

# Photoelectron spectroscopy of lithium hydride anion

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(Received 14 September 1993; accepted 5 October 1993)

We present negative ion photoelectron spectra of the smallest stable molecular negative ion, the lithium hydride anion. Photoelectron spectra, recorded using 2.540 eV photons, are reported for the  $\text{LiH(D)} [X^1\Sigma^+] + e^- \leftarrow \text{LiH(D)}^- [X^2\Sigma^+]$  transitions of  $^7\text{LiH}^-$  and  $^7\text{LiD}^-$ . Adiabatic electron affinities of  $0.342 \pm 0.012$  eV and  $0.337 \pm 0.012$  eV were determined for  $^7\text{LiH}^-$  and  $^7\text{LiD}^-$ , respectively. The experimentally determined electron affinities led to anion dissociation energy ( $D_0$ ) values of  $2.017 \pm 0.021$  eV for  $^7\text{LiH}^-$  and  $2.034 \pm 0.021$  eV for  $^7\text{LiD}^-$  relative to their  $\text{Li}[^2S_{1/2}] + \text{H}^-(\text{D}^-)[^1S_0]$  asymptotes. Franck-Condon analyses yielded the following molecular parameters for the ground state of  $^7\text{LiH}^-$ :  $B_e = 6.43 \pm 0.18$   $\text{cm}^{-1}$ ,  $r_e = 1.724 \pm 0.025$  Å, and  $\omega_e = 920 \pm 80$   $\text{cm}^{-1}$ ; and the following parameters for the ground state of  $^7\text{LiD}^-$ :  $B_e = 3.62 \pm 0.06$   $\text{cm}^{-1}$ ,  $r_e = 1.724 \pm 0.015$  Å, and  $\omega_e = 650 \pm 45$   $\text{cm}^{-1}$ . In addition, we have observed the alkali hydride anions:  $^7\text{LiH}_2^-$ ,  $^7\text{LiD}_2^-$ ,  $\text{Li}_2\text{D}^-$ ,  $\text{NaD}^-$ ,  $\text{NaD}_2^-$ ,  $\text{NaD}_3^-$ , and  $\text{NaD}_4^-$ . No photo-detachment signal was observed for the lithium dihydride anion,  $^7\text{LiD}_2^-$ , using 2.540 eV photons.

## I. INTRODUCTION

The lithium hydride anion is the smallest, stable molecular negative ion. Interest in this anion stems not only from its fundamental nature, but also from its kinship to other systems in which polar, closed shell molecules interact with electrons. Considerable theoretical attention<sup>1-23</sup> has been focused on the negative ion states of polar molecules due to the unique types of electron binding available to these systems. In the case of polar ionic molecules, which include the alkali hydrides and halides, the nature of electron binding in the anion ground states has been described in terms of a molecular orbital picture. For alkali halide negative ions, theoretical studies by Jordan and Simons,<sup>4,12</sup> together with photodetachment studies by Lineberger and co-workers<sup>24-26</sup> have yielded ground state descriptions in which the excess electron is localized on the electropositive alkali atom in a low-lying, nonbonding orbital of the neutral molecule. *Ab initio* calculations on the ground state ( $^2\Sigma^+$ ) of  $\text{LiH}^-$  have been performed by Simons and Jordan,<sup>3,4</sup> Jordan,<sup>5,6</sup> Liu and co-workers,<sup>7</sup> Karo *et al.*,<sup>8</sup> and R smus and Meyer.<sup>9</sup> The electron binding in  $\text{LiH}^-$  is expected to be similar to that in the alkali halide anions, but with a reduced localization of charge on the alkali atom.<sup>4</sup> To date, the considerable difficulty associated with the generation of  $\text{LiH}^-$  has precluded its spectroscopic characterization. Here, we present the photoelectron spectra of  $^7\text{LiH}^-$  and  $^7\text{LiD}^-$  which were recorded using 2.540 eV photons. Adiabatic electron affinities as well as bond dissociation energies, rotational constants, equilibrium bond distances, and vibrational frequencies for the ground states of these negative ions are also reported.

