Solvent resonance effect on the anisotropy of NO$^-$($\text{N}_2\text{O}$)$_n$ cluster anion photodetachment

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Photodetachment from NO$^-$($\text{N}_2\text{O}$)$_n$ cluster anions ($n \leq 7$) is investigated using photoelectron imaging at 786, 532, and 355 nm. Compared to unsolvated NO$^-$, the photoelectron anisotropy with respect to the laser polarization direction diminishes drastically in the presence of the N$_2$O solvent, especially in the 355 nm data. In contrast, a less significant anisotropy loss is observed for NO$^-$($\text{H}_2\text{O}$)$_n$. The effect is attributed to photoelectron scattering on the solvent, which in the N$_2$O case is mediated by the $^2$I anionic resonance. No anionic resonances exist for H$_2$O in the applicable photoelectron energy range, in line with the observed difference between the photoelectron images obtained with the two solvents. The momentum-transfer cross section, rather than the total scattering cross section, is argued to be an appropriate physical parameter predicting the solvent effects on the photoelectron angular distributions in these cluster anions. © 2007 American Institute of Physics. [DOI: 10.1063/1.2766948]

I. INTRODUCTION

Studies of negatively charged clusters provide molecular-level views of chemical interactions relevant to anions in condensed environments. Recent advances in photoelectron imaging have renewed interest in solvation effects on cluster anion photodetachment, emphasizing the photoelectron angular distributions (PADs) measured simultaneously with the photoelectron spectra. Disappointingly, however, it is becoming a rather prevailing view that despite some notable exceptions the PADs merely tend to become more isotropic with increasing cluster size. This leads to a perception that the information content of photoelectron images is limited for larger clusters.

To counter this perception, consider the loss of photodetachment anisotropy when the departing electron’s kinetic energy (eKE) falls within the range of anionic resonances associated with the solvent network. As a general explanation, a resonance temporarily captures the photodetached electron before it is released into the continuum, scrambling its phase and angular momentum. Considering the complex electronic structures and aggregate properties of many solvents, it is not surprising that the solvent-induced, scattering-mediated loss of photoelectron anisotropy is a frequent occurrence in cluster chemistry. The diminished anisotropy, therefore, illuminates the role of photoelectron scattering on the solvent, complementing the information commonly derived from electron attachment and scattering spectra.

For example, the photodetachment of the $\Gamma$·CH$_3$I cluster anion at 267 nm yields a PAD with a markedly low anisotropy magnitude, compared to other monosolvated iodide species, such as $\Gamma$·Ar, $\Gamma$·H$_2$O, and $\Gamma$·CH$_3$CN. The anisotropy loss has been attributed, among other possibilities, to scattering of the departing electron by the CH$_3$I solvent molecule. This mechanism has been argued on the basis of the high scattering cross section associated with a CH$_3$I$^-$ shape resonance found close to the detached electron energy. More recently, Nakanishi et al. observed a similar effect in the detachment of acetone (Acn) cluster anions, (Acn)$_n$$^-\,$, where the PADs are found to be nearly isotropic for $n \approx 5$. Analogous to the $\Gamma$·CH$_3$I case, the acetone molecules possess an anionic resonance in the photoelectron energy range.

In this paper, we discuss the solvent-induced photoelectron anisotropy effects in the photodetachment of the NO$^-$($\text{N}_2\text{O}$)$_n$ cluster anions, with $n$ ranging from 0 up to 7, depending on the laser wavelength. The photodetachment of some of these clusters has been studied previously without angular resolution, using traditional photoelectron spectroscopy and photofragment-photoelectron coincidence techniques. Unsolvated NO$^-$ is adiabatically stable with respect to autodetachment only in its ground vibrational state. Although it is an important anion in itself, the main focus of the present work is on the solvent role in electron photoemission from the NO$^-$ cluster core. As the photoelectrons with specific eKE profiles propagate across the N$_2$O solvent shell, both elastic and inelastic scattering could, in general, lead to the reduction in the PAD anisotropy. It is expected that large-angle scattering, contributing the most to the momentum-transfer cross section, should have the greatest effect on the measured PADs.

