

Theoretical investigation of the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of LiAr and LiKr

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(Received 28 January 2002; accepted 7 March 2002)

The $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of the LiAr and LiKr molecules have been examined theoretically employing the coupled cluster method combined with augmented correlation consistent basis sets of double through sextuple zeta quality. After constructing basis set superposition error-free potential energy curves for the above states, dissociation energies (D_e), bond distances (r_e), and common spectroscopic parameters are extracted through the numerical solution of the one-dimensional rovibrational Schrödinger equation. For the “bound” $A^2\Pi$ states of LiAr and LiKr, the D_e values can be considered in harmony with experimental values: $D_e=890.4$ (957 ± 30) and 1220.0 (1200) cm^{-1} (experimental values in parentheses), respectively. Corresponding bond lengths, $r_e=2.545$ (2.50 ± 0.08) and 2.673 (3.27) Å indicate that the experimental bond distance of the LiKr $A^2\Pi$ state is rather too large. © 2002 American Institute of Physics. [DOI: 10.1063/1.1473809]

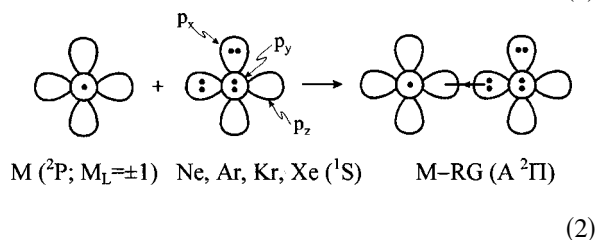
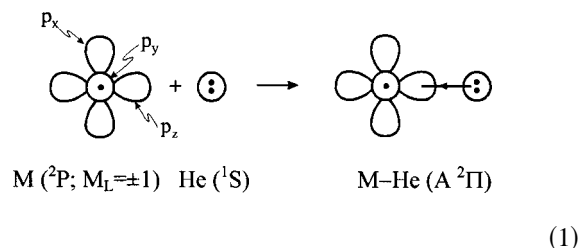
I. INTRODUCTION

The interaction of alkali metals (M) with rare gases (RG) has become a very fruitful topic of research for both experimentalists and theoreticians, mainly since the beginning of the 1960s.^{1–79} Due to their simplicity, these molecules serve as models for understanding different kinds of collisional processes such as line broadening, quenching, and electronic energy transfer. This has been assisted significantly by the recent progress in molecular beam technology and cold-atom trapping,⁵¹ which has made available many experimental data for these molecules. There have also been numerous attempts to incorporate this experimental information in the design of semiempirical model potentials in order to describe these weak interactions in a universal way.^{52–67} Furthermore, increasing interest exists in the study of the excitation and ionization of alkali metal atoms doped in helium nanodroplets.^{78,79}

Because of the relative “simplicity” of the alkali-metal atom(s), fascinating properties are revealed for the diatomic M-RG systems; for instance, their Rydberg states show spectacular potential energy curves with alternating wells and barriers.^{68–71} Although some of these undulations can clearly be attributed to avoided crossings between states of the same symmetry, most of them seem to be related to the atomic orbital structure of the alkali atom’s Rydberg states.⁷² Interest also exists in their low-lying (valence) states. Apart from the repulsive and well-separated ground $X^2\Sigma^+$ state emanating from the ground state atomic fragments, M ($ns^1;^2S$) + RG (1S), excitation of the alkali atom to the M ($np^1;^2P$) state provides for the rest two valence molecular states, namely, a relatively strongly bound $A^2\Pi$ ($2p\pi$) and a repulsive $B^2\Sigma^+$ ($2p\sigma$) state. The $A^2\Pi$ state has been the subject of extensive theoretical and experimental research for

quite a long time. The experimentally observed $A^2\Pi_{3/2} - A^2\Pi_{1/2}$ spin-orbit splitting is much larger compared to what is expected from the $^2P_{3/2} - ^2P_{1/2}$ splitting of the alkali-metal atom, something which has been called the “heavy atom effect,”⁷⁵ and much discussion and controversy^{74–77} have been devoted to the nature of this effect since its first experimental observation in NaAr in 1977.⁷³

The $A^2\Pi$ state can be pictorially described by the following valence-bond–Lewis icons:



Obviously, the $M(^2P; M_L = 0) + \text{RG}(^1S)$ fragments give rise to the $B^2\Sigma^+$ repulsive states.

Experimental bond dissociation energies and bond lengths exist for all LiRG (RG=He–Xe) $A^2\Pi$ molecules (Table I). Examination of the bonding implies that the observed trend in bond strengths results from the interplay between the polarizability of the RG atom and its ability to approach as much as possible the alkali-metal center. This is clearly demonstrated in the LiHe case,⁴⁷ where despite the very small polarizability of the He atom, the absence of $p\pi-p\pi$ Pauli repulsion, present in the other rare-gas atoms,

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TABLE I. Dissociation energies (D_e), bond lengths (r_e), harmonic frequencies (ω_e), and dipole moments (μ) of “best” experimental literature data on the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of the LiRG (RG = He, Ne, Ar, Kr, Xe) molecules. Theoretical results are in parenthesis.

State	Molecule	D_e (cm $^{-1}$)	r_e (Å)	ω_e (cm $^{-1}$) ^a	μ (D)
$X^2\Sigma^+$	LiHe	1.14±0.01 ^b (1.42) ^c	6.010±0.016 ^b (6.1) ^c		
	LiNe	9.43±0.16 ^b (6.96) ^d	4.924±0.016 ^b (5.2) ^d		
	LiAr	42.15±0.20 ^e (39.1) ^g	4.893±0.008 ^e (4.94) ^g	22.0267 ^f (20.9) ^g	
	LiKr	71.9±3.2 ^b (60.0) ^g	4.803±0.056 ^b (4.90) ^g	(22.3) ^g	
	LiXe	111.6±3.6 ^b (96) ^h	4.767±0.041 ^b (4.91) ^h	(29) ^h	
$A^2\Pi$	LiHe	1020±20 ⁱ (1011.2±2.8) ^c	1.783±0.016 ⁱ (1.791) ^c	356.8±1.1 ⁱ (354.9±1.2) ^c	(0.231) ^c
	LiNe	212±5 ^j (212.0±3.2) ^d	2.307±0.011 ^j (2.311±0.002) ^d	108.1±1.3 ^j (105.3±0.1) ^d	(0.441) ^d
	LiAr	957±30 ^k (890.4±4.7) ^g	2.50±0.08 ^k (2.545±0.001) ^g	196.9 ^k (175.6±0.2) ^l	(0.969) ^g
	LiKr	1200 ^m (1220.0±3.7) ^g	3.27 ^m (2.673±0.001) ^g	(186.1±0.6) ^g	(1.131) ^g
	LiXe	1650 ^m (1461) ⁿ	3.17 ^m (2.86) ⁿ	(196) ⁿ	
$B^2\Sigma^+$	LiHe	(0.50) ^c	(8.6) ^c		
	LiNe	(3.47) ^d	(7.1) ^d		
	LiAr	33.8±1.0 ^k (29.3) ^g	6.24±0.05 ^k (6.28) ^g	16.18 ^j (15.2) ^g	
	LiKr	(49.2) ^g	(6.16) ^g	(18.9) ^g	

^a⁷Li⁴He, ⁷Li²⁰Ne, ⁷Li⁴⁰Ar, ⁷Li⁸⁴Kr, and ⁷Li¹³²Xe isotopomers.

