

## THE NEGATIVE ION PHOTOELECTRON (PHOTODETACHMENT) SPECTRA OF $\text{NO}^-(\text{H}_2\text{O})_{n=1,2}$

J.G. EATON, S.T. ARNOLD and K.H. BOWEN

*The Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218 (U.S.A.)*

(First received 22 December 1989; in final form 13 April 1990)

### ABSTRACT

We have recorded the negative ion photoelectron spectra of  $\text{NO}^-(\text{H}_2\text{O})_{n=1,2}$  and  $\text{NO}^-(\text{D}_2\text{O})_1$  using 2.540 eV photons. Vertical detachment energies, adiabatic electron affinities, and anion–single solvent dissociation (sequential solvation) energies were determined from these spectra. For  $\text{NO}^-(\text{H}_2\text{O})_1$  and  $\text{NO}^-(\text{H}_2\text{O})_2$ , the ion–solvent dissociation energies for the loss of single water molecules were found to be 0.72 and 0.68 eV, respectively. This system is discussed in relation both to other hydrated-anion complexes and to other  $\text{NO}^-$  complexes.

### INTRODUCTION

The microscopic nature of anion solvation is strongly influenced by the interactions between negative ions and the first few neutral solvent molecules surrounding them. Because of this, small gas-phase anion–molecule complexes,  $\text{X}^-(\text{Y})_n$ , comprised of only a few solvent molecules, Y, are of fundamental importance in understanding solvation phenomena. Furthermore, the study of gas-phase anion–molecule complexes as a function of cluster size allows ion solvation to be explored in a stepwise manner, revealing the evolution of energetic properties from those of the free anion toward those of the anion in solution.

Because of water's significance as a solvent, anion–molecule complexes of the form  $\text{X}^-(\text{H}_2\text{O})_n$  are of particular interest. While theoretical treatments [1] and thermochemical studies [2–4] have yielded considerable data on the clustering of water about negative ions, there have been fewer spectroscopic (photodissociation, photodestruction, and photodetachment) studies of hydrated-anion complexes [5,6]. In a continuation of our ongoing studies of anion–molecule complexes, we have recorded the size-selected negative ion photoelectron (photodetachment) spectra of complexes comprised of a nitric oxide anion and neutral water solvent molecules. To a first approximation, the photoelectron spectrum of an anion–molecule complex may be viewed as that of its perturbed sub-ion, and the cluster anion spectrum often closely

resembles that of the sub-ion except for its spectral features being broadened and shifted to higher electron binding energies. These spectra provide energetic information, including vertical detachment energies, adiabatic electron affinities, and anion-single solvent dissociation (sequential solvation) energies, and they also provide insight into the nature of the ion-neutral interactions. Here, we present the spectra of  $\text{NO}^- (\text{H}_2\text{O})_{n=1,2}$  and discuss the results of this study in relation both to other hydrated-anion complexes and to other  $\text{NO}^-$  complexes we have examined.

## EXPERIMENTAL

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. By subtracting the center-of-mass photoelectron kinetic energy of an observed spectral feature from the photon energy, one obtains the electron binding energy for a transition from an occupied level in the negative ion to an energetically accessible level in the corresponding neutral. Our negative ion photoelectron spectrometer has been described previously [7]. Briefly, negative ions are generated in a supersonic expansion cluster ion source, skimmed, and transported through a series of ion optical components into an  $E \times B$  Wien velocity filter where they are mass-selected. Upon being focused into the field-free, collision-free ion-photon interaction region, the mass-selected ion beam is crossed with the intracavity photon beam of an argon ion laser at visible wavelengths. A small solid angle of the resulting photodetached electrons is accepted into the input optics of a magnetically shielded, hemispherical electron energy analyzer, where the electrons are energy-analyzed and counted. In the present experiment, photoelectron spectra were recorded with a photon energy of 2.540 eV, a channel spacing of 8.5 meV, and an instrumental resolution of 30 meV.

