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Photoelectron spectroscopy of the molecular anions, Li_3O^- and Na_3O^-

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The molecular anions, Li_3O^- and Na_3O^- were produced by laser vaporization and studied via anion photoelectron spectroscopy. Li_3O^- and Na_3O^- are the negative ions of the super-alkali neutral molecules, Li_3O and Na_3O . A two-photon process involving the photodetachment of electrons from the Li_3O^- and Na_3O^- anions and the photoionization of electrons from the resulting Li_3O and Na_3O neutral states was observed. The assignment of the Li_3O^- photoelectron spectrum was based on computational results provided by Zein and Ortiz [J. Chem. Phys. **135**, 164307 (2011)]. © 2011 American Institute of Physics. [doi:10.1063/1.3657854]

INTRODUCTION

A super-alkali is a molecule or cluster with an ionization potential (IP) that is less than that of the cesium atom, which is 3.9 eV.¹ The alkali sub-oxides, Li_3O and Na_3O , both satisfy this condition, these molecules being, respectively, described as Li_3O^+ and Na_3O^+ closed shell cations, each with a hydrogenic electron.² Modern theoretical work on the structures of neutral Li_3O and Na_3O and on cationic Li_3O^+ and Na_3O^+ find them all to exhibit D_{3h} symmetries.^{3–8} Moreover, the bond lengths of the neutral molecules and their cations are similar in both cases. The ionization potentials of Li_3O and Na_3O have been studied both experimentally and theoretically,^{1–5,8–16} with a recent value of 3.55 eV (Refs. 11 and 12) being measured for Li_3O (3.69 eV (Ref. 13) is the most recent value for Na_3O). The excited neutral states of Na_3O and Li_3O have been mapped by the experiments of Hampe *et al.*¹³ and Neukermans *et al.*,⁷ respectively.

The anion, Li_3O^- , together with the ground and excited states of its Li_3O neutral counterpart have been studied theoretically by Simons and Gutowski⁴ and recently by Zein and Ortiz.²² Simons and Gutowski showed the Li_3O^- anion to have two bound states, a $^1A_1'$ state with D_{3h} symmetry and a pseudo-rotating $^3E'$ state. Zein and Ortiz also found two bound states for the Li_3O^- anion, a singlet $^1A_1'$ state with D_{3h} symmetry and a triplet 3A_1 state with C_{2v} symmetry. Simons and Gutowski reported the vertical detachment energy (VDE) of Li_3O^- to be 0.656 eV, while Zein and Ortiz found the VDE values of the anions' singlet and triplet states to be 0.65 eV and 0.45 eV, respectively. Both groups found the VDE values to be essentially the same as their electron affinity (EA) values.

Here, we present an anion photoelectron spectroscopic study of Li_3O^- and its isoelectronic analog, Na_3O^- . As alkali-like molecules, Li_3O and Na_3O are expected to have both low ionization potential and low electron affinity values. (The EA values of alkali atoms lie in the range 0.4–0.6 eV.) Thus, with ~ 3.5 eV photons, one should be able to pho-

totdetach electrons from Li_3O^- and Na_3O^- anions and then with another photon to photoionize electrons from resulting Li_3O and Na_3O neutral states, thereby producing electrons from both photodetachment and photoionization in the same photoelectron spectrum. As a result of this two photon process, Li_3O^- anions, Li_3O neutral ground and excited states, Li_3O^+ cations, and free electrons all exist together in the anion-photon interaction region at essentially the same time. An analogous situation occurs for the tri-sodium mono-oxide case.

EXPERIMENTAL

Anion 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. This technique is governed by the energy-conserving relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the measured electron kinetic energy. Our apparatus consists of a laser vaporization anion source, a linear time-of-flight mass spectrometer for mass analysis and mass selection, a momentum decelerator, a magnetic bottle electron energy analyzer, and a Nd:YAG laser. The magnetic bottle has a resolution of ~ 50 meV at $\text{EKE} = 1$ eV. In these experiments, photoelectron spectra were recorded with 355 nm (3.49 eV) photons, i.e., the 3rd harmonic of a Nd:YAG laser. The photoelectron spectra were calibrated against the well-known transitions of atomic Cu^- .

In this work, Li_3O^- anions were prepared by laser-ablating a translating, rotating, 12.7 mm rod of 99.9% lithium metal with 532 nm (2.33 eV) photons, i.e., 2nd harmonic of another Nd:YAG laser. To promote the formation of Li_3O^- anions, water vapor was entrained in 110 psi of helium carrier gas and expanded over the ablation region. Na_3O^- anions were produced in a similar manner with pieces of 99.9% sodium pressed into the shape of a ~ 6 mm rod, which was then ablated.

