The ultraviolet photoelectron spectrum of SO⁻

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Ultraviolet photoelectron spectroscopy has been used to obtain the SO $(X\,^3\Sigma^-, a\,^1\Delta, b\,^1\Sigma^+; v') + e^- \leftarrow SO^- (X\,^2\Pi; v'')$ spectrum. The photoelectron spectrum provides the most accurate geometric, vibrational, and spin-orbit constants available for SO⁻, and accesses the three lowest lying electronic states of SO, all of which possess the same electronic configuration, $(\sigma_g^2)(\pi_u^4)(\pi_g^2)$.

The three low lying electronic states of SO are well-characterized experimentally[1-4] and theoretically.[5,6] Reference 4 contains a thorough review of recent spectroscopic studies of these states. The electronic term energy of the $^1\Sigma^+$ state has been determined from high resolution spectroscopy,[7] while the $^1\Delta$ term energy has been determined from low resolution infrared emission studies.[3] Similar low resolution infrared emission experiments[8] involving S_2 have been controversial[6] because of possible ambiguities regarding vibrational assignments, indicating a need for independent confirmation of both the SO and S_2 results. Photoelectron spectroscopy provides unambiguous electronic origin assignments, offering an independent test of the vibrational assignment determined in the IR emission studies.

Previously, Bennett[9,10] measured the 488 nm photoelectron spectrum of SO⁻. Our work improves the electron energy resolution from 56 meV available previously, to 8 meV, enabling more accurate determination of molecular constants as well as resolution of SO⁻ spin-orbit splittings. Additionally, we use a higher photon energy (3.53 eV vs 2.54 eV), providing access to higher energy states of the SO neutral molecule.

The negative ion photoelectron spectrometer used in this study is described in detail elsewhere;[11] only a brief description is given here. Negative ions are formed in a microwave discharge flowing afterglow source, focused, accelerated into a Wien velocity filter for mass selection, and decelerated before entering the laser interaction region. An argon ion laser, operated at single frequency (351.1 nm) and on a single cavity mode, provides the UV radiation, and electron energy analysis is accomplished using a hemispherical electrostatic energy analyzer with 8 meV resolution.[12]

SO⁻ is formed in the flowing afterglow source using trace amounts of SO_2 seeded in helium, and added upstream of the microwave discharge. The photoelectron spectrum is illustrated in Fig. 1; 57 lines were measured and given vibronic assignments. Selected vibrational assignments are also shown on Fig. 1; the large difference (> 150 cm⁻¹) between the neutral and anion vibrational

frequencies made these assignments unambiguous.

The molecular constants for SO⁻ were determined through Franck-Condon simulations of the spectrum for each of the three electronic bands observed. Both the anion and neutral were modeled as Morse oscillators, where the neutral geometries, frequencies and anharmonicities are fixed at the literature values.[1,2] The Franck-Condon factors are calculated by numerically integrating the overlap between the Laguerre wave functions[13] of the neutral and trial Laguerre wave functions for the anion. The anion geometry (r_e), harmonic frequency (ω_e), anharmonicity ($\omega_e x_e$), spin-orbit splitting (A), and vibrational temperature are allowed to vary in a least-squares fit to the data. By fitting directly to the data, both the energy and intensity information provided by the photoelectron spectrum are simultaneously used to determine the anion molecular constants. The results of the analysis are summarized in Table I. The uncertainties shown are assigned based on using different SO neutral electronic states to determine the anion constants, on the reproducibility of the spectrum, as well as on possible systematic errors in the experiment; they approximately represent a 2σ level of uncertainty. Throughout the fit, the anion bond length is assumed to be larger than that of the neutral, as is expected from simple

