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

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ABSTRACT: Slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI) is a high-resolution variant of anion photoelectron spectroscopy that has been applied with considerable success over the years to the study of radicals, size-selected clusters, and transition states for unimolecular and bimolecular reactions. Cryo-SEVI retains the versatility of conventional anion 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, mass-selected 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 size-selected clusters.7–11 Finally, photodetachment of stable anions can access the transition states of unimolecular12,13 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 complex, and it is not yet clear how it can be applied to anions.

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complex than first believed and involves field ionization of high-
ly 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 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 \( \Gamma^+(\text{H}_2\text{O})^− \), FeO\(^+\), and other anions.24,25

These experiments proved very challenging and were limited
in generality by the Wigner threshold law26,27,

\[
\sigma \propto (\text{eKE})^{1/2}
\]

which dictates that at low electron kinetic energy (eKE), the
photodetachment cross section \( \sigma \) scales with \( (\text{eKE})^{1/2} \), 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 photodetach-
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 measure-
ment. 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
\( \text{cm}−1 \) for the slowest electrons with kinetic energy below 100
\( \text{cm}−1 \). 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
pressures 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
umerous laboratories, including those of Gibson,35,36 Wang,37,38
Garand,39,40 Ning,41,42 and Heaven.43,44 The instruments used in
those studies have also achieved sub-meV electron energy
resolution. More specialized techniques such as photodetach-
cross section microscopy24,45 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\(_3^−\) and ZrO\(_2\)H\(_2^+\),47

\[ \text{H}_2\text{CC}^− \text{ and F}^−(\text{NH}_3)_{13,50} \]

In addition, a new experimental direction is discussed in which anions are pre-excited with an infrared (IR) laser prior to photodetachment.31,52 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 instrument32,46 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 co-
workers52 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 \( \sim 40 \text{ ms} \) in the trap, where they
are cooled to roughly 10 K via collisions with a helium/H\(_2\) 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 ×
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
\( \Delta v \) in velocity space and kinetic energy is proportional to \( v^2 \),
the slowest photoelectrons are measured with the highest kinetic
energy resolution \( \Delta \text{eKE} \). 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
ergies 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 (e\(\text{BE}\)), determined by e\(\text{BE} = \nu - \text{eKE} \),
which is independent of the detachment photon energy.

Along with their kinetic energy distributions, VMI gives
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Along with their kinetic energy distributions, VMI gives information about the angular distribution of the detached photoelectrons (PAD) for each transition. For single-phonon
detachment using linearly polarized light, the PAD is given by
\[ \sigma_{\text{tot}} = \frac{\sigma_{\text{tot}}}{4\pi} (1 + \beta P_2(\cos \theta)) \] (2)

where \( \sigma_{\text{tot}} \) is the total photodetachment cross section; \( P_2(x) \) is the second-order Legendre polynomial; \( \theta \) is the angle of the photoelectron velocity vector relative to the laser polarization axis; and \( \beta \) 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 NO\(_3\) Radical. NO\(_3\) was one of the first radicals to be spectroscopically observed, and it plays a key role in atmospheric chemistry as an oxidizing agent in the nighttime troposphere. Its spectroscopy is complex owing to the presence of two excited states, the \( \tilde{A}^2E'' \) and \( \tilde{B}^2E' \) states, that lie 0.876 and 1.873 eV, respectively, above the ground \( \tilde{X}^2A'_1 \) state. While the \( \tilde{B}^2E' - \tilde{X}^2A'_1 \) electronic transition has been studied by absorption, laser-induced fluorescence, and dispersed fluorescence, the \( \tilde{A}^2E'' - \tilde{X}^2A'_1 \) transition is optically forbidden and thus very weak. Figure 2 shows an energy level diagram of electronic states of NO\(_3\) and its vibrational modes.

In 1991, we reported the photoelectron spectrum of the nitrate anion, NO\(_3^-\), in order to explore the vibrational and electronic spectroscopy of the NO\(_3\) radical.\(^{47}\) The anion photoelectron (PE) spectrum yielded several notable results. We saw photodetachment not only to the ground \( \tilde{X}^2A'_1 \) state of NO\(_3\), but also to the previously unobserved \( \tilde{A}^2E'' \) state; while the \( \tilde{A} \) state is optically dark with respect to the neutral \( X \) state, it is accessible via one-electron photodetachment from the anion \( \tilde{X}^1A'_1 \) state.

