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Spectroscopy of Radicals, Clusters, and Transition States Using Slow Electron Velocity-Map Imaging of Cryogenically Cooled Anions

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photoelectron spectroscopy while offering sub-meV resolution, thereby enabling the resolution of vibrational structure in the photoelectron spectra of complex anions. This Feature Article describes recent experiments in our laboratory using cryo-SEVI, including a new research direction in which anions are vibrationally pre-excited with an infrared laser pulse prior to photodetachment.

I. INTRODUCTION

Anion photoelectron spectroscopy (PES) is a versatile experimental technique that enables detailed characterization of the neutral species created when an electron is photodetached from a negative ion.¹ In its canonical manifestation, massselected anions are photodetached at a fixed photon energy. The resulting photoelectron kinetic energy and angular distributions reveal information on the energetics, structure, and vibronic spectroscopy of the neutral species. Anion PES has provided electron affinities for a wide range of atomic and molecular species.^{2,3} Depending on the photon energy, PES can characterize the ground and electronically excited states of a neutral in a single experimental measurement, yielding term energies and, in favorable cases, vibrational structure in each of the accessible electronic states. Since photodetachment can access neutral electronic states of different spin multiplicity, PES provides a direct measure of singlet-triplet splittings and other spectroscopically challenging energetics.⁴ In addition to these appealing capabilities, the neutral species that one can access by photodetachment are of considerable interest. PES is well suited to study open-shell radicals, which can be difficult to study experimentally due to their transient nature, through photodetachment of their closed-shell anions.^{5,6} Since anion PES is inherently a mass-selective technique, it can also be applied to the anion clusters generated by laser-vaporization or electron impact sources and thus yield photoelectron spectra of sizeselected clusters.⁷⁻¹¹ Finally, photodetachment of stable anions can access the transition states of unimolecular^{12,13} and bimolecular chemical reactions,^{14,15} in which case anion PES serves as a powerful spectroscopic probe of transition states.



The versatility of anion PES is, however, limited by its energy resolution, which is typically on the order of 10-30 meV, or 100-300 cm⁻¹. At this resolution, one can readily resolve electronic structure, but the observation of vibrational structure in clusters and polyatomic molecules can be more challenging, particularly in the presence of low-frequency vibrations and Franck–Condon (FC) activity in multiple vibrational modes. These considerations have led to efforts in our laboratory and elsewhere to improve the resolution of anion PES while retaining its versatility.¹⁶

Our first attempts at higher-resolution experiments focused on anion zero electron kinetic energy (ZEKE) spectroscopy, inspired by the work by Muller-Dethlefs and Schlag on the photoionization of neutral molecules.^{17,18} In their demonstration of this technique, NO was ionized via resonant two-color ionization, and electrons with nearly zero electron kinetic energy were detected as the photon energy was scanned. The underlying idea is that whenever the ionizing laser energy is just enough to access a cation state, one observes zero energy electrons. In this way, they were able to resolve individual rotationally resolved transitions between NO and NO⁺, achieving an energy resolution on the order of 1 cm^{-1} . The mechanism of ZEKE electron production of neutrals is more

Received: March 6, 2023 **Revised:** April 10, 2023 Published: April 24, 2023





complex than first believed and involves field ionization of highlying Rydberg states rather than direct ionization.¹⁹ Negative ions, on the other hand, do not have Rydberg states. Nonetheless, we initiated analogous experiments on negative ions starting in the late 1980s based on the selective detection of near-zero energy electrons produced by photodetachment with a tunable laser²⁰ and were able to obtain ZEKE spectra with an energy resolution of $1-2 \text{ cm}^{-1}$ for a series of semiconductor clusters,²¹ open-shell van der Waals clusters,²² and, by photodetachment of IHI⁻, the transition state of the I + HI reaction in which reactive resonances were spectroscopically resolved for the first time.²³ Anion ZEKE experiments with similar resolution were also carried out by Boesl on I⁻(H₂O), FeO⁻, and other anions.^{24,25}

These experiments proved very challenging and were limited in generality by the Wigner threshold $law^{26,27}$

$$\sigma \propto (eKE)^{l+1/2} \tag{1}$$

which dictates that at low electron kinetic energy (eKE), the photodetachment cross section σ scales with (eKE)^{*l*+1/2}, where *l* is the orbital angular momentum of the photoelectron. For anion ZEKE spectroscopy, where only electrons with near zero kinetic energies are detected, the near-threshold photodetachment cross section becomes vanishingly small with increasing angular momentum, so the technique works only for s-wave (*l* = 0) detachment.

These constraints led to the development of slow-electron velocity-map imaging (SEVI) in our laboratory.²⁸ This technique was enabled by the many advances in ion and photoelectron imaging since the advent of ion imaging experiments in 1987,²⁹ particularly the development of velocity-map imaging (VMI) by Eppink and Parker³⁰ and its application to negative ions by Sanov.³¹ In photoelectron VMI experiments, one typically images all of the photoelectrons onto a CCD camera and in principle can obtain the full photoelectron kinetic energy and angular distribution with a single measurement. In SEVI, we take advantage of the fact that the energy resolution of VMI is best for slow electrons, so our VMI electron optical setup is designed to preferentially detect electrons with low kinetic energies, yielding an energy resolution as high as 1-2 cm^{-1} for the slowest electrons with kinetic energy below 100 cm^{-1} . Further improvements result from trapping the anions in a radio frequency octupole trap held at 5 K and periodically filled with a low-pressure He/H_2 gas mixture.³² The trapped ions then undergo buffer gas collisions that cool them to internal temperatures as low as 10 K, resulting in nearly all the anions being in their vibrational ground state and low rotational states. This improved version of the experiment, cryo-SEVI, leads to near-complete suppression of vibrational hot bands and narrow rotational profiles, enabling one to obtain high-resolution spectra even for complex molecular anions and clusters.^{33,34}

Variants of anion SEVI and cryo-SEVI have been reported by several laboratories, including those of Gibson,^{35,36} Wang,^{37,38} Garand,^{39,40} Ning,^{3,41} and Heaven;^{42,43} the instruments used in those studies have also achieved sub-meV electron energy resolution. More specialized techniques such as photodetachment microscopy^{44,45} yield even better resolution but are less universally applicable.

Cryo-SEVI experiments in our laboratory and elsewhere were reviewed in 2018.⁴⁶ This Feature Article focuses on results obtained since then, with particular focus on the cryo-SEVI spectra of $NO_3^{-,47}$ the hydrated metal oxide clusters $TiO_3H_2^{-}$ and $ZrO_2H_2^{-,48,49}$ and the transition state precursor anions

 $\rm H_2CC^-$ and $\rm F^-(\rm NH_3)$.^{13,50} In addition, a new experimental direction is discussed in which anions are pre-excited with an infrared (IR) laser prior to photodetachment.^{51,52} This IR cryo-SEVI experiment probes the effect of vibrational excitation on the anion photoelectron spectrum and also provides a new means to measure the vibrational spectrum of a gas phase negative ion.

