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# *Ab initio* calculation on the analytic potential energy functions for the state $a^3\Sigma_u^+$ and the state $b^3\Pi_u$ of spin-aligned trimer $^7Li_2$*

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The energies, equilibrium geometries and harmonic frequencies of the triplet excited states ($a^3\Sigma_u^+$ and $b^3\Pi_u$) of spin-aligned trimer $^7Li_2$ are firstly calculated by using a symmetry adapted cluster-configuration interaction method. The potential curves for the two excited states have least squares fitted by the Murrell–Sorbie function. The spectroscopic data ($B_e$, $\alpha_e$, $\omega_e$, and $\omega_e\chi_e$) and the force constants ($f_2$, $f_3$ and $f_4$) are calculated. It is found that the spin-aligned triplet excited state $b^3\Pi_u$ is more stable than the ground state $X^1\Sigma_g^+$, and that the Murrell–Sorbie function form is suitable not only for the ground state but also for the spin-aligned triplet excited states. Comparison between the theoretical determinations of dissociation energies, equilibrium interatomic distances and harmonic frequencies with the experimental data about $a^3\Sigma_u^+$ and $b^3\Pi_u$ clearly shows that the present work represents a significant improvement in agreement between theories and experiments.

**Keywords:** molecular structure and potential function, atomic and molecular collision, trimer, spin-aligned excited state, Murrell-Sorbie function

**PACC:** 3410, 3420

## 1. Introduction

Potential energy function (PEF) plays a fundamental role in the understanding of collision processes between atoms and molecules[1] since the relatively slow nuclear motion is very sensitive to the details of the electronic PEF. In order to produce trustworthy dynamics, accurate PEF is always needed. Though PEF calculation for small molecules can be made by solving the electronic Schrödinger equation, the computation of a highly accurate PEF, especially a highly accurate PEF for excited states, is still a formidable task.

There are several methods for obtaining the PEF of a molecule, which avoid directly solving the electronic Schrödinger equation. In this paper, we are interested in the symmetry adapted cluster-configuration interaction (SAC-CI) method. The spin-aligned alkali metal trimer $^7Li_2$ is selected as target molecule, because, on the one hand, the alkali metal atom has only one valence electron in the $s$ orbital, on the other hand, with the discovery of Bose–Einstein condensation (BEC) in ultracold hydrogen,[2] lithium,[3] sodium[4] and rubidium,[5] these kinds of trimers have recently received a great deal of attention. In experiments, atomic densities are sufficiently low that two-body interactions dominate and BEC formation for $^7Li_2$ depends on the potential of the triplet excited states. But to the best of our knowledge, previous studies of spin-aligned states for $^7Li_2$ have been incomplete in some aspect, such as inadequate treatment of electron correlation, or considering only a small range of interaction distances. And most of the work done has been devoted to understanding the properties of the low energy elastic scattering and other features of two Li atoms of the lithium trimer.[6–21] The present work is the most complete effort dealing with the PEFs, force constants and spectroscopic data of the spin-aligned states for trimer $^7Li_2$

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and can be directly used in collision processes between atoms and molecules.[22,23]

In this paper, the energies, equilibrium geometries and harmonic frequencies of the triplet excited states ($a^3\Sigma_u^-$ and $b^1\Pi_u$) are calculated using the SAC-CI method in full active space. The work described here represents a significant improvement over previous theoretical results. Calculations have been carried out for a range of interatomic distances (0.15–1.3nm). In the next section, we describe in detail the dissociation limit of each involved electronic state. In Section 3, we present the calculated results for the PEFs, force constants and spectroscopic data, and make some useful discussion about each involved electronic state. Concluding remarks are made in Section 4.

## 2. Dissociation limits and electronic states

For trimer $^7Li_2$, the calculated results show that the ground and the first singlet excited states are $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$, and the first and the second triplet excited states are $a^3\Sigma_u^+$ and $b^3\Pi_u$ respectively.

