

# Photoelectron spectroscopy of SF<sup>-</sup>

Mark L. Polak, Mary K. Gilles, and W. C. Lineberger

Joint Institute for Laboratory Astrophysics, Department of Chemistry and Biochemistry,  
University of Colorado, Boulder, Colorado 80309-0440

(Received 17 December 1991; accepted 13 January 1992)

Because of its role in industrial plasma processing and etching, the SF molecule has been studied extensively, both theoretically and experimentally. Theoretical work on SF includes SCF and CEPA *ab initio* calculations.<sup>1,2</sup> Gas phase microwave<sup>3</sup> and infrared<sup>4</sup> spectroscopy by Endo *et al.* has provided precise molecular constants for the SF <sup>2</sup>Π<sub>3/2</sub> ground state. In earlier studies, Carrington *et al.*<sup>5</sup> and Di Lonardo and Trombetti<sup>6</sup> used lower resolution spectroscopic techniques to estimate the spin-orbit splitting of the inverted <sup>2</sup>Π ground state to be  $-387 \pm 25$  and  $-398 \pm 8$  cm<sup>-1</sup>, respectively. In addition, Hildenbrand<sup>7</sup> employed mass spectrometric measurements of high temperature equilibria to determine  $D_0(\text{SF}) = 81.2 \pm 2.0$  kcal/mol. On the other hand, very little is known about the corresponding negative ion. O'Hare and Wahl<sup>8</sup> used Hartree-Fock calculations to estimate the electron affinity of SF (2.5 ± 0.5 eV). Recently, Peterson and Woods<sup>9</sup> performed high level CI, MP4SDQ, and CEPA calculations to investigate the properties of SF<sup>-</sup>. In this study, we examine the 351 nm photoelectron spectrum of SF<sup>-</sup>. The molecular properties determined include the adiabatic electron affinity of SF, the anion bond length and vibrational frequency, as well as the spin-orbit splitting of the SF ground state.

The photoelectron spectrometer has been described previously.<sup>10,11</sup> SF<sup>-</sup> is produced by introducing trace quantities of SO<sub>2</sub> and NF<sub>3</sub>, along with helium buffer gas, upstream of the microwave discharge flowing afterglow source.<sup>10</sup> Ions are gently extracted, focused, accelerated, and mass selected with a Wien filter before entering the interaction region. The ion beam is crossed by the single frequency (351.1 nm) output of an argon ion laser which is coupled into a high finesse build up cavity.<sup>11</sup> Photodetached electrons are energy analyzed in a hemispherical energy analyzer with 9 meV resolution. The S<sup>-</sup> ion, with an electron affinity<sup>12</sup> of 2.077 104(1) eV, is used to calibrate the absolute electron energy scale.

The 351.1 nm photoelectron spectrum of SF<sup>-</sup> is shown in Fig. 1. Vibrational structure is observed from SF(<sup>2</sup>Π<sub>3/2</sub>, <sup>2</sup>Π<sub>1/2</sub>; v') + e<sup>-</sup> ← SF<sup>-</sup>(<sup>1</sup>Σ<sup>+</sup>; v'') transitions. The electron binding energy (eBE) shown on the top scale, is obtained by subtracting the photoelectron kinetic energy from the photon energy (eBE =  $h\nu - eKE$ ). The vibrational assignments of the spectrum are unambiguous, due to the difference between the vibrational frequency of the anion and neutral species. The observed vibrational spacings confirmed the identity of the signal carrier to be SF<sup>-</sup>.

SF<sup>-</sup> molecular constants are determined from Franck-Condon simulations of the vibrational progression. All of the electronic states are modeled as Morse oscillators; the simulation procedure has been described previously.<sup>13</sup> For the analysis, spectroscopic constants for the ground state of SF are fixed at literature experimental values<sup>4</sup> and  $\omega_e \chi_e(\text{anion})$  is fixed at the *ab initio* value.<sup>9</sup> The constants extracted from the analysis are  $r_e(\text{anion})$ ,  $\omega_e(\text{anion})$ , and  $T_{\text{vib}}(\text{anion}) = 375(50)$  K. The bond length of the anion is assumed to be longer than that of the neutral, because the extra electron is in a π\* orbital. This assumption is confirmed by the lowered vibrational frequency observed in the anion. In addition, the neutral spin-orbit splitting is determined from the doublet splitting illustrated in Fig. 1. The molecular constants obtained are summarized in Table I. The CEPA-1 *ab initio* SF<sup>-</sup> molecular constants ( $r_e = 1.7217$  Å and  $\omega_e = 642$  cm<sup>-1</sup>) calculated by Peterson and Woods<sup>9</sup> are in excellent agreement with our experimental measurements.