II. EXPERIMENTAL SECTION

The current configuration of the cryo-SEVI instrument^{32,46} is shown in Figure 1. Anions are generated using a pulsed molecular beam combined with either an electron impact ionizer or a Smalley-type laser ablation source. Recently, Wang and coworkers³⁸ have coupled an electrospray source to a cryo-SEVI instrument. In our experiment, the anions pass through a series of ion optics including a skimmer held at a small negative voltage, a collimating radiofrequency (RF) hexapole, and a mass-selecting RF quadrupole, before entering an RF octupole ion trap held at 5 K. Ions spend \sim 40 ms in the trap, where they are cooled to roughly 10 K via collisions with a helium/H₂ buffer gas mixture before being extracted from the trap into a Wiley-McLaren mass spectrometer.⁵³ After traveling along a perpendicular time-of-flight path, the ions of interest are photodetached inside a seven-plate VMI spectrometer by a pulsed laser beam from a dye laser. In IR cryo-SEVI experiments, the tunable infrared laser used to pre-excite the anions is spatially and temporally overlapped with the photodetachment pulse, as this configuration was found to give the highest IR-induced signals.

Photoelectrons are analyzed with a position-sensitive detector comprising two chevron-stacked microchannel plates coupled to a phosphor screen. A CCD camera takes a 768×768 pixel image of the phosphor screen each experimental cycle. The electron spots are event-counted, centroided, and binned into a $1024 \times$ 1024 pixel grid. We have recently implemented new additions to the event-counting and centroiding algorithm that enable centroid analysis of overlapping electron spots, thereby improving the rate of data collection.⁵⁴ Photoelectron centroids are accumulated over several thousand experimental cycles into a single velocity-mapped image, and the radial and angular distributions of the images are calculated using the Maximum Entropy Velocity Legendre Reconstruction (MEVELER) method⁵⁵ or the more recently developed MELEXIR (Legendre Expanded Image Reconstruction) method.⁵⁶ The electron kinetic energy (eKE) distributions are related to the radial distributions by acquiring images of the well characterized photodetachment transitions of various atomic anions such as O⁻ at several different photon energies.⁵⁷

Since the VMI spectrometer has a roughly constant resolution Δv in velocity space and kinetic energy is proportional to v^2 , the slowest photoelectrons are measured with the highest kinetic energy resolution $\Delta e KE$. For this reason, cryo-SEVI spectra are acquired by first taking an overview spectrum at a relatively high detachment energy and taking subsequent spectra at detachment energies slightly above the features of interest. Narrow high-resolution windows of these spectra are concatenated and appropriately scaled to create one high-resolution photoelectron spectrum. Cryo-SEVI spectra are plotted as a function of electron binding energy (eBE), determined by eBE = hv - eKE, which is independent of the detachment photon energy.

Along with their kinetic energy distributions, VMI gives information about the angular distribution of the detached photoelectrons (PAD) for each transition. For single-photon



Figure 1. Schematic of current configuration of cryo-SEVI instrument, including the capability of infrared excitation with a tunable laser (IR optical parameter oscillator/amplifier) of the anions prior to photodetachment.

detachment using linearly polarized light, the PAD is given by $^{\rm S8, S9}$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\sigma_{\mathrm{tot}}}{4\pi} (1 + \beta P_2(\cos\theta)) \tag{2}$$

where σ_{tot} is the total photodetachment cross section; $P_2(x)$ is the second-order Legendre polynomial; θ is the angle of the photoelectron velocity vector relative to the laser polarization axis; and β is the anisotropy parameter, which ranges between -1 for perpendicular and +2 for parallel detachment. The variation of the anisotropy parameter as a function of eKE reflects the symmetry and angular momentum of the orbital from which the electron is detached.

III. RESULTS AND DISCUSSION

A. Vibronic Coupling in the NO₃ Radical. NO₃ was one of the first radicals to be spectroscopically observed,⁶⁰ and it plays a key role in atmospheric chemistry as an oxidizing agent in the nightime troposphere.⁶¹ Its spectroscopy is complex owing to the presence of two excited states, the $\tilde{A}^2 E''$ and $\tilde{B}^2 E'$ states, that lie 0.876 and 1.873 eV, respectively, above the ground $\tilde{X}^2 A'_2$ state. While the $\tilde{B}^2 E' - \tilde{X}^2 A'_2$ electronic transition has been studied by absorption, laser-induced fluorescence, and dispersed fluorescence, ^{62–66} the $\tilde{A}^2 E'' - \tilde{X}^2 A'_2$ transition is optically forbidden and is thus very weak. ^{67,68} Figure 2 shows an energy level diagram of electronic states of NO₃ and its vibrational modes.

In 1991, we reported the photoelectron spectrum of the nitrate anion, NO₃⁻, in order to explore the vibrational and electronic spectroscopy of the NO₃ radical.⁶⁹ The anion photoelectron (PE) spectrum yielded several notable results. We saw photodetachment not only to the ground $\tilde{X}^2A'_2$ state of NO₃, but also to the previously unobserved \tilde{A}^2E'' state; while the \tilde{A} state is optically dark with respect to the neutral \tilde{X} state, it is accessible via one-electron photodetachment from the anion \tilde{X}^1A_1 state.



Figure 2. Schematic of the electronic energy levels of NO_3^- and NO_3 (left) and the vibrational modes of NO_3 (right). The ν_1 and ν_2 modes are totally symmetric whereas the ν_3 and ν_4 modes are degenerate, each having e' symmetry. Reproduced from ref 47. Copyright 2020 American Chemical Society.

The ground state band obtained by photodetachment at 266 nm is shown in Figure 3a. From the vibrational origin, labeled 0_0^0 we obtained an electron affinity (EA) of 3.937 eV for the NO₃ radical. This band also reveals considerable vibrational structure. Peak b, lying 1057 cm⁻¹ above the vibrational origin, was assigned to the 1_0^1 transition based on the ν_1 symmetric stretch frequency inferred from dispersed fluorescence from the NO₃ $\tilde{B}^2 E'$ state. Most surprising, however, was the observation of a progression of peaks spaced by $\sim 360 \text{ cm}^{-1}$, assigned to transitions involving the ν_4 in-plane bend as indicated in Figure 3a. In the D_{3h} point group, this is a nontotally symmetric mode with e' symmetry. Photodetachment transitions involving odd changes in the quantum number of this mode, such as the 4_0^1 transition, are Franck-Condon forbidden and thus should not appear in the photoelectron spectrum. We attributed these nominally forbidden peaks to pseudo-Jahn-Teller coupling with the $NO_3 B$ state, based on similar reasoning by Cederbaum



Figure 3. Anion photoelectron spectrum of NO_3^- with original assignments (a) and cryo-SEVI spectrum (b). Stick spectrum in bottom panel is calculation showing transitions to Franck–Condon allowed (red) and forbidden (blue) levels of NO_3 . Inset shows prediction of Wigner threshold law for s- and p-wave detachment. As discussed in the text, the main contribution to peak D in the cryo-SEVI spectrum is now believed to be the 3_0^1 transition. Reproduced from ref 47. Copyright 2020 American Chemical Society.

and co-workers⁷⁰ used to explain the photoelectron spectrum of isoelectronic BF₃, an interpretation supported by subsequent theoretical work on NO_3 .⁷¹

In 2007, Stanton⁷² analyzed the spectroscopic data involving the ground state of NO₃ and proposed that the previously observed feature⁷³ at 1492 cm⁻¹ in its infrared spectrum was not the $\nu_3 = 1$ fundamental of the degenerate antisymmetric stretch but instead was the $\nu_1 + \nu_4$ combination band. Subsequent work by Stanton^{74,75} suggested that the ν_1 and ν_3 frequencies are both just above 1000 cm⁻¹ and that the feature assigned to the 1_0^1 transition in Figure 3a was predominantly the Franck–Condon forbidden 3_0^1 transition. A paper in 2018 by Hirota⁷⁶ questioned the existence of strong vibronic coupling between the \tilde{X} and \tilde{B} states and proposed that peak a in the photoelectron spectrum was the Franck–Condon allowed 4_1^1 hot band transition rather than the FC forbidden 4_0^1 transition.

