LETTERS TO THE EDITOR

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COMMUNICATIONS

Measurement of the $X\,^2\Sigma^+$–$A\,^2\Pi$ splitting in CsO via photoelectron spectroscopy of CsO^-

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We present the photoelectron spectrum of CsO^-, recorded using 2.540 eV photons. This spectrum provides a direct measurement of the $X\,^2\Sigma^+$–$A\,^2\Pi$ energy splitting in CsO, which is found to be 0.135 ± 0.025 eV. This work also establishes that the ground state of CsO^- is $^1\Sigma^+$. In addition, the adiabatic electron affinity of CsO is found to be 0.273 ± 0.012 eV, while the D_0 value for the $X\,^1\Sigma^+$ state of CsO^- (with respect to $Cs+O^-$) is found to be 1.84 ± 0.15 eV. Molecular parameter estimates for CsO^- are also extracted from the spectrum.

I. INTRODUCTION

The electronic structures of the alkali monoxides has been a topic of longstanding interest in chemical physics. The bonding in these systems is best described as highly ionic with the alkali atom donating its valence electron to the p orbitals of the oxygen atom. This leads to configurations in which a hole can exist either in a π molecular orbital, or in a σ orbital along the bond axis. The resulting $^2\Pi$ and $^2\Sigma^+$ states correspond to the ground and first excited states of the alkali monoxides with the unusual behavior that the ground state changes from $^2\Pi$ to $^2\Sigma^+$ upon traversing the periodic series, LiO...CsO.[1–10] Goddard and co-workers have attributed the reversal in ground state electronic symmetries to a competition between an attractive quadrupole interaction which favors a $^2\Pi$ ground state, and Pauli repulsion which favors a $^2\Sigma^+$ ground state.[7,8]

There have been no direct measurements of the $^2\Sigma^+$–$^2\Pi$ splittings in any of the alkali monoxides, and the small transition moments predicted by theory indicate that a direct spectroscopic observation of these splittings may be difficult.[11,12] Consistent with this, Hirota and co-workers searched without success for the $A\,^2\Sigma^+\leftarrow X\,^2\Pi$ transition in NaO.[5] Furthermore, theoretical studies by Langhoff, Partidge, and Bauschlicher found that the measurement of transitions to the $^2\Sigma^+$ and $^2\Pi$ states from higher excited states of the alkali monoxides also does not offer a likely route for determining the $^2\Sigma^+$–$^2\Pi$ energy separations by difference.[13] Nevertheless, important, and probably rather accurate, indirect experimental measurements of this splitting have been made. It has been estimated for LiO by Klemperer[3] and by Hirota,[6] and for NaO by Hirota.[5] These A–X energy splittings were derived from the Λ-type doubling in these molecules assuming a pure-precession hypothesis. Also, in matrix ESR experiments, Lindsay, Herschbach, and Kwiram used the observed shift in $g_\perp$ to estimate an upper bound for the splitting in RbO.[4]

Photoelectron spectroscopy of the alkali monoxide negative ions is an alternative method for measuring the $^2\Sigma^+$–$^2\Pi$ energy splittings in neutral alkali monoxides. With this in mind, we have recorded the photoelectron spectra of NaO^-, KO^-, RbO^-, and CsO^- using visible photons. Calculations on alkali monoxide anions have been carried out by O'Hare and Wahl[14] on NaO^- and more recently by Bauschlicher, Partridge, and Pettersson[15] on LiO^-, NaO^-, and KO^-. The calculations of Bauschlicher and co-workers on these anions and the corresponding neutrals have been invaluable in guiding the analysis of our photoelectron spectra. Their calculations find a $^3\Pi$ ground state for LiO^- and a $^1\Sigma^+$ ground state for KO^-. In the case of NaO^-, the calculations find a $^3\Pi$ ground state but the possibility of a $^1\Sigma^+$ ground state could not be ruled out. There is a broad consistency between the theoretical results and our experimental data, and the two taken together indicate a change (from $^3\Pi$ to $^1\Sigma^+$) in alkali monoxide anion ground states in going from light to heavy alkali atoms that is analogous to the ground state reversal seen in the neutrals. Here, we present the photoelectron spectrum of CsO^- which provides a direct measurement of the $X\,^2\Sigma^+$–$A\,^2\Pi$ energy splitting in CsO, and establishes that the ground state of CsO^- is $^1\Sigma^+$. In addition, we report values for the electron affinity of CsO and the dissociation energy of CsO^-. Molecular parameter estimates for CsO^- are also extracted from the spectrum. The photoelectron spectra of NaO^-, KO^-, RbO^-, and CsO^- will be discussed in detail in a future publication.[16]