Previous electron scattering studies of N$_2$O are extensive (see, for example, Refs. 16 and 17 and references therein), providing evidence for two shape resonances in the low-eKE range: a $\Pi$ symmetry resonance around 2.4 eV and a $\Sigma$ resonance around 8 eV. Vibrational Feshbach resonances near zero eKE have also been observed. In the present work, the photoelectron imaging results for NO$^-$($\text{N}_2\text{O}$)$_n$ are reported alongside the corresponding NO$^-$($\text{H}_2\text{O}$)$_n$ data, high-

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lighting the differences between the N₂O and H₂O solvents in their effects on the photodetachment anisotropies of the respective cluster anions.

II. EXPERIMENT

The experiments are performed on a negative-ion spectrometer described in detail elsewhere. The instrument employs the ion techniques of Johnson and Lineberger, combined with velocity-mapped imaging detection of photoelectrons. The cluster anions of interest are prepared starting with a pulsed supersonic expansion of a 20%–50% N₂O/Ar mixture into vacuum, with water contamination within the gas delivery lines as the source of H₂O. Anions are formed by secondary electron attachment to neutrals after ionizing the supersonic expansion with a 1 keV electron gun. The core NO⁻ anions are formed via the N₂O+→N₂O⁻+N₂ reaction sequence. 23,24

The resultant anions are pulse extracted into a mass-spectrometer flight tube, at the end of which the ions of selected mass are intercepted with a linearly polarized laser pulse. Pulses of 786 nm (100 fs, <1 mJ) are derived from a Ti:sapphire laser system (Spectra Physics, Inc.). The harmonics of a nanosecond neodymium-doped yttrium aluminum garnet laser (Spectra Physics, Inc., Quanta-Ray Lab 130-50) provide 532, 355, and 266 nm pulses (approximately 30, 20, and 10 mJ/pulse, respectively). The photoelectrons are projected on a 40 mm diameter imaging detector (Burle, Inc.) in the direction perpendicular to the ion and laser beams. In all cases, the laser polarization direction is set parallel to the imaging detector plane. To discriminate against background, the detector is pulsed on for a 200 ns window coinciding with the arrival of the photoelectrons. The photoelectron images are recorded by a computer-controlled charge coupled device camera for (1–5) × 10⁴ experimental cycles. The known vibrational lines of the bare NO⁻ photoelectron spectrum 25,26 are used for energy calibration. The PADs are analyzed using the basis set expansion (BASEX) program obtained from Dribinski et al. 27

III. RESULTS AND ANALYSIS

A. Photoelectron images and energy spectra

Figure 1 shows the raw and Abel-inverted photoelectron images of unsolvated NO⁻, collected at 786, 532, and 355 nm, along with the corresponding eKE spectra. The perceptible rings in the images correspond to the well-characterized 10,23,25,26 progression of transitions to the X²Π, v' = 0–5 vibrational states of NO from the ground X³Σ⁻, v'' = 0 state of NO⁻. The rings appear congested at 355 nm, but the vibrational structure remains resolved, as emphasized in the magnified part of the image in Fig. 1(c). The outermost rings in all images correspond to the 0→0 transition, peaking at an electron binding energy (eBE = hν−eKE) of 0.04±0.01 eV. Subject to rotational and spin-orbit corrections, this determination is consistent with the literature value of 0.026±0.005 eV for the adiabatic electron affinity of NO. 25

Figure 2 shows the 355 nm photoelectron images and the corresponding spectra for the NO⁺(N₂O)ₙ, n = 0–5 cluster anions. In addition to the data shown, the photoelectron images obtained at 355 nm for n up to 7, at 532 nm for n = 0–5, and at 786 nm for n = 0–3 are included in the foregoing analysis. 28 With the exception of the low-eKE spectral regions (discussed below), the energetic characteristics of the NO⁺(N₂O)ₙ photoelectron spectra in Fig. 2 are consistent with the electrostatically bound ion-neutral complexes studied previously by Bowen and co-workers. 10,11 where the excess electron is localized on the nitric oxide component of the cluster. The addition of each solvent N₂O molecule causes a spectral shift of about 0.2 eV to lower eKEs, accompanied by progressive broadening of the image rings and spectral peaks.