This body of work motivated us to reinvestigate the NO₃⁻ photoelectron spectrum using cryo-SEVI.⁴⁷ A representative set of spectra is shown in Figure 3b. The gray spectrum is an overview spectrum taken at $h\nu = 35137$ cm⁻¹, while the black spectra represent three higher-resolution composite spectra that have been concatenated and normalized to the overview spectrum. There are several key points of comparison between the cryo-SEVI in Figure 3b and photoelectron spectra in Figure 3a. First, the peaks in the cryo-SEVI spectra, particularly in the black spectra, are on average 10 cm⁻¹ wide, considerably narrower than the corresponding features in the PE spectrum. The position of the vibrational origin, peak A, yields a refined value of 3.9289(14) eV for the electron affinity of NO₃. Second, the 4¹₁ hot band in the photoelectron spectrum has disappeared

in the cryo-SEVI spectrum, a consequence of better vibrational cooling in the latter spectrum. In contrast, peak a in the PE spectrum, assigned to the 4_0^1 transition, is clearly present in the cryo-SEVI spectrum as peak B and thus is not a hot band. Hence, the alternative assignment proposed by Hirota is incorrect.

The third point is that the relative intensities of the peaks in the cryo-SEVI spectra differ markedly from those in the PE spectrum. Moreover, the relative intensities in the overview and high-resolution cryo-SEVI spectra are very different. For example, the relative intensity of the vibrational origin, peak A, clearly drops relatively to that of peak B, the 4_0^1 transition, as we progress from the PE spectrum to the overview spectrum and then to the high-resolution composite spectrum. These spectra are taken at progressively lower photon energies, so the eKEs of the two peaks are dropping in this progression of spectra. According to the Wigner threshold law, eq 1, the photodetachment cross section drops with decreasing eKE, but it drops more abruptly at higher values of *l*. Hence, peak A appears to undergo photodetachment at a higher value of *l* than peak B.

These results can be explained through consideration of the selection rules for molecular photodetachment.77,78 Photodetachment to the NO3 ground state involves removal of an electron from an a_2' molecular orbital and can occur by p-wave but not s-wave detachment. Hence, near the threshold, p-wave detachment is the lowest allowed partial wave for the vibrational origin and all Franck-Condon allowed transitions. Peak B, the 4_0^1 transition, is allowed only through vibronic coupling to the higher-lying $\tilde{B}^2 E'$ state, and photodetachment to the $\tilde{B}^2 E'$ state, in which an e' electron is removed, can occur via s-wave detachment. Since the vibronic wave function for the $\nu_{A} = 1$ level of the $X^2A'_2$ state is mixed with the ground vibrational level (or other totally symmetric vibrational levels) of the $\tilde{B}^2 E'$ state, the 4_0^1 transition can occur via s-wave detachment. These considerations explain the experimental result that the intensity of peak A drops off more rapidly than that of peak B as the eKE is lowered and lead to the somewhat counterintuitive result that at low eKE, the cryo-SEVI spectrum is dominated by vibronically allowed rather than FC allowed transitions.

One also notes that the intensity dependence of peak D on eKE is more similar to peak B than peak A. Peak D is thus also assigned to a vibronically allowed rather than FC allowed transition. This peak corresponds to an NO₃ vibrational frequency of 1044 cm⁻¹, which could be either the ν_1 fundamental or the ν_3 fundamental proposed by Stanton. The intensity dependence of this peak supports its assignment to the vibronically allowed 3_0^1 transition rather than the FC allowed 1_0^1 transition, in agreement with Stanton's value for the ν_3 frequency. Moreover, the eKE-dependent photoelectron angular distributions for peaks B and D are similar to one another and differ considerably from that of peak A.⁴⁷ Differing PADs across a photodetachment band are a well-known means of distinguishing FC allowed transitions from those allowed by vibronic coupling,^{79,80} and in this case offer further support for the assignment of peaks B and D to the latter type of transition.

B. Water Splitting by TiO_2^{-} and ZrO_2^{-} . There is considerable interest in understanding the interaction of water with TiO_2 and $ZrO_2^{.81,82}$ For example, photocatalyzed water splitting on TiO_2 and ZrO_2 surfaces has the potential to play a key role in solar-powered fuel cells.^{83–85} These considerations have motivated theoretical^{86–89} and experimental^{90–93} investigations of clusters of water with TiO_2 and ZrO_2 . Electronic structure calculations by Dixon and co-workers on neutral TiO_2 ·H₂O and ZrO_2 ·H₂O clusters show that water splitting to form a



Figure 4. Cryo-SEVi spectrum of $TiO(OH)_2^-$. The blue trace is an overview spectrum, and the black trace is a high-resolution composite spectrum. The red sticks are from a Franck–Condon (FC) simulation. Peaks labeled "B" appear only in the high-resolution spectrum. They are FC forbidden transitions and thus are absent in the FC simulation. Reproduced with permission from ref 49. Copyright 2018 American Institute of Physics.

dihydroxy species (i.e., TiO(OH)₂) is highly exothermic and proceeds over a small barrier.^{86,87} By carrying out photoelectron spectroscopy of the anions TiO₂⁻·H₂O and ZrO₂⁻·H₂O, one can determine whether dissociative chemisorption occurs in the anions and if it does, explore the spectroscopy of the neutral dihydroxy species. Previous conventional anion photoelectron spectra did indeed suggest that TiO₂⁻·H₂O is a dihydroxide,⁹⁰ but no vibrational structure was resolved. We thus decided to investigate both TiO₂⁻·H₂O and ZrO₂⁻·H₂O with cryo-SEVI combined with electronic structure calculations.

