ELSEVIER

Ab initio calculation of the $a\,^3\Sigma_u^+$ interaction potential and vibrational levels of $^7Li_2$

M.D. Halls [a], H.B. Schlegel [a,*], M.J. DeWitt [b], G.W.F. Drake [c]

[a] *Department of Chemistry, Wayne State University, Detroit, MI 48202, USA*
[b] *Center for Atomic, Molecular and Optical Sciences, University of Virginia, Charlottesville, VA 22904, USA*
[c] *Department of Physics, University of Windsor, Windsor, Canada ON N9B 3P4*

Abstract

The interaction potential of the lowest triplet excited state, $a\,^3\Sigma_u^+$, for Li_2 has been calculated using the ab initio method, QCISD(T) and the correlation-consistent valence polarised quintuple zeta basis set, cc-pV5Z. Equilibrium constants and vibrational levels for $^7Li_2$ are in good agreement with experimental determinations. The $a\,^3\Sigma_u^+$ energy curve for Li_2 is characterised at the QCISD(T, full)/cc-pV5Z level of theory by the parameters D_e, D_o, R_e, ω_e and $\omega_e x_e$ which are found to be 334.145 cm^{-1}, 301.989 cm^{-1}, 4.1686 Å, 65.400 cm^{-1} and 3.208 cm^{-1}, respectively. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years, advances in laser cooling and trapping have increased interest in the spin-polarised states of alkali species. The lithium dimer, $^7Li_2$, is currently under active investigation, following the observation by Hulet and co-workers [1] of Bose–Einstein condensation (BEC) for this system. In experiments, atomic densities are sufficiently low that two-body interactions dominate and BEC formation for $^7Li_2$ is dependent on the interaction potential of the lowest triplet excited state, $a\,^3\Sigma_u^+$. The stability of the $^7Li_2$ BEC is sensitive to the binding energy of the least bound vibrational level [2]. For $^7Li_2$, the $a\,^3\Sigma_u^+$ potential is predicted to support 11 vibrational states [3].

Experimental studies of the $a\,^3\Sigma_u^+$ state for $^7Li_2$ have been reported. Linton et al. [4] analysed spectra of the $1\,^3\Sigma_g^+$–$a\,^3\Sigma_u^+$ transition, collected using a high-resolution Fourier-transform spectrometer, to determine accurate vibrational and rotational constants and a dissociation energy for the $a\,^3\Sigma_u^+$ state of $D_e = 333 \pm 1$ cm^{-1}. Using a 'dense' RKR potential to reanalyse the data from Linton et al., Zemke and Stwalley [3] obtained a revised dissociation energy of $D_e = 333.4 \pm 0.6$ cm^{-1}. Most recently Linton et al. [5] calculated an improved RKR potential curve using data from high-resolution fluorescence measurements of transitions from the $2\,^3\Pi_g$ to the $a\,^3\Sigma_u^+$ state of $^7Li_2$ which allowed the observation of vibrational levels, including those high-lying levels that were previously unobserved ($v = 8, 9$). The most recent experimentally derived dissociation energy for the $a\,^3\Sigma_u^+$ state for $^7Li_2$ is $D_e = 333.69 \pm 0.10$ cm^{-1} [5].

---

* Corresponding author. Fax: +1-313-577-8822.
 E-mail address: hbs@chem.wayne.edu (H.B. Schlegel).

From a theoretical standpoint the lithium dimer is interesting because it is the simplest system in which triplet pairing gives rise to a favourable interaction, referred to as 'no-pair bonding' [6]. The potential used to compute vibrational levels for $^7Li_2$ in the $a\,^3\Sigma_u^+$ state has usually had a hybrid form derived from the experimental data of Linton et al. [3,7,8]. Previous first-principle studies of the $a\,^3\Sigma_u^+$ state of Li_2 have been incomplete in some respect; such as inadequate treatment of electron correlation, use of limited basis sets and/or considering only a small range of interatomic distances. Konowalow et al. [9] combined the results of three previous computational studies [10–12] to obtain an estimated 'most likely' potential energy curve for the $a\,^3\Sigma_u^+$ state of Li_2. Schmidt-Mink et al. [13] have used a valence configuration interaction (CI) approach along with effective core polarisation potentials to compute the $a\,^3\Sigma_u^+$ curve. To date, the most sophisticated first-principle calculations of the $a\,^3\Sigma_u^+$ state of Li_2 have employed a coupled-cluster approach to incorporate electron correlation effects. Kaldor [14] used the coupled-cluster method including single and double substitutions (CCSD) with a 74-CGTO basis set to compute a small section of the $a\,^3\Sigma_u^+$ curve for Li_2 (~2–6 Å). Bartlett and co-workers [15] used basis sets of double-ζ quality and the single-reference CCSD approach and compared it to results obtained from a multireference-CCSD and an FCI calculation, also considering only a limited section of the potential energy curve (~2–7 Å). Most recently, Donavich et al. [6] carried out a variety of sophisticated correlated calculations using the Dunning correlation consistent double- and triple-ζ basis sets, including complete active space-SCF (CASSCF) and the coupled-cluster method including single and double substitutions and perturbative triples (CCSD(T)), to study the interaction in the $a\,^3\Sigma_u^+$ state, computing the dissociation energy, equilibrium bond length and harmonic vibrational frequency for $^7Li_2$.