^bAtomic beam scattering, fit to Lennard-Jones (12,6) potential (Ref. 16).

^cMRCI (Ref. 47).

^dRCCSD(T) (Ref. 48).

^eRotationally resolved laser spectroscopy (RRLS) (Ref. 50).

^fRRLS (Ref. 40).

^gPresent work.

^hMRCI (Ref. 77).

ⁱRRLS (Ref. 32).

^jRRLS (Ref. 33).

^kRRLS (Ref. 49).

^lPresent work, but see text.

^mFar-wing line broadening (Ref. 20).

ⁿMRCI, $A^2\Pi_{1/2}$ state; corresponding D_e , r_e , ω_e values for the $A^2\Pi_{3/2}$ state: 1332 cm $^{-1}$, 2.88 Å, 174 cm $^{-1}$ (Ref. 77).

schemes (1) and (2), leads to a LiHe $A^2\Pi$ bond strength larger than that in LiNe and LiAr (Table I and Fig. 1).

In two previous papers,^{47,48} we have carefully examined the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ valence states of the LiHe (Ref. 47) and LiNe (Ref. 48) molecules. Concluding our studies towards a quantitative investigation of the LiRG molecules, we present similar results for the LiAr and LiKr systems. Regarding LiAr, the experimental work of Brühl and Zimmermann^{40,49,50} in these three states appears to be the most systematic and accurate so far in the literature (see Table II). These authors have studied the transitions $A^2\Pi \leftarrow X^2\Sigma^+$ and $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ by rotationally resolving the absorption spectrum of ⁶Li²⁰Ar and ⁷Li²⁰Ar using laser-induced fluorescence spectroscopy.^{40,49,50} For the repulsive $^2\Sigma^+$ states they have found shallow van der Waals minima at large internuclear distances ($X^2\Sigma^+$: $D_e=42.15$ cm $^{-1}$ at $r_e=4.893$ Å;⁵⁰ $B^2\Sigma^+$: $D_e=32.1$ cm $^{-1}$ at $r_e=6.24$ Å,⁴⁹ Table II). For the $A^2\Pi$ state, they have also presented more accurate spectroscopic values than the ones in the rather old line-

broadening experiments of Scheps *et al.* of 1975,²⁰ the latter work reporting dissociation energies of modest accuracy and suffering from too large bond lengths (Table II). The Brühl–Zimmermann $A^2\Pi$ preliminary results⁴⁰ in 1995 gave $D_e=925\pm 40$ cm $^{-1}$ and $r_e=2.48\pm 0.06$ Å, while their very recent higher resolution spectroscopic results⁴⁹ are $D_e=957\pm 30$ cm $^{-1}$ at $r_e=2.50\pm 0.08$ Å (but see below). Notice that in neither case could the lowest five ($\nu=0-4$) vibrational levels of the $A^2\Pi$ curve be observed.

Now, there also exist a number of *ab initio* results in the literature (Table II). Most of these results consistently underestimate the binding energy and overestimate the bond length; in addition, and with the exception of Ref. 46, in the rest of these works the basis set superposition error^{80(a),80(b)} (BSSE) has not been taken into account. We have already shown^{47,48} that correcting for BSSE⁸⁰ in the LiRG systems is of paramount importance, for, otherwise, it can lead to spurious agreement with experiment (*vide infra*).

Literature data on LiKr are scarcer (Table III). The line-

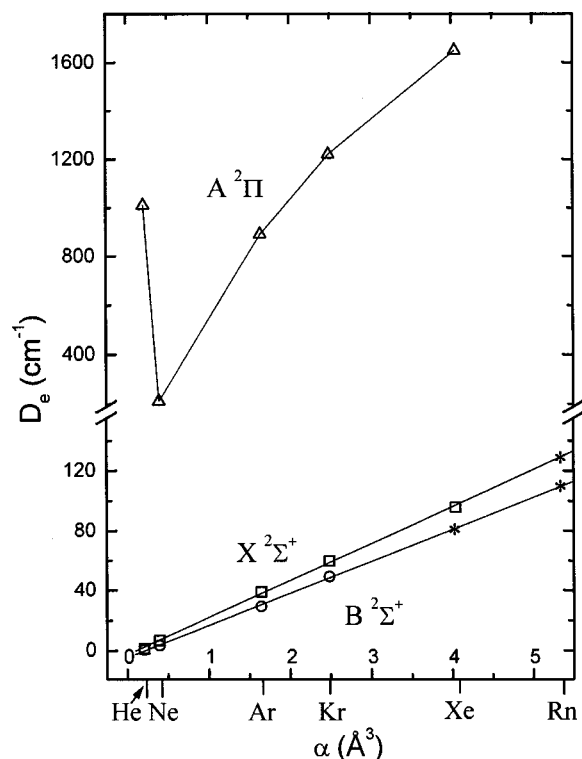


FIG. 1. Plot of the theoretically predicted (Table I) dissociation energies (D_e) of the LiRG $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states as a function of the (experimental) RG polarizabilities. The $A^2\Pi$ LiXe D_e is of experimental origin. Extrapolated D_e values for LiRn ($X^2\Sigma^+$, $B^2\Sigma^+$) and LiXe ($B^2\Sigma^+$) are denoted with a star (*).

broadening experiments of Scheps *et al.*²⁰ are the only experimental source of information regarding the $A^2\Pi$ state. As mentioned previously, these values are of modest accuracy especially with respect to bond distances, which in the LiKr case are overestimated by at least 0.3 \AA , as shown by the recent, moderate-sized multireference configuration-interaction (MRCI) calculations of Park *et al.*⁷⁷ (Table III).