## II. EXPERIMENTAL METHOD

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.<sup>27,28</sup> Briefly, negative ions are generated in a high temperature, supersonic expansion ion source. The details of this source and of ion production are discussed below. Anions generated in the 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 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 at circulating powers of  $\sim 100$  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. The resulting photoelectron spectra were calibrated by recording  $\text{Li}^-$  spectra before and after each  $^7\text{LiH}^-$  or  $^7\text{LiD}^-$  spectrum and comparing the measured electron binding energies to the established electron affinity of the lithium atom.<sup>29,30</sup>

## III. PRODUCTION OF LITHIUM HYDRIDE ANION

Preceding this study, only two observations of  $\text{LiH}^-$  have been reported. Some time ago, Heinicke and co-workers reported observing  $\text{LiH}^-$  produced in a Penning ion source.<sup>31</sup> More recently, Middleton reported observing  $\text{LiH}^-$  produced in a cesium cation sputter source using a cathode containing lithium hydride powder.<sup>32</sup> Since both of these approaches have been shown to produce an astonishingly wide variety of molecular anions, we placed them both in our queue of prospective ion sources for producing  $\text{LiH}^-$  for the present study. Our initial attempts to produce this ion utilized a Penning ion source, similar in design to that used by Heinicke, since we already had considerable experience using this type of source to produce molecular anions.<sup>33,34</sup> Employing this source and Hein-

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icke's source conditions, we were able to produce substantial currents of both  $\text{Li}^-$  and  $\text{LiH}_2^-$ ; just as he reported. Despite numerous attempts, however, we were unable to produce  $\text{LiH}^-$  via this route.

While the sputter ion source of Middleton is a proven approach for generating  $^7\text{LiH}^-$ , this type of source is known to produce ions with extremely high internal temperatures.<sup>35</sup> With this in mind, we placed the sputter ion source approach further down our queue in favor of ion production schemes which were more likely to produce anions with internal temperatures appropriate for spectroscopic studies. Our next several attempts to produce the lithium hydride anion involved an array of hot cathode discharge source configurations followed by a variety of "pickup" ion source schemes in which hydrogen or hydrogen-containing gases (including  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ ) were reacted with lithium beams. In none of these cases, however, did we make a definitive observation of  $\text{LiH}^-$ .

The ion source configuration which eventually produced  $\text{LiH}^-$  is based on coexpanding intimately mixed lithium vapor and hydrogen gas in a supersonic jet. A coexpansion scheme had been earlier employed by Dagdigan to produce *neutral* beams of lithium hydride.<sup>36</sup> Our approach for producing the anions was carried out using the same high temperature, supersonic expansion ion source used in our study of  $\text{Li}_2^-$ .<sup>37</sup> The main portion of this source consists of a stainless steel (SS 304) high temperature oven divided into separately heated reservoir and nozzle sections. Both sections are heated by evenly spaced tantalum wire (0.5 mm diameter) heaters insulated using high purity, multihole alumina rods (99.9%  $\text{Al}_2\text{O}_3$ , McDaniel). High purity lithium metal (99.9% Aldrich) is heated in the reservoir to 1210 K to yield approximately 20 torr of lithium vapor which is coexpanded with 100–200 torr of preheated  $\text{H}_2$  or  $\text{D}_2$  (99.9%) into high vacuum through a 0.15 mm diameter nozzle. The nozzle section is maintained at 1300 K in order to avoid clogging. A negatively biased, hot thoriated iridium filament injects low energy electrons directly into the expanding jet in the presence of a predominantly axial magnetic field, thereby generating negative ions. Typical conditions include negative filament bias voltages of 70–110 V along with emission currents of 40–70 mA. The beam is skimmed by a high temperature conical skimmer maintained at 1000 K, and ions are extracted into the spectrometer. Under these conditions, typical currents measured downstream of the ion-photon interaction region (at beam energies of 500 eV) were 1.0–3.0 pA for  $^7\text{LiH}^-$  and 2.0–6.0 pA for  $^7\text{LiD}^-$ . A representative mass spectrum showing  $^7\text{LiH}^-$  is presented in Fig. 1. A mass spectrum showing  $^7\text{LiD}^-$ , which was recorded using a different Wien filter electric field setting, is presented in Fig. 2. Both spectra show peaks corresponding to the lithium monohydride anions while also showing much weaker intensities of the dihydride anions. In this respect, our production scheme differs from those of Heinicke and Middleton, both of whom report substantially higher intensities of the dihydride anions than of the monohydride anions. We have also utilized this approach to