The ground state band obtained by photodetachment at 266 nm is shown in Figure 3a. From the vibrational origin, labeled 0, we obtained an electron affinity (EA) of 3.937 eV for the NO\(_3\) radical. This band also reveals considerable vibrational structure. Peak b, lying 1057 cm\(^{-1}\) above the vibrational origin, was assigned to the \( \nu_1 \) transition based on the \( \nu_1 \) symmetric stretch frequency inferred from dispersed fluorescence from the NO\(_3\) \( \tilde{B}^2E' \) state. Most surprising, however, was the observation of a progression of peaks spaced by \( \sim 360 \) cm\(^{-1}\), assigned to transitions involving the \( \nu_4 \) in-plane bend as indicated in Figure 3b. 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 \( \nu_4 \) 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\(_3\) \( \tilde{B} \) state, based on similar reasoning by Cederbaum.

![Figure 1](https://example.com/figure1.png)

**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.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Schematic of the electronic energy levels of NO\(_3^-\) and NO\(_3\) (left) and the vibrational modes of NO\(_3\) (right). The \( \nu_1 \) and \( \nu_2 \) modes are totally symmetric whereas the \( \nu_3 \) and \( \nu_4 \) modes are degenerate, each having \( e' \) symmetry. Reproduced from ref 47. Copyright 2020 American Chemical Society.
and co-workers used to explain the photoelectron spectrum of isoelectronic BF, an interpretation supported by subsequent theoretical work on NO.

In 2007, Stanton analyzed the spectroscopic data involving the ground state of NO, and proposed that the previously observed feature at 1492 cm$^{-1}$ in its infrared spectrum was not the $\nu_3 = 1$ fundamental of the degenerate antisymmetric stretch but instead was the $\nu_3 + \nu_4$ combination band. Subsequent work by Stanton suggested that the $\nu_4$ and $\nu_5$ frequencies are both just above 1000 cm$^{-1}$ and that the feature assigned to the $^3\Sigma_g^+$ transition in Figure 3a was predominantly the Franck-Condon forbidden $^3\Sigma_g^+$ transition. A paper in 2018 by Hirota questioned the existence of strong vibronic coupling between the $X$ and $B$ states and proposed that peak a in the photoelectron spectrum was the Franck-Condon allowed $4\Sigma_u^+$ hot band transition rather than the FC forbidden $4\Sigma_u^+$ transition.

This body of work motivated us to reinvestigate the NO$_3^-$ photoelectron spectrum using cryo-SEVI. 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 NO$_3$.

Second, the $4\Sigma_u^+$ 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 $4\Sigma_u^+$ 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 $4\Sigma_u^+$ 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. Molecular photodetachment to the NO$_3$ ground state involves removal of an electron from an $\alpha\Sigma_u^+$ 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 $4\Sigma_u^+$ transition, is allowed only through vibronic coupling to the higher-lying $B^2\Pi$ state, and photodetachment to the $B^2\Pi$ state, in which an e$^-$ electron is removed, can occur via s-wave detachment. Since the vibronic wave function for the $\nu_4 = 1$ level of the $X^2\Sigma_g^+$ state is mixed with the ground vibrational level (or other totally symmetric vibrational levels) of the $B^2\Pi$ state, the $4\Sigma_u^+$ 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 transition rather than FC allowed transition. This peak corresponds to an NO$_3$ vibrational frequency of 1044 cm$^{-1}$, which could be either the $\nu_3$ fundamental or the $\nu_4$ fundamental proposed by Stanton. The intensity dependence of this peak supports its assignment to the vibronically allowed $3\Sigma_g^+$ transition rather than the FC allowed $3\Sigma_g^+$ transition, in agreement with Stanton’s value for the $\nu_4$ 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. Differing PADs across a photodetachment band are a well-known means of distinguishing FC allowed transitions from those allowed by vibronic coupling 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$_2$. 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. These considerations have motivated theoretical and experimental investigations of clusters of water with TiO$_2$ and ZrO$_2$. Electronic structure calculations by Dixon and co-workers on neutral TiO$_2$:H$_2$O and ZrO$_2$:H$_2$O clusters show that water splitting to form a...
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 TiO\(_2^−\)-H\(_2\)O and ZrO\(_2^−\)-H\(_2\)O, 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 TiO\(_2^−\)-H\(_2\)O is a dihydroxide,\(^{90}\) but no vibrational structure was resolved. We thus decided to investigate both TiO\(_2^−\)-H\(_2\)O and ZrO\(_2^−\)-H\(_2\)O 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\(_2^−\)-H\(_2\)O and ZrO\(_2^−\)-H\(_2\)O shown in Figures 4 and 5, respectively, are considerably more complex and differ substantially from one another.\(^{48,49}\) The overview TiO\(_2^−\)-H\(_2\)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 \(\beta\) is around 1.5 for the A peaks and 0 for the B peaks. The ZrO\(_2^−\)-H\(_2\)O spectrum is much more congested, and there are several doublets (B/C, O/P, etc.) where the peak spacing is only \(\sim 5\) cm\(^{-1}\).