The adiabatic electron affinity corresponds to the transition from the lowest quantum state (v = 0, J = 0) of the anion to the lowest quantum state of the neutral. Because the spectrometer lacks rotational resolution, the rotational

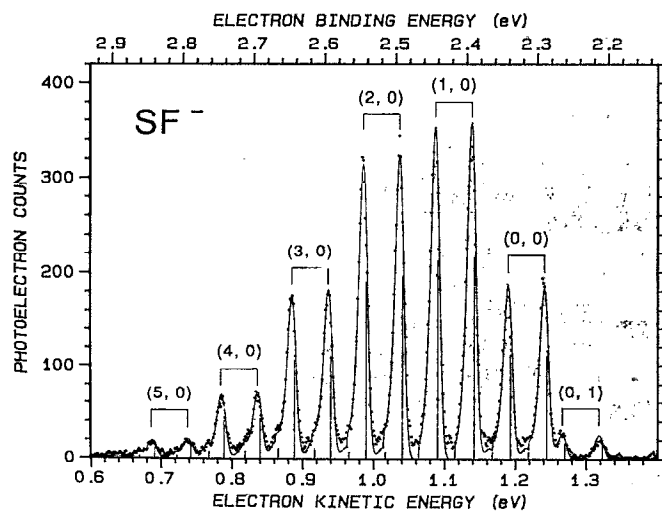


FIG. 1. The photoelectron spectrum of SF<sup>-</sup>, taken with  $h\nu = 3.531$  eV photon energy. Transitions to both spin-orbit states (<sup>2</sup>Π<sub>1/2</sub>, <sup>2</sup>Π<sub>3/2</sub>) of the ground state neutral from the ground state anion (<sup>1</sup>Σ<sup>+</sup>) are observed. Each spin-orbit doublet is designated (v', v''), where v' and v'' denote the vibrational state of the neutral and anion, respectively. The doublet components at higher electron kinetic energy correspond to transitions to the <sup>2</sup>Π<sub>3/2</sub> state. The data are represented by points, the Franck-Condon simulation is illustrated with a solid curve, and the solid vertical lines represent the rotationless origin for each vibrational transition.

TABLE I. Spectroscopic constants for the  $X^2\Pi_{3/2}$  and  $X^2\Pi_{1/2}$  states of neutral SF and for the  $X^1\Sigma^+$  state of  $SF^-$ .

| State                         | Energy (cm <sup>-1</sup> ) | $r_e$ (Å)          | $\omega_e$ (cm <sup>-1</sup> ) | $\omega_e x_e$ (cm <sup>-1</sup> ) |
|-------------------------------|----------------------------|--------------------|--------------------------------|------------------------------------|
| SF $X^2\Pi_{1/2}$             | 417(10)                    | 1.596 <sup>a</sup> | 837.64 <sup>a</sup>            | 4.46 <sup>a</sup>                  |
| SF $X^2\Pi_{3/2}$             | 0                          | 1.596 <sup>a</sup> | 837.64 <sup>a</sup>            | 4.46 <sup>a</sup>                  |
| SF <sup>-</sup> $X^1\Sigma^+$ | -18 430(48) <sup>b</sup>   | 1.717(15)          | 635(15) <sup>c</sup>           | 4.34 <sup>d</sup>                  |

<sup>a</sup>Not determined in this work, but constrained to this value, from Ref. 4, in the Franck-Condon analysis.

<sup>b</sup>Corresponds to EA(SF) = 2.285(6) eV.

<sup>c</sup>Because  $\omega_e x_e$ (anion) is constrained, the uncertainty for  $\omega_e$  reflects the uncertainty in  $\nu_0 = \omega_e - 2\omega_e x_e$ .

<sup>d</sup>Constrained to the value from Ref. 9.

envelope for each vibrational transition must be simulated<sup>13</sup> based on the bond lengths determined in the Franck-Condon analysis. The rotational contour simulation indicates that the rotationless origin of each transition is shifted by +3.0 meV (eKE) from the peak center. The simulation shown in Fig. 1 is performed using a calculated rotational contour for each peak. The resulting adiabatic electron affinity is 2.285(6) eV. Previous theoretical estimates of the electron affinity of SF come from Hartree-Fock calculations<sup>8</sup> (2.5±0.5 eV), application<sup>1</sup> of Koopmans' theorem (1.7 eV), and combining calculated values with experimental values in a thermochemical cycle<sup>9</sup> (2.15 eV). By examining trends in the electron affinities of SF<sub>x</sub> compounds, an electron affinity of 2.0±0.5 eV was estimated.<sup>14</sup> All of the theoretical values and our measurement are in strong disagreement with a recent<sup>15</sup> double-charge-transfer spectroscopy investigation of SF<sup>+</sup> which measured a lower limit, EA(SF) > 4.1 eV.

