

NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF  $\text{N}_2\text{O}^-$  AND  $(\text{N}_2\text{O})_2^-$ J.V. COE, J.T. SNODGRASS, C.B. FREIDHOFF,  
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We have recorded the photoelectron spectra of the gas phase negative ions  $\text{N}_2\text{O}^-$  and  $(\text{N}_2\text{O})_2^-$  both of which were prepared in a nozzle ion source. The shift between the maxima of the two spectra is interpreted in terms of the dissociation energy of the dimer ion.

## 1. Introduction

Electron attachment and related processes in nitrous oxide have been studied extensively [1–7]. The existence of the gas-phase negative ion  $\text{N}_2\text{O}^-$  was first established in 1966 when Paulson identified it in mass spectra [8]. The subsequent work of both Chantry [9,10] and Paulson [11] found that  $\text{N}_2\text{O}^-$  was formed by charge transfer between  $\text{NO}^-$  and  $\text{N}_2\text{O}$ . The formation of  $\text{N}_2\text{O}^-$  has been discussed by Ferguson et al. [12] in terms of Walsh's rules and the structural changes involved in forming bent  $\text{N}_2\text{O}^-$  from linear neutral  $\text{N}_2\text{O}$ . They noted that, since  $\text{N}_2\text{O}^-$  and  $\text{NO}_2$  are isoelectronic species,  $\text{N}_2\text{O}^-$  can be expected to be bent by approximately  $134^\circ$ . The energy required to bend neutral  $\text{N}_2\text{O}$  from  $180^\circ$  to  $\approx 134^\circ$  has been estimated to be about 1 eV. This, it was argued, presents a substantial activation barrier to three-body electron attachment, and thus explains why many ion source environments do not readily form  $\text{N}_2\text{O}^-$ . Theoretical studies by Hopper et al. [13] and by Yarkony [14] have determined the equilibrium structure and vibrational frequencies of  $\text{N}_2\text{O}^-$ . These studies confirm the expected bond angle in  $\text{N}_2\text{O}^-$  and also find significant differences between the bond distance in  $\text{N}_2\text{O}$  and  $\text{N}_2\text{O}^-$ . In addition, the characteristics of the three lowest electronic states of  $\text{N}_2\text{O}^-$  have been discussed by Bardsley [15]. Over the years the electron affinity of  $\text{N}_2\text{O}$  has been measured by charge exchange, electron attachment, and collisional

ionization methods [16]. Presently, however, the most widely accepted value for the adiabatic electron affinity of  $\text{N}_2\text{O}$  is  $+0.22 \pm 0.1$  eV, which is based on the beam-collision-chamber experiments of Hopper et al. [13]. Their combined experimental and theoretical results also gave a value for the vertical electron affinity of  $\text{N}_2\text{O}$  of  $-2.23 \pm 0.2$  eV.

To our knowledge there have been neither observations of nor calculations on the negative dimer ion,  $(\text{N}_2\text{O})_2^-$ . Both Klots and Compton [17] and Knapp et al. [18] have performed experiments in which supersonic beams of carbon dioxide and of nitrous oxide were bombarded with electrons to yield various negative cluster ions. While both groups observed the ions  $(\text{CO}_2)_n^-$ ,  $n \geq 2$ , neither saw any ions of the stoichiometry  $(\text{N}_2\text{O})_n^-$ . In this paper we report the observation of  $(\text{N}_2\text{O})_2^-$  and the photoelectron spectra of  $\text{N}_2\text{O}^-$  and  $(\text{N}_2\text{O})_2^-$ .

## 2. Experimental

In negative ion photoelectron spectroscopy, a mass-selected negative ion beam is crossed with a fixed-frequency laser beam under field-free and collision-free conditions, and the resulting photo-detached electrons are subjected to energy analysis. The difference between the photon energy and the center-of-mass photoelectron kinetic energy of a given feature in the photoelectron spectrum corre-

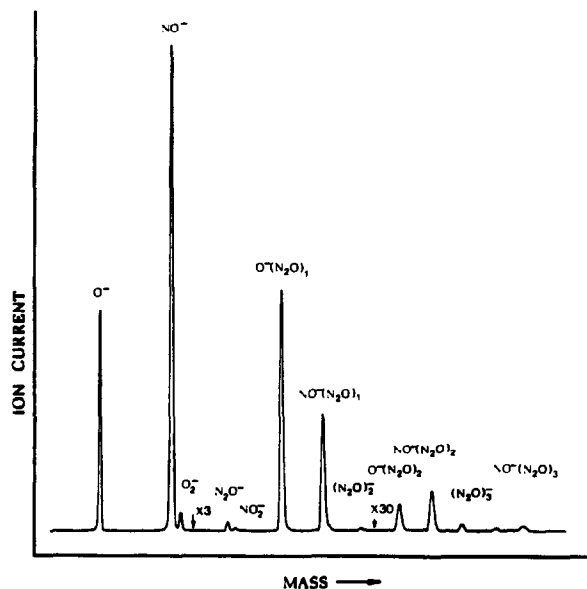


Fig. 1. A negative ion mass spectrum generated using neat  $N_2O$  as the source gas in our nozzle ion source.

