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# New insights into catalytic sites from slow-electron velocity map imaging of cryogenically cooled transition metal oxide anion clusters

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Spectroscopy and dynamics of bare and complexed transition metal oxide clusters has been investigated using slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI). This research program is motivated by the importance of transition metal oxide catalysts in many key chemical reactions. Understanding the reactive sites in catalysts is of prime importance in chemistry, and transition metal oxide clusters represent tractable model systems for these catalysts. Cryo-SEVI is a high resolution (sub-meV) variant of anion photoelectron spectroscopy that provides a unique probe of size-selected transition metal oxide clusters and their complexes with reactants, reactive intermediates, and products. It has been shown to yield highly vibrationally resolved spectra even for clusters comprising multiple transition metal atoms. Comparison of these spectra with Franck-Condon simulations enables one to distinguish among possible isomeric structure and to make definitive structural assignments. First targets for this effort were the suboxide clusters $Fe_nO$, $V_nO$, and $Co_nO$. We've also targeted the product formed by reaction of $TiO_2$ with water. SEVI experiments on both bare metal oxide clusters and reactive intermediates have been complemented by infrared spectroscopy.

**15. SUBJECT TERMS**
SEVI, catalysis, cluster, photoelectron

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## 1. FINAL TECHNICAL REPORT

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## 2. OBJECTIVES

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## 3. STATUS OF EFFORT

Primary research efforts during the last three years have focused on achieving a molecular understanding of bare transition metal oxide clusters, catalytic intermediates, and transition states, with particular emphasis on the spectroscopic signatures of water splitting induced by transition metal oxide clusters and the transition state spectroscopy of benchmark bimolecular and unimolecular chemical reactions. These interconnected goals are addressed in gas phase chemical physics experiments using two complementary techniques: slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI) and, in collaboration with Knut Asmis at the University of Leipzig, infrared photodissociation spectroscopy (IRPD). Cryo-SEVI is a high resolution variant of anion photoelectron spectroscopy that has been developed and perfected in our laboratory; the combination of novel photoelectron imaging methodology with anion trapping and cooling results in photoelectron spectra of complex anions with resolution as high as 1-2 $cm^{-1}$, an improvement of approximately two orders of magnitude over more conventional photoelectron spectroscopy experiments. The IRPD experiments are also performed on cryogenically cooled ions and use either an infrared free electron laser or a tabletop IR laser to obtain infrared spectra of mass-selected ions over a broad frequency range. Key results are summarized below.

## 4. ACCOMPLISHMENTS/NEW FINDINGS

### *A. Spectroscopy of bare and complexed metal oxide clusters:*

Cryo-SEVI and IRPD have been used in tandem to characterize the vibrational and electronic spectroscopy of bare metal oxide clusters in order to ascertain their structure. This information serves as the basis for interpreting ongoing and planned experiments on more complex species in which we characterize the intermediates formed when these clusters react with water and other species.

Thus far, experiments have focused on bare and complexed $(TiO_2)_n^-$ clusters. Gas-phase complexes of water on small titanium oxide clusters are model systems to examine the molecular-level mechanism of dissociative water adsorption at defect sites on bulk titania surfaces.[1] Previously, cryo-SEVI has been used to characterize the n=1 and 2 species.[2-3] The extensive vibrational structure observed for $Ti_2O_4^-$ showed that the anion has a $C_{2v}$ ground state and a very low-lying excited state with $C_{2h}$ symmetry. Following up on this work, IRPD experiments were carried out on the n=3-8 clusters in the spectral region from 450-1200 $cm^{-1}$.[4] The experiments were interpreted with the aid of extensive density functional theory calculations at the BP86/6-311+G* level of theory to identify the lowest-lying cluster isomers and their infrared spectra. The IR spectra of the *n*=3 cluster was conclusively assigned to the predicted most stable $C_s$ structure and the *n*=6 cluster to the predicted $C_2$ structure. The vibrational spectra of the *n*=4 and *n*=7 clusters was attributed to contributions of at most two low-lying structures. While our calculations indicate that the *n*=5 and *n*=8 clusters have many more low-lying isomers than the other clusters, the dominant contributions to their spectra were assigned to the lowest energy structure.

