°C:

$$X_2S_2 + B \xrightarrow{\Delta} XB{=}S$$

$$X = F, Cl, Br, CH_3$$

Essentially the same technique has been applied to the detection of the selenium analogue ClB=Se which appears to be the first member of this class of molecule to be detected. In this case the reaction is:

$$Cl_2Se_2 + B \xrightarrow{\Delta} ClB{=}Se$$

The photoelectron data using very fast flow methods show that high yields of these species can be produced. Other techniques for producing these molecules have also been studied.

In general detailed structural, vibration-rotation, dipole moment and quadrupole data have been determined from the microwave spectra and ionisation potential and associated electronic structure information derived from the photoelectron studies.

L 6 KCN: ISOTOPIC SUBSTITUTION, STRUCTURE AND NUCLEAR HYPERFINE EFFECTS

J.J. van Vaals, W. Leo Meerts and A. Dymanus
Fysisch Laboratorium, Katholieke Universiteit
6525 ED Nijmegen, The Netherlands

The microwave spectra between 12 and 38 GHz of the ^{13}C and ^{15}N isotopically substituted species of potassium cyanide in the ground vibrational state were measured by molecular-beam electric-resonance spectroscopy. For both isotopic species we observed over 20 rotational transitions and determined the rotational, the 5 quartic and 2 sextic distortion constants. The rotational constants of the ^{13}C and ^{15}N substituted species combined with those of the normal isotopic species [1] allowed an accurate and unambiguous determination of the structure, which was confirmed to be T-shaped. Both the effective structure of the ground vibrational state and the substitution structure were evaluated. The results for the substitution structure in Å are: r_{CN} = 1.174(2), r_{KC} = 2.711(5), r_{KN} = 2.532(5).

The hyperfine spectrum of KCN has been unravelled with the help of double resonance techniques. One hundred and twentyfive hyperfine transitions in 8 rotational transitions have been assigned. The quadrupole coupling constants (in MHz) of potassium are: eQq_{aa} = -5.605(4), eQq_{bb} = 2.600(8) and of nitrogen are: eQq_{aa} = 1.922(3), eQq_{bb} = -4.068(7).

From the asymmetric rotor spectrum it could be deduced, using the semirigid bender model described by Bunker [2], that the potential energy surface in the bending direction has very low barriers for internal rotation. This is confirmed by recent ab initio potential energy surface calculations [3,4]. The potential energy barriers for linear cyanide and linear isocyanide are estimated to be 2000 cm^{-1} and 500 cm^{-1} with respect to the minimum at the T-shaped geometry. The zero-point KCN bending vibrational amplitude is ± 10°.

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L 7

DIPOLE MOMENTS OF $^{15}NH_3$, ND_3 AND PH_3 BY LASER STARK SATURATION SPECTROSCOPY.

G.Di Lonardo and A. Trombetti.

Istituto di Spettroscopia Molecolare del C.N.R., Via de' Castagnoli 1 - 40126 Bologna, Italy and Istituto di Chimica Fisica e Spettroscopia, Viale Risorgimento, 4 - 40136 Bologna, Italy.

Inverse Lamb dips (full width at half maximum <1 MHz) of several transitions of $^{15}NH_3$, ND_3 ν_2 bands and of PH_3 ν_2 and ν_4 bands, saturated by $^{12}C\,^{16}O_2$, $^{13}C\,^{16}O_2$ and $^{12}C\,^{18}O_2$ laser lines have been observed in an intracavity Stark cell. Accurate values of the electric dipole moments of the ground state ($^{15}NH_3$ and ND_3), $v_2=1$ state ($^{15}NH_3$, ND_3, PH_3) and $v_4=1$ state (PH_3) have been obtained directly from the resonance voltages of the $\Delta M_J = \pm 1$ Stark components. The results are summarized in the following table.

	(v_2, J, K)	μ (D)		(v_2, J, K)	μ (D)
	(0, 5, 3)	1.4760 (9)		(1, 4, 3)	0.5746 (3)
	(1, 4, 4)	1.253 (6)		(1, 3, 3)	0.5732 (3)
$^{15}NH_3$	(1, 7, 7)	1.241 (10)		(1, 8, 4)	0.5740 (2)
	(1, 8, 8)	1.230 (5)		(1, 14, 12)	0.5740 (5)
	(1, 11, 9)	1.271 (6)		(1, 6, 5)	0.5743 (3)
			PH_3	(1, 10, 7)	0.5741 (1)
				(1, 10, 8)	0.5737 (1)
	(0, 13, 11)	1. 492 (8)			
	(0, 13, 13)	1. 497 (11)		(v_4, J, K)	
ND_3	(1, 14, 11)	1. 352 (3)		$(1^{-l}, 7, 7)$	0.5785 (1)
	(1, 14, 13)	1. 355 (5)		$(1^{-l}, 6, 6)$	0.5783 (1)

L 8 THE ν_2, $2\nu_2$, $3\nu_2$, ν_4 AND $\nu_2 + \nu_4$ BANDS OF $^{15}NH_3$

G.Di Lonardo, L.Fusina and A.Trombetti

Istituto di Spettroscopia Molecolare del C.N.R., via Castagnoli 1 e Istituto
di Chimica Fisica e Spettroscopia - Universita' di Bologna - 40100 BOLOGNA - ITALIA

The i.r. absorption of gaseous $^{15}NH_3$ between 510 cm^{-1} and 3040 cm^{-1} has been recorded with a resolution of 0.06 cm^{-1}.

Transitions belonging to the ν_2, $2\nu_2$, $3\nu_2$, $\nu_2 + \nu_4$ bands and to the hot bands $2\nu_2 \leftarrow \nu_2$, and $\nu_3 \leftarrow \nu_2$ have been measured and assigned for both the components of the inversion doubling.

The observed F.T. transition wavenumbers together with very high resolution laser - Stark and two photon measurements of the ν_2 band reported in the literature or newly measured by us have been used simultaneously in a weighted damped least-squares analysis.

The effective spectroscopic parameters and the *interaction constants* between $\nu_2^{\pm}$, $2\nu_2^{\pm}$, $3\nu_2^{\pm}$, $\nu_4^{\mp}$ and $(\nu_2 + \nu_4)^{\mp}$ vibrational states have been obtained.

The analysis followed essentially the mainline outlined in ref.[1].

The ground state rotational parameters were constrained to the values obtained by Carlotti et al [2].

About 880 transitions of $\nu_2^{\pm}$, $2\nu_2^{\pm}$, and $3\nu_2^{\pm}$ were fitted with a standard deviation of 6.0×10^{-3} cm^{-1} (nearly the accuracy of the experimental measurements).

About 600 transitions of $\nu_4^{\pm}$ and $(\nu_2 + \nu_4)^{\pm}$ were fitted with a standard deviations of about 16.6×10^{-3} cm^{-1}. This is 4 times the accuracy of the experimental data and it is indication that only the most significant part of the rovibration interaction was taken into account.

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L 9 The Vibration-Rotation Infra-Red Emission Spectrum of Hydrogen Isocyanide, HNC

W.J. Jones and M.J. Winter

The Edward Davies Chemical Laboratories
U.C.W. Aberystwyth SY23 1NE U.K.

Infra-red emission from gaseous HNC has previously been reported by Arrington and Ogryzlo (1). However, using a conventional slit monochromator, they could achieve a spectral resolution of only ~ 2 cm^{-1}. More recently, Maki and Sams (2) have recorded the absorption spectrum of HNC in equilibrium with HNC at temperatures up to 1300 K.

In this work, vibrationally excited HNC has been produced by the reaction of discharged nitrogen with methyl bromide, CH_3Br, in a flow system at pressures of 1-3 torr. The resulting infra-red emission, at around 2.75 μm, has been recorded with a resolution of 0.15 cm^{-1} using our SISAM interferometer. The following transitions have been observed:

$10^{0}0 - 00^{0}0$
$11^{1}0 - 01^{1}0$
$12^{0}0 - 02^{0}0$
$10^{0}1 - 00^{0}1$

allowing the determination of several sets of molecular constants.

References

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L 10

Molecular Beam Electric Resonance Spectroscopy of the Argon-Nitric Oxide van der Waals Complex

C. M. Western, P. A. Mills and B.J. Howard

The argon-nitric oxide system has been the subject of a number of studies. Calculations based on the electron gas model [1] and molecular beam scattering data [2] have been used to construct intermolecular potential energy surfaces. Although quantitatively different, both surfaces gave a potential minimum corresponding to a T-shaped configuration.

A molecular beam electric resonance study on the complex Ar-NO, the first such investigation of an open shell van der Walls molecule, is presented here. This technique has yielded much useful information for atom-diatom systems with a linear equilibrium geometry such as Ar-HCl [3].

The microwave and radiofrequency spectra are shown to be compatible with a T-shaped complex with only partially quenched orbital angular momentum, in contrast to chemically bonded non-linear molecules.

The theory for this novel angular momentum coupling scheme will be described. It explicitly includes both orbital and spin angular momenta and differs greatly from the normal approach for asymmetric rotors for which the orbital contribution is included indirectly through the spin rotation term in the hamiltonian. In our treatment the spin and orbital angular momenta are quantised along the molecule-fixed b-axis. The analysis of the complex hyperfine structure will also be represented.

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L 11 Laser Spectroscopy of Supersonic Expansions of ICl

S.G. Hansen, J.D. Thompson and B.J. Howard

High resolution fluorescence excitation spectra of both the $B\ ^3\Pi(0^+) - X\ ^1\Sigma^+$ and $A\ ^3\Pi(1) - X\ ^1\Sigma^+$ systems of rotationally cooled ICl have been obtained using a single mode cw-dye laser. Because of the large degree of coooling which occurs in the expansion, problems due to overlap with nearby ICl and impurity I_2 bands were drastically reduced. This allowed for theobservation of a number of previously unreported B-X bands for both $I^{35}Cl$ and $I^{37}Cl$, including the fundamental 0-0 band. Improved molecular constants were calculated for the B states of both isotopes and the X state of $I^{37}Cl$.

For low J lines of the A-X transition, quadrupole hyperfine splitting patterns were completely resolved by working at sub-Doppler resolution. To aid in the analysis of these spectra, as well as improve on their precision, microwave-optical double resonance experiments were performed. Pure rotational transitions between various F levels in both the A and X states have been observed by monitoring the change in fluorescence from individual optical hyperfine lines as a function of applied microwave frequency. These data shoud provide enough information to completely assign the high resolution optical spectrum and accurately give a value for eQq in the A state

L 12 Infrared Spectrum of CO_2 in the 5 μm Region

Ph. Arcas and E. Arie
Laboratoire d'Infra-rouge,
Bat 350, Faculté des Sciences,
91405 Orsay-Cedex

A. Henry and A Valentin
Laboratoire de Spectronomie
moléculaire,
Tour 13,
Université P. et M. Curie,
4 Place Jussieu,
75230 Paris-Cedex 05

We have recorded the spectrum of CO_2 with the Fourier Transform spectrometer of the "laboratoire de spectronomie moléculaire" in the 5 μm region. The apparatus function of the spectrometer has been chosen to take account the widths of lines in the experimental condition. Pressures of 10 and 20 torr were used with a 12 m optical length.

Effective rotational spectroscopic constants are calculated for the $(11^10,03^10)_I$, $(20^00,04^00)_I$ and $(12^20,04^20)$ levels. These effective constants reproduce the wavenumbers of vibration-rotation transitions with a R.M.S. deviation between 5.6×10^{-5} and 3.6×10^{-4} cm^{-1} in accordance to the intensities and number of lines for the different bands.

In addition the values of the band center wavenumber are determined using data of CO_2 (Pine and Guelachvili) and N_2O (Amiot). These values will be compared with the results obtained by different authors specially for the $(12^20,04^20)$ transition for which the results given in the literature differ rather widely.

L 13 INFRARED SPECTRUM OF CO_2 IN THE 2 μm REGION.

Ph.ARCAS[+],E.ARIÉ[+]
J.CHAUVILLE[°],M.CUISENIER[°],and J.P.MAILLARD[°]

In order to carry on the study of the infrared spectrum of CO_2 *(1) we present preliminary results obtained with the Fourier Transform Spectrometer of Meudon at very high resolution.*

This allows to determine the effective spectroscopic constants of the levels involved in the transitions:

the triade $(20^01,04^01)_{I,II,III} - (00^00)$ *and*

the associated "hot" bands $(21^11,05^11)_{I,II,III} - (01^10)$.

The effective constants reproduce the frequencies of the observed transitions within an accuracy of 0.001 cm^{-1} .

(1) J.P.MAILLARD,M.CUISENIER,Ph;ARCAS,E.ARIÉ and C.AMIOT
Can.J.Physics <u>*58*</u> *,1560 (1980).*

[+] Laboratoire d'Infrarouge ,Bat.350,Université PARIS-XI,
91405-ORSAY. (FRANCE)

[°] Télescope Infrarouge,Observatoire de Meudon,Place J.Janssen
92190-MEUDON. (FRANCE)

L 14

The infrared vibration-rotation spectrum of trans- and cis-nitrous acid

C.M. Deeley and I.M. Mills
Department of Chemistry
University of Reading
RG6 2AD, U.K.

Infrared spectra of the trans- and cis- isomers of nitrous Acid were obtained using a Fourier Transform Interferometer, with 0.06 cm^{-1} resolution.

Analysis was achieved using an asymetric top refinement program in conjunction with a band-contour plotting program. Constraining ground-state rotational and quartic centrifugal distortion constants to microwave values[1] and constraining excited-state quartic centrifugal distortion constants to ground-state values, excited-state rotational constants and band origin were refined until good agreement was obtained between calculated and observed spectra.

Accurate values of band origins and differences in rotational constants are of future use in harmonic and anharmonic force constant calculations.

A summary of the results for bands studied so far is given below:

Trans	ν_o/cm^{-1}	$A'-A''/cm^{-1}$	$B'-B''/cm^{-1}$	$C'-C''/cm^{-1}$
ν_2	1699.80(1)	-0.0140(1)	-0.00085(7)	-0.00071(6)
ν_3	1263.183(5)	0.01597(7)	-0.01101(5)	-0.00175(5)
ν_4	790.118(5)	0.0195(2)	-0.0020(1)	-0.0025(1)
Cis				
ν_4	851.928(4)	0.020049(83)	-0.002795(108)	-0.003367(95)

Results on several other bands will be presented in the poster. Also, our results will be compared with those obtained recently by laser Stark[2] and diode laser spectroscopy[3], and the comparison will be discussed.

1. Finnigan, Cox, Brittain and Smith, JCS Faraday II, 68, 548 (1972).
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3. Maki and Sams, to be published.

L 15

The infrared spectrum, equilibrium structure, and harmonic and anharmonic force field of thioborine, HBS.

