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Structure and Reactivity of Transient Species in Homogeneous Catalytic Water Splitting and CO2 Reduction Using Cryogenic Ion Spectroscopy

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14. ABSTRACT

Under this grant, we have designed, commissioned and exploited new and general experimental methods for the purpose of identifying the reaction pathways that govern the catalytic transformations of small molecules like H_2O, N_2 and CO_2. We accomplished this by trapping key fragile chemical species deep in the catalytic cycle that have been calculated or inferred to play an important role in chemical transformation but have never been isolated. Our approach involved the development of a new type of instrument that combines high resolution mass spectrometry, cryogenic ion processing, and laser photofragmentation spectroscopy. One major accomplishment from this effort is the successful application of the new methods to determine how the degree of CO_2 activation by a homogeneous Ni coordination compound depends on oxidation state and ligand structure. Another important result is the determination of the mode of activation of an Ir-based water splitting catalyst in which unsuspected ligand oxidation of the monometallic precursor yields the active bimetallic catalyst. Because mobile protons are usually involved in covalent bond formation of activated species, we have developed a theoretical framework that extracts structural information from the diffuse vibrational bands that are the usual signatures of charge translocation through hydrogen bonded networks.

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AFOSR Final Performance Report

FA9550-13-1-0007

Structure and Reactivity of Transient Species in Homogeneous Catalytic Water Splitting and CO2 Reduction Using Cryogenic Ion Spectroscopy

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Department of Chemistry
Yale University
New Haven, CT
28 February 2013

Under this grant, we have designed, commissioned and exploited new and general experimental methods for the purpose of identifying the reaction pathways that govern the catalytic activation of small, stable molecules like H_2O, N_2 and CO_2. We accomplished this by trapping key chemical species deep in the catalytic cycle that have been calculated or inferred to play an important role but have never been isolated. This endeavor involved the development of a new type of instrument that combines high resolution mass spectrometry, cryogenic ion processing, and laser photofragmentation spectroscopy. In our approach, we first extract the resting state of the catalyst from solution and transport it into vacuum where collisional dissociation exposes the reactive metal center. Substrate molecules are then introduced directly to the active site by temperature controlled, gas phase condensation in a radio frequency ion trap, and the extent of their activation is monitored as a function of ligand structure and oxidation state of the metal center. The method is general, as illustrated by its application to N_2, CO and N_2O molecules attached to the open coordination site of a Ni coordination compound specifically designed to facilitate control of the metal oxidation states. Transformation of these stable species to useful chemicals (NH_3, CH_3OH, etc.) involves formation of NH, CH and OH chemical bonds. Therefore, during this grant period, we also established a theoretical framework that allows experimental determination of bond forming events involving mobile protons by analyzing their diffuse vibrational signatures. Finally, we demonstrated a method for monitoring the reductive activation of CO_2 starting from the fully reduced radical anion, and applied this technique to reveal the structures of intermediates invoked to understand the different mechanisms displayed by imidazole and pyridine in the photoelectrocatalytic transformation of CO_2 to formic acid.

IA. Instrument development

The work described below was carried out during the past five years (2013-2018) under this grant. A key aspect of our program is the design and implementation of innovative instrumentation specifically tailored to capture and spectroscopically characterize very fragile reaction intermediates invoked in the mechanisms of catalytic systems *currently under development* by synthetic groups. This required the development of a custom apparatus which involves the interface of versatile atmospheric electrospray ionization (ESI) sources to a cryogenic ion processing stage coupled to a triple focusing time-of-flight (TOF) photofragmentation mass spectrometer. The overall schematic is displayed in Fig. 1a. To overcome the limited mass resolution of the TOF-based photodissociation spectrometer, we augmented this instrument with a customized, very high resolution 7T FT ICR (based on a Bruker Apex II modified with the Predator data acquisition system from the National Magnet Laboratory, Fig. 1b).

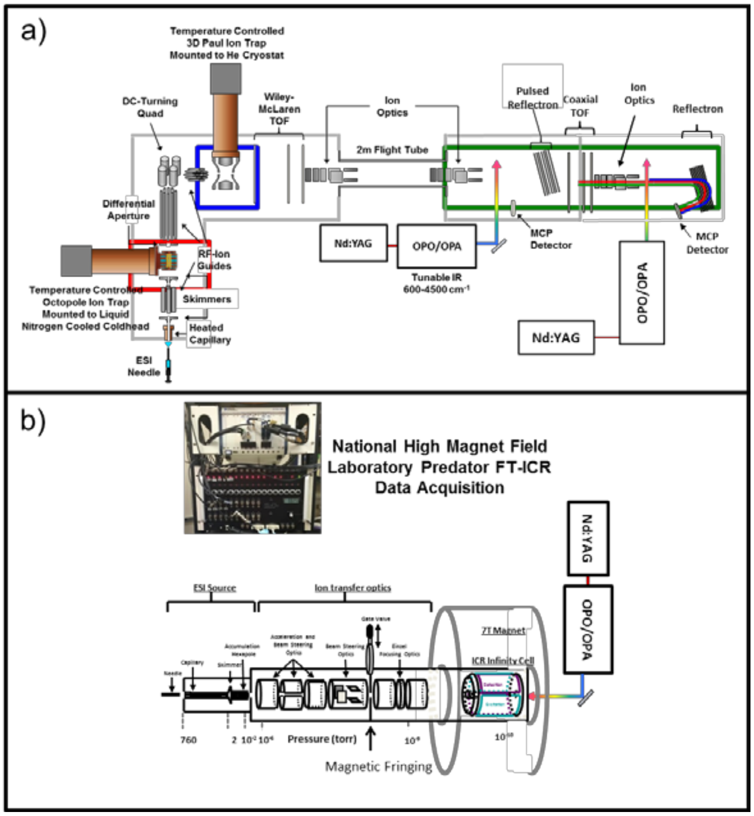
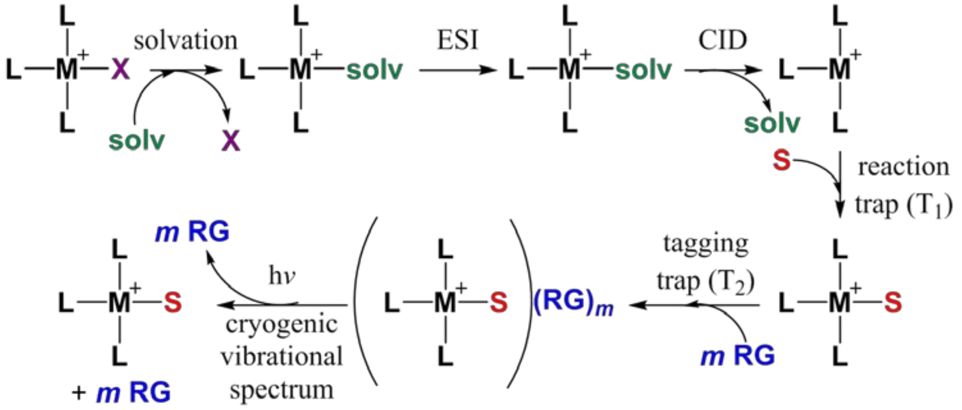


