

Calculation of adiabatic potentials of Li₂

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Abstract

We report adiabatic potential energy curves of the lithium dimer. Our curves are tabulated according to internuclear distance from $3.2a_0$ to $88a_0$. We compare our theoretical results with the ones calculated by other authors and potential energy curves derived from experiments. In our approach we use the configuration interaction method where only the valence electrons of Li atom are treated explicitly. The core electrons are represented by pseudopotential. All calculations are performed by means of MOLPRO program package.

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1. Introduction

The lithium dimer has attracted attention of experimentalists and theoreticians for many years, mainly because it is the second, just after the molecular hydrogen, smallest stable homonuclear molecule. It can serve as a convenient prototype for testing theoretical methods, which can be further applied to heavier alkali dimers. The first ab initio calculations on Li₂ were performed by Konowalow and co-workers [1–5], including the work of Konowalow and Fish [5] where they computed and analyzed the potential energy curves in the long-range region of the 26 lowest lying states. They accounted for atomic polarizabilities in order to describe the atomic multiple interaction and the molecular valence-shell polarization. By using the atomic effective-core potential (ECP) and high quality basis set they were able to perform self-consistent-field (SCF) and configuration-interaction (CI) calculations. Obtained results allowed for valuable comparisons with experimental spectroscopic

data of He et al. [6]. Nevertheless, as discussed by Müller and Mayer [7] the usage by Konowalow and co-workers of the originally atomic ECP leads to defect of an unbalanced treatment of core polarization effects in molecule since it lacks electron–other core polarization contributions. Next, Schmidt-Mink et al. [8] performed SCF/valence CI calculation where they implemented the effective potential to reduce the above defect. In this approach, they employed the technique of self-consistent electron pairs (SCEP) to simultaneously optimize several electronic states, combined with a core polarization potential (CPP) for an efficient treatment of inter-shell correlation effect. Their results also achieved very good agreement with experimental data of He et al. [6]. In turn, Poteau and Spiegelmann [9] reported results for 49 states obtained by calculations, where effective core pseudopotentials and *l*-dependent core polarization potentials were employed. Recently, Song et al. [10] studied both theoretically and experimentally the $5^1\Sigma_g^+$ and $6^1\Sigma_g^+$ Rydberg states. Several spectroscopic studies of lithium dimer were repeated. These include analysis of the $1^1\Sigma_u^+ - 1^1\Sigma_g^+$ band system [11], near infrared two-photon laser spectroscopy of the $2^1\Sigma_g^+$ state [6], ultrafast spectroscopy of wavelength-dependent coherent photoionization in the $5^1\Sigma_g^+$ state [12], state to state

collision energy transfer in singlet state [13] and observation of predissociation in the $2^1\Pi_u$ state in the $^6\text{Li}^7\text{Li}$ isotopomer [14]. Quite recently need for theoretical description of long range potential curves has been caused by molecular photoassociative spectroscopy of cold alkali atoms [15]. Two-photon photoassociation of colliding ultracold lithium atoms was used by Abraham et al. [16] to probe the lowest triplet state $1^3\Sigma_u^+$ of Li_2 in order to determine the scattering lengths necessary to predict the Bose–Einstein condensate (BEC). Also photoassociative spectroscopy was used to obtain high-lying vibrational levels of $1^1\Sigma_u^+$ and $1^3\Sigma_g^+$ states [17] and the intensity dependent rate and shift of a transition in a quantum degenerate gas [18]. Very recently our motivation to calculate the potential curves of highly excited states of the lithium dimer was strengthened by Johim et al. [19] who reported on the BEC of more than 10^5 Li_2 molecules in an optical dipole trap and Chin et al. [20] who studied fermionic pairing in an ultracold two-component degenerate gas of lithium atoms by observing a pairing gap in radio-frequency excitation spectra. The experimentally observed states can be characterized by their potential curves which may serve for direct comparison with theoretical curves. For instance, the application of Doppler-free UV–visible optical–optical double resonance polarization spectroscopy allowed for determination of $2^1\Sigma_u^+$ and $C^1\Pi_u$ states [21]. Quite recently, Jastrzębski et al. [22] and Pashov et al. [23] reported potential curves for the $3^1\Sigma_g^+$ and $4^1\Sigma_g^+$ states. They used the inverted perturbation approach (IPA) developed by Pashov et al. [24]. In turn, Bouloufa et al. [25] constructed the potential energy curve for the $1^1\Pi_u$ state by combining a short-range potential obtained by direct fit of accurate spectroscopic measurements with a long-range potential generated by asymptotic calculation of Coulombic and exchange energies. Our present calculations are based on the self-consistent-field configuration interaction (SCF CI) scheme. We use a substantially richer basis set than in our first report [26]. The present calculation also use the ECP which enables us to provide high lying adiabatic potential curves not calculated in previous theoretical approaches.

2. Theoretical method

We consider the interaction between two alkali atoms. Let \mathbf{R} be the separation between the nuclei of these atoms. In the Born–Oppenheimer approximation we seek for the solutions of the Schrödinger equation

$$H\Psi_i(\mathbf{r}, \mathbf{R}) = E_i(R)\Psi_i(\mathbf{r}, \mathbf{R}), \quad (1)$$

where H is the Hamiltonian of a diatomic system, $E_i(R)$ is the i -th adiabatic energy and $\Psi_i(\mathbf{r}, \mathbf{R})$ describes the state of the system related to this energy, \mathbf{r} represents the electronic coordinates and \mathbf{R} is the relative position of the first atom to the second one. The Hamiltonian of the system can be written as

$$H = H_A + H_B + V_{AB}, \quad (2)$$

where H_A and H_B are the Hamiltonians of the isolated atoms and V_{AB} is the interaction between them. In the present approach only the valence electrons are treated explicitly, but the atomic cores are represented by l -dependent pseudopotentials. Consequently the total Hamiltonian in Eqs. (1), (2) can be expressed as

$$H = T + V, \quad (3)$$

where T stands for the kinetic energy operator of the valence electrons and V represents the interaction operator. The latter is put into the form

$$V = \sum_{\lambda} (V^{\lambda} + V_{\text{pol}}^{\lambda}) + \sum_{j>l=1}^N \frac{1}{r_{ij}} + V_{\text{cc}}. \quad (4)$$

Here V^{λ} describes Coulomb and exchange interaction as well as the Pauli repulsion between the valence electrons and core λ and is defined as

$$V^{\lambda} = \sum_{i=1}^N -\frac{Q_{\lambda}}{r_{\lambda i}} + \sum_{lk} B_{lk}^{\lambda} \exp(-\beta_{lk}^{\lambda} r_{\lambda i}^2) P_l^i, \quad (5)$$

where $Q_{\lambda} = 1$ denotes the net charge of lithium core λ , P_l^i is the projection operator onto the Hilbert subspace of angular symmetry l with respect to the Li^+ -core and N is the number of the valence electrons. The parameters B_{lk}^{λ} and β_{lk}^{λ} define the semi-local energy-consistent pseudopotentials. The second interaction term in Eq. (4) is the polarization term which describes, among others, core–valence correlation effects [20] and, in the case of atom A, is taken as

$$V_{\text{pol}}^A = -\frac{1}{2} \alpha_A \mathbf{F}_A^2, \quad (6)$$

where $\alpha_A = 0.1915a_0$ [27] is the dipole polarizability of the A^+ core and \mathbf{F}_A is the electric field generated at its site by the valence electrons and the other core. The latter can be written as

$$\mathbf{F}_A = \sum_i \frac{\mathbf{r}_{Ai}}{r_{Ai}^3} [1 - \exp(-\delta_A r_{Ai}^2)] - \frac{Q_B \mathbf{R}}{R^3} [1 - \exp(-\delta_A R^2)], \quad (7)$$

where $\delta_A = 0.831a_0^{-2}$ [27] is the cutoff parameter. The third term in Eq. (4) represents the Coulomb repulsion between the valence electrons, whereas the last term describes the core–core interaction. Since the alkali atoms cores are well separated, we choose a simple point–charge Coulomb interaction in the latter case. Detailed formulas are given in the papers of Czuchaj and co-workers [28–33].

Table 1
Comparison of asymptotic energies with other theoretical and experimental results

| | Present work | Schmidt-Mink [8] | Poteau [9] | Bashkin [39] |
|---------|--------------|------------------|------------|--------------|
| 2s + 2p | 14911 | 14924 | 14904 | 14904 |
| 2s + 3s | 27201 | 27209 | 27212 | 27206 |
| 2p + 2p | 29822 | 29876 | – | 29808 |
| 2s + 3p | 30931 | 30934 | 30927 | 30925 |

Energies are shown in cm^{-1} units.

