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Ab initio calculation on accurate analytic potential energy functions and harmonic frequencies of $c^3\Sigma_g^+$ and $B^1\Pi_u$ states of dimer $^7Li_2$*

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The comparison between single-point energy scanning (SPES) and geometry optimization (OPT) in determining the equilibrium geometries of $c^3\Sigma_g^+$ and $B^1\Pi_u$ states of dimer $^7Li_2$ is made at numerous basis sets by using a symmetry-adapted-cluster configuration-interaction (SAC-CI) method in the Gaussian 03 program package. In this paper the difference of the equilibrium geometries obtained by SPES and by OPT is reported. The results obtained by SPES are found to be more reasonable than those obtained by OPT in full active space at the present SAC-CI level of theory. And the conclusion is attained that the cc-PVTZ is a most suitable basis set for these states. The calculated dissociation energies and equilibrium geometries are 0.8818 eV and 0.3090 nm for $c^3\Sigma_g^+$ state, and 0.3668 eV and 0.2932 nm for $B^1\Pi_u$ state respectively. The potential energy curves are calculated over a wide internuclear distance range from about $2.5a_0$ to $37a_0$ and have a least-squares fit into the Murrell–Sorbie function. According to the calculated analytic potential energy functions, the harmonic frequencies (ω_e) and other spectroscopic data ($\omega_e\chi_e$, B_e and α_e) are calculated. Comparison of the theoretical determinations at present work with the experiments and other theories clearly shows that the present work is the most complete effort and thus represents an improvement over previous theoretical results.

Keywords: molecular structure and potential energy function, atomic and molecular collision, dimer, excited state

PACC: 3420

1. Introduction

With the discovery of Bose–Einstein condensation in ultracold hydrogen,[1] lithium,[2] sodium,[3] potassium[4] and rubidium,[3] the analytic potential energy functions (PEFs) of alkali metal dimers, especially the analytic PEF of dimer $^7Li_2$, have been the subject of numerous investigations[5] since the relatively slow nuclear motion is very sensitive to the details of the PEFs. To produce trustworthy dynamics, various cross sections and scattering lengths at ultralow energies always need to use accurate PEFs for calculations in high accuracy. But to our knowledge, previous studies on the PEFs for the $c^3\Sigma_g^+$ and $B^1\Pi_u$ states of dimer $^7Li_2$ are incomplete in some respects, such as giving incomplete spectroscopic data, inadequately accurate equilibrium geometry and/or dissociation energy.[6−12] The work described here is the most complete effort to deal with the analytic PEFs, force constants and spectroscopic data, and represents an improvement over previous theoretical results of the $c^3\Sigma_g^+$ and $B^1\Pi_u$ states for dimer $^7Li_2$.

In this paper, the dissociation energies and equilibrium geometries of the $c^3\Sigma_g^+$ and $B^1\Pi_u$ states of dimer $^7Li_2$ are calculated by using the SAC-CI method[13] in full active space in the Gaussian 03 program package.[14] Calculations have been carried out over a wide internuclear distance range from about $2.5a_0$ to $37a_0$. In the next section, we shall determine the suitable basis set of each involved electronic state for further accurate calculations. In Section 3, we shall present the calculated results for the PEFs, force con-

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stants, harmonic frequencies and other spectroscopic data, and make some useful discussions about each involved state. Concluding remarks are made in Section 4.

2. Determination of the suitable basis set for further calculations

To obtain the accurate equilibrium geometry, our calculations are divided into two steps. First, the OPT calculations[13,14] are adopted so as to attain the equilibrium internuclear distances at the numerous basis sets such as cc-PVTZ, D95V, AUG-cc-PVTZ, 6-311++G, D95(d,p), 6-311G(3df,3pd), D95++, D95V(d,p), 6-311++G(3df,3pd) and the complete basis set tabulated in Ref.[6]. By comparing the computed equilibrium internuclear distances and the experimental ones,[15−18] we select some of them for further calculations. Then, we make the SPES calculations near the optimized equilibrium geometry by a very tiny step at the selected basis sets. Some of our computed results about the $c^3\Sigma_g^+$ and $B^1\Pi_u$ states are presented in Table 1. We also carry out the same calculations for the ground state for comparison, and the computed results are also tabulated in Table 1.