The cryo-SEVI spectra of the bare anions TiO_2^- and $ZrO_2^$ are very simple, each showing short progressions in the totally symmetric stretch and bend modes.⁹⁴ The corresponding spectra of $TiO_2^- \cdot H_2O$ and $ZrO_2^- \cdot H_2O$ shown in Figures 4 and 5, respectively, are considerably more complex and differ



Figure 5. Cryo-SEVI spectra of $ZrO(OH)_2^-$. Blue and black traces are overview and high-resolution composite spectra. Red and blue sticks are FC simulations starting from cis- and trans- anion isomers, respectively (see Figure 6). Peak assignments are discussed in the main text. Reproduced with permission from ref 48. Copyright 2020 American Institute of Physics.

substantially from one another.^{48,49} The overview $\text{TiO}_2^- \cdot \text{H}_2\text{O}$ spectrum (in blue) has a pronounced progression (A1, A3, A7, A11) with a characteristic peak spacing of 678 cm⁻¹, along with multiple smaller features. Higher-resolution spectra (in black) reveal an additional series of peaks B1–B11 that are not evident in the overview spectrum. Moreover, the photoelectron angular distributions (PADs) for the A and B peaks are quite distinct; the anisotropy parameter β is around 1.5 for the A peaks and 0 for

the B peaks. The $ZrO_2^{-}H_2O$ spectrum is much more congested, and there are several doublets (B/C, O/P, etc.) where the peak spacing is only ~5 cm⁻¹.

To interpret these results, Franck–Condon simulations based on electronic structure calculations were carried out. Results from ZrO_2^- ·H₂O are shown in Figure 6 and are very similar to



Figure 6. Calculated structures and energetics for *cis, trans,* and physisorbed isomers of $ZrO(OH)_2^-$ (top) and $ZrO(OH)_2$ (bottom). Reproduced with permission from ref 48. Copyright 2020 American Institute of Physics.

those found for $\text{TiO}_2^{-}\cdot\text{H}_2\text{O}$. For both species, the lowest-energy anions and neutrals are the "chemisorbed" *cis*-dihyrodroxy MO(OH)₂ structures, with *trans* structures lying less than 10 meV higher. The barriers for *cis*- \rightarrow *trans* conversion are calculated to be 0.100 and 0.091 eV for Ti and Zr, respectively. The "physisorbed" MO₂⁻·H₂O structures are higher in energy by 2–3 eV. In light of these results, we will refer to these clusters from now on as MO(OH)₂^{0/-}. While the TiO(OH)₂^{0/-} complexes are planar, the ZrO(OH)₂^{0/-} complexes are not, with dihedral angles of 23.0° and 29.2°, respectively.⁴⁸ This nonplanarity has a significant effect on the cryo-SEVI spectra as discussed below.

Franck–Condon simulations of the $TiO(OH)_2^-$ spectrum are shown as red sticks in Figure 4. The simulations assume all anions are in their vibrational ground state and have the *cis*-

isomeric form. They match the structure in the overview spectrum, including the labeled A peaks, very well, and enable assignment of the A peaks to progressions in totally symmetric vibrational modes of TiO(OH)₂. Peak A1 is assigned to the vibrational origin (0_0^0) , yielding an adiabatic electron affinity of 1.259(4) eV for TiO(OH)₂. The peaks spaced by 413 cm⁻¹ (A1, A3, A7, A11) are assigned to the 3_0^n progression in the Ti–OH symmetric stretch. Additional peaks (A2, A6, A10) are assigned to the $4_0^1 3_0^n$ progression involving excitation of the ν_4 Ti–OH symmetric wag at 413 cm⁻¹, and several smaller peaks are assigned to excitation of other totally symmetric vibrations.

However, none of the B peaks appear in the FC simulations. This observation, along with the different PADs seen for the B peaks,⁴⁹ suggests that they involve FC-forbidden transitions of nontotally symmetric vibrational modes that become allowed only through Herzberg-Teller coupling with a low-lying excited state of neutral $TiO(OH)_2$. As seen in NO₃, effects of this type also lead to differences in the low-energy photodetachment cross sections for peaks that are vibronically versus FC-allowed, and indeed the B peaks are seen only in the high-resolution scans where the eKE is low. The spacing between peaks A1 and B1 is 60 cm⁻¹, which is close to the calculated frequency for the ν_8 umbrella mode of $TiO(OH)_{2}$, a nontotally symmetric mode with b_1 symmetry, and in fact all the B peaks can be assigned to excitations of this mode. Hence, we attribute the B peaks to the presence of Herzberg-Teller coupling between the ¹A₁ ground state and an as yet unidentified ${}^{1}B_{1}$ excited state of TiO(OH)₂.

FC analysis of the $ZrO(OH)_2^-$ spectrum revealed two major differences that explain why its appearance is so different from the $TiO(OH)_2^{-}$ spectrum. First, as mentioned above, the anion and neutral Zr complexes are nonplanar with different dihedral angles. Hence, a progression in the low-frequency umbrella mode (ν_{12}) of the neutral is FC allowed, as opposed to being only vibronically allowed as was the case in the $TiO(OH)_2^$ spectrum, leading to many more closely spaced peaks in the $ZrO(OH)_2$ spectrum. This effect alone, however, does not explain the closely spaced doublets in the $ZrO(OH)_2^$ spectrum. These doublets and most other features can be explained by assuming equal population of the nearly degenerate cis and trans isomers of $ZrO(OH)_2^-$. Electronic structure calculations find the two isomers to have nearly identical electron affinities but slightly different vibrational frequencies in several low-frequency, FC active modes. Hence, only one vibrational origin is observed, peak A at 1.1616(7) eV, but peaks B and C are split by 4 cm⁻¹ because the vibrational frequency of the ν_{12} umbrella mode is 65 cm⁻¹ for the *cis* isomer and 69 cm⁻¹ for the *trans* isomers.

The FC simulations for the two isomers are shown by the red (*cis*) and blue (*trans*) sticks in Figure 5. While the fit is not perfect, it enables assignments of most of the experimental features and shows that there is more FC activity from the *trans* than from the *cis* isomer. This enhanced activity arises primarily from the larger change in dihedral angle upon photodetachment of the *trans* isomer. Hence, the *cis* spectrum is dominated by transitions to neutral states involving single excitations of vibrational modes, i.e., peaks B (12_0^1) , F (11_0^1) , I $(11_0^112_0^1)$, and P (9_0^1) . In contrast, in the *trans* spectrum, peaks C, E, and H are a progression in the ν_{12} mode of the *trans* isomer (i.e., $12_0^1-12_0^3$), and there are several combination bands built on this progression such as peak M, assigned to the $11_0^112_0^3$ transition.

Taken together, the $TiO(OH)_2^-$ and $ZrO(OH)_2^-$ spectra show how subtle changes in structure can have major effects on the photoelectron spectrum. Each spectrum has its own

complexities: $TiO(OH)_2^-$ from Herzberg–Teller coupling and $ZrO(OH)_2^-$ from the combination of two isomers being present as well as nonplanar anion and neutral geometries.