P. H. Turner and I. M. Mills

Department of Chemistry
University of Reading
RG6 2AD, U.K.

The infrared absorption spectrum of thioborine, HBS, has been observed using a flow system to generate the sample and a Nicolet Fourier transform system to collect the spectrum. The sample was prepared by passing a mixture of Ar and H_2S (or D_2S) over metallic B at about 1200 K and then pumping fast through a multiple reflection cell set to a 6 m path at a total pressure of less than 1 Torr. ^{10}B and ^{11}B species were observed in natural abundance, and both HBS and DBS have been studied. The ν_1 BH or BD stretch and ν_3 BS stretch have been observed; for *DBS* the ν_3 fundamental appears as two parallel bands of comparable intensity due to a strong Fermi resonance with $2\nu_2{}^0$. The ν_2 bending fundamental has not been directly observed despite a careful search using a Hg-Cd-Te detector in the region in which we know the band must lie; we estimate its intensity to be less than 5% of either ν_1 or ν_3, which have comparable intensities.

Analysis of the observed spectra, in conjunction with previous microwave[1] and infrared[2] observations, has allowed us to determine the equilibrium structure and harmonic and anharmonic force field. Preliminary results are summarised in the table over page. The constraint $f_{\alpha\alpha\alpha\alpha} = 4f_{\alpha\alpha}$, where $\alpha = \sin\theta$ and θ is the angular deviation from linearity, corresponds to requiring the angle bending potential to be quadratic in θ (see eq.(4) of Strey and Mills[3]; this point will be discussed in the poster).

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2. Sams and Maki, J.Mol.Structure, 26, 107-115 (1975).
3. Strey and Mills, Molecular Physics, 26, 129 (1973).

Spectroscopic constants, all in cm^{-1} Thioborine , HBS

Constant	1-11-32	1-10-32	2-11-32	2-10-32
B_o(ref 1)	0.636540	0.669804	0.531632	0.552495
D_o(ref 1)	0.000730	0.000801	0.000475	0.000521
ν_1	2735.80	2751.44	2077.71	2104.48
ΔB_1	-0.002958	-0.003376	-0.003195	-0.003523
ν_3	1172.39	1207.07	1144.66	1171.70
ΔB_3	-0.003484	-0.003520	-0.000868	-0.000978
$2\nu_2^o$			1073.92	1091.47
ΔB_{22}			+0.000551	+0.000968
ν_3^*			1119.98	1147.20
ΔB_3^*			-0.002506	-0.002505
$2\nu_2^*$			1098.60	1115.97
ΔB_{22}^*			+0.002189	+0.002495
ν_2	[702]	[709]	[553]	[562]
ΔB_2	+0.000785	+0.000944	+0.001095	+0.001247
B_e	0.638976	0.672308	0.533388	0.554261

*Deperturbed from the Fermi resonance $\Delta B = B' - B''$

Structure and force field

r_e (BH)	1.1698(3) Å	f_{rrr}	-21.596 aJ $Å^{-3}$
r_e (BS)	1.5978(1) Å	f_{rrR}	-0.287 aJ $Å^{-3}$
		f_{rRR}	0.0 constrained
f_{rr}(BH)	4.3685 aJ $Å^{-2}$	f_{RRR}	-35.598 aJ $Å^{-3}$
f_{rR}	0.0134 aJ $Å^{-2}$		
f_{RR}(BS)	7.3589 aJ $Å^{-2}$	$f_{r\alpha\alpha}$	-0.109 aJ $Å^{-1}$
		$f_{R\alpha\alpha}$	-0.296 aJ $Å^{-1}$
$f_{\alpha\alpha}$(bend)	0.3232 aJ		
		f_{rrrr}	72.6 aJ $Å^{-4}$
$f_{\alpha\alpha\alpha\alpha} = 4f_{\alpha\alpha}$	constrained	f_{RRRR}	135.4 aJ $Å^{-4}$

L 16

New set of Dunham coefficients for isotopically susbtituted carbon monoxide from high information Fourier Transform Spectroscopy

D. DE VILLENEUVE-LEFEVRE[1], R. FARRENQ[1], G. GUELACHVILI[1],
W. URBAN[2], J. VERGES[3]

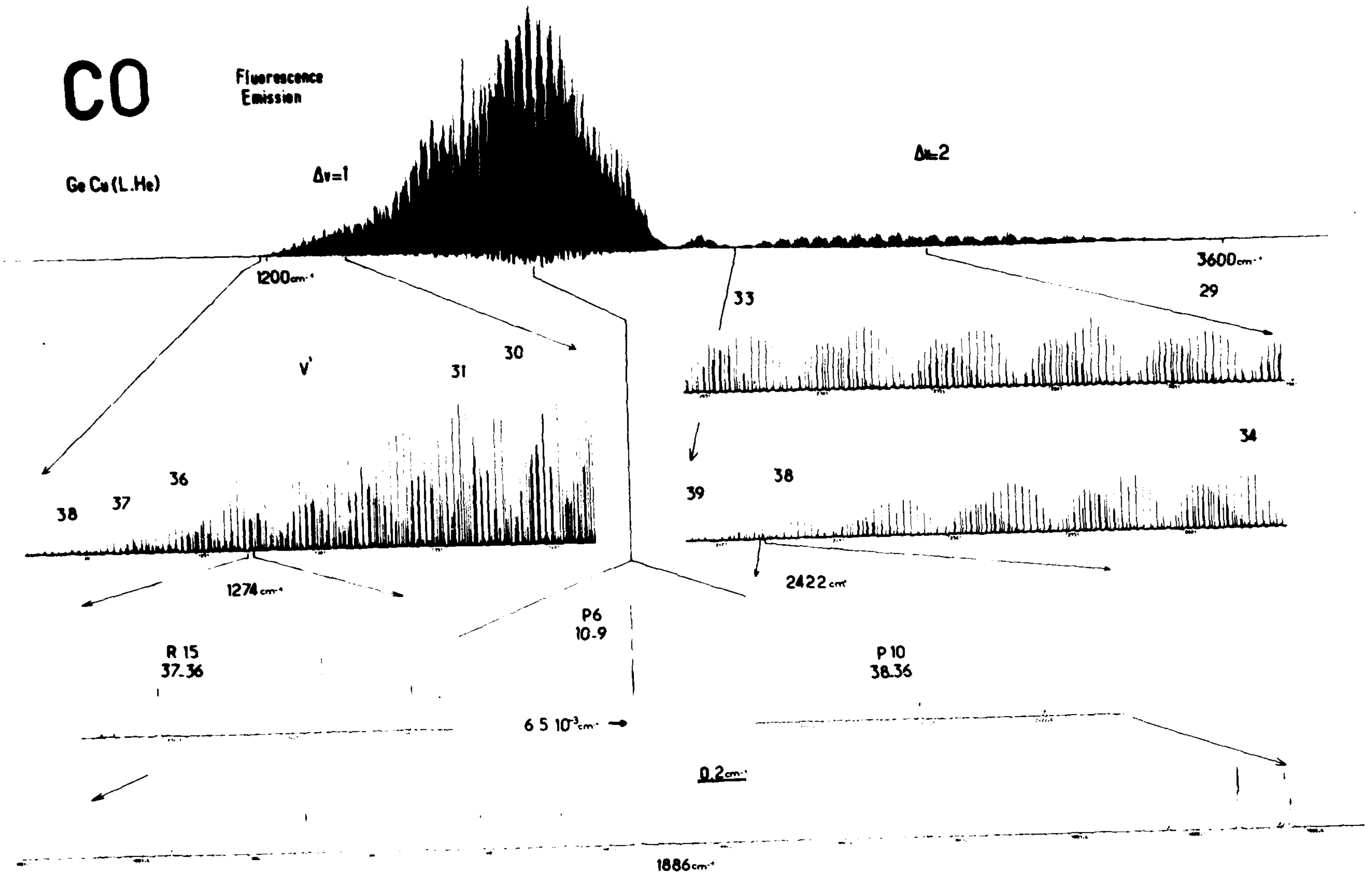
An extensive work on the vibration-rotation bands of CO in the fundamental electronic state : X $^1\Sigma$ has been undertaken in order to determine accurate Dunham coefficients available for all the isotopic species of this molecule and for a wide range of v and J quantum mumbers.

The great amount of experimental data has several origins. Most of the lines come from High Information Fourier transform measurements. Various types of sources have been used in order to reach either high J (up to 93) or high v (up to 40) (or both) vibrational states. Laser measurements are also included in the fit which takes also into account microwave and grating spectra.

A global non linear least squares fit of all the available data, with adequate weights gives a set of improved Dunham coefficients when compared to the best previous results (I).

(I) R.M. DALE, M. HERMAN, J.W.C. JONES, A.R.W. Mc KELLAR, S. NAGLER and I.K.M. STRATHY Can. J. Phys. 57, 5, 677-686, 1979

1) Laboratoire d'Infrarouge Associé au CNRS, Bât. 350, Université Paris-Sud
91405 ORSAY, France
2) Institut Für Angewandte Physik, Wegelestrasse, 8-D-3500 BONN 1, Germany
3) Laboratoire A. Cotton, CNRS II, Bât.505, 91405 ORSAY, France



<u>Latest High Information results on CO</u> :

Source : L.N. cooled laser-type CO tube with d.c. excitation

Detector : L.He cooled Ge Cu

Spectrum : 1.5 10^6 samples, resolution 6.0 10^{-3} cm^{-1} ; spectral range 0-4200cm^{-1}

L 17

ROTATIONAL ANALYSIS OF THE 7576 Å AND 7463 Å ABSORPTION BAND OF NO_2 BY MEANS OF FOURIER TRANSFORM SPECTROSCOPY

A. PERRIN, J.M. FLAUD, C. CAMY-PEYRET
Laboratoire de Physique Moléculaire et d'Optique Atmosphérique
Bâtiment 221, Campus d'Orsay, 91405 ORSAY, France

and

P. LUC
Laboratoire Aimé Cotton, C.N.R.S. II
Bâtiment 505, Campus d'Orsay, 91405 ORSAY, France

We report an extension of our analysis of Fourier Transform absorption spectra of NO_2 between 12400 abd 13900 cm^{-1} [1] .

The rotational analysis of two parallel bands, respectively at 7576 Å and 7464 Å has been performed.

We have assigned lines involving the K_a = 0,1,2,3,4 stacks for the 7576 Å band, and K_a = 0,1,2,3, and 4 stacks for the 7463 Å. band. Furthermore a lot of spin-orbit induced transitions have been detected.

Tentative vibrational assignments are discussed.

[1] A. PERRIN, C. CAMY-PEYRET, J.-M. FLAUD and P. LUC
J. Mol. Spectrosc. (in press).

L 18

THE VUV ABSORPTION SPECTRUM OF CO_2 AT HIGH RESOLUTION. ASSIGNMENT AND ROTATIONAL ANALYSIS OF A $^3\Sigma_u^- \leftarrow \tilde{X}^1\Sigma_g^+$ RYDBERG TRANSITION AT 1106 Å.

C. Cossart-Magos*, M. Eidelsberg**, F. Launay**, S. Leach*
and F. Rostas**

* Laboratoire de Photophysique Moléculaire du C.N.R.S.●
Bâtiment 213, Université de Paris-Sud,
91405 - ORSAY - CEDEX - France.

** Observatoire de Paris-Meudon,
92190 - MEUDON - France -

The gas phase absorption spectrum of $^{12}CO_2$ and $^{13}CO_2$ between 900 and 1820 Å, at a resolution of 0.005 Å was obtained at the Observatoire de Meudon (France), using a spectrograph of 10 m focal length (1) and a continuum source of the B.R.V. type (2).

A considerable increase in resolution (x 40) was gained relative to the previous highest resolution work due to Nakata et al (3). At our higher resolution, the diffuse character of most of the bands in the 900 - 1820 Å region is confirmed. However, for the first time in VUV CO_2 absorption, rotational structure was observed for some bands. The most complete analysis was achieved for a band at about 1106 Å in both isotopic species, which we assign as the origin band of a forbidden transition $^3\Sigma_u^- \leftarrow \tilde{X}^1\Sigma_g^+$. We consider that the excited state belongs to the Rydberg configuration ... $\pi_g^3\ 3p\pi_u$: it is only 0.2 ev above the $^{1,3}\Sigma_u^+$ states of the same configuration, assigned by Greening and King (4) in low resolution spectra. Using the ground state constants of Mandin (5), the excited state term values were determined and, from least squares fitting, the following constants were obtained :

$^{12}CO_2$: $T_0' = 90438.87 \pm 0.06\ cm^{-1}$; $B_0' = 0.38213 \pm 0.00010\ cm^{-1}$

$^{13}CO_2$: $T_0' = 90453.26 \pm 0.05\ cm^{-1}$; $B_0' = 0.38233 \pm 0.00008\ cm^{-1}$

● Laboratoire associé à l'Université de Paris-Sud.

The B' values, situated in between the ground state values of the corresponding neutral molecules (0.3902 $^{(5)}$) and ions (0.3803 $^{(6)}$) are well within the range expected from consideration of the electronic configurations. The bending vibration frequency ν_2' was also determined for the same excited state, through the observation of the 2_1^1 sequence band ; the values obtained (498 and 483 cm^{-1}, respectively in $^{12}CO_2$ and $^{13}CO_2$) compare well with the deperturbed values of this fundamental in the ground state of the corresponding ions (509 and 495 cm^{-1}, respectively in $^{12}CO_2$ and $^{13}CO_2$ $^{(7)}$).

Finally, it should be noted that the observation of fine structure for the band at 1106 Å explains its absence in the photodissociation excitation spectrum of Koyano _et al._ $^{(8)}$ and rules out the interpretation of that peak given by Greening and King $^{(4)}$ who assigned it as a member of the ν_1 progression of the completely dissociative absorption (π_g^3 $3p\pi_u$) $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$. Reassignment of this progression will be discussed.

