Photoelectron Spectroscopy of CS$^-$ and NS$^-$

Susan M. Burnett, C. S. Felgerle, Amy E. Stevens, and W. C. Lineberger*

Department of Chemistry, University of Colorado and Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80309 (Received: September 1, 1982)

Laser photoelectron spectroscopy is used to study NS$^-$ and CS$^-$ ions. Analysis of the photoelectron spectra yields electron affinities of 1.194 $\pm$ 0.011 and 0.205 $\pm$ 0.021 eV for the corresponding neutral molecules. Equilibrium bond lengths for the negative ions are obtained from a Franck-Condon analysis of the relative intensities of the observed transitions. The NS$^-$ spectrum shows photodetachment from several vibrational levels, allowing determination of the NS$^-$ vibrational frequency as 880 $\pm$ 70 cm$^{-1}$.

Introduction

Photoelectron spectroscopy and threshold photodetachment of negative ions have proven to be among the most reliable methods of obtaining electron affinities (EAs).$^{1-10}$ These quantities are important thermodynamic data for determining reactivity and gas-phase acidities.$^{11}$ Since so few experimental molecular EAs are known, it is useful to develop models regarding negative ion formation and periodic trends$^{12,13}$ in molecular electron affinities; for this purpose an increased data base is necessary. Previous to this work, SH,$^{13}$ SD,$^{13}$ S$_2$,$^{14}$ and SO$^{15}$ were the only diatomic sulfur compounds with accurately known EA's. Here we report the photoelectron spectra of NS$^-$ and CS$^-$, and the resulting EA's for the corresponding negatives, as well as some spectroscopic constants for the negative ions. CS$^-$ is a particularly interesting ion in that its parent molecule CS has a closed shell configuration and, unlike the isoelectronic CO, will bind an electron to form a stable ion.

Experimental Section

The photoelectron spectroscopy technique and apparatus have been previously described in detail.$^{14,16}$ Negative ions are produced in a gas discharge source, extracted, and accelerated into a 680-eV beam. Mass selection is achieved by use of crossed electric and magnetic fields, and the beam then intersects the 488-nm intracavity radiation of an Ar II laser. Electrons photodetached into the 0.006 sr acceptance angle of the hemispherical electron monochromator (resolution 55-meV fwhm) are energy analyzed and counted to produce the photoelectron spectrum. The recorded spectrum is converted to an absolute energy scale by calibration against a simultaneously produced ion of known EA. An energy scale compression factor$^{17}$ of 1.022 is also included in conversion of the data; this number was obtained by comparing the known NO vibrational splittings$^{18}$ to an NO$^-$ photoelectron spectrum. Laser polarization is set at the "magic" angle such that the spectra are proportional to average photodetachment cross sections; relative peak intensities are then independent of the angular distribution, so that they can be used for a Franck-Condon factor analysis.

The most stable beams of CS$^-$ were produced by use of a tantalum filament with a mixture of source gases CO and CS$_2$ (ratio approximately 3:1) at a total pressure of about 0.1 torr. These conditions also produced an intense beam of S$^-$, which made a convenient calibration ion$^{19}$ for the CS$^-$ spectrum. For the NS$^-$ spectrum a thoriated iridium filament was used, with N$_2$O and a trace of CS$_2$. A beam of simultaneously produced O$^-$ provided the calibration$^{20}$ for NS$^-$.