The difference between the anion and neutral dissociation energies is very accurately determined to be 1.114(7) eV using the literature<sup>12</sup> value for EA(F) and our experimental value for EA(SF) in the relation

$$D_0^{\cdot}(\text{SF}) - D_0^{\cdot}(\text{SF}^-) = \text{EA}(\text{F}) - \text{EA}(\text{SF}).$$

Combining this with the literature<sup>7</sup> value for  $D_0^{\cdot}(\text{SF})$  of 81.2±2.0 kcal/mol (3.52±0.09 eV),  $D_0^{\cdot}(\text{SF}^-)$  is calculated to be 2.40(9) eV. The dissociation energy of the an-

ion is less than that of the neutral, again as expected for addition of an electron into an antibonding orbital.

This work is supported by National Science Foundation Grants No. PHY90-12244 and No. CHE88-19444. Contribution from the Fall 1991 Experimental Physical Chemistry Class. The following members of the class made essential contributions to the work reported here: Michael G. Adams, Eric J. Arndt, Jennifer A. Ashby, Paul R. Baker, Vito F. Bavaro, Michael W. Buckley, Elizabeth A. Carley, Robert K. De Buse, Michael K. Dennis, Richard A. Drawhorn, Marc S. Helouin, Karen J. Herendeen, Mary G. Hewes, Shinil Kim, Michelle Manning, Rupa Nalitham, Simon C. Parfett, Derek A. Pflum, Lyn D. Pierce, David R. Rowe, Andrew H. Spetzler, Clifton W. Tuck, Ryan S. Watson, and Michael J. Widlar.

<sup>1</sup>P. A. G. O'Hare, *J. Chem. Phys.* **59**, 3842 (1973).

<sup>2</sup>V. Staemmler, *Theoret. Chim. Acta* **62**, 69 (1982).

<sup>3</sup>Y. Endo, S. Saito, and E. Hirota, *J. Mol. Spectrosc.* **92**, 443 (1982).

<sup>4</sup>Y. Endo, K. Nagai, C. Yamada, and E. Hirota, *J. Mol. Spectrosc.* **97**, 213 (1983).

<sup>5</sup>A. Carrington, G. N. Currie, T. A. Miller, and D. H. Levy, *J. Chem. Phys.* **50**, 2726 (1969).

<sup>6</sup>G. Di Lonardo and A. Trombetti, *Trans. Faraday Soc.* **66**, 2694 (1970).

<sup>7</sup>(a) D. L. Hildenbrand, *J. Phys. Chem.* **77**, 897 (1973); (b) M. W. Chase, Jr., J. L. Curnutt, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data* **7**, 897 (1978). [The value we quote for  $D_0^{\cdot}$ , is from Chase *et al.* (JANAF tables), and is a slightly revised interpretation of the data presented by Hildenbrand.]

<sup>8</sup>P. A. G. O'Hare and A. C. Wahl, *J. Chem. Phys.* **53**, 2834 (1970).

<sup>9</sup>K. A. Peterson and R. C. Woods, *J. Chem. Phys.* **92**, 7412 (1990).

<sup>10</sup>D. G. Leopold, K. K. Murray, A. E. Stevens-Miller, and W. C. Lineberger, *J. Chem. Phys.* **83**, 4849 (1985).

<sup>11</sup>K. M. Ervin, J. Ho, and W. C. Lineberger, *J. Chem. Phys.* **91**, 5974 (1989).

<sup>12</sup>H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **14**, 731 (1985).

<sup>13</sup>K. M. Ervin and W. C. Lineberger, in *Advances in Gas Phase Ion Chemistry*, Vol. 1, edited by N. G. Adams and L. M. Babcock (JAI, Greenwich, CN, in press).

<sup>14</sup>M. W. Chase, Jr., J. L. Curnutt, J. R. Downey, Jr., R. A. McDonald, A. N. Syverud, and E. A. Valenzuela, *J. Phys. Chem. Ref. Data* **11**, 800 (1982).

<sup>15</sup>M. L. Langford, D. P. Almeida, and F. M. Harris, *Int. J. Mass Spectrom. Ion Proc.* **98**, 147 (1990).