sponds in general to the transition energy or the electron binding energy from an occupied negative ion energy level to a level in its neutral counterpart. Our apparatus, which has been described previously [19], employs a Wien ( $E \times B$ ) velocity filter for mass selection, an argon ion laser operated intracavity through the ion-photon interaction region, and a magnetically shielded hemispherical electron energy analyzer.

Both  $N_2O^-$  and  $(N_2O)_2^-$  ions were generated in a nozzle ion source similar to that developed by Haberland et al. [20]. This source involves the injection of electrons from a hot biased filament into an expanding supersonic jet, and our version of it has been described previously [21]. Source operating parameters during these experiments were a nozzle diameter of  $18 \mu m$ , a nozzle stagnation pressure of 2 atm (neat  $N_2O$ ), a source bias of  $-500$  V, a filament bias of  $-85$  V relative to the source, a filament emission current of  $\approx 14$  mA, and a nozzle temperature of  $0^\circ C$ . A typical mass spectrum is presented in fig. 1.

### 3. Results

The negative ion photoelectron spectra of  $N_2O^-$

and  $(N_2O)_2^-$  are presented in fig. 2. Both spectra were recorded with  $2.540$  eV photons and with a channel spacing of  $8.5$  meV. The spectrum of  $N_2O^-$  represents 7 h of integration with  $1 \times 10^{-11}$  A of  $N_2O^-$  while that of  $(N_2O)_2^-$  represents 3 h of integration with  $3 \times 10^{-12}$  A of  $(N_2O)_2^-$ . Both spectra were calibrated by photodetaching  $O^-$ . The instrumental resolution of the electron energy analyzer was  $30$  meV during these experiments.

The photoelectron spectrum of  $N_2O^-$  is a single broad peak with a fitted maximum at a c.m. photoelectron kinetic energy of  $1.06$  eV and an apparent photodetachment onset at an electron binding energy of  $0.76 \pm 0.10$  eV. The upper scan in the spectrum of  $N_2O^-$  (fig. 2a) has 2.5 times the signal of the lower full-range scan. It shows that some of the structure in the  $N_2O^-$  envelope is real.

The photoelectron spectrum of  $(N_2O)_2^-$  in fig. 2b

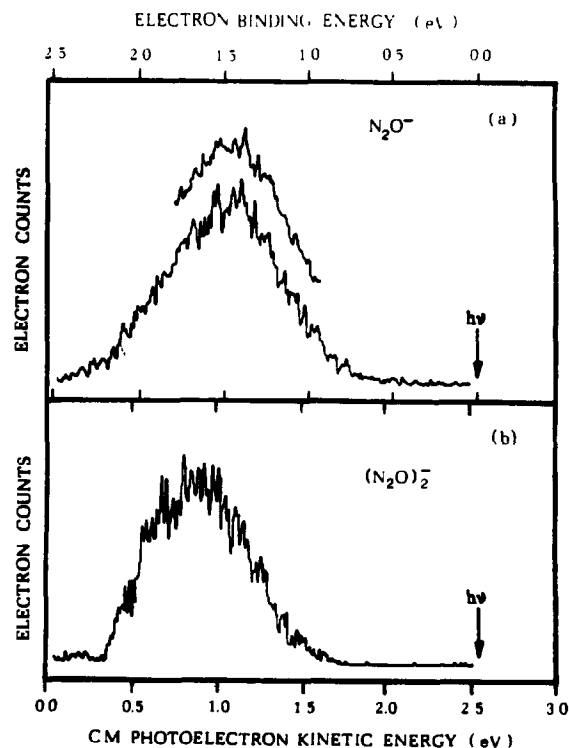


Fig. 2. The photoelectron spectrum of (a)  $N_2O^-$  and (b)  $(N_2O)_2^-$  presented in terms of center-of-mass electron kinetic energies and electron binding energies. Both spectra were recorded with  $2.540$  eV photons. The limited range scan above the full spectrum of  $N_2O^-$  has 2.5 times more signal.