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(2) E. Boursey and H. Damany, Appl. Opt., 13, 589 (1974),

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L 19 COLLISIONALLY INDUCED DOUBLE RESONANCE IN IODINE : ANALYSIS OF THE D'(2g) - A' (2u) TRANSITION (340 nm IODINE LASER)

J.B. KOFFEND, A. SIBAI , R. BACIS
Laboratoire de Spectrométrie Ionique et Moléculaire
Université Lyon I, 43 boulevard du 11 Novembre 1918 - 69622 Villeurbanne (France)

Numerous studies have been devoted to the D'2g - A'2u transition in I_2 . TELLINGHUISEN has made a vibrational analysis of this system excited by high frequency discharge in Argon (1). Recently it has been shown that optical pumping of the D'2g state by an ArF laser at 193 nm results in a D' - A' laser with a 50 % photon conversion officiency (2). We have made a high resolution spectroscopic study of the D'2g - A'2u transition. Fluorescence from the D'2g state is produced by sequential absorption of two visible photons. The first photon (514,5, 520,8 or 530,9 nm) populates several B 0_u^+ state rovibronic levels. However, collisions with a buffer gas (or I_2 itself) result in a redistribution of population in numerous B 0_u^+ state vibrational levels. A second photon excites the E $0_g^+ \leftarrow$ B 0_u^+ system. Due to the population distribution in the B 0_u^+ state we observe that any ion laser line with $\lambda < 480$ nm may be used for the second step. Collisional E - E transfer from E 0_u^+ levels populate the D' 2g state and D'2g - A' 2u U.V. fluorescence is observed. We have rotationally analyzed the D' - A' system and have obtained spectroscopic constants for more than 50 vibrational levels of the A' 2u state. We have been able to examine the structure of A'2u state near its dissociation limit and the long range behavior of the internuclear potential has been characterized.

(1) J. TELLINGHUISEN
Chem. Phys. Lett. 49, 485 (1977)

(2) M.J. SHAW, C.B. EDWARDS, F. O'NEILL, C. FOTAKIS and R.J. DOROVAN
Appl. Phys. Lett. 37, 4, (1980)

L 20

Fourier Transform Spectra of ν_5 and ν_6 of CH_2NH

G.Duxbury Department of Natural Philosophy
University of Strathclyde
107 Rottenrow, Glasgow, G4 0NG

and M.L.LeLerre
School of Chemistry,
University of Bristol,
Cantock's Close,
Bristol, BS8 1TS

High resolution (0.006 cm^{-1}) spectra of methyleneimine, CH_2NH, have been recorded using the McMath F.T.S. developed by Dr.J.W. Brault at the Kitt Peak National Observatory, Arizona. Methyleneimine, a short-lived molecule, was produced by the pyrolysis of methylamine at ca 1000^oC in a flow system, the total pressure in the 60cm multipass absorption cell being ca 500 mtorr. The spectra cover the frequency range of the ν_4 to ν_9 fundamentals and are currently being analysed in conjunction with CO_2 laser Stark data. New constants for ν_4, previously observed in the gas phase by Allegrini et al. (1), and preliminary constants for ν_5 and ν_6 have already been reported (2).

Both ν_5 and ν_6 are totally symmetric (A') vibrations of the planar (C_s) point group and are in principle hybrid (A+B) bands. Approximately 200 parallel transitions have been assigned to the weak ν_5 band at 1453 cm^{-1}. For the stronger ν_6 band at 1344 cm^{-1} ca 640 transitions have been assigned, including a number of perpendicular lines. In fitting these lines, the isolated band model proved inadequate due to a c-type Coriolis interaction which became important at high values of K_a. Inclusion of the interaction yielded a satisfactory fit with a standard deviation of 0.0009 cm^{-1} and an optimum value of ξ_c of 0.691 cm^{-1}.

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L 21

Rotational Analyses in the Ultraviolet Spectra of Benzene and Sym-Triazine

J.H. Callomon, J.E. Parkin and J. Sellors

Department of Chemistry, University College London, 20 Gordon Street,
London WC1H 0AJ, U.K.

1. As part of a continuing investigation of the 2600 Å system of benzene vapour we have re-examined the rotational structure of some of the prominent bands in the absorption spectrum. We do this partly to obtain improved rotational constants and thereby geometry of the excited state, and partly to investigate the pressure dependence of the rotational structure. Computer programs have been developed for simulating the rotational contour of the absorption bands as obtained from a microdensitometer trace of the photographic plate. We find that we can reproduce bands in the spectrum of both C_6H_6 and C_6D_6 with high precision.

2. We have re-examined the spectrum of sym-triazine-h_3 and -d_3 from our photographic plates taken at high resolution ($\delta\nu \sim 0.1$ cm^{-1}) and at long path lengths. In particular we have studied bands up to 1200 cm^{-1} to low frequency of the electronic origin as assigned by Fischer and Small (1). We have made new assignments in this region based upon combination differences involving ground state fundamentals and upon examination of the rotational contours. The analysis points to the existence of a level, possibly of A_1'' symmetry, which lies some 26 cm^{-1} below the assigned electronic origin. There is some support for this in a recent 2-photon study (2) where a possible explanation is given. Further information concerning the dynamics of the excited state arises from the analysis, notably that the electronic angular momentum associated with the E" levels appears to be quenched. This supports arguments in favour of strong Jahn-Teller and/or pseudo-Jahn-Teller activity in the excited state.

1. Fischer and Small, J. Chem. Phys., 56, 5934 (1972)
2. Webb, Swift and Bernstein, J. Chem. Phys., 73, 4891 (1981)

L 22 An infrared $^2\Sigma^+$ - $X^2\Pi_i$ electronic transition of CuO

Y. LEFEBVRE, B. PINCHEMEL, J.M. DELAVAL and J. SCHAMPS

Laboratoire de Spectroscopie des Molécules Diatomiques
Equipe de recherche associée au C.N.R.S. n° 303
Université de Lille I - Bât. P.5.
59655 VILLENEUVE D'ASCQ CEDEX - FRANCE

Detailed ab initio SCF - CI calculations in progress in our laboratory predict existence of a $^2\Sigma^+$ state of CuO lying less than 10 000 cm^{-1} above the $X^2\Pi_i$ ground state with which it forms an unique perturber pair of levels interacting on oxygen - centered 2pσ - 2pπ orbitals.

Observation of this $^2\Sigma^+$ state would be expecially important as a key for the interpretation of the Λ - doubling parameter of the $X^2\Pi_{1/2}$ component, the sign of which is still a subject of controversy.

In order to look for this hypothetical new $^2\Sigma^+$ state we carried out systematic investigations of the near infrared (0.8 to 3.0 μm) fluorescence of CuO via collision energy transfer from the $A^2\Sigma^+$ state easily populated by broadband (1 cm^{-1}) output of a c.w. dye - laser on the wavelength of the A - X transition (Rhodamine 6 G) - Electronic bands separated by the spin - orbit splitting of the $X^2\Pi_i$ state (280 cm^{-1}), and on this account typical of a transition between an unknown $^2\Sigma$ state and the $X^2\Pi_i$ ground state of CuO, where observed in the near infrared at 7 800 cm^{-1} (λ = 1.3 μm) exactly in the region where they were predicted to lie according to our ab initio calculations.

In the frame of this interpretation, the theoretical magnitude of the $X^2\Pi_{1/2}$ Λ - type splitting deduced from the ab initio wavefunctions is in good agreement with the spectroscopic value. It fixes a positive sign for the corresponding p parameter and determines definitively the electronic parities of all the $^2\Sigma$ levels of CuO.

L 23 THE OBSERVATION AND ANALYSIS OF HYPERFINE STRUCTURE IN THE YELLOW SYSTEM OF COPPER MONOFLUORIDE

by

C. R. Brazier, J. M. Brown and T. C. Steimle
Department of Chemistry, Southampton University, Southampton SO9 5NH.

Two spectroscopic studies[1,2] of the closely spaced yellow bands (567.7nm and 569.5nm) of copper monofluoride have recently been reported. Both analyses raised questions about the nature of the excited electronic state. It was assumed that the yellow bands involved a transition between the ground $^1\Sigma^+$ state and an excited state "p-complex", although it was recognized that they could equally well have been analysed by assigning the excited state as $^3\Sigma^-$. Recent ab initio calculations[3] would prefer to find a $^3\Pi$ state in this region. We have studied the nuclear hyperfine structure of the lines in this spectrum in an attempt to decide between the various, alternative assignments.

The spectrum has been studied by the detection of weak fluorescences excited by a tunable dye laser. Under our experimental conditions, it was possible to resolve Cu hyperfine structure even in the Doppler-limited excitation spectrum. We have also studied lines in the spectrum at sub-Doppler resolution by the techniques of Microwave Optical Double Resonance, (MODR) and by Intermodulated Fluorescence (IMF). In this way, we have been able to resolve splittings due to both ^{63}Cu and ^{19}F. An analysis of our observations will be reported, along with the implications for the assignment of the excited electronic state.

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2) A. H. Chojnicki, F. Ahmed and R. F. Barrow, (to be published).
3) J. Schamps, private communication.

L 24 Analysis and Interpretation of the Spectrum of the CuF Molecule

Fakhruddin Ahmed,[*] R.F. Barrow,[*] A.H. Chojnicki,[*]
C Dufour[†] and J. Schamps[†]

[*]Physical Chemistry Laboratory, Oxford University,
South Parks Road, Oxford, OX1 3QZ, England

[†]U.E.R. de Physique Fondamentale, Universite des Sciences
et Techniques de Lille, 59655 Villeneuve d'Ascq, France

Abstract

The electronic spectrum of the CuF molecule has been photographed at moderate resolution in absorption and some regions have been studied in emission, using spectra excited at reduced rotational temperature in a composite wall hollow cathode discharge. Three new systems, all with the ground state as lower state, have been discovered: their upper states are a $^3\Sigma^+$, A(Ω=0$^+$,1) and D(Ω=1). Constants for ^{63}Cu^{19}F are as follows:

State	T_e	ω_e	$x_e\omega_e$	B_e	$10^3\alpha_e$	r_e (Å)	
D(Ω=1)	22805.15	616.42	3.33	0.35942	2.81	1.7928	
C $^1\Pi$	20258.70	643.42	3.66	0.37556	2.98	1.7539	
B $^1\Sigma^+$	19717.48	656.04	3.63	0.37134	3.86	1.7638	
A(Ω=0$^+$,1)	17562.27	647.08	3.46	0.37609 0.37729	2.91 2.97	1.7512	(a)
a $^3\Sigma^+$	14580.52	674.20	4.14	0.38248	2.98	1.7379	(b)
X $^1\Sigma^+$	0	621.55	3.494	0.379408	3.2297	1.7450	(c)

(a) $\Delta\nu$, v=0, $\Omega 0^+ - \Omega 1$, = 55.38 cm^{-1}

The upper figures refer to the e, the lower to the f components.

(b) λ_o = 22.17 cm^{-1}.

(c) Ground state rotational constants are from the microwave spectrum.

The results of detailed *ab initio* calculations on the low-lying states of CuF are reported and the characters of the states are discussed.

M1

HIGH TEMPERATURE AND INTERSTELLAR MOLECULES IN RARE GAS MATRICES AT 4°K

William Weltner, Jr.

Department of Chemistry, University of Florida, Gainesville,
Florida 32611.

The trapping of reactive molecules in solid rare-gas matrices at cryogenic temperatures is now a well established technique. The transparency of such matrices to radiation extending from the far uv to the far ir makes possible optical studies throughout that range. There is the distinct advantage of simplification of the spectra of the cold molecule with, however, loss of rotational structure. Solid state shifts of molecular parameters are almost always small and generally qualitatively understood. The greatest advantage of this technique is that it makes possible the observation of short-lived molecules present in unobservably low concentrations in the gas phase. It then allows, for example, electron-spin-resonance to be applied where such measurements in the gas phase would be very difficult.

This talk will briefly review the spectroscopy of selected molecules where matrix-isolation has been successful in providing unique information, often at the level of high-resolution gas-phase spectroscopy, and often on new molecules. It may include optical and ESR studies of such molecules as $C_4, \ldots, C_n$, C_2H, C_4H, BC_2, Be_2, BeH, BaF, CrH, TiF_2, MnO, MnF_2, CrCu, and Mn_2. It will stress the breadth of information obtained: characterization of the ground and, less informatively, excited electronic states, zero-field splitting, hyperfine interaction, quadrupole coupling, spin-rotation interaction, and exchange interaction constants. Solid-state measurements then complement those in the gaseous state and provide less accurate but perhaps unobtainable data at the present time.

M2 High Resolution Infrared Matrix Spectroscopy

H.H. Gunthard

Physical Chemistry ETHZ
ETHZ Zentrum
8092 Zurich, Switzerland

(no abstract)

N1 Anticrossing and Double Resonance Studies in Glyoxal

M. Lombardi

Laboratoire de Spectrometrie Physique
USMG BP 53X
38041 Grenoble-cedex
France

(no abstract)

N2 Infrared Laser Spectroscopy of Transient Species

R. J. Saykally

Department of Chemistry
University of California
Berkeley, California 94720
U.S.A.

(no abstract)

0 1 The microwave spectrum of isotopic species of thietane

C. Castro and I.M. Mills and H. Wieser

Department of Chemistry
University of Reading
Reading RG6 2AD, U.K.

Department of Chemistry
University of Calgary
Calgary 44, Alberta, Canada

This work deals with the microwave spectra of a small ring molecule, trimethylene sulfide or thietane, and its three deuterated isotopic species β-d_2, $\alpha\alpha'$-d_4 and d_6, in excited vibrational states. The vibration of interest in each of the above molecules is the highly anharmonic out of plane ring puckering deformation, which gives rise to vibrational spectra at low wavenumbers. These molecules have been measured for the v = 0,1,2,3,4 and 5 states of the puckering vibration in the region 18 to 40 GHz. The spectra have been assigned and analysed up to J > 50 so that we have been able to determine centrifugal distortion constants in each vibrational state. Although the spectra are mostly Q-transitions, 3 or 4 low J R-transitions have been observed in each vibrational state.

The main purposes of this work are to obtain (a) knowledge of the potential function of the puckering vibration; (b) values for $a_r^{(ac)} = (\partial I_{ac}/\partial Q_r)$ for the puckering coordinate Q_r, and hence information on the form of Q_r and its isotopic dependence; (c) structural information on the molecule both in the planar configuration of the ring atoms at the top of the barrier, and in either of the two puckered equilibrium configurations. Each puckering state with $v \geq 4$ has been fitted to a separate effective Hamiltonian and the vibrational dependence of both the rotational constants and the quartic centrifugal distortion constants has been observed and analysed. The close lying pairs of states v = 0 and 1, and v = 2 and 3 are treated with a vibration-rotation Hamiltonian which includes on off-diagonal coupling term in v_r. The variation of the centrifugal distortion constants with v_r follows the model of Creswell and Mills.

0 2 Microwave spectra of SiH_3 CCH in excited states

A. BAUER and J. CARLIER
Laboratoire de Spectroscopie Hertzienne
Université de LILLE I
59655 VILLENEUVE D'ASCQ Cedex - FRANCE

Silyl acetylene is a C_{3v} symmetry type molecule, whose lowest vibrational modes are ν_{10}(E) : 220 cm^{-1}. SiC ≡ C bend, ν_5(A) : 659 cm^{-1} and ν_9(E) : 668 cm^{-1}. Due to the low dipole moment (μ = 0,316 D) of this molecule and the high excited states and isotopic species which had to be studied, high sensitivity was required for the observation of the microwave spectrum. Stark spectroscopy was used for the lowest frequencies. For higher frequencies, a new video method using the Stark displacement of the lines was carried out during the averaging, in order to minimize the effect of the standing waves in the cell on the detected signal.