C. Transition State Spectroscopy on H₂CC Isomerization and the F + NH₃ Reaction. Negative ion photodetachment has been shown to be a novel method of probing the transition states of benchmark unimolecular and bimolecular reactions.^{14,95,96} The underlying concept is that if a stable negative ion has a geometry similar to the neutral transition state for a chemical reaction, then photodetachment of the anion will access the transition state, and the resulting photoelectron spectrum can reveal a resolved vibrational structure characteristic of the transition state region. Early examples include using the photoelectron spectroscopy of the vinylidene anion, H_2CC^- , to probe the dynamics of neutral vinylidene isomerization to acetylene (HCCH).^{12,97} There have also been numerous studies of several bimolecular hydrogen transfer reactions via photodetachment of the appropriate hydrogen bonded negative ion, such as photodetaching FH₂⁻ to investigate the transition state of the $F + H_2$ reaction.⁹⁸ The higher resolution offered initially by anion ZEKE spectroscopy and, more recently, cryo-SEVI has revealed additional vibrational features not seen in conventional photoelectron spectra, most notably the spectroscopic observation of reactive resonances in the I + HI and F + H₂ reactions via photodetachment of IHI⁻ and FH₂^{-.23,99} Entrance channels for the Cl + H_2 and F + CH₄ reactions have also been probed.^{100,101} Here, recent results are described in which cryo-SEVI spectra of H_2CC^- and FNH_3 are used to probe the transition states for the unimolecular H₂CC·HCCH isomerization reaction¹³ and the bimolecular reaction $F + NH_3 \cdot HF + NH_2 \cdot {}^{50}$

Vinylidene, H₂CC, is the simplest carbene and as such is of considerable interest in organic chemistry.¹⁰² As shown schematically in Figure 7a, it lies 1.925 eV above acetylene and can isomerize to HCCH over a small (0.13 eV) barrier.^{103–105} The isomerization reaction is the simplest 1,2hydrogen shift and is thus a benchmark chemical reaction.¹ This consideration has motivated many experimental^{12,107-109} and theoretical¹¹⁰⁻¹¹⁴ studies of how the vibrational energy levels of H₂CC and HCCH are coupled to one another. One approach to this problem has been to map out the excited vibrational energy levels of HCCH that lie above the H₂CC minimum and search for perturbations with H2CC levels.^{108,115,116} A more direct approach, developed by Lineberger, ¹² makes use of the fact that H_2CC^- is the stable anionic form of H₂CC and that photodetachment of this species directly accesses the neutral H₂CC well, corresponding to the $X^{1}A_{1}$ state of vinylidene. The resulting photoelectron spectrum shows resolved vibrational structure. Remarkably, the peaks in the singlet band are notably broader than those seen upon photodetachment to the higher-lying $\tilde{a}^{-3}B_2$ triplet state of H₂CC that is known to have a much larger barrier to isomerization.¹¹⁷ On this basis, the broadening of the peaks in the singlet spectrum was attributed to isomerization to acetylene on a subpicosecond time scale. This result motivated multiple investigations of H₂CC⁻ in our laboratory and in Canberra to map out photodetachment to both single and triplet states of H₂CC with high resolution and to explore vibrational autodetachment in H₂CC^{-.13,117,118} Below, results are described in which cryo-SEVI combined with quantum dynamics calculations probes how (or if) H₂CC vibrations mix with high-lying HCCH vibrational states.

Figure 7b shows cryo-SEVI spectra of H_2CC^- and D_2CC^- along with their peak assignments; blue, black, and red traces are



Figure 7. Schematic of $H_2CC \leftrightarrow HCCH$ isomerization coordinate (top), showing how photodetachment from H_2CC^- accesses the vinylidene structure. Bottom panels show cryo-SEVI spectra of H_2CC^- and D_2CC^- . Overview and high-resolution spectra are shown as blue and black traces, respectively. Top and bottom panels are adapted from ref 114, Copyright 2015 American Chemical Society, and with permission from ref 13, Copyright 2017 American Association for the Advancement of Science.

overview spectra, high-resolution composite spectra, and FC simulations, respectively.¹³ The high-resolution D_2CC^- spectra show no evidence of spectral broadening beyond that consistent with an unresolved rotational profile, and this is also the case for most features in the H₂CC⁻ spectrum. However, the situation is more complex upon excitation of the ν_5 antisymmetric stretch or ν_6 rocking vibration of H₂CC, both of which are nontotally symmetric. The weak 6_0^1 and 6_0^2 peaks in the H₂CC⁻ spectrum are notably broader than the corresponding peaks in the D₂CC⁻ spectrum. The 5_0^1 transition, which is a single peak in the D₂CC⁻ spectrum, looks to be a multiplet of closely spaced peaks in the H_2CC^- spectrum. Hence, excitation of the ν_5 and ν_6 vibrations appears to yield much stronger coupling to the HCCH well than excitation of the totally symmetric ν_2 and ν_3 vibrations. This interpretation is supported by quantum dynamics calculations, displayed in Figure 8, that show that the wave functions of the 6^2 and 5^1 H₂CC vibrational levels have substantial amplitude at the HCCH geometry (upper right corner). The overall interpretation of these results is that there is coupling between H₂CC and HCCH vibrational energy levels, but this coupling is vibrationally state-specific and only activated upon excitation of the ν_5 and ν_6 modes of H₂CC.

The cryo-SEVI results on H_2CC^- differ from the earlier photoelectron spectra obtained by Lineberger¹² in that most of the vibrational features do not exhibit any broadening that one might attribute to mixing with HCCH vibrational energy levels. The origin of this discrepancy is unclear; it is not due to the higher energy resolution of the cryo-SEVI spectrum. However, the anion rotational temperature characteristic of the ion source (a flowing afterglow) used in the photoelectron spectroscopy experiment is higher than in cryo-SEVI, so it is possible that rotation promotes mixing with acetylene and thus leads to broader spectral features. Further theoretical investigation of this hypothesis would be of considerable interest.

As mentioned above, negative ion photodetachment is uniquely suited to carry out transition state spectroscopy experiments on bimolecular reactions. Much of this work has been carried out on triatomic systems. However, a cryo-SEVI experiment on CH_3OHF^- successfully mapped out a series of exit channel Feshbach resonances corresponding to metastable



Figure 8. Calculated wave functions for vibrational ground state (left), $v_6 = 2$ (center), and $v_5 = 1$ (right) vibrational states of H₂CC, projected onto H₂CC (top) and HCCH geometries (bottom). The angles θ_1 and θ_2 are defined in the inset. Reproduced with permission from ref 13. Copyright 2017 American Association for the Advancement of Science.

We recently measured cryo-SEVI spectra of the related system FNH_3^- to investigate the bimolecular F + NH₃ reaction.⁵⁰ This reaction has been studied previously by infrared chemiluminescence^{121–123} and with crossed molecular beams scattering.¹²⁴ Potential energy surfaces for this reaction have been reported, ^{125,126} and the dynamics on these surfaces were explored using quasi-classical trajectory calculations.^{126,127}

The relevant energetics and geometries for this system are shown in Figure 9. 50 The reaction is exothermic by 1.3 eV and



Reaction coordinate

Figure 9. Calculated reaction coordinate and energetics for $F + NH_3$ reaction (top) and FNH_3^- anion (bottom). RC, TS, and PC refer to the reactant complex, transition state, and product complex, respectively. Energies are given in wavenumbers relative to the $F + NH_3$ reactant asymptote. Reproduced with permission from ref 50. Copyright 2023 Springer Nature.

has a submerged barrier between reactant $F \cdot NH_3$ and product $FH \cdot NH_2$ complexes. The anion is strongly hydrogen-bonded with a calculated dissociation energy of 0.70 eV and has good geometric overlap with the neutral transition state. The goal of the experiment, then, was to observe vibrational structure associated with not only the product complex, as was seen in CH_3OHF^- , but also the transition state and reactive complex, and, possibly, dynamical resonances lying above the F + NH_3 reactant asymptote.

