

# Ab initio study of the electronic structures of lithium containing diatomic molecules and ions

Alexander I. Boldyrev and Jack Simons

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

Paul von R. Schleyer

Institut für Organische Chemie der Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, 8520 Erlangen, Germany

(Received 7 May 1993; accepted 11 August 1993)

*Ab initio* calculations are used to provide bond lengths, harmonic frequencies, and dissociation energies of low-lying electronic states for  $\text{LiX}$ ,  $\text{LiX}^+$ , and  $\text{LiX}^-$  (with  $X=\text{Li}$  through  $\text{F}$  and  $\text{Na}$  through  $\text{Cl}$ ). Most of these species represent hitherto experimentally unknown molecules or ions, which provides the focus of the work presented here. All of these species are stable to dissociation and the anions are stable to loss of an electron. Differences among the electronic structures of the valence isoelectronic  $\text{LiX}$ ; and  $\text{HX}$ ,  $\text{LiX}^+$ , and  $\text{HX}^+$ ; and  $\text{LiX}^-$  and  $\text{HX}^-$  species are analyzed. Optimized geometries, dissociation energies, ionization potentials, and electron affinities were calculated for the following ground states of the respective species:  $^1\Sigma^+$  for  $\text{Li}_2(^1\Sigma_g^+)$ ,  $\text{LiNa}$ ,  $\text{LiBe}^+$ ,  $\text{LiBe}^-$ ,  $\text{LiMg}^+$ ,  $\text{LiMg}^-$ ,  $\text{LiF}$ ,  $\text{LiAl}$ ,  $\text{LiS}^-$ , and  $\text{LiCl}$ ;  $^2\Sigma^+$  for  $\text{Li}_2(^2\Sigma_g^+)$ ,  $\text{Li}_2(^2\Sigma_u^+)$ ,  $\text{LiBe}$ ,  $\text{LiB}^+$ ,  $\text{LiF}^-$ ,  $\text{LiNa}^+$ ,  $\text{LiNa}^-$ ,  $\text{LiMg}$ ,  $\text{LiAl}^+$ , and  $\text{LiCl}^-$ ;  $^2\Pi_r$  for  $\text{LiB}^-$ ,  $\text{LiAl}^-$ ;  $^2\Pi_i$  for  $\text{LiO}$ ,  $\text{LiF}^+$ ,  $\text{LiS}$ , and  $\text{LiCl}^+$ ;  $^3\Pi_r$  for  $\text{LiB}$ ,  $\text{LiC}^+$ , and  $\text{LiSi}^+$ ;  $^3\Sigma^-$  for  $\text{LiN}$ ,  $\text{LiO}^+$ ,  $\text{LiSi}^-$ ,  $\text{LiP}$ , and  $\text{LiS}^+$ ;  $^4\Sigma^-$  for  $\text{LiC}$ ,  $\text{LiN}^+$ ,  $\text{LiN}^-$ ,  $\text{LiSi}$ ,  $\text{LiP}^+$ , and  $\text{LiP}^-$ ; and  $^5\Sigma^-$  for  $\text{LiC}^-$ .

## I. INTRODUCTION

While alkali metals and hydrogen atoms have only one valence electron, the electronic structures of hydrides and alkali metal compounds often are very different. The multiplicities of the  $\text{XH}$  ground electronic states are usually lower by 1 than the multiplicities of the corresponding atoms  $X$  except when  $X=\text{Be}$  or  $\text{Mg}$ , in which case, the  $X\text{-H}$  bonds are formed by coupling one unpaired electron of  $X$  with the  $\text{H}$  atom electron. However, the spin multiplicities of diatomic  $\text{XLi}$  molecules are sometimes higher by 1 than the  $X$  multiplicities<sup>2,3</sup> [e.g.,  $\text{B}(^2P)$  and  $\text{LiB}(^3\Pi_r)$ ,  $\text{C}(^3P)$ , and  $\text{LiC}(^4\Sigma^-)$ ]. While all the  $\text{HX}$ ,  $\text{HX}^+$ , and  $\text{HX}^-$  species have been studied very well experimentally and theoretically, data for  $\text{LiX}$ ,  $\text{LiX}^+$ , and  $\text{LiX}^-$  species remain sparse.

Here we present a systematic study of the ground electronic states, structures, and stabilities of the diatomic  $\text{LiX}$ ,  $\text{LiX}^+$ , and  $\text{LiX}^-$  ( $X=\text{Li-F}$  and  $\text{Na-Cl}$ ) species and analyze differences in the ground states of the  $\text{XH}$  and  $\text{XLi}$  species.

## II. COMPUTATIONAL DETAILS

The bond lengths of  $\text{LiX}$ ,  $\text{LiX}^+$ , and  $\text{LiX}^-$  ( $X=\text{Li-F}$ ,  $\text{Na-Cl}$ ) were optimized by employing analytical gradients<sup>4</sup> using the Gaussian 92 program (see below) with polarized split-valence basis sets  $\{6\text{-}31+\text{G}^*$  and  $6\text{-}311+\text{G}^*\}$  (Refs. 5–7) at self-consistent field (SCF) and correlated second-order Møller–Plesset (MP2) (full) levels [unrestricted self-consistent field (USCF)] and [unrestricted second-order Møller–Plesset (UMP2) (full)] for open shell systems. Our results are summarized in Table I together with the available experimental data. Harmonic fundamental vibrational frequencies were calculated analytically at the

MP2(full)/6-311+G\* level and are also presented in Table I with the corresponding experimental data.

The MP2 (full)/6-31+G\* equilibrium geometries were used to evaluate electron correlation corrections in the frozen-core approximation by full fourth order<sup>8</sup> Møller–Plesset perturbation theory and by the (U)Q-CISD(T) method<sup>9</sup> using the 6-31+G\* basis sets for  $\text{Li-F}$  and  $\text{Na-Cl}$ . These same MP2(full)/6-311+G\* geometries were used for the MP4 and QCISD(T) calculations with the 6-311+G(2df) basis sets. The unrestricted Hartree–Fock (UHF) wave functions for open shell systems were projected to pure spectroscopic states for which the corresponding results are denoted PUHF, PMP2, PMP3, and PMP4.<sup>12</sup> Tables II and III summarize our calculated first ionization potentials (I.P.s) and electron affinities (E.A.s) for the first row ( $\text{Li-F}$ ) and second row ( $\text{Na-Cl}$ ) atoms with 6-311+G(2df) basis sets at different correlation levels, as well as the available experimental data.<sup>13,14</sup> Our computed dissociation energies, ionization potentials, and electron affinities for the  $\text{LiX}$  diatomics are given in Tables IV, V, and VI, respectively. The relative energies of the low-lying excited states of the  $\text{LiX}$ ,  $\text{LiX}^+$ , and  $\text{LiX}^-$  species are represented in Figs. 1–6.

At the correlated QCISD(T)/6-311+G(2df) level, the calculated atomic I.P.s are close experimental values, but the average deviation is 0.23 eV and the largest discrepancy is 0.46 eV for O. The calculated atomic E.A.s at the QCISD(T)/6-311+G(2df) level were found with average and maximal errors of 0.20 and 0.45 eV for N. However, it is well known how difficult it is to calculate E.A.s of atoms with high accuracy (see, e.g., Refs. 15–19). All calculations were carried out with the Gaussian 92 program.<sup>20</sup>

TABLE I. Calculated and experimental bond length (in Ångstroms) and frequencies (cm<sup>-1</sup>) of LiX, LiX<sup>+</sup>, and LiX<sup>-</sup> species.

Species state		MP2(full)/ 6-311+G* R(Li-X)	MP2(full)/ 6-311+G* (S <sup>2</sup> )	Expt. R(LiX)	MP2(full)/ 6-311+G* ω <sub>e</sub>	Expt. ω <sub>e</sub>
Li <sub>2</sub> <sup>+</sup>	( <sup>2</sup> Σ <sub>g</sub> <sup>+</sup> , 1σ <sub>g</sub> <sup>2</sup> )	3.139	(0.750)	3.12 <sup>a</sup>	259	262.2 ± 1.5 <sup>a</sup>
Li <sub>2</sub>	( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> , 1σ <sub>g</sub> <sup>2</sup> )	2.737	(0.0)	2.672 <sup>b</sup>	342	351.43 <sup>b</sup>
Li <sub>2</sub> <sup>-</sup>	( <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> , 1σ <sub>u</sub> <sup>2</sup> 1σ <sub>u</sub> <sup>1</sup> )	3.176	(1.304)		212	
LiBe <sup>+</sup>	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> )	2.629	(0.0)		320	
LiBe	( <sup>2</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 1π <sup>1</sup> )	2.196	(0.865)		512	
LiBe <sup>-</sup>	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> )	2.545	(0.875)	2.59 <sup>c</sup>	354	295 <sup>c</sup>
	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> )	2.951	(0.0)		196	
	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 1π <sup>2</sup> )	2.216	(2.363)		508	
	( <sup>3</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>1</sup> )	2.533	(2.278)		391	
LiB <sup>+</sup>	( <sup>2</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 1π <sup>1</sup> )	2.567	(0.846)		289	
LiB	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> )	2.459	(0.760)		352	
LiB <sup>-</sup>	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> )	2.403	(0.0)		446	
	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 1π <sup>2</sup> )	1.936	(2.056)		783	
	( <sup>3</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>1</sup> )	2.130	(2.007)		562	
	( <sup>4</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>2</sup> )	2.138	(3.840)		546	
	( <sup>2</sup> Π <sub>i</sub> , 1σ <sup>2</sup> 1π <sup>3</sup> )	1.954	(1.778)		746	
	( <sup>2</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>1</sup> )	2.266	(1.729)		434	
	( <sup>4</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>3</sup> σ <sup>1</sup> )	2.232	(3.757)		460	
LiC <sup>+</sup>	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> )	2.296	(0.0)		414	
	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 1π <sup>2</sup> )	Diss.				
	( <sup>3</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>1</sup> )	2.298	(2.007)		331	
LiC	( <sup>2</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>1</sup> )	2.047	(0.793)		847	
	( <sup>2</sup> Π <sub>i</sub> , 1σ <sup>2</sup> 1π <sup>3</sup> )	1.771	(0.787)			
	( <sup>4</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>2</sup> )	1.884	(3.755)		703	
	( <sup>4</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>3</sup> σ <sup>1</sup> )	Diss.				
LiC <sup>-</sup>	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>2</sup> )	1.988	(2.997)		556	
	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> )	1.757	(0.0)		700	
	( <sup>3</sup> Π <sub>i</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>3</sup> )	1.896	(2.011)		682	
	( <sup>3</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>3</sup> σ <sup>1</sup> )	2.129	(2.991)		515	
	( <sup>5</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>2</sup> 3σ <sup>1</sup> )	1.972	(6.006)		575	
LiN <sup>+</sup>	( <sup>2</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>1</sup> )	2.173	(0.755)		393	
	( <sup>2</sup> Π <sub>i</sub> , 1σ <sup>2</sup> 1π <sup>3</sup> )	Diss.				
	( <sup>4</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>2</sup> )	2.243	(3.757)		267	
LiN	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>2</sup> )	1.874	(2.025)		681	
	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> )	1.640	(0.0)		1099	
	( <sup>3</sup> Π <sub>i</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>3</sup> )	1.728	(2.054)		787	
	( <sup>3</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>3</sup> σ <sup>1</sup> )	2.308	(2.005)			
	( <sup>5</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>2</sup> 3σ <sup>1</sup> )	Diss.				
LiN <sup>-</sup>	( <sup>2</sup> Π <sub>i</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>3</sup> )	1.817	(1.815)		676	
	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> 2σ <sup>1</sup> )	1.665	(2.075)		811	
	( <sup>4</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>2</sup> 3σ <sup>1</sup> )	1.932	(3.770)		593	
	( <sup>4</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>3</sup> 3σ <sup>1</sup> 4σ <sup>1</sup> )	2.247	(3.755)		302	
LiO <sup>+</sup>	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>2</sup> )	2.106	(2.009)		355	
	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> )	Diss.				
	( <sup>3</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>3</sup> )	2.410	(2.007)		123	
LiO	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> 2σ <sup>1</sup> )	1.612	(0.761)		850	
	( <sup>2</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>3</sup> )	1.710	(0.758)	1.688 <sup>d</sup>	801	813.48 ± 0.26 <sup>d</sup>
LiO <sup>-</sup>	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>4</sup> )	1.688	(0.0)		751	
	( <sup>3</sup> Π <sub>i</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>3</sup> 3σ <sup>1</sup> )	1.768	(2.007)		690	
	( <sup>3</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>4</sup> 3σ <sup>1</sup> )	1.682	(2.009)		699	
LiF <sup>+</sup>	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> 2σ <sup>1</sup> )	Diss.				
	( <sup>2</sup> Π <sub>i</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>3</sup> )	2.074	(0.753)		293	
LiF	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>4</sup> )	1.595	(0.0)	1.564 <sup>b</sup>	886	910.34 <sup>b</sup>
LiF <sup>-</sup>	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>4</sup> 3σ <sup>1</sup> )	1.646	(0.750)		767	
LiNa <sup>+</sup>	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>1</sup> )	3.410	(0.750)		190	
LiNa	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> )	2.941	(0.0)	2.815 <sup>b</sup>	254	256.8 <sup>b</sup>
LiNa <sup>-</sup>	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> )	3.411	(1.231)		153	
LiMg <sup>+</sup>	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> )	2.935	(0.0)		261	
LiMg	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> )	3.245	(0.858)		121	
	( <sup>2</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 1π <sup>1</sup> )	2.588	(1.062)		398	
LiMg <sup>-</sup>	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> )	3.519	(0.0)		124	
	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 1π <sup>2</sup> )	2.590	(2.401)		345	
	( <sup>3</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 3σ <sup>1</sup> )	3.139	(2.036)		199	
	( <sup>3</sup> Π <sub>r</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>1</sup> )	3.077	(2.167)		218	
LiAl <sup>+</sup>	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> )	3.005	(0.775)		242	