RESULTS

The photoelectron spectra of Li_3O^- and Na_3O^- are presented in Figure 1. In the photoelectron spectrum of Li_3O^- ,

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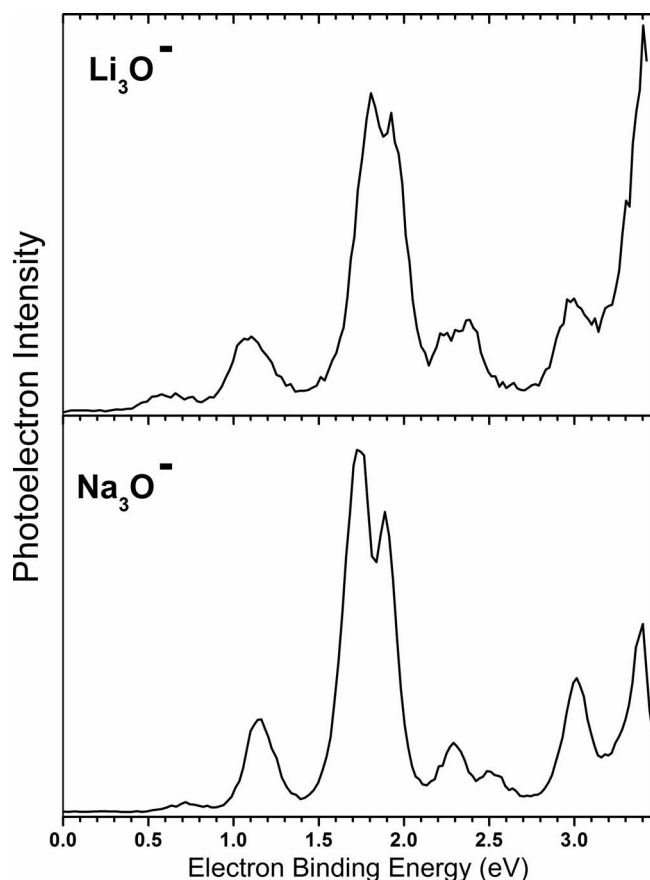


FIG. 1. Photoelectron spectra of Li_3O^- (top) and Na_3O^- (bottom) each recorded with 3.49 eV photons.

transitions are observed which are centered at $\text{EBE} = 0.6, 1.1, 1.8, 1.9, 2.3, 3.0,$ and 3.5 eV. The peaks at $\text{EBE} = 1.8, 1.9,$ and 3.5 eV are much more intense than the others, and the feature at $\text{EBE} = 2.3$ eV shows evidence of additional sub-structure.

An almost identical set of peaks appears in the isoelectronic Na_3O^- spectrum, although most peaks are shifted by ~ 0.05 eV toward higher electron binding energies. However, the two strongest peaks (at $\text{EBE} = 1.75$ and 1.85 eV) are exceptions; they are shifted ~ 0.05 eV toward lower electron binding energies than the analogous Li_3O^- peaks. There are also other differences. The peak near $\text{EBE} = 3.5$ eV is less intense in the Na_3O^- spectrum than in the Li_3O^- spectrum, and two distinct peaks are present at $\text{EBE} = 2.3$ and 2.5 eV in the Na_3O^- spectrum, compared to the less defined feature at $\text{EBE} = 2.3$ eV in the Li_3O^- spectrum.

In both Li_3O^- and Na_3O^- photoelectron spectra, the observed transitions are due to both photodetachment and photoionization. As described above, the energetics for such a two photon process are feasible for these two anions. In addition, most pulsed lasers easily have enough power for two photon processes. Another two photon process that can sometimes compete with photodetachment is photodissociation. There, the mass-selected anion is decomposed into neutral and anion fragments, with the latter in turn undergoing photodetachment. We see no evidence for this process having contributed electrons to the photoelectron spectra of Li_3O^- and Na_3O^- . Anionic products of photodissociation would likely include

the atomic anions, Li^- , Na^- , and/or O^- . All of these would have sharp peaks that would likely protrude out of the observed bands at well-known EBE values, but none do. Moreover, all possible neutral photodissociation products have ionization potentials that are significantly greater than the 3.49 eV photon energy used in these experiments.