The experimental spectra are shown as blue (overview) and black (high-resolution composite) traces in Figure 10; the lower two traces are simulated spectra from reduced dimensionality quantum dynamics calculations. The energies of the transition state and reactant asymptote are shown as gray and black arrows, respectively. There is substantial vibrational structure in the spectrum whose appearance evolves notably with increasing electron binding energy. Peaks a-j are spaced by about 300 cm⁻¹. They lie below the transition state energy and are attributed to resonances associated with the product complex that can undergo vibrational predissociation to NH₂ + HF.

Quantum dynamics calculations of the resonance wave functions⁵⁰ show that the peaks correspond to progressions in the NH₂·HF hindered translational mode at 251 cm⁻¹ and a more complex vibration at 829 cm⁻¹ in which pseudorotation of the HF is coupled to NH₂ out-of-plane wagging. The out-of-plane motion is activated by the flattening of the NH₃ pyrimidal structure in the anion upon photodetachment to the NH₂·HF product complex.

At higher binding energy, peaks k–o are considerably broader. They lie in the energy range just above the transition state barrier in Figure 9; hence, the neutral states have amplitude on both sides of the barrier. The vibrational structure responsible for these peaks is quite complex; quantum dynamics calculations show that the neutral states have three quanta of excitation in the HF stretch, along with excitations in the out-ofplane wagging mode of the NH₂ (~318 cm⁻¹) and a pseudorotation of the HF moiety (655 cm⁻¹). Finally, peaks q–t lie above the reactant asymptote and thus represent reactive resonances that can in principle be accessed in F + NH₃ reactive scattering. Additional structure in the experimental spectrum beyond peak t is also likely to be from reactive resonances, but the poorer agreement with theory in this region precludes a definitive assignment.

Overall, the F^-NH_3 cryo-SEVI spectrum comprises a very rich resonance structure spanning the exit channel, the transition state region, and states above the reactant asymptote. In contrast to other bimolecular transition states studied with this technique,¹¹⁹ the vibrational structure cannot be explained in terms of a high-frequency hydrogen atom motion and a much lower frequency stretching motion involving the heavier atoms. The complexity of the spectrum reflects the fact that $F + NH_3$ is not a simple hydrogen transfer reaction because the geometry of the NH_3 moiety evolves significantly en route to the $HF + NH_2$ products. Hence, assignment of the vibrational structure is possible only by comparison with multidimensional quantum dynamics calculations.

D. Vibrational Pre-excitation of Anions: IR Cryo-SEVI. A primary goal of cryo-SEVI is to use cryogenic cooling to bring the anions into their ground vibrational state, thereby eliminating vibrational hot bands in the photoelectron spectrum, and to rotationally cool the anions as much as possible to obtain narrow rotational profiles. However, the extent to which one can extract vibrational frequencies from these spectra and, more generally, learn about the neutral potential energy surface accessed by photodetachment is limited by the selection rules that govern photoelectron spectroscopy.

The intensities of vibrational transitions in photoelectron spectra are typically governed by Franck-Condon factors. In the absence of vibronic coupling, this means that starting from the anion ground vibrational state, one only observes progressions in totally symmetric vibrational modes for which there is a normal coordinate displacement upon photodetachment. For symmetry reasons, there is no such displacement for nontotally symmetric modes, and while CH, NH, and OH stretches in molecules can be totally symmetric, changes in the corresponding bond lengths upon anion photodetachment are generally very small.^{128–130} Hence, the situation on the left side of Figure 11 holds, in which transition intensities from the anion ground state to the v = 1 level of a nontotally symmetric mode or a mode in which there is no normal coordinate displacement are either zero by symmetry or negligibly small. However, excitation of the v = 1 level of one of these modes in the anion results in a fully FC-allowed transition to the neutral v = 1 level, as shown on the



Figure 10. Experimental (top two traces) and simulated (bottom two traces) cryo-SEVI spectra of FNH_3 . Aqua vertical lines are energies of $HF(v) + NH_2$ product states. Gray and black arrows are energies of transition state and $F + NH_3$ reactant asymptote, respectively. Peak assignments are discussed in text. Reproduced with permission from ref 50. Copyright 2023 Springer Nature.



Figure 11. Principle of IR cryo-SEVI experiment. The v = 1 level of a nontotally symmetric mode is generally inaccessible from the anion vibrational ground state (left). Vibrational pre-excitation of a nontotally symmetric mode activates new features in the cryo-SEVI spectrum (right). Reproduced from ref 52. Copyright 2023 American Chemical Society.

right side of Figure 11, leading to new features in the photoelectron spectrum. Hence, IR pre-excitation of negative ions has the potential to access previously unseen neutral vibrational states and, more generally, expand the range of nuclear configurations probed on the neutral potential energy surface.

In order to carry out experiments of this type, we have incorporated a tunable IR laser into our experiment that excites the cryogenically cooled anions prior to photodetachment. This new experimental configuration, IR cryo-SEVI, has been carried out on a diatomic anion, $OH^{-,51}$ and, more recently, on the polyatomic vinoxide anion $CH_2CHO^{-,52}$ The OH^{-} anion served as a first demonstration of the technique; it is a special case in the sense that the cryo-SEVI spectrum is fully rotationally resolved⁵¹ and the gas phase infrared spectrum is well characterized.^{131,132} The vinoxide results illustrate the potential and complexity of IR cryo-SEVI, most notably the observation of effects associated with anharmonic coupling between vibrational modes in the anion and neutral as well as the dependence of these effects on the vibrational frequency of the pre-excited mode.

The hydroxide anion OH⁻ has been extensively studied by photodetachment, including rotationally resolved threshold photodetachment measurements by Lineberger¹³³ and Wester¹³⁴ as well as photodetachment microscopy experiments by Blondel.¹³⁰ The rotationally resolved infrared spectrum of OH⁻ was measured by Saykally using velocity-modulated IR spectroscopy,^{131,135} while the open-shell $X^2\Pi$ ground state of the OH radical has been characterized extensively using microwave spectroscopy^{136,137} and other methods.^{138,139} This body of work leads to the energy level diagram in Figure 12, showing the rovibrational structure of the X ¹ Σ ⁺ anion ground state and the two spin–orbit manifolds of OH.