TABLE I. (Continued.)

Species state	MP2(full)/ 6-311+G* R(Li-X)	MP2(full)/ 6-311+G* (S <sup>2</sup> )	Expt. R(LiX)	MP2(full)/ 6-311+G* ω <sub>e</sub>	Expt. ω <sub>e</sub>
LiAl	( <sup>2</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 1π <sup>1</sup> )	2.821	(0.822)	205	
	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> )	2.869	(0.0)	322	
	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 1π <sup>2</sup> )	2.340	(2.014)	625	
LiAl <sup>-</sup>	( <sup>3</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>1</sup> )	2.623	(2.018)	351	
	( <sup>2</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 1π <sup>3</sup> )	2.382	(1.580)	504	
	( <sup>2</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>1</sup> )	2.832	(0.762)	268	
LiSi <sup>+</sup>	( <sup>4</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>2</sup> )	2.438	(3.799)	461	
	( <sup>4</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>1</sup> 3σ <sup>1</sup> )	2.773	(3.761)	283	
	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> )	2.720	(0.0)	360	
LiSi	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 1π <sup>2</sup> )	Diss.			
	( <sup>3</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>1</sup> )	2.740	(2.009)	283	
	( <sup>4</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>2</sup> )	2.355	(3.752)	472	
LiSi <sup>-</sup>	( <sup>2</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 1π <sup>3</sup> )	2.220	(0.787)	599	
	( <sup>2</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>1</sup> )	2.545	(0.773)	464	
	( <sup>4</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>1</sup> 3σ <sup>1</sup> )	Diss.			
LiP <sup>+</sup>	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>2</sup> )	2.502	(2.030)	395	
	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> )	2.155	(0.0)	670	
	( <sup>3</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>1</sup> 3σ <sup>1</sup> )	2.615	(2.008)	366	
LiP	( <sup>3</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>3</sup> )	2.344	(2.082)	476	
	( <sup>5</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>2</sup> 3σ <sup>1</sup> )	2.505	(6.001)	359	
	( <sup>2</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>1</sup> )	2.555	(0.758)	372	
LiP <sup>-</sup>	( <sup>2</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 1π <sup>3</sup> )	Diss.			
	( <sup>4</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>2</sup> )	2.602	(3.751)	278	
	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> )	2.072	(0.0)	544	
LiS <sup>+</sup>	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>2</sup> )	2.331	(2.014)	495	
	( <sup>3</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>1</sup> 3σ <sup>1</sup> )	2.694	(2.007)	313	
	( <sup>3</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>3</sup> )	2.189	(2.012)	541	
LiS	( <sup>5</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>2</sup> 3σ <sup>1</sup> )	Diss.			
	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> 2σ <sup>1</sup> )	2.065	(1.071)	740	
	( <sup>2</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>3</sup> )	2.331	(1.704)	479	
LiS <sup>-</sup>	( <sup>4</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>2</sup> 3σ <sup>1</sup> )	2.412	(3.761)	423	
	( <sup>4</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>1</sup> 3σ <sup>1</sup> 4σ <sup>1</sup> )	No convergency			
	( <sup>3</sup> Σ <sup>-</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>2</sup> )	2.447	(2.010)	367	
LiS <sup>-</sup>	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> )	Diss.			
	( <sup>3</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>3</sup> )	2.578	(2.007)	227	
	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> 2σ <sup>1</sup> )	2.063	(0.759)	597	
LiS <sup>-</sup>	( <sup>2</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>3</sup> )	2.147	(0.757)	597	
	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>4</sup> )	2.058	(0.0)	660	
	( <sup>3</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>4</sup> 2π <sup>1</sup> )	2.237	(2.006)	491	
LiCl <sup>+</sup>	( <sup>3</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>1</sup> 1π <sup>4</sup> 3σ <sup>1</sup> )	2.204	(2.009)	438	
	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 1π <sup>4</sup> 2σ <sup>1</sup> )	2.727	(0.756)	107	
	( <sup>2</sup> Π <sub>u</sub> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>3</sup> )	2.354	(0.756)	352	
LiCl	( <sup>1</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>4</sup> )	2.016	(0.0)	664	643.3 <sup>b</sup>
	( <sup>2</sup> Σ <sup>+</sup> , 1σ <sup>2</sup> 2σ <sup>2</sup> 1π <sup>4</sup> 3σ <sup>1</sup> )	2.104	(0.750)	541	500 <sup>c</sup>

<sup>a</sup>Data from Ref. 21.<sup>b</sup>Data from Ref. 1.<sup>c</sup>Data from Ref. 24.<sup>d</sup>Data from Ref. 40(e).<sup>e</sup>Data from Ref. 42(b).

### III. RESULTS AND DISCUSSIONS

#### A. Li<sub>2</sub>, Li<sub>2</sub><sup>+</sup>, Li<sub>2</sub><sup>-</sup>, LiNa, LiNa<sup>+</sup>, and LiNa<sup>-</sup>

All of these species have been studied theoretically and experimentally.<sup>1</sup> Li<sub>2</sub><sup>+</sup> and LiNa<sup>+</sup> have <sup>2</sup>Σ<sub>g</sub><sup>+</sup>(1σ<sub>g</sub><sup>1</sup>) and <sup>2</sup>Σ<sup>+</sup>(1σ<sup>1</sup>) ground electronic states with only one valence electron and therefore have no valence correlation energy. Molecular constants for the ground X <sup>2</sup>Σ<sub>g</sub><sup>+</sup> state of Li<sub>2</sub><sup>+</sup> have been deduced from the molecular constants of n=8–11 members of the Rydberg ndπ<sup>1</sup>Π<sub>g</sub><sup>-</sup> series of neutral Li<sub>2</sub>

by Bernheim, Gold, and Tipton.<sup>21</sup> Our bond length, vibrational frequency, and dissociation energy agree well with these data (see Tables I and IV) and with the previous best *ab initio* results.<sup>22(a)–22(d)</sup> For the LiNa<sup>+</sup> cation, only the dissociation energy (22.9 kcal/mol) is experimentally known<sup>1</sup> and is close to our 20.3 kcal/mol value. Our bond length and frequency agree well with the pseudopotential calculations of Preuss *et al.*<sup>23(a),23(b)</sup>

The Li<sub>2</sub> and LiNa neutral molecules have been well

TABLE II. Calculated and experimental I.P.s (in electron volts) of Li-F and Na-Cl atoms.

Atom	6-311+G PMP4	(2df) QCISD(T)	Expt. <sup>a</sup>
Li	5.34 <sup>b</sup>		5.39
Be	9.17	9.28	9.32
B	8.26	8.19	8.30
C	11.22	11.17	11.26
N	14.52	14.47	14.53
O	13.38	13.37	13.62
F	17.22	17.21	17.42
Na	4.94 <sup>b</sup>		5.14
Mg	7.46	7.52	7.65
Al	5.94	5.93	5.99
Si	8.09	8.08	8.15
P	10.45	10.43	10.49
S	10.06	10.06	10.36
Cl	12.71	12.70	12.97

<sup>a</sup>Data from Ref. 13.<sup>b</sup>Data at PUHF.

studied and references may be found in Huber and Herzberg.<sup>1</sup> These molecules have only two valence electrons and the ground electronic states are  $^1\Sigma_g^+$  (Li<sub>2</sub>) and  $^1\Sigma^+$  (LiNa). Our largest discrepancies in the bond lengths of both Li<sub>2</sub> and LiNa probably arise because of the flat potential energy curves and the importance of electron correlation. For example, our calculated  $R(\text{Li-Li})$  in Li<sub>2</sub> decreases from 2.784 Å at the SCF/6-311+G\* level to 2.737 Å at the MP2/6-311+G\* level, then to 2.723 Å at the MP3/6-311+G\* level, and to 2.710 Å at the MP4/6-311+G\* level. The convergence of our calculated bond lengths to the experimental value 2.673 Å is rather slow. Similar results have been found by Scuseria, Hamiton, and Schaefer.<sup>22(c)</sup> Large basis sets and a high level of correlation are needed to reach experimental accuracy {see high level *ab initio* calculations for Li<sub>2</sub> [Refs. 22(f) and 22(g)] and LiNa [Ref. 23(c)]}.

Experimental molecular constants for Li<sub>2</sub><sup>-</sup> and LiNa<sup>-</sup> are not known; however, several high quality *ab initio* calculations have been carried out for Li<sub>2</sub><sup>-</sup> [Refs. 22(c) and

TABLE III. Calculated and experimental E.A.s (in electron volts) of Li-F and Na-Cl atoms.

Atom	6-311+G PMP4	(2df) QCISD(T)	Expt. <sup>a</sup>
Li	0.54	0.61	0.62
B	0.17	0.14	0.28
C	1.18	1.14	1.26
N	-0.47	-0.48	-0.07
O	1.18	1.13	1.46
F	3.22	3.11	3.40
Na	0.49	0.54	0.55
Al	0.29	0.28	0.44
Si	1.28	1.26	1.39
P	0.41	0.40	0.75
S	1.77	1.76	2.08
Cl	3.36	3.36	3.62

<sup>a</sup>Data from Ref. 14.

22(g)] and for LiNa<sup>-</sup>.<sup>23(d)</sup> The ground electronic states are  $^2\Sigma_u^+$  (Li<sub>2</sub><sup>-</sup>) and  $^2\Sigma^+$  (LiNa<sup>-</sup>) and our dissociation energies and harmonic vibrational frequencies for both of these anions agree well with the experimental dissociation energies<sup>1</sup> and with the previous calculations. However, as in the case of the neutrals (Li<sub>2</sub> and LiNa), our bond lengths for the anions are ~0.1 Å, too long with respect to the best calculations.

Our calculated I.P.s for Li<sub>2</sub> (5.09 eV) and for LiNa (4.87 eV) are less than the I.P.s of the atoms Li (5.39 eV) and Na (5.14 eV). Likewise, our E.A.s for Li<sub>2</sub> (0.41 eV) and LiNa (0.44 eV) are less than the E.A.s of Li (0.62 eV) and Na (0.55 eV). Our adiabatic I.P. and E.A. of Li<sub>2</sub> agree well with the best *ab initio* calculations 5.16 [Ref. 22(c)] and 0.43 eV,<sup>22(c),22(g)</sup> respectively.