The cryo-SEVI and IRP D experiments, in combination with theory, yielded geometrical structures and vibrational frequencies for $(TiO_2)_n^-$ clusters from n=1-8. The next step was to determine what happens when these clusters complex with $H_2O$ and to characterize the spectroscopic signatures of physisorbed vs. dissociatively chemisorbed water molecules. This work was motivated by the calculations by Dixon[5-6] on $(TiO_2)_n + H_2O$ that predicted water would in fact be split by the $TiO_2$ clusters. To this end, cryo-SEVI of $TiO_3H_2^-$ anions was used to probe the simplest titania/water reaction, $TiO_2^{0/-} + H_2O$.[7] The resultant spectra, shown in Fig. 1, revealed vibrationally-resolved structure assigned to detachment from the *cis*-dihydroxide $TiO(OH)_2^-$ geometry. This result demonstrates that for reaction of the anionic $TiO_2^-$ monomer with a single water molecule, the dissociative adduct, where the water is split, is energetically preferred over a molecularly adsorbed geometry. The spectrum in Fig. 1 is a significant improvement in resolution over previous measurements (which showed no vibrational structure at all),[8] yielding an electron affinity of 1.2529(4) eV as well as several vibrational frequencies for neutral $TiO(OH)_2$. Comparison to the previously measured cryo-SEVI spectrum of bare $TiO_2^-$ shows that reaction with water stabilizes neutral $TiO_2$ more than the anion,[2] providing insight into the fundamental chemical interactions between titania and water.

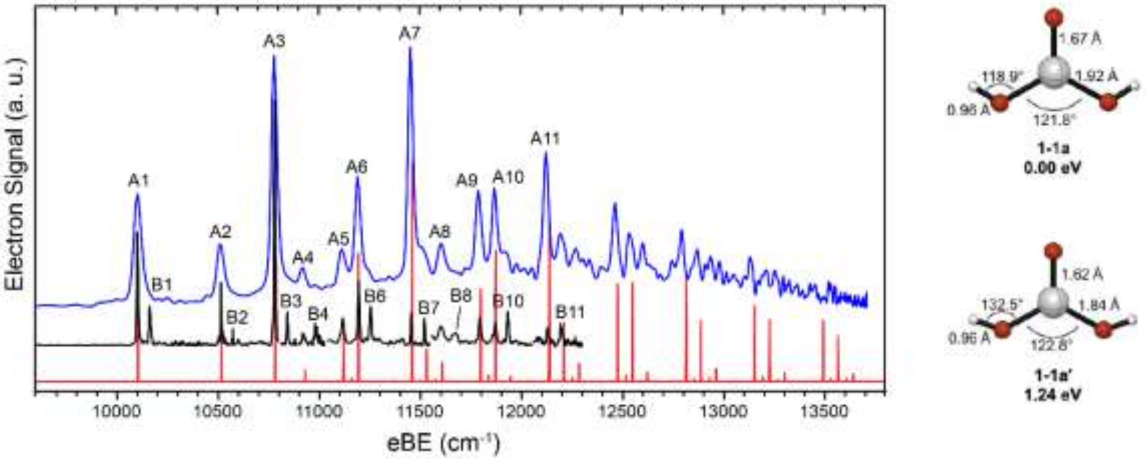

Fig. 1. Cryo-SEVI spectrum of $TiO_3H_2^-$ and calculated dihydroxy structures for anion and neutral. Blue line is experimental overview spectrum, black trace is high resolution experimental composite spectrum and red trace is Franck-Condon simulation.

To explore similar effects in larger clusters, the infrared spectroscopy of $[(TiO_2)_n(H_2O)_m]^-$ clusters (n=2-4, m=1-3) was explored by IRPD of the corresponding $D_2$ messenger-tagged clusters.[9] Vibrational features were reported in the spectral windows of 400-1200 $cm^{-1}$ and 2600-3000 $cm^{-1}$, capturing both fingerprint cluster modes and O-D stretching modes. The IRPD spectra were interpreted with the aid of $\omega$B97X-D/aug-cc-pVDZ density functional calculations. We conclusively assigned the IRPD spectra of the $n$=2,$m$=1,2 clusters and the $n$=3,$m$=1-3 clusters with up to three water molecules to dissociatively adsorbed global minimum energy structures. The clearest indicator of dissociative water adsorption was the disappearance of structure in the Ti-O stretching regime from 900-1000 $cm^{-1}$, as terminal Ti-O moieties react to form Ti-O-D groups with sequential addition of $D_2O$. The $n$=4 clusters exhibited more complex spectra, possibly reflecting contributions from a trapped intermediate along with the global energy minimum. The facile dissociative adsorption of water on the undercoordinated Ti atoms in these clusters illuminates at the molecular level how hydrolysis reactions may be initiated at reactive $TiO_2$ defect sites.[1]