II. EXPERIMENT

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy analyzing the resultant photodetached electrons. Our negative ion photoelectron spectrometer has been described previously.[17] Anions generated in an appropriate ion source are accelerated, collimated, and transported via a series of ion optical components before being mass-selected using an $\mathbf{E}\times\mathbf{B}$ Wien

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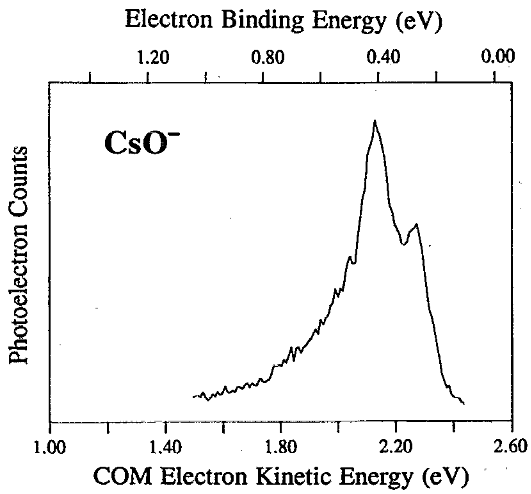

FIG. 1. The photoelectron spectrum of CsO^- recorded using 2.540 eV photons. This spectrum was calibrated using the photoelectron spectrum of Cs^-. No signal was observed outside the displayed energy window. (COM ≡ center-of-mass)

velocity filter. The mass-selected ion beam is then focused into a field-free, collision-free interaction region, where it is crossed with the intracavity photon beam of an argon ion laser operated at 488 nm (2.540 eV) and circulating powers of ~100 W. A small solid angle of the resulting photodetached electrons is accepted into the input optics of a magnetically shielded, hemispherical electron energy analyzer, where the electrons are energy analyzed and counted.

Cesium monoxide anions were generated using an ion source developed here for producing alkali monoxide and associated negative ions which circumvents many of the source problems associated with such high temperature species.[18] In this source, cesium monoxide anions are formed in an expanding supersonic jet in the region just outside its nozzle orifice. Essentially, this is achieved by interacting a cesium-argon jet with an effusive flow of nitrous oxide near the nozzle while injecting relatively low energy electrons into this region in the presence of a magnetic field. Alkali monoxide anions have been previously observed mass spectrometrically in two other environments.[19,20]

III. RESULTS AND DISCUSSION

The 488 nm photoelectron spectrum of CsO^- is presented in Fig. 1. The two peaks in this spectrum are assigned to different electronic bands resulting from photodetachment transitions from CsO^- to the ground and first excited states of CsO. Experimentally derived information pertaining to neutral CsO has been provided by the crossed molecular beam magnetic deflection experiments of Herm and Herschbach[2] which found CsO to be paramagnetic indicating a $^2\Sigma^+$ ground state; by the ESR experiments of Lindsay, Herschbach, and Kwiram[4] on matrix isolated CsO which gave signals indicative of a $^2\Sigma^+$ ground state; by infrared studies on matrix isolated CsO carried out by Spiker and Andrews which provided the vibrational frequency for the ground state of CsO;[21,22] and by the chemiluminescence studies of Woodward, Hayden, and Gole in which emission from the B state of CsO was observed.[23] The establishment of a $^2\Sigma^+$ ground state for CsO led us to assign the lower electron binding energy (EBE) feature to transitions from the ground state of CsO^- to the $X\,^2\Sigma^+$ state of CsO and the higher EBE feature to transitions from the ground state of CsO^- to the $A\,^2\Pi$ state of CsO.