Fig. 1. Schematics of a) the Yale cryogenic ion trap and time of flight photofragmentation mass spectrometer and b) FT-ICR coupled to a tunable infrared laser.

It is useful to emphasize that this research direction represented a substantial departure from our long standing emphasis on microhydration, in both chemical scope and required instrumentation. The capabilities of the photofragmentation spectrometer developed at Yale for this purpose were optimized to extract air sensitive species from solution in an encapsulated electrospray interface and deliver them to two temperature-controlled ion traps for further ion processing. The overall scheme at the heart of our approach is illustrated in Scheme I. This creates a systematic way to expose the active sites of homogeneous catalysts isolated in the gas phase so that a variety of substrate molecules can be docked onto the open coordination site using a temperature controlled ion trap. The second trap is cooled below 10K where either inert rare gas atoms or weakly interacting molecules (e.g. H_2 or N_2) are condensed on the substrate/catalyst complex so that its vibrational spectrum can be acquired in a linear action regime using IR photodissociation. This cryogenic variation of the so-called “tagging” method for structurally characterizing cold, mass selected ions was awarded a US Patent (USPTO #8890059 B2) during this grant period (2014). The typical performance of this cryogenic ion vibrational predissociation (CIVP) approach is illustrated by a recent application to characterize molecular ionophores (in this case, D_3O^+ embedded in the 18-crown-6 scaffold) in Fig. 2. These results were



Scheme 1. The resting state of the catalyst is extracted from solution with an ESI interface. The anion X is exchanged with a solvent molecule (solv) under ESI extraction of the cation. Collisional induced dissociation (CID) leads to desolvation and exposes an open coordination site of the compound. In a second step, a substrate molecule (S) is introduced to the active site in a temperature-controlled (T_1) ion trap. This complex is then cooled in a second, cryogenically cooled ion trap (T_2) where an inert “mass tag” (rare gas (RG), e.g. N_2, H_2) is formed by condensation, which is then injected into a time-of-flight photofragmentation mass spectrometer for structural characterization with IR and UV/vis spectroscopy.

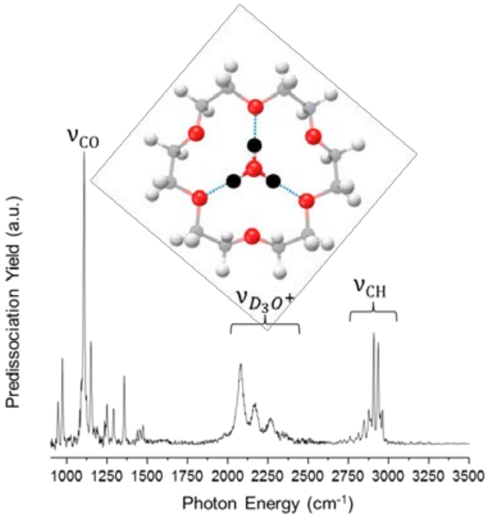


Fig. 2. A representative D_2-predissociation vibrational spectrum of cryogenically cooled (10 K) D_3O^+(18-crown-6 ether). The broad spectral coverage and sharp features provides an FTIR like capability with the sensitivity of mass spectrometry.

reported in publication (15), which addresses the important role that vibrationally adiabatic processes play in systems involving a mobile proton. That work was undertaken in the course of our AFOSR program as part of the fundamental background required to understand the new paradigms required to decode the spectroscopic signatures of mobile protons at the heart of proton-coupled electron transfer, a ubiquitous charge transport process in a variety of bio-mimetic catalysis platforms. This instrument also has the capability to record isomer and conformer-specific spectra in the case that several distinct species contribute to a particular mass. This aspect was originally developed a decade ago under AFOSR support and has recently been implemented on a similar system currently online at the IR free electron laser at the Fritz-Haber Institute in Berlin. Because of the close overlap with our work, we have an active and on-going collaboration with that group so that we can gain access to the much larger spectral (150-2000 cm^{-1}) range afforded by that facility.