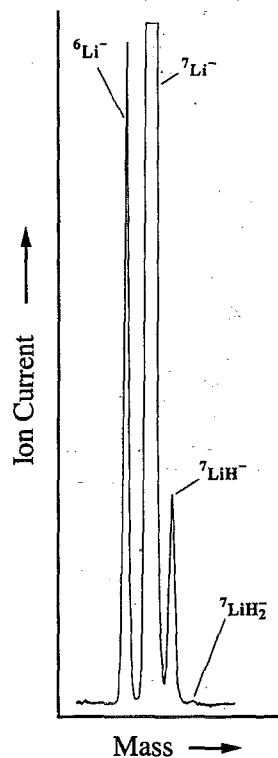


FIG. 1. Mass spectrum of the negative ions generated in our high temperature, supersonic expansion ion source by coexpansion of lithium and hydrogen. This spectrum shows the production of  $^7\text{LiH}^-$  along with a very small amount of  $^7\text{LiH}_2^-$ .

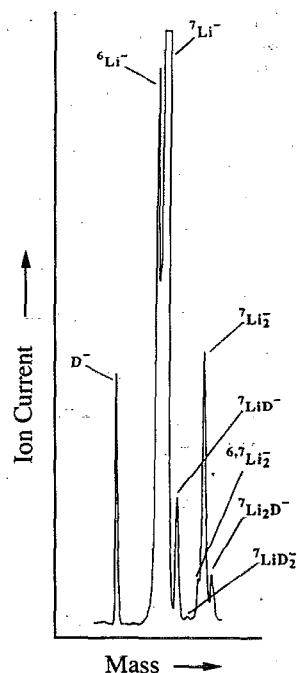


FIG. 2. Mass spectrum of the negative ions generated in our high temperature, supersonic expansion ion source by coexpansion of lithium and deuterium. The molecular anions present in the spectrum are  $^7\text{LiD}^-$ ,  $^7\text{LiD}_2^-$ ,  $\text{Li}_2^-$ , and  $\text{Li}_2\text{D}^-$ .

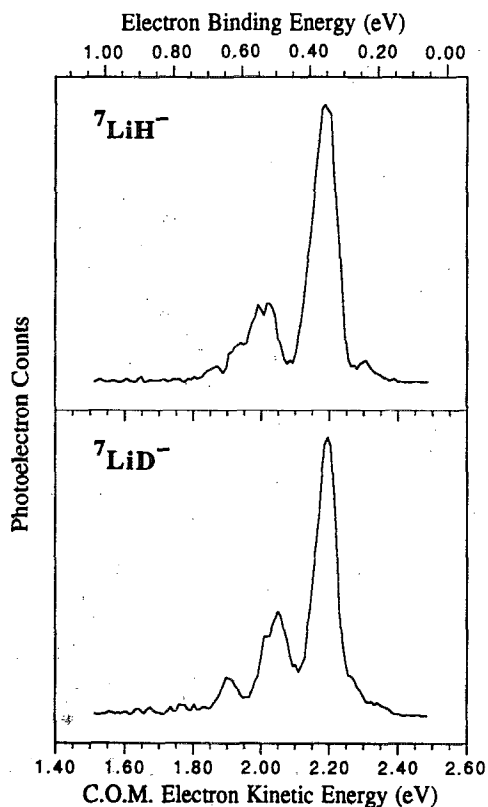


FIG. 3. Photoelectron spectra of  ${}^7\text{LiH}^-$  and  ${}^7\text{LiD}^-$  recorded using 2.540 eV photons. Electron binding energy is obtained by subtracting the center-of-mass electron kinetic energy from the photon energy. No signal was observed outside the energy window shown in the spectra.

generate currents of 0.1–3.0 pA of other alkali hydride anions, e.g.,  $\text{Li}_2\text{D}^-$  (see Fig. 2),  $\text{NaD}^-$ ,  $\text{NaD}_2^-$ ,  $\text{NaD}_3^-$ , and  $\text{NaD}_4^-$ .

