

Photoelectron spectroscopy of lithium dimer anion

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ABSTRACT

We have recorded the photoelectron spectrum of ${}^7\text{Li}_2^-$ at 488 nm and 457.9 nm. Photodetachment transitions are observed between the $X^2\Sigma_u^+$ state of ${}^7\text{Li}_2^-$ and the $X^1\Sigma_g^+$, $a^3\Sigma_u^+$, and $A^1\Sigma_u^+$ states of ${}^7\text{Li}_2$. The electron affinity of ${}^7\text{Li}_2$ was determined to be 0.437 ± 0.009 eV. Additional spectroscopic parameters for the $X^2\Sigma_u^+$ of ${}^7\text{Li}_2^-$ determined in this work are: $B_e = 0.502\pm 0.005$ cm^{-1} which leads to $r_e = 3.094\pm 0.015$ Å, $\omega_e = 232\pm 35$ cm^{-1} , and $D_0 = 0.865\pm 0.022$ eV.

1. INTRODUCTION

The lithium molecule is the smallest homonuclear diatomic capable of forming a stable negative ion. Although H_2 is isoelectronic to Li_2 in the valence shell, the $X^2\Sigma_u^+$ state of H_2^- is not stable with respect to autodetachment and thus exists only as a resonance.¹ In addition, He_2^- has only been observed as a high-lying metastable in a ${}^4\Pi_u$ state.²⁻⁴ Due to its fundamental nature, Li_2^- has been the subject of a number of theoretical studies,⁵⁻¹³ nearly all of which predict a bound ground state of ${}^2\Sigma_u^+$ symmetry. Despite this theoretical interest, experimental information regarding the bound nature of this species has thus far been limited to two mass spectrometric observations of Li_2^- .^{14,15} Other information regarding the interaction of electrons with Li_2 has been provided by dissociative electron attachment studies and the observation of electron scattering resonances.^{16,17} Here, we present the photoelectron spectrum of Li_2^- along with spectroscopic constants for the $X^2\Sigma_u^+$ Li_2^- ground state which were extracted from a Franck-Condon analysis of the photoelectron spectrum.

2. EXPERIMENTAL

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.¹⁸ Briefly, anions are generated in a supersonic expansion cluster ion source, skimmed, and transported through a series of ion optical components through an $\mathbf{E} \times \mathbf{B}$ Wien velocity filter where they are mass selected. After being focused into the field-free, collision-free ion/photon interaction region, the mass selected cluster ion beam is crossed with the intracavity photon beam of an argon ion laser operated at visible wavelengths. 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. The photoelectron spectra of lithium dimer anion were recorded with an instrumental resolution of 30 meV at photon energies of 2.540 eV and 2.709 eV.

Beams of lithium dimer anion were generated using a specially designed high temperature seeded beam supersonic expansion ion source which is shown schematically in Fig.1. The main portion of this source consists of a high temperature oven with separately heated reservoir and nozzle sections. The oven is constructed of stainless steel (type 304) with evenly

