

# Photoelectron Spectroscopy of CS<sup>-</sup> and NS<sup>-</sup>

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Laser photoelectron spectroscopy is used to study NS<sup>-</sup> and CS<sup>-</sup> 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<sup>-</sup> spectrum shows photodetachment from several vibrational levels, allowing determination of the NS<sup>-</sup> vibrational frequency as  $880 \pm 70$  cm<sup>-1</sup>.

## Introduction

Photoelectron spectroscopy and threshold photodetachment of negative ions have proven to be among the most reliable methods of obtaining electron affinities (EA's).<sup>1-10</sup> These quantities are important thermodynamic data for determining reactivity and gas-phase acidities.<sup>11</sup> Since so few experimental molecular EA's are known, it is useful to develop models regarding negative ion formation and periodic trends<sup>8,9,12</sup> in molecular electron affinities; for this purpose an increased data base is necessary. Previous to this work, SH,<sup>13</sup> SD,<sup>13</sup> S<sub>2</sub>,<sup>14</sup> and SO<sup>15</sup> were the only diatomic sulfur compounds with accurately known EA's. Here we report the photoelectron spectra of NS<sup>-</sup> and CS<sup>-</sup>, and the resulting EA's for the corresponding neutrals, as well as some spectroscopic constants for the negative ions. CS<sup>-</sup> 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.<sup>4,14,16</sup> 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<sup>17</sup> of 1.022 is also included in conversion of the data; this number was obtained by comparing the known NO vibrational splittings<sup>18</sup> to an NO<sup>-</sup> 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.

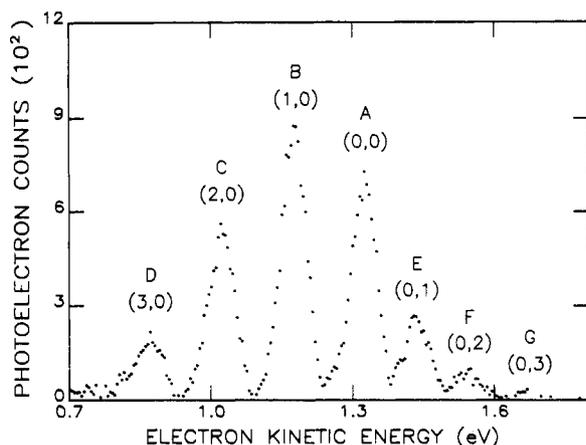
The most stable beams of CS<sup>-</sup> were produced by use of a tantalum filament with a mixture of source gases CO and CS<sub>2</sub> (ratio approximately 3:1) at a total pressure of about 0.1 torr. These conditions also produced an intense beam of S<sup>-</sup>, which made a convenient calibration ion<sup>19</sup> for the CS<sup>-</sup> spectrum. For the NS<sup>-</sup> spectrum a thoriated iridium filament was used, with N<sub>2</sub>O and a trace of CS<sub>2</sub>. A beam of simultaneously produced O<sup>-</sup> provided the calibration<sup>20</sup> for NS<sup>-</sup>. Mass selected beam currents were between 12 and 15 pA during the two experiments.

## Results and Discussion

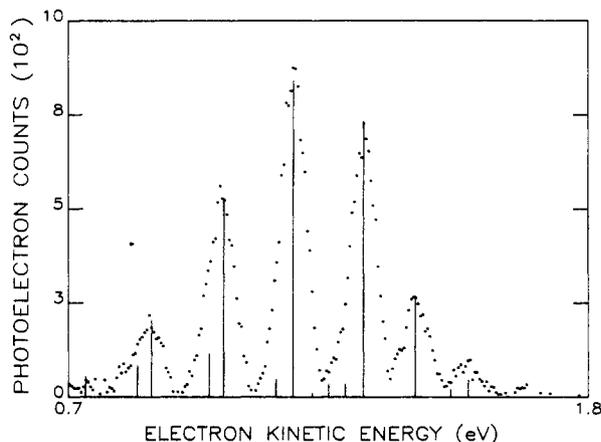
The ground electronic state of NS is a <sup>2</sup>II with an electron configuration ... $(7\sigma)^2(2\pi)^4(3\pi)^1$  such that an electron is added to a  $\pi^*$  orbital ( $3\pi$ ) to form the negative ion. We thus expect to see a significant bond lengthening upon ion formation, with the result that one should find a long Franck-Condon progression of vibrational peaks in the photoelectron spectrum. This expectation is analogous to the well-known NO<sup>-</sup> case.<sup>16</sup> Figure 1 shows the NS<sup>-</sup> 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<sup>-</sup>( $v''=0$ ) to four