## B. LiBe, LiBe<sup>+</sup>, LiBe<sup>-</sup>, LiMg, LiMg<sup>+</sup>, and LiMg<sup>-</sup>

The neutral LiBe and LiMg molecules have recently been studied experimentally.<sup>24,25</sup> For LiBe, the  $X^2\Sigma^+ \rightarrow C^2\Pi$  electronic transition with an origin at 19 203 cm<sup>-1</sup> has been observed by laser-induced fluorescence, and vibrational analysis yields  $G'_{1/2} = 295$  cm<sup>-1</sup> and  $G''_{1/2} = 188$  cm<sup>-1</sup>. A preliminary rotational analysis of the 0-0 band gives  $r''_0 = 2.59$  Å and  $r'_0 = 3.04$  Å.<sup>24</sup> Neutral LiMg and charged LiMg<sup>+</sup> have been identified in mass-spectrometric experiments and the neutral's dissociation energy  $D_0(\text{MgLi}) = 15.2 \pm 2.0$  kcal/mol and I.P.(MgLi) = 5.96 ± 0.10 eV have been determined.<sup>25(a)</sup> Laser-induced chemiluminescence of the LiMg excimer<sup>25(b)</sup> provided potential parameters for the  $C^2\Pi$  (e.g.,  $R_e = 3.882$  Å) and  $D^2\Sigma^+$  ( $R_e = 4.536$  Å) states of LiMg. The electronic structures of LiBe, LiBe<sup>+</sup>, LiBe<sup>-</sup>, LiMg, LiMg<sup>+</sup>, and LiMg<sup>-</sup> have been theoretically investigated.<sup>26</sup>

The expected single occupancy of the  $\sigma^*$  molecular orbital (MO) of LiBe and LiMg lead to  $^2\Sigma^+$  ground states (with  $1\sigma^2 2\sigma^1$  valence configurations). The first excited  $^2\Pi_r$  state ( $1\sigma^2 1\pi^1$ ) correlates with the Li(<sup>2</sup>P) + Be(Mg)(<sup>1</sup>S) dissociation limit. For charged LiBe<sup>+</sup> and LiMg<sup>+</sup> species, a ground  $^1\Sigma^+$  state (with  $1\sigma^2$  configurations) is expected. For LiBe<sup>-</sup> and LiMg<sup>-</sup>, the ground electronic state may be  $^1\Sigma^+(1\sigma^2 2\sigma^2)$  or  $^3\Pi_r(1\sigma^2 2\sigma^1 \pi^1)$  as in the isoelectronic LiB molecule. For neutral LiBe and LiMg, the above two electronic states ( $^2\Sigma^+$  and  $^2\Pi$ ) were investigated, and for the negative ions LiBe<sup>-</sup> and LiMg<sup>-</sup>, three low-lying  $^1\Sigma^+(1\sigma^2 2\sigma^2)$ ,  $^3\Sigma^+(1\sigma^2 1\pi^2)$ , and  $^3\Pi_r(1\sigma^2 2\sigma^1 \pi^1)$  were studied; for the positive ions LiBe<sup>+</sup> and LiMg<sup>+</sup>, only the  $^1\Sigma^+$  state has been studied.

In contrast with earlier SCF<sup>26(a),26(c)</sup> and multireference data configuration interaction (MRDCI)<sup>26(d)</sup> results, but in accordance with higher level *ab initio* [complete active space self-consistent field multireference configuration interaction (CASSCF/MRC)]<sup>24,26(h)</sup> and full CI,<sup>26(g)</sup> calculations, we have found attractive potential energy curves for the  $^2\Sigma^+$  configuration of LiBe at the UHF/6-31+G\*, UMP2(full)/6-31+G\*, and at MP2(full)/6-311+G\* levels. Our best calculated equilibrium bond lengths 2.545 Å for LiBe ( $^2\Sigma^+$ ) and 3.245 Å for LiMg [ $^2\Sigma^+$ , both at MP2(full)/6-311+G\*] are in a reasonable

TABLE IV. Calculated and experimental dissociation energies (in kcal/mol) of the LiX, LiX<sup>+</sup>, and LiX<sup>-</sup> species.

Reaction	PMP4	QCISD(T)	Expt.
	6-311+G(2df)	6-311+G(2df)	
Li <sub>2</sub> <sup>+</sup> ( <sup>2</sup> Σ <sub>g</sub> <sup>+</sup> )—Li+Li <sup>+</sup>	29.4 <sup>a</sup>		33.2, <sup>b</sup> 29.93 <sup>c</sup>
Li <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )—Li+Li	22.1	23.6	24.1 <sup>b</sup>
Li <sub>2</sub> <sup>-</sup> ( <sup>2</sup> Σ <sub>u</sub> <sup>-</sup> )—Li+Li <sup>-</sup>	17.2	19.0	20.2 <sup>b</sup>
LiBe <sup>+</sup> ( <sup>1</sup> Σ <sup>+</sup> )—Be+Li <sup>+</sup>	13.6	13.2	
LiBe( <sup>2</sup> Σ <sup>+</sup> )—Li+Be	6.4	6.1	
LiBe <sup>-</sup> ( <sup>1</sup> Σ <sup>+</sup> )—Be+Li <sup>-</sup>	7.7	7.4	
LiB <sup>+</sup> ( <sup>2</sup> Σ <sup>+</sup> )—B+Li <sup>+</sup>	18.2	18.2	
LiB( <sup>3</sup> Π <sub>g</sub> )—B+Li	27.7	27.2	
LiB <sup>-</sup> ( <sup>2</sup> Π <sub>g</sub> )—B+Li	37.0	37.2	
LiC <sup>+</sup> ( <sup>3</sup> Π <sub>g</sub> )—C+Li <sup>+</sup>	10.2	9.0	
LiC( <sup>4</sup> Σ <sup>-</sup> )—C+Li	60.1	59.6	
LiC <sup>-</sup> ( <sup>3</sup> Σ <sup>-</sup> )—C <sup>-</sup> +Li	44.4	44.7	
LiN <sup>+</sup> ( <sup>4</sup> Σ <sup>-</sup> )—N+Li <sup>+</sup>	4.7	4.8	
LiN( <sup>3</sup> Σ <sup>-</sup> )—N+Li	34.8	34.4	
LiN <sup>-</sup> ( <sup>4</sup> Σ <sup>-</sup> )—N+Li <sup>-</sup>	32.9	31.4	
LiO <sup>+</sup> ( <sup>3</sup> Σ <sup>-</sup> )—O+Li <sup>+</sup>	11.5	11.5	
LiO( <sup>2</sup> Π <sub>g</sub> )—O+Li	81.0	80.3	80.5 <sup>b</sup>
LiO <sup>-</sup> ( <sup>3</sup> Π <sub>g</sub> )—O <sup>-</sup> +Li	62.9	63.8	
LiF <sup>+</sup> ( <sup>2</sup> Π <sub>g</sub> )—F+Li <sup>+</sup>	6.8	6.8	
LiF( <sup>1</sup> Σ <sup>+</sup> )—F+Li	135.8	134.0	136.3 <sup>b</sup>
LiF <sup>-</sup> ( <sup>2</sup> Σ <sup>-</sup> )—F <sup>-</sup> +Li	69.7	70.5	
LiNa <sup>+</sup> ( <sup>2</sup> Σ <sup>-</sup> )—Na <sup>+</sup> +Li	21.3 <sup>a</sup>		22.9 <sup>b</sup>
LiNa( <sup>1</sup> Σ <sup>+</sup> )—Li+Na	18.4	19.7	20.8 <sup>b</sup>
LiNa <sup>-</sup> ( <sup>2</sup> Σ <sup>+</sup> )—Li <sup>-</sup> +Na	14.4	15.6	
LiMg <sup>+</sup> ( <sup>1</sup> Σ <sup>+</sup> )—Mg+Li <sup>+</sup>	18.5	18.5	
LiMg( <sup>2</sup> Σ <sup>+</sup> )—Mg+Li	3.9	4.1	
LiMg <sup>-</sup> ( <sup>1</sup> Σ <sup>+</sup> )—Mg+Li <sup>-</sup>	7.5	7.2	
LiAl <sup>+</sup> ( <sup>2</sup> Σ <sup>+</sup> )—Al+Li <sup>+</sup>	27.1	27.0	
LiAl( <sup>1</sup> Σ <sup>+</sup> )—Al+Li	21.9	23.3	
LiAl <sup>-</sup> ( <sup>2</sup> Π <sub>g</sub> )—Al <sup>-</sup> +Li	29.1	31.2	
LiSi <sup>+</sup> ( <sup>3</sup> Π <sub>g</sub> )—Si+Li <sup>+</sup>	16.8	16.8	
LiSi( <sup>4</sup> Σ <sup>-</sup> )—Si+Li	42.5	42.2	35.5 <sup>d</sup>
LiSi <sup>-</sup> ( <sup>3</sup> Σ <sup>-</sup> )—Si <sup>-</sup> +Li	28.0	28.2	
LiP <sup>+</sup> ( <sup>4</sup> Σ <sup>-</sup> )—P+Li <sup>+</sup>	9.5	9.6	
LiP( <sup>3</sup> Σ <sup>+</sup> )—P+Li	38.2	38.3	58.3±5.5 <sup>e</sup>
LiP <sup>-</sup> ( <sup>4</sup> Σ <sup>-</sup> )—P <sup>-</sup> +Li	41.7	42.3	
LiS <sup>+</sup> ( <sup>3</sup> Σ <sup>-</sup> )—S+Li <sup>+</sup>	19.2	19.2	
LiS( <sup>2</sup> Π <sub>g</sub> )—S+Li	71.3	71.0	73.8±1.8 <sup>f</sup> 77.7±8.8 <sup>g</sup>
LiS <sup>-</sup> ( <sup>1</sup> Σ <sup>+</sup> )—S <sup>-</sup> +Li	56.5	56.3	
LiCl <sup>+</sup> ( <sup>2</sup> Π <sub>g</sub> )—Cl+Li <sup>+</sup>	12.5	12.5	
LiCl( <sup>1</sup> Σ <sup>+</sup> )—Cl+Li	109.8	109.7	113.0 <sup>b</sup>
LiCl <sup>-</sup> ( <sup>2</sup> Σ <sup>+</sup> )—Cl <sup>-</sup> +Li	45.3	45.4	40.4 <sup>h</sup>

<sup>a</sup>Data at PUHF.<sup>b</sup>Data from Ref. 1.<sup>c</sup>Data from Ref. 21.<sup>d</sup>Data from Ref. 32.<sup>e</sup>Data from Ref. 36.<sup>f</sup>Data from Ref. 40(f).<sup>g</sup>Data from Ref. 40(g).<sup>h</sup>Data from Ref. 42(b).

agreement with the experimental data for LiBe [ $R(\text{LiBe}) = 2.59 \text{ \AA}$ ] and with the best *ab initio* values 2.619 (Ref. 24) and 2.607  $\text{\AA}$  [Ref. 26(h)] for LiBe and 3.110  $\text{\AA}$  [Ref. 26(h)] for LiMg. Our harmonic vibrational frequencies 354  $\text{cm}^{-1}$  (LiBe) and 121  $\text{cm}^{-1}$  (LiMg), compare well with the experimental  $G_{1/2} = 295 \text{ cm}^{-1}$  for LiBe and with the previous high level *ab initio* frequencies 282 (Ref. 24) and 300  $\text{cm}^{-1}$  [Ref. 26(g)] for LiBe and 183  $\text{cm}^{-1}$  [Ref. 26(g)] for LiMg. Our dissociation energies  $D_e(\text{LiBe}) = 6.1 \text{ kcal/mol}$  and  $D_e(\text{LiMg}) = 4.1 \text{ kcal/mol}$  [both at

QCISD(T)/6-311+G(2df)//MP2 (full)/6-311+G\*] do not differ much from the best theoretical values 7.1 (Ref. 24) and 6.7 kcal/mol [Ref. 26(g)] for LiBe as well as 4.6 kcal/mol [Ref. 26(g)] for LiMg.