The supersonic expansion ion source used in these experiments has also been described previously [8]. In this source, high-pressure gas in the stagnation chamber is expanded through a pinhole aperture into high vacuum, while a negatively biased, hot filament ( $\text{ThO}_2/\text{Ir}$ ) injects relatively low-energy electrons directly into the condensation-prone environment of the expanding jet. There, the primary electrons collide with the expansion gas, producing still lower energy secondary electrons, which are probably the prime agents of electron attachment. Ion currents are enhanced considerably when the expansion occurs in the presence of a magnetic field. To generate the  $\text{NO}^- (\text{H}_2\text{O})_n$  cluster ions, the source was typically operated with a stagnation pressure of 3.6 atm of  $\text{N}_2\text{O}$  containing 1%  $\text{H}_2\text{O}$ , a nozzle diameter of 25  $\mu\text{m}$ , a filament emission current of 5 mA, a beam voltage of 500 V, an extraction voltage of

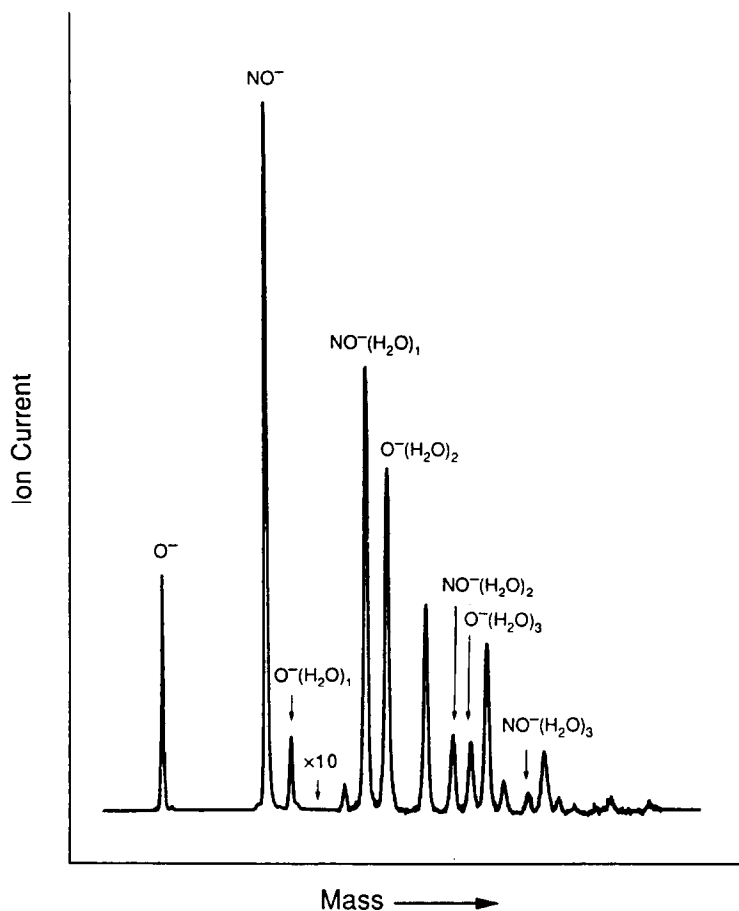


Fig. 1. A mass spectrum showing the negative ions produced by the supersonic expansion source when water vapor is expanded with  $\text{N}_2\text{O}$ .

500 V, a skimmer voltage of 10 V, and a filament bias voltage of  $-40$  V, with these last three voltages being referenced to the beam voltage. A mass spectrum obtained under these source conditions is shown in Fig. 1. It includes the homologous series  $\text{NO}^-(\text{H}_2\text{O})_{n=1-3}$ , with other prominent species being  $\text{O}^-$ ,  $\text{NO}^-$ ,  $\text{O}^-(\text{N}_2\text{O})_n$ ,  $\text{NO}^-(\text{N}_2\text{O})_n$ , and the series  $\text{O}^-(\text{H}_2\text{O})_n$ . The photoelectron spectra of  $\text{NO}^-(\text{H}_2\text{O})_1$  and  $\text{NO}^-(\text{H}_2\text{O})_2$  were recorded with ion currents of  $\sim 4.1 \times 10^{-10}$  and  $\sim 0.5 \times 10^{-10}$  A, respectively.