The microwave spectrum of the ground state has been observed from J = 0 to J = 23 and some transitions of isotopic species have also been measured.
For the ν_{10} state, ten rotational transitions have been observed from J = 0 to J = 11.
For the $2\nu_{10}$ state, sixteen rotational transitions up to 232 GHz have been measured.

Several sets of contants corresponding to the different states could be derived from the analysis. In addition to the classical rotation and vibration-rotation parameters, some H sextic distortion constants were obtained and also the $\chi_{\ell\ell}$ vibrational aharmonic constant.

03

MILLIMETER WAVE SPECTRUM OF ACETONITRILE OXIDE CH_3CNO IN THE VIBRATIONAL STATES $v_{10} = 2$ and $v_{10} = 3$

J. Galica, B. P. Winnewisser and M. Winnewisser
Physikalisch Chemisches Institut
Justus-Liebig-Universität
Heinrich-Buff-Ring 58
D-63 Giessen, West Germany

The measurement of the millimeter wave spectrum of acetonitrile oxide, CH_3CNO, has been extended to the states $v_{10} = 2$ and $v_{10} = 3$ in the vibrational manifold of the lowest bending mode. The spectrum has been analyzed in terms of the off-diagonal matrix elements expected for a C_{3v} symmetric top, in particular $\Delta K = \pm 2$, $\Delta \ell = \pm 2$ and $\Delta K = \pm 1$, $\Delta \ell = \mp 2$. Prominent resonances not explained by these matrix elements can be attributed to interactions with another set of vibrational energy levels, as will be shown.

04 ROTATION-INVERSION SPECTRUM OF ISOCYANAMIDE NH_2NC AND MILLIMETER WAVE SPECTRUM OF DIAZOMETHANE CH_2N_2

E. Schäfer and M. Winnewisser
Physikalisch Chemisches Institut
Justus Liebig Universität Giessen
Heinrich-Buff-Ring 58
D-6300 Giessen

The a-type rotational spectrum and the c-type rotation-inversion spectrum of isocyanamide were observed in the frequency range 147 to 300 GHz. Ether extraction of the hydrolysis products of diazomethyllithium was employed to isolate the isocyanamide.

Rotational constants and centrifugal distortion constants have been obtained for the groundvibrational state (NH_2-inversion state 0^+) and for the lowest excited vibrational state (NH_2-inversion state 0^-). The inversion splitting was determined to be 0.366 cm^{-1} (11 GHz).

The symmetry group and selection rules will be illustrated.

128 ground state transitions of the a-type R branch of diazomethane have been measured in the frequency range 100 to 400 GHz. The data were analyzed using Watson's S-reduced Hamiltonian.

05

AVOIDED-CROSSING MOLECULAR-BEAM STUDY OF THE INTERNAL ROTATION IN METHYL SILANE

W. Leo Meerts
Fysisch Laboratorium, Katholieke Universiteit
Toernooiveld, 6525 ED Nijmegen, The Netherlands

and

Irving Ozier
Department of Physics, University of British Columbia
Vancouver, B.C., Canada V6T 1W5

The avoided crossing molecular-beam electric-resonance technique 1) has been applied to methyl silane (CH_3SiH_3) in the ground torsional state. A new type of anticrossing was observed which breaks the torsional symmetry and obeys the selection rules $\Delta J=0$, $K=+1 \rightarrow -1$. These avoided crossings yield directly the pure internal rotation splittings in a given rotational state, regardless of the value of (A_0-B_0). Such 'barrier' crossings were observed for J from 1 to 6. In addition several $(J_K=1_1 \rightarrow 2_0)$ anticrossings were studied.

The present data combined with microwave spectra 2) allowed accurate determination of many of the parameters entering the rotational and internal-rotation Hamiltonian. Besides the rotational constants A_0 and B_0, three of the most interesting molecular constants obtained are the barrier height to internal rotation $V_3=593.14(34)$ cm^{-1}, the moment of inertia of the CH_3 top $I_\alpha=3.1607(12)$ amu Å^2 and the ratio of I_α to the moment of inertia along the symmetry axis of the entire molecule $\rho=0.351814(10)$. In addition to the most abundant isotopic species the ^{30}Si substituted species was studied in natural abundance, and an accurate value of the isotopic shift in the barrier height was determined: $V_3(CH_3{}^{30}SiH_3)-V_3(SH_3{}^{28}SiH_3)=0.105(23)$ cm^{-1}.

The molecular beam results together with the microwave data provide an excellent test of the currently used model for the description of the barrier to internal rotation in symmetric tops.

1) W.L. Meerts and I. Ozier, Phys.Rev.Lett. 41, 1109 (1978)

2) E. Hirota, J.Mol.Spectrosc. 43, 36 (1972)

0 6 INFRARED SPECTRA OF CF_3Br: INTERPRETATION OF THE RELEVANT STRUCTURE

A. BALDACCI, A. PASSERINI and S. GHERSETTI

Department of Organic Chemistry, University of Venice
Calle Larga S. Marta 2137, Venezia (Italy)

Under the context of a research work on halomethanes undertaken in this laboratory, the results of an extensive investigation in medium resolution of the gas-phase i.r. spectrum of CF_3Br are presented here.

In this study (range 4000-400 cm^{-1}) a natural sample containing $^{79/81}Br$ isotopic variants (both belonging to the C_{3v} point group) in almost equal percentage was used.

Of the six fundamentals, three of symmetry $\underline{a}_1(\nu_1-\nu_3)$ and three of symmetry $\underline{e}(\nu_4-\nu_6)$, all infrared active, the ν_2 at 761.9 cm^{-1} and the ν_5 at 548.9 cm^{-1} were studied from the observed spectrum, while ν_3, lying below 400 cm^{-1}, was evaluated by applying the Ritz rule. The location of ν_6 was tentatively estimated at 303.3 cm^{-1} ($CF_3{}^{79}Br$) and at 303.0 cm^{-1} ($CF_3{}^{81}Br$) respectively. The ν_1 and ν_4 modes, already investigated in detail (1,2), were not considered here.

The assignment of more than one hundred overtones, combinations, and "hot" bands, the latter mainly by the means of anharmonic constants and intensity considerations, is characterized by a satisfactory internal consistency throughout the range investigated.

Under the present experimental conditions most of the absorption bands of such symmetric tops present an unresolved contour; only for few perpendiculars (i.e. ν_5, $\nu_2+\nu_5$, $2\nu_4^2$) the rotational structure appears as a set of Q sub-branches superimposed on the P,R background; for the latter, the vibrational origins and the $\xi_{eff.}$ could be evaluated by the usual analysis.

(1) K. BURCZYK, H. BURGER, A. RUOFF and P. PINSON; J. Mol. Spectrosc. 77 109-116 (1979)

(2) L.C. HOSKINS and C.J. LEE; J. Chem. Soc. 59 4932-4936 (1973)

07 THE ν_1 BANDS OF $CH_3C\ell$ AND THEIR APPLICATIONS TO STRATOSPHERIC PROBLEMS

M. MORILLON-CHAPEY and M. DANG-NHU
Laboratoire d'Infrarouge
Université de Paris-Sud
Bâtiment 350

F 91405 ORSAY CEDEX, FRANCE

$CH_3C\ell$ has not been detected so far in the atmosphere by optical methods in spite of its importance in atmospheric studies. We have shown that the most favorable spectral range for this detection seems to be located in the region of the Q branches of the ν_1 parallel bands (3.4 μm).

With the parameters determined in a previous study (1) for both $CH_3{}^{35}C\ell$ and $CH_3{}^{37}C\ell$ we have computed the positions and intensities of all the lines which form the Q branches for K = 1 to K = 6. We have plotted the calculated branches for 2 temperatures :
T = 300 K for comparison with the experimental F.T. spectrum and
T = 216 K, which is the temperature of the optimal altitude for detection of $CH_3C\ell$.

It is now possible for experimentalists to use our accurate predictions of line strenghts and wavenumbers for both isotopic species of $CH_3C\ell$ under a variety of pressure, temperature, and concentration conditions pertinent to further stratospheric observations.

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(1) Intensities of the ν_1 - bands of $^{12}CH_3{}^{35}C\ell$ and $^{12}CH_3{}^{37}C\ell$ near 3 μm. To be published in J.Q.S.R.T. (1981) by M. DANG-NHU, M. MORILLON-CHAPEY, G. GRANER and G. GUELACHVILI.

08

Single Vibronic Level Fluorescence and Two-Photon Excitation Spectra with a Pulsed Dye Laser

J.M. Hollas, H. Musa and T. Ridley

Chemistry Department, Reading University, Whiteknights, Reading,
RG6 2AD, England

Single vibronic level (SVL) fluorescence spectra have been obtained using exciting radiation from a dye laser, with oscillator and amplifier dye cells, pumped with a 500 kW nitrogen laser. When necessary the radiation is frequency doubled using an appropriate angle-tuned crystal.

SVL spectra of the $\tilde{A}$-$\tilde{X}$ system of styrene ($C_6H_5CH{=}CH_2$) and styrene-β-D_2 have been obtained with the aim of determining the C(1)-C(α) torsional potential function in the $\tilde{X}$ state. Observation of the lowest five levels of ν_{42}, the torsional vibration, and observation of the gas-phase Raman spectrum for each molecule leads to the potential function

$$\frac{V(\phi)}{cm^{-1}} = (1070\pm8)\cos2\phi-(274\pm2)\cos4\phi+(7.0\pm0.2)\cos6\phi$$

for styrene, and

$$\frac{V(\phi)}{cm^{-1}} = (1070\pm8)\cos2\phi-(270\pm2)\cos4\phi+(4.5\pm0.2)\cos6\phi$$

for styrene-β-D_2.

In the $\tilde{A}(\pi^*\pi)$-$\tilde{X}$ system of 2-aminopyridine SVL fluorescence spectra involve transitions to several levels of the NH_2-inversion vibration, ν_I, in the $\tilde{X}$ state. These are compared with observations of direct transitions within the ν_I manifold in the far infrared spectrum from which the parameters of the W-shaped potential function have been obtained.†

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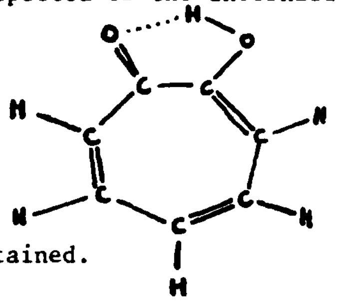
† R A Kydd, Spectrochim.Acta, 35A, 409 (1979)

SVL fluorescence spectra of the internally hydrogen-bonded molecule tropolone



have also been obtained.

Fluorescence excitation following the simultaneous absorption of two photons has been observed in the $\tilde{A}$-$\tilde{X}$ electronic systems of 1,2- and 1,3-difluorobenzene. As in the corresponding system of benzene ν_{14}, the 'Kekulé vibration' of the ring is involved in considerable intensity stealing. In 1,2-difluorobenzene this vibration is totally symmetric and this is the first example of intensity stealing by such a vibration in two photon spectra.

The problem of calibration of the dye laser wavelength has been solved by using the neon lines, observed in the optogalvanic effect, for absolute wavelength measurements and a Fabry-Perot etalon to provide fringes for interpolation between the neon lines.

0 9 OPTICALLY PUMPED CW FIR LASER EMISSIONS FROM $H^{13}COOH$: MEASUREMENTS AND ASSIGNMENTS

Didier DANGOISSE and Pierre GLORIEUX

Laboratoire de Spectroscopie Hertzienne, associé au CNRS
Université de Lille I, 59655 VILLENEUVE D'ASCQ Cédex, France

Twenty one emissions have been obtained from the $H^{13}COOH$ laser pumped by a cw CO_2 laser. Some of them are very powerful and are observed with a low threshold pump power (<1 W).

Frequency measurements by beating the FIR radiation with the output of a mmwave klystron provided high accuracy information (∿ 1 MHz).

However contrary to previously investigated molecules [1], there was almost no high resolution data on this molecule : values of vibrational energy are from matrix isolation spectroscopy and only the ground state rotational energy levels have been investigated by microwave spectroscopy.

Using the strong analogy between this molecule and $H^{12}COOH$ we are able a) using a graphical method, to assign J and Ka values of levels from which FIR laser emission originates.

b) to recalculate one approximate IR spectrum and using additional information (polarisation selection rules, cascade emissions...) to assign the transition pumped by the laser.

c) by fitting all available information, to deduce a set of rotational constants and the ν_6 vibrational energy.

The validity of this method has been decked by comparing these results with those obtained from radiofrequency spectroscopy inside the cavity of a CO_2 laser. The latter work provides the frequency of K-doubling transitions and possibly the J and Ka values of the levels connected by the CO_2 laser lines.

The good agreement between double resonance and FIR laser assignments proves the consistency of the assignment procedure.

[1] see for instance
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O 10 The Infrared Stretching Fundamentals of SiF_2

G.L. Caldow, C.M. Deeley, P.H. Turner and I.M. Mills

Department of Chemistry, University of Reading
Reading, RG6 2AD, U.K.

The infrared spectrum of the stretching fundamentals of SiF_2 has been obtained at a resolution of about 0.1 cm^{-1} using a Nicolet FTIR spectrometer. The SiF_2 was prepared by passing an equimolar mixture of SiF_4 and Ar over metallic Si at about 1300 K, and pumping fast through a multiple reflection absorption cell set to a path of 6m. The pressure in the cell was about 1 Torr. Each spectrum was obtained by co-adding 24 interferograms in about 5 minutes, after which the cell had to be dismantled and cleaned to remove polymer.

The spectrum was analysed using computer simulation based on a coupled Hamiltonian for ν_1 and ν_3, making use of previously published microwave results[1,2]. The new results obtained are the vibrational band origins, and the relative sign and magnitude of the vibrational transition moments (determined through the effect of the ζ_{13}^{c} Coriolis coupling). The molecular parameters obtained (combined with the results of the earlier work) are summarised below in cm^{-1}.

	ground state	ν_1 state	ν_3 state
ν_o:	0.0	855.010 (5)	870.405 (5)
A :	1.0207752 (18)	1.0224337 (14)	1.0107307 (14)
B :	0.2943211 (6)	0.2924576 (21)	0.2938542 (21)
C :	0.2278335 (4)	0.2267635 (12)	0.2270575 (12)

$10^6 D_J$:	0.3492 (60)	fixed for all vibrational states.	D:	−0.192507
$10^6 D_{JK}$:	−2.8054 (645)		F:	0.0021338
$10^6 D_K$:	19.03 (3)		$\nu_1 - \nu_3$:	−15.395
$10^6 d_1$:	−0.1203 (8)		M_1/M_3:	1.22 ± 0.24
$10^6 d_2$:	−0.0078 (2)		$(\zeta_{31}^{c})(\partial\mu_a/\partial Q_3)(\partial\mu_b/\partial Q_1)$ =	positive

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2. Shoji, Tanaka and Hirota, J.Mol.Spectrosc. 47, 268 (1973)

O 11

ROTATIONAL ENERGY TRANSFER STUDY OF CO PERTURBED BY H_2 AND He : A TEST FOR AB-INITIO CALCULATIONS PROVIDING POTENTIAL ENERGY SURFACES.