The LiBe<sup>+</sup> and LiMg<sup>+</sup> cations in their ground state <sup>1</sup>Σ<sup>+</sup> ( $1\sigma^2$ ) are remarkably stable species. Our calculated dissociation energies 13.2 (LiBe<sup>+</sup>) and 18.5 kcal/mol [LiMg<sup>+</sup>, both at QCISD(T)/6-311+G(2df)//MP2(full)/6-311+G\*] are larger than those for the neutral counterparts. This contradicts mass spectroscopic

TABLE V. Calculated and experimental adiabatic I.P.s (in electron volts) of the LiX species.

Reaction	PMP4	QCISD(T)	Expt.
	6-311+G(2df)	6-311+G(2df)	
Li <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	5.02	5.09	5.00, <sup>a</sup> 5.14 <sup>b</sup>
LiBe( <sup>2</sup> Σ <sup>+</sup> )	5.03	5.03	
LiB( <sup>3</sup> Π <sub>g</sub> )	5.75	5.73	
LiC( <sup>4</sup> Σ <sup>-</sup> )	7.50	7.48	
LiN( <sup>3</sup> Σ <sup>-</sup> )	6.63	6.62	
LiO( <sup>2</sup> Π <sub>g</sub> )	8.35	8.32	8.45±0.2 <sup>c</sup>
LiF( <sup>1</sup> Σ <sup>+</sup> )	10.93	10.86	
LiNa( <sup>1</sup> Σ <sup>+</sup> )	4.82	4.87	
LiMg( <sup>2</sup> Σ <sup>+</sup> )	4.71	4.71	5.96±0.1 <sup>d</sup>
LiAl( <sup>1</sup> Σ <sup>+</sup> )	5.11	5.18	
LiSi( <sup>4</sup> Σ <sup>-</sup> )	6.45	6.44	
LiP( <sup>3</sup> Σ <sup>-</sup> )	6.58	6.59	
LiS( <sup>2</sup> Π <sub>g</sub> )	7.60	7.59	
LiCl( <sup>1</sup> Σ <sup>+</sup> )	9.56	9.55	

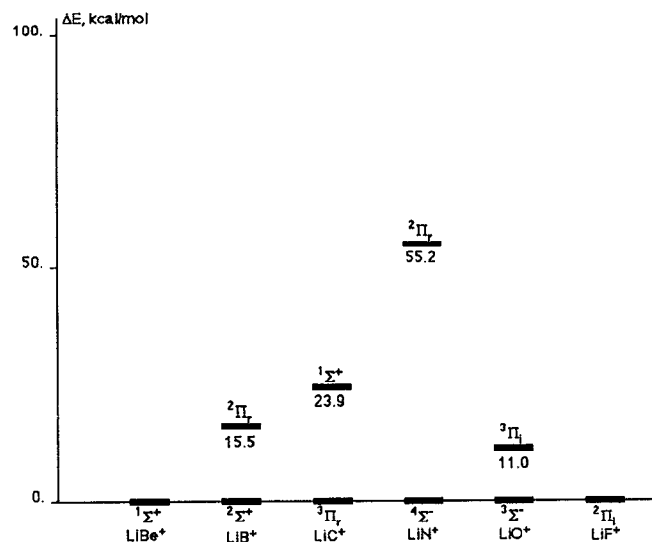
<sup>a</sup>Data from Ref. 1.<sup>c</sup>Data from Ref. 40(b).<sup>b</sup>Data from Ref. 21.<sup>d</sup>Data from Ref. 25(a).

measurements on LiMg and LiMg<sup>+</sup> which result in the claim that the neutral molecule is more stable than the cation.<sup>25(a)</sup> The first adiabatic I.P.s for LiBe and LiMg are 5.03 and 4.71 eV [at the QCISD(T)/6-311+G(2df)//MP2(full)/6-311+G\*], respectively, which are lower than the I.P. of the Li atom (I.P.=5.39 eV). Our LiMg I.P. is more than 1 eV lower than the I.P.(LiMg)=5.96±0.1 eV found by Wu and Ihle.<sup>25(a)</sup>

The anions LiBe<sup>-</sup> and LiMg<sup>-</sup> are valence isoelectronic with the LiB molecule, so a high-spin <sup>3</sup>Π electronic ground state might be expected for these species. However, both anions are found to have low-spin <sup>1</sup>Σ<sup>+</sup>(1σ<sup>2</sup>2σ<sup>2</sup>) ground electronic states which are stable towards dissociation into Li<sup>-</sup>+Be or into Li<sup>-</sup>+Mg. Electron correlation corrections to these dissociation energies are not important for the neutral species and for the cations, but are very important for the anions. Our calculated dissociation energies are 7.4 kcal/mol for LiBe<sup>-</sup> and 7.2 kcal/mol for

TABLE VI. Calculated and experimental adiabatic E.A.s (in electron volts) of the LiX species.

Species	PMP4	QCISD(T)
	6-311+G(2df)	6-311+G(2df)
Li <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	0.32	0.41
LiBe( <sup>2</sup> Σ <sup>+</sup> )	0.59	0.67
LiB( <sup>3</sup> Π <sub>g</sub> )	0.58	0.58
LiC( <sup>4</sup> Σ <sup>-</sup> )	0.49	0.50
LiN( <sup>3</sup> Σ <sup>-</sup> )	0.46	0.48
LiO( <sup>2</sup> Π <sub>g</sub> )	0.40 <sup>b</sup>	0.42 <sup>b</sup>
LiF( <sup>1</sup> Σ <sup>+</sup> )	0.35	0.36
LiNa( <sup>1</sup> Σ <sup>+</sup> )	0.36	0.44
LiMg( <sup>2</sup> Σ <sup>+</sup> )	0.69	0.75
LiAl( <sup>1</sup> Σ <sup>+</sup> )	0.60	0.62
LiSi( <sup>4</sup> Σ <sup>-</sup> )	0.65	0.65
LiP( <sup>3</sup> Σ <sup>-</sup> )	0.56	0.57
LiS( <sup>2</sup> Π <sub>g</sub> )	1.13	1.12
LiCl( <sup>1</sup> Σ <sup>+</sup> ) <sup>a</sup>	0.57	0.57

<sup>a</sup>Experimental value is 0.593±0.010 eV [Ref. 42(b)].<sup>b</sup>LiO(<sup>3</sup>Π<sub>g</sub>) final state.FIG. 1. Energies of ground and low-lying excited states of LiX<sup>+</sup> species with X ranging across the first row [at the QCISD(T)/6-311+G(2df) level].

LiMg<sup>-</sup>. Both anions are very stable electronically; in fact, the calculated adiabatic E.A.s of LiBe and LiMg are 0.67 and 0.75 eV, respectively [all data at the QCISD(T)/6-311+G(2df) level]. Therefore, LiBe<sup>-</sup> and LiMg<sup>-</sup> are viable species and are good candidates for experimental study.

### C. LiB, LiB<sup>+</sup>, LiB<sup>-</sup>, LiAl, LiAl<sup>+</sup>, and LiAl<sup>-</sup>

Earlier *ab initio* calculations on neutral LiB (Refs. 2, 27–30) have yielded conflicting results. The first *ab initio* study on LiB by Kaufman and Sach at the HF level<sup>27</sup> assumed a <sup>1</sup>Σ<sup>+</sup> ground state and gave a minimum at 2.40 Å. However, the energy was above that of the separated

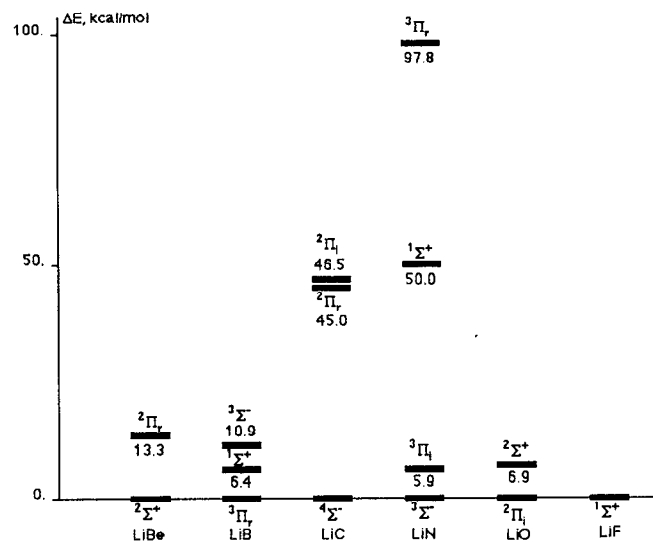


FIG. 2. Energies of ground and low-lying excited states of LiX species with X ranging across the first row [at the QCISD(T)/6-311+G(2df) level].

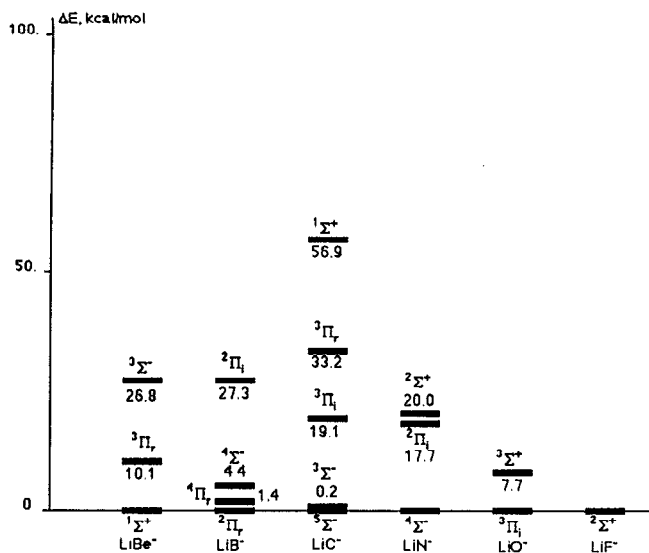


FIG. 3. Energies of ground and low-lying excited states of LiX<sup>-</sup> species with X ranging across the first row [at the QCISD(T)/6-311+G(2df) level].

atoms. Cade and Huo, using a large Slater basis set, also calculated only the  $1\Sigma^+$  state for LiB. Their energy at the minimum at 2.38 Å was slightly lower than that of the separated atoms.<sup>28</sup> Nemukhin *et al.*<sup>2</sup> studied three electronic states of LiB— $1\Sigma^+(1\sigma^22\sigma^2)$ ,  $3\Sigma^+(1\sigma^21\pi^2)$ , and  $3\Pi_g(1\sigma^22\sigma^11\pi^1)$  at the CASSCF level, with double zeta (DZ) basis sets and with the  $1\sigma$ ,  $2\sigma$ ,  $3\sigma$ ,  $4\sigma$ ,  $1\pi$ , and  $2\pi$  orbitals in the active space. They found the  $3\Pi$  state to be the most stable with  $1\Sigma^+$  as the first excited state. Their predicted bond lengths were 2.22 and 2.52 Å and the dissociation energies were 16.2 and 12.6 kcal/mol for the  $3\Pi_g$  and  $1\Sigma^+$  states, respectively. The  $3\Sigma^+$  and  $1\Pi_g$  states were found to be repulsive. Knowles and Murrell repeated

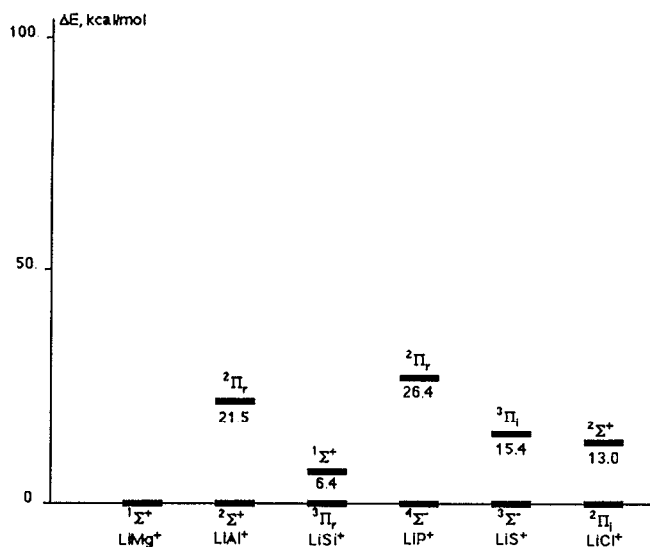


FIG. 4. Energies of ground and low-lying excited states of LiX<sup>+</sup> species with X ranging across the second row [at the QCISD(T)/6-311+G(2df) level].