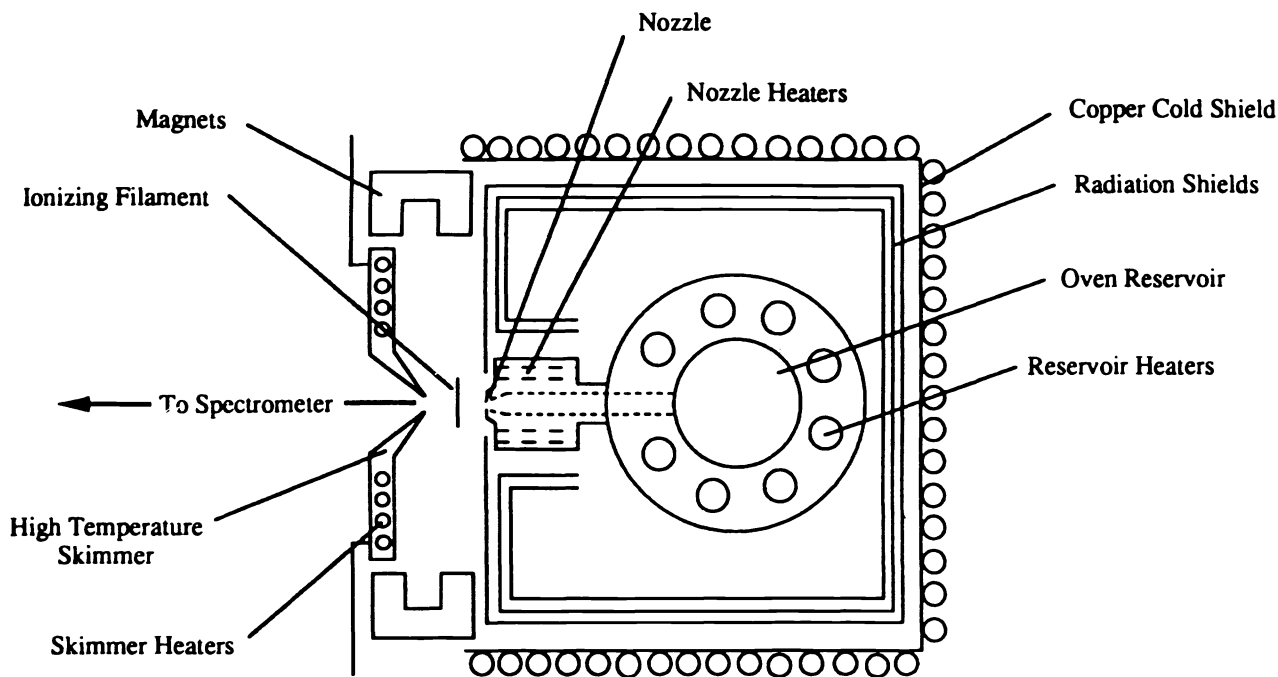


Figure 1. Schematic diagram of our high temperature supersonic expansion ion source.

spaced holes in each section for inserting heaters. The heaters for both sections consist of tantalum wires (0.5 mm diameter) insulated by high purity multi-hole ceramic rods (99.9% Al_2O_3 , McDaniel). The oven is surrounded by several layers of tantalum foil and stainless steel foil radiation shields and by a water cooled copper cold shield. High purity lithium metal (99.9% Aldrich) is heated in the reservoir section to 1300 K, giving approximately 50 torr of lithium vapor. The lithium vapor is then coexpanded with preheated high purity argon (99.99%) carrier gas through the nozzle (0.15 mm diameter) into high vacuum. The temperature of the nozzle section is maintained 30-70 degrees hotter than the temperature of the reservoir at all times in order to prevent nozzle clogging. A negatively biased hot thoriated iridium filament placed on the high vacuum side of the nozzle injects low energy electrons directly into the condensation prone region of the expanding lithium/argon jet. An axial magnetic field in the expansion region was used to enhance ionization efficiency and to confine and concentrate the microplasma. The resultant beam is then skimmed by a high temperature conical skimmer, and ions are extracted into the spectrometer. The skimmer is heated in a similar manner to the oven, and the design employed allows temperatures of 1000 K to be maintained at the skimmer tip. This was found to be a necessary condition for producing stable beams. Other source conditions included a beam energy of -500 eV, a negative filament bias of 40-90 V, a filament emission current of 2-60 mA, and argon carrier gas pressures of 50-150 torr. The use of higher carrier gas pressures was found to induce beam instabilities and to drastically reduce the observed ion currents. Under these conditions, typical currents (monitored downstream of the ion-photon interaction region) of 10-60 picoamperes of Li_2^- are measured along with slightly larger currents of the atomic anion. In addition, beams of higher lithium clusters ($\text{Li}_{n=3-11}^-$) are concurrently produced, with the intensities of $\text{Li}_{n=3-7}^-$ being comparable to those of the dimer anion. The photoelectron spectroscopy of these cluster anions will be discussed in a future publication.¹⁹ The use of hydrogen and deuterium as carrier gases allows the production of the anions LiH^- and LiD^- , and the photoelectron spectroscopy of these species will also be reported in a future publication.²⁰

3. RESULTS AND ANALYSIS

3.1 Spectral Assignment

The 488 nm (2.540 eV) photoelectron spectrum of ${}^7\text{Li}_2^-$ is presented in Fig. 2. This spectrum was recorded over about 3.5 hours with a ${}^7\text{Li}_2^-$ current of 10-60 picoamperes and a circulating laser power of 120 W. The absolute kinetic energy scale was calibrated by comparing the electron binding energy of ${}^7\text{Li}^-$, recorded immediately before and after the ${}^7\text{Li}_2^-$ spectrum, to the established literature value.²¹ The ${}^7\text{Li}_2^-$ spectrum is highly structured, with individual peaks arising due to photodetachment transitions between the $X^2\Sigma_u^+$ ground state of ${}^7\text{Li}_2^-$ and the ground and energetically accessible low-lying excited electronic states of ${}^7\text{Li}_2$. All of the features in this spectrum have been assigned, guidance having been provided by available theoretical data and optical data.^{9,22-26} Assignments of the photodetachment transitions giving rise to each feature in the photoelectron spectrum are given in Fig.2 above each corresponding spectral feature. The lowest electron binding energy (EBE) feature corresponds to the photodetachment transition from the $X^2\Sigma_u^+$ of ${}^7\text{Li}_2^-$ to the $X^1\Sigma_g^+$ ground state of ${}^7\text{Li}_2$.