## RESULTS AND INTERPRETATION

The negative ion photoelectron (photodetachment) spectra of  $\text{NO}^-(\text{H}_2\text{O})_{n=1,2}$  are presented in Fig. 2. The spectrum of  $\text{NO}^-$  was recorded

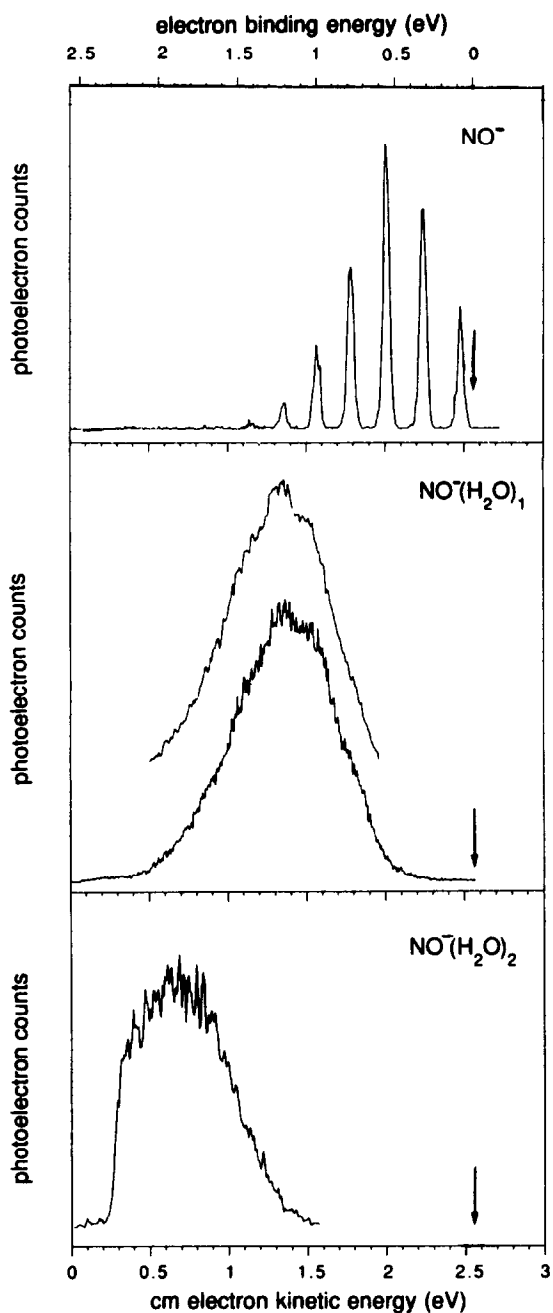


Fig. 2. The negative ion photoelectron spectra of  $\text{NO}^-$ ,  $\text{NO}^-(\text{H}_2\text{O})_1$ , and  $\text{NO}^-(\text{H}_2\text{O})_2$  are all presented on the same center of mass electron kinetic energy and electron binding energy scales. All three spectra were recorded with 2.540 eV photons, and the photon energy is indicated by arrows. The upper scan in the spectrum of  $\text{NO}^-(\text{H}_2\text{O})_1$  has  $\sim 10$  times the signal of the lower full-range scan.

before and after each cluster anion spectrum for calibration purposes and is presented for comparison. The  $\text{NO}^-(\text{H}_2\text{O})_1$  and  $\text{NO}^-(\text{H}_2\text{O})_2$  cluster anion spectra each consist of a single broad peak with fitted maxima at electron binding energies of  $1.18 \pm 0.01$  and  $1.86 \pm 0.02$  eV, respectively, and these are interpreted as their vertical detachment energies (VDEs). The upper scan in the spectrum of  $\text{NO}^-(\text{H}_2\text{O})_1$  has approximately ten times the signal of the lower full-range scan and shows some structure at the top of this peak. The signal in the  $\text{NO}^-(\text{H}_2\text{O})_2$  spectra is artificially truncated at low electron kinetic energies due to the unavoidable and rapid decrease in the transmission functions of electron energy analyzers at low electron kinetic energies. As mentioned earlier, the main features in the photoelectron spectra of anion-molecule complexes typically resemble those of their uncomplexed sub-ions except for being broadened and shifted to higher electron binding energies. In the case of  $\text{NO}^-(\text{H}_2\text{O})_n$ , however, the spectra are broadened, and no characteristic  $\text{NO}^-$  vibrational features are resolved. The photoelectron spectrum of  $\text{NO}^-(\text{D}_2\text{O})_1$  is similar to that of  $\text{NO}^-(\text{H}_2\text{O})_1$ , containing a single broad peak of essentially the same width. Its VDE was determined to be  $1.24 \pm 0.01$  eV.