Table 2

The Li₂ molecule adiabatic potential energy curves for $1^1\Sigma_g^+$, $2^1\Sigma_g^+$, $3^1\Sigma_g^+$, $4^1\Sigma_g^+$, $1^1\Sigma_u^+$, $2^1\Sigma_u^+$ and $3^1\Sigma_u^+$ states

| $R(a_0)$ | $1^1\Sigma_g^+$ | $2^1\Sigma_g^+$ | $3^1\Sigma_g^+$ | $4^1\Sigma_g^+$ | $1^1\Sigma_u^+$ | $2^1\Sigma_u^+$ | $3^1\Sigma_u^+$ |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 3.20 | 3152.98 | 30025.64 | 36910.79 | 38600.08 | 23805.44 | 40291.92 | 45645.37 |
| 3.40 | 113.42 | 26708.38 | 33099.65 | 35351.71 | 19921.24 | 36302.24 | 41591.55 |
| 3.60 | -2360.41 | 23815.65 | 29908.77 | 33081.52 | 16686.71 | 32977.51 | 38214.89 |
| 3.80 | -4319.57 | 21350.95 | 27280.51 | 31283.14 | 14031.58 | 30250.43 | 35445.64 |
| 4.00 | -5825.09 | 19290.59 | 25147.36 | 29559.44 | 11878.69 | 28043.92 | 33204.93 |
| 4.20 | -6940.40 | 17594.63 | 23440.98 | 27802.53 | 10154.24 | 26282.04 | 31415.18 |
| 4.40 | -7 725.27 | 16217.03 | 22097.39 | 26395.05 | 8792.34 | 24895.49 | 30005.55 |
| 4.60 | -8234.16 | 15111.26 | 21059.21 | 25275.40 | 7734.62 | 23823.01 | 28913.55 |
| 4.80 | -8515.69 | 14233.49 | 20276.19 | 24388.85 | 6930.38 | 23011.62 | 28085.09 |
| 5.00 | -8612.28 | 13544.32 | 19704.92 | 23687.39 | 6336.43 | 22416.30 | 27473.47 |
| 5.20 | -8560.29 | 13009.42 | 19308.30 | 23129.82 | 5916.51 | 21999.21 | 27035.66 |
| 5.40 | -8390.55 | 12599.50 | 19054.76 | 22682.32 | 5640.35 | 21728.76 | 26710.54 |
| 5.60 | -8129.00 | 12289.97 | 18917.43 | 22319.40 | 5482.83 | 21578.71 | 26423.57 |
| 5.80 | -7797.39 | 12060.44 | 18873.29 | 22024.42 | 5423.09 | 21527.25 | 26203.19 |
| 6.00 | -7413.95 | 11894.19 | 18902.28 | 21788.77 | 5443.79 | 21556.19 | 26053.22 |
| 6.20 | -6994.00 | 11777.77 | 18986.63 | 21609.86 | 5530.44 | 21650.18 | 25958.83 |
| 6.40 | -6550.41 | 11700.50 | 19110.35 | 21488.64 | 5670.92 | 21796.22 | 25903.36 |
| 6.60 | -6094.00 | 11654.19 | 19259.04 | 21427.35 | 5855.04 | 21983.12 | 25869.93 |
| 6.80 | -5633.86 | 11632.74 | 19420.33 | 21427.67 | 6074.28 | 22201.13 | 25841.35 |
| 7.00 | -5177.55 | 11631.90 | 19584.69 | 21489.02 | 6321.42 | 22441.53 | 25800.41 |
| 7.25 | -4621.95 | 11655.68 | 19786.12 | 21644.86 | 6660.47 | 22760.95 | 25708.88 |
| 7.50 | -4091.69 | 11704.33 | 19980.75 | 21873.31 | 7023.90 | 23085.33 | 25558.10 |
| 7.75 | -3593.92 | 11776.54 | 20170.75 | 22153.53 | 7403.70 | 23391.57 | 25360.50 |
| 8.00 | -3133.66 | 11871.87 | 20358.27 | 22465.18 | 7793.30 | 23638.05 | 25168.37 |
| 8.25 | -2713.92 | 11990.01 | 20542.62 | 22791.55 | 8187.28 | 23748.75 | 25077.64 |
| 8.50 | -2336.04 | 12130.31 | 20720.04 | 23120.19 | 8581.13 | 23668.09 | 25161.95 |
| 8.75 | -1999.86 | 12291.43 | 20884.64 | 23442.59 | 8971.14 | 23456.53 | 25373.24 |
| 9.00 | -1704.02 | 12471.31 | 21029.85 | 23753.80 | 9354.22 | 23198.46 | 25634.13 |
| 9.50 | -1223.52 | 12875.55 | 21240.84 | 24338.50 | 10089.61 | 22693.47 | 26164.63 |
| 10.00 | -869.96 | 13314.59 | 21337.98 | 24886.61 | 10771.22 | 22284.85 | 26626.13 |
| 10.50 | -615.93 | 13756.34 | 21355.05 | 25417.22 | 11388.01 | 21998.86 | 26988.21 |
| 11.00 | -436.27 | 14170.58 | 21350.53 | 25930.29 | 11933.40 | 21836.14 | 27251.50 |
| 11.50 | -310.36 | 14533.24 | 21375.63 | 26407.47 | 12405.03 | 21788.15 | 27432.13 |
| 12.00 | -222.46 | 14829.31 | 21461.25 | 26822.23 | 12804.56 | 21842.02 | 27551.08 |
| 12.50 | -161.08 | 15054.13 | 21618.56 | 27148.37 | 13137.09 | 21982.53 | 27627.17 |
| 13.00 | -118.08 | 15212.27 | 21844.20 | 27373.47 | 13410.12 | 22193.45 | 27674.38 |
| 13.50 | -87.76 | 15314.24 | 22126.37 | 27510.51 | 13632.32 | 22458.78 | 27702.26 |
| 14.00 | -66.21 | 15372.76 | 22450.24 | 27587.01 | 13812.42 | 22763.65 | 27717.05 |
| 14.50 | -50.70 | 15399.83 | 22801.54 | 27626.90 | 13958.49 | 23095.07 | 27722.89 |
| 15.00 | -39.41 | 15405.41 | 23168.32 | 27645.62 | 14077.49 | 23442.27 | 27722.72 |
| 16.00 | -24.77 | 15380.14 | 23913.39 | 27652.98 | 14256.23 | 24151.54 | 27712.76 |
| 17.00 | -16.31 | 15334.30 | 24636.13 | 27649.11 | 14381.82 | 24843.40 | 27701.26 |
| 18.00 | -11.14 | 15284.80 | 25308.41 | 27654.44 | 14473.99 | 25487.80 | 27701.50 |
| 19.00 | -7.84 | 15238.37 | 25908.46 | 27687.70 | 14544.17 | 26059.95 | 27731.69 |
| 20.00 | -5.65 | 15197.18 | 26407.30 | 27777.87 | 14599.15 | 26527.49 | 27823.15 |
| 22.00 | -3.11 | 15130.94 | 26970.36 | 28265.30 | 14679.00 | 27026.23 | 28320.66 |
| 24.00 | -1.82 | 15082.47 | 27123.67 | 29004.87 | 14733.24 | 27150.08 | 29050.11 |
| 26.00 | -1.42 | 15063.32 | 27150.98 | 29370.28 | 14771.65 | 27181.42 | 29747.75 |
| 28.00 | -0.72 | 15020.30 | 27182.53 | 29811.97 | 14799.70 | 27191.52 | 30346.21 |
| 30.00 | -0.48 | 15000.18 | 27189.78 | 29815.96 | 14820.67 | 27195.55 | 30766.47 |
| 32.00 | -0.33 | 14984.68 | 27193.64 | 29818.17 | 14836.68 | 27197.49 | 30896.14 |
| 34.00 | -0.24 | 14972.55 | 27195.91 | 29819.52 | 14849.12 | 27198.56 | 30919.88 |
| 36.00 | -0.17 | 14962.94 | 27197.35 | 29820.37 | 14858.93 | 27199.21 | 30926.13 |
| 38.00 | -0.13 | 14955.23 | 27198.30 | 29820.94 | 14866.77 | 27199.64 | 30928.35 |
| 40.00 | -0.10 | 14948.97 | 27198.95 | 29821.33 | 14873.12 | 27199.93 | 30929.36 |
| 42.00 | -0.08 | 14943.84 | 27199.41 | 29821.59 | 14878.31 | 27200.13 | 30929.92 |
| 44.00 | -0.07 | 14939.60 | 27199.74 | 29821.78 | 14882.60 | 27200.28 | 30930.26 |
| 46.00 | -0.06 | 14936.06 | 27199.98 | 29821.92 | 14886.17 | 27200.39 | 30930.49 |
| 48.00 | -0.05 | 14933.08 | 27200.15 | 29822.02 | 14889.17 | 27200.47 | 30930.66 |
| 50.00 | -0.05 | 14930.56 | 27200.28 | 29822.10 | 14891.71 | 27200.54 | 30930.78 |
| 52.00 | -0.04 | 14928.41 | 27200.39 | 29822.15 | 14893.87 | 27200.59 | 30930.87 |
| 54.00 | -0.04 | 14926.57 | 27200.46 | 29822.19 | 14895.72 | 27200.62 | 30930.94 |
| 56.00 | -0.03 | 14924.98 | 27200.52 | 29822.22 | 14897.32 | 27200.65 | 30931.00 |
| 58.00 | -0.03 | 14923.60 | 27200.57 | 29822.25 | 14898.70 | 27200.67 | 30931.04 |

(continued on next page)

