

Calculation of adiabatic potentials of Li_2^+

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Introduction

The lithium dimer and lithium ion dimer have attracted attention of experimentalists and theoreticians for many years, mainly because they are the next, just after the molecular hydrogen, smallest stable homonuclear molecules. It can serve as a convenient prototype for testing theoretical methods, which can be further applied to heavier alkali dimers. The first useful *ab initio* calculations on Li_2^+ using the RHF method (restricted Hartree-Fock-Roothaan) were performed by Konowalow and co-workers [1]. Next, Schmidt-Mink *et al.* [2] performed SCF/valence CI calculation where they obtained the 8 lowest lying states of Li_2^+ molecule. The last theoretical results were presented by Magnier *et al.* [3] where authors calculated adiabatic potential energy curves of 58 states of lithium ion dimer. The most important experimental works where only ground state of Li_2^+ molecule was taken into account were performed by Bernheim *et al.* [4, 5] and McGeoch *et al.* [6]. Our present calculations are based on the self-consistent-field configuration interaction (SCF CI) scheme which was used in our previous reports [7, 8].

Computational method

All calculations reported in this poster were performed by means of the MOLPRO program package [9]. The core electrons of Li atoms are represented by pseudopotential ECP2SDF [10]. The basis for the s and p orbitals, which comes with this potential is enlarged by functions for d and f orbitals given by O. Ross [11] and assigned by ROOS. 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 (10.495627, 3.673469, 1.285714). Also, we added to the basis a set of nine diffused functions: three s functions (0.010159, 0.003894, 0.001493), three p functions (0.007058, 0.002598, 0.000956) and three d function (0.006753, 0.002364, 0.000827). 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) ground atomic asymptote and (2p), (3s), (3p) and (3d) 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.

Table 1. Comparison of asymptotic energies with other theoretical and experimental results. Energies are shown in a.u. units.

Dissociation limit	Bashkin (exp.) [12]	Present work	Magnier (theory) [3]
$Li^+ + Li(2s)$	-0.198142	-0.198101	-0.198107
$Li^+ + Li(2p)$	-0.130235	-0.130172	-0.130200
$Li^+ + Li(3s)$	-0.074182	-0.074188	-0.074299
$Li^+ + Li(3p)$	-0.057236	-0.057390	-0.057303
$Li^+ + Li(3d)$	-0.055606	-0.055523	-0.055570
$Li^+ + Li(4s)$	-0.038615	-0.055439	-0.038672
$Li^+ + Li(4p)$	-0.039747	-0.038762	-0.032013

Calculations of the adiabatic potential energy curves are performed for the internuclear separation R in the range from $2 a_0$ to $100 a_0$ with the various steps adjusted to the internuclear distance.

Spectroscopic parameters

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 2. As it is seen, overall agreement of all our spectroscopic constants and other theoretical and experimental data is very reasonable.

Table 2. Spectroscopic parameters R_e (Å), D_e , ω_e and T_e (cm^{-1}) for the ground and excited states of Li_2^+ molecule.

State	R_e	D_e	ω_e	T_e
$1^2\Sigma_g^+$				
Exp.[5, 4]	3.110	10464(6)	262(2)	0
Exp.[6]	3.032	10807	263.45	0
Theory[2]	3.099	10441	263.76	0
Theory[1]	3.127	10324	-	0
Theory[3]	3.122	10466	263.08	0
Present work	3.093	10498	263.39	0
$2^2\Sigma_g^+$				
Theory[2]	6.654	2390	82.94	22987
Theory[3]	6.879	2525	84.16	22844
Present work	6.819	2516.5	79.04	22800
$3^2\Sigma_g^+$				
Theory[3]	11.113	3143	56.62	34496
Present work	10.947	3058	57.90	34533
$4^2\Sigma_g^+$				
Theory[3]	16.404	1724	22.14	39644
Present work	16.600	1512	24.03	39768
$1^2\Sigma_u^+$				
Theory[2]	9.950	90	20.10	10350
Theory[1]	10.300	86	-	-
Theory[3]	10.001	90	16.01	10376
Present work	9.942	89	15.92	10285
$2^2\Sigma_u^+$				
Theory[3]	13.229	131	13.07	25239
Present work	13.225	127.5	12.96	25156
$3^2\Sigma_u^+$				
Present work	19.492	162	10.94	37405
$4^2\Sigma_u^+$				
Present work	23	383.5	11.25	40885
$2^2\Pi_g$				
Present work	19.144	349	12.14	40920
$1^2\Pi_u$				
Theory[2]	3.976	2103	105.58	23277
Theory[1]	4.014	1852	-	-
Theory[3]	4.022	2100	108.26	23270
Present work	3.981	2133	105.25	23197
$2^2\Pi_u$				
Theory[3]	9.631	3330	50.79	38039
Present work	9.107	3008	60.06	38285
$1^2\Delta_g$				
Theory[3]	9.578	324	28.14	41425
Present work	repulsive potential			