II. METHODS AND COMPUTATIONAL APPROACH

In order to exploit the convergence properties of Dunning's correlation-consistent (cc) basis sets⁸¹ to the estimation of complete basis set (CBS) limit properties,⁸² we have used them in both LiAr and LiKr.⁸³ For the Li atom, we have employed the aug-cc-pCVnZ basis, $n=2$ (D), 3(T), 4(Q), and 5, where n is the cardinal number defining the quality of the plain cc-pVnZ basis sets.^{81(a),83} We have used the same diffuse (aug-) and core-valence (C) functions on Li as in Refs. 47 and 48. For the rare-gas atoms we have used the aug-cc-pVnZ bases,^{81(b)-81(e),83} where $n=2, 3, 4, 5$, and 6 (Ar only). Our largest generally contracted basis sets $[11s10p8d6f4g2h]_{\text{Li}}/[9s8p6d5f4g3h2i]_{\text{Ar}}$ and $[9s8p6d4f3g2h]_{\text{Kr}}$ contain 374 and 321 contracted spherical Gaussian functions (5d,7f,9g,11h,13i) for LiAr and LiKr, respectively. Recently, a revision of the second-row atom (Al-Ar) basis sets was published by Dunning and co-workers.⁸⁴ These basis sets, named (aug-)cc-pV($n+d$)Z, were constructed by adding an extra primitive d function to the normal (aug-)cc-pVnZ basis sets followed by a

reoptimization of all d -function exponents, in order to improve the convergence to the CBS limit. For this reason we have also tested the convergence properties of these revised bases by performing calculations around the equilibrium bond distance of the LiAr $A^2\Pi$ state.

As in the LiNe case, we have calculated the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ potential energy curves for both LiAr and LiKr at the coupled-cluster+single+double excitations with a perturbative estimate of the connected triples out of a restricted Hartree-Fock reference wave function, RHF-RCCSD(T) level of theory.⁸⁵ In both molecules, the 8 ($s+p$) valence e^- of the rare-gas atom+all 3 e^- of the Li atom (total 11 e^-) were allowed to correlate. An attempt was also made to estimate the core/valence effects in the LiAr system by calculating the energy with the $2s^22p^6$ core electrons of Ar included in the coupled-cluster calculation using unpublished correlation-consistent core/valence functions for Ar.⁸⁶

CBS limits for selected properties were estimated using the two well-known extrapolation formulas, namely, the simple exponential,⁸²

$$P_n = P_\infty + Ae^{-Bn}$$

and the mixed exponential/Gaussian,⁸⁷

$$P_n = P_\infty + Ae^{-(n-1)} + Be^{-(n-1)^2},$$

where P is a generic property, P_∞ its CBS limit, n the cardinal basis set number, while A and B are freely adjustable parameters.

The basis set superposition error^{80(a),80(b)} (BSSE) has been taken into account in every calculated point of all potential energy curves (PEC) using the counterpoise method of Boys and Bernardi.^{80(c)} The significance of correcting for BSSE in these weakly interacting systems was very vividly exhibited in our LiNe paper⁴⁸ where, in fact, with the increase of the basis set, the BSSE-uncorrected D_e for the $A^2\Pi$ state as a function of the basis set size (n) presented a maximum [at the aug-cc-p(C)VQZ basis] before converging to the CBS limit value. Bond lengths for all states were determined by fitting the three lowest-energy points of the corresponding PEC and then repeating the calculation at the determined r_e . Spectroscopic constants for all states were extracted by solving numerically the nuclear Schrödinger equation using a Numerov technique.⁸⁸ In the integration procedure 900 points were used for all PECs, followed by a cubic spline interpolation. All our calculations were performed with the MOLPRO 2000 suite of codes.⁸⁹

III. RESULTS AND DISCUSSION

A. Atoms

Table IV presents our numerical findings for the Li(2S), Ar(1S), and Kr(1S) atoms, as well as the excitation energy Li($^2P \leftarrow ^2S$), in a series of increasing-size basis sets. For the largest bases, the restricted Hartree-Fock (RHF) values are higher than the numerical Hartree-Fock (HF) ones⁹⁰ by 4, 30, and 200 $\mu\text{hartree}$ for Li(2S), Ar(1S), and Kr(1S), respectively. Our best RCCSD(T) result for the total energy of Li is only 0.714 mhartree higher than the "exact" nonrela-

TABLE II. Experimental and theoretical (*ab initio*) literature data on the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of LiAr. Methods, dissociation energies D_e , bond lengths r_e , and harmonic, anharmonic frequencies ω_e , $\omega_e x_e$.

State	Authors, year, reference	Method	D_e (cm ⁻¹) ^a	r_e (Å)	ω_e (cm ⁻¹) ^{a,b}	$\omega_e x_e$ (cm ⁻¹) ^{a,b}
$X^2\Sigma^+$	Rothe <i>et al.</i> , 1963, Ref. 6	Expt. ^c	41.0 ^d	5.27 ^d		
	Buck and Pauly, 1968, Ref. 9	Expt. ^c	43	4.95		
	Schlier, 1969, Ref. 12	Expt. ^c	42.8	4.80		
	Ury and Wharton, 1972, Ref. 15	Expt. ^c	45.5(8) ^d	4.893(23) ^d		
	Klingbeil, 1972, Ref. 17	Expt. ^c	43.64	4.843		
	Brühl and Zimmermann, 1995, Ref. 40	Expt. ^e	42.5(1.2)	4.888(15)	22.0267	3.0198
	Brühl and Zimmermann, 2001, Ref. 50	Expt. ^e	42.15(20)	4.893(8)		
	[Kerner, 1995] ^f	[CPP] ^g	[40.66] ^f	[4.927] ^f		
	Sadlej and Edwards, 1995, Ref. 39	ACPF ^h	77	4.8866		
	Park <i>et al.</i> , 1997, Ref. 69	MRCI ⁱ	27	5.39	15	
		MRCI+Q ^j	37	5.22	18	
	[Czuchaj, 1999] ^f		[36.8] ^f	[5.10] ^f		
	Lee and Lee, 2000, Ref. 45	MP2 (full) ^k	36.98	5.08		
	Park <i>et al.</i> , 2000, Ref. 77	MRCI ⁱ	40	4.90	21	
	Ahokas <i>et al.</i> , 2000, Ref. 46	UCCSD(T) ^m	34.4	5.01		
	El Hadj Rhouma <i>et al.</i> , 2002, Ref. 67	CPP ^g	62	4.64	27.11	3.65
	Present work	RCCSD(T) ⁿ	39.1	4.94	20.9	2.82
$A^2\Pi$	Scheps <i>et al.</i> , 1975, Ref. 20	Expt. ^o	790	2.97		
			810	3.18		
	Brühl and Zimmermann, 1995, Ref. 40	Expt. ^e	925(40)	2.48(6)		
	Brühl and Zimmermann, 2001, Ref. 49	Expt. ^e	957(30)	2.50(8)	196.9	
	Gu <i>et al.</i> , 1994, Ref. 37	MRDCI ^p	418	2.73	161.6	15.0
	Sadlej and Edwards, 1995, Ref. 39	ACPF ^h	811	2.5813	169	-11.52
	[Kerner, 1995] ^f	[CPP] ^g	[943] ^f	[2.47] ^f		
	Sohlberg and Yarkony, 1997, Ref. 76	SOCI+Q ^q	640	2.59	148	9.9
	Park <i>et al.</i> , 1997, Ref. 69	MRCI ⁱ	582	2.65		
		MRCI+Q ^j	714	2.61	138	
	[Czuchaj, 1999] ^f		[893] ^f	[2.54] ^f		
	Park <i>et al.</i> , 2000, Ref. 77	MRCI ⁱ	697 ^r	2.59 ^r	212 ^r	
			690 ^s	2.61 ^s	210 ^s	
	[Buenker, 2001] ^f		[757] ^f	[2.61] ^f		
	El Hadj Rhouma <i>et al.</i> , 2002, Ref. 67	CPP ^g	966	2.64	161.7	
	Present work	RCCSD(T) ⁿ	890.4(4.7) ^t	2.545(1) ^t	175.6(2) ^t	10.0
	$B^2\Sigma^+$	Brühl and Zimmermann, 2001, Ref. 49	Expt. ^e	33.8(1.0)	6.24(5)	16.18
[Kerner, 1995] ^f		[CPP] ^k	[34.2] ^f	[6.30] ^f		
Park <i>et al.</i> , 1997, Ref. 69		MRCI ⁱ	16	7.04		
		MRCI+Q ^j	23	6.77		
[Czuchaj, 1999] ^f			[27.4] ^f	[6.72] ^f		
[Buenker, 2001] ^f			[134] ^f	[8.06] ^f		
El Hadj Rhouma <i>et al.</i> , 2002, Ref. 67		CPP ^g	39	6.21	16.2	
Present work		RCCSD(T) ⁿ	29.3	6.28	15.2	1.95