Table 2 (continued)

| $R(a_0)$ | $1^1\Sigma_g^+$ | $2^1\Sigma_g^+$ | $3^1\Sigma_g^+$ | $4^1\Sigma_g^+$ | $1^1\Sigma_u^+$ | $2^1\Sigma_u^+$ | $3^1\Sigma_u^+$ |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 60.00 | -0.03 | 14922.40 | 27200.61 | 29822.27 | 14899.91 | 27200.69 | 30931.07 |
| 62.00 | -0.03 | 14921.35 | 27200.64 | 29822.29 | 14900.97 | 27200.70 | 30931.10 |
| 64.00 | -0.03 | 14920.42 | 27200.66 | 29822.30 | 14901.89 | 27200.71 | 30931.11 |
| 66.00 | -0.03 | 14919.61 | 27200.68 | 29822.31 | 14902.71 | 27200.72 | 30931.13 |
| 68.00 | -0.03 | 14918.89 | 27200.69 | 29822.32 | 14903.44 | 27200.73 | 30931.14 |
| 70.00 | -0.03 | 14918.24 | 27200.70 | 29822.33 | 14904.08 | 27200.73 | 30931.15 |
| 72.00 | -0.03 | 14917.67 | 27200.71 | 29822.37 | 14904.65 | 27200.74 | 30931.16 |
| 74.00 | -0.03 | 14917.16 | 27200.72 | 29822.37 | 14905.17 | 27200.74 | 30931.17 |
| 76.00 | -0.03 | 14916.70 | 27200.72 | 29822.37 | 14905.63 | 27200.75 | 30931.17 |
| 78.00 | -0.03 | 14916.28 | 27200.73 | 29822.37 | 14906.05 | 27200.75 | 30931.18 |
| 80.00 | -0.03 | 14915.91 | 27200.73 | 29822.37 | 14906.42 | 27200.75 | 30931.18 |
| 82.00 | -0.03 | 14915.57 | 27200.74 | 29822.37 | 14906.76 | 27200.75 | 30931.18 |
| 84.00 | -0.03 | 14915.26 | 27200.74 | 29822.36 | 14907.07 | 27200.75 | 30931.19 |
| 86.00 | -0.03 | 14914.99 | 27200.74 | 29822.36 | 14907.35 | 27200.75 | 30931.19 |
| 88.00 | -0.03 | 14914.73 | 27200.75 | 29822.36 | 14907.60 | 27200.75 | 30931.19 |

Energies are shown in cm^{-1} units.

Table 3

The Li_2 molecule adiabatic potential energy curves for $1^3\Sigma_u^+$, $2^3\Sigma_u^+$, $3^3\Sigma_u^+$, $4^3\Sigma_u^+$, $5^3\Sigma_u^+$, $1^3\Sigma_g^+$, $2^3\Sigma_g^+$ and $3^3\Sigma_g^+$ states

| $R(a_0)$ | $1^3\Sigma_u^+$ | $2^3\Sigma_u^+$ | $3^3\Sigma_u^+$ | $4^3\Sigma_u^+$ | $5^3\Sigma_u^+$ | $1^3\Sigma_g^+$ | $2^3\Sigma_g^+$ | $3^3\Sigma_g^+$ |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 3.20 | 18614.28 | 39539.21 | 44903.74 | 46180.63 | 47733.56 | 26768.74 | 37336.86 | 41348.13 |
| 3.40 | 15220.69 | 35578.15 | 40941.79 | 42286.27 | 43471.91 | 22450.56 | 33454.56 | 37235.96 |
| 3.60 | 12325.19 | 32280.65 | 37637.68 | 39032.05 | 39863.70 | 18944.63 | 30193.81 | 33830.75 |
| 3.80 | 9888.40 | 29573.41 | 34914.35 | 36317.32 | 36890.23 | 16133.01 | 27500.96 | 31054.29 |
| 4.00 | 7860.91 | 27377.86 | 32693.66 | 34032.97 | 34479.41 | 13903.37 | 25309.34 | 28821.74 |
| 4.20 | 6189.69 | 25618.25 | 30899.16 | 32093.77 | 32535.04 | 12155.91 | 23550.17 | 27051.27 |
| 4.40 | 4823.09 | 24225.63 | 29456.02 | 30468.32 | 30963.96 | 10805.34 | 22158.81 | 25668.83 |
| 4.60 | 3713.33 | 23139.25 | 28288.01 | 29138.88 | 29692.76 | 9779.72 | 21077.39 | 24609.73 |
| 4.80 | 2817.77 | 22306.78 | 27310.75 | 28084.03 | 28679.93 | 9018.96 | 20255.56 | 23818.56 |
| 5.00 | 2099.34 | 21683.63 | 26440.01 | 27287.72 | 27899.72 | 8473.24 | 19650.27 | 23248.54 |
| 5.20 | 1526.41 | 21232.21 | 25631.62 | 26713.55 | 27327.29 | 8101.53 | 19225.13 | 22860.53 |
| 5.40 | 1072.32 | 20920.97 | 24882.01 | 26306.22 | 26934.63 | 7870.21 | 18949.60 | 22621.99 |
| 5.60 | 714.85 | 20723.50 | 24193.44 | 26021.55 | 26692.34 | 7751.86 | 18798.25 | 22506.00 |
| 5.80 | 435.64 | 20617.53 | 23564.08 | 25831.08 | 26572.39 | 7724.11 | 18749.88 | 22490.31 |
| 6.00 | 219.51 | 20583.86 | 22990.12 | 25715.50 | 26550.21 | 7768.58 | 18786.78 | 22556.45 |
| 6.20 | 54.03 | 20604.97 | 22468.36 | 25660.12 | 26605.55 | 7870.17 | 18894.07 | 22688.99 |
| 6.40 | -71.00 | 20661.94 | 21999.57 | 25652.86 | 26722.06 | 8016.36 | 19059.16 | 22875.00 |
| 6.60 | -163.90 | 20723.64 | 21599.26 | 25683.60 | 26886.60 | 8196.80 | 19271.33 | 23103.59 |
| 6.80 | -231.40 | 20704.47 | 21339.88 | 25743.95 | 27088.44 | 8402.92 | 19521.49 | 23365.57 |
| 7.00 | -278.94 | 20495.35 | 21319.56 | 25827.09 | 27318.76 | 8627.69 | 19801.88 | 23653.24 |
| 7.25 | -316.85 | 20108.86 | 21474.81 | 25955.01 | 27635.58 | 8926.12 | 20184.88 | 24039.12 |
| 7.50 | -336.93 | 19713.34 | 21688.21 | 26102.36 | 27973.41 | 9235.62 | 20593.98 | 24444.51 |
| 7.75 | -344.17 | 19337.42 | 21920.94 | 26263.37 | 28321.98 | 9549.13 | 21020.19 | 24860.83 |
| 8.00 | -342.32 | 18986.23 | 22160.57 | 26433.52 | 28671.86 | 9861.22 | 21456.07 | 25281.10 |
| 8.25 | -334.14 | 18660.34 | 22401.42 | 26608.73 | 29013.28 | 10167.75 | 21895.37 | 25699.56 |
| 8.50 | -321.69 | 18359.20 | 22640.56 | 26784.90 | 29334.58 | 10465.62 | 22332.82 | 26111.46 |
| 8.75 | -306.48 | 18081.92 | 22876.46 | 26957.81 | 29619.93 | 10752.59 | 22763.95 | 26512.85 |
| 9.00 | -289.58 | 17827.46 | 23108.40 | 27123.21 | 29848.21 | 11027.08 | 23184.88 | 26900.42 |
| 9.50 | -253.70 | 17382.36 | 23559.11 | 27416.28 | 29630.18 | 11534.96 | 23983.00 | 27623.46 |
| 10.00 | -218.09 | 17013.92 | 23990.84 | 27642.77 | 29605.01 | 11985.51 | 24704.06 | 28263.03 |
| 10.50 | -184.84 | 16711.40 | 24401.11 | 27801.53 | 29598.00 | 12379.25 | 25328.47 | 28802.14 |
| 11.00 | -154.92 | 16464.07 | 24786.13 | 27910.07 | 29603.89 | 12719.34 | 25839.36 | 29137.83 |
| 11.50 | -128.71 | 16261.99 | 25141.32 | 27992.84 | 29618.10 | 12874.97 | 25953.40 | 29223.78 |
| 12.00 | -106.24 | 16096.38 | 25461.95 | 28071.00 | 29636.94 | 13030.58 | 26067.43 | 29309.71 |
| 12.50 | -87.29 | 15959.83 | 25744.10 | 28158.45 | 29657.70 | 13186.18 | 26181.45 | 29395.64 |
| 13.00 | -71.55 | 15846.31 | 25985.65 | 28262.02 | 29678.50 | 13341.78 | 26295.48 | 29481.57 |
| 13.50 | -58.60 | 15750.95 | 26187.27 | 28382.69 | 29698.18 | 13497.39 | 26409.50 | 29567.50 |
| 14.00 | -48.04 | 15669.95 | 26352.51 | 28517.27 | 29716.12 | 13652.99 | 26523.52 | 29653.43 |
| 14.50 | -39.44 | 15600.34 | 26486.84 | 28660.25 | 29732.03 | 13808.60 | 26637.55 | 29739.36 |
| 15.00 | -32.46 | 15539.84 | 26596.19 | 28805.45 | 29745.87 | 13964.20 | 26751.57 | 29825.30 |
| 16.00 | -22.16 | 15439.78 | 26760.40 | 29081.20 | 29767.88 | 14275.52 | 26979.70 | 29997.22 |