In this communication, the ab initio calculation of the $a\,^3\Sigma_u^+$ interaction potential, the associated vibrational levels and the equilibrium constants for $^7Li_2$ are reported. The work described here represents a significant improvement over previous theoretical results. Calculations have been carried out for a range of interatomic distances (2–32 Å) to provide the most complete first-principle determination of the $a\,^3\Sigma_u^+$ interaction potential for Li_2 thus far.

2. Methods

The calculations described here were carried out using the GAUSSIAN suite of programs [16]. The interaction energies were computed by a single-reference-determinant, size extensive, all electron ab initio method, using quadratic configuration interaction including contributions from single and double excitations and perturbative triple excitations (QCISD(T, full)) [17], and employing a correlation consistent quintuple-ζ basis set, cc-pV5Z [6s,5p,4d,3f,2g,1h] [18], which provides a total of 182 AOs for the Li dimer. To ensure basis set consistency between the dimer and atomic calculations, the interaction energy, E_{int}, for two Li atoms in the $a\,^3\Sigma_u^+$ state was obtained by subtracting the atomic energy corrected for basis set superposition, E_{atom}, from the dimer energy, E_{dimer},

$$E_{int}(R) = E_{dimer}(R) - 2E_{atom}(R),$$

where R is the interatomic separation and E_{atom} is R dependent through the counterpoise correction procedure of Boys and Bernardi [19]. The energies from unrestricted Hartree–Fock (UHF), and Møller–Plesset perturbation theory up to third order (MP$_n$, $n = 2, 3$) were also obtained during the course of the QCISD(T) calculations. The interaction energy was calculated at 0.125 Å intervals from 2 to 32 Å. Spin contamination was negligible for the UHF wavefunctions with typical S^2 values for the atom and dimer calculations of 0.7500 and 2.0000. The potential minimum was determined using a seventh-order polynomial interpolation of the potential. Rotationless vibrational energies were obtained by solving the finite difference equation for nuclear motion using Mathematica [20]. A five-point formula was used for the second derivatives; three additional points between grid points were obtained by seventh-order polynomial interpolation and $1/R^6$ extrapolation. The vibrational energies were converged to 0.01 cm^{-1} or better.

3. Results and discussion

Advances in the efficiency of correlated ab initio quantum chemistry programs, and the increased performance of computing workstations over the past decade, now allow the quantitative first-principle determination of properties for molecular systems with tremendously improved accuracy. In studying the lowest energy $a\,^3\Sigma_u^+$ excited state of Li_2, we obtain the added benefit of being immune to variational collapse, thus allowing treatment using robust ground-state correlated methods [21,22].

Conventional wisdom, using H_2 as a model system, associates singlet electron pairing as a requirement for a favourable interaction, whereas triplet-pairing gives rise to a repulsive anti-bonding state. Li_2 is the simplest system in which the lowest triplet excited state is bound. The theoretical potential energy curves for the $a\,^3\Sigma_u^+$ state of Li_2 are shown in Fig. 1. Previous authors have noted that in addition to the adequate treatment of electron correlation, a basis set rich in polarisation functions is required to accurately describe the $a\,^3\Sigma_u^+$ interaction in Li_2 [14]. In this work we have employed the most extensive basis set to date, the cc-pV5Z basis set, which includes up to h-type functions for Li with a total of 182 AOs for the Li dimer. At the Hartree–Fock (SCF) level of theory the interaction is repulsive throughout. Compari-
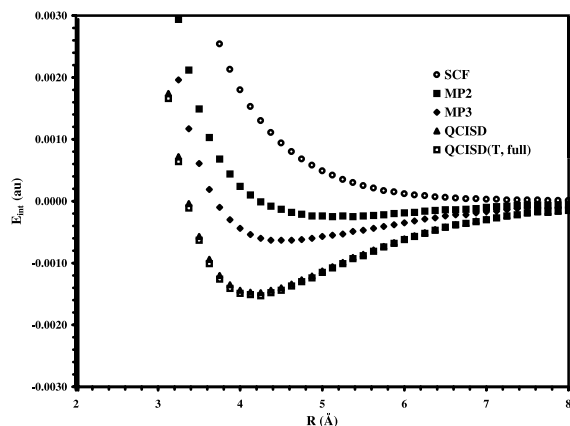
son of the interaction curves at the various levels of theory shows that as the treatment of electron correlation becomes more complete the attractive nature of the interaction increases. The curves show that perturbative correlation methods are insufficient to describe the interaction and a comparison of the iterative methods, QCISD and QCISD(T), suggests good convergence with respect to level of theory. The interaction energy, E_{int}, of the $a\,^3\Sigma_u^+$ state of Li_2 computed at the QCISD(T, full)/cc-pV5Z level of theory for interatomic distances of 2–32 Å at 0.5 Å intervals is summarised in Table 1 [23].