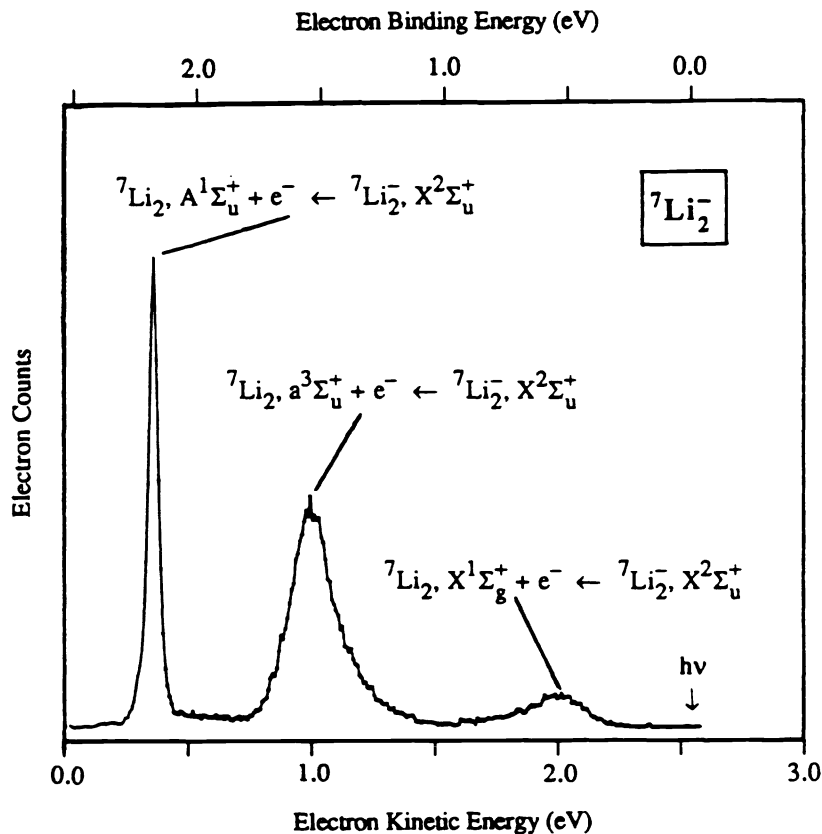


Figure 2. The 488 nm photoelectron spectrum of ${}^7\text{Li}_2^-$. The assignment for each photodetachment transition is designated above its corresponding spectral feature.

The spectral width of this feature is a consequence of a vibrational progression, and the appearance of several vibrational features in this band has allowed a detailed analysis to be carried out which will be discussed below. The next highest EBE feature in the spectrum is due to the ${}^7\text{Li}_2, a^3\Sigma_u^+ + e^- \leftarrow {}^7\text{Li}_2^-, X^2\Sigma_u^+$ transition. A comparison of the determined

spectroscopic constants for the $X^2\Sigma_u^+$ state of ${}^7\text{Li}_2^-$ with high level calculations on the $a^3\Sigma_u^+$ of ${}^7\text{Li}_2$ ²³ suggests that the spectral shape of this feature on the low EBE side reflects access of the weakly bound portion of the $a^3\Sigma_u^+$ potential while the shape of the high EBE side reflects access of the repulsive portion of this potential at smaller internuclear distances. The highest EBE feature in the spectrum arises due to the transition to the $A^1\Sigma_u^+$ state of ${}^7\text{Li}_2$. The width of this feature suggests that the equilibrium bond distances of the $X^2\Sigma_u^+$ of ${}^7\text{Li}_2^-$ and $A^1\Sigma_u^+$ state of ${}^7\text{Li}_2$ the are very similar. The photoelectron spectrum of ${}^7\text{Li}_2^-$ displays the same qualitative features, with one notable exception, as the spectra of the heavier alkali dimer anions which we have reported previously.²⁷ At the photon energies employed in this study and in our previous work, the $M_2, b^3\Pi_u + e^- \leftarrow M_2, X^2\Sigma_u^+$ transition should be energetically accessible for all alkali dimer anions. The feature corresponding to this transition appears clearly as a shoulder on the low EBE side of the $M_2, A^1\Sigma_u^+ + e^- \leftarrow M_2, X^2\Sigma_u^+$ transition in the spectra of $\text{Na}_2^-, \text{K}_2^-, \text{Rb}_2^-,$ and Cs_2^- . In the photoelectron spectrum of Li_2^- , however, no such feature is observed. Since the $M_2, b^3\Pi_u + e^- \leftarrow M_2, X^2\Sigma_u^+$ transition is a two electron process, its apparent absence in the spectrum of Li_2^- may indicate that the contributions of π orbital-containing configurations to the ground state configuration of Li_2^- are significantly smaller than those to the ground state configurations of the heavier alkali dimer anions.