### *B. Transition state spectroscopy:*

While the work on complexed metal oxides enables one to characterize the intermediates formed in water splitting reactions, cryo-SEVI has also been used to great effect in transition state spectroscopy (TSS) experiments in which negative ion photodetachment probes the transition state itself, not reactants or products.[10-11] TSS has been a long-running project in our group, but the enhanced resolution of cryo-SEVI has led to significant recent advances in our ability to characterize the transition state for benchmark chemical reactions, including the bimolecular $F+H_2$ and $F+CH_3OH$ reactions and the unimolecular isomerization of vinylidene ($H_2CC$) to acetylene.

For example, the cryo-SEVI spectra of $FH_2^-$ and $FD_2^-$ resulted in the first direct observation of reactive resonances in the $F+H_2$ reaction.[12] The spectra revealed several narrow peaks that were not seen in previous photoelectron spectroscopy experiments of these anions. Theoretical calculations, based on a highly accurate $F + H_2$ potential energy surface, convincingly assigned these peaks to resonances associated with quasibound states in the HF+H and DF+D product regions and with a quasibound state in the transition state region of the $F+H_2$ reaction. The observation of these sharp peaks represents a major advance in transition state spectroscopy, in which such structure is extremely sensitive to the potential energy surface in the transition state region. Comparison with recent reactive scattering experiments by Yang[13] suggests that the same set of resonances are manifested in the two types of experiments.

Cryo-SEVI has also been applied to the $CH_3OHF^-$ anion in order to investigate the transition state region of the polyatomic reaction $F+CH_3OH \rightarrow CH_3O+HF$.[14] The experimental results were accompanied by a high-level simulation of the $CH_3OHF^-$ photodetachment spectrum calculated by Guo by running quantum dynamics trajectories on a 6-dimensional subsurface of a new 15-dimensional PES constructed for the F + $CH_3OH$ reaction. The experimental spectra were dominated by broad steps with a spacing of ~3600 $cm^{-1}$ for $CH_3OHF^-$ detachment and ~2700 $cm^{-1}$ for $CH_3ODF^-$. Previous photodetachment experiments[15-16] also observed this stepped structure and assigned it to an H−F stretching progression of the $CH_3O$−HF product complex (PC). With cryo-SEVI, additional fine structure was newly resolved, superimposed on the broad steps and spaced by ~200 $cm^{-1}$. This fine structure is well-reproduced by the simulation. These newly observed peaks were assigned to progressions in exit channel Feshbach resonances with excitation in the low frequency $CH_3O$−HF van der Waals stretching mode.

This methodology has also been applied to a benchmark unimolecular reaction. Vinylidene-acetylene isomerization is the prototypical example of a 1,2-hydrogen shift, one of the most important classes of isomerization reactions in organic chemistry. This reaction was investigated with quantum state specificity by cryo-SEVI of the $H_2CC^-$ and $D_2CC^-$ anions and quantum dynamics calculations.[17-18] Peaks in the cryo-SEVI spectra, shown in Fig. 2, are considerably narrower than in previous work[19] and reveal subtleties in the isomerization dynamics of neutral vinylidene, as well as vibronic coupling with an excited state of vinylidene. Comparison with theory permitted assignment of most spectral features to eigenstates dominated by vinylidene character. However, excitation of the $\nu_6$ in-plane rocking mode in $H_2CC$ (present in peaks B, C, and I) led to appreciable tunneling-facilitated mixing with highly vibrationally-excited states of acetylene. This mixing was manifested as broadening and/or spectral fine structure that was largely suppressed for analogous vibrational levels of $D_2CC$. The state-specificity implied by these results forms the basis of one of the research directions outlined in this proposal, in which anion vibrational excitation prior to photodetachment probes