A. Bersellini-Picard, R. Charneau and Ph. Bréchignac,
Laboratoire de Photophysique Moléculaire du C.N.R.S.*
Bâtiment 213 - Université de Paris-Sud
91405 - ORSAY CEDEX France.

The aim of this work is an attempt to test ab initio calculations providing potential energy surfaces in the case of $CO-H_2$ (1) and CO-He (2)(3).

Rotational relaxation cross sections for CO perturbed by H_2 and He deduced from experiments presented in this work give information on the intermolecular potential through comparison with results of dynamical calculations. We present here results of infrared linewidths measurements at low and room temperatures for CO diluted in H_2 and He using a tunable diode laser in the 4.7 μm spectral region. These results are discussed in connection to infrared double resonance measurements and theoretical results of inelastic cross sections.

In a first part, for the system $CO-H_2$, pressure-broadening data are compared with direct measurements of inelastic cross sections deduced from a time resolved infrared double resonance technique using CO lasers (4).

In a second part, CO-He measurements are compared to the cross sections derived from two ab-initio potential energy surfaces : the first obtained by Green and Thaddeus (2) and the second by Thomas et al (3).

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Green and P. Thaddeus, Astrophys. J., 205, (1976) 766,

Thomas, W.P. Kraemer and G.H.F. Diercksen, Chem. Phys., 51, (1980)

[illegible] ard-Bersellini, R. Charneau and J.M. Launay,
[illegible]

0 12 A METHOD FOR SIMULTANEOUS MEASUREMENTS OF STRENGTHS AND COLLISIONAL LINEWIDTHS FROM FOURIER TRANSFORM SPECTRA.

N. LACOME, A. LEVY,
Laboratoire d'Infrarouge,
Associé au C.N.R.S.,
Université de Paris-Sud
Bâtiment 350,
91405 ORSAY CEDEX, FRANCE

J.P. HOUDEAU and C. BOULET
Département de Physique Atomique et Moléculaire
Université de Rennes I
35042 RENNES CEDEX

On account of the considerable increase in high resolution Fourier Transform spectra, a practical method has been set up in order to derive individual line parameters from Fourier data. This method concerns mainly spectra exhibiting moderately dense structure, so that spectral analysis can be carried out under pressure conditions where collisional broadening dominates.

Under these conditions :

a) For any line under study, the strength and width values can be determined simultaneously from the same spectrum,

b) Instrumental distortions can be reduced by pressurizing the gas to sufficient extent. In the present case the relevant corrections do not exceed 3 percent, and in a few cases reach 5 percent,

c) Thus, from the analytic expression of the apodized apparatus function, it is possible by the means of a convolution calculation to draw up a series of tabulations. These give the true linewidth and the dimensionless quantity $K(\sigma_0)\ell$ respectively, as functions of the width and maximum transmission of the observed contour.

The calculation has been extended to the case of doublets of same intensities and widths and of known spacing.

The method has been tested by investigating a few self-broadened lines in the 12°0-00°0 transition of N_2O, and some nitrogen-broadened lines in the fundamental band of NO recorded at the laboratory by G. GUELACHVILI.

O 13 The ν_3 and ν_4 IR Bands of SiH_3F: Analysis, Contour Simulation and Si-isotope Displacements

R. Escribano
Inst. Estructura de la Materia
C.S.I.C., Serrano
119, Madrid-6
Spain

R. J. Butcher
Cavendish Laboratory
Madingley Road
Cambridge, CB3 OHE
U.K.

and I. M. Mills
Department of Chemistry
University of Reading
Reading, RG6 2AD
U.K.

The IR spectrum of SiH_3F has been recorded at Reading with the Nicolet 7199 Fourier Transform Spectrophotometer. The spectral resolution is around 0.06 cm^{-1}. We report here the analysis of the ν_3 (Si-F stretching) and ν_4 (Si-H asymmetric stretching) bands.

These bands provide beautiful examples of nearly unperturbed, symmetric top parallel and perpendicular bands with isotopic structure. We have assigned over 200 transitions in each band. For ν_3, these data correspond to P and R sub-band maxima of all three species with ^{28}Si, ^{29}Si, ^{30}Si. The data have been analyzed using a least squares fitting programme, yielding the band origins and the A, B, D_J and D_{JK} constants in the $v_3 = 1$ state for all three species.

For the ν_4 band, the data correspond to individual transitions of the ^{28}Si species as well as to ^PQ and ^rQ maxima of all three molecules. The analysis therefore provides the band origin isotopic displacements for the ^{29}Si and ^{30}Si species, and a whole set of parameters for the ^{28}Si molecule.

The results will be presented at the meeting.

0 14

FOURIER TRANSFORM ANALYSIS OF THE $^{129}I_2$ and $^{127-129}I_2$ X STATE CLOSE TO THE DISSOCIATION LIMIT

D. CERNY*, R. BACIS*, C. EFFANTIN*, J. VERGES**
* Laboratoire de Spectrométrie Ionique et Moléculaire
Université LYON I, 43, Boulevard du 11 Novembre 1918 - 69622 Villeurbanne (France)
**Laboratoire Aimé COTTON
C.N.R.S. II - Bâtiment 505, 91405 Orsay (France)

In order to complement results obtained at the dissociation limit of the ground state of the $^{127}I_2$ (1) we have undertaken the study of $^{129}I_2$ and $^{127-129}I_2$ from their Laser Induced Fluorescence analysed with a Fourier Transform Spectrometer (LIF-FTS). Various records were obtained using Kr^+ (520.8 and 530.9 nm) and Ar^+ (514.5 and 501.7 nm) laser lines. The fluorescence induced by these lines spans the 0.5 - 1.4 μm region. A precise description of the X state of both molecules is obtained. In particular, the 501.7 nm line excite the levels (v' = 61, J' = 8 and 5) (v' = 62, J' = 25) of the B state and we observe B-X transitions having v" as high as 110. From single mode excitation spectra it has been possible to rotationally analyse levels quite near the dissociation limit and we have shown that the $^{127-129}I_2$ last vibrational level has $v_D = 114$.

Perturbation of the X state by the 0_g^+ and 1g states which occur very near the dissociation limit, may limit the reliability of a long range analysis since complete deperturbation of $X^1\Sigma_g^+$ constants obtained is difficult (1). However, the mass-reduced long range behavior for both $^{127}I_2$ and $^{127-129}I_2$ determined from our measurements is identical and thus lends credence to the long range analysis performed.

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(1) F. MARTIN, S. CHURASSY, R. BACIS, R.W. FIELD and J. VERGES to be published

O 15 ZEEMAN QUANTUM BEATS IN THE NO_2 $^2\tilde{B}_2$ EXCITED STATE: A STUDY OF POPULATION AND ALIGNMENT DECAY

P. J. Brucat and R. N. Zare
Department of Chemistry
Stanford University
Stanford, California 94305

Single rotational levels in the $^2\tilde{B}_2$ excited electronic state of NO_2 are prepared by absorption of polarized single frequency pulses from an acousto-optically modulated R6G CW dye laser. Subsequent emission from the laser-excited level is time resolved in the presence of an applied magnetic field. The Fourier transform of the decay signal contains well resolved frequency components corresponding to the Larmor precession of the hyperfine levels which lie within the Doppler limited excitation envelope. This Zeeman Quantum Beat spectrum contains information on the overall population decay of the excited rotational level, the decay of the alignment of the individual hyperfine levels, and the Landé g factors for these hyperfine levels. At low pressures ($\leq 10^{-4}$ torr) the population and alignment decays are exponential with a lifetime of ≈ 40 μs. As the pressure is increased, the alignment of the excited state decays faster than the total emission but the total emission decays non-exponentially with time. Approximate depolarization cross sections have been obtained.

0 16

LASER EXCITATION STUDY OF THE CO_2^+ $\tilde{A}$ and $\tilde{B}$ INTERELECTRONIC STATE MIXING

Mark Johnson, Joëlle Rostas, and R. N. Zare

Rotational levels of the $\tilde{B}\ ^2\Sigma_\mu^+(000)$ state are selectively excited with a doubled Rhodamine dye laser (3 GHz bandwidth) which is scanned over the 2890Å $\tilde{B}^2\Sigma_\mu^+(000)$ - $\tilde{X}\ ^2\Pi_g(000)$ band. Filter combinations are used to isolate different emission regions. Fluorescence from these levels is observed in the 3000 - 4500Å region, corresponding to the $\tilde{A}$ - $\tilde{X}$ bands. The fraction of the fluorescence quantum yield in the $\tilde{A}$ - $\tilde{X}$ region can be related to mixing coefficients for the coupled $\tilde{A}$ and $\tilde{B}$ states using the unperturbed $\tilde{A}$ and $\tilde{B}$ state radiative lifetimes. The unperturbed $\tilde{B}$ state lifetime is obtained by selective laser excitation of the $\tilde{B}(010)$ - $\tilde{X}(010)$ band. The radiative lifetime of some strongly perturbed $\tilde{B}(000)$ levels is also determined. Mixing coefficients for rotational levels in the vicinity of extra lines are derived for the f symmetry levels.

The $\tilde{A}(202)$ - $\tilde{X}(000)$ band is reported for the first time. Its position 1270 cm^{-1} to the blue of the $\tilde{B}$ - $\tilde{X}$ origin suggests either strong anharmonic coupling or a new value for $2\nu_3'$.

0 17 Interactions between the electronic sextet states of $\mathrm{FeC}\ell$

J.M. DELAVAL and J. SCHAMPS

Laboratoire des Molécules Diatomiques CNRS ERA 303
U.E.R. de Physique Fondamentale, Université de Lille I
59655 VILLENEUVE D'ASCQ Cedex - France

From combination of rotational analysis and ab initio calculations, the two most intense ultraviolet systems of the emission spectrum of $\mathrm{FeC}\ell$ have been assigned to $^6\Phi_i - {}^6\Delta_i$ and $^6\Pi_i - {}^6\Delta_i$ transitions.

The lower $^6\Delta$ state is most likely the ground state of the molecule, with $\mathrm{Fe}^+(3d^6 4s)\ \mathrm{C}\ell^-$ configuration, while the excited states are obtained from it via a $4s - 4p$ electron jump.

Interactions between the states find expression in anomalies in their fine structure : non-equal spin-orbit intervals, non-linear Ω-variation of the effective rotational constants of the spin-orbit components, unexpectedly large Λ-doubling splittings.

These effects are theoretically interpreted as the result of intense perturbations between the close-lying sextet states of the lower $\mathrm{Fe}^+(3d^6 4s)\ \mathrm{C}\ell^-$ structure on the one hand, and between those of the upper $\mathrm{Fe}^+(3d^6 4p)\ \mathrm{C}\ell^-$ structure on the other hand.

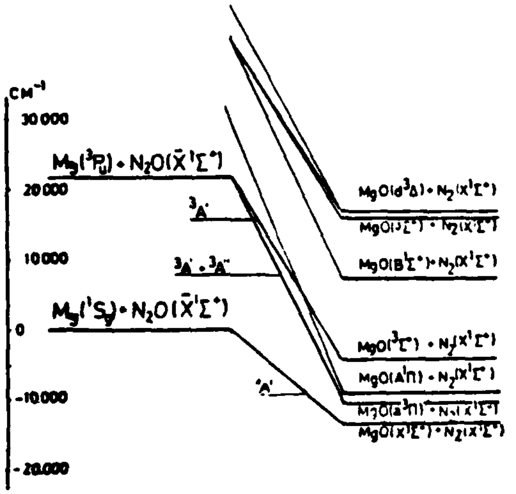
0 18

SPECTROSCOPIC STUDY OF MgO PRODUCED BY CHEMICAL REACTION.

Bernard BOURGUIGNON, Joëlle ROSTAS and Guy TAIEB
Laboratoire de Photophysique Moléculaire du C.N.R.S.*
Bâtiment 213, Université de Paris-Sud
91405 - ORSAY - CEDEX - France.

The reaction of Mg with N_2O has been studied by chemiluminescence and laser induced spectroscopy. When the reactant Mg formed in a Broïda oven, is in the ground state (^1S), no chemiluminescence was observed and the translation temperature in the reacting zone was measured to be ∿ 300 °K.

High concentration of metastable 3^3P Mg was obtained from a discharge through Mg vapor with He as a carrier gas. The reaction of the Mg metastable state with N_2O yielded chemiluminescence of MgO. The $B^1\Sigma^+-X^1\Sigma^+$ system ($\Delta v = 0$, $v = 0$ to 4 and $\Delta v = \pm 1$) shows up predominantly, but the $B^1\Sigma^+-A^1\Pi$ and $d^3\Delta-a^3\Pi$ ($\Delta v = 0$ sequence) are also observed. The non observation or observation of MgO excited electronic states when the reactant is in the ground or metastable state respectively is expected from the simple correlation diagram given beside.



Comparison of the B-X chemiluminescence with simulated spectra yielded high rotational and vibrational temperature.

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* Laboratoire associé à l'Université de Paris-Sud.

0 19

Level Crossing and Level Anticrossing Spectroscopy in Laser Excited NO_2

H. G. Weber
Physikalisches Institut, Universität Heidelberg,
Philosophenweg 12, D-6900 Heidelberg, Germany

The excited electronic states of NO_2 are well known for its complicated structure. We study internal couplings in these states and the effect of external perturbations on these states using the techniques of level crossing and level anticrossing. We report decoupling experiments (zero field level anticrossing) and Hanle experiments (zero field level crossing) in magnetic fields on NO_2 under beam conditions and under static gas conditions /1/. The Hanle experiments reveal the excited state lifetime in good agreement with radiative decay measurements.
The decoupling experiments reveal a narrow level structure of about 10 kHz which we attribute to the nonrigidity of NO_2 in the excited electronic state.
Our experiments reveal some novel properties of NO_2 in the excited electronic states. These investigations may therefore help to support our understanding of the complicated dynamic in excited electronic states of polyatomic systems.