The dissociation energies and equilibrium constants derived from the computed potential are presented in Table 2, along with experimental determinations and previous theoretical results for comparison. The most recent experimental characterisation of the $a\,^3\Sigma_u^+$ state of Li_2 by Linton et al. [5] obtained 333.69 ± 0.10 cm^{-1} and 301.829 ± 0.015 cm^{-1} for D_e and D_o, respectively. Comparison of the theoretical determinations of the dissociation energy and the experimental data clearly shows that the present work represents a significant improvement in level of agreement. At the QCISD(T, full)/cc-pV5Z level of theory, the predicted dissociation energy is in agreement with the experimentally determined value within 0.5 cm^{-1}. The next closest theoretical determination, that of Schmidt-Mink et al. [13], underestimates the dissociation energy by ca. 12 cm^{-1}. The results of Shaik and co-workers [6] using a comparable theoretical method of electron correlation to that employed here, are in disagreement with the experimental data by more than ca. 18 cm^{-1}. This can be attributed to the use of basis sets that were not sufficiently large. Because of uncertainties in the experimental determination of the potential minimum, the experimental value of D_o is better determined than D_e. Our computed D_o is in excellent agreement with the experimental determination with a difference of only 0.16 cm^{-1}. The equilibrium bond distance, harmonic and anharmonic spectroscopic constants also show excellent agreement with experimental determinations.

Theoretical QCISD(T, full)/cc-pV5Z vibrational levels and Linton et al.'s most recent RKR levels determined from experimental data for $^7Li_2$ in the

Fig. 1. Theoretical potential energy curves for $^7Li_2$ in the $a\,^3\Sigma_u^+$ state.

Table 1
The QCISD(T, full) values for $E_{int}(R)$ using the cc-pV5Z basis set[a]

R (Å)	$E_{int}(R)$ (a.u.)	R (Å)	$E_{int}(R)$ (a.u.)	$E_{int}(R)$ (asymp) (a.u.)
2.000	4.728E−02	17.500	−1.124E−06	
2.500	1.489E−02	18.000	−9.482E−07	
3.000	3.063E−03	18.500	−8.040E−07	
3.500	−6.433E−04	19.000	−6.844E−07	
4.000	−1.488E−03	19.500	−5.856E−07	
4.500	−1.437E−03	20.000	−5.066E−07	
5.000	−1.160E−03	20.500	−4.366E−07	
5.500	−8.664E−04	21.000	−3.786E−07	
6.000	−6.191E−04	21.500	−3.286E−07	
6.500	−4.304E−04	22.000	−2.866E−07	
7.000	−2.947E−04	22.500	−2.506E−07	
7.500	−2.009E−04	23.000	−2.196E−07	
8.000	−1.376E−04	23.500	−1.936E−07	
8.500	−9.534E−05	24.000	−1.706E−07	
9.000	−6.710E−05	24.500	−1.516E−07	
9.500	−4.801E−05	25.000	−1.346E−07	
10.000	−3.491E−05	25.500	−1.196E−07	
10.500	−2.578E−05	26.000	−1.066E−07	
11.000	−1.931E−05	26.500	−9.460E−08	
11.500	−1.466E−05	27.000	−8.160E−08	−8.085(3)E−8
12.000	−1.127E−05	27.500	−7.260E−08	−7.236(3)E−8
12.500	−8.763E−06	28.000	−6.560E−08	−6.489(2)E−8
13.000	−6.885E−06	28.500	−5.860E−08	−5.831(2)E−8
13.500	−5.462E−06	29.000	−5.260E−08	−5.249(2)E−8
14.000	−4.370E−06	29.500	−4.760E−08	−4.734(1)E−8
14.500	−3.527E−06	30.000	−4.260E−08	−4.277(1)E−8
15.000	−2.868E−06	30.500	−3.860E−08	−3.871(1)E−8
15.500	−2.348E−06	31.000	−3.560E−08	−3.509(1)E−8
16.000	−1.936E−06	31.500	−3.160E−08	−3.186(1)E−8
16.500	−1.606E−06	32.000	−2.960E−08	−2.897(1)E−8
17.000	−1.340E−06	∞	0.000E + 00	

[a] The last column gives the asymptotic interaction potential calculated from Eq. (1). The figures in brackets give the uncertainty in the final figure quoted.