^aValues in parentheses denote uncertainties in the last digits.^b⁷Li⁴⁰Ar isotope.^cAtomic beam scattering results.^dFit to Lennard-Jones (12,6) potential.^eRotationally resolved laser spectroscopy results.^fValues in square brackets indicate unpublished results, as mentioned in Refs. 49 ($X^2\Sigma^+$) and 48 ($A^2\Pi, B^2\Sigma^+$).^gCore polarization potential.^hAveraged coupled-pair functional, (14s9p4d3f)→[5s4p3d2f]_{Li,Ar} basis, BSSE-uncorrected results.ⁱMultireference configuration interaction (MRCI), (12s8p5d3f)→[9s8p5d3f]_{Li} and (14s10p3d)→[10s7p3d]_{Ar} basis, BSSE-uncorrected results.^jMRCI+multireference Davidson correction.^kMöller Plesset second-order perturbation theory with all electrons correlated, 6-311++G(3df,3pd)_{Li,Ar} basis, BSSE-uncorrected results.^lMRCI with relativistic effective core potentials, [6s6p2d]_{Li}/[6s6p3d]_{Ar} basis, BSSE-uncorrected results.^m(Unrestricted) coupled-cluster, [5s4p3d2f1g]_{Li}/[augmented Stuttgart effective core potentials]_{Ar} basis, BSSE-corrected results.ⁿ(Restricted) coupled-cluster results from present work, [11s10p8d6f4g2h]_{Li}/[9s8p7d5f4g3h2i]_{Ar} basis, BSSE-corrected results.^oFar-wing line-broadening results.^pMultireference doubles configuration interaction, (11s6p2d)→[6s4p2d]_{Li} and (14s11p2d)→[8s7p2d]_{Ar} basis, BSSE-uncorrected results.^qSecond-order configuration interaction+multireference Davidson correction, [4s3p2d1f]_{Li}/[6s5p3d2f]_{Ar} BSSE-uncorrected results.^r $A^2\Pi_{1/2}$ state.^s $A^2\Pi_{3/2}$ state.^tBSSE-corrected CBS limit results (see text for details).

TABLE III. Experimental and theoretical (*ab initio*) literature data on the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of LiKr. Methods, energies, dissociation energies D_e , bond lengths r_e , and harmonic, anharmonic frequencies ω_e , $\omega_e x_e$.

State	Authors, year, reference	Method	D_e (cm ⁻¹) ^a	r_e (Å) ^a	ω_e (cm ⁻¹) ^{a,b}	$\omega_e x_e$ (cm ⁻¹) ^{a,b}	
$X^2\Sigma^+$	Rothe <i>et al.</i> , 1963, Ref. 6	Expt. ^c	66.5 ^d	5.18 ^d			
	Bernstein and Muckerman, 1967, Ref. 8	Expt. ^c	75.5	4.0			
	Buck and Pauly, 1968, Ref. 9	Expt. ^c	69.0	4.87			
	Düren <i>et al.</i> , 1968, Ref. 10	Expt. ^c	63.9(6.5)	4.65(35)			
	Schlier, 1969, Ref. 12	Expt. ^c	65.4	4.75			
	Dehmer and Wharton, 1972, Ref. 16	Expt. ^c	71.9(3.2) ^d	4.803(56) ^d			
				69.6(2.7) ^e	4.908(185) ^e		
				67.2(0.8) ^f	4.871(47) ^f		
				67.1(0.7) ^g	4.875(40) ^g		
				68.1(0.6) ^h	4.953(19) ^h		
	Auerbach, 1974, Ref. 18	Expt. ^c	68.0(7.6) ^d	4.78(3) ^d			
	Park <i>et al.</i> , 2000, Ref. 77	MRCI ⁱ	59	4.87	25		
	Present work	RCCSD(T) ^j	60.0	4.90	22.3	0.57	
$A^2\Pi$	Scheps <i>et al.</i> , 1975, Ref. 20	Expt. ^k	1200	3.27			
	Park <i>et al.</i> , 2000, Ref. 77	MRCI ⁱ	917 ^l	2.73 ^l	114 ^l		
			867 ^m	2.75 ^m	107 ^m		
	Present work	RCCSD(T) ^j	1220.0(3.7) ⁿ	2.673(1) ⁿ	186.1(6) ⁿ	8.1	
$B^2\Sigma^+$	Present work	RCCSD(T) ^j	49.2	6.16	18.9	1.92	

^aValues in parentheses denote uncertainties in the last digits.^b⁷Li:⁸⁴Kr isotopomer.^cAtomic beam scattering results.^dFit to Lennard-Jones (12,6) potential.^eFit to Buckingham-Corner (6,8) potential ($\beta=0.7$).^fFit to Buckingham-Corner (6,8) potential ($\beta=2.325$).^gFit to Buckingham-Corner (6,8,10) potential.^hFit to Morse-Spline-van der Waals potential.ⁱMultireference configuration interaction with relativistic effective core potentials, $[6s6p2d]_{\text{Li}}/[7s7p3d]_{\text{Kr}}$ basis, BSSE-uncorrected results.^j(Restricted) coupled-cluster results from present work, $[11s10p8d6f4g2h]_{\text{Li}}/[9s8p6d4f3g2h]_{\text{Kr}}$ basis, BSSE-corrected results, see text for details.^kFar-wing line-broadening results.^l $A^2\Pi_{1/2}$ state.^m $A^2\Pi_{3/2}$ state.ⁿComplete basis set limit, see text for details.

tivistic energy,⁹¹ while the predicted energy gap $^2P \leftarrow ^2S$ is in practical agreement with the experimental (M_J averaged) one.⁹²

B. $X^2\Sigma^+$ and $B^2\Sigma^+$ repulsive states

Figure 2 depicts a compilation of BSSE-corrected potential energy curves for the three lowest-lying states ($X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$) of the LiRG (RG=He,Ne,Ar,Kr) series at the respective highest level of theory. The LiHe and LiNe curves have been taken from our previous work on the LiRG series^{47,48} and are shown here for comparison purposes. No-

tice how the $X^2\Sigma^+$ curves become steeper in the order LiHe, LiNe, LiAr, LiKr (Fig. 2), in accordance with the size of the rare-gas atom.