/1/ F. Bylicki and H.G.Weber, Chem.Phys.Lett. 79, 355
ibidem 79, 517 (1981)

0 20

Deperturbation of the State $B^3\Sigma_u^-$ in S_2

P. Patino and R.F. Barrow, Physical Chemistry Laboratory, Oxford

The rotational analysis of eight absorption bands of the main system $B^3\Sigma_u^-$ - $X^3\Sigma_g^-$ of $^{32}S_2$ has been completed. They arise from the vibrational levels 1, 2 and 3 of the excited state. All these levels are perturbed, v' = 3 having one perturbation in each F_i level and v'=1 and 2 two perturbations in each F_i component of $^3\Sigma_u^-$.

Previous deperturbation procedures performed in this laboratory have shown a $^3\Pi_u$ state to be responsible for the perturbations in the $B^3\Sigma_u^-$ state. From a qualitative consideration of the magnitudes of the interactions between the components of a $^3\Pi_u$ state with those of a $^3\Sigma_u^-$ state, the perturbations have been identified by plotting the diminished term values versus J(J+1).

The deperturbation of the three vibrational levels has been being carried out following a nonlinear least squares procedure. The feature of this procedure is that the experimental measurements are fitted by simultaneous variation of all free parameters of the appropriate Hamiltonian matrix. Both the standard deviation of the parameters involved and the variance of the fit have been satisfactory in v'=2 where two consecutive levels of $^3\Pi_u$ are the perturbing states. With regard to the levels 1 and 3, however, the fit has not yet proved to be entirely satisfactory.

Direct observations of some transitions assigned to B'' $^3\Pi_u$-$X^3\Sigma_g^-$ are also reported.

0 21

Local mode overtone structure in some symmetrical molecules

L. Halonen and M.S. Child
Theoretical Chemistry Department, 1 South Parks Road,
Oxford, OX1 3TG

Calculated fundamental and overtone eigenvalues for the CH and CD stretching vibrations of C_2H_2, C_2D_2, CH_4, CD_4, SiH_4, GeH_4 and C_6H_6 have been derived from a minimum parameter local mode model including harmonic potential and kinetic energy coupling between anharmonic bond oscillators. Matrices were diagonalised in a bond product Morse basis for the CH and CD stretching vibrations, with matrix sizes up to 330 x 330. Least squares fits were used to reproduce available experimental data to within 2-3 cm^{-1}, except for the highest overtones of C_2H_2 and C_2D_2. A feature of all the calculations is a trend with increasing energy towards increasing local mode degeneracy of the two lowest members of each overtone manifold.

Correlation diagrams showing the transition from a harmonic normal mode to a local mode limit as a function of the ratio

$$\xi = (\nu_1 - \nu_3)/x_e$$

where x_e is the C-H(D) bond anharmonicity, will be presented for the tetrahedral molecules. SiH_4 and GeH_4 lie close to the local mode limit, $\xi \to 0$, despite substantial interbond harmonic coupling due to compensation by the kinetic energy coupling which acts in the opposite sense. The two coupling terms also act in opposite senses for CH_4 and CD_4, but the kinetic energy coupling is relatively larger, with the result that ξ is of order unity for both molecules, but with $\xi(CH_4) < \xi(CD_4)$. A similar ordering on the appropriate correlation diagram is also seen for C_2H_2 and C_2D_2.

0 22 Local and normal vibrational states

M.S. Child and R.T. Lawton

Theoretical Chemistry Department, 1 South Parks Road,
Oxford, U.K.

Recent quantum mechanical [1,3] and classical [2,3] calculations on a realistic potential energy surface for H_2O show that the higher OH stretching vibrational states the better described in a local mode rather than a normal coordinate picture. The following specific local mode features have been identified.

(a) A series of local progressions, showing an increasing local mode degeneracy with increasing energy. The local mode splitting in the first progression decreases from 100 cm^{-1} at $v = 1$ to <0.001 cm^{-1} at $v = 8$ for example.

(b) Corresponding wavefunctions closely approximated in the symmetrised local mode form $\Psi^{\pm}_{nm}(R_1,R_2) \approx \frac{1}{\sqrt{2}}(\psi_n(R_1)\psi_m(R_2) \pm \psi_m(r_1)\psi_n(R_2)$, where R_1 and R_2 are bond coordinates.

(c) Local mode rather than normal coordinate selection rules, for transition between the highly excited states.

(d) Localised classical motions, with a permanent imbalance in the energy associated with different chemically equivalent bonds.

This picture has recently been explained in simple terms [4] by the quenching of interbond coupling due to the large bond anharmonicity $x\omega$ associated with X-H vibrations. With the interbond coupling conveniently measured by the X-H fundamental splitting, $|\nu_1-\nu_3|$, the ratio $|\nu_1-\nu_3|/x\omega$ therefore provides a convenient experimental measure of bond localisation in any molecule containing the equivalent X-H bonds , local mode behaviour being predicted for $[(\nu_1-\nu_3)/x\omega]<2$.

[1] R.T. Lawton and M.S. Child, Mol. Phys. 40, 773 (1980).
[2] R.T. Lawton and M.S. Child, Mol. Phys. 37, 1799 (1979).
[3] R.T. Lawton (D.Phil Thesis, Oxford University) (1980).
[4] M.S. Child and R.T. Lawton, Far. Disc. 71, (in press).

O 23

Spin-Orbit and Coriolis Interactions in Rydberg States with $^2\Pi$ Cores: The $b^3\Pi$ and $C^1\Pi$ States of DCl

K. P. Huber, Herzberg Institute of Astrophysics, National Research
Council of Canada, Ottawa, Ontario, K1A 0R6

The rotational structure in the lowest stable excited states of $D^{35}Cl$, $b^3\Pi$ and $C^1\Pi$, has been reinvestigated. The Λ-type doubling is small and results from the uncoupling of the core rather than Rydberg orbital angular momentum. The spin-orbit interaction of the $^2\Pi$ core strongly mixes the $\Omega=1$ components of the two states and leads to an avoided crossing between the nearly coinciding levels $^3\Pi_0$ of v=1 and $^1\Pi_1$ of v=0, a perturbation already noticed by Tilford, Ginter, and Vanderslice[1]. The spin-orbit interaction is also responsible for intensity anomalies in the P and R branches of the $b^3\Pi_0 \leftarrow X^1\Sigma^+$ transition. Similar anomalies have been found in the absorption spectra of HBr and DBr[2] and feature prominently in the analogous transitions of ClF. The latter have been observed in this laboratory[3]; molecular constants for two Rydberg states of ClF will be reported.

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[1] S. G. Tilford, M. L. Ginter, J. T. Vanderslice, J. Mol. Spectrosc. 33, 505 (1970).

[2] M. L. Ginter, S. G. Tilford, J. Mol. Spectrosc. 34, 206 (1970).

[3] F. Alberti, A. E. Douglas, E. C. Looi (1977); unpublished.

O 24

ANALYSIS OF THE SPECTRUM OF PF_5 AT 946 cm^{-1} WITH .014 cm^{-1} RESOLUTION

M.L. Palma, J. Bordé and J. Dupré, C. Meyer

Laboratoire de Spectroscopie Moléculaire
Université Pierre et Marie Curie
4, Place Jussieu
75230 PARIS CEDEX 05, France

Laboratoire d'Infrarouge
Bâtiment 350
Université Paris-Sud
91405 ORSAY CEDEX, France

The infrared spectrum of PF_5 was recorded between 931 and 958 cm^{-1} using a SISAM spectrometer with an absorption path of 3.35 m (p = 0.15 torr, T = 235° K). The ν_3 and $\nu_3 + \nu_7 - \nu_7$ parallel bands have been assigned and fitted but some unexplained features may come from other fairly intense hot bands ($\nu_3 + 2\nu_7 - 2\nu_7$, $\nu_3 + \nu_6 - \nu_6$ and $\nu_3 + \nu_8 - \nu_8$). At .014 cm^{-1} resolution the J structures in P and R branches of ν_3 and $\nu_3 + \nu_7 - \nu_7$ are clearly resolved except that they blend each other in some places. Unfortunately the K structure is not well resolved but shows up only through bumps in the wide R(J) or P(J) peaks and through some wavy features in the Q branches. So the following method was used : first a least-squares fit on P(J) and R(J) peaks yielded a first set of spectroscopic constants ; the observed frequencies of this fit are the maxima of the peaks which are assigned to K = 3 lines for ν_3 and K = 4 lines for $\nu_3 + \nu_7 - \nu_7$; second, contour fits on the Q branches and on R(J) and P(J) peaks were made to estimate the parameters responsible for the K structure ; this step gave an estimate of α_3^A which helped assigning 14 transitions with $K \neq 3$ in the ν_3 band. In a third step, these 14 new data made possible for this band a least-squares fit which involved both J and K with ν_0, B", α_3^B, α_3^A and D_J as adjustable parameters ; we obtained an average 5 mK obs. - calc. from 87 data.

Unfortunately, the $\nu_3 + \nu_7 - \nu_7$ is far less clearly observed and we could only achieve a least-squares fit on 46 R(J) and P(J) peaks with 3 adjustable parameters ν_0, B" and α_3^B while D_J and α_3^A were held fixed to the ν_3 values.

Synthetic contours will be presented in the P, Q and R branches and compared to the experimental spectrum.

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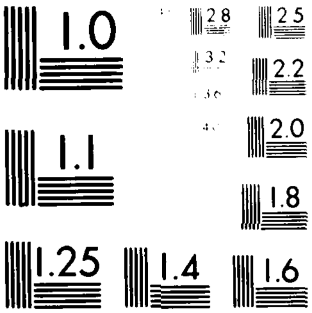

MICROCOPY RESOLUTION TEST CHART

P 1 The Importance of Spectroscopy for Infrared Multiphoton Excitation

W. Fuss and K.L. Kompa

Max-Planck-Institut für Quantenoptik
D-8046 Garching b. München, W.Germany

It is substantiated by examples that the infrared spectra of molecules in high vibrational states are similar in width to those of the ground states. Assumption of even narrower structures in spectra of SF_6 of energy up to 30000 cm^{-1} allows to explain published picosecond absorption measurements most readily. Therefore in order to explain collisionless infrared multiphoton excitation, the existence of resonance has to be checked, not only for the first three steps, but for all of them. Among ten contributing mechanisms considered, the most powerful one is the cooperation of rotational compensation with anharmonic splitting. It explains why a strongly anharmonic molecule can behave in absorption like a harmonic oscillator; why the isotope selectivity strongly drops if two frequencies are applied without delay, and several effects of temperature and collisions. Consideration of the other mechanisms and knowledge of relatively few spectroscopic details helps to understand many other details and variations in multiphoton excitation. Much of the discussion makes use of level diagrams which only display the anharmonic defects and which also account for rotation in a simple way.

P 2 Infrared Photochemistry: Dynamics and Infrared Spectroscopy

M. Quack

Institut für Physikalische Chemie
Universitat Göttingen
D-3400 Gottingen, W. Germany

(no abstract)

Q 1

INFRARED SPECTROSCOPY WITH A MICROWAVE SPECTROMETER:

IR-MW DOUBLE RESONANCE OF HCOF AND ClO_2

Harold Jones
Dept. of Chemistry, University of Ulm, D-7900 Ulm

The combination of a CO_2-laser with a microwave spectrometer allows very precise infrared measurements to be carried out via the technique of IR-MW double resonance. This is demonstrated with reference to results obtained on ClO_2 (in collaboration with John Brown, University Southampton) and on DCOF. It has proved possible to determine the band-constants of all the intense bands of these two molecules (both fundamental and hot-bands) which fall within the operating range of the CO_2-laser.

Examples of the extensive data which can be obtained by this technique will be given.

Q 2

THE 923 cm^{-1} BAND OF TWO ISOTOPIC FORMS OF FREON 12 BY LASER-MICROWAVE DOUBLE RESONANCE

Harold Jones[1] and Mireille Morillon-Chapey[2]

1 = Dept. of Chemistry, University of Ulm, D-7900 Ulm
2 = Laboratoire d'Infrarouge, Université de Paris,
F-91405 Orsay

The constants of the 923 cm^{-1} band (ν_6) of $CF_2{}^{35}Cl_2$ and $CF_2{}^{35}Cl^{37}Cl$ have been accurately determined by application of infrared-microwave double resonance spectroscopy with CO_2 and N_2O lasers. Using this technique sufficient rotational transitions in the v_6=1 excited states of these two isotopic species were measured to determine the rotational and distortion parameters of this state. The frequencies of a considerable number of infrared transitions were also determined from the double resonance observations and from IR-MW two-photon measurements. This data was combined with ground state data from this work and from conventional measurements to enable all transitions up to $J \simeq 40$ to be calculated with an accuracy of approximately ±1 Doppler width.

This work also allowed a useful double resonance line-shape phenomena to be clearly characterized.

Q 3

Pressure - broadening in the millimeter wave Spectrum of ozone.

N. MONNANTEUIL and J.M. COLMONT

Laboratoire de Spectroscopie Hertzienne - L.A. C.N.R.S. 249
Université des Sciences et Techniques de Lille
59655 Villeneuve d'Ascq Cédex - FRANCE

Line shapes of four rotational lines of ozone in the range 95 - 120 GHz have been measured at different pressures of ozone between 0.02 and 0.4 Torr. Temperature behavior of the self-broadened linewidth was investigated over a range $245°K \leqslant T \leqslant 295°K$. The temperature dependence of the linewidth parameters can be described by a power law αT^{-n}, a value of exponent n is proposed.

N_2 - broadening of three of these lines has been observed at room temperature, for different partial presssures of ozone. N_2 - broadening coefficients of the three transitions are proposed.

Q 4

LASERSPECTROSCOPIC INVESTIGATION OF THE VAN DER WAALS MOLECULE SODIUM - ARGON

G. Aepfelbach, A. Nunnemann, D. Zimmermann
Institut für Strahlungs- und Kernphysik, Technische Universität
Berlin, Rondellstr. 5, D - 1000 Berlin 37, Germany

Precise information about the interaction potential between an alkali and a rare gas atom may be deduced from a measurement of the optical spectrum of the corresponding diatomic weakly bound van der Waals molecule. Investigations of this kind have recently been performed for NaNe [1] and for NaAr [2,3] using laser spectroscopy. The present work dealing equally with NaAr was mainly carried out as a test of a newly built apparatus being intended to measure the absorption spectra of other alkali-rare gas-molecules. Similar to the previous work [1,3] the sodium-argon-molecules were produced by supersonic expansion of a mixture of pure argon of 6 bar pressure and of sodium at a temperature of about 800 K through a nozzle of 30 µm diameter. The supersonic beam crossed the beam of a tunable dye laser at right angles and the resulting fluorescence light of the molecule was detected by a photomultiplier. Our measurements covered a frequency range of about 3000 GHz extending from the D_1-line of atomic sodium to lower frequencies.