For the calculations and description of full PEFs of diatomic molecules, first and foremost, we must determine the reasonable dissociation limits. If two Li atoms are in the ground state $^2S_g$, based on the group theory and atomic and molecular reaction statics,[24] the representation $^2S_g$ of the atomic group is resolved into those of $D_{\infty h}(Li_2)$ as follows:

$$^2S_g \rightarrow {}^2\Sigma_g^+. \tag{1}$$

Their direct product and its reduction are

$$^2\Sigma_g^+ \otimes {}^2\Sigma_g^+ \rightarrow {}^1\Sigma_g^+ \oplus {}^3\Sigma_u^+. \tag{2}$$

We can see that Eq.(2) contains $^1\Sigma_g^+$ and $^3\Sigma_u^+$. According to the principle of reversibility for the microscopic process,[24] the dissociation limits for $Li_2(X^1\Sigma_g^+)$ and $Li_2(a^3\Sigma_u^+)$ are

$$Li_2(X^1\Sigma_g^+) \rightarrow Li(^2S_g) + Li(^2S_g), \tag{3}$$

$$Li_2(a^3\Sigma_u^+) \rightarrow Li(^2S_g) + Li(^2S_g). \tag{4}$$

When one of two Li atoms is in the excited state, or two Li atoms are both in the excited states, we can also derive $X^1\Sigma_g^+$ and $a^3\Sigma_u^+$, but their dissociation energies must be higher than the ones of channels (3) and (4). So, according to the principle of the optimum energy dissociation,[24] only channel (3) is the most optimal for $X^1\Sigma_g^+$ and channel (4) is the most optimal for $a^3\Sigma_u^+$.

When one Li atom is in the ground state $^2S_g$ and the other in the first excited state $^2P_u$, based on the above-mentioned reason, the representation $^2P_u$ of the atomic group is resolved into those of $D_{\infty h}(Li_2)$ as follows

$$^2P_u \rightarrow {}^2\Sigma_u^+ \oplus {}^2\Pi_u. \tag{5}$$

Their direct product and its reduction are

$$^2\Sigma_g^+ \otimes ({}^2\Sigma_u^+ \oplus {}^2\Pi_u) \rightarrow {}^1\Sigma_u^+ \oplus {}^3\Sigma_u^+ \oplus {}^1\Pi_u \oplus {}^3\Pi_u. \tag{6}$$

According to the principle of reversibility for the microscopic process and the principle of the optimum energy dissociation,[24] we conclude that the most optimal dissociation processes for $A^1\Sigma_u^+$ and $b^3\Pi_u$ are

$$Li_2(b^3\Pi_u) \rightarrow Li(^2S_g) + Li(^2P_u), \tag{7}$$

$$Li_2(A^1\Sigma_u^+) \rightarrow Li(^2S_g) + Li(^2P_u). \tag{8}$$

## 3. Results and discussion

The calculations described here are carried out in Gaussian 03 program. Firstly, by comparing the optimized energies, equilibrium geometries and harmonic frequencies of the first and the second triplet excited states between theories and experiments, we select D95(d) basis for further calculations. Then, using the selected D95(d) basis, we calculate the potential energy curves of spin-aligned $Li_2(a^3\Sigma_u^+)$ and $Li_2(b^3\Pi_u)$. These curves of *ab initio* calculated points are shown in Figs.1, 2, where the solid lines are fitted by the Murrell–Sorbie function[26]

$$V = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho), \tag{9}$$

where $\rho = R - R_e$, $R$ is the interatomic distance of the two atoms, and $R_e$ is its equilibrium distance.

By iterating a system of normal equations based on a least-squares fit, the parameters $a_1$, $a_2$ and $a_3$ of Eq.(9) have been calculated for spin-aligned states $a^3\Sigma_u^+$ and $b^3\Pi_u$ and listed in Table 1 together with the dissociation energies and the equilibrium interatomic distances. From these we can easily calculate the force constants ($f_2$, $f_3$ and $f_4$), and then calculate the spectroscopic data ($\omega_e$, $\omega_e\chi_e$, $B_e$ and $\alpha_e$) of each involved electronic state using Eqs.(10)–(15). The calculated results are listed in Table 2. At the same time, we also carry out the same calculations for the ground state $X^1\Sigma_g^+$ and the first singlet excited state $A^1\Sigma_u^+$ under the same conditions for comparison. These calculated results are listed in Tables 1 and 2:

$$f_2 = D_e(a_1^2 - 2a_2), \tag{10}$$

$$f_3 = -6D_e(a_3 - a_1a_2 + a_1^3/3), \tag{11}$$

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

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \tag{13}$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(\frac{f_3R_e}{3f_2} + 1\right), \tag{14}$$