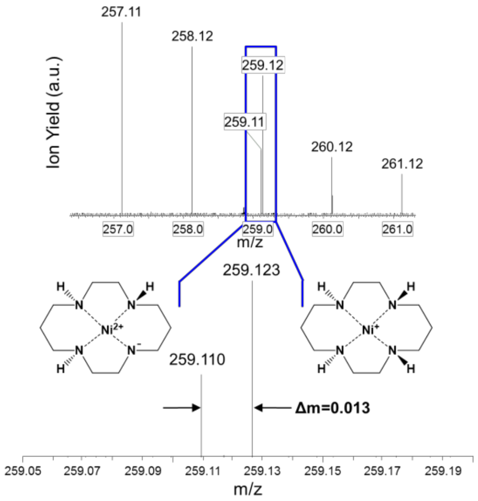


Fig. 3. A solution of Ni(II)Cyclam and the chemical reductant agent dodecamethyl-cobaltocene in acetonitrile is electrosprayed into a high-resolution mass spectrometer. The resolution of the instrument (50,000) is required to separate the peaks originating from overlapping isotopologues of different molecules: the deprotonated $[Ni(II)Cyclam\text{-}H]^+$ (left structure) and the its chemically reduced form $[Ni(I)Cyclam]^+$.

The other significant advance in our instrumentation has been the integration of high resolution mass spectrometry. The importance of this capability is illustrated in Fig. 3, which highlights an example where this performance was essential in a study of the controlled reduction of Ni(II)Cyclam to the Ni(I) oxidation state critical for activating CO_2. The key obstacle in this project is to suppress a competitive deprotonation reaction that dominates production of the desired Ni(I) species, and is less than 0.02 amu away from the target peak. The mass peaks are easily separated, however, using our high resolution instruments as illustrated in Fig. 3.

An additional refinement of our methods under this grant period concerns the control of temperature to determine the binding energies of trapped intermediates as well as the spectral evolution of floppy systems as they are warmed to enable large amplitude motion in the potential energy landscape. An example of the temperature dependent trapping of a CO_2 molecule onto the open coordination site of a specifically designed ligand to support this Ni(I) oxidation state is presented in Fig. 4. We have also introduced a cryogenically cooled octopole trap as an alternative scheme to achieve even better temperature control. This is indeed a superior methodology over the commercially available 3D Paul trap (Jordan) as evidenced by our successful execution of He tagging in several molecular ion systems.

IB. Applications to activation mechanisms in homogeneous water splitting catalysts

Coincident with the instrumentation development, we have engaged several productive collaborations with synthesis groups (Miller, Crabtree, Holland, and Brudvig at Yale, Krüger at TU Kaiserslautern, Jackson at University of Kansas) in order to maximize the impact of the new methods and indeed tailor them to meet the needs presented by specific “real world” systems. An early example of this involved the understanding of the mechanism of an Ir-based homogeneous water splitting catalyst recently introduced by the Yale Solar Group (Crabtree/Brudvig). The initial goal was to capture the elusive Ir(V)=O species invoked in the initial hypothesis of the catalytic cycle indicated in red at the top of Fig. 5. Working in close collaboration with Zare’s high resolution mass spectrometry team at Stanford, we established that the atomically correct assembly created upon initial activation of the catalyst actually corresponds to oxidation of the Cp* ring as opposed to the metal-oxo species. This was immediately clear in the vibrational spectrum of the putative intermediate with the appearance of strong OH stretching vibrations (black trace in the middle of Fig. 5). This observation, in turn, led to a re-evaluation of the mechanism of action, from which emerged the current hypothesis that the bi-metallic, μ-oxo

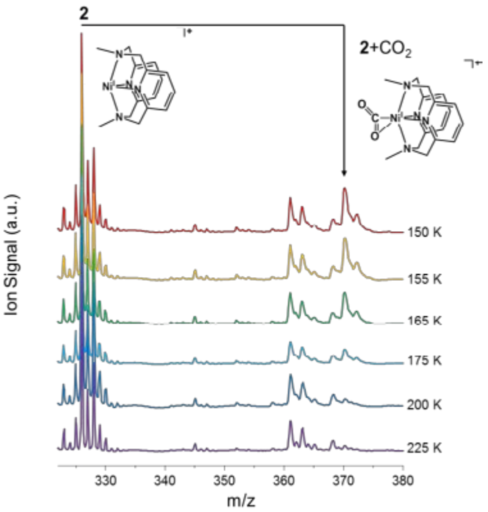


Fig. 4. Mass spectrometry reveals the temperature dependence of the uptake of CO_2 by the Ni(I)(L-N_4Me_2)$^+$ compound, where the onset for CO_2 addition occurs at ~ 200 K.

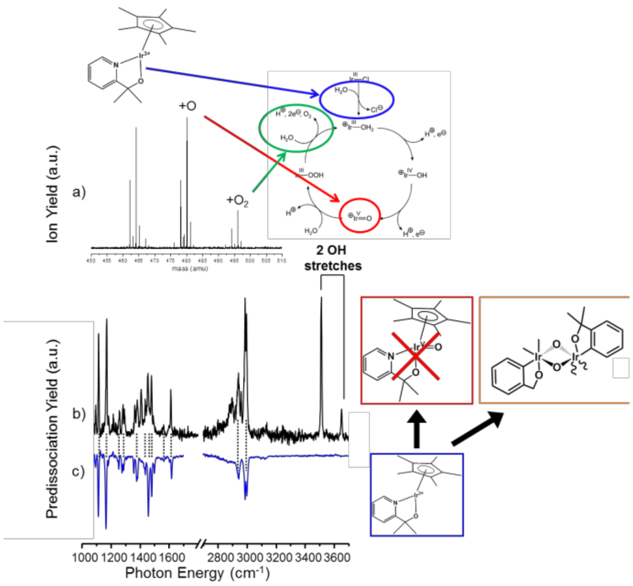


Fig. 5. Mass spectra (a) and vibrational predissociation spectrum (b) of the putative intermediate iridium oxide compound (red box) demonstrated that it is actually comprised of an oxidized Cp* group. The new mechanism involves the formation of a μ-oxo bridged Ir complex (in orange) rather than the metal-oxo species (in red). The blue trace in (c) corresponds to the spectrum of the cationic form of the precursor (blue box and top).

bridged species (orange box in Fig. 5) is actually the activated form of the catalyst. This work appeared on the cover of the January 6th, 2014 issue of *Inorganic Chemistry* in a joint publication along with the Zare and Crabtree groups.