#### IV. PHOTOELECTRON SPECTRA AND ANALYSIS

The photoelectron spectra of  ${}^7\text{LiH}^-$  and  ${}^7\text{LiD}^-$  are presented in Fig. 3. These spectra were recorded using 2.540 eV photons. The features in both spectra belong to single electronic band systems due to the  $\text{LiH(D)} [X^1\Sigma^+] + e^- \leftarrow \text{LiH(D)}^- [X^2\Sigma^+]$  photodetachment transitions. In both spectra, the most intense feature corresponds to the vibrational origin ( $\nu'=0 \leftarrow \nu''=0$ ) band. The dominant features to the high electron binding energy (EBE) sides of the origin bands in both spectra are due to transitions from  $\nu''=0$  of the anions to  $\nu'=1$  and  $\nu'=2$  of the neutral molecules. Hot band transitions are also present in the spectra, the most evident being the  $\nu'=0 \leftarrow \nu''=1,2$  bands which appear to the low EBE sides of the origin peaks. These assignments are supported by the results of anharmonic Franck–Condon analyses which were generated by using the known values of  $\omega_e$ ,  $\omega_e x_e$ , and  $r_e$  for both  ${}^7\text{LiH}$  and  ${}^7\text{LiD}$ .<sup>38</sup> In these simulations, the vibrational frequencies, vibrational anharmonicities, equilibrium bond distances, and vibrational temperatures of the anions as well as the origin transition energies were independently varied. In addition, the contours resulting from unresolved rota-

tional structure were simulated for each vibrational feature since rotational effects are expected to play a visible role in these particularly light systems. The spectral peak widths for individual rotational features were set equal to the experimental energy width of the  $\text{Li}[{}^2S_{1/2}] + e^- \leftarrow \text{Li}^- [{}^1S_0]$  peaks in the calibrant spectra. The simulations suggest that the peak widths in both spectra are largely the result of unresolved rotational structure.

Several spectroscopic parameters for the electronic ground states of  ${}^7\text{LiH}^-$  and  ${}^7\text{LiD}^-$  were determined from the simulations. A rotational constant of  $6.43 \pm 0.18 \text{ cm}^{-1}$  was found for  ${}^7\text{LiH}^-$ , while for  ${}^7\text{LiD}^-$ , this parameter was found to be  $3.62 \pm 0.06 \text{ cm}^{-1}$ . These values both lead to an equilibrium bond distance of 1.724 Å. Vibrational frequencies for  ${}^7\text{LiH}^-$  and  ${}^7\text{LiD}^-$  were found to be  $920 \pm 80 \text{ cm}^{-1}$  and  $650 \pm 45 \text{ cm}^{-1}$ , respectively. In addition, vibrational temperatures of 840 K were found for both anions.

Adiabatic electron affinities for  ${}^7\text{LiH}$  and  ${}^7\text{LiD}$  were obtained essentially from the energies of the vibrational origin bands in the photoelectron spectra. The rotational analyses allowed refinements to be made to the electron affinity values, placing the true origins (i.e., the energy differences between the anion and neutral rovibronic ground states) just to the low EBE sides of the  $\nu'=0 \leftarrow \nu''=0$  peak centers. This rotational correction is made since photodetachment is expected to be dominated by transitions which approximately preserve rotational quantum number.<sup>39,40</sup> Also, the most highly populated rotational levels of  ${}^7\text{LiH}^-$  and  ${}^7\text{LiD}^-$  correspond to  $J=6$  and  $J=9$ , respectively, at a temperature of 840 K. The values obtained here for the adiabatic electron affinities of  ${}^7\text{LiH}$  and  ${}^7\text{LiD}$  are  $0.342 \pm 0.012 \text{ eV}$  and  $0.337 \pm 0.012 \text{ eV}$ , respectively. The error bars are chosen to account for errors in absolute kinetic energy scale calibrations, errors in determining the energy scale compression factors, and errors in the peak fitting procedures.