Results and Discussion

The ground electronic state of NS is a $^2$II with an electron configuration ...$(7s)^2(2\pi)^4(3\pi)$ such that an electron is added to a $\pi^*$ orbital (3\pi) to form the negative ion. We thus expect to see a significant bond lengthening upon ion formation, with the result that one should find a long Franck-Condon progression of vibrational peaks in the photoelectron spectrum. This expectation is analogous to the well-known NO$^-$ case.$^{16}$ Figure 1 shows the NS$^-$ photoelectron spectrum obtained with 488-nm photons (2.54 eV). The observed peaks are due to various vibrational transitions from the ground electronic state of the ion to the ground electronic state of the neutral molecule. In particular, peaks A-D are the result of detachment from the ground vibrational state of the ion, NS$^-(v'=0)$ to four

the remaining peak spacings are considerably smaller. This matrix element, or possible transmission distortion in the vibrational level of the final state (neutral) and obscured noticeably with changes in assumptions (such as transitions from vibronic transition and peaks E through G potential. Known values of the constants for the Morse oscillator approximation to the Morse potential yields \( \omega_{\text{vib}} \) (0.02 cm\(^{-1} \)) or (0.002 Å or with changes in \( T_{\text{vib}} \) of 100 K).

The intervals between peaks A–D are consistent with the known values of \( \omega_{\text{vib}} = 1218.7 \) cm\(^{-1} \) and \( r_{\text{e}} = 7.28 \) cm\(^{-1} \) for NS,\(^{18} \) within the limits of our experimental accuracy, and the remaining peak spacings are considerably smaller. This break provides the basis for identifying peak A as the (0,0) vibronic transition and peaks E through G as hot bands. The extended vibrational progression is evidence of the expected geometry change, which is quantified by a Franck–Condon factor analysis. The analysis is based on an anharmonic oscillator approximation to the Morse potential. Known values of the constants \( \omega_{\text{vib}} \) and \( r_{\text{e}} \) for the neutral are used along with \( \omega_{\text{vib}} \) (from the hot band spacings) for the ion, and \( r_{\text{e}} \) and the vibrational temperature of the ion are varied until a good fit to the relative intensities of the (\( \nu', \nu'' \)) peaks is obtained. Figure 2 compares the observed NS\(^{-} \) spectrum with the best fit result. The resulting value is \( r_{\text{e}} \) (NS\(^{-} \)) = 1.589 ± 0.02 Å, based on \( r_{\text{e}} \) (NS) = 1.49402 Å,\(^{18} \) and with \( T_{\text{vib}} = 950 \) K. The quality of the fit deteriorates noticeably with changes in \( r_{\text{e}} \) as small as 0.002 Å, but we use a larger empirical error limit since other assumptions (such as energy independence of the electronic matrix element, or possible transmission distortion in the energy analyzer) have not been quantitatively tested. We also observe a hot band system, peaks E–G, showing transitions from NS\(^{-} \) (\( \nu'' = 1,2,3 \)) to the ground vibrational state of NS. From analysis of this system we determine \( \omega_{\text{vib}} \) for the ion to be 880 ± 70 cm\(^{-1} \); the large change shows substantial weakening of the bond arising from the \( \pi^* \) electron in NS\(^{-} \).

The electron affinity is obtained from the difference between the photon energy and the (0,0) peak energy, with the result that \( \text{EA} \) (NS\(^{-} \)) = 1.194 ± 0.011 eV. This value has been corrected for rotational pulling (discussed in more detail in ref 21) and for the spin orbit splitting of the \( ^2 \Pi \) ground state of NS. Since the (0,0) peak corresponds to a large number of unresolved transitions between various rotational states of the ion and neutral, it is necessary to determine what position relative to the peak center corresponds to the EA, the transition between rotationless levels. The pulling depends on \( \Delta \) and \( T_{\text{vib}} \), and in this case is estimated to be 5 ± 2 meV. We also make a spin–orbit correction. The NS \( ^2 \Pi \) splitting is 221.5 cm\(^{-1} \) (0.0275 eV)\(^{18} \) and a NS\(^{-} \) \( ^3 \Sigma \rightarrow ^2 \Pi \) splitting (by analogy to NO) should have equal intensity in each component of the doublet. The \( ^2 \Pi \) splitting is, however, not resolved in our experiment, so the observed peaks are at a position midway between the transition energies corresponding to the two components. A correction of 0.014 eV, half of the NS \( ^2 \Pi \) splitting, is accordingly subtracted from the observed (0,0) transition energy to obtain the EA reported above.