DISCUSSION

In order to assign the transitions in the photoelectron spectrum of Li_3O^- , we have relied on the calculations of Zein and Ortiz for support.²² While analogous calculations are not available for the tri-sodium mono-oxide case, the spectral similarity between the photoelectron spectra of Na_3O^- and Li_3O^- suggests that a very similar set of computational results would be found, if such calculations were to be conducted. Thus, our assignments herein focus only on the Li_3O^- spectrum. Anticipating both photodetachment and photoionization transitions in the photoelectron spectrum of Li_3O^- , Zein and Ortiz calculated the vertical detachment energies from the anions' singlet and triplet states to the ground state of neutral Li_3O at the coupled-cluster single double triple (CCSD(T)) level of theory (0.65 eV and 0.45 eV, respectively) and the ionization potentials of the ground and excited states of neutral Li_3O , in both D_{3h} and C_{2v} symmetries at the BD-T1 level of theory.

Utilizing their computational results, we constructed an energy level diagram on which the energies of the ground state ($^1A_1'$) Li_3O^- anion, the ground and excited states of the D_{3h} Li_3O neutral, and the ground state of the Li_3O^+ cation were quantitatively placed relative to one another (see Figure 2). In constructing this energy level diagram, the energies of the ground and excited neutral Li_3O states were plotted relative to the ground state of the Li_3O^+ cation based on their IP values as calculated at the BD-T1 level of theory. The energy of the anion's singlet ground state was located on this diagram by placing it below the BD-T1 ionization energy of the neutral Li_3O ground state by an energy equal to its CCSD(T) VDE value.

We did not include the 3A_1 Li_3O^- anion on this diagram for two reasons; there was little indication for a separate peak at $\text{EBE} = 0.45$ eV, the VDE predicted for anion's triplet state, and with an energy separation of 0.22 eV between the anions' singlet and triplet states, an anion temperature of ~ 1100 K would have been required to achieve a 10% population of the excited triplet state. Thus, it is expected that the Li_3O^- anion's triplet played only a minor role in the Li_3O^- photoelectron spectrum, and that the majority of the observed photodetachment transitions originated from the $^1A_1'$ singlet, ground state of the Li_3O^- anion.

Since every photoionization transition originated from a neutral Li_3O state that had itself been formed by the photodetachment of a Li_3O^- anion, all neutral-state-to-cation transitions are paired with singlet anion-to-neutral-state transitions (see corresponding primed and unprimed capital letters in Figure 2). Using these transition energies, we now present the spectral assignment of the Li_3O^- photoelectron spectrum. These are marked with same lettering scheme of the Li_3O^- photoelectron spectrum in Figure 3. The band cen-

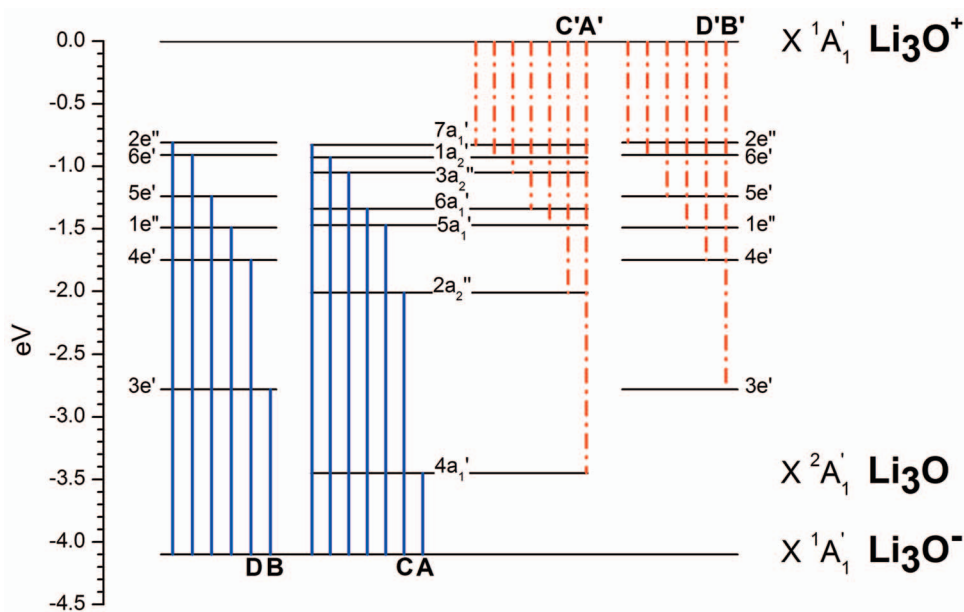


FIG. 2. Energy level diagram on which the energies of the ground state ($^1A_1'$) Li_3O^- anion, the ground and excited states of the D_{3h} Li_3O neutral, and the ground state of the Li_3O^+ cation are quantitatively placed relative to one another. Vertical solid lines denote the anion-to-neutral-state transitions, while vertical dashed lines denote the neutral-state-to-cation transitions.