3.2 Determination of the electron affinity of ${}^7\text{Li}_2$

An accurate determination of the adiabatic electron affinity of ${}^7\text{Li}_2$ was made by subtracting the energy of the $A^1\Sigma_u^+(v''=0) \rightarrow X^1\Sigma_g^+(v'=0)$ optical transition in ${}^7\text{Li}_2$ ²⁵ from the EBE of the center of the spectral feature corresponding to the ${}^7\text{Li}_2, A^1\Sigma_u^+ + e^- \leftarrow {}^7\text{Li}_2^-, X^2\Sigma_u^+$ transition in the photoelectron spectrum of ${}^7\text{Li}_2^-$. This band appears as a single narrow feature in the photoelectron spectrum. A consideration of the magnitude of the vibrational frequency of the $A^1\Sigma_u^+$ state of ${}^7\text{Li}_2$ ^{25,26} reveals that this band must be dominated by a single vibrational feature corresponding to the ${}^7\text{Li}_2, A^1\Sigma_u^+(v''=0) + e^- \leftarrow {}^7\text{Li}_2^-, X^2\Sigma_u^+(v'=0)$ photodetachment transition (along with significantly smaller contributions from other $\Delta v=0$ photodetachment transitions). Thus, subtracting the $A^1\Sigma_u^+(v''=0) \rightarrow X^1\Sigma_g^+(v'=0)$ transition energy for ${}^7\text{Li}_2$, from our measured ${}^7\text{Li}_2, A^1\Sigma_u^+(v''=0) + e^- \leftarrow {}^7\text{Li}_2^-, X^2\Sigma_u^+(v'=0)$ transition energy (EBE) gives the energy difference between the $X^2\Sigma_u^+(v''=0)$ state of ${}^7\text{Li}_2^-$ and the $X^1\Sigma_g^+(v'=0)$ state of ${}^7\text{Li}_2$, ie. the adiabatic electron affinity. In order to ascertain that our measurement of the ${}^7\text{Li}_2, A^1\Sigma_u^+(v''=0) + e^- \leftarrow {}^7\text{Li}_2^-, X^2\Sigma_u^+(v'=0)$ transition energy was not affected by the transmission function for low energy electrons of our energy analyzer, we recorded the spectrum of ${}^7\text{Li}_2^-$ at 457.9 nm (2.709 eV). The measured EBE of the peak center of this transition measured using 2.709 eV photons agreed to within 1 meV with the measured value using 2.540 eV photons. The rotational energy correction²⁸ to the ${}^7\text{Li}_2, A^1\Sigma_u^+(v''=0) + e^- \leftarrow {}^7\text{Li}_2^-, X^2\Sigma_u^+(v''=0)$ transition energy was also considered. Due to the very similar equilibrium bond distances, and thus similar rotational constants of the $X^2\Sigma_u^+$ state of ${}^7\text{Li}_2^-$ and the $A^1\Sigma_u^+$ state of ${}^7\text{Li}_2$, the rotational energy correction here is negligible. In fact, using the spectroscopic constants determined in this study for the $X^2\Sigma_u^+$ state of ${}^7\text{Li}_2^-$ (see below) we estimate this correction to be much less than 1 meV. Thus, the value for the adiabatic electron affinity of ${}^7\text{Li}_2$ determined here is 0.437 ± 0.009 eV. The stated uncertainty is chosen to account for possible errors in absolute kinetic energy scale calibrations, errors in determining the energy scale compression factor, and errors in the peak fitting procedure. Our experimental value for the adiabatic electron affinity of ${}^7\text{Li}_2$ is in excellent agreement with several theoretical values.⁷⁻¹¹