The NO⁺(N₂O)ₙ, n = 1 image includes a central feature corresponding to slow photoelectrons. This feature is absent for unsolvated NO⁻ (Figs. 1 and 2, n = 0) and nearly unobservable for NO⁺(N₂O)ₙ, n > 1 (Fig. 2). It is attributed to the covalent, w-shaped N₂O⁻ singlet anion, as proposed by Hiraoka et al. 29 and characterized by Resat et al. 12 and Torchio et al. 30 Further confirmation of the presence of the N₂O⁻ isomer in our experiment comes from a small N₂O⁻ photofragment signal, which we observed with our secondary reflectron mass spectrometer 31 in 532 nm dissociation of the NO⁺(N₂O)ₙ, n = 1 cluster. 28 As suggested by Snis and Panas, 32 this photofragment arises from a dissociative excitation of the covalent N₂O⁻ anion. We excluded the low-eKE spectral regions from the anisotropy analysis, which was thus limited to the bands arising from the NO⁻ cluster core only.

Figure 3 shows 355 nm photoelectron images and the corresponding spectra of NO⁺(H₂O)ₙ, n = 0–3. The spectra are in agreement with the previous measurements by Eaton et al. 33 The loss of vibrational structure in the NO⁺(H₂O)ₙ
spectrum is related to the strength of the ion-solvent interaction, where anionic geometries caused by stronger ionic H bonds lead to higher vibrational excitations in the resulting neutral complex. In addition, Myshakin et al. found two isomeric species for NO−/H2O, with the H bonds forming with either the N or O atom of the NO− core, contributing to additional line broadening.

B. Photoelectron angular distributions for unsolvated NO−

The PADs resulting from one-photon detachment with linearly polarized light are generally described as \( I(\theta) \propto 1 + \beta P_2(\cos \theta) \), where \( \beta \) is the anisotropy parameter, \( \theta \) is the angle between the photoelectron velocity and the laser polarization vectors, and \( P_2 \) is the second-order Legendre polynomial. Inspection of Fig. 1 reveals a perpendicular (\( \beta < 0 \)) nature of the NO− PADs. Negative \( \beta \) values are generally expected in the detachment from antibonding \( \pi \) orbitals of diatomic anions, as discussed, for example, in regard to \( \pi^1 \) photodetachment of O2− (Ref. 37) and S2−.21 Although NO− lacks inversion symmetry, its 2p\( \pi^* \) highest occupied molecular orbital (HOMO) (shown in the inset in Fig. 4) is qualitatively similar to O2− and the observed negative anisotropy is therefore not surprising.

The \( \beta \) values for the individual vibrationally resolved rings in the 786, 532, and 355 nm NO− photoelectron images (Fig. 1) are plotted versus the corresponding eKE values in Fig. 4 gray open circles. The results for each wavelength appear to follow parabolic patterns, consistent between multiple experimental runs on two different instruments in our laboratory. The patterns are indicated by dashed parabolas in Fig. 4, fitted to the corresponding data; however, this intriguing observation falls outside the scope of this report. Averaged \( \beta \) values corresponding to the PADs integrated over the entire Franck-Condon envelope of the transition are shown in Fig. 4 as black filled circles. In addition, the averaged \( \beta \) value from a 266 nm NO− photoelectron image28 is included at average eKE=4.11 eV, as well as the vibrationally resolved 488 nm results of Siegel et al., indicated by crosses.

The \( \beta \) values in Fig. 4 are compared to a solid curve obtained by a nonlinear fit to the data using the Cooper-Zare central-potential model. We used the simplified version of the model proposed by Hanstorp et al., which assumes no interaction between the departing electron and the neutral residue. The fitting procedure is described in the previous work. Similar to the studies of S2− and O2−, the 2p\( \pi^* \)
HOMO of NO$^-$ is approximated as a d-like orbital with an effective angular momentum quantum number $\ell = 2$. For consistent comparison with the cluster data, only the average $\beta$ values, corresponding to the integrated PADs (filled circles in Fig. 4), were used for the model fit. The resulting Cooper-Zare curve shown in Fig. 4 corresponds to $\cos \phi = 0.881$ for the relative phase $\phi$ of the $\ell' = \ell \pm 1$ partial waves and $A = 0.383$ eV$^{-1}$ for the coefficient related to the spatial extent of the negative ion$^{38}$ [see Eq. (2) in Ref. 8].