The adiabatic electron affinities were then used to obtain bond dissociation energies for the anions relative to their  $\text{Li}[{}^2S_{1/2}] + \text{H}^- (\text{D}^-) [{}^1S_0]$  asymptotes. Values of  $D_0$  for  ${}^7\text{LiH}^-$  and  ${}^7\text{LiD}^-$  in their  ${}^2\Sigma^+$  ground states were calculated from the thermochemical cycle;

$$D_0[{}^7\text{Li}-\text{H}^- (\text{D}^-)] = D_0[{}^7\text{Li}-\text{H}(\text{D})] + \text{EA}[{}^7\text{LiH}(\text{D})] - \text{EA}[\text{H}(\text{D})]$$

using our measured electron affinities, the literature values for the  ${}^7\text{LiH}$  and  ${}^7\text{LiD}$  dissociation energies,<sup>41,42</sup> and the literature value of the atomic electron affinity of hydrogen.<sup>30</sup> The  $D_0$  values determined in this manner are  $2.017 \pm 0.021 \text{ eV}$  for  ${}^7\text{LiH}^-$  and  $2.034 \pm 0.021 \text{ eV}$  for  ${}^7\text{LiD}^-$ .

The modeled spectra of both  ${}^7\text{LiH}^-$  and  ${}^7\text{LiD}^-$ , constructed using the energetic and spectroscopic parameters reported above, are presented in Fig. 4 and Fig. 5, respectively, along with the actual photoelectron spectra. The simulation for  ${}^7\text{LiD}^-$  produces a rather good fit of the real spectrum. In the case of  ${}^7\text{LiH}^-$ , the correspondence is also good with respect to most spectral features, but there is clearly some deviation from the fit on the high EBE side of the  $\nu'=1 \leftarrow \nu''=0$  peak. If the  ${}^7\text{LiD}^-$  spectrum is exam-

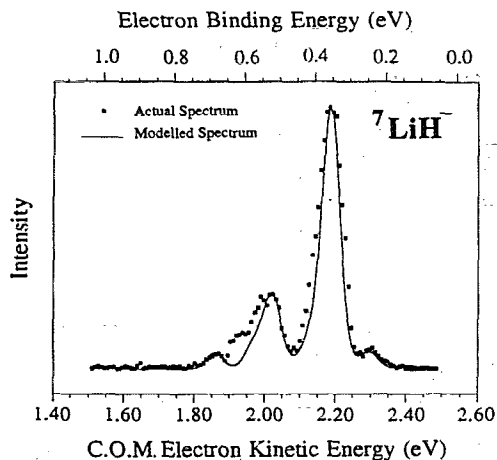


FIG. 4. Modeled and actual photoelectron spectra of  ${}^7\text{LiH}^-$ . The former was generated using the energetic and anion spectroscopic parameters reported in this work. The modeled spectrum is shown as a solid line while the actual spectrum is represented by points.

ined closely, analogous but much smaller deviations can also be seen. We have considered and eliminated all reasonable mechanisms which could account for these features except for autodetachment (to  $\text{LiH}(\text{D}), X^1\Sigma^+$ ) from metastable  $\text{LiH}(\text{D})^-$  anions generated in the ion source. It is possible that small amounts of metastable anions could have been produced in the relatively harsh environments of the hydrogen plasmas of the ion source in these particular experiments. The features indicate that such metastable states would need to be  $\sim 2.3$  eV higher in energy than the anion ground states, and a consideration of lifetimes suggests that such states would likely be  ${}^4\Sigma^+$  or  ${}^4\Pi$ . This type of process is not only plausible, but is also consistent with respect to the relative behavior of the features in the two spectra. If initial state energies are estimated from the features in the  ${}^7\text{LiH}^-$  spectrum and the

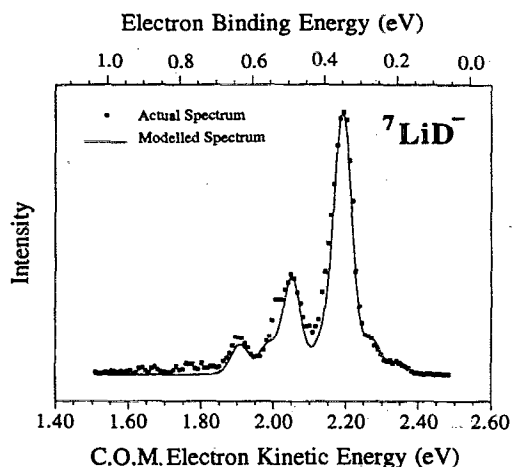


FIG. 5. Modeled and actual photoelectron spectra of  ${}^7\text{LiD}^-$ . The former was generated using the energetic and anion spectroscopic parameters reported in this work. The modeled spectrum is shown as a solid line while the actual spectrum is represented by points.