Although the cluster anion photoelectron spectra do not contain an obvious  $\text{NO}^-$  spectral fingerprint, we have been able to characterize these clusters as being of the form  $\text{NO}^-(\text{H}_2\text{O})_n$ , implying that the excess negative charge is localized on the nitric oxide portion of the cluster and that this sub-ion is solvated by neutral water molecules. This characterization is supported by both mass spectrometric and photoelectron spectroscopic evidence. The mass spectrum exhibits a smoothly decreasing homologous series in  $\text{NO}^-(\text{H}_2\text{O})_n$  beginning at  $\text{NO}^-$  with each of its cluster ions separated by 18 amu. This suggests that water molecules are clustering to a  $\text{NO}^-$  sub-ion, and isotopic substitution confirms these observations. Although the photoelectron spectra of  $\text{NO}^-(\text{H}_2\text{O})_n$  contain no resolved vibrational features, the shape and width of the  $\text{NO}^-$  spectral profile is faithfully retained, as shown in Fig. 3 for  $\text{NO}^-(\text{H}_2\text{O})_1$ . By modeling the spectra, we have demonstrated that uniform broadening of each vibrational feature in the spectrum of  $\text{NO}^-$  yields a profile which closely resembles that of  $\text{NO}^-(\text{H}_2\text{O})_1$ . This model also accounts for the cleft observed near the top of the  $\text{NO}^-(\text{H}_2\text{O})_1$  spectrum and suggests that the sub-ion in this complex is very likely  $\text{NO}^-$ .

Ion-solvent dissociation energies for these anionic complexes and adiabatic electron affinities for their corresponding neutral clusters were determined from these spectra. In the photoelectron spectrum of  $\text{NO}^-$ , the lowest electron binding energy peak corresponds to the  $\text{NO}(X^2\Pi, v' = 0) \leftarrow \text{NO}^-(X^3\Sigma, v'' = 0)$  transition, i.e. its origin peak. When the center-of-mass electron kinetic energy (EKE) corresponding to the center of this peak is subtracted from the photon energy and corrected for rotational and spin-orbit effects,

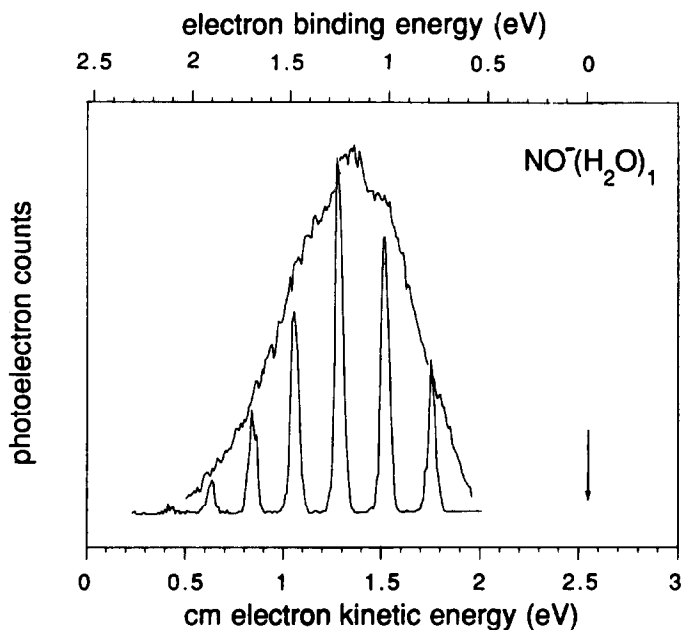


Fig. 3. The spectrum of  $\text{NO}^-$ , overlaid on the spectrum of  $\text{NO}^-(\text{H}_2\text{O})_1$ , demonstrates that the overall shape and width of the cluster anion spectrum strongly resembles that of  $\text{NO}^-$ .

