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 2002 issue.

NOTES

On the photoelectron spectrum of AgO⁻

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Here, we present the 364 nm negative ion photoelectron spectrum of AgO⁻ in an experiment designed to determine the electron affinity of AgO and other properties of AgO⁻. Several experimental[1–8] and theoretical[9–13] investigations have reported bond lengths, vibrational frequencies, spin–orbit splittings, and term energies for the neutral ground state and several electronic excited states. Most of the experimental investigations[1,2,4–8] report spectroscopic constants for the $^2\Pi_i$ ground state of AgO. Two of the experimental investigations[2,4,5] report spectroscopic constants for a $^2\Sigma^+$ state lying about 8428 cm⁻¹ above the ground state. Griffiths and Barrow[6] and O'Brien[2,4] assign the spin–orbit split ground state of AgO to be inverted. There are no reports in the literature, however, of the equilibrium bond length of AgO⁻, the ground state harmonic frequency of AgO⁻, or of the electron affinity of AgO, all of which are presented here.

Negative ion photoelectron spectroscopy is a powerful technique that has provided accurate electron affinities of many species.[14,15] Vibrational frequencies, term energies, spin–orbit splittings, and bond lengths for the anion precursor and neutral may also be determined from a negative ion photoelectron spectrum. The negative ion photoelectron spectrometer used for this experiment has been described in detail elsewhere.[14] Briefly, a beam of anions is produced by sputtering[16] a high purity silver rod (Aldrich, 99.98%) in a variable temperature (180–300 K) flow tube with about 10% argon in helium at a pressure near 500 mTorr. The ions are thermalized, reacted downstream with O_2, extracted from the flow tube, accelerated to ~750 eV, mass selected, and decelerated to ~40 eV. The ion beam (~1 pA of AgO⁻) is crossed with a single frequency 363.789 nm (3.408 14 eV) argon ion laser beam. The interaction region is used as an external build-up cavity[17] for the laser, which increases the circulating power in the interaction region to ~100 W. Photoelectrons that are detached perpendicular to the ion-laser plane are energy analyzed in a hemispherical analyzer with a resolution of about 8 meV full width at half maximum. The absolute energy scale was determined daily by calibration with Ag⁻, whose electron affinity (1.3045 eV) is well known.[18] A small energy scale nonlinearity (~0.1%) was determined and corrected using the well-known[19] atomic transitions in W observed in the W⁻ photoelectron spectrum.

A survey of the photoelectron spectrum of AgO⁻ shows photodetachment in the region between 1.5 eV and 2.8 eV electron binding energy. The features in this range are plotted in Fig. 1. The single peak in Fig. 1(a) at 2.70 eV binding energy is the transition to the $v=0$ level in the A $^2\Sigma^+$ state of AgO. Peaks C, E, and G in Fig. 1(b) are transitions from the anion ground state to the $v=0$, 1, and 2 levels, respectively, in the X $^2\Pi_{3.2}$ state of AgO. Peaks D, F, and H are transitions from the anion ground state to the $v=0$, 1, and 2 levels, respectively, in the X $^2\Pi_{1/2}$ state of AgO. Peaks A and B are vibrational hotbands from the anion $v=1$ state to the ground vibrational level in the X $^2\Pi_{3/2}$ and X $^2\Pi_{1/2}$ states of AgO, respectively. The position of peak C defines the adiabatic electron affinity of AgO as 1.654 (2) eV. The AgO electron affinity error bar represents a 2σ level of uncertainty. Many of the experimental investigations[1,6–8] report a $^2\Pi$ state lying about 24 400 cm⁻¹ above the ground state, which was not accessible with our photon energy.

The peak assignments were confirmed by simulating the vibrational progression in Fig. 1(b). A Frank–Condon simulation of the data in Fig. 1(b) using the program PESCAL[20,21] was carried out as follows. The anion and neutral electronic ground states were modeled as Morse oscillators. The neutral parameters (r_c, ω_e, $\omega_e x_e$) were fixed to known literature values.[2,6] The lack of a vibrational progression for transitions to the A state suggests that the anion bond length and the neutral A state bond lengths are essentially identical. Thus the anion equilibrium bond length was fixed at the 1.935 Å neutral A $^2\Sigma^+$ state literature value,[4] and only the anion harmonic vibrational frequency ω_e was allowed to vary, effectively determining the hot band position. Frank–Condon factors were determined by numerical integration of the Laguerre wave function solutions[22] to the Morse potentials. The instrumental line shape was modeled as a Gaussian with 15 meV full width at half maximum. Other parameters input