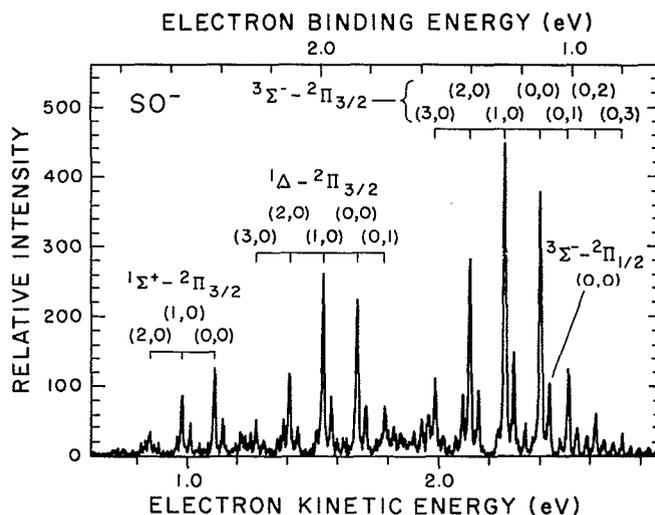

FIG. 1. The 351 nm photoelectron spectrum of SO⁻. Vibrational and electronic assignments for selected transitions in the $\Omega'' = 3/2$ manifold are shown. Transitions from $\Omega'' = 1/2$ spin-orbit levels are clearly visible for the most prominent features; the SO($^3\Sigma^-$, $v' = 0$) ← SO⁻ ($^2\Pi_{1/2}$, $v'' = 0$) assignment is shown. The transitions with unindicated assignments are from vibrationally and/or spin-orbit excited SO⁻ ($v'' = 1-5$, $\Omega'' = 1/2$).

TABLE I. Recommended spectroscopic constants for SO and SO$^-$. The constants with uncertainties indicated were determined in this work. The SO constants are those used in the Franck–Condon analysis. All values are in cm^{-1} unless otherwise noted.

Constant	SO$^-$ $X\,^2\Pi$	SO $X\,^3\Sigma^-$	SO $a\,^1\Delta$	SO $b\,^1\Sigma^+$
r_e	1.570(5) Å	1.481 087 Å[a]	1.488 86 Å[b]	1.5001 Å[a]
ω_e	906(15)	1149.2[a]	1115.349[b]	1068.66[a]
$\omega_e\chi_e$	8.2(20)	5.64[a]	6.978[b]	7.25[a]
A	−272(5)			
T_0	−9074(40)	0	5861(10)[c]	10 469.3[d]

Electron affinity SO = 1.125(5) eV [9074(40) cm^{-1}]
D_0(SO$^-$) = 4.406(7) eV [35 537(56) cm^{-1}][e]

[a]Reference 1.
[b]Reference 2.
[c]Based on this work and Ref. 3, see text.
[d]Derived from constants in Ref. 1.
[e]See discussion of dissociation energy in text.

molecular orbital considerations, and the spin–orbit constant is constrained to be negative based on the π^3 electronic configuration of the SO$^-$ ground state.[14]

The electron affinity of SO was determined from the electron kinetic energy (EKE) of the $X\,^3\Sigma^+$–$X\,^2\Pi$ (0,0) photoelectron peak. A correction of +2.0 meV accounts for the rotational contour of the peak. The correction was determined[15] by simulating the rotational contour as a rigid rotor electronic transition at a rotational temperature of 350 K, and convolving the result with the instrumental resolution of 8 meV. The difference between the resulting peak maximum and the position of the rotationless origin was used as the correction. The electron affinity of SO was then determined by

$$EA = h\nu(\text{laser}) - EKE(\text{corrected origin peak}).$$

The $a\,^1\Delta$ and $b\,^1\Sigma^+$ term energies are obtained from the differences between their respective electronic origin energies and that of the $X\,^3\Sigma^+$ state. Our value of $T_0(^1\Sigma^+) = 10\ 468(26)$ cm^{-1} is in excellent agreement with the more precise literature value[1] of 10 469.3 cm^{-1}. For the $a\,^1\Delta$ state, our term energy [$T_0 = 5858(15)$ cm^{-1}] agrees well with the low resolution IR emission measurement of Barnes et al.[3] of 5865(15) cm^{-1}, confirming their assignments, and suggesting a "best" value of $T_0 = 5861(10)$ cm^{-1}.

Finally, the dissociation energy D_0(SO$^-$) corresponding to

$$SO^-(^3\Sigma^-) \rightarrow S^-(^2P_{3/2}) + O(^3P_2)$$
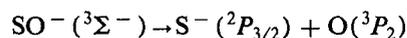
can be calculated from

$$D_0(SO^-) = D_0(SO) + EA(SO) - EA(S).$$

Using literature values for D_0(SO) [5.358(2) eV][16] and EA(S) [2.077 120(1) eV][17] along with our measured value of EA(SO$^-$), we obtain D_0(SO$^-$) = 4.406(7) eV. The dissociation energy we use for SO is obtained from the onset of predissociation in the $B\,^3\Sigma^-$ state, and is generally the preferred value;[1,16] however, Colin[16] points out that ambiguities in the possible atomic spin–orbit components of the dissociation asymptote suggest a plausible range for D_0(SO) of 5.323–5.360 eV. This corresponds to 4.371 eV $< D_0$(SO$^-$) < 4.408 eV.

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