is similar to that of  $\text{N}_2\text{O}^-$  in that it is also a single broad band. Its fitted maximum, however, occurs at a c.m. photoelectron kinetic energy of 0.87 eV, and this represents a shift to lower electron kinetic energy of 0.19 eV relative to the maximum in the  $\text{N}_2\text{O}^-$  spectrum. Also, because the signal in the  $(\text{N}_2\text{O})_2^-$  spectrum is so much lower than in the  $\text{N}_2\text{O}^-$  spectrum, we ascribe the "structure" in the  $(\text{N}_2\text{O})_2^-$  spectrum only to noise

#### 4. Discussion

Because of the large geometrical difference between  $\text{N}_2\text{O}$  and  $\text{N}_2\text{O}^-$ , we do not anticipate appreciable Franck-Condon overlap between the lowest-lying levels in the ion and its neutral. Photodetachment of  $\text{N}_2\text{O}^-$  is expected to access a portion of the neutral's potential roughly 1 eV above the lowest-lying neutral level, thereby resulting in highly excited vibrational states of  $\text{N}_2\text{O}$ . We interpret the photoelectron spectrum of  $\text{N}_2\text{O}^-$  as due to a largely unresolved progression in the bending mode of  $\text{N}_2\text{O}$ , complicated perhaps by combinations of stretches and bends. Even though there is some structure near the maximum of the  $\text{N}_2\text{O}^-$  spectrum, the density of states and our available resolution preclude a more definitive assignment at this point.

As mentioned above, the electron binding (transition) energy corresponding to the observed onset of photodetached electrons in our  $\text{N}_2\text{O}^-$  spectrum is  $0.76 \pm 0.10$  eV. For reasons already stated, this is not thought to be the origin transition. While we cannot rule out the possibility that hot-band transitions from vibrationally excited  $\text{N}_2\text{O}^-$  ions contribute to the signal in the region of the photodetachment onset, the collisionally cooled environment of the nozzle ion source together with the presumed charge transfer formation mechanism would seem to make it unlikely that the  $\text{N}_2\text{O}^-$  ion is highly excited. The observed photodetachment onset energy should probably be interpreted as the transition energy where the Franck-Condon overlap between the lowest (or possibly the lower) energy level(s) of the negative ion and the accessible levels of the neutral first becomes large enough to give a detectable photodetachment signal. The vertical detachment energy (VDE) is usually defined as the minimum energy required to photodetach electrons from a negative ion in its lowest energy state and in

its equilibrium geometry without a change in nuclear coordinates. The photodetachment onset energy reported here is thus a lower limit to the VDE of  $\text{N}_2\text{O}^-$ , and an upper limit to the adiabatic electron affinity of  $\text{N}_2\text{O}$ .

When photodetachment transitions occur from the ground vibrational level of a negative ion one expects (in the diatomic limit, at least) an intensity maximum in the resulting photoelectron spectrum which corresponds to the VDE. The electron binding energy corresponding to the maximum in our  $\text{N}_2\text{O}^-$  spectrum is roughly 1.5 eV and thus is a reasonable estimate of the VDE. In view of the reported adiabatic electron affinity of  $\text{N}_2\text{O}$  and estimates of the energy required to distort  $\text{N}_2\text{O}$  into the  $\text{N}_2\text{O}^-$  configuration, this is also consistent with a reasonable expectation for the value of the VDE of  $\text{N}_2\text{O}^-$ .

While substantial information is available about the structure and bonding of  $\text{N}_2\text{O}^-$ , very little is known about the nature of the bonding interaction in  $(\text{N}_2\text{O})_2^-$ . An important aspect of this problem concerns the distribution of excess negative charge within the negative dimer ion. One can imagine two extreme charge distribution categories where in one the charge is localized on one of the two components of the dimer ion, and where in the other there is a dispersal of the negative charge over both components. The situation where the excess charge is localized on a single component of a dimer ion is reminiscent of the usual notion of a solvated anion. There the primary negative ion (the anion) may be thought of as remaining largely intact even though it is perturbed and stabilized by its solvent molecule. In this case electrostatic interactions between the ion and its solvent presumably dominate the bonding. In other cases, however, charge dispersal effects may also make significant contributions to the bonding. These contributions may arise either in the sense of covalency in the ion-neutral bond or in the sense of excess electron delocalization via electron tunneling between two energetically and structurally equivalent sites within the dimer ion.