All observed molecular lines which are characterized by a line width of about 0.2 GHz could be arranged in pairs of lines separated by the hyperfine splitting of the 3s electron of atomic sodium of 1.7716 GHz. According to the previous analysis [2] the molecular spectrum of sodium argon in this frequency range is due to the rovibronic structure of the molecular transition $X^2\Sigma - A^2\Pi$. As compared to the results of Smalley [3] additional vibronic bands have been observed in our experiment - for example v' = 8 ($A\,^2\Pi_{3/2}$) - v" = 3 and v' = 11 ($A\,^2\Pi_{1/2}$) - v" = 1. The rotational structure of each vibronic band was analysed using rotational energy values given by the diagonal part of the rotational Hamiltonian [4]. Including all molecular lines corresponding to rotational quantum numbers up to about 20 the measured frequency values fit well to the calculated values within limits of experimental error. As an example our results of the rotational constants of several vibronic states are given in the following table together with the results of Smalley (in brackets).

	B_v	D_v	1/2 p + q
$X\,^2\Sigma$ v"=0	1.3302(2)	$7.70(8)\cdot 10^{-5}$	-
	(1.3324(6))	$(7.67(22)\cdot 10^{-5})$	-
v"=1	1.2165(6)	$10.1(2)\cdot 10^{-5}$	-
	(1.2167(19))	$(8.3(2.1)\cdot 10^{-5})$	-
$A\,^2\Pi_{1/2}$ v'=8	2.3742(4)	$1.114(15)\cdot 10^{-4}$	-0.0399(4)
	(2.3770(11))	$(1.326(76)\cdot 10^{-4})$	(-0.0416(18))
$A\,^2\Pi_{3/2}$ v'=9	2.1806(4)	$1.312(20)\cdot 10^{-4}$	-
	(2.1861(8))	$(1.218(31)\cdot 10^{-4})$	-

[1] W. Lapatovich et al., J. Chem.Phys. 73, 5419 (1980)
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[3] R.E. Smalley et al., J. Chem.Phys. 66, 3778 (1977)
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MEASUREMENTS OF INTENSITIES OF SOME ABSORPTION LINES OF WATER VAPOR IN ATMOSPHERE BY INTRACAVITY LASER SPECTROSCOPY

Q 5

Marc CHENEVIER, Marie-Antoinette MELIERES, Frédéric STOECKEL
Laboratoire de Spectrométrie Physique, Université Scientifique et Médicale de Grenoble, B.P. 53 X - 38041 GRENOBLE CEDEX - France.

Intracavity spectroscopy in a broadband, jet stream, C.W. dye laser provides extremely high sensitivity for detection of very weak absorption lines (1,2,3). But before a systematic use of intracavity spectroscopy it is necessary to obtain more information about physical processes governing evolution of the emission spectrum of this type of laser and to see how theories agree with experiments. The generation time, t, of the dye laser is a key-parameter in understanding the dye laser emitted spectra and giving quantitative results. We therefore study as function of t the shape of the emitted spectra without and with absorbant. A jet stream dye laser with a three mirror cavity, operating with Rhodamin 6 G in ethylene glycol is excited by an argon laser. The dye laser spectrum is recorded using a spectrograph with a resolving power of 150 000 and a 1024 photodiodes array. Two light modulators, the first one on the pumping beam, the second one on the output of dye laser permit observation of spectrum versus time of working of the dye laser (generation time).

1. Time evolution of the dye laser emission, without absorbant

We tested (Fig. 1), in the range of a generation time t = 40 µs to 1000 µs (using a gate of 10 µs) that the emitted spectra has a near gaussian shape whose width varies like $1/\sqrt{t}$ and intensity like $\sqrt{t}$. Those results agree with the theoretical predictions relative to an homogeneous broadband dye laser (1,4,5).

2. Time evolution of absorption lines of H_2O vapor in a free atmosphere ; determination of the intensity k_σ^N of the line.

The depth of absorption lines increases with t, following the law : $I=I_o e^{\alpha ct}$ as usually predicted by theories. Experimental values of α allows us to determine k_σ^N in the range of 10^{-25}-10^{-26} cm^{-1}/mol.cm^{-2} corresponding to α : 10^{-7}-10^{-8} cm^{-1} (Fig. 2) good agreements are found with experimental results obtained by other techniques (Table 1). In Fig. 1, the I values are obtained from experimental I values after deconvolution by the apparatus fonction (gaussian shape of half-width at half-height of 0.07 cm^{-1}).

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(2) E.N. ANTONOV, E.B. BERIK, V.G. KOLOSHNIKOV, JQRST 22, 45 (1979).
(3) W.T. HILL, III, R.A. ABREU, T.W. HÄNSCH, A.L. SCHAWLOW Optics Comm. 32, 96 (1980)
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(5) V.R. MIRONENKO, V.I. YUDSON, Optics Comm. 34, 397 (1980)

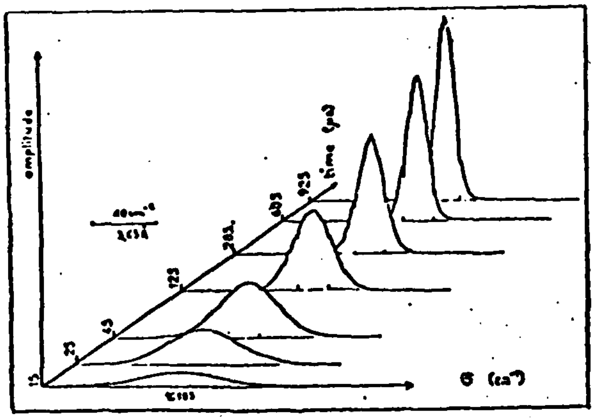


Fig 1.

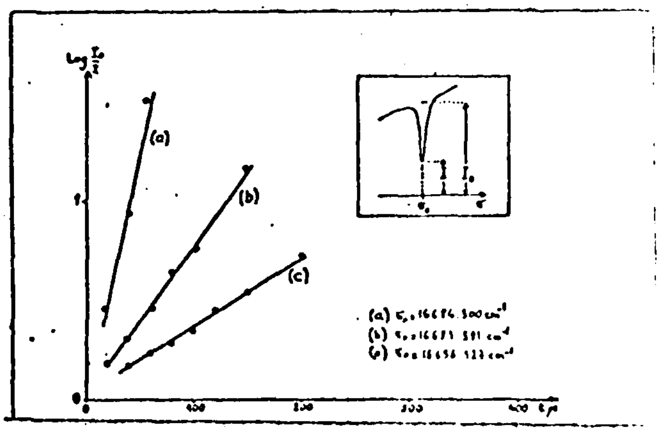


Fig. 2

σ cm^{-1}	$k_\sigma^{N(a)} \times 10^{25}$	$k_\sigma^{N(b)} \times 10^{25}$
16 684.300	9.3	6.800
16 681.381	2.3	2.170
16 679.720	0.6	0.7020
16 678.970	1.7	1.420
16 669.430	6.5	4.700
16 661.636	1.4	1.310
16 654.732	2.6	2.170
16 653.99	0.7	0.693
16.656.127	1.2	1.350

Table 1 : (a) Our result (b) Rothan results Applied Optics, 17, 3517 (1978).
k_σ^N units : cm^{-1}/mol.cm^{-2}

Q 6

LOW TEMPERATURE DIELECTRIC RELAXATION SPECTROSCOPY

John Gilchrist

Study of the dielectric relaxations of molecular species dissolved or dispersed in hydrocarbon media at 4.2 K or lower yields approximate values of their ground-state splittings. Splittings between 15 MHz and 15 GHz can most readily be estimated. The technique has been used to study the internal-rotation splittings of phenols and alcohols and their thio- analogues, the inversion splittings of secondary amines and the rotations/inversions of primary amines. There is generally a satisfactory correlation with far-infra-red and vapour-phase microwave data where these exist, but the technique appears to be of greatest value for molecules which are spectroscopically interesting but unsuitable for microwave study. Examples: a 4-formyl phenol derivative, tricyclohexyl carbinol, 2,2,6,6-tetramethyl piperidine. Alternatively it might be used to aid the interpretation of microwave spectra.

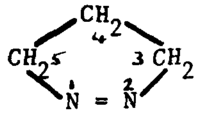
Q 7

The 325 nm Electronic System of 1-Pyrazoline

A.C.P. Alves and J.M. Hollas

Chemistry Department, Reading University, Whiteknights, Reading RG6 2AD
England

1-pyrazoline is a five-membered ring



with the carbon atom in the 4-position out of the plane occupied by the other four heavy atoms. The barrier to planarity is 111 cm^{-1} with many low-lying ring-puckering vibrational levels.[†]

The 325 nm electronic transition involves a π^*-n electron promotion and is either $^1A_2$-$^1A_1$ (forbidden) or $^1B_1$-$^1A_1$ (allowed, type C). Band contour analysis shows that many of the strongest vibronic bands in the system are type A or type B. The fact that 1-pyrazoline is an oblate near-symmetric rotor ($\kappa'' = 0.900$) makes it difficult to distinguish between these two types.

The band system is vibrationally extremely complex and irregular. This must be due, in part, to there being many hot bands involving several puckering vibrational levels in the ground electronic state. It is also possible that the puckering vibration may be anharmonic in the excited electronic state and that it may be involved in Herzberg-Teller intensity stealing.

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Q 8 THE $2\nu_2$, ν_1, AND ν_3 BANDS OF $D_2\,^{16}O$ AND $2\nu_2$, ν_1 OF $HD^{16}O$

par

N. PAPINEAU*, C. CAMY-PEYRET, J.M. FLAUD

Laboratoire de Physique Moléculaire et d'Optique Atmosphérique,
Campus d'Orsay, ORSAY, FRANCE

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Four spectra of pure D_2O and three of a D_2O H_2O mixture have been recorded on a Fourier Transform Spectrometer with a resolution of about 5.10^{-3} cm^{-1}.

For D_2O, a careful analysis of the bands $2\nu_2$, ν_1, ν_3 had led to a largely extended and more precise set of rotational levels belonging to the vibrational states (000), (020), (100) and (001). From this set and the microwave transitions available in the litterature, we have been able to determine improved rotational constants for the ground state and precise vibrational energies, rotational and coupling constants for the three interacting states (020), (100), and (001). Many vibrorotational resonances were detected.

For HDO, we have obtained a largely extended and more precise set of rotational levels belonging to the vibrational states (000), (020), (100). From this set in the same way as for D_2O, we have determined improved rotational constants for the ground state.

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* Present adress : Office National d'Etudes et de Recherches (ONERA), 92320 CHATILLON - FRANCE

Q 9 DOUBLE RESONANCE ON THE ACTIVE MEDIUM OF A FIR LASER : DISPERSION EFFECTS

Didier DANGOISSE, Pierre GLORIEUX and Michel LEFEBVRE

Laboratoire de Spectroscopie Hertzienne, associé au CNRS
Université de Lille I, 59655 VILLENEUVE D'ASCQ Cédex, France

In double resonance experiments on the active medium of a FIR laser emitting molecules are subjected to a resonant electromagnetic field connecting levels involved in the emission process.

Absorption (or emission) changes have been considered in previous works on H COOH [1], D_2CO [2] and CH_3OH [3] lasers. These studies have allowed assignment of unknown FIR laser lines [3], fast modulation of the output of a FIR laser and generation of new emission lines originating from levels which are not directly pumped by the laser [2].

Together with absorption changes, double resonance may also induce refractive index (i.e. dispersion) changes. These dispersion effects cause a change of the optical length of the laser and as a consequence of its emission frequency.

i) This phenomenon may be discriminated by the FIR laser mode and gives rise to lineshapes which are absorption like (i.e. lorentzian) when the laser is tuned on the top of its mode profile, and dispersion like (i.e. derivate of a lorentzian) with reversing sign when the FIR laser is tuned to half-mode width off resonance.

ii) It may also be discriminated by the slope of a frequency marker provided by a superheterodyne detection. This gives a much sharper discriminator and generates stronger signals which are unfortunately distorted by the strong nonlinearity of this discriminator.

iii) They have also been directly exhibited as a change of the emission frequency. By careful measurements of this frequency, changes as small as ± 30 KHz have been measured, corresponding to refractive index changes $\Delta n \lesssim 10^{-7}$.

In the general case, the observed signal is a superposition of absorption and dispersion contributions. It is essential to know the contribution of dispersion effects when one wants to use double resonance on a FIR laser to get accurate spectroscopic information since these effects may distort the observed lineshapes.

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Q 10

AIR BROADENED N_2O LINEWIDTHS : AN IMPROVED CALCULATION AT DIFFERENT TEMPERATURES

N. LACOME, A. LEVY and C. BOULET
Laboratoire d'Infrarouge,
Associé au C.N.R.S.,
Université de Paris-Sud,
Bâtiment 350,
91405 ORSAY CEDEX, FRANCE

The semiclassical theory developed by Robert and Bonamy has been used to obtain the linewidths of N_2O broadened by itself, by N_2 and by O_2. The main features of the formalism are as follows :

a) The anisotropic potential is expressed by using, besides the quadrupole - quadrupole contribution, an atom - atom interaction model (without any adjustable parameter) which takes both long and short range forces into account.

b) The geometry of the collision is described through the so-called "equivalent" straight path more appropriate than the usual one.

c) The matrix elements of the relaxation operator are computed by the means of the linked-cluster theorem, so that the treatment remains non-perturbative and no resort to cut off procedures is needed.

In addition to being more realistic the present formalism has the advantage of making the computation tractable for complex molecular systems such as linear-linear ones.

Careful comparison has been made with the available experimental results. For self broadened N_2O very satisfactory agreement is obtained both at 300 and 204°K. So it is the case for nitrogen broadening at room temperature.

Regarding oxygen broadened linewidths very few experimental data exist. Anyway, the present results reveal substantial improvement as compared to usual calculations based upon Anderson-Tsao Curnutte model.

From these results a predictive tabulation has been obtained for the values of air-broadened N_2O linewidths at 300°K and 204°K. These parameters are of well-known importance in calculations of spectral transmission of the terrestrial atmosphere.

Q 11

HIGH ORDER SPECTROSCOPIC CONSTANTS OF ν_1, $2\nu_2$ AND ASSOCIATED HOT BANDS OF N_2O ISOTOPIC SPECIES FROM HIGH RESOLUTION F.T. SPECTROSCOPY.