The comparable intensities of the two photoelectron bands led us to assign the ground state of CsO^- as $^1\Sigma^+$, and this result is in line with the ground state reversal trend in alkali monoxide anions predicted by Bauschlicher, Partridge, and Pettersson.[15] The leading configuration of the $^1\Sigma^+$ state in alkali monoxide anions is given by Bauschlicher *et al.* as $(1\sigma^2 1\pi^4 + 2\sigma^2 1\pi^4)$ in valence orbital notation. Photodetachment transitions from the $^1\Sigma^+$ state of the anion to both the $^2\Sigma^+$ $(1\sigma^1 1\pi^4)$ and the $^2\Pi$ $(1\sigma^2 1\pi^3)$ states of the neutral result from the removal of single electrons. The remaining candidates for the CsO^- ground state are the $^3\Sigma^+$, $^3\Pi$, and $^1\Pi$ states. In these states, one valence electron can be viewed as residing in an alkali atom-centered orbital as in the alkali halide negative ions[24–27] and in the lithium hydride anion.[27,28] The $^3\Sigma^+$ state has a $(1\sigma^1 2\sigma^1 1\pi^4)$ configuration, while the $^3\Pi$ and $^1\Pi$ states have $(1\sigma^2 2\sigma^1 1\pi^3)$ configurations. For each of these three anion states, the photodetachment transition to one of the two low-lying neutral states ($^2\Sigma^+$ or $^2\Pi$) is a two-electron process while the transition to the other is a single electron process. Since calculations indicate that the $^3\Sigma^+$, $^3\Pi$, and $^1\Pi$ states of alkali monoxide anions are all well described by single configurations,[29] in each case, the spectral feature corresponding to the two-electron process would be significantly less intense than that from the one-electron process. This would result in a spectrum having one strong and one weak feature, but two comparably strong peaks are actually observed in the photoelectron spectrum of CsO^-. Therefore, the lower EBE feature in the spectrum is assigned to the CsO, $X\,^2\Sigma^+ + e^- \leftarrow CsO^-$, $X\,^1\Sigma^+$ photodetachment transition and the higher EBE feature to the CsO, $A\,^2\Pi + e^- \leftarrow CsO^-$, $X\,^1\Sigma^+$ transition.

The electron binding energy difference between the CsO, $X\,^2\Sigma^+ + e^- \leftarrow CsO^-$, $X\,^1\Sigma^+$ and CsO, $A\,^2\Pi + e^- \leftarrow CsO^-$, $X\,^1\Sigma^+$ bands gives the $X\,^2\Sigma^+$–$A\,^2\Pi$ energy splitting in CsO directly. The peaks in the spectra are assigned to the vibrational origin bands in both electronic transitions. This assignment is supported on the strength of calculations by Bauschlicher *et al.*[15] who predict the (0,0) transitions for the MO, $^2\Sigma^+ \leftarrow MO^-$, $^1\Sigma^+$ and MO, $^2\Pi \leftarrow MO^-$, $^1\Sigma^+$ electronic bands to be dominant in the photoelectron spectra of LiO^-, NaO^-, and KO^-. The CsO $X\,^2\Sigma^+$–$A\,^2\Pi$ energy splitting measured from the spectrum is 0.135 ± 0.025 eV. This value is in reasonable agreement with theoretical calculations on CsO by Goddard and co-workers,[7,8] by Laskowski, Langhoff, and Siegbahn,[30] and by Langhoff, Bauschlicher, and Partridge,[9,10] with the experimental value being a little larger than the predicted values, which are all about 0.1 eV.

The EBE of the CsO, $X\,^2\Sigma^+ + e^- \leftarrow CsO^-$, $X\,^1\Sigma^+$ origin transition gives the adiabatic electron affinity (EA_a) of CsO. This value was determined to be 0.273 ± 0.012 eV accounting for rotational energy corrections.[31] With this electron affinity value in hand, a thermochemical cycle was used to determine the dissociation energy of CsO^-. Using our value of EA_a for CsO along with the D_0 value reported by Herm and Herschbach[2] for the $X\,^2\Sigma^+$ state of CsO and the literature value for the electron affinity of the oxygen atom,[32] the D_0 value for the $X\,^1\Sigma^+$ state of CsO^- (with respect to $Cs+O^-$) was found to be 1.84 ± 0.15 eV. In addition, another cycle was used to determine D_0 for the $A\,^2\Pi$ state of CsO, and this value is 2.90 ± 0.15 eV.

Finally, we estimated some of the molecular parameters for the ground state of CsO^- via a Franck–Condon analysis. Of the spectroscopic constants needed for this analysis, the vibrational frequency measured by Spiker and Andrews[21,22] is the only one determined in previous experiments. Accordingly, the remaining parameters for the $X\,^2\Sigma^+$ and $A\,^2\Pi$ states needed for this analysis and not determined in this work were taken from the most recent theoretical study,[9] which was also found to be in excellent agreement with all available experimental spectroscopic constants pertaining to neutral alkali monoxides. Estimated values of 2.516 Å for r_e, 0.1865 cm^{-1} for B_e, and 275 cm^{-1} for ω_e (along with a temperature of 700 K) for CsO^- were found to be consistent with the observed spectral profile, although some of the broadening along the high EBE portion of the spectrum was outside the fit. The bond distance determined for CsO^- was found to be between the theoretically predicted bond distances for the $X\,^2\Sigma^+$ and $A\,^2\Pi$ states of CsO, consistent with the situation predicted by theory for KO and KO^-. In addition, the results of this modeling supported the values for the $X\,^2\Sigma^+$–$A\,^2\Pi$ splitting in CsO and the EA_a of CsO reported above.

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