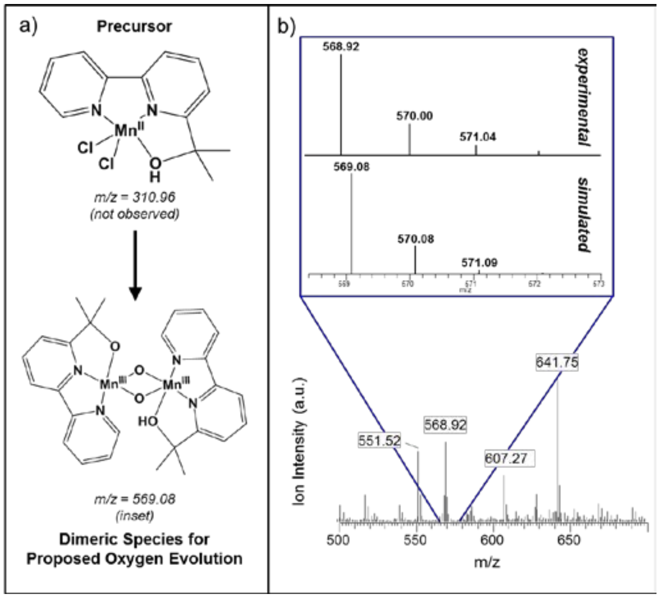
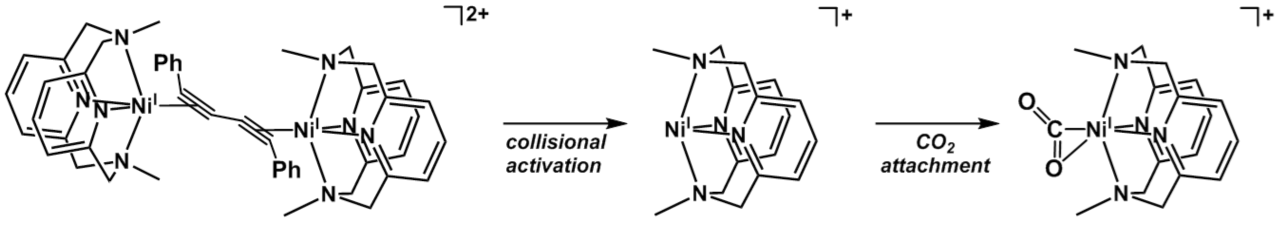


Fig. 6. Mass spectrometry reveals that in the gas phase, the precursor molecule together with Oxone form a variety of high mass species corresponding to dimeric products which are thought to be those involved in oxygen evolution.

With this initial successful contribution to the synthetic effort, we continued to work with the Brudvig group, this time on their Mn-based water splitting catalyst inspired by the multi-metallic oxygen evolving complex (OEC) in photosystem II. Three ligands with highly donating pyridine alkoxide moieties, including 2-(pyridin-2-yl)propan-2-ol (pyalkH), 2,2'- (pyridine-2,6-diyl)bis(propan-2-ol) (pydialkH_2), and 2-[(2,2'-bipyridin)-6-yl]propan-2-ol (bipy- alkH), were screened for activity, and the complexes with the ligand bipy-alkH (such as that shown in Fig. 6a) were shown to evolve O_2 when driven by Oxone (potassium peroxymonosulfate). The catalytic mixture generated from the precursor complex [Mn(bipy-alkH)Cl_2] retained activity in unbuffered solution for more than 160 h. In this case, we were able to characterize the species present in the reaction mixture using high resolution mass spectrometry, and in particular identified a dimeric, μ-oxo species (bottom of Fig. 6a) that appears as a likely candidate for the active species involved in O_2 evolution. These first results were published in ChemPlusChem in 2016 (publication 13).

IC. Characterization of oxidation-state dependent activation of small molecules

Our first efforts in the area of CO_2 activation involved a collaboration with the Kubiak group at UCSD in the context of NiCyclam (see Fig. 3) because it is a well characterized system. The key questions to be addressed regard the mechanism of CO_2 attachment to the metal center and the degree of charge displacement onto the CO_2 moiety held in that coordination site. It became immediately clear, however, that, although Ni(II)Cyclam is readily introduced into the gas phase with an ESI interface, it is not straightforward to isolate the critical reduced Ni(I) form necessary to activate CO_2. Instead, the dominant product by far is due to deprotonation of an NH group with retention of the Ni(II) core. We therefore turned to an alternative, tetra-coordinated ligand platform related to Cyclam but distorted out of plane in such a way that it supports a more stable Ni(I) metal center in addition to the Ni(II) analogue. This unusual compound was accessed using the bimetallic scaffold (left of Fig. 7) synthesized by the Krüger group in Kaiserslautern for the specific purpose of controlling the overall spin in bi- and tri-metallic molecular platforms.



1

2

2+CO$_2$

Fig. 7. Mechanism to release the active Ni(I) compound with an open coordination site on which to trap CO$_2$.