Results

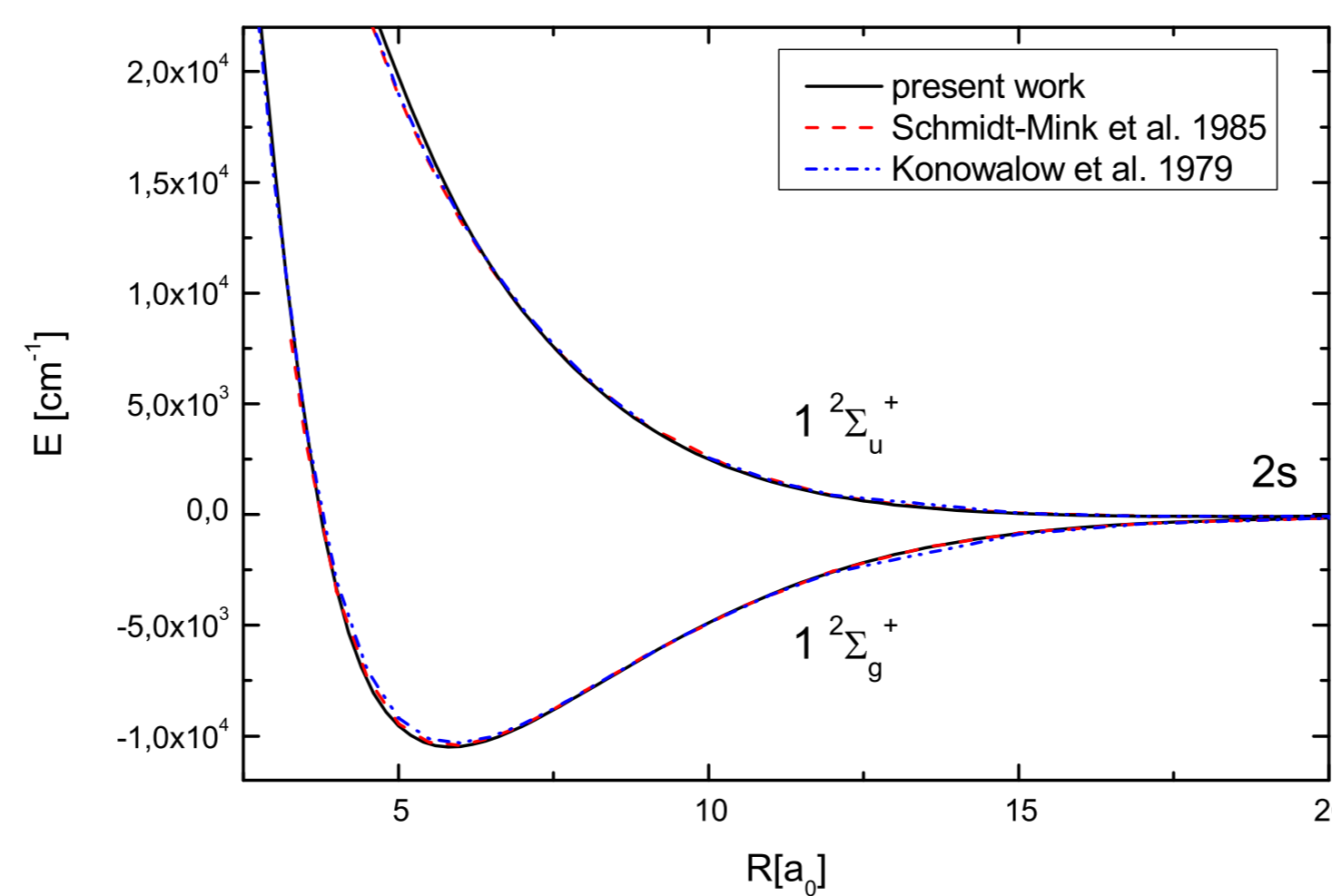


Fig. 1. Comparison of the ground and the first excited molecular state correlating to $Li^+ + Li(2s)$ asymptote with the theoretical results of Konowalow and Rosenkrantz [1] and Schmidt-Mink *et al.* [2].