Table 3 (continued)

| $R(a_0)$ | $1^3\Sigma_u^+$ | $2^3\Sigma_u^+$ | $3^3\Sigma_u^+$ | $4^3\Sigma_u^+$ | $5^3\Sigma_u^+$ | $1^3\Sigma_g^+$ | $2^3\Sigma_g^+$ | $3^3\Sigma_g^+$ |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 17.00 | -15.34 | 15360.42 | 26875.76 | 29313.18 | 29783.62 | 14388.20 | 27028.52 | 30193.17 |
| 18.00 | -10.79 | 15296.12 | 26959.43 | 29488.05 | 29794.70 | 14475.15 | 27069.25 | 30360.25 |
| 19.00 | -7.72 | 15243.23 | 27021.08 | 29607.77 | 29802.47 | 14543.43 | 27101.78 | 30498.53 |
| 20.00 | -5.61 | 15199.24 | 27066.71 | 29684.30 | 29807.93 | 14597.89 | 27126.93 | 30608.26 |
| 22.00 | -3.11 | 15131.31 | 27125.37 | 29761.18 | 29814.55 | 14677.92 | 27160.06 | 30754.00 |
| 24.00 | -1.82 | 15082.53 | 27157.28 | 29791.73 | 29817.99 | 14732.56 | 27178.01 | 30833.31 |
| 26.00 | -1.12 | 15046.86 | 27174.76 | 29805.34 | 29819.83 | 14771.23 | 27187.58 | 30876.67 |
| 28.00 | -0.72 | 15020.30 | 27184.59 | 29812.21 | 29820.87 | 14799.43 | 27192.78 | 30900.55 |
| 30.00 | -0.48 | 15000.18 | 27190.31 | 29815.98 | 29821.46 | 14820.50 | 27195.71 | 30913.63 |
| 32.00 | -0.33 | 14984.68 | 27193.78 | 29818.17 | 29821.81 | 14836.57 | 27197.42 | 30920.80 |
| 34.00 | -0.24 | 14972.55 | 27195.95 | 29819.52 | 29822.02 | 14849.04 | 27198.48 | 30924.77 |
| 36.00 | -0.17 | 14962.94 | 27197.36 | 29820.37 | 29822.15 | 14858.87 | 27199.15 | 30927.03 |
| 38.00 | -0.13 | 14955.23 | 27198.30 | 29820.94 | 29822.23 | 14866.73 | 27199.59 | 30928.36 |
| 40.00 | -0.10 | 14948.97 | 27198.95 | 29821.33 | 29822.28 | 14873.09 | 27199.90 | 30929.20 |
| 42.00 | -0.08 | 14943.84 | 27199.41 | 29821.59 | 29822.31 | 14878.29 | 27200.11 | 30929.75 |
| 44.00 | -0.07 | 14939.60 | 27199.74 | 29821.78 | 29822.33 | 14882.58 | 27200.27 | 30930.12 |
| 46.00 | -0.06 | 14936.06 | 27199.98 | 29821.92 | 29822.35 | 14886.16 | 27200.38 | 30930.38 |
| 48.00 | -0.05 | 14933.08 | 27200.15 | 29822.02 | 29822.36 | 14889.16 | 27200.47 | 30930.57 |
| 50.00 | -0.05 | 14930.56 | 27200.28 | 29822.10 | 29822.36 | 14891.70 | 27200.53 | 30930.71 |
| 52.00 | -0.04 | 14928.41 | 27200.39 | 29822.15 | 29822.37 | 14893.86 | 27200.58 | 30930.82 |
| 54.00 | -0.04 | 14926.57 | 27200.47 | 29822.19 | 29822.37 | 14895.72 | 27200.62 | 30930.90 |
| 56.00 | -0.03 | 14924.98 | 27200.53 | 29822.22 | 29822.37 | 14897.32 | 27200.65 | 30930.96 |
| 58.00 | -0.03 | 14923.60 | 27200.57 | 29822.25 | 29822.37 | 14898.70 | 27200.67 | 30931.01 |
| 60.00 | -0.03 | 14922.40 | 27200.61 | 29822.27 | 29822.37 | 14899.91 | 27200.69 | 30931.05 |
| 62.00 | -0.03 | 14921.35 | 27200.64 | 29822.29 | 29822.37 | 14900.97 | 27200.70 | 30931.08 |
| 64.00 | -0.03 | 14920.42 | 27200.66 | 29822.30 | 29822.37 | 14901.89 | 27200.71 | 30931.10 |
| 66.00 | -0.03 | 14919.61 | 27200.68 | 29822.31 | 29822.37 | 14902.71 | 27200.72 | 30931.12 |
| 68.00 | -0.03 | 14918.89 | 27200.69 | 29822.32 | 29822.37 | 14903.44 | 27200.73 | 30931.13 |
| 70.00 | -0.03 | 14918.24 | 27200.70 | 29822.33 | 29822.37 | 14904.08 | 27200.73 | 30931.14 |
| 72.00 | -0.03 | 14917.67 | 27200.71 | 29822.33 | 29822.37 | 14904.65 | 27200.74 | 30931.15 |
| 74.00 | -0.03 | 14917.16 | 27200.72 | 29822.33 | 29822.37 | 14905.17 | 27200.74 | 30931.16 |
| 76.00 | -0.03 | 14916.70 | 27200.72 | 29822.34 | 29822.37 | 14905.63 | 27200.74 | 30931.17 |
| 78.00 | -0.03 | 14916.28 | 27200.73 | 29822.34 | 29822.37 | 14906.05 | 27200.75 | 30931.17 |
| 80.00 | -0.03 | 14915.91 | 27200.73 | 29822.34 | 29822.37 | 14906.42 | 27200.75 | 30931.18 |
| 82.00 | -0.03 | 14915.57 | 27200.74 | 29822.35 | 29822.37 | 14906.76 | 27200.75 | 30931.18 |
| 84.00 | -0.03 | 14915.26 | 27200.74 | 29822.35 | 29822.36 | 14907.07 | 27200.75 | 30931.19 |
| 86.00 | -0.03 | 14914.99 | 27200.74 | 29822.36 | 29822.37 | 14907.35 | 27200.75 | 30931.19 |
| 88.00 | -0.03 | 14914.73 | 27200.75 | 29822.36 | 29822.37 | 14907.60 | 27200.75 | 30931.19 |

Energies are shown in cm^{-1} units.

Table 4

The Li_2 molecule adiabatic potential energy curves for $1^1\Pi_g$, $2^1\Pi_g$, $1^1\Pi_u$, $2^1\Pi_u$, $1^3\Pi_g$, $2^3\Pi_g$, $1^3\Pi_u$, $2^3\Pi_u$, $1^1\Delta_g$ and $1^3\Delta_u$ states

| $R(a_0)$ | $1^1\Pi_g$ | $2^1\Pi_g$ | $1^1\Pi_u$ | $2^1\Pi_u$ | $1^3\Pi_g$ | $2^3\Pi_g$ | $1^3\Pi_u$ | $2^3\Pi_u$ | $1^1\Delta_g$ | $1^3\Delta_u$ |
|----------|------------|------------|------------|------------|------------|------------|------------|------------|---------------|---------------|
| 3.20 | 31693.55 | 41342.87 | 26364.14 | 37458.06 | 35180.66 | 37947.11 | 11248.38 | 38267.28 | 29252.64 | 50257.52 |
| 3.40 | 28814.78 | 37609.54 | 23321.78 | 34298.10 | 32500.84 | 34449.77 | 8892.35 | 34464.34 | 27501.14 | 47684.43 |
| 3.60 | 26251.45 | 34540.10 | 20690.58 | 31669.37 | 29625.86 | 32111.26 | 6998.49 | 31306.49 | 26026.99 | 45451.03 |
| 3.80 | 24003.14 | 32031.99 | 18488.62 | 29469.27 | 26966.24 | 30400.75 | 5519.10 | 28731.86 | 24787.17 | 43508.25 |
| 4.00 | 22066.05 | 29990.21 | 16697.36 | 27642.17 | 24712.23 | 29009.62 | 4403.12 | 26667.12 | 23754.14 | 41815.81 |
| 4.20 | 20424.10 | 28337.39 | 15277.02 | 26150.95 | 22855.57 | 27837.25 | 3599.88 | 25038.60 | 22910.11 | 40339.73 |
| 4.40 | 19050.60 | 27011.38 | 14179.94 | 24959.86 | 21348.36 | 26834.33 | 3062.04 | 23778.07 | 22241.37 | 39050.84 |
| 4.60 | 17913.54 | 25960.86 | 13357.98 | 24031.10 | 20138.32 | 25967.30 | 2746.67 | 22825.12 | 21734.45 | 37923.87 |
| 4.80 | 16979.96 | 25142.30 | 12766.18 | 23326.83 | 19177.12 | 25210.28 | 2615.66 | 22127.52 | 21374.56 | 36936.94 |
| 5.00 | 16218.71 | 24518.31 | 12364.45 | 22811.48 | 18422.33 | 24544.03 | 2635.93 | 21640.87 | 21145.73 | 36071.19 |
| 5.20 | 15601.78 | 24056.89 | 12118.01 | 22452.97 | 17837.53 | 23956.14 | 2779.10 | 21327.80 | 21031.60 | 35310.50 |
| 5.40 | 15104.77 | 23730.85 | 11997.20 | 22223.27 | 17391.81 | 23438.94 | 3021.14 | 21157.04 | 21016.23 | 34641.14 |
| 5.60 | 14706.91 | 23517.30 | 11976.98 | 22098.27 | 17059.00 | 22986.89 | 3341.75 | 21102.58 | 21084.77 | 34051.44 |
| 5.80 | 14390.72 | 23397.05 | 12036.27 | 22057.44 | 16816.90 | 22595.37 | 3723.91 | 21142.72 | 21223.71 | 33531.48 |
| 6.00 | 14141.63 | 23354.01 | 12157.32 | 22083.37 | 16646.56 | 22260.56 | 4153.32 | 21259.20 | 21420.99 | 33072.77 |
| 6.20 | 13947.53 | 23374.66 | 12325.03 | 22161.33 | 16531.69 | 21979.45 | 4617.93 | 21436.49 | 21665.96 | 32668.03 |
| 6.40 | 13798.44 | 23447.60 | 12526.52 | 22278.93 | 16458.22 | 21749.78 | 5107.56 | 21661.12 | 21949.31 | 32310.97 |
| 6.60 | 13686.10 | 23563.20 | 12750.76 | 22425.95 | 16414.06 | 21569.86 | 5613.59 | 21921.11 | 22262.87 | 31996.11 |