To interpret these results, Franck–Condon simulations based on electronic structure calculations were carried out. Results from ZrO\(_2^−\)-H\(_2\)O are shown in Figure 6 and are very similar to those found for TiO\(_2^−\)-H\(_2\)O. For both species, the lowest-energy anions and neutrals are the “chemisorbed” cis-dihydroxide MO(OH)\(_2^0/−\) 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” MO\(_2^−\)-H\(_2\)O 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 transitions in totally symmetric vibrational modes of TiO(OH)$_2$. Peak A1 is assigned to the vibrational origin (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 3J$_0$ progression in the Ti–OH symmetric stretch. Additional peaks (A2, A6, A10) are assigned to the 4J$_0$ progression involving excitation of the $\nu_4$ 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, suggests that they involve FC-forbidden transitions of non-totally 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 NO$_2$ 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 $\nu_4$ umbrella mode of TiO(OH)$_2$, a non-totally 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 $^1$A$^1$ ground state and an as yet unidentified $^3$B$_2$ 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 ($\nu_{12}$) 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 $\nu_{12}$ 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$^2$, F(11$^1$), I(11,12$^2$), and P(9$^2$)). In contrast, in the trans spectrum, peaks C, E, and H are a progression in the $\nu_{12}$ mode of the trans isomer (i.e., 12$^2-12$), and there are several combination bands built on this progression such as peak M, assigned to the 11$^2$-12$^3$ 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 H$_2$CC Isomerization and the F + NH$_3$ Reaction. Negative ion photodetachment has been shown to be a novel method of probing the transition states of benchmark unimolecular and bimolecular reactions.\textsuperscript{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$_2$CC$^-$, to probe the dynamics of neutral vinylidene isomerization to acetylene (HCCCH).\textsuperscript{12,27} There have also been numerous studies of several bimolecular hydrogen transfer reactions via photodetachment of the appropriate hydrogen bonded negative ion, such as photodetaching FH$_2^-$ to investigate the transition state of the F + H$_2$ reaction.\textsuperscript{96} 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 + H$_2$ reactions via photodetachment of IHI$^+$ and FH$_2^-$.\textsuperscript{23,90} Entrance channels for the CI + H$_2$ and F + CH$_4$ reactions have also been probed.\textsuperscript{100,101}

Here, recent results are described in which cryo-SEVI spectra of H$_2$CC$^-$ and FNH$_3$ are used to probe the transition states for the unimolecular H$_2$CC-HCCH isomerization reaction\textsuperscript{93} and the bimolecular reaction F + NH$_3$·H$_2$ + NH$_2$.\textsuperscript{50}