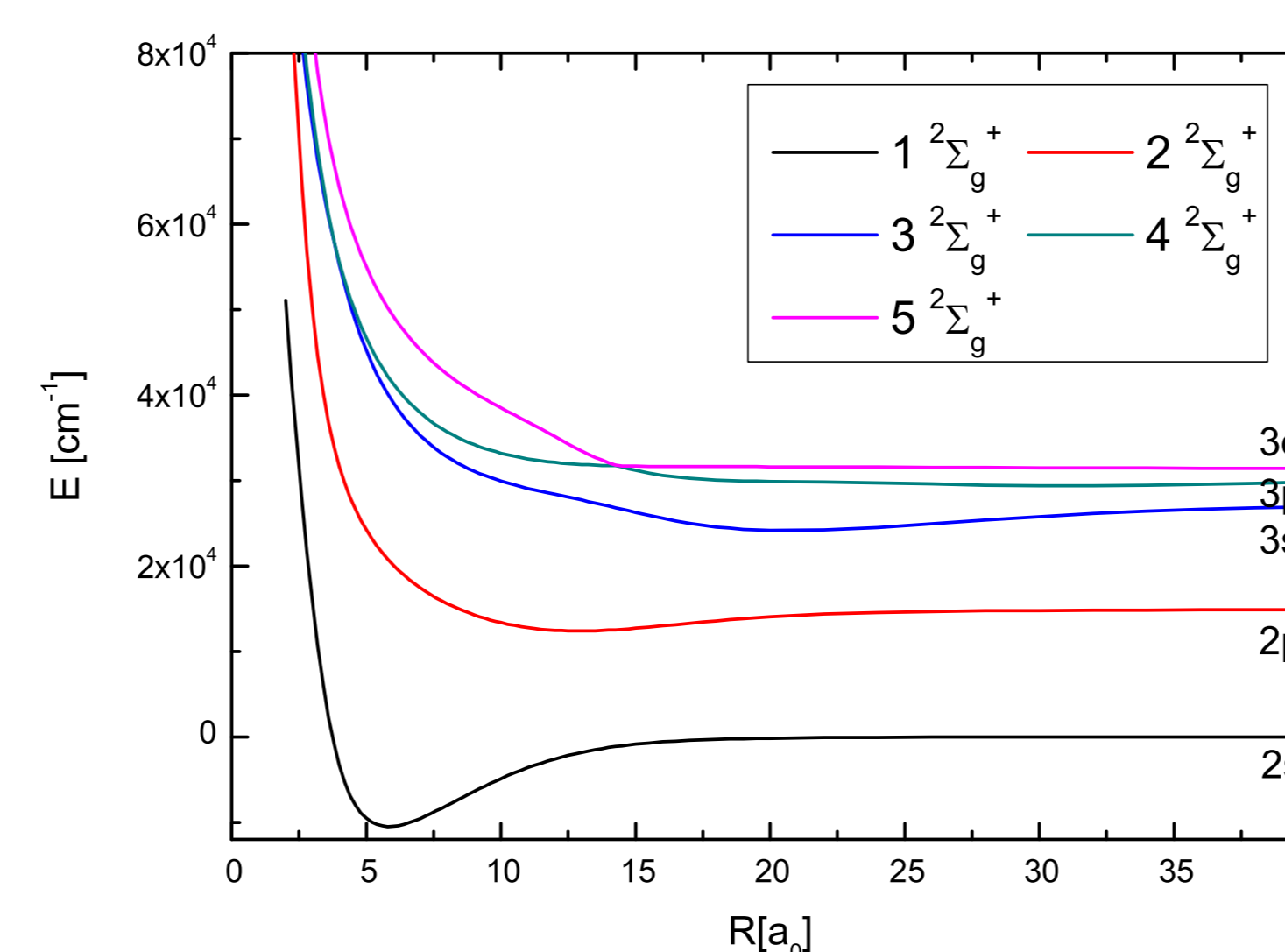


Fig. 2. Adiabatic potential energy curves for the ground and 4 excited states in the symmetry $2^2\Sigma_g^+$ of the Li_2^+ molecule correlating to the $Li^+ + Li(2s)$, $Li^+ + Li(2p)$, $Li^+ + Li(3s)$, $Li^+ + Li(3p)$ and $Li^+ + Li(3d)$ asymptotes.