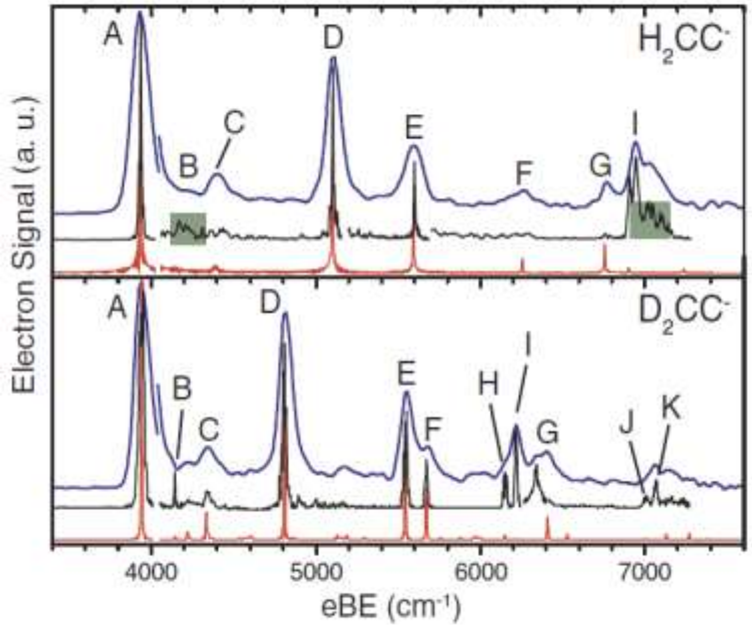

Fig. 2. Cryo-SEVI spectra of $H_2CC^-$ and $D_2CC^-$. Color scheme is same as Fig. 1.

otherwise inaccessible transition state configurations. In addition, we have mapped out the photoelectron kinetic energy distributions resulting from vibrational excitation of $H_2CC^-$ followed by autodetachment.[20] These spectra revealed novel, highly delocalized vibrational levels of $H_2CC$ with amplitude in the theoretically predicted shallow wells along the isomerization coordinate.[21]

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## 5. PERSONNEL REPORTED

*Principle Investigator*
Daniel M. Neumark

*Graduate Students*
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Jessalyn Devine
Marissa Weichman

*Administrative*
Michelle Haskins

## 6. PUBLICATIONS

(1) M. Weichman, J. Devine, D. S. Levine, J. B. Kim, and D. M. Neumark. "Isomer-Specific Vibronic Structure of the 9-, 1-, and 2-Anthracenyl Radicals via Slow Photoelectron Velocity-Map Imaging." PNAS 113, 1698 (2016).

(2) M. L. Weichman, X. Song, M. R. Fagiani, S. Debnath, S. Gewinner, W. Schollkopf, D. M. Neumark, and K. R. Asmis. "Gas Phase Vibrational Spectroscopy of Cold $(TiO_2)_n^-$ (n=3-8) Clusters." J. Chem. Phys. 144, 124308 (2016).

(3) M. L. Weichman, J. Devine, and D. M. Neumark. "High-Resolution Photoelectron Imaging of Cryogenically Cooled $Fe_4O^-$ and $Fe_5O^-$." J. Chem. Phys. 145, 054302 (2016).

(4) J. A. Devine, M. L. Weichman, X. Zhou, J. Ma, B. Jiang, H. Guo, and D. M. Neumark. "Non-Adiabatic Effects on Excited States of Vinylidene Observed with Slow Photoelectron Velocity-Map Imaging." J. Am. Chem. Soc., 138, 16417 (2016).

(5) J. Devine, M. L. Weichman, S. J. Lyle, and D. M. Neumark. "High-Resolution Photoelectron Imaging of Cryogenically Cooled α- and β-Furanyl Anions." J. Mol. Spectrosc. 332, 16 (2017).

(6) J. A. Devine, M. L. Weichman, M. C. Babin, and D. M. Neumark. "Slow-Photoelectron Velocity Map Imaging of Cold tert-butyl Peroxide." J. Chem. Phys. 147, 013915 (2017).

(7) M. L. Weichman, L. Cheng, J. B. Kim, J. F. Stanton, and D. M. Neumark. "Low-lying vibronic level structure of the ground state of the methoxy radical: Slow electron velocity-map imaging (SEVI) spectra and Köppel-Domcke-Cederbaum (KDC) vibronic Hamiltonian calculations." J. Chem. Phys. 146, 224309 (2017).

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(9) J. Devine, M. L. Weichman, B. Laws, J. Chang, M. Babin, G. Balerdi, C. Xie, C. L. Malbon, W. C. Lineberger, D. R. Yarkony, R. W. Field, S. T. Gibson, J. Ma, H. Guo, and D. M. Neumark. "Encoding of Vinylidene Isomerization in its Anion Photoelectron Spectrum." Science 358, 336 (2017).