(continued on next page)

Table 4 (continued)

| $R(a_0)$ | $1^1\Pi_g$ | $2^1\Pi_g$ | $1^1\Pi_u$ | $2^1\Pi_u$ | $1^3\Pi_g$ | $2^3\Pi_g$ | $1^3\Pi_u$ | $2^3\Pi_u$ | $1^1\Delta_g$ | $1^3\Delta_u$ |
|----------|------------|------------|------------|------------|------------|------------|------------|------------|---------------|---------------|
| 6.80 | 13603.76 | 23713.32 | 12988.40 | 22594.23 | 16388.98 | 21438.30 | 6128.70 | 22205.34 | 22599.58 | 31718.66 |
| 7.00 | 13545.89 | 23891.11 | 13231.53 | 22777.54 | 16374.56 | 21353.71 | 6646.66 | 22502.85 | 22953.29 | 31474.41 |
| 7.25 | 13501.17 | 24143.54 | 13533.23 | 23021.24 | 16361.63 | 21311.39 | 7290.12 | 22875.14 | 23411.34 | 31210.13 |
| 7.50 | 13480.64 | 24420.86 | 13823.05 | 23276.41 | 16346.18 | 21335.28 | 7921.12 | 23221.07 | 23878.88 | 30985.57 |
| 7.75 | 13478.84 | 24715.44 | 14093.36 | 23540.74 | 16323.17 | 21419.32 | 8532.57 | 23505.04 | 24348.47 | 30795.21 |
| 8.00 | 13491.47 | 25021.04 | 14338.99 | 23813.69 | 16290.79 | 21556.19 | 9118.67 | 23697.08 | 24813.81 | 30634.27 |
| 8.25 | 13515.17 | 25332.49 | 14556.87 | 24095.46 | 16249.45 | 21737.83 | 9674.77 | 23800.94 | 25269.54 | 30498.59 |
| 8.50 | 13547.27 | 25645.51 | 14745.81 | 24386.08 | 16200.76 | 21956.23 | 10197.24 | 23852.81 | 25711.07 | 30384.55 |
| 8.75 | 13585.64 | 25956.51 | 14906.11 | 24685.04 | 16146.84 | 22203.88 | 10683.45 | 23889.46 | 26134.42 | 30288.97 |
| 9.00 | 13628.60 | 26262.42 | 15039.22 | 24991.02 | 16089.77 | 22474.11 | 11131.69 | 23933.98 | 26536.23 | 30209.11 |
| 9.50 | 13723.01 | 26848.89 | 15233.22 | 25615.56 | 15973.01 | 23060.36 | 11911.89 | 24088.17 | 27264.44 | 30087.26 |
| 10.00 | 13822.39 | 27387.79 | 15349.37 | 26238.51 | 15860.54 | 23679.57 | 12541.53 | 24348.75 | 27880.00 | 30003.50 |
| 10.50 | 13921.40 | 27866.27 | 15409.31 | 26836.07 | 15757.44 | 24307.58 | 13035.34 | 24708.06 | 28377.57 | 29946.43 |
| 11.00 | 14016.57 | 28275.57 | 15431.09 | 27385.96 | 15665.51 | 24928.10 | 13414.74 | 25143.59 | 28762.79 | 29907.85 |
| 11.50 | 14105.77 | 28611.94 | 15428.32 | 27869.99 | 15584.71 | 25530.08 | 13702.90 | 25628.97 | 29050.33 | 29881.93 |
| 12.00 | 14187.84 | 28877.65 | 15410.63 | 28276.32 | 15514.14 | 26106.06 | 13921.19 | 26139.54 | 29259.43 | 29864.60 |
| 12.50 | 14262.28 | 29080.68 | 15384.54 | 28602.17 | 15452.59 | 26650.80 | 14087.35 | 26654.71 | 29409.28 | 29853.02 |
| 13.00 | 14329.12 | 29232.64 | 15354.34 | 28854.65 | 15398.83 | 27160.26 | 14215.15 | 27158.28 | 29516.16 | 29845.27 |
| 13.50 | 14388.69 | 29345.79 | 15322.79 | 29047.51 | 15351.73 | 27630.72 | 14314.86 | 27637.46 | 29592.59 | 29840.04 |
| 14.00 | 14441.52 | 29430.82 | 15291.58 | 29195.56 | 15310.32 | 28058.11 | 14393.92 | 28081.67 | 29647.65 | 29836.45 |
| 14.50 | 14488.25 | 29495.98 | 15261.71 | 29310.98 | 15273.80 | 28437.65 | 14457.69 | 28480.99 | 29687.74 | 29833.96 |
| 15.00 | 14529.51 | 29547.12 | 15233.73 | 29402.49 | 15241.50 | 28763.99 | 14509.96 | 28825.24 | 29717.28 | 29832.18 |
| 16.00 | 14598.10 | 29621.94 | 15184.16 | 29535.75 | 15187.33 | 29242.05 | 14590.18 | 29315.15 | 29756.01 | 29829.89 |
| 17.00 | 14651.72 | 29673.69 | 15142.89 | 29624.42 | 15144.16 | 29507.73 | 14648.55 | 29559.54 | 29778.71 | 29828.49 |
| 18.00 | 14693.94 | 29710.84 | 15108.85 | 29684.10 | 15109.35 | 29639.94 | 14692.68 | 29668.12 | 29792.67 | 29827.51 |
| 19.00 | 14727.51 | 29737.92 | 15080.81 | 29724.44 | 15081.00 | 29707.63 | 14727.01 | 29721.27 | 29801.64 | 29826.74 |
| 20.00 | 14754.47 | 29757.78 | 15057.63 | 29751.85 | 15057.70 | 29745.34 | 14754.28 | 29751.09 | 29807.59 | 29826.11 |
| 22.00 | 14794.35 | 29783.36 | 15022.28 | 29783.86 | 15022.29 | 29782.82 | 14794.32 | 29782.22 | 29814.49 | 29825.12 |
| 24.00 | 14821.68 | 29797.77 | 14997.30 | 29799.97 | 14997.30 | 29799.79 | 14821.68 | 29797.57 | 29817.98 | 29824.39 |
| 26.00 | 14841.06 | 29806.24 | 14979.21 | 29808.66 | 14979.21 | 29808.63 | 14841.06 | 29806.20 | 29819.83 | 29823.86 |
| 28.00 | 14855.20 | 29811.44 | 14965.82 | 29813.64 | 14965.82 | 29813.63 | 14855.20 | 29811.43 | 29820.87 | 29823.48 |
| 30.00 | 14865.76 | 29814.74 | 14955.71 | 29816.62 | 14955.71 | 29816.62 | 14865.76 | 29814.74 | 29821.46 | 29823.20 |
| 32.00 | 14873.81 | 29816.91 | 14947.93 | 29818.48 | 14947.93 | 29818.48 | 14873.81 | 29816.91 | 29821.81 | 29823.00 |
| 34.00 | 14880.06 | 29818.38 | 14941.86 | 29819.67 | 14941.86 | 29819.67 | 14880.06 | 29818.38 | 29822.02 | 29822.85 |
| 36.00 | 14884.99 | 29819.39 | 14937.05 | 29820.45 | 14937.05 | 29820.45 | 14884.99 | 29819.39 | 29822.15 | 29822.75 |
| 38.00 | 14888.93 | 29820.11 | 14933.20 | 29820.98 | 14933.20 | 29820.98 | 14888.93 | 29820.11 | 29822.23 | 29822.66 |
| 40.00 | 14892.11 | 29820.63 | 14930.07 | 29821.35 | 14930.07 | 29821.35 | 14892.11 | 29820.63 | 29822.28 | 29822.60 |
| 42.00 | 14894.72 | 29821.01 | 14927.50 | 29821.60 | 14927.50 | 29821.60 | 14894.72 | 29821.01 | 29822.31 | 29822.55 |
| 44.00 | 14896.87 | 29821.30 | 14925.38 | 29821.79 | 14925.38 | 29821.79 | 14896.87 | 29821.30 | 29822.33 | 29822.52 |
| 46.00 | 14898.65 | 29821.51 | 14923.61 | 29821.92 | 14923.61 | 29821.92 | 14898.65 | 29821.51 | 29822.35 | 29822.49 |
| 48.00 | 14900.16 | 29821.68 | 14922.12 | 29822.02 | 14922.12 | 29822.02 | 14900.16 | 29821.68 | 29822.36 | 29822.46 |
| 50.00 | 14901.43 | 29821.80 | 14920.86 | 29822.09 | 14920.86 | 29822.09 | 14901.43 | 29821.81 | 29822.36 | 29822.45 |
| 52.00 | 14902.51 | 29821.90 | 14919.79 | 29822.15 | 14919.79 | 29822.15 | 14902.51 | 29821.90 | 29822.36 | 29822.43 |
| 54.00 | 14903.44 | 29821.99 | 14918.87 | 29822.19 | 14918.87 | 29822.19 | 14903.44 | 29821.99 | 29822.37 | 29822.42 |
| 56.00 | 14904.24 | 29822.05 | 14918.07 | 29822.22 | 14918.07 | 29822.22 | 14904.24 | 29822.05 | 29822.37 | 29822.41 |
| 58.00 | 14904.93 | 29822.10 | 14917.38 | 29822.25 | 14917.38 | 29822.25 | 14904.93 | 29822.10 | 29822.37 | 29822.40 |
| 60.00 | 14905.54 | 29822.14 | 14916.78 | 29822.27 | 14916.78 | 29822.27 | 14905.54 | 29822.14 | 29822.37 | 29822.39 |
| 62.00 | 14906.06 | 29822.17 | 14916.26 | 29822.28 | 14916.26 | 29822.28 | 14906.06 | 29822.17 | 29822.37 | 29822.39 |
| 64.00 | 14906.53 | 29822.20 | 14915.80 | 29822.30 | 14915.80 | 29822.30 | 14906.53 | 29822.20 | 29822.37 | 29822.39 |
| 66.00 | 14906.94 | 29822.23 | 14915.39 | 29822.31 | 14915.39 | 29822.31 | 14906.94 | 29822.23 | 29822.37 | 29822.38 |
| 68.00 | 14907.30 | 29822.24 | 14915.03 | 29822.32 | 14915.03 | 29822.32 | 14907.30 | 29822.24 | 29822.37 | 29822.38 |
| 70.00 | 14907.62 | 29822.26 | 14914.70 | 29822.32 | 14914.70 | 29822.32 | 14907.62 | 29822.26 | 29822.37 | 29822.37 |
| 72.00 | 14907.91 | 29822.27 | 14914.42 | 29822.33 | 14914.42 | 29822.33 | 14907.91 | 29822.27 | 29822.36 | 29822.37 |
| 74.00 | 14908.17 | 29822.28 | 14914.16 | 29822.33 | 14914.16 | 29822.33 | 14908.17 | 29822.28 | 29822.37 | 29822.37 |
| 76.00 | 14908.40 | 29822.29 | 14913.93 | 29822.33 | 14913.93 | 29822.33 | 14908.40 | 29822.29 | 29822.37 | 29822.37 |
| 78.00 | 14908.61 | 29822.30 | 14913.72 | 29822.35 | 14913.72 | 29822.34 | 14908.61 | 29822.30 | 29822.37 | 29822.37 |
| 80.00 | 14908.79 | 29822.31 | 14913.54 | 29822.35 | 14913.54 | 29822.35 | 14908.79 | 29822.31 | 29822.37 | 29822.37 |
| 82.00 | 14908.96 | 29822.31 | 14913.37 | 29822.35 | 14913.37 | 29822.35 | 14908.96 | 29822.31 | 29822.36 | 29822.37 |
| 84.00 | 14909.12 | 29822.32 | 14913.21 | 29822.35 | 14913.21 | 29822.35 | 14909.12 | 29822.32 | 29822.37 | 29822.37 |
| 86.00 | 14909.26 | 29822.32 | 14913.08 | 29822.35 | 14913.08 | 29822.35 | 14909.26 | 29822.32 | 29822.37 | 29822.37 |
| 88.00 | 14909.38 | 29822.33 | 14912.95 | 29822.35 | 14912.95 | 29822.35 | 14909.38 | 29822.33 | 29822.36 | 29822.36 |