For the $X^2\Sigma^+$ state, weak van der Waals minima are found for both LiAr ($D_e=39.1$ cm⁻¹; $r_e=4.94$ Å) and LiKr ($D_e=60.0$ cm⁻¹; $r_e=4.90$ Å) at the BSSE-corrected RCCSD(T) level of theory (Tables II and III), using our largest basis sets (aug-cc-pCV5Z for Li, aug-cc-pV6Z for Ar, and aug-cc-pV5Z for Kr). Considering the weakness of the van der Waals interaction in both molecules, we observe very good agreement with the existing experimental values, espe-

TABLE IV. Absolute energies E (hartree) of the ground states of the Li(2S) and RG(1S) atoms and energy gaps (cm⁻¹) of the first excited state of Li at the RHF and CCSD(T)/(aug-cc-pCVnZ)_{Li}/(aug-cc-pVnZ)_{RG}, $n=2, 3, 4, 5$ and 6 (Ar), level (RG=Ar,Kr).

Basis set ^a	Li				Ar			Kr	
	$E(^2S; 2s^1)$		$^2P(2p^1) \leftarrow ^2S(2s^1)$		$E(^1S)$			$E(^1S)$	
	RHF	CCSD(T)	RHF	CCSD(T)	RHF	CCSD(T)	CCSD(T) ^b	RHF	CCSD(T)
aug-cc-p(C)VDZ	-7.432426	-7.466114	14883.7	14908.8	-526.80097	-526.96968	-526.97719	-2751.97775	-2752.11802
aug-cc-p(C)VTZ	-7.432681	-7.474267	14855.1	14924.4	-526.81335	-527.04876	-527.05115	-2752.05222	-2752.24963
aug-cc-p(C)VQZ	-7.432696	-7.476370	14850.6	14911.0	-526.81680	-527.07506	-527.07669	-2752.05472	-2752.27348
aug-cc-p(C)V5Z	-7.432723	-7.477346	14849.7	14907.8	-526.81735	-527.08344	-527.08421	-2752.05478	-2752.28086
aug-cc-p(C)V6Z					-526.81748	-527.08781	-527.08817		
NHF ^c	-7.432727				-526.81751			-2752.05498	
Exact ^d		-7.4780603							
Expt.		-7.4780604 ^e		14903.89 ^f					

^a“Core” (C) functions apply to Li only.^baug-cc-pV($n+d$)Z basis, $n=D, T, Q, 5$, and 6.^cNumerical Hartree-Fock calculation (Ref. 90).^dNonrelativistic “exact” calculation (Ref. 91).^eNonrelativistic “experimental” estimate (Ref. 91).^f M_J average (Ref. 92).

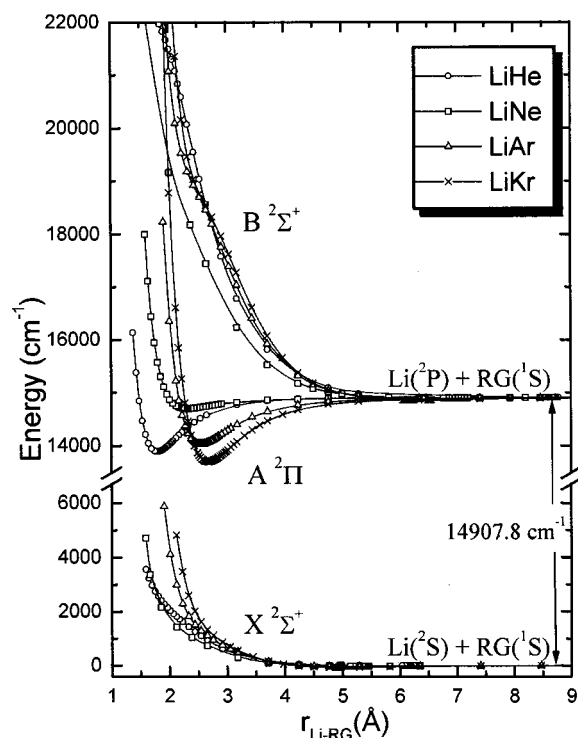


FIG. 2. Potential energy curves of the LiRG $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states, RG=He, Ne, Ar, and Kr, at the MRCI (LiHe) and RCCSD(T) (LiNe, LiAr, LiKr) level of theory.

cially with the very recent high-resolution data of Brühl and Zimmermann⁵⁰ for LiAr (Table II). In fact, four vibrational levels have been experimentally observed for the $X^2\Sigma^+$ $^7\text{Li}^{40}\text{Ar}$ system with transitions $\Delta\nu(1,2,3\leftarrow 0)=16.0876$, 26.4140, and 31.1668 cm^{-1} , respectively.⁵⁰ We calculate instead three vibrational levels, with corresponding transitions 15.3 and 24.9 cm^{-1} , the third transition ($3\leftarrow 0$) being 0.2 cm^{-1} above our dissociation limit, $\Delta\nu(3\leftarrow 0)+\Delta G(0)=39.3\text{ cm}^{-1}$.

For the $^7\text{Li}^{84}\text{Kr}$ $X^2\Sigma^+$ state no experimental vibrational levels have been reported in the literature. At the highest level of theory we obtain five vibrational levels ($\nu=0-4$) with transitions $\Delta\nu(1,2,3,4\leftarrow 0)=19.4$, 34.0, 43.2, and 48.2 cm^{-1} , respectively. However, because the experimental D_e value(s) is rather larger than 60.0 cm^{-1} (ranging from 65–70 cm^{-1} , Table III), at least an additional ν level ($\nu=5$) can be sustained, located approximately 5 cm^{-1} above our dissociation limit.