(10) M. L. Weichman, B. Vlaisavljevich, J. DeVine, N. Shuman, S. Ard, T. Shiozaki, D. M. Neumark, and A. Viggiano. "Electronic Structure of SmO and $SmO^-$ via Slow Photoelectron Velocity-Map Imaging Spectroscopy and Spin-Orbit CASPT2 Calculations." J. Chem. Phys. 147, 234311 (2017).

(11) M. L. Weichman, S. Debnath, J. T. Kelly, S. Gewinner, W. Schollkoft, D. M. Neumark, and K. R. Asmis. "Dissociative Water Absorption on Gas-Phase Titanium Dioxide Cluster Anions Probed with Infrared Photodissociation Spectroscopy." Top. Catal. 61, 92 (2018).

(12) J. DeVine, M. Weichman, C. Xie, M. Babin, M. Johnson, J. Ma, H. Guo, D. M. Neumark. "Autodetachment from Vibrationally Excited Vinylidene Anions." J. Phys. Chem. Lett. 9, 1068 (2018).

(13) J. DeVine, A. Taka, M. Babin, M. Weichman, H. Hratchian, and D. M. Neumark.

"High-Resolution Photoelectron Spectroscopy of $TiO_3H_2^-$: Probing the $TiO_2^-$ + $H_2O$ Dissociative Adduct". J. Chem. Phys. 148, 222810 (2018).

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## 7. INTERACTIONS/TRANSITIONS

May 5, 2016
Evanston, IL
"Slow Electron Velocity Map Imaging of Cryogenically Cooled Anions"
Northwestern University
Invited Lecture

May 26, 2016-May 30, 2016
Shanghai, China
"Spectroscopy of Cryogenically Cooled Transition Metal Oxide Cluster Anions by Slow Electron Velocity Map Imaging and Infrared Photodissociation"
International Symposium on New Molecules and Clusters
Invited Lecture

May 31, 2016-June 3, 2016
Leesburg, VA
DOE Meeting
Attended Meeting

June 17-24, 2016
Rehovot, Israel
"Slow Electron Velocity Map Imaging of Cryogenically Cooled Anions"
Weizman Institute
Invited Lecture

June 17-24, 2016
Tel Aviv, Israel
"Slow Electron Velocity Map Imaging of Cryogenically Cooled Anions"
Tel Aviv University
Invited Lecture

July 4-9, 2016
Geneva, Switzerland
"Dynamics of Electron Solvation in Clusters and Liquid Jets"
CECAM: Computational Methods for Modeling Multiply-Charged Droplets

Invited Lecturer

August 7-12, 2016
Telluride, CO
“Slow Electron Velocity Map Imaging of Cryogenically Cooled Anions”
Conference on Advanced Particle Imaging Techniques: 1986-2016 and Beyond
Invited Lecturer

August 31, 2016-September 2, 2016
Edinburgh, Scotland, UK
“Attosecond Science in Atomic, Molecular, and Condensed Matter Physics”
Faraday Discussion
Invited Lecturer

September 28-29, 2016
Berkeley, CA
PULSE Quarterly Meeting
Attended Meeting

October 23-26, 2016
Gaithersburg, MD
AMOS/DOE Meeting
Attended Meeting

November 6-11, 2016
Taipei, Taiwan
“Bimolecular and Unimolecular Transition State Dynamics Studied by Cryo-SEVI”
16th International Conference on Stereodynamics
Invited Lecturer

November 13-15, 2016
Tucson, AZ
“Femtosecond and Attosecond Dynamics in Liquid Jets”
MURI 2016 Meeting
Invited Lecturer

January 23-25, 2017
Rehovot, Israel
“Nonlinear Spectroscopy with Attosecond Laser Pulses”
Conference on Ultrafast and Ultraslow Dynamics
Weizmann Institute of Science, Israel
Invited Lecturer

January 26, 2017
Jerusalem, Israel
“Slow Electron Velocity-Map Imaging of Cryogenically Cooled Anions (Cryo-SEVI)”

Hebrew University
Invited Lecturer

April 4-7, 2017
NSF MRI Spectroscopy Virtual Panel
Attended Meeting

April 28, 2017-May 2, 2 017
Washington, D. C.
National Academy of Science
Attended Meeting