Vinylidene, H$_2$CC, is the simplest carbene and as such is of considerable interest in organic chemistry.\textsuperscript{102} As shown schematically in Figure 7a, it lies 1.925 eV above acetylene and can isomerize to HCCCH over a small (0.13 eV) barrier.\textsuperscript{103–105} The isomerization reaction is the simplest 1,2-hydrogen shift and is thus a benchmark chemical reaction.\textsuperscript{106} This consideration has motivated many experimental\textsuperscript{102,107–109} and theoretical\textsuperscript{110–114} studies of how the vibrational energy levels of H$_2$CC and HCCCH are coupled to one another. One approach to this problem has been to map out the excited vibrational energy levels of HCCCH that lie above the H$_2$CC minimum and search for perturbations with H$_2$CC levels.\textsuperscript{108,115,116} A more direct approach, developed by Lineberger,\textsuperscript{12} makes use of the fact that H$_2$CC$^-$ is the stable anionic form of H$_2$CC and that photodetachment of this species directly accesses the neutral H$_2$CC well, corresponding to the $^3$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 $^3$B$_2$ triplet state of H$_2$CC that is known to have a much larger barrier to isomerization.\textsuperscript{117} On this basis, the broadening of the peaks in the singlet band was attributed to isomerization to acetylene on a subpicosecond time scale. This result motivated multiple investigations of H$_2$CC$^-$ in our laboratory and in Canberra to map out photodetachment to both single and triplet states of H$_2$CC with high resolution and to explore vibrational autodetachment in H$_2$CC$^-$-\textsuperscript{13,117,118} Below, results are described in which cryo-SEVI combined with quantum dynamics calculations probes how (or if) H$_2$CC vibrations mix with high-lying HCCCH vibrational states.

Figure 7b shows cryo-SEVI spectra of H$_2$CC$^-$ and D$_2$CC$^-$ along with their peak assignments; blue, black, and red traces are
overview spectra, high-resolution composite spectra, and FC simulations, respectively. The high-resolution D$_2$CC$^-$ 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 H$_2$CC$^-$ spectrum. However, the situation is more complex upon excitation of the $\nu_5$ antisymmetric stretch or $\nu_6$ rocking vibration of H$_2$CC$^-$, both of which are nontotally symmetric. The weak $6^2_0$ and $6^2_1$ peaks in the H$_2$CC$^-$ spectrum are notably broader than the corresponding peaks in the D$_2$CC$^-$ spectrum. The $S^0_5$ transition, which is a single peak in the D$_2$CC$^-$ spectrum, looks to be a multiplet of closely spaced peaks in the H$_2$CC$^-$ spectrum. Hence, excitation of the $\nu_5$ and $\nu_6$ vibrations appears to yield much stronger coupling to the HCCH well than excitation of the totally symmetric $\nu_2$ and $\nu_3$ vibrations. This interpretation is supported by quantum dynamics calculations, displayed in Figure 8, that show that the wave functions of the $6^2$ and $5^1$ H$_2$CC vibrational levels have substantial amplitude at the HCCH geometry (upper right corner). The overall interpretation of these results is that there is coupling between H$_2$CC and HCCH vibrational energy levels, but this coupling is vibrationally state-specific and only activated upon excitation of the $\nu_5$ and $\nu_6$ modes of H$_2$CC.

The cryo-SEVI results on H$_2$CC$^-$ differ from the earlier photoelectron spectra obtained by Lineberger$^{12}$ 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$_3$OHF$^-$ successfully mapped out a series of exit channel Feshbach resonances corresponding to metastable

Figure 7. Schematic of H$_2$CC $\leftrightarrow$ HCCH isomerization coordinate (top), showing how photodetachment from H$_2$CC$^-$ accesses the vinylidene structure. Bottom panels show cryo-SEVI spectra of H$_2$CC$^-$ and D$_2$CC$^-$. 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.

Figure 8. Calculated wave functions for vibrational ground state (left), $\nu_5 = 2$ (center), and $\nu_6 = 1$ (right) vibrational states of H$_2$CC, projected onto H$_2$CC (top) and HCCH geometries (bottom). The angles $\theta_1$ and $\theta_2$ are defined in the inset. Reproduced with permission from ref 13. Copyright 2017 American Association for the Advancement of Science.
vibrational states of the CH₃O-HF complex that predissociate to CH₃O + HF, yielding considerably higher resolution than a previous study of this system via conventional photoelectron spectroscopy. We recently measured cryo-SEVI spectra of the related system FNH₃ to investigate the bimolecular F + NH₃ reaction. This reaction has been studied previously by infrared chemiluminescence and with crossed molecular beams scattering. Potential energy surfaces for this reaction have been reported, and the dynamics on these surfaces were explored using quasi-classical trajectory calculations. The relevant energetics and geometries for this system are shown in Figure 9. The reaction is exothermic by 1.3 eV and has a submerged barrier between reactant F-NH₃ and product FH-NH₂ 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 CH₃OHF⁻, but also the transition state and reactive complex, and, possibly, dynamical resonances lying above the F + NH₃ 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 functions 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 pyramidal 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-of-plane wagging mode of the NH₃ (≈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−NH₃ 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, 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 + NH₃ is not a simple hydrogen transfer reaction because the geometry of the NH₃ moiety evolves significantly en route to the HF + NH₂ products. Hence, assignment of the vibrational structure is possible only by comparison with multidimensional quantum dynamics calculations.