In the CS\(^{-} \) photoelectron spectrum, we would expect to see the (0,0) peak at the high end of the electron energy scale (low EA) because CS is isoelectronic with CO, which has a negative EA.\(^{22} \) We assume the ground state of CS\(^{-} \) to be a \( ^4 \Pi \) state, in analogy to NO. Then the additional electron in the CS\(^{-} \) ion is in an antibonding orbital, and its spectrum ought to have a fairly long vibrational series, as in the NS\(^{-} \) case. Figure 3 shows the CS\(^{-} \) photoelectron spectrum, again obtained with 2.54-eV photons. It does contain the features mentioned above, and vibrational spacings are consistent with the known spectroscopic constants for CS. Peaks A through E represent the transitions CS(X \(^1 \Sigma, \nu'' = 0,1,2,3,4 \) ← CS(X \(^2 \Pi, \nu'' = 0 \)) as labeled, and no detachment is observed from vibrationally excited ions. A similar Franck–Condon analysis of the spectrum yields the value \( r_{\text{e}} \) (CS\(^{-} \)) = 1.627 ± 0.02 Å based on \( r_{\text{e}} \) (CS) = 1.53949 Å.\(^{18} \) Since no hot bands are observed, we cannot determine \( \omega_{\text{vib}} \) for CS\(^{-} \); values of 900–1300 cm\(^{-1} \) were used for the Franck–Condon analysis with little change in the predicted spectrum. The nonoccurrence of hot bands is not terribly surprising since the CS\(^{-} \) (\( \nu'' = 1 \)) level is likely bound by only about 50 meV. The energy of the

(0,0) peak indicates that $EA(CS) = 0.205 \pm 0.021$ eV, which as before includes a rotational correction of $-0.004$ eV, and spin–orbit correction of $+0.016$ eV. Here the spin–orbit correction was based on an estimated value of the $^2I$ splitting in CS$^-$ (250 ± 100 cm$^{-1}$) obtained by comparison with the splitting in isoelectronic molecules NS (221.5 cm$^{-1}$) and CCl (135 cm$^{-1}$). Because we assume that the negative charge resides primarily on the S in CS$^-$, the spin–orbit splitting of S$^-$ (482 cm$^{-1}$) was also considered, and used as an upper bound. A value of 250 cm$^{-1}$ was chosen, and provides the major source of error in the EA.

The following quantities are determined by these experiments:

$$EA(CS) = 0.205 \pm 0.021 \text{ eV}$$
$$EA(NS) = 1.194 \pm 0.011 \text{ eV}$$
$$r_a(CS^-) = 1.627 \pm 0.02 \text{ Å} \quad r_a(NS^-) = 1.589 \pm 0.02 \text{ Å}$$
$$\omega_a(NS^-) = 880 \pm 70 \text{ cm}^{-1}$$

Comparing our results to previously reported values of the electron affinities of CS and NS, we find reasonable agreement. MacNeil and Thynne$^{23}$ reported $EA(CS) \leq 1.2$ eV, from observation of the appearance potential for CS$^-$ by dissociative attachment to COS; the present work provides the first quantitative data. Our result of 1.194 eV for $EA(NS)$ also is remarkably close to O'Hare's value of $1.3 \pm 0.3$ eV, obtained from an SCF calculation near the Hartree–Fock$^{24}$ limit (which assumed the ion geometry to be that of the neutral).

Acknowledgment. This work was supported by Grants PHY79-04928 and CHE78-18424 from the National Science Foundation. W.C.L. is pleased to acknowledge the award of a Faculty Fellowship by the University of Colorado Council on Research and Creative Work and support by the J. S. Guggenheim Foundation (1981–2). C.S.F. received support from an Exxon Foundation Fellowship.