Energies are shown in cm^{-1} units.



Table 5
Spectroscopic parameters R_e (Å), D_e , ω_e and T_e (cm⁻¹) for the ground and excited states of Li₂ molecule

| State | Dissociation | Method | R_e | D_e | ω_e | T_e |
|------------------------------|--------------|-----------------|-----------|--------------|------------|-----------|
| $1^1\Sigma_g^+$ | (2s + 2s) | Present work | 2.658 | 8613 | 352.41 | 0 |
| | | Exp. [36] | 2.673 | 8600 | 351.39 | 0 |
| | | Exp. [37] | 2.673 | 8516.78 | | |
| | | Exp. [40] | | 8615 | | |
| | | Theory [9] | 2.660 | 8510 | 353 | 0 |
| | | Theory [8] | 2.675 | 8466 | 351.01 | 0 |
| $1^3\Sigma_u^+$ | | Present work | 4.134 | 344 | 65.95 | 8126 |
| | | Exp. [41] | 4.127 | 336 | 67.58 | 8180.9 |
| | | Exp. [38] | 4.171 | 333 | 65.13 | 8183.8 |
| | | Theory [9] | 4.159 | 321 | 66.1 | 8189 |
| | | Theory [8] | 4.182 | 322 | 63.73 | 8144 |
| | | $2^1\Sigma_g^+$ | (2s + 2p) | Present work | 3.655 | 3274 |
| Exp. [42] | 3.651 | | | 3319 | 128.67 | 20101 |
| Theory [9] | 3.667 | | | 3161 | 126.3 | 20253 |
| Theory [8] | 3.655 | | | 3276 | 129.04 | 20128 |
| $1^3\Sigma_g^+$ | | | | Present work | 3.053 | 7184 |
| | | Exp. [38] | 3.068 | 7091.5 | 251.5 | 16328.8 |
| | | Theory [9] | 3.055 | 7137 | 253.3 | 16277 |
| | | Theory [8] | 3.067 | 7071 | 252.2 | 16333 |
| $1^1\Sigma_u^+$ | | Present work | 3.092 | 9483 | 257.54 | 13994 |
| | | Exp. [11] | 3.108 | 9352.5 | 257.47 | 14068 |
| | | Theory [9] | 3.094 | 9466 | 257.4 | 13948 |
| | | Theory [8] | 3.108 | 9356 | 256.06 | 14048 |
| $2^3\Sigma_u^+$ | | Present work | 3.181 | -5669 | 193.73 | |
| | | Theory [9] | 3.185 | -5712 | 213.1 | |
| | | Theory [8] | 3.166 | -5709 | | |
| $1^1\Pi_g$ | | Present work | 4.048 | 1426 | 93.37 | 21968 |
| | | Exp. [43] | 4.058 | 1422.5 | 93.35 | 21988.5 |
| | | Exp. [44] | | 1421.9 | 92.77 | 21998.8 |
| | | Theory [9] | 4.063 | 1400 | 92.5 | 22013 |
| | | Theory [8] | 4.073 | 1406 | 91.85 | 21998 |
| $1^3\Pi_g$ | | Present work | repulsive | | | |
| $1^1\Pi_u$ | | Present work | 2.934 | 2930 | 269.49 | 20553 |
| | | Exp. [25] | | 2984.42 | | |
| | | Exp. [36] | 2.936 | 2984.5 | 270.69 | 20436 |
| | | Theory [9] | 2.939 | 2716 | 269.7 | 20698 |
| | | Theory [8] | 2.942 | 2903 | 270.28 | 20501 |
| $1^3\Pi_u$ | | Present work | 2.577 | 12297 | 348.15 | 11225 |
| | | Exp. [45] | 2.590 | 12145 | 345.6 | |
| | | Theory [9] | 2.581 | 12178 | 348.7 | 11236 |
| | | Theory [8] | 2.595 | 12148 | 345.88 | 11256 |
| $3^1\Sigma_g^+$ | (2s + 3s) | Present work | 3.076 | 8333 | 246.62 | 27428 |
| | | Exp. [46] | 3.086 | 8312.8 | 245.9 | 27410 |
| | | Theory [9] | 3.074 | 8289 | 250.4 | 27434 |
| | | Theory [8] | 3.085 | 8279 | 245.7 | 27396 |
| $2^3\Sigma_g^+$ | | Present work | 3.073 | 8451 | 270.07 | 27322 |
| | | Theory [9] | 3.075 | 8428 | 270.4 | 27294 |
| | | Theory [8] | 3.079 | 8379 | 270.68 | 27296 |
| $2^1\Sigma_u^+$, inner well | | Present work | 3.081 | 5674 | 259.82 | 30094 |
| | | Exp. [21] | 3.096 | | 259.003 | 30101.407 |
| | | Exp. [47] | 3.094 | | 259.9 | 30100.3 |
| | | Theory [9] | 3.083 | 5660 | 260.1 | 30062 |
| | | Theory [8] | 3.089 | 5598 | 259.2 | 30077 |
| $2^1\Sigma_u^+$, outer well | | Present work | 6.072 | 5413 | 119.05 | 30285 |
| | | Exp. [21] | 6.037 | | | 30400.137 |
| | | Theory [9] | 6.080 | 5453 | 117 | 30269 |
| | | Theory [8] | 6.052 | 5329 | 121.96 | |

(continued on next page)

