LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 2000 issue.

NOTES

Photoelectron spectroscopy of SnO^-

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Negative ion laser photoelectron spectroscopy has provided accurate electron affinities for a wide variety of species, ranging from atoms to complex molecular systems.[1,2] Data from these studies frequently determine several spectroscopic constants for the neutral as well as the precursor anion, including vibrational frequencies, term energies for low-lying electronic states, spin–orbit splittings, and singlet–triplet gaps.[2] Continuing a study of metal oxides, we report the 364 nm photoelectron spectra of SnO^-. The properties of the neutral SnO have been the focus of sporadic attention over the last 30 years.[3–7] While there are several reports on the higher excited states, virtually nothing is known concerning electronic states of SnO lying below ~4 eV.[8–15] Balasubramanian and Pitzer[3] report calculations of a $^3\Sigma$ state lying 2.3 eV above the ground state, but this state has never been observed.

The negative ion photoelectron spectrometer used in this work has been described in detail.[2] Anions are generated in a variable temperature (180–300 K) flowing afterglow ion source and thermalized. Tin anions, generated by sputtering[16] a tin rod (Goodfellow, 99.75%) are allowed to react with O_2 added downstream to produce several tin oxide anions. The anions are extracted from the flow tube, mass analyzed (~3 pA of SnO^-), and crossed with ~100 W of 364 nm radiation (3.408 eV) from an Argon ion laser in a high finesse build-up cavity. Photoelectrons detached perpendicular to both beams are energy analyzed with a hemispherical analyzer having ~7 meV resolution. The absolute electron energy scale is determined by calibration with O^-, whose electron affinity is well determined[17] and a small energy scale nonlinearity is determined and corrected using the well-known W atom fine structure intervals[18] observed in the photoelectron spectrum of W^-.

The SnO molecule has a formal triple bond and a $^1\Sigma$ ground state, in analogy to CO. The added electron in the anion must reside in a π^* orbital, giving rise to a $^2\Pi_{1/2,3/2}$ anion ground state, with increased bond length and a reduced vibrational frequency compared with ground-state SnO. The electron affinity of SnO is expected to be rather low, as, e.g., EA(CO)<0.

A survey of the entire 3.408 eV accessible photoelectron spectrum indicates photodetached electrons were observed only between 1.7 and 0.3 eV electron binding energy. The cold photoelectron spectra of SnO^- taken between these electron energy limits is shown in Fig. 1. Three intense peaks (A–C) and a number of weak features are observed in this region; the uniform ≅810 cm^{-1} spacing between the ten peaks A–J identifies them as arising from transitions to $v=0\ldots9$ in the $X\,^1\Sigma^+$ ground state of SnO. This very long progression is the result of the 364 nm photon producing both direct photodetachment and also exciting an autoionizing (probably $^2\Sigma$) excited state of SnO^-; thus simple, calculated Franck–Condon intensity profiles cannot be used to obtain an accurate anion bond length. Another readily assignable feature of the spectrum is the progression A*–C*, arising from the spin–orbit excited $^2\Pi_{3/2}$ state of SnO^-. The S–O excited state will exhibit a progression of peaks similar to A–J, shifted to lower binding energy by the spin–orbit excitation energy, and reduced in intensity as a result of the

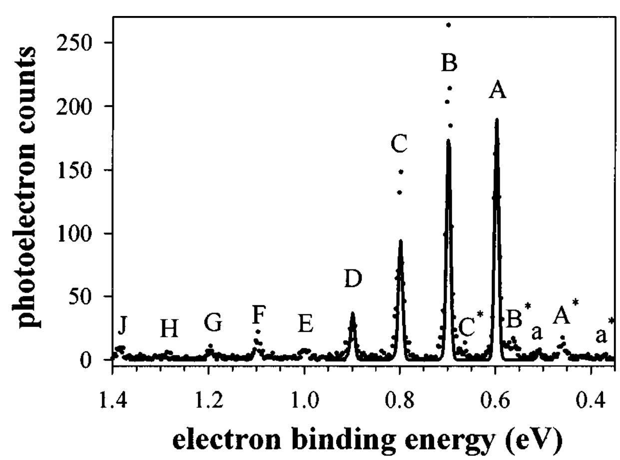

FIG. 1. 364 nm photoelectron spectrum of SnO^- taken at 180 K (dotted line) and Franck–Condon simulation (solid line).