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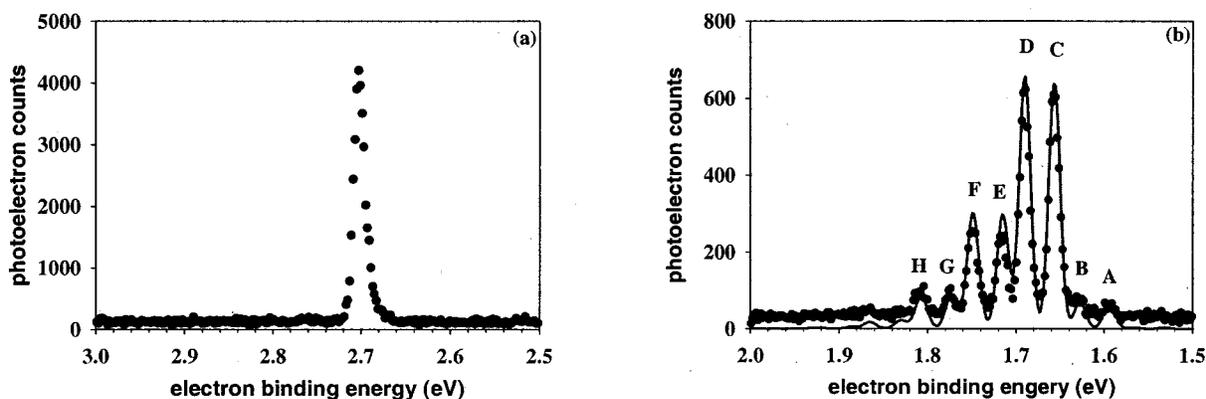[a)]Author to whom correspondence should be addressed. Electronic mail: wcl@jila.colorado.edu

FIG. 1. 364 nm photoelectron spectra showing transitions to the $A\ ^2\Sigma^+$ (a) and $X\ ^2\Pi_i$ (b) states of AgO. The points are the data and the solid line is a Frank–Condon simulation as described in the text.

into the simulation were the 0–0 transition position and height and the anion temperature (~300 K). The simulated spectrum is plotted in Fig. 1(b) as a solid line. With no adjustment to the anion bond length, the simulated ground state vibrational progression is essentially identical with that of the observed progression, continuing the anion bond length determination. Molecular constants and electronic state splittings derived from the transition assignments and the Frank–Condon simulation are summarized in Table I, along with recent literature values for comparison. The error bars in Table I represent a 2σ level of uncertainty. The electronic ground state of AgO⁻ is found to have a vibrational frequency of 497 (20) cm⁻¹ and an equilibrium bond length of 1.935(15) Å. The adiabatic electron affinity of AgO is found to be 1.654(2). Since the peaks in our photoelectron spectrum of AgO⁻ are not rotationally resolved, a rotational correction[23] of −1.76 meV was made to the AgO adiabatic electron affinity. The neutral A state term energy and the X state spin–orbit splitting and vibrational frequency reported here are in excellent agreement with the known literature values,[4] confirming our electronic state assignments.

AgO is well described[13] by a $Ag^+(4d^{10})O^-(2s^22p^5)$ ionic configuration with a $2p\sigma^22p\pi^3\ ^2\Pi_i$ ground state and a $2p\sigma^12p\pi^4\ ^2\Sigma^+$ excited state. The observation of transitions to both of these states in the photoelectron spectrum confirms that AgO⁻ has a $2p\sigma^22p\pi^4$ configuration with a $^1\Sigma^+$ ground state. Removal of a $2p\pi$ electron gives the $^2\Pi_i$ ground state with a bond length increase of 0.07 Å, suggesting that these electrons are slightly bonding in AgO⁻. This is

similar to the bond length increase observed for detachment of a $2p\pi$ electron in CuO⁻.[24] Removal of a $2p\sigma$ electron gives the $^2\Sigma^+$ excited state with no measured bond length change. This suggests that the $2p\sigma$ electrons are nonbonding in AgO⁻, even though a simple molecular orbital description predicts these electrons to be strongly bonding. While detachment of a $2p\sigma$ electron from CuO⁻ does lead to a small increase in bond length, the increase is not as large as for detachment of a $2p\pi$ electron.

The adiabatic dissociation energy of AgO⁻ to Ag+O⁻ can be obtained from a thermodynamic cycle,

$$D_0(AgO^-) = D_0(AgO) - EA(O^-) + EA(AgO). \qquad (1)$$

The dissociation energy of AgO has been determined to be 2.29(15) eV from a mass spectrometric Knudsen cell measurement,[25] while the electron affinity of O⁻[1.461 122(3) eV] is well known.[26] Using the EA(AgO⁻) measured in this work, the $D_0(AgO^-)$ obtained is 2.48(15) eV [57.2 (3.5) kcal/mol]. The accuracy of this dissociation energy is limited by the mass spectrometric Knudsen cell measurement. A quantity we measure with more accuracy is the difference in bond strengths:

$$D_0(AgO^-) - D_0(AgO) = 0.193(2)\ \text{eV}\ [4.45(5)\ \text{kcal/mol}].$$

This difference in dissociation energies clearly shows that AgO⁻ is more strongly bound than AgO.

TABLE I. Spectroscopic constants for AgO⁻ and AgO.

State	T_0 (cm⁻¹)		ω_e (cm⁻¹)		r_e (Å)	B_e cm⁻¹
	This work	Literature[a]	This work	Literature[a]		
AgO⁻ $X\ ^1\Sigma^+$	−13340(16)[b]		497 (20)		1.935 (15)	0.323 (50)
AgO $X\ ^2\Pi_{3/2}$	0	0	481 (15)	485	2.005[a]	0.301[a]
AgO $^2\Pi_{1/2}$	270 (15)	269	481 (15)	485	2.005[a]	0.301[a]
AgO $A\ ^2\Sigma^+$	8429 (40)	8428			1.935[a]	0.323[a]

[a]From Ref. 4.
[b]Corresponds to EA (AgO)=1.654(2) eV.

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