Figure 13 shows the cryo-SEVI spectrum of OH⁻ without (black) and with (red) IR pre-excitation.⁵¹ Both spectra are fully rotationally resolved and assigned; selected transitions are indicated in Figures 12 and 13. The two most intense IR-off transitions, the R3(0) and R1(0) transitions, originate from the (v = 0, J = 0) state of the anion (labeled as (0,0) in Figure 12). The relative intensities of these peaks compared to those originating from higher-lying anion rotational states yield a rotational temperature of \sim 20 K. The red trace shows the IR cryo-SEVI spectrum where the IR laser is tuned to the R(0)transition of the anion at 3591 cm⁻¹, exciting anions from the (0,0) level to (1,1) level. One observes significant depletion of the R3(0) and R1(0) transitions, while five new transitions originating from the (1,1) anion appear that are assigned in Figure 13. These are "sequence band" transitions between the ν = 1 anion and neutral levels and are interspersed with the transitions originating from the anion v = 0 level. One can also obtain a "vibrational action spectrum" by scanning the IR laser and following the change in intensity of one of the red IR-on features, as was done for the R3(1) peak at 14799 cm^{-1,51}

While the idea of IR cryo-SEVI seems simple in principle, the spectra in Figure 13 illustrate that at least for OH^- , very cold ions and high photoelectron kinetic energy resolution are required. The red peaks resulting from vibrationally excited anions all lie within a few cm⁻¹ of the nearest ground state feature and would



Figure 12. Vibration–rotation levels of OH⁻ (bottom) and the two spin–orbit manifolds of OH (top). Selected photodetachment transitions (green) from the OH⁻(0,0) and (1,1) states are shown. The IR laser vibrationally excites OH⁻ via the R(0) transition. Reproduced from ref 51. Copyright 2021 American Chemical Society.



Figure 13. Cryo-SEVI spectrum of cold (black) and vibrationally excited (red) OH⁻. Upon vibrational excitation, the R3(0) and R1(0) features are depleted and several new peaks appear. Adapted from ref 51. Copyright 2021 American Chemical Society.

thus be obscured if the resolution were suboptimal or if the anions were warmer; the latter scenario would lead to more rotational features in the IR-off spectrum that overlap spectrally with the IR-on peaks. In addition, the fraction of vibrationally excited molecules would be reduced when higher rotational levels of the vibrational ground state are populated, as those require slightly different IR excitation frequencies.

The extension of IR cryo-SEVI to polyatomic molecules presents several challenges. First, although infrared spectra of several negative ions have been obtained through "tagging" experiments,^{140,141} it is still the case that relatively few vibrational frequencies are known for gas phase anions. Second, at the few-cm⁻¹ resolution of the cryo-SEVI instrument, one does not expect to resolve individual ro-vibrational transitions in polyatomic anions. Finally, the anion vibrational state excited by



Figure 14. Excitation of the $\nu_4 = 1$ level of the vinoxide anion at 1570 cm⁻¹. IR-off (a) and IR-on (b) photoelectron images show additional rings from IR excitation. Panel c compares IR-on (red) and IR-off (black) cryo-SEVI spectra, while panel d shows (IR-on) – (IR-off) difference spectrum. Positive and negative peaks originate from $\nu_4 = 1$ and $\nu_4 = 0$ levels of vinoxide, respectively. Panel e shows a simulated photoelectron spectrum from the anion $\nu_4 = 1$ level within harmonic and FC approximations. Adapted from ref 52. Copyright 2023 American Chemical Society.

the IR laser may be anharmonically coupled to nearby vibrational levels,¹⁴² and similar coupling may be at play in the neutral vibrational levels accessed by photodetachment. Both effects can lead to more complexity in the resulting photoelectron spectrum than implied by the simple picture in Figure 11.

The vinoxide anion was selected as a suitable polyatomic since both the anion and neutral are reasonably well characterized. Photodetachment of the anion has been investigated in several experiments,^{143–146} including a SEVI study in our group prior to the installation of cryogenic cooling.¹⁴⁷ The microwave,¹⁴⁸ infrared,^{149,150} and electronic spectra^{151–155} of the vinoxy radical and its photodissociation dynamics¹⁵⁶ have also been reported. The electron affinity of vinoxy is 1.825 eV, which is convenient for photodetachment with a dye laser, and the SEVI spectrum exhibits some vibrational structure but is relatively sparse. Quantum chemistry calculations on the vinoxide anion at the B2PLYP-D3/aug-cc-pVTZ level of theory including anharmonicity find two strong infrared transitions, the ν_4 CO stretch at 1560 cm⁻¹ and the ν_3 carbonyl CH stretch at 2512



Figure 15. Effect of excitation of the $\nu_3 = 1$ mode of vinoxide at 2546 cm⁻¹. Panel a shows IR-on (red) and IR-off (black) cryo-SEVI spectra. Panel b shows the IR (on–off) difference spectrum. Panel c shows an FC simulation of the spectrum from the vinoxide $\nu_3 = 1$ level within the harmonic approximation. Structure below and above the vibrational origin (0_0^0 , see Figure 14) in panel b is from anharmonic coupling effects in the anion and neutral, respectively. Reproduced from ref 52. Copyright 2023 American Chemical Society.

cm^{-1,52} These two modes were thus targeted for our IR cryo-SEVI experiment,⁵² with the calculated frequencies taken as starting points for our search.

Figure 14a,b shows photoelectron images of vinoxide with the IR laser off (a) and tuned to the ν_4 transition at 1570 cm⁻¹ (b). The corresponding photoelectron spectra are shown in black and red, respectively, in Figure 14c. The vibrational origin (0_0^0) is the largest peak in the IR-off spectrum, and there is FC activity in the totally symmetric ν_9 (CCO bend), ν_7 (CC stretch), and ν_4 (CO stretch) modes. The additional rings in Figure 14b, indicated with arrows, represent hot-band transitions from the vibrationally excited anion and appear as small peaks below the vibrational origin in the red trace in Figure 14c. Figure 14d shows the (IR on) - (IR off) difference spectrum; here, the negative peaks represent ground state features that are depleted by the IR laser pulse, while the positive peaks are transitions from vibrationally excited anions. Peak assignments for the positive features are shown; the peak at lowest eBE is the 4_1^0 transition, and the other peaks are transitions from the $\nu_4 = 1$ level of the anion to various vibrational states of vinoxy. The low eBE region of the IR-on photoelectron spectrum, showing a progression in the ν_9 mode $(4_1^0 9_0^n)$, is very similar to the IR-off spectrum, except that the peaks in the IR-on spectrum are shifted to lower eBE by the anion ν_4 frequency. At larger eBE, however, the IR-on photoelectron spectrum is markedly different, showing FC activity in the ν_5 and ν_8 modes, which are not observed in the IR-off spectrum. A harmonic Franck-Condon simulation (Figure 14e) assuming all anions are in the $\nu_4 = 1$ level simulates the IR-on spectrum very well. This agreement

shows vibrational excitation of the anion ν_4 mode remains "in place" on the time scale of our experiment (~10 ns) and is well described within the harmonic approximation typically used for the interpretation of photoelectron spectra.