Table 1. Comparison of equilibrium geometries (in nm) obtained by OPT and by SPES calculations for $c^3\Sigma_g^+$, $B^1\Pi_u$ and $X^1\Sigma_g^+$ states of dimer $^7Li_2$.

		D95(3df,3pd)	D95(d,p)	6-311G(3df,3pd)	6-311++G	6-311++G(3df,3pd)	AUG-cc-PVTZ	cc-PVTZ
OPT	$c^3\Sigma_g^+$	0.3140	0.3158	0.3121	0.3160	0.3115	0.3107	0.3119
	$B\ ^1\Pi_u$	0.2991	0.3045	0.2973	0.3090	0.2982	0.2981	0.2967
	$X\ ^1\Sigma_g^+$	0.2704	0.2700	0.2705	0.2717	0.2706	0.2694	0.2700
SPES	$c^3\Sigma_g^+$	0.3112	0.3143	0.3100	0.3154	0.3196	0.3069	0.3090
	$B\ ^1\Pi_u$	0.2963	0.3037	0.2942	0.3080	0.2963	0.2942	0.2932
	$X\ ^1\Sigma_g^+$	0.2688	0.2699	0.2688	0.2720	0.2694	0.2678	0.2678

From Table 1, the equilibrium internuclear distance obtained by OPT is easily found to be different from the one obtained by SPES at the same set. For example, at the cc-PVTZ, the results obtained by OPT are 0.3119 nm for $c^3\Sigma_g^+$ state, and 0.2967 nm for $B^1\Pi_u$ state respectively, whereas the ones obtained by SPES are 0.3090 nm for $c^3\Sigma_g^+$ state and 0.2932 nm for $B^1\Pi_u$ state respectively. Careful examination has found that the unique Group Sum of Operators (GSUM) method used in the SPES calculations is incompletely identical with the one used in the geometry optimization,[13,14] thus the differences of the above results are easy to be understood. In detail, the GSUM method is not automatically done in OPT calculations in this SAC-CI Gaussian version[13,14] because it is difficult in general to say where is the unknown optimized geometry. Though after optimization, we can again do perturbation selection and repeat optimization by using freshly selected operators, the OPT method only does an additional single-point SAC-CI calculation.[13,14] This is why the result obtained by SPES calculations is quite integrated into the potential energy curve, and should be more reasonable.

Table 2. Dissociation energies (in eV) for $c^3\Sigma_g^+$, $B^1\Pi_u$ and $X^1\Sigma_g^+$ states at different basis sets.

state	D95(3df,3pd)	D95(d,p)	6-311G(3df,3pd)	6-311++G	6-311++G(3df,3pd)	AUG-cc-PVTZ	cc-PVTZ
$D_e c^3\Sigma_g^+$	0.8791	0.8233	0.8857	0.7795	0.8955	2.6483	0.8818
$B\ ^1\Pi_u$	0.3465	0.1606	0.3641	0.1255	0.3785	0.3665	0.3668
$X\ ^1\Sigma_g^+$	1.1163	1.0176	1.1044	0.9626	1.1103	1.1037	1.1105

Furthermore, we have calculated the dissociation energies for each involved state by using the selected basis sets listed in Table 1, and give our calculation results in Table 2. By comparing the dissociation energies and equilibrium geometries between theory and experiment,[15−18] we instantly find that the cc-PVTZ is a most suitable basis set for the $B^1\Pi_u$ state in full active space. It is easy to see that the calculation values for this state are in excellent agreement with the experiments.[16−18]

The cc-PVTZ and the D95(3df,3pd) almost give identical accuracy as to the $c^3\Sigma_g^+$ state. In detail, the cc-PVTZ set gives more accurate equilibrium geometry but slightly poorer dissociation energy, whereas the D95(3df,3pd) set gives more accurate dissociation energy but poorer equilibrium geometry. By detailed comparison, we finally determine to use the cc-PVTZ for further calculations.