This compound can be crystalized with intact Ni(I) centers that survive ESI injection in the mass spectrometer as a di-cation. The open coordination site was exposed using collision induced dissociation (CID) of the bi-metallic compound as illustrated in Fig. 7. This was carried out in the high pressure region of the ion source. Substrate molecules such as CO, N_2 and N_2O were next coordinated in the active site in a temperature-controlled reactive trap (red box in Fig. 1. These complexes were then transferred to the low temperature cryogenic ion trap (blue box in Fig. 1) where the weakly bound mass tags, needed for characterization with vibrational predissociation spectroscopy, were condensed onto the cold ions. Finally, the tagged ions were injected in to the time-of-flight photofragmentation mass spectrometer for acquisition of their vibrational spectra.

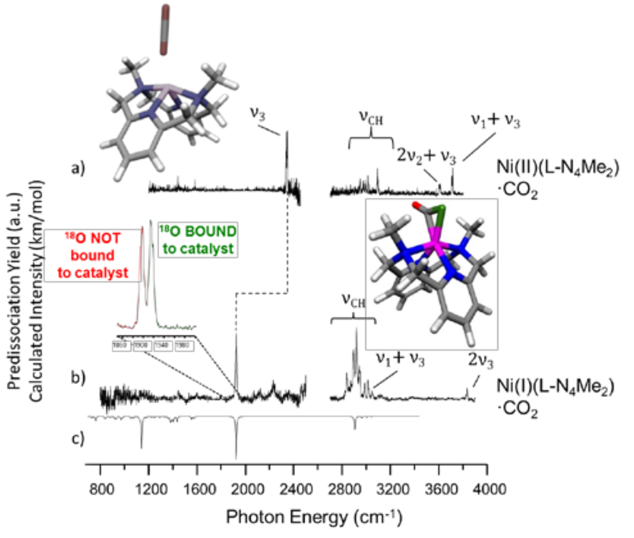


Fig. 8. Vibrational predissociation spectra of a) Ni(II)(L-$N_4Me_2)^{2+}CO_2$ and b) Ni(I)(L-$N_4Me_2)^{+}CO_2$. A large shift of the asymmetric CO_2 stretch (ν_3) is observed from the Ni(II) to Ni(I) species, indicating activation of the CO_2 in the Ni(I) case. Isotopically labeled CO_2 was used to confirm the η^2-C,O binding motif shown as insets in b).

Figure 8 presents representative spectroscopic results from the CO_2 activation study. The top trace (8a) confirms that CO_2 is not activated by the Ni(II) atom in the macrocycle by the fact that the antisymmetric stretch (ν_3) is essentially unchanged from that in the isolated neutral molecule. On the other hand, the Ni(I) complex yields a very strongly red-shifted antisymmetric stretch consistent with a strongly bent (148°) CO_2 in the binding site. Interestingly, the calculated structure (inset in Fig. 8b) indicates that the molecule binds to the metal center in a η^2-C,O coordination motif. This was confirmed using partial isotopic labeling in the $C^{18}O^{16}O$

isotopologue, which yields a doubling of the all-important antisymmetric stretch highlighted in the colored inset in (Fig. 8b). These results were published as a “hot paper” in *Ang. Chem. Int. Ed.* (publication 11) in 2016 as a joint effort with Prof. Kruger’s group.

We then followed up the CO_2 work with a second paper (publication 14) in which we compared the distortions displayed by N_2 and CO with that observed for CO_2. All of these systems attach directly to the metal center with significant reduction in their bond strengths as evidenced by their shifts relative to the fundamentals in the isolated molecules (horizontal arrows in Fig. 9). Interestingly, N_2 actually displays a larger perturbation than does CO. We also explored the reactive uptake of N_2O, which does not feature a Ni-O bond but rather occurs by oxidation of the ligand to yield an OH group on the ring.

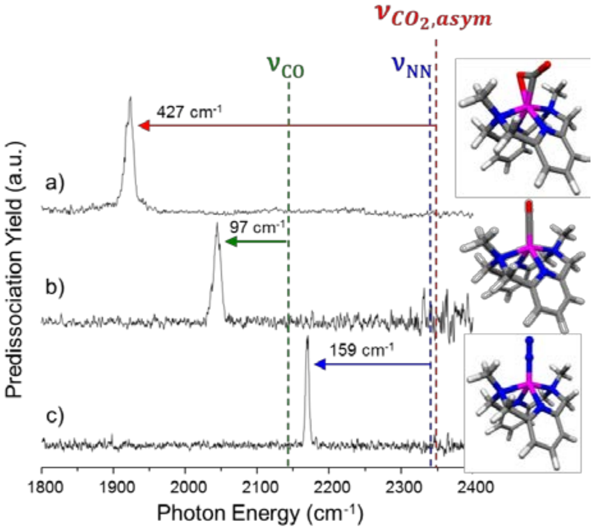


Fig. 9. Vibrational spectra of a) CO_2, b) CO and c) N_2 on $Ni(I)(L\text{-}N_4Me_2)^+$ show significant redshifts of the corresponding adduct stretches from those of the isolated neutral molecules, implying transfer of electron density to the small molecule upon complexation to the metal.