- (1) Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* 1975, 4, 539.
- (2) Corderman, R. R.; Lineberger, W. C. *Annu. Rev. Phys. Chem.* 1979, 30, 347.
- (3) Engelking, P. C.; Corderman, R. R.; Wendoloski, J. J.; Ellison, G. B.; O'Neil, S. V.; Lineberger, W. C. *J. Chem. Phys.* 1981, 74, 5460.
- (4) Kasdan, A.; Herbst, E.; Lineberger, W. C. *J. Chem. Phys.* 1975, 62, 541.
- (5) Slater, J.; Read, F. H.; Novick, S. E.; Lineberger, W. C. *Phys. Rev. A* 1978, 17, 201.
- (6) Novick, S. E.; Engelking, P. C.; Jones, P. L.; Futrell, J. H.; Lineberger, W. C. *J. Chem. Phys.* 1979, 70, 2652.
- (7) Hotop, H.; Patterson, T. A.; Lineberger, W. C.; *Phys. Rev. A* 1973, 8, 762.
- (8) Lowe, J. P. *J. Am. Chem. Soc.* 1977, 99, 5557.
- (9) Janousek, B. K.; Brauman, J. I. "Gas Phase Ion Chemistry"; Academic Press: New York, 1979; Vol. 2, Chapter 10.
- (10) Jackson, R. L.; Hiberty, P. C.; Brauman, J. I. *J. Chem. Phys.* 1981, 7, 3705.
- (11) Bartmess, J. E.; McIver, Jr., R. T. "Gas Phase Ion Chemistry"; Academic Press: New York, 1979; Chapter 11.
- (12) Zittel, P. F.; Lineberger, W. C. *J. Chem. Phys.* 1976, 65, 1932.
- (13) Brauman, J. I.; Smith, K. C. *J. Am. Chem. Soc.* 1969, 91, 7778.
- (14) Breyer, F.; Frey, P.; Hotop, H. *Z. Phys. A* 1981, 300, 7.
- (15) Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* 1974, 60, 1740.
- (16) Lineberger, W. C. "Chemical and Biochemical Applications of Layers"; Academic Press: New York, 1974; Vol. I, pp 71-101.
- (17) Siegel, M. W.; Celotta, R. J.; Hall, J. L.; Levine, J.; Bennett, R. A. *Phys. Rev. A* 1972, 6, 607.

- (17) Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* 1976, 65, 4323.
- (18) Huber, K. P.; Herzberg, G. "Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules"; Van Nostrand-Reinhold: New York, 1979.
- (19) Lineberger, W. C.; Woodward, B. W. *Phys. Rev. Lett.* 1970, 25, 424.
- (20) Hotop, H.; Bennett, R. A.; Lineberger, W. C. *J. Chem. Phys.* 1973, 58, 2373.

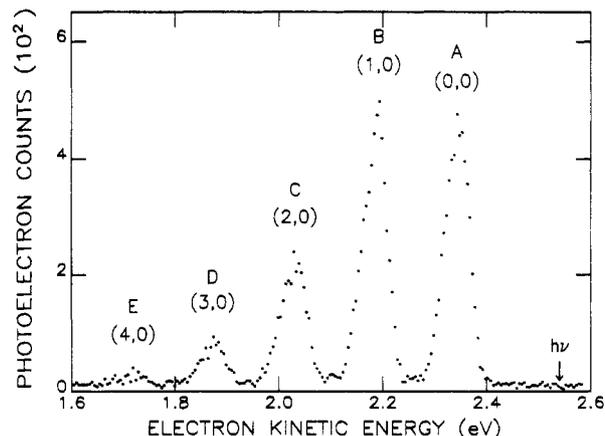


**Figure 1.** Photoelectron spectrum of  $\text{NS}^-$ , with 2.54-eV photons and 15-pA beam current. Peaks are labeled  $(v', v'')$ , where  $v'$  is the vibrational level of the final state (neutral) and  $v''$  is that of the initial state (ion).



**Figure 2.** Franck-Condon fit for  $\text{NS}^-$  spectrum, with  $T_{\text{vib}} = 950 \pm 100$  K, and  $r_e'' = 1.589 \pm 0.02$  Å. Vertical lines are the calculated peak intensities, based on the analysis model discussed in the text. The quality of the fit deteriorates noticeably with changes in  $r_e''$  of 0.002 Å or with changes in  $T_{\text{vib}}$  of 100 K.

vibrational states of the neutral,  $\text{NS}(X^2\Pi, v'=0,1,2,3)$ . The intervals between peaks A–D are consistent with the known values of  $\omega_e = 1218.7 \text{ cm}^{-1}$  and  $x_e\omega_e = 7.28 \text{ cm}^{-1}$  for  $\text{NS}$ ,<sup>18</sup> 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  $\omega_e$  and  $r_e$  for the neutral are used along with  $\omega_e$  (from the hot band spacings) for the ion, and  $r_e$  and the vibrational temperature of the ion are varied until a good fit to the relative intensities of the  $(v', v'')$  peaks is obtained. Figure 2 compares the observed  $\text{NS}^-$  spectrum with the best fit result. The resulting value is  $r_e''(\text{NS}^-) = 1.589 \pm 0.02$  Å, based on  $r_e'(\text{NS}) = 1.49402$  Å,<sup>18</sup> and with  $T_{\text{vib}} = 950$  K. The quality of the fit deteriorates noticeably with changes in  $r_e''$  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  $\text{NS}^-(v''=1,2,3)$  to the ground vibrational state of  $\text{NS}$ . From analysis of this system we determine



**Figure 3.** Photoelectron spectrum of  $\text{CS}^-$ , with 2.54-eV photons and 12-pA beam current. Peaks are labeled as in Figure 1. A Franck-Condon analysis yielded fits of comparable quality to that shown in Figure 2 for  $\text{NS}^-$ .