3. Results and discussion

3.1. Potential energies and potential energy functions

Using the selected cc-PVTZ basis set,[19−21] we calculate the potential energy curves of the $c^3\Sigma_g^+$ and $B^1\Pi_u$ states in full active space over the internuclear separation range from about $2.5a_0$ to $37a_0$. The computed potential energies at selected values of the internuclear separation are tabulated in Tables 3 and 4 respectively. And the curves of the *ab initio* computed points over this range are shown in Figs.1 and 2, where the solid line are fitted by the Murrell–Sorbie (M-S) function[22]

$$V = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho). \quad (1)$$

Here $\rho = R - R_e$, R is the internuclear separation of the diatomics, and R_e is its equilibrium distance.

Table 3. Potential energies $E(R)$ at different internuclear separations R for the $c^3\Sigma_g^+$ state of dimer $^7Li_2$ at cc-PVTZ basis set.

R/a_0	$E(R)$/hartree	R/a_0	$E(R)$/hartree	R/a_0	$E(R)$/hartree	R/a_0	$E(R)$/hartree
2.44	−14.648755	7.44	−14.849974	15.84	−14.826418	24.84	−14.824002
3.04	−14.748422	8.04	−14.846684	16.64	−14.825942	26.04	−14.823901
3.64	−14.806544	8.64	−14.843486	17.44	−14.825557	27.24	−14.823817
4.24	−14.836387	9.44	−14.839628	18.24	−14.825243	28.44	−14.823747
4.84	−14.850095	10.24	−14.836362	19.04	−14.824984	29.64	−14.823688
5.24	−14.854139	11.04	−14.833705	19.84	−14.824769	30.84	−14.823638
5.64	−14.855726	11.84	−14.831605	20.64	−14.824589	32.04	−14.823596
5.84	−14.855880	12.64	−14.829976	21.44	−14.824438	33.04	−14.823565
6.04	−14.855718	13.44	−14.828725	22.24	−14.824309	34.04	−14.823538
6.44	−14.854691	14.24	−14.827761	23.04	−14.824199	35.04	−14.823513
6.84	−14.853042	15.04	−14.827012	23.84	−14.824104	37.04	−14.823492

Table 4. Potential energies $E(R)$ at different internuclear separations R for the $B^1\Pi_u$ state of dimer $^7Li_2$ at cc-PVTZ basis set.

R/a_0	$E(R)$/hartree	R/a_0	$E(R)$/hartree	R/a_0	$E(R)$/hartree	R/a_0	$E(R)$/hartree
2.54	−14.713798	6.54	−14.833283	11.74	−14.820749	21.94	−14.822633
3.14	−14.767856	7.14	−14.829964	12.14	−14.820835	23.34	−14.822660
3.74	−14.804472	7.94	−14.825911	12.74	−14.820998	24.74	−14.822790
4.34	−14.825169	8.74	−14.823089	13.54	−14.821237	26.14	−14.822844
4.74	−14.832175	9.54	−14.821521	14.54	−14.821532	27.54	−14.822889
5.14	−14.835564	10.14	−14.820952	15.54	−14.821790	29.14	−14.822930
5.34	−14.836284	10.54	−14.820769	16.54	−14.821993	30.54	−14.822959
5.54	−14.836514	10.94	−14.820694	17.54	−14.822164	32.14	−14.822986
5.74	−14.836351	11.14	−14.820687	18.94	−14.822355	34.14	−14.823013
6.14	−14.835171	11.34	−14.820695	20.34	−14.822503	37.14	−14.823035

By iterating a system of normal equations based on a least-squares fit, the parameters a_1, a_2 and a_3 of Eq.(1) have been calculated for $c^3\Sigma_g^+$ and $B^1\Pi_u$ states and tabulated in Table 5 together with the dissociation energies and the equilibrium internuclear separations for convenient comparison. By the way, we have also made the same calculations for the ground state, and made simple comparison with experimental data[16,23] and other theoretical results.[6,7,9]