In the last year of this grant, we carried out two experiments designed to control the oxidation states of both the catalysts and the substrate independently, which are reported in publications 18 and 19. Of particular interest is the successful generation of the critical Ni(I) oxidation state in the gas phase using ion chemistry techniques borrowed from bioanalytical mass spectrometry. This involved first generating the Ni(II) cyclam precursor (which carries a +2 charge) and storing it in an ion trap. We then merged these ions with molecular anions in order to directly inject one electron in the Ni(II) species by ion-ion recombination, thus generating the Ni(I) single charged cation,. The hot nascent product ions were cooled by collisions with the buffer gas in the trap and structurally characterized with vibrational spectroscopy, carried out in collaboration with the FELIX team at Radboud University in The Netherlands. This verified that the coordination environment was preserved after exothermic electron transfer. This is an important development because it

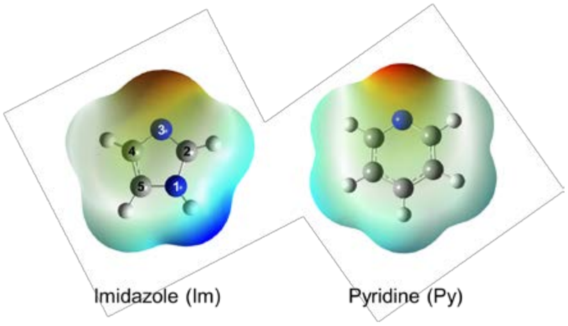


Fig. 10. Structures and electrostatic potentials, calculated at the B3LYP/aug-cc-pVDZ level of theory, of imidazole (Im) and pyridine (Py) with red and blue indicating negative and positive electrostatic domains, respectively.

provides a rational scheme for the preparation of extremely reactive oxidation states in an isolated environment where one can introduce substrates in a controlled fashion. In another study, we followed how a fully reduced (activated) CO_2 molecule (the $CO_2^{-\bullet}$ radical anion) interacts with the N atoms on the heterocycles imidazole and pyridine (Fig. 10), which are both effective catalysts for CO_2 reduction. In this case, vibrational spectroscopy was used to monitor covalent C-N bond formation. Interestingly, only pyridine appears to operate by this mechanism, indicating that the imidazole likely involves the acidic $C_{(2)}$-H group rather than the ring N atom, supporting the suggestion raised by Bocarsly and co-workers in their kinetic analysis of the bulk electrochemistry.

II. Papers Acknowledging Support Under this Grant (#FA9550-13-1-0007)

1. **Ionic Liquids from the Bottom Up: Local Assembly Motifs in [EMIM][BF_4] Through Cryogenic Ion Spectroscopy**
   Christopher J. Johnson, Joseph A. Fournier, Conrad T. Wolke, and Mark A. Johnson
   The Journal of Chemical Physics **2013**, *139* 224305.
   DOI: 10.1063/1.4838475

2. **Communication: He tagged Vibrational Spectra of the SarGlyH^+ and $H^+(H_2O)_{2,3}$ Ions: Quantifying Tag Effects in Cryogenic Ion Vibrational Predissociation (CIVP) Spectroscopy**
   Christopher J. Johnson, Arron B. Wolk, Joseph A. Fournier, Erin N. Sullivan, Gary H. Weddle, and Mark A. Johnson
   The Journal of Chemical Physics **2014**, *140* 221101.
   DOI: 10.1063/1.4880475

3. **Vibrational Spectral Signatures of the Proton Defect in the Three-Dimensional $H^+(H_2O)_{21}$ Cluster**
   Joseph A. Fournier, Christopher J. Johnson, Conrad T. Wolke, Gary H. Weddle, Arron B. Wolk, and Mark A. Johnson
   Science **2014**, *334* (6187) 1009-1012.
   DOI: 10.1126/science.1253788

4. **Microhydration of Contact Ion Pairs in $M^{2+}OH^-(H_2O)_{n=1-5}$ (M=Mg, Ca) Clusters: Spectral Manifestations of a Mobile Proton Defect in the First Hydration Shell**
   Christopher J. Johnson, Laura C. Dzugan, Arron B. Wolk, Christopher M. Leavitt, Joseph A. Fournier, Anne B. McCoy, and Mark A. Johnson
   The Journal of Physical Chemistry A **2014**, *118* (35) 7590-7597.
   DOI: 10.1021/jp504139j

5. **Site-Specific Vibrational Spectral Signatures of Water Molecules in the Magic $H_3O^+(H_2O)_{20}$ and $Cs^+(H_2O)_{20}$ Clusters**
Joseph A. Fournier, Conrad T. Wolke, Christopher J. Johnson, Mark A. Johnson, Nadja Heine, Sandy Gewinner, Wieland Schollkopf, Tim K. Esser, Matias R. Fagiani, Harald Knorke, and Knut R. Asmis
Proceedings of the National Academy of Sciences of the United States **2014**, *111* (51) 18132-18137.
DOI: 10.1073/pnas.1420734111

6. **Thermodynamics of Water Dimer Dissociation in the Primary Hydration Shell of the Iodide Ion with Temperature-Dependent Vibrational Predissociation Spectroscopy**
Conrad T. Wolke, Fabian S. Menges, Niklas Tötsch, Olga Gorlova, Joseph A. Fournier, Gary H. Weddle, Mark A. Johnson, Nadja Heine, Tim K. Esser, Harald Knorke, Knut R. Asmis, Anne B. McCoy, Daniel J. Arismendi-Arrieta, Rita Prosmiti, and Francesco Paesani
The Journal of Physical Chemistry A **2015**, *119* (10) 1859-1866.
DOI: 10.1021/jp510250n

7. **Persistence of Dual Free Internal Rotation in $NH_4^+(H_2O)\cdot He_{n=0-3}$ Ion–Molecule Complexes: Expanding the Case for Quantum Delocalization in He Tagging**
Patrick J. Kelleher, Christopher J. Johnson, Joseph A. Fournier, Mark A. Johnson, and Anne B. McCoy
The Journal of Physical Chemistry A **2015**, *119* (18) 4170-4176.
DOI: 10.1021/acs.jpca.5b03114