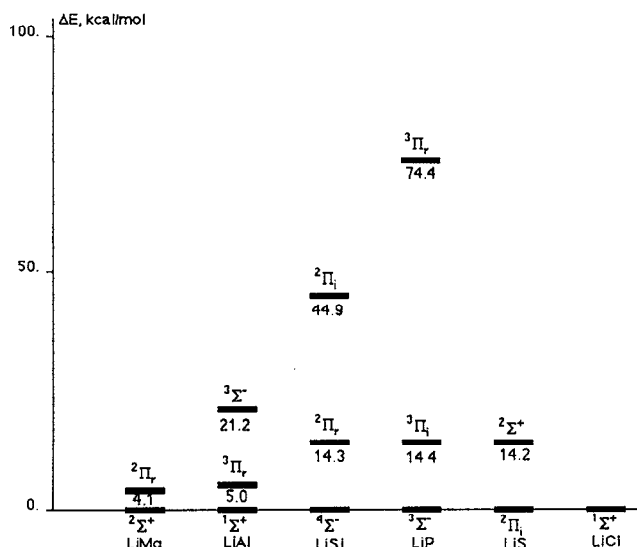


FIG. 5. Energies of ground and low-lying excited states of LiX species with X ranging across the second row [at the QCISD(T)/6-311+G(2df) level].

these calculations with larger basis sets ( $10s7p2d/5s5p2d$ )B+( $10s4p2d/4s4p2d$ )Li and using the MRCI method with CASSCF orbitals as a starting point.<sup>30</sup> They also found a  $3\Pi_g$  ground state for LiB with a minimum at  $R_e=2.142$  Å and a dissociation energy of  $D_e=25.5$  kcal/mol. The first excited  $1\Sigma^+$  state (with  $R_e=2.424$  Å) was found to lie only 6.3 kcal/mol above the ground state. In contrast to the CASSCF calculations,<sup>2</sup> the  $1\Pi_g$  state was found at the MRCI level to be weakly bound having a minimum at 2.219 Å and an energy 20.4 kcal/mol above the ground state. However, the  $3\Sigma^+$  state was also found to be totally repulsive.

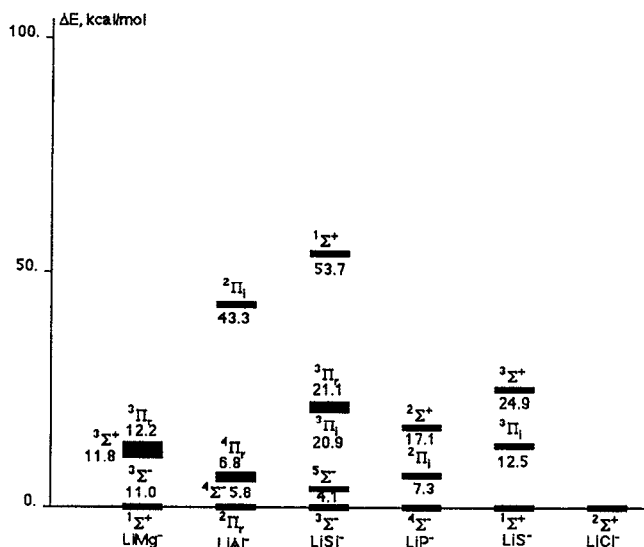


FIG. 6. Energies of ground and low-lying excited states of LiX<sup>-</sup> species with X ranging across the second row [at the QCISD(T)/6-311+G(2df) level].

Nemukhin *et al.*<sup>2</sup> studied the  $^2\Sigma^+$  and  $^2\Pi_r$  states of LiB<sup>+</sup> at the CASSCF level with DZ basis sets. The  $^2\Sigma^+$  ground state was 15.5 kcal/mol lower than the  $^2\Pi_r$  state. The calculated dissociation energy of LiB<sup>+</sup> ( $^2\Sigma^+$ ) into Li<sup>+</sup>+Be is 16.7 kcal/mol and the calculated equilibrium bond length of LiB<sup>+</sup> in this state is 2.575 Å, which is larger than in neutral LiB ( $^3\Pi_r$ ) by more than 0.3 Å (see Table I).

We studied three low-lying states  $^1\Sigma^+$ ,  $^3\Sigma^-$ , and  $^3\Pi_r$  for neutral LiB and LiAl. It already has been found that the coefficients of the SCF configuration in the CI expansions of these states were more than 0.95,<sup>2</sup> therefore, the MPn and QCISD(T) approximations should be adequate. According to our best calculations for LiB,  $^3\Pi$  is the ground state and the  $^1\Sigma^+$  and  $^3\Sigma^-$  states lie 6.4 and 10.9 kcal/mol [at QCISD(T)/6-311+G(2df)] higher, respectively. Our relative energy for the  $^1\Sigma^+$  state (6.4 kcal/mol) is very close to the 6.3 kcal/mol obtained by Knowles and Murrell.<sup>30</sup> However, in contrast to all previous *ab initio* calculations, we found the  $^3\Sigma^-$  state to be bound having a minimum at 1.948 Å [at MP2(full)6-31+G\*] with a dissociation energy of 14.8 kcal/mol [QCISD(T)/6-311+G(2df)]. Combining our results with the data of Knowles and Murrell for the  $^1\Pi_r$  state,<sup>30</sup> we predict the following energy ordering (in kcal/mol) of the low-lying states for LiB:  $^3\Pi_r(0) < ^1\Sigma^+(6.4) < ^3\Sigma^-(10.9) < ^1\Pi_r(20.4)$ . The relative energies for LiB differ from those of the corresponding BH states  $^1\Sigma^+ < ^3\Pi_r < ^1\Pi_r < ^3\Sigma^-$ .<sup>31</sup> Along the  $^1\Sigma^+ - ^3\Pi_r - ^3\Sigma^-$  series, the LiB bond length decreases from 2.424 Å ( $^1\Sigma^+$ ) to 2.219 Å ( $^3\Pi_r$ ) (Ref. 30) and then to 1.948 Å ( $^3\Sigma^-$ ) when one and two electrons, respectively, are transferred from the antibonding  $2\sigma^*$  MO into the bonding  $1\pi$  MO. However, all the calculated states of LiB (as well as for LiAl) are highly ionic. Thus, the NBO charges are approximately Li<sup>+0.85</sup>B<sup>-0.85</sup>. Therefore, more than 95% of the electron density in the  $2\sigma$  and  $1\pi$  MOs is localized on B (or Al), so these MOs are mainly nonbonding. However, because the potential energy curves are very flat for all states of LiB and LiAl, even small changes in the linear combination of atomic orbitals (LCAO)-MO coefficients can lead to significant changes in distance. The dissociation energy for LiB is greatest for the  $^3\Pi_r$  state, where only one electron is transferred from the  $2\sigma$  MO into the  $1\pi$  MO. Our highest level dissociation energy for the LiB ( $^3\Pi_r$ ) ground state into the neutral atoms in their ground states 27.2 kcal/mol [at QCISD(T)/6-311+G(2df)] agrees well with the  $D_e(\text{LiB})=25.5$  kcal/mol of Knowles and Murrell.<sup>30</sup>

The results for LiAl were unexpected. Unlike LiB, which has a high-spin  $^3\Pi$  ground state, LiAl prefers the low-spin  $^1\Sigma^+$  electronic configuration. However, the high-spin  $^3\Pi_r$  state is only 5.1 kcal/mol higher and the  $^3\Sigma^-$  state lies above the  $^1\Sigma^+$  state by 21.2 kcal/mol. Our calculated dissociation energy of LiAl ( $^1\Sigma^+$ ) into the neutral atoms in their ground states is 23.3 kcal/mol at the QCISD(T)/6-311+G(2df) level.

We studied both the  $^2\Sigma^+(1\sigma^22\sigma^1)$  and  $^2\Pi_r(1\sigma^21\pi^1)$  states of LiB<sup>+</sup> and LiAl<sup>+</sup>. The  $^2\Sigma^+$  ground states of LiB<sup>+</sup> and LiAl<sup>+</sup> are bound with dissociation energies of 18.2

kcal/mol (LiB<sup>+</sup>→Li<sup>+</sup>+B) and 23.3 kcal/mol (LiAl<sup>+</sup>→Li<sup>+</sup>+Al). As expected, the removal of an electron from the bonding  $1\pi$  MO of LiB( $^3\Pi_r$ ) increases the bond length in LiB<sup>+</sup>( $^2\Sigma^+$ ) by more than 0.4 Å.

Our calculated first adiabatic I.P.s of LiB and LiAl are 5.73 and 5.18 eV [at the QCISD(T)/6-311+G(2df) level], respectively.

We studied four  $^4\Sigma^-(1\sigma^22\sigma^11\pi^2)$ ,  $^4\Pi_r(1\sigma^22\sigma^11\pi^13\sigma^1)$ ,  $^2\Pi_r(1\sigma^21\pi^3)$ , and  $^2\Pi_r(1\sigma^22\sigma^21\pi^1)$  states of LiB<sup>-</sup> and LiAl<sup>-</sup>. The  $^2\Pi_r(1\sigma^22\sigma^21\pi^1)$  state is the most stable for LiB<sup>-</sup>, however, the  $^4\Pi_r$  state is practically degenerate and the  $^4\Sigma^-$  configuration is only 4.4 kcal/mol (see Fig. 3) higher. The  $^2\Pi_r(1\sigma^22\sigma^21\pi^1)$  state of LiAl<sup>-</sup> is the most stable; the  $^4\Sigma^-$  (5.8 kcal/mol) and  $^4\Pi_r$  (6.8 kcal/mol) states are slightly higher in energy. The calculated dissociation energies for LiB<sup>-</sup>( $^2\Pi_r$ ) and LiAl<sup>-</sup>( $^2\Pi_r$ ) into Li+B<sup>-</sup> and Li+Al<sup>-</sup> are 37.2 and 31.2 kcal/mol, respectively [at the QCISD(T)/6-31+G(2df) level]. Both anions are also stable to loss of an electron; the calculated adiabatic E.A.s are 0.58 eV for LiB and 0.62 eV for LiAl [at the QCISD(T)/6-311+G(2df) level] therefore these anions are viable species and which may be found in mass-spectroscopic measurements. The charge distributions for both anions are close to Li<sup>0</sup>B<sup>-1</sup> and Li<sup>0</sup>Al<sup>-1</sup> which compares with the charge distributions Li<sup>+</sup>B<sup>-</sup> and Li<sup>+</sup>Al<sup>-</sup> in the neutral species.

#### D. LiC, LiC<sup>+</sup>, LiC<sup>-</sup>, LiSi, LiSi<sup>+</sup>, and LiSi<sup>-</sup>

The LiSi diatomic was identified mass spectrometrically and a dissociation energy of  $D_0^0=67\pm 6$  kcal/mol has been determined.<sup>32</sup> However, this dissociation energy has been revised to a much lower value 35.5 kcal/mol.<sup>33</sup> *Ab initio* computations on LiC and LiSi [for  $^2\Pi_r(1\sigma^22\sigma^21\pi^1)$  and  $^4\Sigma^-(1\sigma^22\sigma^11\pi^2)$  states] were performed at the multi-configuration self-consistent field single and double excitation configuration interaction (MCSCF-CISD) level by including all single and double excitations from the reference configurations (six for  $^2\Pi_r$  and three for  $^4\Sigma^-$ ).<sup>3</sup> High-spin  $^4\Sigma^-$  ground states were found for both molecules. The first excited  $^2\Pi_r$  states lie 33.3 kcal/mol (for LiC) and 14.5 kcal/mol (for LiSi) above the ground states. These findings are in contrast to those for the corresponding hydrides, where, e.g., the  $^2\Pi_r$  states are the most stable and the  $^4\Sigma^-$  states are higher in energy by 17.5 kcal/mol for CH (Refs. 1 and 34) and by 40.9 kcal/mol for SiH.<sup>1</sup> Mavridis and Harrison<sup>3</sup> clarified the reasons for these differences. The  $^4\Sigma^-$  LiC state results from transfer of an electron from Li to an empty *p* orbital of carbon. C<sup>-</sup> is then stabilized by the Li<sup>+</sup> ion's electric field. The calculated dissociation energies are LiC ( $D_e=50.9$  kcal/mol) and LiSi ( $D_e=35.2$  kcal/mol).<sup>3</sup> The latter agrees well with the revised experimental value<sup>33</sup> (see Table V). The ions of LiC and LiSi, to the best of our knowledge, have not been studied before.