From Table 5, we can easily see that the computed dissociation energy is in agreement with the experimental values[15−18] within 0.0024 eV or 0.273% for the $c^3\Sigma_g^+$ state, and within 0.0033 eV or 0.891% for the $B^1\Pi_u$ state, respectively. And the computed equilibrium internuclear distance is in accord with the experimental data[15−18] within 0.0022 nm or 0.717% for the $c^3\Sigma_g^+$ state, and 0.0004 nm or 0.136% for the $B^1\Pi_u$ state at the present SAC-CI/cc-PVTZ level of theory in full active space, respectively. Comparison of the theoretical determinations of the dissociation energies and the equilibrium internuclear distances with the previous theoretical results[6−12] clearly shows that the present work represents an improvement in agreement between theories and experiments. The dissociation energy given in Ref.[7] is equivalent to our result in accuracy for the $c^3\Sigma_g^+$ state, but inferior to our result for the $B^1\Pi_u$ state.

Table 5. Parameters of the analytical PEFs of the $c^3\Sigma_g^+$, $B^1\Pi_u$ and $X^1\Sigma_g^+$ states of dimer $^7Li_2$.

Dissociation limits	source	T_e/eV	R_e/nm	D_e/eV	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	
$Li_2(X^1\Sigma_g^+) \rightarrow Li(^2S_g) + Li(^2S_g)$	This work	0.000	0.2678	1.1105	17.470	75.669	119.37	
	Exp.[16]	0.000	0.2673	1.0561	—	—	—	
	Exp.[23]	0.000	—	1.0561	—	—	—	
	Theory[6]	0.000	0.2660	1.0552	—	—	—	
	Theory[7]	0.000	0.2675	1.0497	—	—	—	
	Theory[9]	0.000	0.2692	1.0288	—	—	—	
$Li_2(c^3\Sigma_g^+) \rightarrow Li(^2S_g) + Li(^2P_u)$	This work	2.029	0.3090	0.8818	9.1256	-4.785	41.637	
	Exp.[15]	2.002	0.3068	0.8794	—	—	—	
	Theory[6]	2.218	0.3055	0.8850	—	—	—	
	Theory[7]	2.025	0.3067	0.8768	—	—	—	
	Theory[8]	—-	0.3096	0.8446	—	—	—	
	Theory[9]	—-	0.3032	0.9071	—	—	—	
	Theory[10]	—-	0.3150	0.8308	—	—	—	
$Li_2(B^1\Pi_u) \rightarrow Li(^2S_g) + Li(^2P_u)$	This work	2.554	0.2932	0.3668	28.145	241.79	703.99	
	Exp.[16]	2.534	0.2936	0.3701	—	—	—	
	Exp.[17]	2.531	0.2936	0.3701	—	—	—	
	Exp.[18]	—-	0.2936	0.3701	—	—	—	
	Theory[6]	2.567	0.2939	0.3368	—	—	—	
	Theory[7]	2.542	0.2942	0.3560	—	—	—	
	Theory[9]	—-	0.2921	0.3218	—	—	—	
	Theory[10]	—-	0.3090	0.1612	—	—	—	
	Theory[11]	—-	0.2970	0.3026	—	—	—	
	Theory[12]	—-	0.3050	0.1969	—	—	—	

Figure 2 shows that the potential energy curve for the $B^1\Pi_u$ state of dimer $^7Li_2$ exhibits a long-range hump which protrudes above its energy asymptote. It has been known for a long time that this potential hump is caused by the long range repulsive dipole–dipole resonance interaction and the competing electron exchange interaction.[24−26] In order to see the details of this barrier clearly, the curve around the hump in Fig.2 over the internuclear distance range from about 0.45 to 1.95 nm is afresh shown in Fig.3. From Fig.3 we can clearly see that the potential hump maximum is located at 0.5895 nm, and its height is 0.064 eV, which is larger than recent experimental values[18,26] only by 0.002eV or 3.23%.