TABLE I. Spectroscopic constants for SnO^- and SnO.

State	T_0 (cm^{-1})	r_e (Å) Experimental	r_e (Å) *Ab initio*[a]	Vibrational frequency (cm^{-1}) Experimental	Vibrational frequency (cm^{-1}) *Ab initio*[a]
$SnO^-(^2\Pi_{1/2})$	0	1.91±0.02	1.907	720±25	680[b]
$SnO^-(^2\Pi_{3/2})$	1120±15				
SnO ($^1\Sigma^+$)	4825±50[c]	1.832 505[d]	1.830	810±10	810[b]

[a]B3LYP/SDD/aug-cc-pVTZ.
[b]Frequencies are not scaled.
[c]Corresponds to EA (SnO)=0.598±0.006 eV.
[d]From Ref. 20.

lower population in the excited state. Finally, by comparison of this 180 K photoelectron spectrum with a room temperature spectrum (not shown), one can identify vibrational hot bands. Peaks a and a* are such vibrational hot bands, arising from the first vibrational excited states of the ground and the first S–O excited states, respectively. The position of peak A determines the electron affinity of SnO, 0.598±0.006 eV. Other molecular constants directly obtained are the spin–orbit excitation energy and vibrational frequency for the anion, and the neutral vibrational frequency. These results are summarized in Table I.

The suspicion that the extended vibrational progression arises as a consequence of autoionization is confirmed by the observation that the photoelectron angular distributions[19] of the intense peaks exhibit significant anisotropy ($\beta \cong 0.4$) while the extended weak features exhibit isotropic ($\beta \cong 0$) distributions, consistent with originating from a long-lived state. As the autoionizing contributions to the spectrum render a simple, direct Franck–Condon simulation of the spectrum inappropriate, we have chosen to estimate of the anion bond length via a simulation[2] of only the intense portion of the spectrum (Peaks A–C) that has the largest direct photodetachment component. The change in bond length obtained by the limited simulation, combined with the known bond length of the neutral[20] allowed us to calculate the internuclear distance in the anion, as reported in Table I. The simulated spectrum is displayed in Fig. 1.

To assist in the analysis, *ab initio* calculations for SnO and SnO^- were carried out using the B3LYP hybrid density-functional method and the SDD (Stuttgart–Dresden effective core potential) and aug-cc-pVTZ basis sets for Sn and O, respectively, as implemented in the GAUSSIAN 98W suite of programs.[21] The value for the vibrational frequency found for the ground-state of SnO is consistent with other experimental and theoretical results,[3,7,9–11] including our theoretical value, as shown in Table I. The vibrational frequency for the anion is also in reasonable agreement with our theoretical result (Table I). The calculated bond lengths for the anion and the neutral molecule agree reasonably with the experimental values. The agreement suggests that relativistic effects, which are expected to be important in this system, are incorporated successfully in the SDD pseudopotential.

The 1120 cm^{-1} spin–orbit excitation in SnO^- is comparable with similar systems. For example, the isoelectronic species SnF shows a spin orbit splitting of 2317 cm^{-1}.[20] In contrast to observations[22] on PbO^-, the absence of bands at higher electron binding energies indicates that the first excited state of SnO lies above 2.7 eV, the difference between the photon energy and the EA(SnO). Calculations by Balasubramanian and Pitzer[3] indicate the $^3\Sigma^+$ state to be the first excited state in SnO, with a excitation value of 2.3 eV; however, the lowest exited state observed experimentally has an excitation energy of 2.6 eV.[10]

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