Similar arguments hold for the excited $B^2\Sigma^+$ state correlating to the $\text{Li}(2p^1,^2P;M_L=0)+\text{RG}(^1S)$ atomic fragments, although due to the diffuseness and the size of the $2p_\sigma$ orbital of Li, repulsion sets in at larger internuclear distances (Fig. 2). The calculated van der Waals well depths are comparable to the ones in the $X^2\Sigma^+$ state, but shallower by $\sim 10\text{ cm}^{-1}$ and at larger distances in both LiAr and LiKr molecules. For $^7\text{Li}^{40}\text{Ar}$ ($B^2\Sigma^+$) our theoretical (experimental⁴⁹) D_e and r_e values are 29.3 (33.8 ± 1.0) cm^{-1} and 6.28 (6.24 ± 0.05) Å, respectively. In addition, four ν levels ($\nu=0-3$) have been observed experimentally⁴⁹ with $\Delta\nu(1,2,3\leftarrow 0)=12.3$, 20.6, and 24.9 cm^{-1} , as compared to our theoretical numbers $\Delta\nu(1,2,3$

$\leftarrow 0\right)=11.3$, 18.8, and 25.0 cm^{-1} , the last transition being 2.6 cm^{-1} above our $D_e(=29.3\text{ cm}^{-1})$ value.

We are not aware of any published results, either experimental or theoretical, for the $B^2\Sigma^+$ state of LiKr. Theoretically, we obtain $D_e=49.2\text{ cm}^{-1}$, $r_e=6.16\text{ Å}$ (Table III), and four vibrational levels ($\nu=0-3$), with $\Delta\nu(1,2,3\leftarrow 0)=15.1$, 26.7, and 34.7 cm^{-1} ; a fifth one ($\nu=4$) is located at 50.6 cm^{-1} , 1.4 cm^{-1} above the D_e value, with $\Delta\nu(4\leftarrow 0)=41.6\text{ cm}^{-1}$.

In general, the D_e and r_e trends for both X and $B^2\Sigma^+$ repulsive states of the LiRG series follow the trend in the polarizability change in the RG (He–Xe) atoms (Table I). In fact, the van der Waals stabilization increases linearly as a function of the RG polarizabilities^{93,94} as shown in Fig. 1. Using the experimental polarizabilities of Xe ($\alpha=4.04\text{ Å}^3$) (Ref. 93) and Rn ($\alpha=5.3\text{ Å}^3$) (Ref. 94), simple extrapolation of the D_e 's as a function of α furnishes relatively reliable D_e values for the LiRn $X^2\Sigma^+$ state ($D_e=128\pm 3\text{ cm}^{-1}$), and for the LiXe ($D_e=82\pm 3\text{ cm}^{-1}$) and LiRn ($D_e=109\pm 4\text{ cm}^{-1}$) $B^2\Sigma^+$ states (Fig. 1). The $B^2\Sigma^+$ curves show a shoulder around $\sim 3\text{ Å}$ (Fig. 2), which is more pronounced in the cases of LiAr and LiKr, but of unclear origin.

C. $A^2\Pi$ state

This first excited state in the LiRG series traces its lineage to the $\text{Li}(^2P;M_L=\pm 1)+\text{RG}(^1S)$ fragments; the bonding is described pictorially in schemes (1) and (2) of the Introduction, while Fig. 2 shows the calculated $A^2\Pi$ potential energy curves for LiAr and LiKr. The LiHe and LiNe curves from our previous work^{47,48} are also presented for easy comparison. Table V lists our RCCSD(T) calculated values for total energies, dissociation energies (D_e), and bond lengths (r_e), for both LiAr and LiKr at their $A^2\Pi$ state using the aug-cc-p(C)VnZ series of basis sets, $n=2, 3, 4, 5$, and 6 (Ar only). CBS limits for the BSSE-corrected D_e 's and r_e 's using the exponential and the mixed exponential/Gaussian formulas are also displayed for both molecules. Other spectroscopic constants (frequencies ω_e , $\omega_e x_e$, rotational-vibrational coupling constants α_e , and centrifugal distortion constants, $\overline{D_e}$) for the most important isotopomers $^6,7\text{Li}^{40}\text{Ar}$ and $^6,7\text{Li}^{84}\text{Kr}$ are summarized in Table VI.

LiAr. The behavior of the dissociation energy in the $A^2\Pi$ state of LiAr with respect to the size of the basis set shows remarkable similarities with the LiNe case;⁴⁸ as the size of the basis set increases, the D_e uncorrected for BSSE exhibits a *maximum* at the RCCSD(T)/aug-cc-p(C)V5Z level of theory ($D_e=920.5\text{ cm}^{-1}$, Table V), creating an apparent agreement with the Brühl–Zimmermann first experimental D_e ($=925\pm 40\text{ cm}^{-1}$) value.⁴⁰ The same type of maximum has also been observed in LiNe ($A^2\Pi$),⁴⁸ but at the RCCSD(T)/aug-cc-p(C)VQZ level of theory. Keeping the same aug-cc-pCV5Z basis set on Li and increasing the basis set on Ar to aug-cc-pV6Z actually *reduces* the D_e to 898.5 cm^{-1} (Table V), thus rendering an extrapolation to the CBS limit untenable. A similar trend is also observed for the BSSE-uncorrected bond length, but now with a *minimum* r_e value at the aug-cc-p(C)V5Z basis (Table V). Obviously, an

TABLE V. RCCSD(T) results on the $A^2\Pi$ states of LiAr and LiKr. Energies E (hartree), dissociation energies D_e (cm^{-1}), equilibrium bond distances r_e (\AA), and CBS limits, in a series of increasing-size basis sets. Experimental results are also shown for comparison.

Basis set ^a	LiAr							LiKr				
	E	D_e	D_e^b	$D_e(+d)^{b,c}$	r_e	r_e^b	$r_e(+d)^{b,c}$	E	D_e	D_e^b	r_e	r_e^b
aug-cc-p(C)VDZ	-534.370629	605.6	440.4	461.0	2.703	2.770	2.756	-2759.520209	879.0	653.1	2.818	2.881
aug-cc-p(C)VTZ	-534.458970	865.9	743.5	761.1	2.570	2.595	2.587	-2759.661408	1210.8	1075.9	2.683	2.708
aug-cc-p(C)VQZ	-534.487588	900.3	841.2	852.4	2.550	2.562	2.558	-2759.687537	1234.1	1173.9	2.673	2.684
aug-cc-p(C)V5Z	-534.497052	920.5	872.7	874.7	2.539	2.550	2.549	-2759.695925	1238.6	1200.0	2.668	2.676
aug-cc-p(C)V6Z	-534.501321	898.5	878.6	879.3	2.544	2.548	2.548					
CBS/ e^{-n} ^d	-534.5023(5)		885.0(1.7)	884.2(2.3)		2.549(2)	2.548(1)			1206.4(1.9)		2.677(2)
CBS/mixed ^e	-534.5033(3)		889.7(3.2)	890.4(4.7)		2.545(1)	2.545(1)			1220.0(3.7)		2.763(1)
Expt. ^f				810			3.17			1200 ^f		3.27 ^f
Expt. ^g				925(40)			2.48(6)					
Expt. ^h				957(30)			2.50(8)					

^aaug-cc-p(C) $VnZ = (\text{aug-cc-pCVnZ})_{\text{Li}} / (\text{aug-cc-pVnZ})_{\text{Ar,Kr}}$, $n = \text{D, T, Q, 5}$ and 6 (Ar only).