Table 5 (continued)

| State | Dissociation | Method | R_e | D_e | ω_e | T_e |
|------------------------------|--------------|--------------|-----------|--------|------------|---------|
| $3^3\Sigma_u^+$ | | Present work | 3.658 | 5903 | 373.15 | 29922 |
| | | Theory [9] | 3.667 | 5866 | 356.4 | 29853 |
| | | Theory [8] | 3.695 | 5839 | 392.69 | 29836 |
| $4^1\Sigma_g^+$, inner well | (2p + 2p) | Present work | 3.545 | 8388 | 229.19 | 29985 |
| | | Exp. [48] | 3.548 | 8349.3 | 227.3 | 29975 |
| | | Theory [9] | 3.543 | 8377 | 231.1 | 29941 |
| | | Theory [8] | 3.551 | 8319 | 229.55 | 30023 |
| $4^1\Sigma_g^+$, outer well | | Present work | 9.107 | 2159 | 19.38 | 36110 |
| | | Theory [9] | 8.750 | 2158 | 17 | 36160 |
| | | Theory [8] | 8.940 | 2166 | | |
| $4^3\Sigma_u^+$ | | Present work | 3.351 | 4157 | 187.36 | 34195 |
| | | Theory [9] | 3.267 | 4395 | 206.4 | 33923 |
| | | Theory [8] | 3.371 | 4075 | 186.17 | 34267 |
| $5^3\Sigma_u^+$ | | Present work | 3.149 | 3260 | 265.39 | 35132 |
| | | Theory [9] | 3.126 | 3079 | 264.9 | 35240 |
| $2^1\Pi_g$ | | Present work | 3.191 | 6469 | 230.70 | 31905 |
| | | Exp. [49] | 3.2014 | 6455 | 229.26 | 31868.4 |
| | | Theory [9] | 3.201 | 6398 | 229.1 | 31920 |
| $2^3\Pi_g$ | | Present work | 3.853 | 8511 | 189.83 | 29842 |
| | | Exp. [50] | 3.816 | 8484 | 189.1 | 29840.5 |
| | | Theory [9] | 3.851 | 8435 | 191.3 | 29883 |
| $2^1\Pi_u$ | | Present work | 3.077 | 7751 | 236.47 | 30627 |
| | | Exp. [51] | 3.074 | 7648.4 | 239.1 | 30549 |
| | | Theory [9] | 3.089 | 7641 | 231.3 | 30677 |
| $2^3\Pi_u$ | | Present work | 2.968 | 8720 | 283.82 | 29681 |
| | | Theory [9] | 2.965 | 8671 | 284.1 | 29647 |
| $1^1\Delta_g$ | | Present work | 2.822 | 8811 | 276.30 | 29586 |
| | | Exp. [52] | | 9579 | 271.44 | |
| | | Theory [9] | 2.919 | 9368 | 273.1 | 28950 |
| $1^3\Delta_u$ | | Present work | repulsive | | | |
| | | Theory [9] | 3.126 | 3430 | 251.6 | 34888 |
| $3^3\Sigma_g^+$ | (2s + 3p) | Present work | 3.034 | 8446 | 274.49 | 31060 |
| | | Exp. [50] | 3.081 | 8401 | 273.3 | 31041.7 |
| | | Theory [9] | 3.034 | 8346 | 274.4 | 31091 |
| | | Theory [8] | 3.030 | 8396 | 278.89 | 31149 |
| $3^1\Sigma_u^+$ | | Present work | 4.369 | 5848 | 295.30 | 33668 |
| | | Theory [9] | 4.340 | 5839 | 258 | 33594 |
| | | Theory [8] | 4.315 | 5875 | 256.16 | 33670 |

3. Computational method

All calculations reported in this paper were performed by means of the MOLPRO program package [34]. The core electrons of Li atoms are represented by pseudopotential ECP2SDF [27], which was formed from the uncontracted (9s9p8d3f) basis set. The basis for the s and p orbitals, which comes with this potential is enlarged by functions for d and f orbitals given by P. Feller [35] and assigned by CC-PV5Z. Additionally, our basis set was augmented by three s short range correlation functions (392.169555, 77.676373, 15.38523), three p functions (96.625417, 19.845562, 4.076012) and three d functions (3.751948, 1.9783, 1.043103). Also, we added to the basis a set of five diffused functions: two s functions (0.010159, 0.003894), two p functions (0.007058, 0.002598) and one d function (0.026579).

We checked the quality of our basis set performing the CI calculations for the ground and several excited states of isolated lithium atom. The calculated Li_2 adiabatic potentials correlate to the (2s + 2s) ground atomic asymptote and (2s + 2p), (2s + 3s), (2p + 2p), (2s + 3p) excited atomic asymptotes. The comparison of experimental and theoretical asymptotic energies for different states is shown in Table 1. The spin-orbit coupling (SO) and core-core polarization effect contribute insignificant part to energy of our system, so we do not take them into consideration in our calculations. The potential energy curves for Li_2 are calculated using the complete-active-space self-consistent-field (CASSCF) method to generate the orbitals for the subsequent CI calculations. The corresponding active space in the D_{2h} point group involved the molecular counterparts of the 2s, 2p, 3s, 3p and 3d valence orbitals of the Li atom.

4. Results and discussion

Calculations of the adiabatic energy curves are performed for the internuclear separation R in the range from $3.2a_0$ to $88a_0$ with the various steps adjusted to the internuclear distance. Numerical values of the calculated potential energies are shown in Tables 2–4. Equilibrium positions R_e and depths of the potential wells D_e are obtained using cubic spline approximation to the calculated potentials around their equilibrium positions. Spectroscopic parameters ω_e and T_e are calculated by solving the Schrödinger equation with calculated adiabatic potentials. These values are shown in Table 5. As it is seen, overall agreement of all our spectroscopic constants and other theoretical and

experimental data is very reasonable. Particularly, what is worth noting, there is a good agreement for the spectroscopic constants in the case of double wells for two states $2^1\Sigma_u^+$ and $4^1\Sigma_g^+$. Present results for all singlet and triplet states are plotted relative to the corresponding experimental values of the atomic terms in Figs. 1–3. The states $5^3\Sigma_u^+$, $2^1\Pi_u$, $2^1\Pi_g$, $2^3\Pi_u$, $2^3\Pi_g$, $1^1\Delta_g$ and $1^3\Delta_u$ are calculated for the second time (besides Poteau and Spiegelmann [9]). All our states are calculated for the first time, for large internuclear separations R (up to $88a_0$). We obtain asymptotic energies for ground and excited states, which are in very good agreement with experimental and other theoretical values (Table 1.) We also present almost all states corresponding to the $2p + 2p$ asymptote (Fig. 3), except $1^1\Sigma_u^-$ and $1^3\Sigma_g^-$ states, which are not available by methods of the MOLPRO program package [34]. In Fig. 4, we

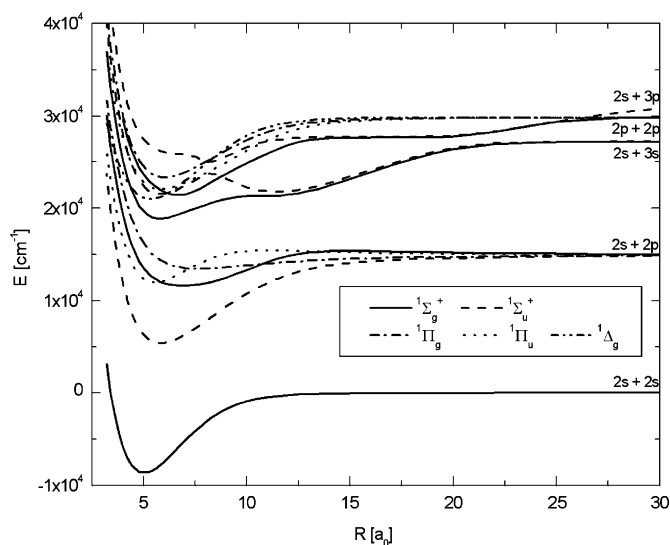


Fig. 1. Adiabatic potential energy curves for the ground and excited singlet states of the Li_2 molecule correlating to the $2s + 2s$, $2s + 2p$, $2s + 3s$, $2p + 2p$ and $2s + 3p$ asymptotes.

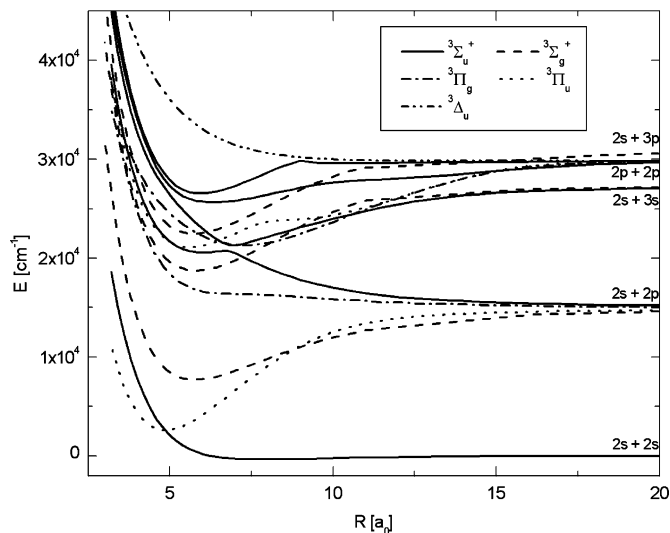


Fig. 2. Adiabatic potential energy curves for excited triplet states of the Li_2 molecule correlating to the $2s + 2s$, $2s + 2p$, $2s + 3s$, $2p + 2p$ and $2s + 3p$ asymptotes.

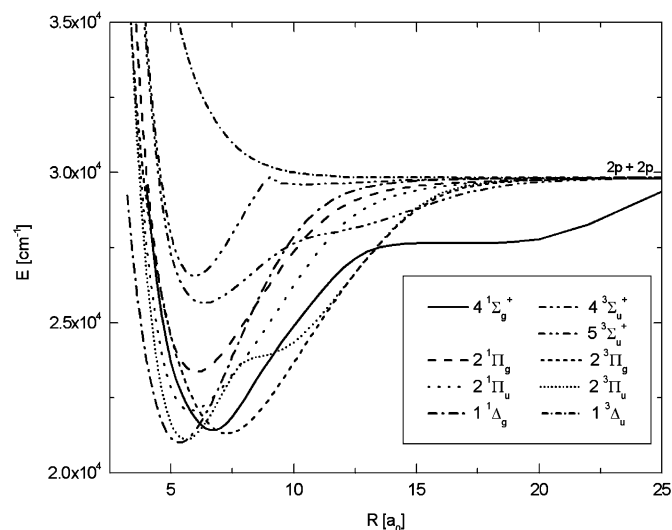


Fig. 3. Adiabatic potential energy curves for excited states of the Li_2 molecule correlating to the $2p + 2p$ asymptote.