energies are adjusted only for isotope shifts, the resultant autodetachment transition energies correspond to the electron kinetic energies of excess intensity in the  ${}^7\text{LiD}^-$  spectrum. There are precedents for this type of process in other metastable anions. For example, Compton and co-workers observed autodetachment from  $\text{He}_2^- [{}^4\Pi_g]$  to  $\text{He}_2[X^1\Sigma_g^+]$ .<sup>43</sup>

Finally, we note that we attempted to record the photoelectron spectrum of  ${}^7\text{LiD}_2^-$ . The lithium dihydride anion is somewhat analogous to the hydrogen bialide anions,<sup>44</sup> and is thus one of the simplest examples of a negative ion possessing a geometry which allows the transition state region of a neutral reaction to be probed via photodetachment.<sup>45</sup> The exposure of a 0.5 pA beam of  ${}^7\text{LiD}_2^-$  to 2.540 eV photons, however, failed to produce any measurable photodetachment signal. This observation is consistent with both the vertical detachment energy of 3.1 eV calculated for  $\text{LiH}_2^-$  by Rosmus<sup>44</sup> and with the prediction of Heinicke that the electron affinity of  $\text{LiH}_2$  should exceed 3 eV.<sup>31</sup>

## V. DISCUSSION

The results of this work are consistent with the picture, provided by theory, that the excess electron resides in the low-lying nonbonding lowest unoccupied molecular orbital (LUMO) of neutral lithium hydride. The anion dissociation energies determined here are found to be 83% of the neutral dissociation energies. Furthermore, the equilibrium bond lengths determined in this work indicate that only an 8% bond elongation accompanies the attachment of an excess electron to lithium hydride.

The results presented here agree rather well with the parameters predicted by theory. The adiabatic electron affinity determined here for  $\text{LiH}^-$  is in good agreement with several *ab initio* calculations<sup>3-9</sup> and with the pseudopotential calculation of Garrett.<sup>23</sup> When a zero point energy correction is made to the electron affinity value reported by Jordan and Simons, nearly perfect agreement is achieved.<sup>4</sup> The  $\text{LiH}^-$  dissociation energy found here is in excellent agreement with theoretical predictions. The anion equilibrium bond distance found here is also in accord with theoretical predictions, although most theoretical studies expected a slightly smaller bond elongation ( $\sim 5\%$ ) relative to the neutral molecule. The only significant deviation from theoretical predictions is with respect to vibrational frequencies, where the predicted frequencies are  $\sim 20\%$  larger than those reported here.

In summary, we have presented the 488 nm photoelectron spectra of  ${}^7\text{LiH}^-$  and  ${}^7\text{LiD}^-$ . Adiabatic electron affinities of  $0.342 \pm 0.012$  eV and  $0.337 \pm 0.012$  eV were determined for  ${}^7\text{LiH}^-$  and  ${}^7\text{LiD}^-$ , respectively. The experimentally determined electron affinities led to dissociation energy ( $D_0$ ) values of  $2.017 \pm 0.021$  eV for  ${}^7\text{LiH}^-$  and  $2.034 \pm 0.021$  eV for  ${}^7\text{LiD}^-$ . Franck-Condon analyses yielded the following spectroscopic parameters for the ground state of  ${}^7\text{LiH}^-$ :  $B_e = 6.43 \pm 0.18$   $\text{cm}^{-1}$ ,  $r_e = 1.724 \pm 0.025$  Å, and  $\omega_e = 920 \pm 80$   $\text{cm}^{-1}$ ; and the following parameters for  ${}^7\text{LiD}^-$ :  $B_e = 3.62 \pm 0.06$   $\text{cm}^{-1}$ ,  $r_e = 1.724 \pm 0.015$  Å, and  $\omega_e = 650 \pm 45$   $\text{cm}^{-1}$ .

## ACKNOWLEDGMENTS

We wish to thank J. V. Coe, P. J. Dagdigan, K. D. Jordan, W. Klemperer, W. S. Koski, W. C. Lineberger, and J. Simons for stimulating discussions. We also thank V. L. Slager for assisting with some aspects of the Franck-Condon analyses and G. Pisiello and his machine shop staff for expert fabrication of the ion source components. Grateful acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the National Science Foundation under Grant No. CHE-9007445.

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