3.3 Determination of spectroscopic constants for the $X^2\Sigma_u^+$ state of ${}^7\text{Li}_2^-$

Spectroscopic constants for the ground state of ${}^7\text{Li}_2^-$ were obtained by performing anharmonic Franck-Condon spectral simulations of the ${}^7\text{Li}_2, X^1\Sigma_g^+ \leftarrow {}^7\text{Li}_2^-, X^2\Sigma_u^+$ band. In order to facilitate this procedure, a long integration time scan was performed on this band using 2.540 eV photons, and this spectrum is shown in Fig.3, along with assignments of several vibrational features. Simulations were generated using the known values of $\omega_e, \omega_e x_e,$ and r_e for ${}^7\text{Li}_2$ ²⁵ and by varying the origin band position, and the vibrational frequency, vibrational anharmonicity, equilibrium bond distance, and vibrational temperature of the anion. The simulated spectra were then compared to the empirical spectrum in a least squares sense. This

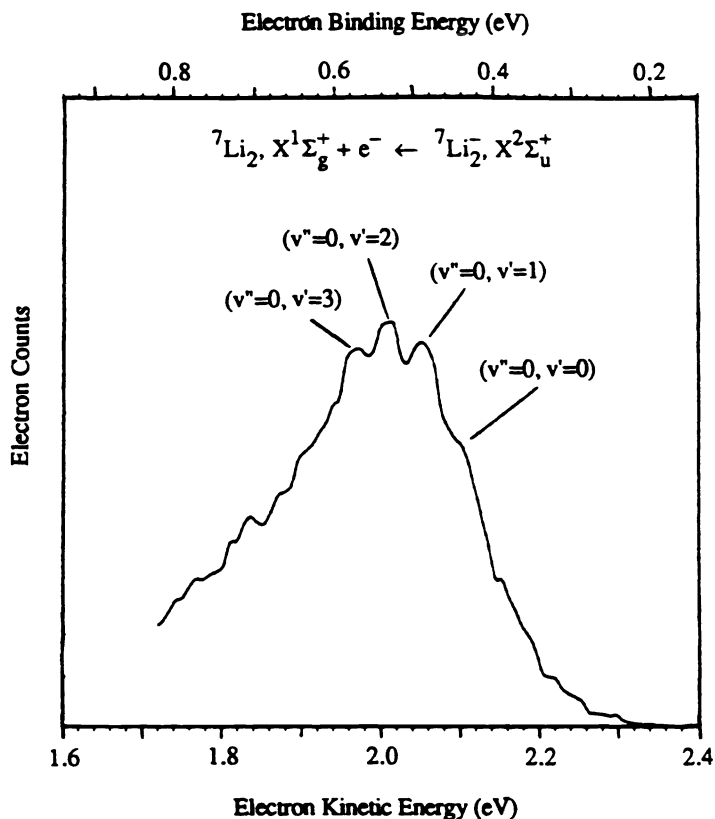


Figure 3. A long integration time scan over the ${}^7\text{Li}_2, X^1\Sigma_g^+ \leftarrow {}^7\text{Li}_2^-, X^2\Sigma_u^+$ taken at 488 nm. The assignments of several vibrational features in this band are also given where " denotes an anion state and ' denotes a neutral state.

procedure yielded a confirmation of the previously determined adiabatic electron affinity, as well as the following spectroscopic constants for the ground state of ${}^7\text{Li}_2^-$: $B_e = 0.502 \pm 0.005 \text{ cm}^{-1}$, $r_e = 3.094 \pm 0.015 \text{ \AA}$, and $\omega_e = 232 \pm 35 \text{ cm}^{-1}$. The anion vibrational anharmonicity was not determined here since this quantity had no significant effect on the fit. In addition, a vibrational temperature, assuming a Boltzmann distribution, of 280 K was determined for ${}^7\text{Li}_2^-$. Finally, using the experimental value for the electron affinity of ${}^7\text{Li}_2$, the dissociation energy of ${}^7\text{Li}_2^-$ can be determined via thermochemical cycle using the following relation:

$$D_0 [{}^7\text{Li}_2^-, X^2\Sigma_u^+] = D_0 [{}^7\text{Li}_2, X^1\Sigma_g^+] + \text{E.A.} [{}^7\text{Li}_2] - \text{E.A.} [\text{Li}] \quad (1)$$

Using the recommended value for the dissociation energy of ${}^7\text{Li}_2$ ²⁹ and the established literature value for the electron affinity of Li,²¹ a value of $0.865 \pm 0.022 \text{ eV}$ is obtained for $D_0 [{}^7\text{Li}_2^-, X^2\Sigma_u^+]$. This value along with the other spectroscopic constants for the $X^2\Sigma_u^+$ of ${}^7\text{Li}_2^-$ are in excellent agreement those determined in several theoretical investigations.⁷⁻¹¹

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