$a\,^3\Sigma_u^+$ state are shown in Table 3 along with the classical turning points for comparison. The theoretically derived vibrational levels slightly overestimate the RKR levels, but overall are in good agreement with an average difference of ca. 1.3 cm^{-1} and a maximum difference of ca. 2 cm^{-1}. Previous ab initio $a\,^3\Sigma_u^+$ state potentials for Li$_2$ were either incomplete or not of sufficient accuracy. For example, the work of Schmidt-Mink et al. [13] predicted only nine bound levels for ^{7}Li$_2$ in the $a\,^3\Sigma_u^+$ state. The results presented here are in agreement with the prediction of Zemke and Stwalley [3], with the $a\,^3\Sigma_u^+$ state supporting 11 bound vibrational levels for ^{7}Li$_2$. Of particular interest is the binding

energy of the least bound vibrational level for ^{7}Li$_2$ in the $a\,^3\Sigma_u^+$ state, $v = 10$. Moerdijk et al. [7] calculated an inverse perturbation analysis (IPA) potential curve for the $a\,^3\Sigma_u^+$ state combining a number of experimental results [4,5]. They predicted a binding energy of 0.38 cm^{-1} (11.4 GHz) for $v = 10$ of ^{7}Li$_2$. The most recent experimentally determined RKR potential of Linton et al. [5] predicts a least bound level binding energy of 0.394 cm^{-1}. However, in ultracold photoassociation experiments, Abraham et al. [2] determined $v = 10$ to be bound by 0.416 cm^{-1} (12.47 ± 0.04 GHz). Our QCISD(T, full)/cc-pV5Z results predict a $v = 10$ binding energy of 0.297 cm^{-1}.

Table 2
Equilibrium constants for the $a\,^3\Sigma_u^+$ state of $^7Li_2$

	D_e (cm^{-1})	D_o (cm^{-1})	R_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
Experiment[a]	333.690	301.829	4.173		
	333	301.083	4.1716	65.130	3.267
QCISD(T, full)/cc-pV5Z	334.145	301.989	4.1686[b]	65.400	3.208
CCSD(T, full)/cc-pCVTZ[c]	315		4.193	65.24	
CCSD(T, full)/cc-pVTZ[c]	368		4.103	69.92	
CCSD(T, full)/cc-pCVDZ[c]	273		4.152	66.84	
CCSD(T, full)/cc-pVDZ[c]	261		4.188	64.92	
CCSD/74-CGTO[d]	306		4.050	75	
CPP + CI[e]	322		4.182	63.73	3.202

[a] From Linton et al. [4,5].
[b] From BSSE corrected QCISD(T, full)/cc-pV5Z potential.
[c] From Danovich et al. [6].
[d] From Kaldor [14].
[e] From Schmidt-Mink et al. [13].

Table 3
Comparison of the QCISD(T, full)/cc-pV5Z and vibrational levels from RKR potential fit to experimental data for the $a\,^3\Sigma_u^+$ state of $^7Li_2$

v	QCISD(T, full)/cc-pV5Z			RKR[a]		
	$G(v)$ (cm^{-1})	R_{min} (Å)	R_{max} (Å)	$G(v)$ (cm^{-1})	R_{min} (Å)	R_{max} (Å)
0	32.156	3.844	4.627	31.857	3.846	4.630
1	91.174	3.668	5.087	90.453	3.668	5.092
2	143.597	3.571	5.497	142.523	3.571	5.503
3	189.637	3.504	5.912	188.240	3.505	5.922
4	229.371	3.456	6.360	227.679	3.458	6.373
5	262.768	3.420	6.871	260.837	3.422	6.885
6	289.706	3.393	7.490	287.665	3.395	7.501
7	310.027	3.375	8.304	308.098	3.377	8.297
8	323.681	3.362	9.511	322.155	3.365	9.441
9	331.144	3.356	11.631	330.170	3.358	11.392
10	333.848	3.354	16.974	333.269	3.356	16.052

[a] RKR vibrational energies from Linton et al. [5].