one obtains the adiabatic electron affinity of  $\text{NO}$  [9]. Because the  $\text{NO}^-(\text{H}_2\text{O})_n$  spectral profiles strongly resemble that of  $\text{NO}^-$ , the electron affinities of their corresponding neutral clusters were determined by comparing their vibrationally unresolved spectral profiles with the Franck–Condon envelope of  $\text{NO}^-$ . For example, Fig. 3 illustrates how the shifted vibrational envelope of the  $\text{NO}^-(\text{H}_2\text{O})_1$  spectrum exhibits the same shape and width as that of  $\text{NO}^-$ , allowing the origin in the  $\text{NO}^-(\text{H}_2\text{O})_1$  spectrum to be determined via a comparison with the location of the origin in the  $\text{NO}^-$  profile, i.e. by find the corresponding point on its spectral profile. For  $\text{NO}^-(\text{H}_2\text{O})_{n=1,2}$ , the adiabatic electron affinities (EAs) were found to be  $0.75 \pm 0.05$  and  $1.43 \pm 0.06$  eV, respectively, while the EA of  $\text{NO}^-(\text{D}_2\text{O})_1$  was found to be  $0.80 \pm 0.05$  eV. Ion–single solvent dissociation energies were also extracted from these spectra using the relation

$$\text{EA}[\text{X}(\text{Y})_n] - \text{EA}[\text{X}(\text{Y})_{n-1}] = D[\text{X}^-(\text{Y})_{n-1} \cdots \text{Y}] - D_{\text{WB}}[\text{X}(\text{Y})_{n-1} \cdots \text{Y}]$$

where  $\text{EA}[\text{X}(\text{Y})_n]$  denotes the adiabatic electron affinity of the  $\text{X}(\text{Y})_n$  cluster,  $D[\text{X}^-(\text{Y})_{n-1} \cdots \text{Y}]$  is the ion–neutral dissociation energy (the absolute value of the solvation energy) for the loss of a single solvent  $\text{Y}$  from a given cluster ion, and  $D_{\text{WB}}[\text{X}(\text{Y})_{n-1} \cdots \text{Y}]$  is the weak bond dissociation energy for the loss of a single solvent  $\text{Y}$  from its corresponding neutral cluster. Because ion–solvent

TABLE 1

Vertical detachment energies, adiabatic electron affinities, and anion–single solvent dissociation energies for  $\text{NO}^-(\text{H}_2\text{O})_{n=1,2}$  and  $\text{NO}^-(\text{D}_2\text{O})_1$

	Vertical detachment energy (eV)	Adiabatic electron affinity (eV)	Ion–single solvent dissociation energy (eV)
$\text{NO}^-(\text{H}_2\text{O})_1$	$1.18 \pm 0.01$	$0.75 \pm 0.05$	0.72
$\text{NO}^-(\text{H}_2\text{O})_2$	$1.86 \pm 0.02$	$1.43 \pm 0.06$	0.68
$\text{NO}^-(\text{D}_2\text{O})_1$	$1.24 \pm 0.01$	$0.80 \pm 0.05$	0.77

interaction energies are generally somewhat larger than van der Waals bond strengths, the energy difference (the spectral shift) between the origins of adjacent-sized cluster anions is approximately equal to (and is a lower limit to) the dissociation energy for the larger of the species losing a single solvent molecule. In this way, the anion–single solvent dissociation (sequential solvation) energies were determined to be 0.72 and 0.68 eV for  $\text{NO}^-(\text{H}_2\text{O})_1$  and  $\text{NO}^-(\text{H}_2\text{O})_2$ , respectively, and 0.77 eV for  $\text{NO}^-(\text{D}_2\text{O})_1$ . As expected, the dissociation energy for the deuterated cluster anion is slightly larger than that of its hydrated analog. The VDEs, EAs, and ion–single solvent dissociation energies for these systems are summarized in Table 1.