$\bar{\omega}_e$  for the ion to be  $880 \pm 70 \text{ cm}^{-1}$ ; the large change shows substantial weakening of the bond arising from the  $\pi^*$  electron in  $\text{NS}^-$ .

The electron affinity is obtained from the difference between the photon energy and the (0,0) peak energy, with the result that  $\text{EA}(\text{NS}) = 1.194 \pm 0.011$  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  $\text{NS}$ . 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  $\Delta B$  and on  $T_{\text{rot}}$ , and in this case is estimated to be  $5 \pm 2$  meV. We also make a spin-orbit correction. The  $\text{NS } ^2\Pi$  splitting is  $221.5 \text{ cm}^{-1}$  ( $0.0275$  eV)<sup>18</sup> and a  $\text{NS}^- ^3\Sigma \rightarrow \text{NS } ^2\Pi$  transition (by analogy to  $\text{NO}$ ) 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  $\text{NS } ^2\Pi$  splitting, is accordingly subtracted from the observed (0,0) transition energy to obtain the EA reported above.

In the  $\text{CS}^-$  photoelectron spectrum, we would expect to see the (0,0) peak at the high end of the electron energy scale (low EA) because  $\text{CS}$  is isoelectronic with  $\text{CO}$ , which has a negative EA.<sup>22</sup> We assume the ground state of  $\text{CS}^-$  to be a  $^2\Pi$  state, in analogy to  $\text{NS}$ . Then the additional electron in the  $\text{CS}^-$  ion is in an antibonding orbital, and its spectrum ought to have a fairly long vibrational series, as in the  $\text{NS}^-$  case. Figure 3 shows the  $\text{CS}^-$  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  $\text{CS}$ . Peaks A through E represent the transitions  $\text{CS}(X^1\Sigma, v''=0,1,2,3,4) \leftarrow \text{CS}^-(X^2\Pi, v'=0)$ , as labeled, and no detachment is observed from vibrationally excited ions. A similar Franck-Condon analysis of the spectrum yields the value  $r_e''(\text{CS}^-) = 1.627 \pm 0.02$  Å based on  $r_e'(\text{CS}) = 1.534941$  Å.<sup>18</sup> Since no hot bands are observed, we cannot determine  $\bar{\omega}_e$  for  $\text{CS}^-$ ; values of 900–1300  $\text{cm}^{-1}$  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  $\text{CS}^-(v=1)$  level is likely bound by only about 50 meV. The energy of the

(21) Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* 1977, 66, 5054.

(22) Schulz, G. *J. Phys. Rev. A* 1964, 135 988.

(0,0) peak indicates that  $EA(\text{CS}) = 0.205 \pm 0.021$  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  ${}^2\Pi$  splitting in  $\text{CS}^-$  ( $250 \pm 100$   $\text{cm}^{-1}$ ) obtained by comparison with the splitting in isoelectronic molecules  $\text{NS}$  ( $221.5$   $\text{cm}^{-1}$ ) and  $\text{CCl}$  ( $135$   $\text{cm}^{-1}$ ).<sup>18</sup> Because we assume that the negative charge resides primarily on the S in  $\text{CS}^-$ , the spin-orbit splitting of  $\text{S}^-$  ( $482$   $\text{cm}^{-1}$ )<sup>18</sup> was also considered, and used as an upper bound. A value of  $250$   $\text{cm}^{-1}$  was chosen, and provides the major source of error in the EA.

The following quantities are determined by these experiments:

$$EA(\text{CS}) = 0.205 \pm 0.021 \text{ eV}$$

$$EA(\text{NS}) = 1.194 \pm 0.011 \text{ eV}$$

$$r_e(\text{CS}^-) = 1.627 \pm 0.02 \text{ \AA} \quad r_e(\text{NS}^-) = 1.589 \pm 0.02 \text{ \AA}$$

$$\bar{\omega}_e(\text{NS}^-) = 880 \pm 70 \text{ cm}^{-1}$$

Comparing our results to previously reported values of the electron affinities of CS and NS, we find reasonable agreement. MacNeil and Thynne<sup>23</sup> reported  $EA(\text{CS}) \leq 1.2$  eV, from observation of the appearance potential for  $\text{CS}^-$  by dissociative attachment to COS; the present work provides the first quantitative data. Our result of 1.194 eV for  $EA(\text{NS})$  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<sup>24</sup> limit (which assumed the ion geometry to be that of the neutral).

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(23) MacNeil, K. A. G.; Thynne, J. C. J. *J. Chem. Phys.* 1979, 73, 2960.

(24) O'Hare, P. A. G. *J. Chem. Phys.* 1971, 54, 4124.