We studied LiC in three electronic  $^4\Sigma^-(1\sigma^21\pi^22\sigma^1)$ ,  $^2\Pi_r(1\sigma^21\pi^3)$ , and  $^2\Pi_r(1\sigma^22\sigma^21\pi^1)$  states as well as the LiC<sup>+</sup> and LiSi<sup>+</sup> cations in three  $^3\Sigma^-(1\sigma^21\pi^2)$ ,  $^3\Pi_r(1\sigma^22\sigma^11\pi^1)$ , and  $^1\Sigma^+(1\sigma^22\sigma^2)$  states and the LiC<sup>-</sup> and LiSi<sup>-</sup> anions in five  $^5\Sigma^-(1\sigma^22\sigma^11\pi^23\sigma^1)$ ,



$^3\Sigma^-(1\sigma^22\sigma^21\pi^2)$ ,  $^3\Pi_r(1\sigma^22\sigma^21\pi^13\sigma^1)$ ,  $^3\Pi_i(1\sigma^22\sigma^11\pi^3)$ , and  $^1\Sigma^+(1\sigma^21\pi^4)$  states. The LiSi molecule was examined previously by us.<sup>35</sup>

We confirm<sup>3</sup> that LiC and LiSi have high-spin  $^4\Sigma^-$  ground electronic states with excited  $^2\Pi_r$  states that lie 45.0 kcal/mol (LiC) and 14.3 kcal/mol (LiSi) higher in energy. Our calculated equilibrium bond lengths and dissociation energies for LiC and LiSi agree well with the earlier findings<sup>3,33</sup> (see Tables I and IV).

Both the LiC<sup>+</sup> and LiSi<sup>+</sup> cations have  $^3\Pi_r$  ground electronic states, as does the isovalent LiB cation. However, this is *not* the case with LiAl, LiBe<sup>-</sup>, and LiMg<sup>-</sup>. The  $^1\Sigma^+$  states of LiC<sup>+</sup> and LiSi<sup>+</sup> both have minima which lie 23.9 kcal/mol (LiC<sup>+</sup>) and 6.4 kcal/mol (LiSi<sup>+</sup>) above the corresponding ground state energies. The LiC<sup>+</sup> and LiSi<sup>+</sup> ground states are stable to dissociation into Li<sup>+</sup>+C (by 9.0 kcal/mol) and into Li<sup>+</sup>+Si (by 16.8 kcal/mol), respectively. The calculated first adiabatic I.P.s are 7.48 eV (LiC) and 6.44 eV [LiSi, at QCISD(T)/6-311+G(2df)].

Because the LiC<sup>-</sup> anion has two very nearly degenerate electronic states  $^5\Sigma^-$  and  $^3\Sigma^+$ , we were unable to predict with certainty which is the most stable. The LiSi<sup>-</sup> anion has a  $^3\Sigma^-$  ground state. The orders of the electronic states (see Figs. 1 and 4) are  $^5\Sigma^-(0.0) \approx ^3\Sigma^-(0.2) < ^3\Pi_i(19.1) < ^3\Pi_r(33.2) < ^1\Sigma^+(56.9)$  for LiC<sup>-</sup> and  $^3\Sigma^-(0.0) < ^5\Sigma^-(4.1) < ^3\Pi_i(20.9) < ^3\Pi_r(21.1) < ^1\Sigma^+(53.7)$  for LiSi<sup>-</sup> (all data in kilocalories per mole at the QCISD(T)/6-311+G(2df) level). The LiC<sup>-</sup> and LiSi<sup>-</sup> anions are very stable with respect to dissociation into Li+C<sup>-</sup> (44.7 kcal/mol) and into Li+Si<sup>-</sup> [28.2 kcal/mol both at the QCISD(T)/6-311+G(2df) level], and therefore should be viable species. The calculated E.A.s are 0.50 eV (LiC) and 0.65 eV (LiSi, at the same level).

### E. LiN, LiN<sup>+</sup>, LiN<sup>-</sup>, LiP, LiP<sup>+</sup>, and LiP<sup>-</sup>

The LiP molecule was studied mass spectrometrically and a preliminary experimental value of the dissociation energy 52.6 ± 4.1 kcal/mol was obtained.<sup>36</sup> Seven low-lying states for the LiN molecule were computed at the SCF-DZ level by Khait and Baranovskii.<sup>37</sup> The LiN  $^1\Sigma^+$  state was calculated by Zhu and Murrell.<sup>29</sup> The most accurate *ab initio* investigation of LiN (with DZ+P basis sets at the CI level) found a  $^3\Sigma^-(1\sigma^22\sigma^21\pi^2)$  ground state and a  $^3\Pi_i(1\sigma^22\sigma^11\pi^3)$  state only 6.9 kcal/mol above. We previously studied<sup>38</sup> four electronic states for LiP— $^3\Sigma^-(1\sigma^22\sigma^21\pi^2)$ ,  $^3\Pi_r(1\sigma^21\pi^32\sigma^1)$ ,  $^1\Sigma^+(1\sigma^21\pi^4)$ , and  $^5\Sigma^-(1\sigma^22\sigma^11\pi^23\sigma^1)$ ; the high-spin  $^3\Sigma^-$  state was found to be the most stable and to have a dissociation energy much smaller than that given in Ref. 36 (which we feel must be in error).

We studied four electronic states  $^3\Sigma^-$ ,  $^3\Pi_i$ ,  $^1\Sigma^+$ , and  $^5\Sigma^-$  for the neutral LiN molecule; three electronic states  $^4\Sigma^-(1\sigma^22\sigma^11\pi^2)$ ,  $^2\Pi_r(1\sigma^22\sigma^21\pi^1)$ , and  $^2\Pi_i(1\sigma^21\pi^3)$  for both the LiN<sup>+</sup> and LiP<sup>+</sup> cations and four electronic states  $^2\Sigma^+(1\sigma^22\sigma^11\pi^4)$ ,  $^2\Pi_r(1\sigma^22\sigma^21\pi^3)$ ,  $^4\Sigma^-(1\sigma^22\sigma^21\pi^23\sigma^1)$ , and  $^4\Pi_i(1\sigma^22\sigma^11\pi^33\sigma^1)$  for the both LiN<sup>-</sup> and LiP<sup>-</sup> anions. In previous calculations of LiN, Dykstra *et al.*<sup>38</sup> found that the Hartree-Fock configurations dominate in

both  $^3\Sigma^-$  (0.984) and  $^3\Pi_i$  (0.970 Cl expansion). Therefore, our single reference configuration calculations for these states should be reliable.

The  $^3\Sigma^-$  state is the most stable for LiN as found earlier for LiP. Our calculated LiN dissociation energy 34.4 kcal/mol is nearly double that of Dykstra *et al.*<sup>39</sup> (19.6 kcal/mol). Our basis set is larger, we take much more electron correlation energy into account and our calculated bond length of LiN ( $^3\Pi_i$ ) is 0.04 Å shorter than in Ref. 39. Both molecules are highly ionic (the NBO charges are Li<sup>+0.85</sup>N<sup>-0.85</sup>, and Li<sup>+0.78</sup>P<sup>-0.78</sup>), and all bonds (bonding  $1\sigma$  and  $1\pi$  and antibonding  $2\sigma$  MOs) are highly polarized (more than 90%) towards N or P.

The  $^3\Pi_i$  and  $^1\Sigma^+$  excited states are higher in energy—5.9 kcal/mol (7.8 kcal/mol by Dykstra *et al.*<sup>39</sup>) and 49.0 kcal/mol, respectively for LiN, and 14.4 and 43.0 kcal/mol for LiP [at the QCISD(T)/6-311+G(2df) level].

Both the LiN<sup>+</sup> and LiP<sup>+</sup> cations are weakly bound and have high-spin  $^4\Sigma^-$  ground electronic states. The dissociation energies are 4.8 kcal/mol for LiN<sup>+</sup> and 9.6 kcal/mol for LiP<sup>+</sup>. The  $^2\Pi_i(1\sigma^21\pi^3)$  states have no minima for either species, but the  $^2\Pi_r(1\sigma^22\sigma^21\pi^1)$  states have minima which lie above the dissociation products Li<sup>+</sup> and (N or P) in their ground states. The adiabatic I.P. are 6.62 eV (LiN) and 6.59 eV (LiP).

The LiN<sup>-</sup> and LiP<sup>-</sup> anions also have  $^4\Sigma^-$  ground electronic states, but both are strongly bound with dissociation energies of 31.4 kcal/mol (LiN<sup>-</sup> into Li<sup>-</sup>+N) and 42.3 kcal/mol (LiP<sup>-</sup> into Li<sup>-</sup>+P). The adiabatic E.A.s are 0.48 eV (LiN) and 0.57 eV (LiP).

### F. LiO, LiO<sup>+</sup>, LiO<sup>-</sup>, LiS, LiS<sup>+</sup>, and LiS<sup>-</sup>

The LiO and LiS molecules have been well characterized experimentally<sup>40</sup> and theoretically.<sup>41</sup> The dissociation energy of LiO was determined to be  $D_0^0 = 80.5 \pm 1.5$  kcal/mol by electron-impact mass spectrometry<sup>40(b)</sup> and  $D_0^0 = 81.4 \pm 3$  kcal/mol by flame photometry.<sup>40(d)</sup> The ionization potential I.P. = 8.45 eV was deduced from the electron-impact appearance potential.<sup>40(b)</sup> The  $^2\Pi_i$  symmetry of the ground state for LiO was established by molecular beam electronic deflection.<sup>40(c)</sup> *Ab initio* calculations of the two doublet states of LiO  $^2\Pi_i(1\sigma^22\sigma^23\sigma^21\pi^3)$  and  $^2\Sigma^+(1\sigma^22\sigma^23\sigma^11\pi^4)$  have been performed by Yoshimine *et al.*<sup>41(a),41(b)</sup> with large Slater-type orbital (STO) basis sets (7s6p3d2 f) Li and O at the CI level, as well as by Langhoff *et al.*<sup>41(e)-41(g)</sup> at the CISD level also with large STO basis sets (7s5p3d2 f) O and Li. The  $^2\Pi_i$  ground state was found to be 6.7 kcal/mol lower in energy than the  $^2\Sigma^+$  state. Langhoff *et al.*'s<sup>41(e)-41(g)</sup> calculated dissociation energy of LiO ( $^2\Pi_i$ ), 87.2 kcal/mol at the CISD level is somewhat higher than the experimental values of 80.5 ± 1.5 [Ref. 40(b)] and 81.4 ± 3 kcal/mol.<sup>40(d)</sup>

Both states of LiO are reasonably well described at the HF level. Differences between the results of the HF and CI calculations are 0.02 Å for  $R_e$  and 0.001 eV for the  $^2\Pi_i-^2\Sigma^+$  excitation energy.<sup>41(e)-41(g)</sup>

The LiS dissociation energy was determined mass spectrometrically to be  $D_0^0 = 77.7 \pm 8.8$  kcal/mol.<sup>40(f)</sup> Two low-lying LiS states  $^2\Pi_i$  and  $^2\Sigma^+$  were studied at the CISD level

with large basis sets  $(8s7p3d2f)_S + (6s8p6d2f)_{Li}$  by Partridge *et al.*<sup>41(f)</sup> The  $^2\Pi_i$  ground state for LiS was predicted to have  $D_e = 76.1$  kcal/mol and  $R_e = 2.147$  Å. The first excited  $^2\Sigma^+$  state of SH with  $T_e = 11.7$  kcal/mol and  $R_e = 2.075$  Å SH is similar;  $^2\Pi_i$  is the ground state and  $^2\Sigma^+$  is the first excited state.<sup>1</sup> However, the energy difference between the  $^2\Pi_i$  and  $^2\Sigma^+$  states for SH ( $T_e = 88.7$  kcal/mol) is larger than for LiS. The calculated LiS dissociation energy 76.1 kcal/mol of Partridge *et al.*<sup>41(f)</sup> is very close to the experimental value  $77.7 \pm 8.8$  kcal/mol of Kudo and Wu.<sup>40(f)</sup>

We calculated both the  $^2\Pi_i$  and  $^2\Sigma^+$  states for LiO and LiS, as well as the  $^3\Pi_i(1\sigma^2 2\sigma^1 1\pi^3)$ ,  $^3\Sigma^-(1\sigma^2 2\sigma^2 1\pi^2)$ ,  $^1\Sigma^+(1\sigma^2 1\pi^4)$  states for LiC<sup>+</sup> and LiS<sup>+</sup>, and the  $^1\Sigma^+(1\sigma^2 2\sigma^2 1\pi^4)$  states for LiO<sup>-</sup> and LiS<sup>-</sup>.