C. Solvation effects on photoelectron anisotropy

The NO$^-(\text{N}_2\text{O})_n$ PADs extracted from the images in Fig. 2 reveal a gradual loss of photodetachment anisotropy with increasing solvation. The trend is particularly notable in comparison with the PADs obtained for the NO$^-(\text{H}_2\text{O})_n$ images in Fig. 3. The latter retain a greater degree of anisotropy upon hydration, despite the much larger spectral shifts induced by sequential addition of H$_2$O, compared to N$_2$O. This becomes particularly clear by direct comparison of the anisotropy parameter values obtained for the individual cluster ions by integrating the PADs over the corresponding spectral profiles. The resulting $\beta$ values are plotted in Fig. 5(a) versus average eKE, which is used both as a measure of solvation and as a natural variable for comparison with the Cooper-Zare model. Four separate data sets are shown. Sets 1, 2, and 3, as labeled in Fig. 5, correspond to the NO$^-(\text{N}_2\text{O})_n$ cluster anions studied at 355, 532, and 786 nm, respectively. The cluster sizes, indicated in Fig. 5(a) next to the data points, range from $n=0$ (unsolvated NO$^-$, filled black circles in Fig. 5(a)) to $n=7$, 5, and 3 for sets 1, 2, and 3, respectively. Set 4 corresponds to NO$^-(\text{H}_2\text{O})_n$, $n=0$–3 at 355 nm. The $\beta$ (eKE) trends are compared to the Cooper-Zare curve for unsolvated NO$^-$, determined in Fig. 4 and reproduced as a dashed curve in Fig. 5(a). The greatest deviation from the model prediction is exhibited by set 1, corresponding to NO$^-(\text{N}_2\text{O})_n$ at 355 nm.

To quantify the deviations in $\beta$ and account for the varying number of solvent molecules $n$, we introduce a normalized solvent-induced anisotropy differential $D$ defined as

$$D = \Delta \beta n^\alpha,$$

where $\Delta \beta = \beta_{\text{eKE}} - \beta_{\text{CZ}}(\text{eKE})$, with $\beta_{\text{eKE}}$ and $\beta_{\text{CZ}}(\text{eKE})$ being the $n>0$ data from Fig. 5(a) and the $n=0$ Cooper-Zare predicted values, respectively, and $\alpha$ is an empirical exponent. Thus defined, $D$ is not intended as a rigorous measure of solvation effects. It is proposed only for clarifying the observed trends and discriminating between the factors in play, namely, the eKE dependence and solvent coordination.
Subtracting \( \beta_{\text{CZ}}(e\text{KE}) \) in \( \Delta \beta \) accounts for the expected Cooper-Zare model trend, as applied to the (unperturbed) core NO\(^-\) anion photodetachment, with the balance attributed to the solvent effects. These are expected to depend on the solvent nature and the number of solvent molecules present. Since the scaling of \( \Delta \beta \) with \( n \) is unlikely to be linear, an empirical \( n^n \) normalization is included in Eq. (1), with \( \alpha \) expected to be between 0 and 1.

The four sets of \( D \) values, corresponding to sets 1–4 defined above (\( n > 0 \)), are plotted in Fig. 5(b) using \( \alpha = 0.8 \). This empirical value is chosen arbitrarily to match the \( D \) values for sets 1 and 2 and 3 within the overlapping eKE ranges; however, reasonable variations in \( \alpha \) do not change the foregoing conclusions. The resulting \( D(e\text{KE}) \) variations for sets 1–3, on the one hand, and set 4, on the other, represent the energy-dependent effects on the PADs attributed to the solvation by \( \text{N}_2\text{O} \) and \( \text{H}_2\text{O}\), respectively, normalized (empirically) to the numbers of solvent molecules in the corresponding clusters.

IV. DISCUSSION

Viewing cluster photodetachment as electron ejection from the core anion, followed by its scattering on the solvent, the PADs can be affected by the solvent via the following mechanisms. First is the change in the partial-wave balance due to the solvation-induced decrease in eKE. Second is the solvent-induced perturbation of the initial electronic state, including any distortions of the core-anion geometry and/or symmetry, as well as possible delocalization of the excess electron to the solvent. Third is the departing electron scattering on the solvent molecules.