May 14-16, 2017
Berkeley, CA
LBNL AMOS
Attended Meeting

May 21-23, 2017
Albuquerque, NM
"Studies of Bare and Complexed Metal Oxide Clusters by Slow Photoelectron Imaging and Infrared Photodissociation of Cryogenically Cooled Anions"
AFOSR Meeting
Invited Lecture

May 24-26, 2017
Lausanne, Switzerland
"Femtosecond and Attosecond Dynamics in Atoms, Molecules, and Condensed Matter"
EPFL
Invited Lecture

May 30-June 2, 2017
Gaithersburg, MD
DOE Meeting
Attended Meeting

June 9-15, 2017
New Haven, CT
"Slow Electron Velocity-Map Imaging of Cryogenically Cooled Anions (Cryo-SEVI)"
Yale University
Invited Lecture

June 25-July 1, 2017
Nijmegan, Netherlands
"Transient Absorption and Non-Linear Spectroscopy with Attosecond Light Sources"
ISMB 2017, International Symposium on Molecular Beams
Invited Lecture

July 9-14, 2017
Tahoe City, CA
“Slow Electron Velocity-Map Imaging of Cryogenically Cooled Anions: Applications to Bimolecular and Unimolecular Transition State Spectroscopy"
2017 Dynamics of Molecular Collisions (DMC)
Invited Lecture

July 16-18, 2017
Arlington, VA
DARPA/PULSE Meeting
Attended Meeting

August 11-13, 2017
Cancun, Quintana Roo, Mexico
“Transient Absorption and Nonlinear Spectroscopy with Attosecond Light Pulses”
FEMTO 13
Invited Lecture

September 13-15, 2017
Providence, RI
External Review of Brown University Department of Chemistry
Attended Meeting

October 5-6, 2017
Seminar at the University of Missouri
Invited Lecture

October 22-24, 2017
Gaithersburg, MD
DOE AMOS Meeting
Attended Meeting

October 29, 2017-November 1, 2017
Lubbock, Texas
“Electron Interacting with Nucleic Acid Constituently in Clusters and Liquid Jets”
SWRM 2017
ACS Meeting

November 6, 2017
Kansas
“Ultrafast Dynamics in Atoms, Molecules, and Solids Studies with Attosecond Light Pulses”
Seminar at the Kansas State
Invited Lecture

November 16-17, 2017

Columbus, Ohio
“Attosecond Dynamics in Liquid Jets”
MURI Meeting OSU
Attended Meeting

January 17-21, 2018
Munich, Germany
“Slow Electron Velocity Map Imaging and Infrared Photodissciation on Spectroscopy of Cryogenically Cooled Anions”
2018 Free Electron Laser Workshop “Applications of IR Free-Electron Laser: Latest Development and Future Directions” at Ringberg Castle, Germany
Invited Lecture

January, 22-23, 2018
Cambridge, MA
“Slow Electron Velocity Map Imaging and Infrared Photodissciation on Spectroscopy of Cryogenically Cooled Anions”
Harvard University
Invited Lecture

February 18-23, 2018
“Slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI)”
Galveston, TX
GRC 2018 Photoionization and Photodetachment
Invited Lecture

February 25-March 2, 2018
Lucca (Barga), Italy
GRC 2018 Photoionization and Photodetachment, Renaissance Tuscany Il Ciocco
Session Chair

March 18-22, 2018
New Orleans, LA
“Slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI)”
255th American Chemical Society National Meeting & Exposition
Invited Lecture

April 12-13, 2018
Grand Rapids, Michigan
(1) Chemistry Talk: “Studies of Radicals, Catalytic Intermediates, and Transition States by Slow Electron Velocity-Map Imaging of Cryogenically Cooled Anions (Cryo-SEVI).”
(2) General Talk: Chemical Reactions: What Lies Under the Arrow?
Lectures at the Grand Valley State University
Ott Lecture

May 3-5, 2018

Urbana, Illinois
“Studies of Radicals, Catalytic Intermediates, and Transition States by Slow Electron Velocity-Map Imaging of Cryogenically Cooled Anions (Cryo-SEVI)”
Flygate Lecture University of Illinois

May 15-18, 2018
Berkeley, CA
DOE LBNL Meeting - Triennial Review of GPCP and CPIMS Programs
Attended Meeting

May 21-24, 2018
Albuquerque, NM
AFOSR Meeting
Attended Meeting

May 29-June 1, 2017
Gaithersburg, MD
DOE Meeting
Attended Meeting

June 21-22, 2019
Oxford, UK
Review of Oxford Department of Chemistry
Attended Meeting