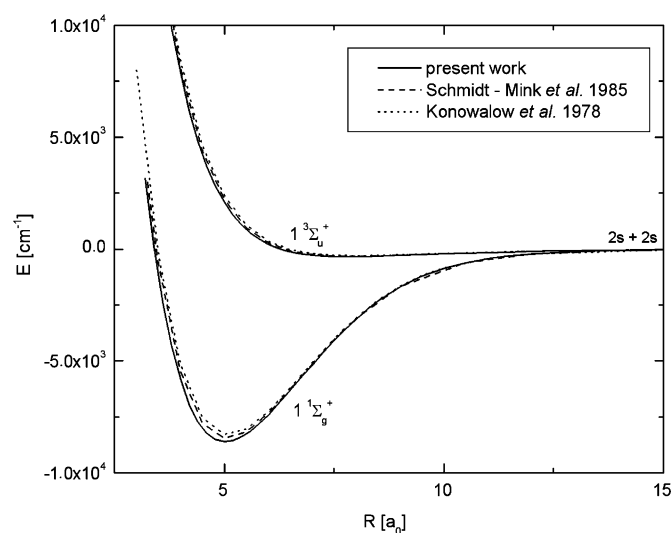


Fig. 4. Comparison of the ground and the first excited molecular state correlating to $2s + 2s$ asymptote with the theoretical results of Olson and Konowalow [3,4] and Schmidt-Mink et al. [8].

compare our ground and the first excited molecular state correlating to ground state of lithium atoms along with the theoretical results of Olson and Konowalow [3,4] and Schmidt-Mink et al. [8]. As one may see, the agreement is very good. In Fig. 5, we compare present results of the ground state $X(1)^1\Sigma_g^+$ with two curves derived from experiments by Hessel and Vidal [36] and Barakat et al. [37]. In the vicinity of the potential well we note better agreement with the curve of Hessel and Vidal [36], but for larger distances we note the perfect fit with the curve of Barakat et al. [37]. In Fig. 6, the comparison for $a(1)^3\Sigma_u^+$ with the curve derived from experiment by Linton et al. [38] shows some discrepancy for the repulsive part of potential curve. Also our theoretical curve displays a deeper well of about 11 cm^{-1} . In Fig. 7 we show our results along with the experimental curve given by Bouloufa et al. [25] and theo-

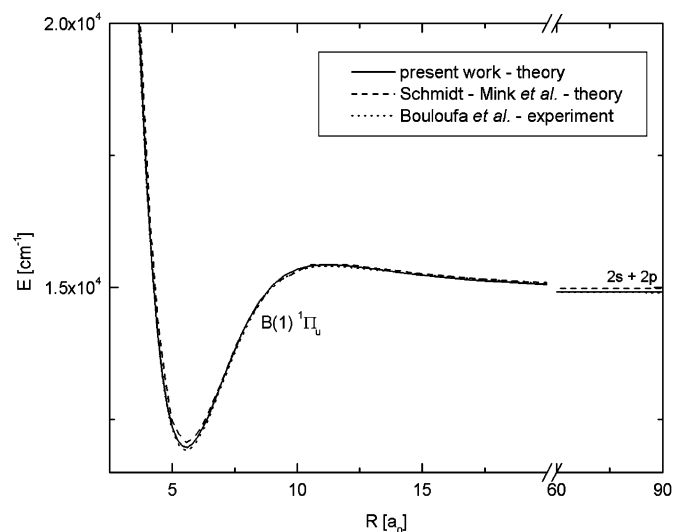


Fig. 7. Comparison of the $B(1)^1\Pi_u$ state correlating to $2s + 2p$ asymptote with results derived from experiment by Bouloufa et al. [25] and theoretical results of Schmidt-Mink et al. [8].

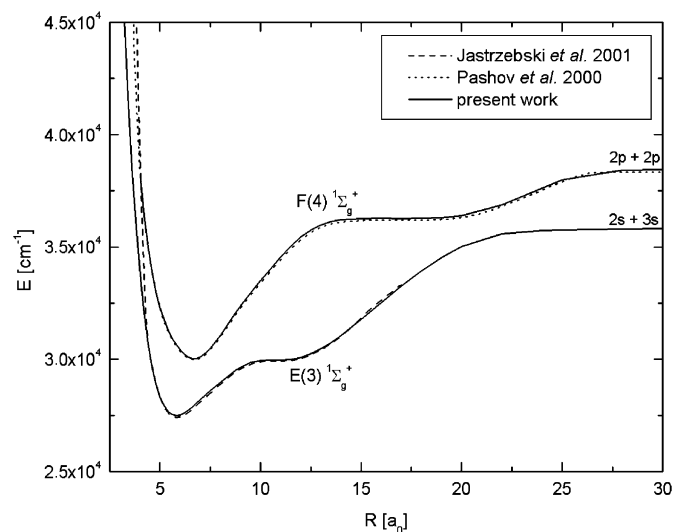


Fig. 8. Comparison of the $E(3)^1\Sigma_g^+$ and $F(4)^1\Sigma_g^+$ states correlating, respectively, to $2s + 3s$ and $2p + 2p$ asymptotes with potential curves derived from experiment by Jastrzebski et al. [22] and Pashov et al. [23].

retical results of Schmidt-Mink et al. [8]. Here, we underline the good agreement in the distinctive hump shape which appears around $10\text{--}13a_0$. In turn, in the Fig. 8, we display the comparison with two $^1\Sigma_g^+$ states derived from experiment. Here, in the case of $4^1\Sigma_g^+$ state once again the agreement is excellent, while in the case of the lower $3^1\Sigma_g^+$ state correlating to $2s + 3s$ atomic energy [22,23] we find a disagreement for small internuclear distance.

5. Conclusion

We have calculated the adiabatic potential energy curves of the lithium dimer using CASSCF/MRCI method. Several curves correlated to the excited atomic states are pre-

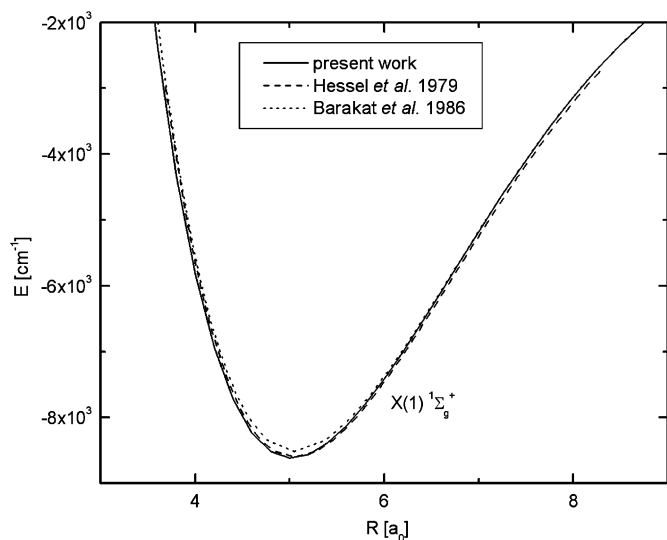


Fig. 5. Comparison of the ground state with the experimental results of Hessel and Vidal [36] and Barakat et al. [37].

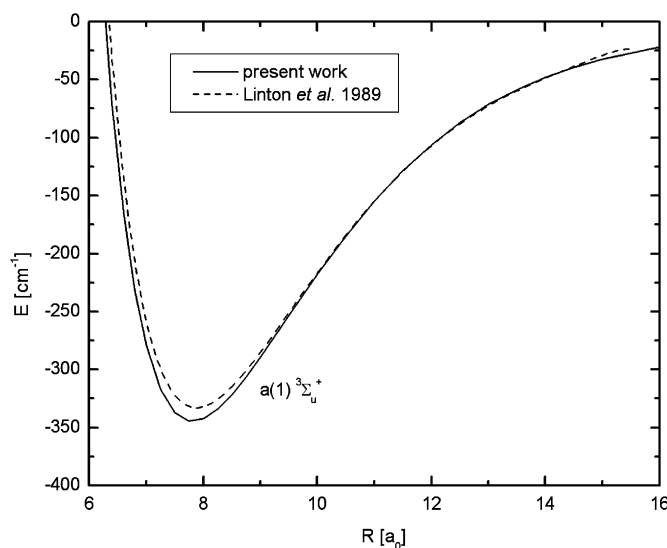


Fig. 6. Comparison of the first excited molecular state correlating to $2s + 2s$ asymptote with the experimental result of Linton et al. [38].

sented for the second time (besides Poteau and Spiegelmann [9]): $5^3\Sigma_u^+$, $2^1\Pi_u$, $2^1\Pi_g$, $2^3\Pi_u$, $2^3\Pi_g$, $1^1\Delta_g$ and $1^3\Delta_u$. Comparisons with available lowly-lying theoretical and experimental curves provide almost perfect agreement. Only in the case of the repulsive part of the $3^1\Sigma_g^+$ state, we note certain disagreement. In the near future, we plan to calculate adiabatic potential energy curves for heavier alkali dimers.

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