In our analysis, the first of the above effects is accounted for by comparing the observed anisotropy values to the Cooper-Zare model predictions. Regarding the second, only minimal distortion of the core-anion structure and/or charge delocalization to the solvent network is indicated in Figs. 2 and 3, where the cluster anion spectra clearly retain the NO\(^-\) character. In addition, \( ab\) \textit{initio} calculations on NO\(^-\)-\text{N}_2\text{O} predicted only a 2% charge delocalization to the solvent molecule.\(^{40}\) This brings our focus to electron scattering on the solvent.

Shown as dashed curves in Fig. 5(c) are the total electron scattering cross sections, \( \sigma(e\text{KE}) \), for \( \text{N}_2\text{O} \) and \( \text{H}_2\text{O} \), based on the data from Refs. 16 and 41, respectively. The \( \text{N}_2\text{O}+e^- \) cross section reveals a resonance with a maximum at 2.25 eV. In contrast, the \( \text{H}_2\text{O}+e^- \) curve reflects a steep decline with increasing eKE in the low-eKE region, with no evidence of resonances in the region of interest. Nonetheless, the total cross section for \( \text{H}_2\text{O} \) \textit{exceeds} that for \( \text{N}_2\text{O} \) in the entire range shown. This seemingly contradicts our principal conclusion ascribing the anisotropy decay in cluster anion photodetachment primarily to electron-solvent scattering.

To reconcile these observations, we consider the qualitatively different electron scattering mechanisms for \( \text{H}_2\text{O} \) and \( \text{N}_2\text{O} \). The \( \text{H}_2\text{O}+e^- \) scattering in the 0–4 eV range is dominated by long-range interaction of the electrons with the molecular dipole moment. Classically speaking, most scattering events occur with large impact parameters and lead to small-angle scattering of the incident electrons. This expectation is confirmed by the dependence of the \( \text{H}_2\text{O}+e^- \) differential cross section \( \sigma_{\text{diff}}(\theta_e,e\text{KE}) \) on the scattering angle \( \theta_e \), which peaks very strongly in the forward direction (i.e., near \( \theta_e = 0^\circ \)).\(^{41,42}\) Specifically, in the vicinity of 2 eV, the differential cross section for \( \text{H}_2\text{O}+e^- \) forward scattering is estimated to exceed that for backward scattering (\( \theta_e = 180^\circ \)) by about two orders of magnitude (Fig. 1 in Ref. 42). In other words, the trajectories of most electrons scattered by \( \text{H}_2\text{O} \) are affected rather little.

In contrast, the \( \text{N}_2\text{O}+e^- \) scattering dynamics in the same energy range are dominated by the \( ^2\text{II} \) symmetry \( \text{N}_2\text{O}^- \) resonance.\(^{18}\) One might think of the resonance as an absorber, which reemits the scattered electrons in varying directions, subject to the conservation of energy and angular momentum.\(^{17}\) Accordingly, the \( \text{N}_2\text{O}+e^- \) differential cross section shows nearly equal probabilities for forward and backward scattering near the resonance maximum [Fig. 3(a) in Ref. 16]. Hence, the electron trajectories get scrambled by the interaction with \( \text{N}_2\text{O} \) in the vicinity of the anionic resonance.

These scattering features align well with the stronger decay of photodetachment anisotropy observed with \( \text{N}_2\text{O} \) solvation, despite the larger total cross section of \( \text{H}_2\text{O} \). Furthermore, we conclude that the total scattering cross section is not necessarily a good measure for evaluating the solvent effects on the PADs in cluster anion photodetachment. Obtained by integrating the differential cross section over all scattering angles, \( \sigma(e\text{KE}) \) does not reflect the most relevant details of the interaction between the emitted electrons and the solvent molecules. A more appropriate measure is the momentum-transfer (or “diffusion”) cross section \( \sigma_m(e\text{KE}) \), calculated by integrating \( \sigma_{\text{diff}}(\theta_e,e\text{KE}) \) with a \((1 - \cos \theta_e)\) weight function.\(^{15}\) The \( \sigma_m(e\text{KE}) \) cross section assigns a greater weight to scattering events that significantly alter the electron trajectories (and thus affect the PAD) and discounts small-angle scattering contributions.