J.L. TEFFO, A. VALENTIN, A. HENRY

Laboratoire de Spectronomie Moléculaire - C.N.R.S.
Université Pierre et Marie Curie
4 place Jussieu
75230 PARIS CEDEX 05
FRANCE

The infrared spectra of four nitrous oxide isotopic species $^{14}N_2{}^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$ and $^{14}N_2{}^{18}O$ were investigated between 1000 and 1350 cm^{-1} with the Fourier Tranform spectrometer of the Laboratory. The width of recorded lines is about 1.4 times the Doppler-Fizeau width.

For each isotopic species, the ν_1-$2\nu_2$ Fermi diad and the corresponding diads in the hot bands from the $01^{1\,e,f}0$ vibrational levels are studied. For the most abundant isotope, data for poliads from 100, 02^00 and $02^{2\,e,f}0$ levels are also obtained.

Spectroscopic constants including sextic centrifugal distorsion constants and ℓ type doubling constants are calculated. Especially effective constants for the levels 12^20 and 04^20 of $^{14}N_2{}^{16}O$ are reported. The wavenumbers computed using the set of calculated spectroscopic constants are in agreement for many bands within 0.1 cm^{-1} (rms) with the observed values. Wavenumbers obtained by combination differences for several bands, by previous authors are in agreement with the data we obtain, wavenumbers presented here being significantly more precise.

In addition the values of D and H constants are in good agreement with microwave measurements.

Q 12 ANALYSIS OF THE DIODE LASER SPECTRUM OF THE ν_3 BAND OF $^{14}N^{16}O_2$

P. Prastault, J. Laurent
O.N.E.R.A
92320 Châtillon sous Bagneux, France

V. Dana
Laboratoire de Spectroscopie Moléculaire
Université Pierre et Marie Curie
4, Place Jussieu
75230 Paris Cedex 05, France

and A. Goldman
Department of Physics
University of Denver
Denver, Colorado 80208, U.S.A

A set up, enabling the record of high resolution spectra with a spectral limit of 10^{-3} cm^{-1}, has been realised and applied to the study of the NO_2 ν_3 band. The device includes a reference beam for wavelength calibration. A tunable diode laser is used in the frequency range between 1580 cm^{-1} - 1615 cm^{-1}. Absorption spectra of NO_2 have been recorded with pressure in the range 0.01 torr - 0.1 torr and with a 30 cm pathlength. Each spectrum covers a spectral interval of about 0.3 cm^{-1}. The relative wavelength calibration is obtained with a solid germanium Fabry-Pérot etalon. The interfringe delivered by this reference beam is 0.04986 cm^{-1} at 1605 cm^{-1}. The wavenumbers of unoverlapped lines observed on a spectrum recorded with a Fourier transform spectrometer have been used to determine the absolute wavenumbers of the diode laser spectrum. Identification of the observed transitions and measurement of the spin-splittings have led to a determination of the effective spin-rotation coupling constants for the (001) vibrational level.

Q 13 SUB - DOPPLER FOURIER TRANSFORM SPECTROSCOPY : VELOCITY CHANGING COLLISIONS IN THE IODINE B STATE

J. VERGES and P. JUNCAR
Laboratoire Aimé Cotton, CNRS II, Bâtiment 505 - 91405 Orsay (France)

P. WEISS and R.W. FIELD
Department of Chemistry , M.I.T., Cambridge, MA 02139 (U.S.A)

C. EFFANTIN, J. d'INCAN and R. BACIS
Laboratoire de Spectrométrie Ionique et Moléculaire
43, Boulevard du 11 Novembre 1918 - 69622 Villeurbanne (France)

Short and long term frequency or amplitude variations of the exciting laser usually seriously degrade both resolution and sensitivity in Sub-Doppler Fourier Transform fluorescence spectroscopy. Nevertheless these problems have been overcome in the following manner.

The 514,5 nm single mode line of a C.W. Ar^+ laser has been locked to a sigmameter. The sigmameter path difference is servo-controlled with a He-Ne laser locked on an iodine saturated absorption line. In that way the frequency of the 514,5 nm line can be fixed for several hours anywhere within the Doppler profile of the P(13) $B\ 0_u^+\ (v'=43) - X\ {}^1\Sigma_g^+\ (v''=0)$ iodine absorption line without any degradation of the recorded lineshapes. The high resolution Fourier Transform spectrometer records the forward and backward fluorescence from the excited hyperfine levels along the axis of the 514,5 nm exciting line. The iodine pressure is of the order of 0,1 torr and even in that range the main fluorescence lines observed in the backward direction are broadened by velocity-changing collisions. The rotational relaxed lines are broader but remain sub-Doppler.

Due to the good signal-to-noise ratio, deconvolution of the observed lineshapes allow the determination of the position of the exciting laser line and of various parameters defining the collision : temperature of the gas, cross section for velocity-changing collisions in the excited levels and parameters for rotational relaxation.

Q 14 Microwave spectra of N-methyl pyrazole

N.K. Narain, S.L. Srivastava, Krishnaji

Physics Department
Allahabad University
Allahabad
INDIA

(no abstract)

Q 15

2-12 μm AMMONIA BANDS RECORDED WITH THE "BRAULT" FOURIER TRANSFORM SPECTROMETER AT KITT PEAK: A FEW HIGHLIGHTS OF THE SPECTRAL CHARACTERISTICS

Jane Mills and K. Narahari Rao
Department of Physics, The Ohio State University
Columbus, Ohio, 43210, U.S.A.

Infrared spectrum of ammonia has always had wide universal interest among spectroscopists, astrophysicists and laser investigators. A strong need exists for updating the basic observational data for this molecule and its isotopic varieties. The effort made in different laboratories to provide better and better wavenumber standards for CO, OCS, and N_2O is ineed very commendable; whenever and wherever possible they are used in wavenumber calibrations. However, when one studies with tunable lasers, often times the experience has been that there is just no calibrating line available when one is needed. It appears therefore imperative that measurements on the spectra of molecular species having rich spectra be made more definitive; often times studies are confined to examine a few specific aspects of such molecular species. Investigators at this time are employing ammonia lines[1] for calibrating tunable laser spectra because they are there and ammonia gas is readily accessible and easy to use. It, therefore, seems almost obligatory to update the measurements on ammonia, methane, and water vapor.

The pathlength for $^{14}NH_3$ data has been as high as 100 meters to enhance their usefulness for molecular structural studies especially in the observation of forbidden transitions. With the availability of measurements for $^{14}NH_3$ by using heterodyne techniques[2] and also because of incorporation of other standards simultaneously with the recording of FTS NH_3 spectra, we believe we are in a position to show not only good maps of the infrared spectra of both $^{14}NH_3$ and $^{15}NH_3$ but also give reasonable estimates of the precision of measurements.

K. K. Lo, Jon Manheim and R. J. Nordstrom from Ohio State, and D. Papousek from Prague are expected to be involved in the interpretative processes. Dr. A. F. Krupnov from the USSR is expected to contribute by providing submillimeter data of $^{15}NH_3$ similar to his previous work on $^{14}NH_3$.

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Q 16 Microwave spectra of CF_3CH_3

J. Baker and R.A. Creswell

(paper withdrawn)

Q 17 Observation of the ν_2 band of CH_2 by laser magnetic resonance

Trevor J. Sears, P.R. Bunker and A.R.W. McKellar
Herzberg Institute of Astrophysics
National Research Council of Canada
Ottawa Ontario Canada K1A 0R6

The ν_2 band of gas phase $^3B_1$ CH_2 has been observed by CO_2 laser magnetic resonance spectroscopy. A preliminary calculation using ab initio potential energy points and a semirigid bender Hamiltonian was used to predict the expected positions of the ν_2 rotation-vibration transitions. Three transitions, $2_{02}\leftarrow 1_{11}$, $2_{02}\leftarrow 2_{11}$, and $1_{01}\leftarrow 1_{10}$, have been assigned. They give no information on the A rotational constant, but do lead to determinations of $\nu_2 - A_0 = 892.2 \pm 0.5$ cm^{-1} and hence $\nu_2 = 957 \pm 10$ cm^{-1}. This value is much lower than previous estimates of the bending frequency of CH_2, and it has a crucial bearing on the interpretation of its photoelectric spectrum.

Q 18

THE PURE ROTATIONAL SPECTRUM OF PH_3 BETWEEN 8 AND 80 CM^{-1} WITH A RESOLUTION OF 0.005 CM^{-1}.

A.BONETTI; Istituto di Fisica, Univ. di Firenze, L. E. Fermi 2 50125-Firenze
B. CARLI, F. MENCARAGLIA; Istituto di Ricerca sulle Onde Elettromagnetiche
(IROE) Via Panciatichi 64 50127-Firenze
M.CARLOTTI, G. DI LONARDO, A. TROMBETTI; Istituto di Chimica-Fisica e spettroscopia, Univ. di Bologna Viale
Risorgimento 4 40136-Bologna

A Fourier spectrometer with a resolution better than 0.005 cm^{-1} (unapodized) and a wavenumber precision better than 0.00015 cm^{-1}, constructed at the IROE of the C.N.R. in Florence, is operating in the range 8 - 80 cm^{-1}. In this region, the pure rotational spectrum of PH_3 was measured and transitions up to J=8 were observed.

Accurate rotational and centrifugal distortion constants for the ground state of this molecule were derived from these measurements.

An extension of the spectrometer sensibility up to 200 cm^{-1} is in progress.

Q 19 ANALYSIS OF THE ISOTOPE SUBSTITUTION EFFECT ON VIBRATION-ROTATION MOLECULAR SPECTRA IN THE CASE OF HEAVY ATOM SUBSTITUTION

A.D.Bykov, Yu.S.Makushkin, O.N.Ulenikov
The Institute of Atmospheric Optics, Siberian Branch,
U.S.S.R. Academy of Sciences, Tomsk, 634055, USSR

An analysis of isotope effects in polyatomic molecules is essentially simplified in the case when the atom with great mass number undergoes isotope substitution. In this case the parameter $\mathcal{E} = (m' - m)/m'$ can be introduced, where m and m' are the masses of atom before and after isotope substitution. The value $\mathcal{E}$ in the majority of practical cases (O,N,S, etc.) is small (of the order of the Born-Oppenheimer parameter and even less). The presence of small parameter enables one to simplify the method of investigation of isotope dependence of molecular and spectroscopic constants, suggested earlier by the authors [1,2], and to obtain simple relationships between energy levels and probabilities of dipole transitions of various isotopic modifications of molecules.

The Hamiltonian of isotopic modification of a molecule is of the form [1]

$$\mathcal{H} = H + \Delta h,$$

where H is the Hamiltonian of the basic molecule, Δh is the operator addition due to isotope substitution. The operator Δh is of the order of smallness of $\mathcal{E}$ and can be considered as a perturbation relative to the Hamiltonian H. In this case, diagonalization of the Hamiltonian $\mathcal{H}$ matrix can be performed, taking into account possible degeneracies and accidental resonances in the basic molecule. As a result, the relationships, describing the band center shifts, vibration-rotation line shifts and line intensity changes are presented also as functions of molecular or spectroscopic constants of the basic molecule. As an illustration, the paper presents the results of numerical calculations of shifts of the bands and individual lines for the molecules O_3,H_2O,CO_2.

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Q 20

STUDY OF THE METHANE ABSORPTION SPECTRUM IN THE 1.08 μm REGION

A.E.Cheglokov, Yu.S.Makushkin, L.N.Sinitsa, O.N.Ulenikov,
V.E.Zuev
The Institute of Atmospheric Optics, Siberian Branch of
the U.S.S.R. Academy of Sciences, Tomsk,634055, U.S.S.R.

The $^{12}CH_4$ and $^{13}CH_4$ methane absorption spectra have been investigated using the Nd-glass laser intracavity spectrometer. The $^{12}CH_4$ absorption spectrum was registered in the 9100-9350cm^{-1} region. As in Ref.(1) the lines of three absorption bands were observed. The lines of R-branch in the $3\nu_3$ band have been registered for larger quantum numbers J than in [1]. The analysis of the results obtained is presented. In particular, the work on identifying the vibrational bands is carried out.

The $^{13}CH_4$ absorption spectrum was investigated in the 9150-9300 cm^{-1} range. The absorption spectrum obtained has been interpreted. For this purpose, the data on the $^{12}CH_4$ absorption spectrum and the calculated theoretically line center shifts, due to isotopic substitution of heavy atom, were used.

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Q 21

ANALYSIS OF HEAVY WATER VAPOR ABSORPTION SPECTRUM IN THE 9161-9392 cm^{-1} REGION

A.D.Bykov, V.E.Zuev, V.P.Lopasov, Yu.S.Makushkin,
L.N.Sinitsa, O.N.Ulenikov
The Institute of Atmospheric Optics, Siberian Branch,
U.S.S.R. Academy of Sciences, Tomsk, 634055, U.S.S.R.

The paper presents the results of complex study of the HDO and D_2O vapor absorption spectrum in the 9161-9392 cm^{-1} region. The measurements were made using the Nd-glass intracavity spectrometer whose construction and general characteristics are given in [1]. In the range investigated more than 400 absorption lines were recorded. These lines are referred to the bands (310) and (121) of HDO, (112) and (013) of D_2O (some of these 400 absorption lines are related to the H_2O bands (111) and (012)). The uncertainty in determining the line centers is about 0.07 cm^{-1}.

The spectrum obtained was interpreted and about 80% of all the lines were identified. The vibration-rotation energy levels were determined for the above bands: for the (310) band of HDO the separate energy levels were up to $J = 14$; for the (121) band of HDO - up to $J = 6$; for the (112) band of D_2O - up to $J = 9$; for the (013) band of D_2O - up to $J = 6$. It is shown that if the determined values of energy levels are taken into account then the above vibrational states can be considered as isolated ones with a sufficient degree of correctness. The rotational and centrifugal constants are determined for all four bands. The set of the constants obtained describes the spectrum within the experimental error.

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Q 22 THE THEORY OF RESONANCE VIBRATION-ROTATION INTERACTIONS IN THE METHANE MOLECULE

V.I. Perevalov, Vl.G. Tyuterev, V.I. Zhelinskii

The Institute of Atmospheric Optics
Siberian Branch of the U.S.S.R.
Academy of Sciences
Tomsk 634055 U.S.S.R.

The effective Hamiltonians for simultaneous fitting of the bands (ν_2, ν_4) and the bands (ν_1 , ν_3 , $2\nu_2$, $2\nu_4$, $\nu_2+\nu_4$) were obtained using the contact transformations in the representation of irreducible tensor operators [1] from a reference vibration-rotation Hamiltonian. In these Hamiltonians expressions for the parameters of the q^3J, q^2J^3 type operators were obtained using the molecular parameters ω , B_e , ζ and the cubic anharmonicity constants. The numerical calculations of these parameters with different force fields were made. The detailed analysis of comparison of the values calculated and fitted is given.

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AUTHORS - AUTEURS

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