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

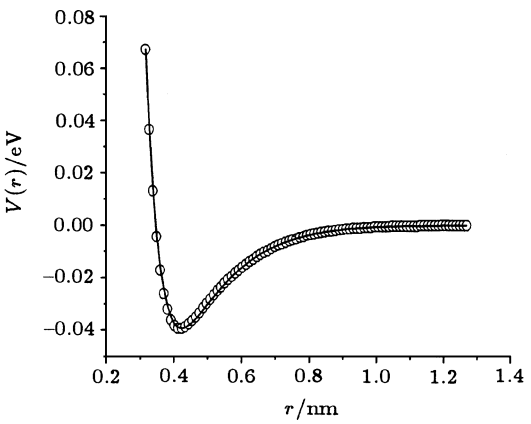



**Fig.1.** Potential energy curve of the first triplet excited state of trimer $Li_2$. solid line: curve fitted by Murrell–Sorbie function; circle line: single-point energy scanning results.

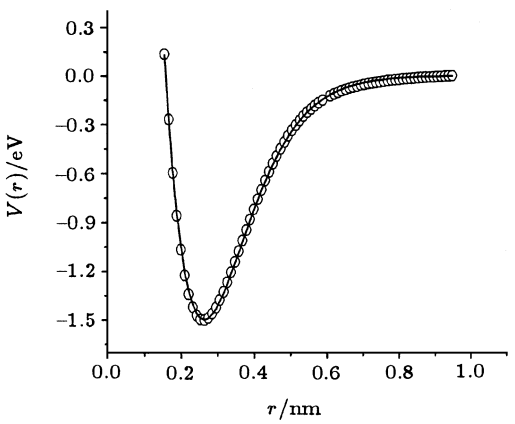



**Fig.2.** Potential energy curve of the second triplet excited state of trimer $Li_2$. solid line: curve fitted by Murrell–Sorbie function; circle line: single-point energy scanning results.

**Table 1.** Parameters of the analytical potential function (8) of the ground state $X^1\Sigma_g^+$, the first singlet excited state $A^1\Sigma_u^+$, the spin-aligned excited states $a^3\Sigma_u^+$ and $b^3\Pi_u$.

| Dissociation limits | source | $T_e$/ eV | $R_e$/nm | $D_e$/eV | $a_1/\mathrm{nm}^{-1}$ | $a_2/\mathrm{nm}^{-2}$ | $a_3/\mathrm{nm}^{-3}$ |
|---|---|---|---|---|---|---|---|
| $Li_2(X^1\Sigma_g^+) \rightarrow Li(^2S_g) + Li(^2S_g)$ | This work | 0.00 | 0.269 | 1.034 | 20.166 | 116.61 | 236.50 |
| | Ref.[25] | 0.00 | 0.267 | 1.059 | — | — | — |
| | Theory[16] | 0.00 | 0.270 | 0.992 | — | — | — |
| | Theory[21] | 0.00 | 0.266 | 1.055 | — | — | — |
| $Li_2(A^1\Sigma_u^+) \rightarrow Li(^2S_g) + Li(^2P_u)$ | This work | 1.56 | 0.315 | 1.100 | 13.422 | 48.84 | 75.70 |
| | Ref.[25] | 1.74 | 0.311 | 1.109 | — | — | — |
| | Theory[18] | — | 0.307 | 1.200 | — | — | — |
| $Li_2(a^3\Sigma_u^+) \rightarrow Li(^2S_g) + Li(^2S_g)$ | This work | 1.016 | 0.418 | 0.0411 | 13.202 | 9.892 | 114.08 |
| | Exp.[12] | 1.015 | 0.417 | 0.0413 | — | — | — |
| | Exp.[17] | — | 0.417 | 0.0414 | — | — | — |
| | Theory[9] | — | 0.405 | 0.0379 | — | — | — |
| | Theory[11] | — | 0.419 | 0.0324 | — | — | — |
| | Theory[18] | — | 0.407 | 0.0439 | — | — | — |
| | Theory[19] | — | 0.411 | 0.0422 | — | — | — |
| $Li_2(b^3\Pi_u) \rightarrow Li(^2S_g) + Li(^2P_u)$ | This work | 1.395 | 0.258 | 1.501 | 16.439 | 83.055 | 173.39 |
| | Exp.[20] | — | 0.259 | 1.505 | — | — | — |
| | Theory[6] | — | 0.263 | 1.424 | — | — | — |
| | Theory[21] | 1.393 | 0.258 | 1.510 | — | — | — |