We also find the  $^2\Pi_i$  state to be the ground state for both LiO and LiS. The first excited  $^2\Sigma^+$  state is higher in energy by 6.9 kcal/mol for LiO and by 14.2 kcal/mol for LiS. Our calculated dissociation energies for both molecules 80.3 kcal/mol (LiO) and 71.0 kcal/mol (LiS) agree well with experimental values (see Table IV).

Both LiO<sup>+</sup> and LiS<sup>+</sup> cations have  $^3\Sigma^-$  ground electronic states and their first excited  $^3\Pi_i$  states lie at 11.0 kcal/mol (LiO<sup>+</sup>) and 15.4 kcal/mol (LiS<sup>+</sup>), but neither cation is very strongly bound. The dissociation energies of LiO<sup>+</sup> and LiS<sup>+</sup> are 11.5 and 19.2 kcal/mol, respectively. Our calculated adiabatic I.P. for LiO (8.32 eV) agrees well with the experimental value  $(8.45 \pm 0.2$  eV).<sup>40(b)</sup>

For LiO<sup>-</sup> and LiS<sup>-</sup>, only the  $^1\Sigma^+$  ground state is expected to be stable, however, we studied three electronic states  $^1\Sigma^+(1\sigma^2 2\sigma^2 1\pi^4)$ ,  $^3\Sigma^+(1\sigma^2 2\sigma^1 1\pi^4 3\sigma^1)$ , and  $^3\Pi_r(1\sigma^2 1\pi^4 2\sigma^1 2\pi^1)$ . Our calculated dissociation energy of LiO<sup>-</sup>( $^1\Sigma^+$ ) oscillates strongly along the PMP2–PMP3–PMP4 expansion and at the QCISD(T) level we were not able to achieve convergence. Therefore, our data for this molecule are not reliable for this state. However, for both the triplet  $^3\Pi_i$  and  $^3\Sigma^+$  states of LiO MP4 and QCISD(T) data should be reliable. Both these states are electronically bound (adiabatic E.A. are 0.42 and 0.08 eV, respectively). The dissociation energy computed for LiS<sup>-</sup>( $^1\Sigma^+$ ) displays good convergence along the same MP series. The difference between the PMP4 and QCISD(T) results is only 0.2 kcal/mol. Therefore our calculated molecular properties for LiS<sup>-</sup> should be reliable. The dissociation energy of LiS<sup>-</sup> is 56.3 kcal/mol and our calculated adiabatic E.A. for LiS is 1.12 eV. The  $^3\Pi_i$  and  $^3\Sigma^+$  excited states are also electronically bound with the adiabatic E.A. 0.58 and 0.05 eV, respectively.

### G. LiF, LiF<sup>+</sup>, LiF<sup>-</sup>, LiCl, LiCl<sup>+</sup>, and LiCl<sup>-</sup>

The neutral LiF and LiCl molecules are well known.<sup>1</sup> Experimental bond lengths 1.564 Å (LiF) and 2.021 Å (LiCl) as well as dissociation energies 136.3 kcal/mol (LiF) and 111.6 kcal/mol (LiCl) in their  $^1\Sigma^+$  ground state are available.<sup>1</sup> Photodetachment studies of LiCl<sup>-</sup> (Ref. 42) gave an equilibrium bond distance of 2.123 Å, a dissociation energy of  $D_0^0 = 40.4$  kcal/mol and E.A. = 0.593 eV. Numerous *ab initio* investigations of the neutral and charged species have been reported (see Ref. 43 and refer-

ences therein). The calculated dissociation energies at high *ab initio* levels (CISD with large basis set) 139.7 kcal/mol (LiF) and 111.2 kcal/mol (LiCl), and computed bond lengths 1.571 Å (LiF) and 2.033 Å (LiCl) are in good agreement with the experimental data. In their ground electronic states, the molecular anions LX<sup>-</sup> are generally described<sup>43(d),43(e)</sup> as a neutral alkali atom strongly polarized by the halide ion  $L^0X^{-1}$ . Electron affinities, bond lengths, and vibrational frequencies for LiF<sup>-</sup>, LiCl<sup>-</sup>, NaF<sup>-</sup>, and NaCl<sup>-</sup> have been computed by Simons,<sup>43(d)</sup> by Jordan,<sup>43(f)</sup> and by Adamowicz and McCullough<sup>43(g)</sup> at the Hartree–Fock level. Single and double excitation coupled-cluster (CCSD) theory was applied to LiF<sup>-</sup> by Adamowicz and Bartlett.<sup>43(h)</sup> For all four systems, electron affinities approximated using Koopmans' theorem agree within 0.2 eV with Lineberger *et al.*<sup>42</sup> experimental data. Inclusion of orbital relaxation and electron correlation reduced the discrepancies to 0.1 eV. The small contribution of electron relaxation and electron correlation to the E.A.s of the alkali halides can be ascribed to the electronic structure. The extra electron in each radical anion occupies the empty region behind the alkali metal atom. Excellent agreement also is obtained between observed<sup>42</sup> and calculated<sup>43</sup> bond lengths and frequencies.

Our results for LiF and LiCl agree reasonably well with previous *ab initio* results and for anions with Lineberger's experimental data (see Tables I, IV–VI). In addition, we predict that LiF<sup>+</sup>( $^1\Sigma^+$ ) and LiC<sup>+</sup>( $^1\Sigma^+$ ) are only weakly bound cations with 6.8 and 12.5 kcal/mol dissociation energies, respectively.

## IV. OVERVIEW

All atoms from the first (Li–F) and second (Na–Cl) rows (except Ne and Ar) form chemical bonds with lithium atoms. Be and Mg form weak bonds because the  $2s^2$  and  $3s^2$  shells are filled in these atoms, so rearrangement to  $-2s^1 2p^1$  or  $-3s^1 3p^1$  is needed in order to form chemical bonds. Because these promotion energies are high and are not adequately compensated by the Li–Be and Li–Mg bonds, LiBe and LiMg are not very thermodynamically stable species.

Dissociation energies increase from LiB and LiAl to the end of rows (except for LiN and LiP) as expected because the electron affinities of the Li-bonded atoms increase in this direction. The charge distributions are nearby  $L^+X^-$  with the more electronegative X's. LiN and LiP have lower dissociation energies than LiC and LiSi, respectively, because N and P have lower E.A.s than C and Si. The dissociation energies are generally lower for diatomics from the second row than for the valence isoelectronic diatomics from the first row, with only one exception [LiP and LiN (see Table V)].

Our results for Li<sub>2</sub><sup>+</sup>, Li<sub>2</sub>, Li<sub>2</sub><sup>-</sup>, LiO, LiF, LiNa, LiSi, LiS, LiCl, and LiCl<sup>-</sup> are in reasonable agreement with the experimental data. However, our dissociation energy for LiP is much lower than Kudo's experimental value,<sup>36</sup> which we believe must be in error. All the LiX molecules except LiB, LiC, and LiSi have the same ground electronic states as do the HX diatomics. The exceptions LiB( $^3\Pi_r$ ),

LiC(<sup>4</sup>Σ<sup>-</sup>), and LiSi(<sup>4</sup>Σ<sup>-</sup>) have high-spin ground electronic states (see Figs. 1 and 4), whereas the corresponding hydrides have low-spin ground electronic states BH(<sup>1</sup>Σ<sup>+</sup>), CH(<sup>2</sup>Π<sub>r</sub>), and SiH(<sup>2</sup>Π<sub>r</sub>). The low-spin states <sup>1</sup>Σ<sup>+</sup> of LiB and <sup>2</sup>Π<sub>r</sub> for LiC and LiSi are only 6.4, 45.0, and 13.1 kcal/mol, respectively, higher in energy. As we have discussed earlier,<sup>39</sup> the main reason is that the 1π<sup>1</sup>(LiB) or 1π<sup>2</sup>(LiC and LiSi) subshell occupancies are very stable. The strong nuclear charges are close enough to make these occupancies more stable than the nonbonding (or antibonding) 2σ<sup>2</sup> subshell. Indeed, the relative stability of the 1π<sup>2</sup> or 1π<sup>1</sup> subshells along the isoelectronic series LiC–LiSi or LiB–LiAl decreases with respect to the 2σ<sup>2</sup> subshell, as do the relative energies of high-spin electronic states (<sup>4</sup>Σ<sup>-</sup> vs <sup>2</sup>Π<sub>r</sub> for LiC and LiSi, and <sup>3</sup>Π<sub>r</sub> vs <sup>1</sup>Σ<sup>+</sup> for LiB and LiAl).

The Li<sup>+</sup> cation forms bound states with all atoms from the first and second rows. However, the LiX<sup>+</sup> dissociation energies decrease from the beginning to the end of a row. These decreases are related to the decreasing polarizability and the increasing electronegativity of the atoms along such a row. However, both LiN<sup>+</sup> and LiP<sup>+</sup> are irregular and have the lowest dissociation energies. The ground electronic states of the LiX<sup>+</sup> cations are the same as those of the isoelectronic neutral species LiX' (where X has one higher nuclear charge than X'). The exception LiSi<sup>+</sup> has a high-spin <sup>3</sup>Π<sub>r</sub> ground electronic state, whereas the isoelectronic neutral analog LiAl has a low-spin <sup>1</sup>Σ<sup>+</sup> ground electronic state.

Only LiC<sup>+</sup>, LiN<sup>+</sup>, LiSi<sup>+</sup>, and LiP<sup>+</sup> have different high-spin electronic states than HO<sup>+</sup>, NH<sup>+</sup>, SiH<sup>+</sup>, and PH<sup>+</sup>, respectively. All other LiX<sup>+</sup> and HX<sup>+</sup> pairs have the same electronic states.

Our calculated adiabatic Li<sub>2</sub>, LiBe, LiNa, LiMg, and LiAl I.P.s are lower than the I.P. of the Li atom and increase from the beginning to the end of each row. The exception LiN has a lower I.P. than LiC. For Li<sub>2</sub> and LiO our calculated I.P.s agree well with the experimental data (see Table V).

All of the LiX<sup>-</sup> anions (X=Li–F and Na–Cl) are stable electronically, geometrically, and thermodynamically. Only LiBe<sup>-</sup> and LiMg<sup>-</sup> have low dissociation energies. However, only the LiCl<sup>-</sup> anion has been studied experimentally.<sup>42</sup> Our LiCl<sup>-</sup> dissociation energy 44.6 kcal/mol, E.A. [0.58 eV also at QCISD(T)/6-311+G(2df) + ZPE], bond length (2.104 Å), and vibrational frequency [541 cm<sup>-1</sup> both at MP2(full)/6-311+G\*] agree reasonably well with the experimental data<sup>42(b)</sup> D<sub>0</sub>=40.4 kcal/mol, E.A.=0.593±0.010 eV, R(Li–Cl)=2.123 Å, and ω<sub>e</sub>=500 cm<sup>-1</sup>.

The electronic structures of all LiX<sup>-</sup> anions (except Li<sub>2</sub><sup>-</sup> and LiNa<sup>-</sup>) involve Li<sup>0</sup>X<sup>-1</sup> charge distributions. Hence, the E.A.s of all LiX diatomics lie between 0.4 and 0.8 eV (see Table VII), close to the E.A. of the Li atom (0.62 eV). LiO and LiS have higher E.A.s because of their intermediate charge distributions between Li<sup>0</sup>X<sup>-</sup> and Li<sup>+1</sup>X<sup>-2</sup>.