^bBSSE-corrected values.

^cResults with the aug-cc-p $V(n+d)Z$ basis on Ar, $n = \text{D, T, Q, 5}$ and 6 .

^dSimple exponential CBS extrapolation (including all basis sets DZ-6Z), see text.

^eMixed exponential/Gaussian CBS extrapolation (including all basis sets DZ-6Z), see text.

^fReference 20.

^gReference 40.

^hReference 49.

extrapolation to the CBS limit can be performed only *after* correcting for BSSE. Observe the $\sim 20 \text{ cm}^{-1}$ ($\sim 2\%$ of the experimental dissociation energy) difference in the D_e due to BSSE, even at the highest [RCCSD(T)/aug-cc-p(C)V6Z] level of theory. Our best CBS values using the mixed exponential/Gaussian formula are $D_e = 889.7 \pm 3.2 \text{ cm}^{-1}$ or $D_e = 890.4 \pm 4.7 \text{ cm}^{-1}$ with the new aug-cc-p(C)V $(n+d)Z$ basis sets (Table V). The single d function added in the previous family of basis sets plays, as expected, a less important role as we move from $(D+d)Z$ to $(6+d)Z$, leaving, practically, the extrapolation procedure unaffected.

Three experimental values exist^{20,40,49} for the D_e and r_e of the LiAr $A^2\Pi$ state (Tables II and V). The data from the line-broadening experiments of Scheps *et al.*²⁰ in 1975 have been known to be of only modest accuracy⁷⁷ (*vide infra*), their values being in general too small for the D_e 's and too large for the r_e 's (Table II; see also the discussion on LiKr). Brühl and Zimmermann report more accurate laser spectro-

scopic data for $A^2\Pi: D_e(1) = 925 \pm 40 \text{ cm}^{-1}$, $r_e(1) = 2.48 \pm 0.06 \text{ \AA}$ in their first paper,⁴⁰ and $D_e(2) = 957 \pm 30 \text{ cm}^{-1}$, $r_e(2) = 2.50 \pm 0.08 \text{ \AA}$ in their very recent, second paper.⁴⁹ Our D_e of $890.4 \pm 4.7 \text{ cm}^{-1}$ (CBS/mixed value) lies inside the $D_e(1)$ range, but deviates significantly from the $957 \pm 30 \text{ cm}^{-1}$ result. The ± 40 and $\pm 30 \text{ cm}^{-1}$ range specified by $D_e(1)$ and $D_e(2)$, respectively, shows the difficulty in assigning experimentally a more accurate D_e for LiAr ($A^2\Pi$). This is also shown by the experimental r_e values; in both studies by Brühl and Zimmermann,^{40,49} the range inside which lies the "true" value of the bond length is as large as 0.12 \AA and 0.16 \AA , respectively. This difficulty arises, apparently, due to the relative position of the $X^2\Sigma^+$ and $A^2\Pi$ curves, leading to the experimental observation of only the highest ($\nu' = 5-10$) vibrational levels (the $\nu' = 10$ level has been observed in their second paper only⁴⁹) of the $A^2\Pi$ curve ($^7\text{Li}^{40}\text{Ar}$ isotopomer).⁴⁹ The difference between the

TABLE VI. BSSE-corrected harmonic ω_e (cm^{-1}), anharmonic $\omega_e x_e$ (cm^{-1}) frequencies, rotational-vibrational coupling constants α_e (cm^{-1}) and centrifugal distortion constants D_e (cm^{-1}) of the $A^2\Pi$ states of the most important isotopic species of LiAr and LiKr, at the RCCSD(T) level of theory.^a

	$^6\text{Li}^{40}\text{Ar}$		$^7\text{Li}^{40}\text{Ar}$		$^6\text{Li}^{84}\text{Kr}$		$^7\text{Li}^{84}\text{Kr}$	
	PW ^b	PW ^b	PW ^{b,c}	Expt. ^{c,d}	PW ^b	PW ^b	PW ^b	PW ^b
ω_e^c	187.6(3) ^f	175.6(2) ^f	199.4 ^g	196.9	199.9(7) ^f	186.1(6) ^f		
$\omega_e x_e^g$	11.4	10.0	15.6	14.72	9.3	8.1		
α_e^g	0.030	0.025		0.028	0.019	0.015		
$D_e (\times 10^{-4})^g$	0.141	0.108			0.074	0.055		

^aThe following reduced masses were used: $^6\text{Li}^{40}\text{Ar}$: 5.228178; $^7\text{Li}^{40}\text{Ar}$: 5.968196; $^6\text{Li}^{84}\text{Kr}$: 5.612774; $^7\text{Li}^{84}\text{Kr}$: 6.474645 amu.

^bValues from present work.

^cValues from fit to $\nu = 5-10$ vibrational levels (see text).

^dExperimental values (Ref. 49).

^eValues in parentheses denote uncertainties in the last digits.

^fValues at the complete basis set (CBS/mixed) limit.

^gTheoretical values at the largest basis set: $(\text{aug-cc-pCV5Z})_{\text{Li}} / (\text{aug-cc-pV6Z})_{\text{Ar}}$ for LiAr, and $(\text{aug-cc-pCV5Z})_{\text{Li}} / (\text{aug-cc-pV5Z})_{\text{Kr}}$ for LiKr.

$D_e(1)$ (Ref. 40) and $D_e(2)$ (Ref. 49) experimental values seems to originate mainly from the different fitting procedures used, as is evidenced from the practically identical vibrational spacings in the two papers.^{40,49} At our highest level of theory, RCCSD(T)/aug-cc-p(C)V6Z, and for the same ${}^7\text{Li}^{40}\text{Ar}$ isotopomer, we predict the existence of 12 vibrational levels, the last one being just $\sim 4\text{ cm}^{-1}$ below the dissociation limit. Although our predicted vibrational spacings are in very good agreement with the experimentally observed ones, the theoretical (experimental⁴⁹) values being 64.0 (65.6), 49.8 (51.4), 37.6 (39.0), 27.0 (28.4), 18.0 (19.3), and 10.9 cm^{-1} for the $\Delta\nu'$ spacings $6\leftarrow 5$, $7\leftarrow 6$, $8\leftarrow 7$, $9\leftarrow 8$, $10\leftarrow 9$, and (the nonobserved) $11\leftarrow 10$, respectively, our ω_e and $\omega_e x_e$ frequencies for ${}^7\text{Li}^{40}\text{Ar}$, 175.6 ± 0.2 and 10.0 cm^{-1} (Table VI) are smaller than the Y_{10} ($=\omega_e$) and Y_{20} ($=\omega_e x_e$) values of 196.9 and 14.72 cm^{-1} reported by Brühl and Zimmermann after fitting their $\nu'=5-10$ levels to a Dunham polynomial.⁴⁹ On the other hand, a similar fit to our theoretically predicted $\nu=5-10$ levels leads to almost complete agreement with the aforementioned experimental results (Table VI).⁴⁹ In other words, comparison with the experimental values would probably be more favorable if all vibrational levels could be observed experimentally.