June 24-29, 2018
Smithfield, RI
“Nonlinear and multidimensional spectroscopy with attosecond XUV pulses”
GRC 2018 Multiphoton Processes
Invited Lecture

July 16-21, 2018
Telluride, CO
“Studies of Radicals, Catalytic Intermediates, and Transition States by Slow Electron Velocity-Map Imaging of Cryogenically Cooled Anions (Cryo-SEVI)”
Spectroscopy and Dynamics on Multiple Potential Energy Surfaces
Invited Lecture

August 12-17, 2018
“Spectroscopy of Metal and Metal Oxide Clusters Using Slow Electron Velocity-Map Imaging of Cryogenically Cooled Anions”
ISSPIC Meeting
Hangzhou, China
Invited Lecturer

August 18-20, 2018
“Spectroscopy of Metal and Metal Oxide Clusters Using Slow Electron Velocity-Map Imaging of Cryogenically Cooled Anions”
2nd International Symposium on New Molecules and Clusters
Shanghai, China
Invited Lecture

September 2-8, 2018
“Slow electron velocity-map imaging  of cryogenically cooled anions (cryo-SEVI)”
IMPRA
Cartagena, Columbia
Invited Lecture

September 23-29, 2018
“Solvation dynamics in clusters and liquid jets”
Bochum. Germany
Meeting

October 12, 2018
Sonoma State University Lecture
“Chemistry Under the Arrow”
Rohnert Park, CA
Invited Lecture

October 16, 2018
“Attosecond science and applications to chemical dynamics”
California Institute of Technology
Pasadena, CA
Invited Lecture

October 21-24, 2018
DOE Meeting
Gaithersburg, MD
Attended Meeting

November 15-16, 2018
“Attosecond XUV probing of electronic coherences in atoms and molecules”
“Attosecond and femtosecond dynamics
in solids and liquids”
MURI 1 and 9 Meetings
Arlington, VA
Invited Lectures

## 8. NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

None

## 9. HONORS/AWARDS

Peter Debye Award in Physical Chemistry, American Chemical Society, 2019
Bourke Award, Royal Society of Chemistry, 2018
Ott Lecture, Grand Valley State University, 2018
Flygate Lecture, University of Illinois, 2018

# AFOSR Deliverables Submission Survey

Response ID:10958 Data

## 1.

**Report Type**

Final Report

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

dneumark@berkeley.edu

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

5106423502

**Organization / Institution name**

University of California, Berkeley

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

"New insights into catalytic sites from slow-electron velocity map"

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

FA9550-XX-X-XXXX

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

Daniel Milton Neumark

**Program Officer**
**The AFOSR Program Officer currently assigned to the award**

Michael Berman

**Reporting Period Start Date**

12/01/2015

**Reporting Period End Date**

11/30/2018

**Abstract**

Spectroscopy and dynamics of bare and complexed transition metal oxide clusters has been investigated using slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI). This research program is motivated by the importance of transition metal oxide catalysts in many key chemical reactions. Understanding the reactive sites in catalysts is of prime importance in chemistry, and transition metal oxide clusters represent tractable model systems for these catalysts. Cryo-SEVI is a high resolution (sub-meV) variant of anion photoelectron spectroscopy that provides a unique probe of size-selected transition metal oxide clusters and their complexes with reactants, reactive intermediates, and products. It has been shown to yield highly vibrationally resolved spectra even for clusters comprising multiple transition metal atoms. Comparison of these spectra with Franck-Condon simulations enables one to distinguish among possible isomeric structure and to make definitive

structural assignments. First targets for this effort were the suboxide clusters Fe n O$^-$, V n O$^-$, and Co n O$^-$. We've also targeted the product formed by reaction of TiO 2 with water. SEVI experiments on both bare metal oxide clusters and reactive intermediates have been complemented by infrared spectroscopy.

### Distribution Statement

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### Explanation for Distribution Statement

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### Archival Publications (published) during reporting period:

### New discoveries, inventions, or patent disclosures:

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

No

**Please describe and include any notable dates**

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

### Changes in research objectives (if any):

### Change in AFOSR Program Officer, if any:

### Extensions granted or milestones slipped, if any:

### 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**

**Report Document - Text Analysis**

**Appendix Documents**

## 2. Thank You

**E-mail user**

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