The momentum-transfer cross sections for electron collisions with \( \text{H}_2\text{O} \) and \( \text{N}_2\text{O} \) are plotted as solid curves in Fig. 5(c), using the results of Refs. 41 and 16, respectively. For \( \text{N}_2\text{O} \), \( \sigma_m(e\text{KE}) \) is not very different from the corresponding total cross section, implicating that most \( \text{N}_2\text{O}+e^- \) collisions in the relevant energy range are “momentum-transfer” collisions. For \( \text{H}_2\text{O}+e^- \), however, \( \sigma_m \) is reduced by orders of magnitude relative to \( \sigma \), as most scattering events are long-range electron-dipole interactions, not causing significant changes to the electron trajectories.

The normalized anisotropy differentials for the \( \text{N}_2\text{O} \) and \( \text{H}_2\text{O} \) solvents, shown in Fig. 5(b), mirror the main trends of the corresponding momentum-transfer cross sections in Fig. 5(c). For \( \text{N}_2\text{O} \) (sets 1–3), \( D(e\text{KE}) \) peaks near the \(^2\text{II} \) resonance maximum, while the less significant anisotropy loss in \( \text{NO}^-/(\text{H}_2\text{O})_n \) is consistent with the smaller \( \sigma_m(e\text{KE}) \) values for \( \text{H}_2\text{O} \). While the agreement is by no means quantitative, it does bring out the role of the \( \text{N}_2\text{O}^- \) resonance.

A major limitation of the above analysis is the empirical nature of Eq. (1). In addition, one must consider that electron-solvent scattering interactions in cluster anion photodetachment occur in the short range, while the measured
eKEs correspond to final (far-field) energies of the detached electrons. Assuming attractive electron-neutral interactions, the effective energy of the outgoing electrons in the solvent-scattering process is greater than the measured eKE, which should result in a redshift or reddening broadening of the scattering profile. This effect possibly contributes to the low-eKE slope of \( D(eKE) \) in Fig. 5(b), which extends beyond the unsolvated resonance curve. Resonance broadening by the cluster environment and collective many-body effects are also likely to contribute to the broadening of the \( D(eKE) \) curve.\(^{43,44}\)

The suggested role of the \( \text{N}_2\text{O}^- \) resonance echoes with the past work on solvated iodide cluster anions, in which a marked loss of anisotropy with a single \( \text{CH}_4\text{I}^- \) solvent molecule implicated a \( \text{CH}_4\text{I}^- \) scattering resonance.\(^8\) In general, we believe that in many cases the solvent-induced reduction of photoelectron anisotropy can be traced to a large electron-solvent momentum-transfer cross section, such as expected in the case of a resonance found in the outgoing photoelectron energy range. As one more case in point, a marked loss of photodetachment anisotropy upon solvation was previously observed by our group for the \( \text{OCS}^- \) cluster anions. Although we did not explicitly comment on it at the time, the trend is clearly seen in the outer rings of the 400 nm photoelectron images of \( \text{OCS}_n^- \) in Fig. 1 in Ref. 45. In that case, eKE falls in the vicinity of the \( ^1\text{II} \) shape resonance of OCS peaking at 1.15 eV.\(^{46}\) This example is particularly relevant here, because of the similarities between OCS and \( \text{N}_2\text{O} \), including their structures and electron affinities.\(^{47}\)

V. SUMMARY

Photoelectron images of solvated \( \text{NO}^- \) obtained at several laser wavelengths reveal a greater reduction in the photodetachment anisotropy in the presence of \( \text{N}_2\text{O} \) solvent molecules, compared to \( \text{H}_2\text{O} \). The effect is attributed to an \( \text{N}_2\text{O} \) solvent anionic resonance that falls within the departing electron kinetic energy range. The momentum-transfer cross section, rather than the total scattering cross section, is shown to be a better predictor of the solvent effects on the photoelectron angular distributions in these cluster anions.

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