LiKr. We will now discuss our findings for the $A^2\Pi$ state of LiKr. Our BSSE-corrected dissociation energy converges to $D_e=1220.0\pm 3.7\text{ cm}^{-1}$ (CBS/mixed formula, Table V). The BSSE-uncorrected D_e 's seem to converge too, but to a larger CBS D_e value. Now based on (a) this difference between the D_e 's, (b) the quite "large" D_e difference between the two extrapolation formulas, exponential versus mixed exponential/Gaussian, in the BSSE-corrected CBS limits, $1206.4\pm 1.9\text{ cm}^{-1}$ vs $1220.0\pm 3.7\text{ cm}^{-1}$, respectively (Table V), (c) the quite "large" BSSE of $\sim 39\text{ cm}^{-1}$ ($\sim 3\%$ of the "true" binding energy) at our highest RCCSD(T)/aug-cc-pV5Z level of theory, and (d) our experience with LiNe (Ref. 48) and LiAr, we surmise that if the one-electron basis set were larger (i.e., if the aug-cc-pV6Z basis set for Kr were available), then the BSSE-uncorrected D_e value using the aug-cc-p(C)V6Z basis would rather be lower than the D_e of 1238.6 cm^{-1} using the aug-cc-pV5Z basis (Table V), i.e., presenting the same type of maximum in the binding energy as in the LiNe ($A^2\Pi$) (Ref. 48) and LiAr ($A^2\Pi$) cases. Furthermore, there would be better agreement between the two extrapolation schemes using the BSSE-corrected results. Our most trusted value for the equilibrium bond length is $2.673\pm 0.001\text{ \AA}$, obtained at the BSSE-corrected CBS/mixed limit. This value is in disagreement with the only available experimental value of Scheps *et al.*, 3.27 \AA .²⁰ The accuracy of the latter line-broadening experimental results has been recently questioned by Park *et al.*,⁷⁷ whose spin-orbit MRCI calculations have shown that the experimental r_e value (see Table III) is rather overestimated. On the other hand, our calculated D_e is in good agreement with the experimental $D_e=1200\text{ cm}^{-1}$ from the same experimental work, their D_e value being consistently lower than our calculated value as in the LiAr case (Tables II, III, and V). Calculated values for some common spectroscopic constants for two isotopic species, ${}^6\text{Li}^{84}\text{Kr}$ and ${}^7\text{Li}^{84}\text{Kr}$, are shown in Table VI. For the most abundant isotopomer, ${}^7\text{Li}^{84}\text{Kr}$, we predict the existence

of 13 ($\nu=0-12$) vibrational levels at the RCCSD(T)/aug-cc-pV5Z level of theory, the $\nu=12$ level being 14.4 cm^{-1} below the dissociation limit; we are not aware of any experimental rotational/vibrational data on the LiKr $A^2\Pi$ state.

IV. CONCLUDING REMARKS

The present work concludes our theoretical study on the three lowest-lying ($X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$) states of the diatomic lithium-rare-gas molecules. Currently, we report highly accurate BSSE-corrected values for the energetics and the spectroscopic constants of LiAr and LiKr, obtained by using the correlation-consistent family of basis sets,⁸¹ aug-cc-p(C)VnZ, $n=2-6$ for LiAr and $n=2-5$ for LiKr, at the coupled-cluster RCCSD(T) level of theory. Wherever accurate experimental data are available, our predicted values are in very good agreement with them (Tables II and III). Two "discrepancies" are noted: (a) Our predicted bond length for the $A^2\Pi$ state of LiKr is shorter by at least 0.3 \AA (Table III) than the experimental bond length of Scheps *et al.*²⁰ (b) Our predicted (extrapolated) dissociation energy for the $A^2\Pi$ state of LiAr ($890.4\pm 4.7\text{ cm}^{-1}$) is smaller by at least 37 cm^{-1} than the most recent experimental value of $957\pm 30\text{ cm}^{-1}$ reported by Brühl and Zimmermann using high-resolution laser spectroscopy.⁴⁹ On the other hand, there is agreement with their older (1995) measurements of $925\pm 40\text{ cm}^{-1}$.⁴⁰ Two reasons seem to exist for this discrepancy; first, the experimental values were extracted by observing only the highest ($\nu'=5-10$) vibrational levels of the LiAr ($A^2\Pi$) curve due to the relatively unfavorable position of the $X^2\Sigma^+$ and $A^2\Pi$ curves, and second, although we have reached, in essence, the one-electron basis set limit within the RCCSD(T) method, our calculations do not take into account core/valence effects (for Ar), and relativistic corrections. The experimentally observed⁴⁹ $A^2\Pi_{3/2}-A^2\Pi_{1/2}$ spin-orbit splitting of 14 cm^{-1} has already been averaged out in both experimental and our theoretical results. We believe that the main part of any remaining corrections to D_e would originate from the Ar $2s^2 2p^6$ core/valence correlation, relativistic corrections playing a minor role. Trial RCCSD(T) calculations with Ar core/valence basis sets under development⁸⁶ showed that core/valence effects add $\sim 10\text{ cm}^{-1}$ to the dissociation energy of LiAr($A^2\Pi$), bringing it to an estimated value of $D_e\approx 900\text{ cm}^{-1}$, while the bond length shortens by $0.005-0.008\text{ \AA}$, leading to an estimated $r_e\approx 2.54\text{ \AA}$. Core/valence effects are expected to play a crucial role for the case of LiKr ($A^2\Pi$) with the inclusion of the Kr $3d^{10}$ "semicore" shell. The $A^2\Pi_{3/2}-A^2\Pi_{1/2}$ spin-orbit splitting for LiKr has been calculated by Park *et al.*,⁷⁷ at the MRCI level of theory to be as large as 50 cm^{-1} at the equilibrium bond length.

As a final remark, we would like to draw attention to the calculated curves for the LiRG (RG=He, Ne, Ar, and Kr) series (Fig. 2). Notice the similarities in the $A^2\Pi$ curves among LiNe, LiAr, and LiKr, which are shifted to deeper wells and larger bond lengths as the size and polarizability of the rare-gas atom increases [scheme (2) of the Introduction]. LiHe is an exception compared to the three other LiRG

molecules due to the lack of filled $p\pi$ orbitals in He [scheme (1) of the Introduction], thus creating the conditions of a closer approach of He towards Li (smaller r_e), and a more effective binding.

ACKNOWLEDGMENTS

The authors thank Professor K. A. Peterson for providing the core/valence functions for Ar prior to publication. One of the authors (I.S.K.K.) expresses his gratitude to the Hellenic State Scholarships Foundation (IKY) for financial support. The generous computing time provided by the National Center for Scientific Research, DEMOKRITOS, is greatly appreciated.

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- multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.
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