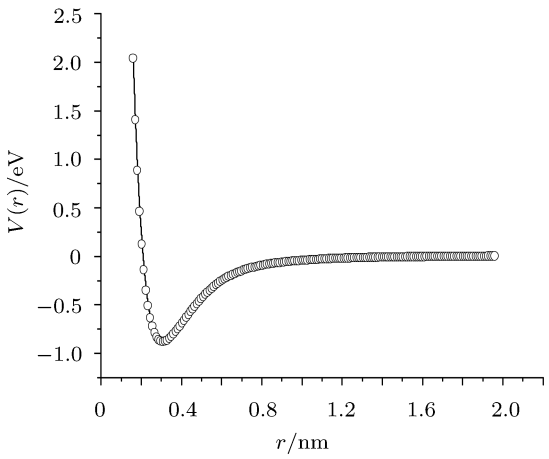


Fig.1. Potential energy curve of the third triplet excited state of dimer ^{7}Li, solid line: fitting results by M-S function; circle line: single-point energy scanning results.

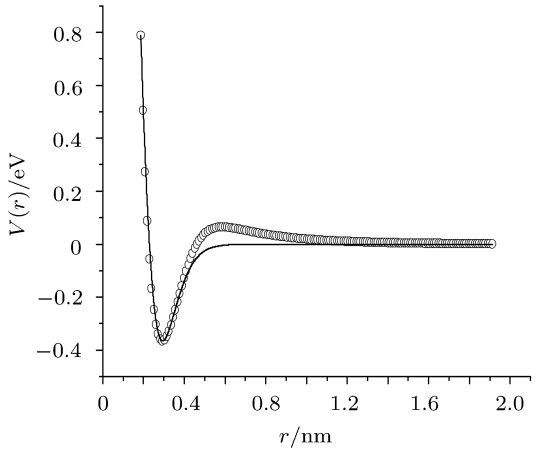


Fig.2. Potential energy curve of the second singlet excited state of dimer ^{7}Li, solid line: fitting results by M-S function; circle line: single-point energy scanning results.

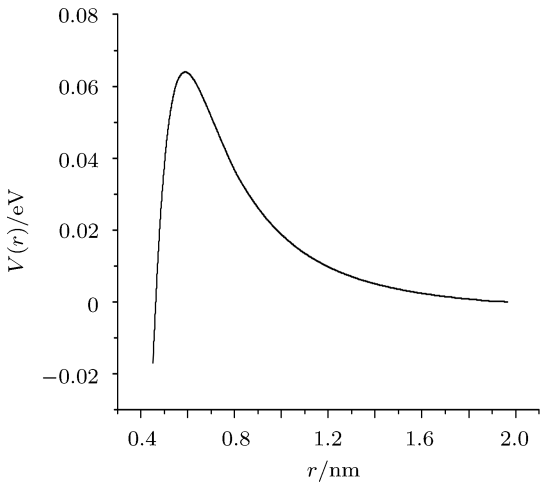


Fig.3. The detailed energy barrier of the second singlet excited state over the internuclear distance range from about 0.45 to 1.95 nm.

3.2. Harmonic frequencies obtained by analytic potential energy functions

Because the OPT calculations cannot give the accurate equilibrium internuclear distance for the $c^3\Sigma_g^+$ and $B^1\Pi_u$ states, we cannot obtain their accurate harmonic frequencies by OPT. But then, employing the analytic PEF given by Eq.(1), we can derive the expression of the force constant f_2 at the equilibrium position,

$$f_2 = D_e(a_1^2 - 2a_2). \tag{2}$$

The following relationship exists according to the Rydberg–Klein–Rees (RKR) method:

$$f_2 = 4\pi^2\omega_e^2\mu c^2. \tag{3}$$

Combining Eq.(2) and Eq.(3), we have

$$\omega_e = \left[\frac{D_e(a_1^2 - 2a_2)}{4\pi^2\mu c^2}\right]^{1/2}. \tag{4}$$

Here, μ is the reduced mass of $^7Li_2$ molecule, and ω_e is the harmonic frequency of the involved state. Employing the known state parameters listed in Table 5, we have calculated the ω_e values of these states and list the calculated results in Table 6.