**Figure 9.** Calculated reaction coordinate and energetics for F + NH₃ reaction (top) and FNH₃⁻ 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 + NH₃ reactant asymptote. Reproduced with permission from ref 50. Copyright 2023 Springer Nature.
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$^-$, and, more recently, on the polyatomic vinoxide anion CH$_2$CHO$^-$. 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 resolved and the gas phase infrared spectrum is well characterized. 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 Lineberger and Wester as well as photodetachment microscopy experiments by Blondel. The rotationally resolved infrared spectrum of OH$^-$ was measured by Saykally using velocity-modulated IR spectroscopy, while the open-shell $X^2\Pi$ ground state of the OH radical has been characterized extensively using microwave spectroscopy and other methods. This body of work leads to the energy level diagram in Figure 12, showing the rovibrational structure of the $X^1\Sigma^+$ 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. 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 $\nu = 0, J = 0$ 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 $\nu = 1$ anion and neutral levels and are interspersed with the transitions originating from the anion $\nu = 0$ 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$^{-1}$. 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
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,\textsuperscript{140,141} it is still the case that relatively few vibrational frequencies are known for gas phase anions. Second, at the few-cm\textsuperscript{−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 the IR laser may be anharmonically coupled to nearby vibrational levels,\textsuperscript{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,\textsuperscript{143–146} including a SEVI study in our group prior to the installation of cryogenic cooling.\textsuperscript{147} The microwave,\textsuperscript{148} infrared,\textsuperscript{149,150} and electronic spectra\textsuperscript{151–155} of the vinoxy radical and its photodissociation dynamics\textsuperscript{156} 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\textsubscript{4} CO stretch at 1560 cm\textsuperscript{−1} and the ν\textsubscript{3} carbonyl CH stretch at 2512 cm\textsuperscript{−1}.

![Figure 12. Vibration—rotation levels of OH\textsuperscript{−} (bottom) and the two spin—orbit manifolds of OH (top). Selected photodetachment transitions (green) from the OH\textsuperscript{−}(0,0) and (1,1) states are shown. The IR laser vibrationally excites OH\textsuperscript{−} via the R(0) transition. Reproduced from ref 51. Copyright 2021 American Chemical Society.](image1)

![Figure 13. Cryo-SEVI spectrum of cold (black) and vibrationally excited (red) OH\textsuperscript{−}. 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.](image2)

![Figure 14. Excitation of the ν\textsubscript{4} = 1 level of the vinoxide anion at 1570 cm\textsuperscript{−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 ν\textsubscript{4} = 1 and ν\textsubscript{4} = 0 levels of vinoxy, respectively. Panel e shows a simulated photoelectron spectrum from the anion ν\textsubscript{4} = 1 level within harmonic and FC approximations. Adapted from ref 52. Copyright 2023 American Chemical Society.](image3)
These two modes were thus targeted for our IR cryo-SEVI experiment, 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 $\nu_4$ transition at 1570 cm$^{-1}$ (b). The corresponding photoelectron spectra are shown in black and red, respectively, in Figure 14c. The vibrational origin ($0^1_00$) is the largest peak in the IR-off spectrum, and there is FC activity in the totally symmetric $\nu_9$ (CCO bend), $\nu_7$ (CC stretch), and $\nu_4$ (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 $4^1_1$ 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 $\nu_9$ mode ($4^1_9^10^0_9$), 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 $\nu_4$ frequency. At larger eBE, however, the IR-on photoelectron spectrum is markedly different, showing FC activity in the $\nu_4$ and $\nu_8$ 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 $\nu_4$ 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 $\nu_3$ mode at 2546 cm$^{-1}$ are shown in Figure 15. The top panel shows IR-off (black) and IR-on 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 $\nu_3$ sequence band transitions ($3^1_1$, 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 $\nu_3$ 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
anharmonic interaction 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.
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