8. **Vibrational Signatures of Solvent-Mediated Deformation of the Ternary Core Ion in Size-Selected $[MgSO_4Mg(H_2O)_{n=4-11}]^{2+}$ Clusters**
Joseph W. DePalma, Patrick J. Kelleher, Christopher J. Johnson, Joseph A. Fournier, and Mark A. Johnson
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    Chemical Physics Letters **2017**, *690* 159-171.
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17. **Trapping and Structural Characterization of the $XNO_2\cdot NO_3^-$ (X = Cl, Br, I) Exit Channel Complexes in the Water-Mediated X^- + N_2O_5 Reactions with Cryogenic Vibrational Spectroscopy**
    Patrick J. Kelleher, Fabian S. Menges , Joseph W. DePalma , Joanna K. Denton, Mark A. Johnson, Gary H. Weddle, Barak Hirshberg and R. Benny Gerber
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    Journal of Physical Chemistry A, **2018**, 122 (15), 3805-3810
    DOI: 10.1021/acs.jpca.8b01883

Graduate Students supported by this grant

Stephanie Craig
Arron Wolk
Nan Yang

Postdoctoral Associates supported by this grant

Fabian Menges, Christopher Johnson

Inventions and patent disclosures

One patent has been granted based on the work supported by this grant. US Patent 8890059, "Use of Cryogenic Ion Chemistry to Add a Structural Characterrization Capability to Mass Spectrometry Through Linear Action Spectroscopy"

Honors and Awards during grant period

2014 Elected member, National Academy of Sciences

Invited Lectures during grant period

2013

1 Tilde Science Café, Public lecture, "The Wild World of Electrified Water," Branford, CT.
2. Lehigh University, Pchem seminar
3. Marquette University, Pchem seminar
4. Telluride meeting on vibrational dynamics
5. Plenary Lecture, German Physical Society
6. Kaiserslautern meeting on trimetallic complexes
7. Bochum symposium on Solvation
8. Molecular energy transfer GRC
9. ACS symposium New Orleans
11. ACS Symosium on Water, Indianapolis

2014

1. SASP, Oberburgl, Austria
2. Oxford spectroscopy and dynamics
3. Molecular and Ionic Clusters GRC
4. ACS Dallas, Irving Langmuir Award Lecture
5. Atomic and molecular interactions GRC
6. ASCONA, Switzerland, Conference on nanostructures
7. Arizona, Dept. Colloquium
8. AFOSR contractor's meeting
9. Student invited talk, U. Indiana
10. Keynote lecture, Gordon research seminar, Vibrational dynamics GRC
11. Pittcon Lectures (2), Duquesne University
12. Department colloquium, Temple University
13. ACS National meeting, Spectroscopy and dynamics symposium, San Francisco
14. Chemistry department seminar, Technical University, Munich

2015

1. McElvain lecture, University Wisconsin
2. Department Colloquium, University of Georgia
3. Plenary lecture, German Physical Chemistry Society (Deutsche Bunsen-Gesellschaft), Bochum
4. Student Invited Lecture, Analytical Division, University of Illinois
5. University of Leipzig
6. Telluride Workshop on Vibrational Spectroscopy

7. Dynamics of Molecular Collisions, Asilomar
8. Gordon Conference on Water
9. Harry Emmet Gunning Lecture Series (3) University of Alberta)
10. Plenary lecture, “Spectroscopy and Dynamics” symposium, Nottingham, England.
11. JILA workshop on Ultracold Chemistry
12. Reilly Lectures in Physical Chemistry (3, Notre Dame)

2016

1. Size selected clusters, Davos, Switzerland
2. University of Mississippi
3. Molecular and Ionic Clusters Gordon Research Conference (Session Chair)
4. Vibrational Spectroscopy Gordon Research Conference (Session Chair)
5. Stauffer Lectures (2, Stanford University)
6. ACS National Meeting in San Diego, Aerosol symposium
7. Malcolm Dole Lectures (2), Northwestern University
8. University of Nijmegen Colloguium
9. International Symposium on Molecular Spectroscopy, Univ. Illinois
10. EMLG-JMLG (European molecular liquids group) ann. meeting, Crete, Greece
11. AFOSR Molecular Dynamics and Theoretical Chemistry Contractor’s meeting

2017

1. Florida State
2. Telluride Vibrational spectroscopy workshop
3. GRC Gaseous Ions
4. APS National meeting symposium on solvation
5. Cross Lectures (2), University of Washington
6. Kahn lecture, University of New Mexico
7. ACS National Meeting, Washington DC, Award symposium for Kit Bowen
8. U. C. Berkeley (2)
9. Frontier Lectures (3) Texas A&M
10. Southwest regional ACS meeting, Keynote lecture
11. NSF CCI site visit, San Diego
12. APS March meeting, New Orleans

2018

1. IR free electron lasers workshop, Munich
2. GRC on Photoions
3. AFOSR workshop on new advances in mass spectrometry (Wright Patterson AFB)
4. Plenary speaker, American Society for Mass Spectrometry, St. Petersburgh, FLA

AFOSR Deliverables Submission Survey

Response ID:10131 Data

1.

Report Type

Final Report

Primary Contact Email
Contact email if there is a problem with the report.

mark.johnson@yale.edu

Primary Contact Phone Number
Contact phone number if there is a problem with the report

2039274763

Organization / Institution name

Yale University

Grant/Contract Title
The full title of the funded effort.

Structure and Reactivity of Transient Species in Water Splitting and CO2 Reduction Using Cryogenic Ion Spectroscopy

Grant/Contract Number
AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-13-1-0007

Principal Investigator Name
The full name of the principal investigator on the grant or contract.