**Table 2.** Derived force constants and spectroscopic data of the ground state $X^1\Sigma_g^+$, the first singlet excited state $A^1\Sigma_u^+$, the spin-aligned excited states $a^3\Sigma_u^+$ and $b^3\Pi_u$(1aJ=$10^{-18}$J).

| state | source | $f_2$/aJ·nm$^{-2}$ | $f_3$/ aJ·nm$^{-3}$ | $f_4$/aJ·nm$^{-4}$ | $\omega_e$/cm$^{-1}$ | $\omega_e\chi_e$/cm$^{-1}$ | $B_e$/cm$^{-1}$ | $\alpha_e$/cm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| $X^1\Sigma_g^+$ | This work | 28.734 | –614.83 | 6881.7 | 361.3 | 3.36 | 0.659 | 0.007 |
| | Ref.[25] | — | — | — | 351.4 | 2.58 | 0.672 | 0.007 |
| | Theory[16] | — | — | — | 365.8 | — | — | — |
| $A^1\Sigma_u^+$ | This work | 14.535 | –239.15 | 2848.9 | 269.7 | 1.67 | 0.482 | 0.004 |
| | Ref.[25] | — | — | — | 255.4 | 1.58 | 0.498 | 0.005 |
| | Theory[18] | — | — | — | 261.3 | 1.77 | — | — |
| $a^3\Sigma_u^+$ | This work | 1.017 | –29.652 | 701.899 | 65.8 | 2.66 | 0.274 | 0.018 |
| | Exp.[12] | — | — | — | 65.13 | 3.26 | — | — |
| | Theory[9] | — | — | — | 75.0 | — | — | — |
| | Theory[11] | — | — | — | 64.92 | — | — | — |
| | Theory[18] | — | — | — | 66.4 | 3.11 | — | — |
| | Theory[19] | — | — | — | 65.6 | 3.16 | — | — |
| $b^3\Pi_u$ | This work | 25.042 | –416.84 | 4367.8 | 344.3 | 1.72 | 0.721 | 0.0059 |
| | Exp.[20] | — | — | — | 345.6 | 1.89 | 0.716 | 0.006 |
| | Theory[6] | — | — | — | 339.0 | 2.5 | — | — |
| | Theory[21] | — | — | — | 348.7 | — | — | — |

From Table 1 we easily see that the dissociation energies and equilibrium interatomic distances derived from the calculated potential curves shown in Figs.1, 2 are in excellent agreement with recent experimental data obtained by Linton *et al*[12,17] for $a^3\Sigma_u^+$, and Engelke and Hage[20] for $b^3\Pi_u$ of trimer $^7Li_2$. From Table 2 we also easily see that the spectroscopic data are in good agreement with the experiments.[12,20] Comparison of the theoretical determinations of the dissociation energies, the equilibrium interatomic distances and the harmonic frequencies with the experimental data clearly show that the present work represents a significant improvement in agreement between theories and experiments. At the SAC-CI/D95(d) level of theory in full active space, the predicted dissociation energies are in agreement with the experimentally determined values within 0.0003eV for $a^3\Sigma_u^+$[12,17] and 0.004eV for $b^3\Pi_u$,[20] and the predicted equilibrium interatomic distances are in accord with the experimentally determined data within 0.001nm for $a^3\Sigma_u^+$[12,17] and 0.001nm for $b^3\Pi_u$,[20] respectively.