tered at $\text{EBE} = 0.6$ eV is attributed to the photodetachment transition from the singlet, ground state, anion to the doublet, ground state, neutral species with a $4a_1'$ electronic configuration; it contains the spectrum's origin transition and corresponds to the transition labeled **A** in Figures 2 and 3. Thus, the VDE value of Li_3O^- is determined to be 0.6 eV. However, since this band is not vibrationally resolved, we cannot precisely determine the EA value of Li_3O from it. Nevertheless, our measured VDE value and the EA value implied by our result are consistent with the VDE and EA values reported

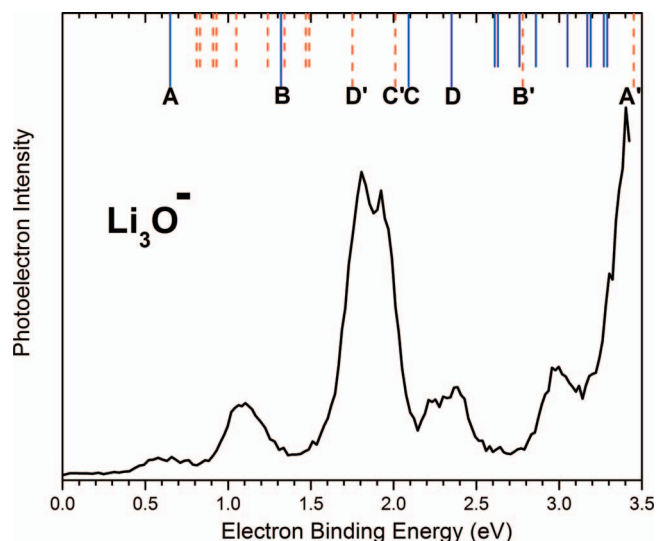


FIG. 3. Spectral assignments for the photoelectron spectrum of Li_3O^- . The vertical solid sticks depict photodetachment transitions, while vertical dashed sticks depict photoionization transitions. Specific photodetachment transitions in Figure 2 are labeled **A**, **B**, **C**, and **D**, while specific photoionization transitions in Figure 2 are labeled **A'**, **B'**, **C'**, and **D'**.

by both Gutowski and Ortiz. The peaks at $\text{EBE} = 1.1$, 2.3, and 2.4 eV are transitions from the anion to excited neutral states with electronic configurations $3e'$, $2a_2''$, and $4e'$, respectively, and these correspond to transitions labeled **B**, **C**, and **D**, respectively. The peak at $\text{EBE} = 3.45$ eV is the photoionization transition from the HOMO of the ground neutral ($4a_1'$) to the cation and is labeled, **A'**. Transitions to the cation originating from the HOMO+1 and HOMO+2 ($3e'$) of the neutral are labeled **B'** and correspond to the observed peak at $\text{EBE} = 3.0$ eV. The peaks at $\text{EBE} = 1.8$ and 1.7 eV are from the HOMO+3 ($2a_2''$) as well as from HOMO+4 and HOMO+5 ($4e'$) of the neutral, and they are labeled **C'** and **D'**, respectively. Additionally, the $\text{EBE} = 1.1$ eV peak could contain photoionization transitions originating from higher (hydrogenic) neutral states. This assignment is in accord with that made by Zein and Ortiz in Ref. 22.

Among the reasons for interest in Li_3O^- is the fact that it is isoelectronic with the elusive, double Rydberg anion, H_3O^- , and studying one might shed light on the other.^{4,17,18} The double Rydberg anion, H_3O^- , would consist of the closed shell, C_{3v} symmetry, H_3O^+ cation core and two Rydberg-like electrons. While the $\text{H}^-(\text{H}_2\text{O})$ and $\text{OH}^-(\text{H}_2)$ complexes have been observed experimentally,^{19,20} the double-Rydberg H_3O^- has not. Because there would be little structural change upon removing an excess electron, the photoelectron spectrum of H_3O^- would be expected to be dominated by a single, narrow peak at $\text{EBE} \sim 0.5$ eV, just as was seen in the photoelectron spectrum of the double Rydberg anion, NH_4^- .²¹ The photoelectron spectra of the Li_3O^- and Na_3O^- anions lack this spectral signature. Moreover, the symmetry of the ground state Li_3O^- anion is D_{3h} and not C_{3v} , as it would be in the case of H_3O^- . It is clear that Li_3O^- is not analogous to the H_3O^- double Rydberg anion.

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