Mark Johnson

Program Officer
The AFOSR Program Officer currently assigned to the award

Michael R. Berman

Reporting Period Start Date

02/01/2013

Reporting Period End Date

04/30/2018

Abstract

Under this grant, we have designed, commissioned and exploited new and general experimental methods for the purpose of identifying the reaction pathways that govern the catalytic activation of small, stable molecules like H2O, N2 and CO2. We accomplished this by trapping key chemical species deep in the catalytic cycle that have been calculated or inferred to play an important role but have never been isolated. This endeavor involved the development of a new type of instrument that combines high resolution mass spectrometry, cryogenic ion processing, and laser photofragmentation spectroscopy. In our approach, we first extract the resting state of the catalyst from solution and transport it into vacuum where collisional dissociation exposes the reactive metal center. Substrate molecules are then introduced directly to the active site by temperature controlled, gas phase condensation in a radio frequency ion trap, and the extent of their activation is monitored as a function of ligand structure and oxidation state of the metal center. The method is general, as illustrated by its application to N2, CO and N2O molecules attached to the open coordination site of a Ni coordination compound specifically designed to facilitate control of the metal

oxidation states. Transformation of these stable species to useful chemicals (NH_3, CH_3OH, etc.) involves formation of NH, CH and OH chemical bonds. Therefore, during this grant period, we also established a theoretical framework that allows experimental determination of bond forming events involving mobile protons by analyzing their diffuse vibrational signatures. Finally, we demonstrated a method for monitoring the reductive activation of CO_2 starting from the fully reduced radical anion, and applied this technique to reveal the structures of intermediates invoked to understand the different mechanisms displayed by imidazole and pyridine in the photoelectrocatalytic transformation of CO_2 to formic acid.

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Archival Publications (published) during reporting period:

1. Ionic Liquids from the Bottom Up: Local Assembly Motifs in [EMIM][BF4] Through Cryogenic Ion Spectroscopy
Christopher J. Johnson, Joseph A. Fournier, Conrad T. Wolke, and Mark A. Johnson
The Journal of Chemical Physics 2013, 139 224305.
DOI: 10.1063/1.4838475

2. Communication: He tagged Vibrational Spectra of the SarGlyH+ and $H^+(H_2O)_{2,3}$ Ions: Quantifying Tag Effects in Cryogenic Ion Vibrational Predissociation (CIVP) Spectroscopy
Christopher J. Johnson, Arron B. Wolk, Joseph A. Fournier, Erin N. Sullivan, Gary H. Weddle, and Mark A. Johnson
The Journal of Chemical Physics 2014, 140 221101.
DOI: 10.1063/1.4880475

3. Vibrational Spectral Signatures of the Proton Defect in the Three-Dimensional $H^+(H_2O)_{21}$ Cluster
Joseph A. Fournier, Christopher J. Johnson, Conrad T. Wolke, Gary H. Weddle, Arron B. Wolk, and Mark A. Johnson
Science 2014, 334 (6187) 1009-1012.
DOI: 10.1126/science.1253788

4. Microhydration of Contact Ion Pairs in $M^{2+}OH^-(H_2O)_{n=1-5}$ (M=Mg, Ca) Clusters: Spectral Manifestations of a Mobile Proton Defect in the First Hydration Shell
Christopher J. Johnson, Laura C. Dzugan, Arron B. Wolk, Christopher M. Leavitt, Joseph A. Fournier, Anne B. McCoy, and Mark A. Johnson
The Journal of Physical Chemistry A 2014, 118 (35) 7590-7597.
DOI: 10.1021/jp504139j

5. Site-Specific Vibrational Spectral Signatures of Water Molecules in the Magic $H_3O^+(H_2O)_{20}$ and $Cs^+(H_2O)_{20}$ Clusters
Joseph A. Fournier, Conrad T. Wolke, Christopher J. Johnson, Mark A. Johnson, Nadja Heine, Sandy

Gewinner, Wieland Schollkopf, Tim K. Esser, Matias R. Fagiani, Harald Knorke, and Knut R. Asmis
Proceedings of the National Academy of Sciences of the United States 2014, 111 (51) 18132-18137.
DOI: 10.1073/pnas.1420734111

6. Thermodynamics of Water Dimer Dissociation in the Primary Hydration Shell of the Iodide Ion with Temperature-Dependent Vibrational Predissociation Spectroscopy
Conrad T. Wolke, Fabian S. Menges, Niklas Tötsch, Olga Gorlova, Joseph A. Fournier, Gary H. Weddle, Mark A. Johnson, Nadja Heine, Tim K. Esser, Harald Knorke, Knut R. Asmis, Anne B. McCoy, Daniel J. Arismendi-Arrieta, Rita Prosmiti, and Francesco Paesani
The Journal of Physical Chemistry A 2015, 119 (10) 1859-1866.
DOI: 10.1021/jp510250n
7. Persistence of Dual Free Internal Rotation in NH4+(H2O)·Hen=0–3 Ion–Molecule Complexes: Expanding the Case for Quantum Delocalization in He Tagging
Patrick J. Kelleher, Christopher J. Johnson, Joseph A. Fournier, Mark A. Johnson, and Anne B. McCoy
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DOI: 10.1021/acs.jpca.8b01883

New discoveries, inventions, or patent disclosures:

Do you have any discoveries, inventions, or patent disclosures to report for this period?

Yes

Please describe and include any notable dates

US Patent 8890059, "Use of Cryogenic Ion Chemistry to Add a Structural Characterrization Capability to Mass Spectrometry Through Linear Action Spectroscopy"

Do you plan to pursue a claim for personal or organizational intellectual property?

No

Changes in research objectives (if any):

None

Change in AFOSR Program Officer, if any:

No

Extensions granted or milestones slipped, if any:

Three month extension granted. This involved delays incurred due to massive reconstruction in the Yale's Sterling Chemistry Laboratory to provide new undergraduate laboratories. My laboratories were often off-line due to dust, power outages, and invasive infrastructure installation.

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

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Appendix Documents

2. Thank You

E-mail user

Jul 29, 2018 13:39:11 Success: Email Sent to: mark.johnson@yale.edu