From Table 6 we can easily see that the ω_e values derived from the calculated PEFs are larger than the experimental data[16] only by 0.37% for the $X^1\Sigma_g^+$ state and smaller than the experimental data[15] by 2.94% for the $c^3\Sigma_g^+$ state. It proves that our fitted PEFs are accurate. The derived ω_e value for the $B^1\Pi_u$ state is somewhat larger than the experimental data[16] since the present M-S analytic function form cannot correctly describe potentials with barriers which protrude above the potential asymptote.

3.3. Force constants and other spectroscopic data

Employing the analytic PEFs and the derived harmonic frequencies, we can easily calculate the force constants (f_2, f_3 and f_4) and the other spectroscopic data ($\omega_e\chi_e$, B_e and α_e) by using Eqs.(5)–(9). The calculated results are presented in Table 6. At the same time, we also carry out the same calculations on the ground state for convenient comparison with other measurements and theories.[6,7,16,27,28] The calculated results are presented in Table 6, also.

$$f_3 = -6D_e(a_3 - a_1a_2 + a_1^3/3)\,, \tag{5}$$

$$f_4 = D_e(3a_1^4 - 12a_1^2a_2 + 24a_1a_3), \tag{6}$$

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \tag{7}$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\Big(\frac{f_3R_e}{3f_2} + 1\Big), \tag{8}$$

$$\omega_e\chi_e = \frac{B_e}{8}\Big[-\frac{f_4R_e^2}{f_2} + 15\Big(1 + \frac{\omega_e\alpha_e}{6B_e^2}\Big)^2\Big]. \tag{9}$$

Table 6. Derived force constants and spectroscopic data of the $c^3\Sigma_g^+$, $B^1\Pi_u$ and $X^1\Sigma_g^+$ states of dimer $^7Li_2$ (1a J $= 10^{-18}$ J).

state	source	f_2/aJ·nm^{-2}	f_3/aJ·nm^{-3}	f_4/aJ·nm^{-4}	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	
$X^1\Sigma_g^+$	This work	27.375	−613.525		9316.261	352.7	2.984	0.670	0.0076
	Exp.[16]	—	—		—	351.4	2.578	0.673	0.0070
	Ref.[27]	—	—		—	351.4	2.610	0.673	0.0070
	Theory[6]	—	—		—	353.0	—	—	—
	Theory[7]	—	—		—	351.0	2.586	0.671	0.0068
	Theory[28]	—	—		—	352.5	2.50	0.675	0.0072
$c^3\Sigma_g^+$	This work	13.117	−287.043		4903.266	244.1	2.549	0.503	0.0078
	Exp.[15]	—	—		—	251.5	—	—	—
	Theory[6]	—	—		—	252.2	—	—	—
	Theory[7]	—	—		—	252.2	2.403	0.511	0.0077
	Theory[8]	—	—		—	245	2.2	—	—
	Theory[9]	—	—		—	256.2	2.24	—	—
	Theory[10]	—	—		—	229.4	—	—	—
$B^1\Pi_u$	This work	18.132	−469.034		3498.488	287.0	5.540	0.559	0.0099
	Exp.[16]	—	—		—	270.7	2.953	0.557	0.0083
	Theory[7]	—	—		—	270.3	2.944	0.555	0.0084
	Theory[9]	—	—		—	273.1	7.19	—	—
	Theory[10]	—	—		—	214.6	—	—	—
	Theory[11]	—	—		—	260	3.8	0.54	0.01
	Theory[12]	—	—		—	288	13	—	—

4. Conclusions

The PEFs of the $c^3\Sigma_g^+$ and $B^1\Pi_u$ states for dimer $^7Li_2$ have been calculated at the present SAC-CI/cc-PVTZ level of theory in full active space in the Gaussian 03 program package and have been used to compute the spectroscopic data and force constants. Favourable agreement is found in comparison with the experimental data. The results about the equilibrium internuclear distance and the dissociation energy obtained here are in better agreement than previous studies. The work described here is the most complete effort to deal with the PEFs, force constants and spectroscopic data, and thus represents an improvement over the previous theoretical results about the $c^3\Sigma_g^+$ and $B^1\Pi_u$ states for dimer $^7Li_2$. As a further investigation, we will employ our derived analytic PEFs to calculate the various cross sections,[29,30] especially at very low energies.[31]

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