Some guidance in considering the bonding in  $(\text{N}_2\text{O})_2^-$  is provided by studies of the isoelectronic species  $(\text{CO}_2)_2^-$ . Jordan et al. [22-24] have performed calculations which found the most stable configuration of  $(\text{CO}_2)_2^-$  to be that of a bent  $\text{CO}_2^-$  sub-ion solvated by a slightly perturbed  $\text{CO}_2$  molecule rather than that of an "oxalate-like" ion. Kafafi et al. [25] have

found spectroscopic evidence for two compounds of stoichiometry  $\text{LiC}_2\text{O}_4$  upon reaction of Li with  $\text{CO}_2$  in argon matrices. They describe these species as  $\text{Li}^+\text{C}_2\text{O}_4^-$  and as the  $(\text{Li}^+\text{CO}_2^-)\text{CO}_2$  adduct. Since  $\text{Li}^+\text{C}_2\text{O}_4^-$  can be photolytically converted to the solvated form  $(\text{Li}^+\text{CO}_2^-)\text{CO}_2$ , the latter is thought to be more stable. A somewhat different picture is suggested by the collisional charge transfer experiments of Quitevis and Herschbach [26] who determined a nominal electron affinity for  $(\text{CO}_2)_2$  of +0.8 eV. Their result implies a stabilization of one eV or more relative to  $\text{CO}_2^- + \text{CO}_2$ , and suggest a stronger interaction than that expected in the solvated ion (ion-molecule complex) model.

The photoelectron spectra of negative cluster ions can sometimes provide clues about their make up. This is especially the case when the excess electron is localized on a single component of the cluster ion. There the intact sub-ion (or primary ion) can act as the "chromophore" for photodetachment. This leads to a cluster-ion photoelectron spectrum which resembles the photoelectron spectrum of the free primary ion except for being *shifted* to a lower electron kinetic energy (higher electron binding energy) due to the stabilizing effect of solvation. In this case of a dimer ion, the magnitude of this shift corresponds to the primary ion-neutral solvent dissociation energy (also the absolute value of the solvation energy) minus the weak-bond dissociation energy of the dimer ion's corresponding neutral dimer. Since ion-solvent interaction energies are usually somewhat larger than van der Waals bond strengths, and since the photodetachment experiment may not always access the weak-bond well of the neutral, the shift is a good approximation to the ion-neutral dissociation (solvation) energy. We have studied several negative cluster ion systems that conform to the expectations of a solvated ion model, and among these are  $\text{NO}^-(\text{N}_2\text{O})_{n=1,2}$  [21],  $\text{H}^-(\text{NH}_3)_{n=1,2}$  [27], and  $\text{NH}_2^-(\text{NH}_3)_{n=1,2}$  [28]. The  $\text{NO}^-(\text{N}_2\text{O})_{n=1,2}$  system is particularly pertinent to a consideration of  $(\text{N}_2\text{O})_2^-$ . In the photoelectron spectra of  $\text{NO}^-(\text{N}_2\text{O})_1$  and  $\text{NO}^-(\text{N}_2\text{O})_2$  the highly structured photoelectron spectral pattern of  $\text{NO}^-$  is preserved in both, even though it is successively shifted to lower electron kinetic energies and broadened. The shifts between the origin peaks of  $\text{NO}^-$  and  $\text{NO}^-(\text{N}_2\text{O})_1$  and between those of  $\text{NO}^-(\text{N}_2\text{O})_1$  and  $\text{NO}^-(\text{N}_2\text{O})_2$  are roughly equal to the first and second solvation energies

for gas-phase nitric oxide negative ions being solvated by nitrous oxide molecules, and they are both  $\approx 0.2$  eV.

The case of  $(\text{N}_2\text{O})_2^-$  is analogous to that of  $\text{NO}^-(\text{N}_2\text{O})_{n=1,2}$  in that the shift between the fitted maxima of the  $\text{N}_2\text{O}^-$  and the  $(\text{N}_2\text{O})_2^-$  spectra is essentially the same as the shift between the  $\text{NO}^-$  and the  $\text{NO}^-(\text{N}_2\text{O})_1$  spectra. The two systems are different, however, in that the  $\text{N}_2\text{O}^-$  spectrum, unlike the  $\text{NO}^-$  spectrum, does not exhibit a "fingerprint" spectral pattern. While this makes a solvation ion interpretation of the  $(\text{N}_2\text{O})_2^-$  spectrum less certain than it was in the case of  $\text{NO}^-(\text{N}_2\text{O})_n$ , the available evidence is nevertheless somewhat supportive of it. Under this interpretation the  $(\text{N}_2\text{O})_2^-$  spectrum is viewed as arising from the photodetachment of an ionic species which is best described as a bent  $\text{N}_2\text{O}^-$  solvated by a neutral linear  $\text{N}_2\text{O}$  molecule, i.e. as  $\text{N}_2\text{O}^-(\text{N}_2\text{O})_1$ , and the  $\approx 0.2$  eV shift between the  $\text{N}_2\text{O}^-$  and the  $(\text{N}_2\text{O})_2^-$  spectra is viewed as a rough measure of the dissociation energy of  $\text{N}_2\text{O}^-(\text{N}_2\text{O})_1$  into  $\text{N}_2\text{O}^-$  and  $\text{N}_2\text{O}$ .

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