Results from excitation of the ν_3 mode at 2546 cm⁻¹ are shown in Figure 15. The top panel shows IR-off (black) and IRon spectra (red), the middle panel is the difference spectrum, and the bottom panel shows a harmonic FC simulation starting from the anion $\nu_3 = 1$ level. Clearly, the difference spectrum is much more complex than the ground state spectrum. Moreover, it is in poor agreement with the FC simulation, which predicts a few ν_3 sequence band transitions (3¹₁, etc.) above the vibrational origin and no transitions below the origin. The experimental difference spectrum, in contrast, shows many small features below the origin, and a comparison to the FC simulation suggests that each ν_3 sequence band appears to be split into four closely spaced transitions.

These effects can be explained within the context of anharmonic coupling within the anion and neutral. Essentially, the nominal $\nu_3 = 1$ anion and neutral levels are mixed with nearby vibrational states, so that the individual vibrational eigenstates are linear combinations of multiple harmonic zero-order vibrational states. A near-quantitative agreement with experiment is obtained using a newly developed implementation of vibrational perturbation theory (VPT)^{52,157–161} that identifies relevant anharmonic couplings among nearly degenerate vibrational states and provides the contributions of the individual harmonic states to the vibrational eigenstate. The underlying concept is illustrated in Figure 16. In the absence of



Figure 16. Mechanism for the appearance of new peaks in the cryo-SEVI spectrum owing to anharmonic coupling between anion vibrational levels. Photodetachment from the zeroth-order $\nu_3 = 1$ anion state (left) only accesses the neutral $\nu_3 = 1$ level (see FC simulation in panel c of Figure 15) while photodetachment of coupled anion state (right) accesses multiple neutral vibrational states. Reproduced from ref 52. Copyright 2023 American Chemical Society.

anharmonic coupling, photodetachment from the anion $\nu_3 = 1$ state $|\phi_{\nu_3}^{"}\rangle$ accesses the corresponding neutral $\nu_3 = 1$ state $|\phi_{\nu_3}^{'}\rangle$, leading to the 3¹₁ transition seen in the FC simulation. However, anharmonic coupling in the anion can mix the zero-order $|\phi_{\nu_3}^{"}\rangle$ and $|\phi_{\nu_4+\nu_8}^{"}\rangle$ states, resulting in a coupled anion eigenstate $|\chi_i^{"}\rangle$ that can undergo photodetachment to the neutral $|\phi_{\nu_4+\nu_8}^{'}\rangle$ state in addition to the $|\phi_{\nu_3}^{'}\rangle$ state. Similarly, owing to anharmonic couplings in the radical, the neutral vibrational eigenstates $|\chi_j^{'}\rangle$ are linear superpositions of the $|\phi_{\nu_3}^{'}\rangle$ zero-order state and other nearby vibrational states, giving each of those neutral eigenstates ν_3 character.

Under these circumstances, the relative intensity of a transition between anion and neutral eigenstates $|\chi_i''\rangle$ and $|\chi_j\rangle$ is given by

$$|\langle \chi_{j}'|\chi_{i}''\rangle|^{2} = \left|\sum_{j,k} c_{k}' c_{j}'' \langle \phi_{k}'|\phi_{j}''\rangle\right|^{2}$$
(3)

The VPT analysis shows that the structure below the vibrational origin results primarily from anharmonic coupling within the anion, whereas above the origin the quartets corresponding to the ν_3 sequence band mostly reflect neutral anharmonic couplings. In fact, three of the peaks within these quartets can be considered to be polyads based on the $\nu_3 = 1$ neutral level, while the fourth peak results from photodetachment to neutral states involving $\nu_4 + \nu_8$ excitation.

The vinoxide study leads to several interesting conclusions. It demonstrates that IR cryo-SEVI can be applied to polyatomic anions. Excitation of the vinoxide CO stretch at 1570 cm⁻¹ yields a photoelectron spectrum that is readily interpreted and assigned within the harmonic approximation that is typically used for the interpretation of photoelectron spectra. The significant differences between the results at 1570 and 2546 cm⁻¹ show that at the higher vibrational frequency, effects attributed to anharmonic coupling in both the vinoxide anion and vinoxy radical are quite prominent but nonetheless can be analyzed using vibrational perturbation theory. The ability to spectroscopically determine which modes are coupled through

anharmonic interactions complements previous work on intramolecular vibrational energy redistribution in polyatomic neutral molecules,^{162,163} most notably the IR chemiluminescence studies of McDonald and co-workers.^{142,164} As further applications of IR cryo-SEVI are explored, the extent to which anharmonic coupling grows in with increasing vibrational excitation and complexity of the molecule will play a major role in understanding this new experimental method.

IV. CONCLUDING REMARKS

Cryo-SEVI continues to be a powerful experimental tool that enables one to obtain high-resolution photoelectron spectra for an array of negative ions ranging from transition metal and lanthanide atoms to complex, polyatomic clusters. While this Feature Article primarily focuses on experiments carried out in Berkeley, cryo-SEVI instruments are operating at several other laboratories in the United States and elsewhere. From a personal perspective, there are two key questions regarding the future directions of the technique. First, what are the limits on the size and complexity of a target system for which cryo-SEVI will yield a well-resolved spectrum? The answer clearly depends on the extent of multimode Franck-Condon activity, or, put another way, how significant the geometry changes of the anion are upon photodetachment. It also depends on how effectively the anions can be cooled, as there is evidence that vibrational cooling in our cryogenic ion trap is incomplete for, say, polyatomic metal oxide cluster anions. Second, the IR cryo-SEVI experiment described herein has considerable potential. A primary goal of this work is its application to both unimolecular and bimolecular transition state spectroscopy systems, since vibrational excitation of the anion enlarges the Franck-Condon accessible transition state region and thus, in principle, enables a more complete mapping of the neutral potential energy surface on which the chemical reaction occurs. On the other hand, as the number of atoms and/ or the infrared excitation energy increases, the interpretation of the resulting spectra becomes more complicated and, at the same time, more interesting, owing to the anharmonic coupling effects seen here for the vinoxide example. We thus hope in the near future to better understand the extent to which this new experiment can be applied to the many anions that have been studied by photoelectron spectroscopy and its variants.

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Notes

The author declares no competing financial interest.

Biography



Daniel M. Neumark was born in 1955 in Chicago, IL. He was an undergraduate at Harvard, then went to graduate school at the University of California, Berkeley. There, he worked in Yuan Lee's research group and received his Ph.D. in 1984. From 1984 to 1986, he was a postdoctoral fellow with Carl Lineberger at the University of Colorado, Boulder. He joined the Berkeley Chemistry Department as an Assistant Professor in 1986 and has been there ever since. His research interests encompass gas phase studies of reaction dynamics via negative ion photodetachment, spectroscopy and scattering experiments involving liquid microjets, and attosecond dynamics of atoms, molecules, and solids.

ACKNOWLEDGMENTS

This research is supported by the Air Force Office of Scientific Research under Grant No. FA9550-23-1-0545. Additional support was provided by the AFOSR Defense University Research Instrumentation Program under Grant FA9550-19-1-0139, DEF. The author thanks Martin DeWitt, Jascha Lau, Tonia Solomis, Mark Babin, Jessalyn Devine, Marissa Weichman, John Stanton, Anne McCoy, Mark Boyer, Hua Guo, Hongwei Song, and Hrant Hratchian for their contributions to the work described in this Feature Article.

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