For sufficiently large R, it is interesting to compare the directly calculated interaction potential with the one obtained from the asymptotic expansion [24]

$$E_{int}(R) = -30.5970(35)/R^6 - 512.989(26)/R^8 - 12694.1(2)/R^{10} \text{ a.u.} \quad (1)$$

with R in Ångstroms. The expansion coefficients are accurate to within the stated uncertainties, and we take one-half of the last term as the truncation uncertainty. The results listed in the last column of Table 1 show that the potentials agree to within the uncertainty of the directly calculated potential for $R \gtrsim 27$ Å, and that the asymptotic potential is to be preferred for larger R. However, use of the asymptotic potential in place of the directly calculated one had no significant effect on the calculated vibrational energy levels. The good agreement shown in Table 1 provides an additional check on the accuracy of the directly calculated potential.

4. Conclusions

The interaction potential of the $a\,^3\Sigma_u^+$ state for Li_2 has been computed at the QCISD(T, full)/ cc-pV5Z level of theory and has been used to compute the equilibrium constants and vibrational levels for $^7Li_2$. Favourable agreement was found in comparing with experimental data and the results obtained are more complete and in better agreement than previous theoretical studies. Also, good agreement was found with the asymptotic expansion for the interaction potential.

References

[1] C.C. Bradley, C.A. Sackett, R.J. Hulet, Phys. Rev. Lett. 78 (1997) 985.

[2] E.R.I. Abraham, W.I. McAlexander, J.M. Gerton, R.G. Hulet, R. Côté, A. Dalgarno, Phys. Rev. A 55 (1997) R3299.

[3] W.T. Zemke, W.C. Stwalley, J. Phys. Chem. 97 (1993) 2053.

[4] C. Linton, T.L. Murphy, F. Martin, R. Bacis, J. Verges, J. Chem. Phys. 91 (1989) 6036.

[5] C. Linton, F. Martin, A.J. Ross, I. Russier, P. Crozet, A. Yiannopoulou, L. Li, A.M. Lyyra, J. Mol. Spectrosc. 196 (1999) 20.

[6] D. Danovich, W. Wu, S. Shaik, J. Am. Chem. Soc. 121 (1999) 3165.

[7] A.J. Moerdijk, W.C. Stwalley, R.G. Hulet, B.J. Verhaar, Phys. Rev. Lett. 71 (1994) 40.

[8] R. Côté, A. Dalgarno, M.J. Jamieson, Phys. Rev. A 50 (1994) 399.

[9] C.C. Konowalow, R.M. Regan, M.E. Rosenkrantz, J. Chem. Phys. 81 (1984) 4534.

[10] M.L. Olson, D.D. Konowalow, Chem. Phys. 21 (1977) 393.

[11] D.D. Konowalow, J.L. Fish, Chem. Phys. 77 (1983) 435.

[12] W. Kutzelnigg, V. Staemmler, M. Gelus, Chem. Phys. Lett. 13 (1972) 496.

[13] I. Schmidt-Mink, W. Müller, W. Meyer, Chem. Phys. 92 (1985) 263.

[14] U. Kaldor, Chem. Phys. 180 (1990) 1.

[15] A. Balkova, S.A. Kucharski, R.J. Bartlett, Chem. Phys. Lett. 182 (1991) 511.

[16] M.J. Frisch, et al., GAUSSIAN 98 Revision A.6, Gaussian, Pittsburgh, PA, USA, 1998.

[17] J.A. Pople, M. Head-Gordon, K. Raghavachari, J. Chem. Phys. 76 (1987) 5968.

[18] The Li cc-pV5Z basis set from D. Feller (unpublished) was obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0 Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA; http://www.emsl.pnl.gov:2080/forms/basisform.html.

[19] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.

[20] S. Wolfram, Mathematica, third ed., Cambridge University Press, Cambridge, UK, 1996 (and associated computer programs, Wolfram Research, Champaign, IL, USA).

[21] K. Raghavachari, Annu. Rev. Phys. Chem. 41 (1991) 615.

[22] W. Kutzelnigg, P. von Herigonte, Adv. Quantum Chem. 36 (2000) 185.

[23] The complete set of QCISD(T,\,full)/cc-pV5Z interaction energies covering the interatomic range 2–32 \accent23{\rm A} at 0.125 \accent23{\rm A} intervals is available at the world-wide web at http://chem.wayne.edu/schlegel/suppmat/.

[24] Z.C. Yan, J.F. Babb, G.W.F. Drake, Phys. Rev. A 54 (1996) 2824.