## DISCUSSION

The anion–solvent dissociation (solvation) energies reported above are consistent with thermochemical determinations for the solvation energies of other hydrated cluster anions, which range from 0.5 to 1.0 eV [2–4]. The solvation energies of these complexes are useful in considering different anion–water interactions and in relating gas-phase properties to bulk parameters. For hydrogen bonded anion–molecule complexes,  $\text{X}^-(\text{Y})_1$ , which have the solvent, Y, in common, a correlation has previously been noted by Yandagori and Kebarle [2(c)] and by Castleman and co-workers [3(a)] between the dissociation energies of these complexes and the gas-phase basicities of their anions, with stronger bases shown to exhibit larger anion–solvent dissociation energies. The strength of the anion–neutral bond in  $\text{NO}^-(\text{H}_2\text{O})_1$  is intermediate between that of  $\text{O}_2^-(\text{H}_2\text{O})_1$  and  $\text{NO}_2^-(\text{H}_2\text{O})_1$ , 0.72 eV vs. 0.80 eV [2(a)] and 0.66 eV [3(b)], respectively. Since the order of basicity parallels that of the dissociation energies, it seems likely that the gas-phase basicity of  $\text{NO}^-$  lies between those of  $\text{O}_2^-$  and  $\text{NO}_2^-$ . An additional correlation has been presented by Castleman and co-workers relating gas-phase solvation energies and the bulk “single ion” heat of solvation [10]. The heat of solvation for an ion  $\text{X}^-$  in water, for example, can be predicted by knowing the first several gas-phase (sequential) solvation energies of

$X^-(H_2O)_n$ . Because the heat of solvation for  $O_2^-$  in water is 4.62 eV [11] while that of  $NO_2^-$  is 3.4 eV [10], it seems likely that the value for  $NO^-$  solvated in water is bracketed by these two numbers.

Further insight into ion-neutral interactions can be gained by comparing anion-neutral complexes comprised of the same sub-ion and different neutral solvents. By studying the series  $NO^-(Ar)$ ,  $NO^-(Kr)$ ,  $NO^-(Xe)$ ,  $NO^-(N_2O)_n$ , and  $NO^-(H_2O)_n$ , we have examined the role of the neutral in ion-neutral interactions which cover a range of strengths. The photoelectron spectra of  $NO^-(Ar)$ ,  $NO^-(Kr)$ , and  $NO^-(Xe)$  are highly structured and exhibit spectral patterns which closely resemble that of  $NO^-$  [12,13]. The ion-atom dissociation energies for these complexes range from 60 to 160 meV and increase with the size of the solvent. The increase in dissociation energy is linearly related to the polarizability of the rare gas atoms, suggesting that weak ion-induced dipole interactions dominate the bonding in these systems. The  $NO^-(N_2O)_{n=1-5}$  cluster ion spectra [7,12] also exhibit highly structured spectral patterns which strongly resemble those of free  $NO^-$ , although the solvation shifts ( $\sim 200$  meV) and the extent of the broadening are greater in these spectra than in the  $NO^-$  (rare gas) cases. This is indicative of a substantially stronger interaction, and presumably, ion-dipole and ion-quadrupole interactions dominate the bonding in  $NO^-(N_2O)_n$ . The present study of  $NO^-(H_2O)_n$  provides examples of ion-neutral complexes which exhibit still stronger interactions, as demonstrated by the larger solvation shifts and the lack of sub-ion spectral structure. The stronger interactions observed in these clusters are probably due to hydrogen bonding and charge transfer effects in addition to electrostatic interactions, and indeed Weinhold and co-workers [1(e)] have demonstrated that both electrostatic and charge transfer effects play important roles in the energetics and the structures of the anionic hydrogen bonded complexes  $X^-(H_2O)_n$ , where  $X^- = F^-$ ,  $Cl^-$ , and  $O_2^-$ .