Generally, a molecule such as trimer $^7Li_2(a^3\Sigma_u^+)$, in which equilibrium interatomic distance is large, is often fitted by the asymptotic Van der Waals potential. However, from Fig.1 we clearly see that the solid curve fitted by the Murrell–Sorbie function coincides very well with the dotted one obtained by *ab initio* calculations. This proves that the Murrell–Sorbie function is suitable for the fitting of the first triplet excited state $a^3\Sigma_u^+$ of trimer $^7Li_2$, though $^7Li_2(a^3\Sigma_u^+)$ looks like a Van de Waals molecule, and the Murrell–Sorbie function is often employed to fit the function of the ground state.

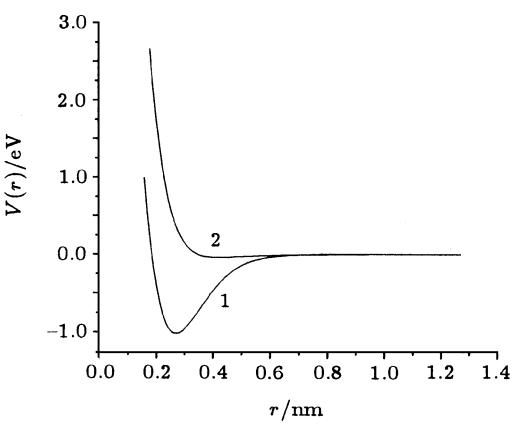



**Fig.3.** Comparison between the ground state and the first triplet excited state of trimer $Li_2$. 1: the ground state; 2: the first triplet excited state.

For convenient analyses, we plot the potential curves of the ground and the first triplet excited states, and the potential curves of the first singlet and the second triplet excited states in Fig.3 and Fig.4 respectively. From Fig.3 and Fig.4, we clearly see that the ground state and the first triplet excited state have same dissociation limit, which is consistent with Eqs.(3) and (4), and that the first singlet and the second triplet excited states have same dissociation limit, which is consistent with Eqs.(7) and (8). These prove that the dissociation limit analyses about the states $X^1\Sigma_g^+$, $A^1\Sigma_u^+$, $a^3\Sigma_u^+$ and $b^3\Pi_u$ are correct and vice versa.

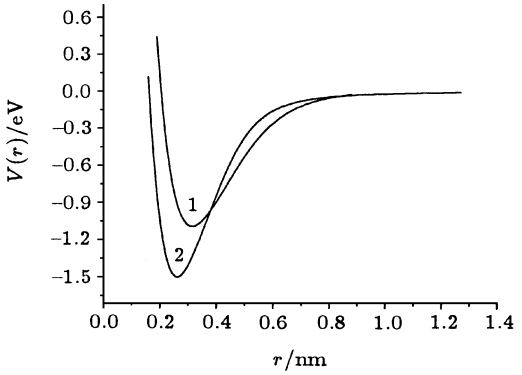



**Fig.4.** Comparison between the first singlet excited state and the second triplet excited state of trimer $Li_2$. 1: the first singlet excited state; 2: the second triplet excited state.

Table 1 shows that the dissociation energy about the state $b^3\Pi_u$ equals 1.501eV, which is higher than that of the ground state, and the equilibrium interatomic distance is 0.258nm, which is shorter than that of the ground state. These values prove that the second triplet excited state $b^3\Pi_u$ is more stable than the ground state $X^1\Sigma_g^+$.

# 4. Conclusion

The potential functions of the first and the second triplet excited states ($a^3\Sigma_u^+$ and $b^3\Pi_u$) for trimer $^7Li_2$ have been calculated at SAC-CI/D95(d) level of theory in full active space and have been used to compute the spectroscopic data and force constants. Favourable agreement is found in comparing with the experimental data. The results obtained here are more competent and in better agreement than previous studies. Also, the Murrell–Sorbie function is found to be well employed to fit the first and the second triplet excited states ($a^3\Sigma_u^+$ and $b^3\Pi_u$), including the first singlet excited state $A^1\Sigma_u^+$.

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