*Note added in proof.* Bauschlicher *et al.*<sup>44</sup> recently published results of CASSCF-MRCI calculations on low lying electronic states of LiO<sup>-</sup>. They found a high-spin (<sup>3</sup>Π)

ground electronic state for LiO<sup>-</sup>. However, three other (<sup>1</sup>π, <sup>1</sup>Σ<sup>+</sup>, and <sup>3</sup>Σ<sup>+</sup>) excited states are also electronically found. The molecular constants and electron detachment energies calculated in the present work for the <sup>3</sup>π and <sup>3</sup>Σ<sup>+</sup> states agree well with data published by Bauschlicher *et al.*<sup>44</sup>

## ACKNOWLEDGMENTS

This work was facilitated by an Alexander von Humboldt Fellowship to AIB in Erlangen, and was supported in part by the Office of Naval Research and by National Science Foundation Grant No. CHE9116286 in Utah and the Deutsche Forschung Gemeinschaft and the Fonds der Chemischen Industrie in Erlangen. The authors thank D. A. Boldyrev for coding the program for drawing the figures shown in this article.

- <sup>1</sup>K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules* (Van Nostrand-Reinhold, New York, 1979).
- <sup>2</sup>A. V. Nemukhin, J. Almlöf, and A. Heiberg, *Chem. Phys. Lett.* **76**, 601 (1980).
- <sup>3</sup>A. Mavridis and J. F. Harrison, *J. Phys. Chem.* **86**, 1979 (1982).
- <sup>4</sup>H. B. Schlegel, *J. Comput. Chem.* **3**, 214 (1982).
- <sup>5</sup>H. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1973).
- <sup>6</sup>(a) M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.* **80**, 3265 (1984); (b) R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *ibid.* **72**, 650 (1980); (c) T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. v. R. Schleyer, *J. Comput. Chem.* **4**, 294 (1983).
- <sup>7</sup>A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **72**, 5639 (1980).
- <sup>8</sup>R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.* **14**, 91 (1978)
- <sup>9</sup>J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5958 (1987).
- <sup>10</sup>S. Huzinaga, technical report, Division of Theoretical Chemistry, University of Alberta, 1971.
- <sup>11</sup>S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations* (Elsevier, Amsterdam, 1984).
- <sup>12</sup>H. B. Schlegel, *J. Chem. Phys.* **84**, 4530 (1984).
- <sup>13</sup>G. L. Sharon, I. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Hallard, *J. Phys. Chem. Ref. Data* **17**, Suppl 1 (1988).
- <sup>14</sup>H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **14**, 731 (1985).
- <sup>15</sup>F. Sasaki and M. Yoshimine, *Phys. Rev. A* **9**, 17, 26 (1974); T. Noro, M. Yoshimine, M. Sekiya, and F. Sasaki, *Phys. Rev. Lett.* **66**, 1157 (1991).
- <sup>16</sup>D. Feller and E. R. Davidson, *J. Chem. Phys.* **82**, 4135 (1985); **90**, 1024 (1989).
- <sup>17</sup>C. W. Bauschlicher, Jr. and P. R. Taylor, *J. Chem. Phys.* **85**, 2779 (1986); C. W. Bauschlicher, Jr., S. R. Langhoff, H. Partridge, and P. R. Taylor, *ibid.* **85**, 3407 (1986).
- <sup>18</sup>B. H. Botch and T. H. Dunning, Jr., *J. Chem. Phys.* **76**, 6046 (1982); R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *ibid.* **96**, 6796 (1992).
- <sup>19</sup>D. Sundholm and J. Olsen, *Chem. Phys. Lett.* **171**, 53 (1990).
- <sup>20</sup>M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, GAUSSIAN 92, Revision c (Gaussian Inc., Pittsburgh, PA, 1990).
- <sup>21</sup>R. A. Bernheim, L. P. Gold, and T. Tipton, *J. Chem. Phys.* **78**, 3635 (1983).
- <sup>22</sup>(a) D. D. Konowalow and M. E. Rozenkrantz, *Chem. Phys. Lett.* **61**, 489 (1979); (b) D. Eisel, W. Demtroder, W. Müller, and P. Botschwina, *Chem. Phys.* **80**, 329 (1983); (c) D. D. Konowalow and J. L. Fish, *Chem. Phys. Lett.* **104**, 210 (1984); (d) W. Müller and W. Meyer, *J. Chem. Phys.* **80**, 3311 (1984); (e) G. E. Scuseria, T. P. Hamilton, and H. F. Schaefer III, *ibid.* **92**, 568 (1990); (f) D. D.

- Konowalow and M. L. Olson, *ibid.* **71**, 450 (1979); (g) H. Partridge, C. W. Bauschlicher, Jr., and P. E. M. Siegbahn, *Chem. Phys. Lett.* **97**, 198 (1983); (h) R. Shepard, K. D. Jordan, and J. Simons, *J. Chem. Phys.* **69**, 1788 (1978).
- <sup>23</sup> (a) R. Fuentealba, H. Preuss, H. Stoll, and L. v. Szentpaly, *Chem. Phys. Lett.* **89**, 418 (1982); (b) L. v. Szentpaly, P. Fuentealba, H. Preuss, and H. Stoll, *ibid.* **93**, 555 (1982); (c) I. Schmidt-Mink, W. Muller, and W. Meyer, *ibid.* **112**, 120 (1984).
- <sup>24</sup> R. Schlachta, I. Fischer, P. Rosmus, and V. E. Bondybey, *Chem. Phys. Lett.* **170**, 485 (1990).
- <sup>25</sup> (a) C. H. Wu and H. R. Ihle, *Proc. 8th Int. Mass Spectrom. Conf., Oslo*, **8A**, 374 (1980); (b) G. Pichler, A. M. Lyyra, P. D. Kleiber, W. C. Stwalley, R. Hammer, K. M. Sando, and H. H. Michels, *Chem. Phys. Lett.* **156**, 467 (1989).
- <sup>26</sup> (a) P. H. Blustin and J. W. Linnett, *J. Chem. Soc. Faraday Trans.* **70**, 826 (1974); (b) R. O. Jones, *J. Chem. Phys.* **72**, 3197 (1980); (c) A. A. Safonov, V. F. Khrustov, and N. F. Stepanov, *Zh. Strukt. Khim.* **24**, 168 (1983); (d) B. K. Rao and P. Jena, *Phys. Rev. B* **37**, 2867 (1988); (e) W. Pewestorf, V. Bonacic-Koutecky, and J. Koutecky, *J. Chem. Phys.* **89**, 5794 (1988); (f) P. Fantucci, V. Bonacic-Koutecky, W. Pewestorf, and J. Koutecky, *ibid.* **91**, 4229 (1989); (g) K. Pak, W. C. Ermler, C. W. Kern, and V. E. Bondybey, *J. Cluster Sci.* (in press); (h) C. W. Bauschlicher, Jr., S. R. Langhoff, and H. Partridge, *J. Chem. Phys.* **96**, 1240 (1992).
- <sup>27</sup> J. J. Kaufman and L. M. Sachs, *J. Chem. Phys.* **52**, 645 (1970).
- <sup>28</sup> P. E. Cade and W. M. Huo, *At. Data Nucl. Data Tables* **15**, 1 (1975).
- <sup>29</sup> Z. H. Zhu and J. N. Murrell, *Chem. Phys. Lett.* **88**, 262 (1982).
- <sup>30</sup> D. B. Knowles and J. N. Murrell, *J. Mol. Struct. (Theochem.)* **135**, 169 (1986).
- <sup>31</sup> M. Jaszunski, B. O. Roos, and P. O. Widmark, *J. Chem. Phys.* **75**, 306 (1981).
- <sup>32</sup> H. R. Ihle, C. H. Wu, M. Miletic, and K. F. Zmbov, *Adv. Mass Spectrom. A* **7**, 670 (1978).
- <sup>33</sup> C. H. Wu (private communication).
- <sup>34</sup> A. Kasdan, E. Herbst, and W. C. Lineberger, *Chem. Phys. Lett.* **31**, 78 (1975).
- <sup>35</sup> A. I. Boldyrev and J. Simons, *J. Phys. Chem.* **97**, 1526 (1993).
- <sup>36</sup> K. F. Zmbov, and C. H. Wu, Abstract of Proceedings of Symposium for the year 1992 on Special Basic Research, March 6, 1993.
- <sup>37</sup> Y. G. Khait and V. I. Baranovskii, *Zh. Strukt. Khim.* **23**, 167 (1982).
- <sup>38</sup> A. I. Boldyrev and J. Simons, *J. Phys. Chem.* **97**, 6149 (1993).
- <sup>39</sup> C. E. Dykstra, P. K. Pearson, and H. F. Schaefer III, *J. Am. Chem. Soc.* **97**, 2321 (1975).
- <sup>40</sup> (a) R. A. Berg, L. Wharton, W. Klemperer, A. Buchler, and J. L. Stauffer, *J. Chem. Phys.* **43**, 2416 (1965); (b) D. L. Hildenbrand, *ibid.* **57**, 4556 (1972); (c) S. M. Freund, E. Herbst, R. P. Mariella, and W. Klemperer, *ibid.* **56**, 1467 (1972); (d) G. J. Dougherty, M. R. Dunn, M. J. McEvan, and L. F. Phillips, *Chem. Phys. Lett.* **11**, 124 (1971); (e) C. Yamada, M. Fujitake, and E. Hirota, *J. Chem. Phys.* **91**, 137 (1989); (f) H. Kudo and C. H. Wu, *Chem. Express* **5**, 633 (1990); (g) H. Kimura, M. Asano, and K. Kubo, *J. Nucl. Mater.* **97**, 259 (1981).
- <sup>41</sup> (a) M. Yoshimine, *J. Chem. Phys.* **57**, 1108 (1972); (b) M. Yoshimine, A. D. McLean, and B. Liu, *ibid.* **58**, 4412 (1973); (c) D. L. Cooper and W. G. Richards, *ibid.* **73**, 3515 (1980); (d) J. N. Allison and W. A. Goddard III, *ibid.* **77**, 4259 (1982); (e) S. R. Langhoff, C. W. Bauschlicher, Jr., and H. Partridge, *ibid.* **84**, 4474 (1986); (f) H. Partridge, S. R. Langhoff, and C. W. Bauschlicher, Jr., *ibid.* **88**, 6431 (1988); (g) S. R. Langhoff, C. W. Bauschlicher, Jr., and H. Partridge, *Comparison of Ab initio Quantum Chemistry with Experiment for Small Molecules* (Reidel, New York, 1985), pp. 357-407.
- <sup>42</sup> (a) J. L. Carlsten, J. R. Peterson, and W. C. Lineberger, *Chem. Phys. Lett.* **37**, 5 (1976); (b) T. M. Miller, D. G. Leopold, K. K. Murray, and W. C. Lineberger, *J. Chem. Phys.* **85**, 2368 (1986).
- <sup>43</sup> (a) J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90**, 5622 (1990); (b) C. W. Bauschlicher, Jr. and S. R. Langhoff, *ibid.* **89**, 4246 (1988); (c) S. R. Langhoff, C. W. Bauschlicher, Jr., and H. Partridge, *ibid.* **84**, 1687 (1986); (d) J. Simons, *Annu. Rev. Phys. Chem.* **28**, 15 (1977); (e) K. D. Jordan, in *Alkali Halide Vapours*, edited by P. Davidovitz and D. L. McFadden (Academic, New York, 1979), Chap. 15, pp. 479-534; (f) L. Adamowicz and E. A. McCullough, Jr., *Chem. Phys. Lett.* **107**, 72 (1984); (g) L. Adamowicz and R. J. Bartlett, *ibid.* **129**, 159 (1986); (h) L. Adamowicz and R. J. Bartlett, *J. Chem. Phys.* **88**, 313 (1988).
- <sup>44</sup> C. W. Bauschlicher, Jr., H. Partridge, and L. G. M. Pettersson, *J. Chem. Phys.* **99**, 3654 (1993).