For all the anion-molecule complexes we have studied to date, some degree of broadening is observed in their photoelectron spectra. Generally, the spectral broadening increases with stronger ion-neutral interactions, and systems with comparable solvation energies often display similar broadening characteristics. On occasion, however, systems which have similar solvation energies may show significant differences in broadening, as in  $NO^-(N_2O)_3$  and  $NO^-(H_2O)_1$  [12]. In these cases, each cluster ion has a total solvation energy of  $\sim 0.7$  eV, yet  $NO^-(N_2O)_3$  retains much of the sub-ion spectral fingerprint while  $NO^-(H_2O)_1$  shows a complete lack of vibrational structure. A number of mechanisms have been proposed to account for the broadening in ion-molecule spectra, including (1) excited weak-bond vibrations in the cluster anion, (2) vibrational excitations in the resulting neutral, and (3) access to a repulsive portion of the neutral's potential energy surface. High density vibrational state manifolds are indigenous to cluster anions due to the pres-



ence of anion-solvent weak bond vibrations, and it is possible that these states are significantly populated. Complexation-induced distortions of the neutral solvent in ion-molecule systems may also account for a portion of the spectral broadening. Distortions may result in the excitation of bending and stretching modes within the neutral solvents, producing features in the photoelectron spectra which correspond to these excitations. Resolved transitions of this type have been observed in the photoelectron spectra of  $\text{H}^-(\text{NH}_3)_{1,2}$  and  $\text{NH}_2^-(\text{NH}_3)_{1,2}$  studied by us [14,15] and  $\text{H}^-(\text{H}_2\text{O})_1$ , studied by Lineberger and co-workers [6(b)]. These vibrational features appear as secondary peaks on the high electron binding energy side of the main spectral peaks, and they probably account for a portion of the observed broadening in the spectra of  $\text{NO}^-(\text{H}_2\text{O})_n$ . Reflection of the cluster anion's vibrational wavefunction onto the repulsive portion of its neutral's potential surface can also broaden the features in the photoelectron spectra, and contributions from this mechanism were found to be significant in the photoelectron spectra of  $\text{H}^-(\text{NH}_3)_n$ . This is probably the mechanism that accounts for the broadening differences in  $\text{NO}^-(\text{H}_2\text{O})_1$  and  $\text{NO}^-(\text{N}_2\text{O})_3$ . In the case of  $\text{NO}^-(\text{H}_2\text{O})_n$ , it seems likely that spectral broadening arises primarily from mechanism (3), secondarily but significantly from (2), and to a minor extent from (1).

## CONCLUSION

In a continuation of our spectroscopic studies of anion-molecule complexes, we have recorded the negative ion photoelectron spectra of  $\text{NO}^-(\text{H}_2\text{O})_{n=1,2}$  and  $\text{NO}^-(\text{D}_2\text{O})_1$ . These spectra were essentially unstructured, with the individual vibrational features of the  $\text{NO}^-$  spectral pattern unresolved. The shape and width of the  $\text{NO}^-$  spectral envelope was faithfully retained, however, and was shifted to progressively higher electron binding energies as the degree of solvation increased. From the photoelectron spectra of these cluster anions, vertical detachment energies, adiabatic electron affinities, and anion-single solvent dissociation energies were determined. Using the energy shifts between the spectral patterns of the  $\text{NO}^-$ ,  $\text{NO}^-(\text{H}_2\text{O})_1$ , and  $\text{NO}^-(\text{H}_2\text{O})_2$  spectra, the first and second ion-solvent dissociation energies were found to be  $0.72 \pm 0.05$  and  $0.68 \pm 0.06$  eV, while the ion-solvent dissociation energy for  $\text{NO}^-(\text{D}_2\text{O})_1$  was found to be  $0.77 \text{ eV} \pm 0.05 \text{ eV}$ . These are among the largest solvation energies that we have encountered thus far, and they probably arise due to a combination of hydrogen bonding, charge transfer effects, and electrostatic interactions between the  $\text{NO}^-$  sub-ion and its water solvent molecule(s).

## ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation under grant CHE-8511320.

## REFERENCES

- 1 (a) E. Clementi, *J. Chem. Phys.*, 61 (1974) 799.  
(b) J.M. Howell, A.M. Sapse, E. Singman and G. Snyder, *J. Phys. Chem.*, 86 (1982) 2345.  
(c) D. Cremer and E. Kraka, *J. Phys. Chem.*, 90 (1986) 33.  
(d) J. Gao, D.S. Garner and W.L. Jorgensen, *J. Am. Chem. Soc.*, 108 (1986) 4784.  
(e) L.A. Curtiss, C.A. Melendres, A.E. Reed and F. Weinhold, *J. Comput. Chem.*, 7 (1986) 294.  
(f) J. Simons and K.D. Jordan, *Chem. Rev.*, 87 (1987) 535 and references cited therein.
- 2 (a) M. Arshadi and P. Kebarle, *J. Phys. Chem.*, 74 (1970) 1483.  
(b) M. Arshadi, R. Yamdagni and P. Kebarle, *J. Phys. Chem.*, 74 (1970) 1475.  
(c) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, 93 (1971) 7139.
- 3 (a) R.G. Keesee, N. Lee and A.W. Castleman, Jr., *J. Chem. Phys.*, 73 (1980) 2195.  
(b) N. Lee, R.G. Keesee and A.W. Castleman, Jr., *J. Chem. Phys.*, 71 (1980) 1089.  
(c) R.G. Keesee, N. Lee and A.W. Castleman, Jr., *J. Am. Chem. Soc.*, 101 (1979) 2599.
- 4 F.C. Fehsenfeld and E.E. Ferguson, *J. Chem. Phys.*, 61 (1974) 3181. R.S. Narcissi, A.D. Bailey, L.E. Wlodyka and C.R. Philbrick, *J. Atmos. Terr. Phys.*, 34 (1972) 647.
- 5 J.A. Burt, *J. Chem. Phys.*, 57 (1972) 4649. P.C. Cosby, J.H. Ling, J.R. Peterson and J.T. Mosely, *J. Chem. Phys.*, 65 (1976) 5267 and references cited therein. L.C. Lee and G.P. Smith, *J. Chem. Phys.*, 70 (1979) 1727. A.W. Castleman, Jr. and R.G. Keesee, *Chem. Rev.*, 86 (1986) 589 and references cited therein. J. Snodgrass, H.-S. Kim and M.T. Bowers, *J. Chem. Phys.*, 88 (1988) 3072.
- 6 (a) S. Golub and B. Steiner, *J. Chem. Phys.*, 49 (1968) 5191.  
(b) T.M. Miller, D.G. Leopold, K.K. Murray and W.C. Lineberger, *Bull. Am. Phys. Soc.*, 30 (1985) 880.  
(c) W.C. Lineberger, private communication, 1989.  
(d) M.J. Johnson, private communication, 1989.
- 7 J.V. Coe, J.T. Snodgrass, C.B. Freidhoff, K.M. McHugh and K.H. Bowen, *J. Chem. Phys.*, 84 (1986) 618.
- 8 J.V. Coe, J.T. Snodgrass, C.B. Freidhoff, K.M. McHugh and K.H. Bowen, *J. Chem. Phys.*, 87 (1987) 4302.
- 9 M.W. Siegel, R.J. Celotta, J.L. Hall, J. Levine and R.A. Bennett, *Phys. Rev. A*, 6 (1972) 607.
- 10 N.L. Lee, R.G. Keesee and A.W. Castleman, Jr., *J. Colloid Interface Sci.*, 75 (1980) 555.
- 11 L.A. Posey, M.J. DeLuca, P.J. Campagnola and M.A. Johnson, *J. Phys. Chem.*, 93 (1989) 1178.
- 12 S.T. Arnold, J.G. Eaton, D. Patel-Misra, H.W. Sarkas and K.H. Bowen, in J.P. Maier (Ed.), *Ion and Cluster Ion Spectroscopy and Structure*, Elsevier, Amsterdam, 1989.
- 13 C.B. Freidhoff, Ph.D. Thesis, The Johns Hopkins University, 1987.
- 14 J.T. Snodgrass, J.V. Coe, C.B. Freidhoff, K.M. McHugh and K.H. Bowen, *Faraday Discuss. Chem. Soc.*, 86 (1988) 241.
- 15 J.T. Snodgrass, Ph.D. Thesis, The Johns Hopkins University, 1986.