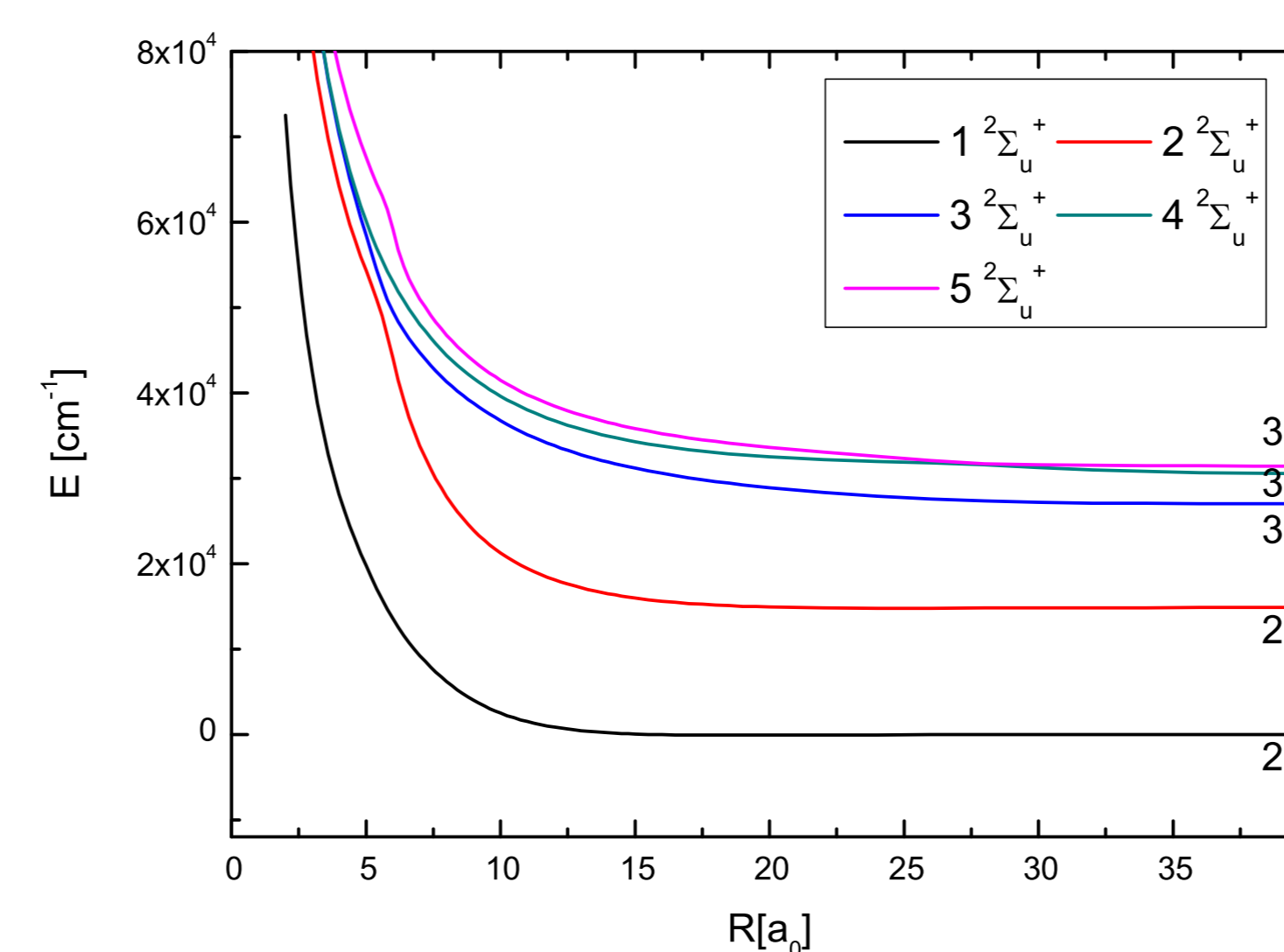


Fig. 3. Adiabatic potential energy curves for 5 excited states in the symmetry $2^2\Sigma_u^+$ of the Li_2^+ molecule correlating to the $Li^+ + Li(2s)$, $Li^+ + Li(2p)$, $Li^+ + Li(3s)$, $Li^+ + Li(3p)$ and $Li^+ + Li(3d)$ asymptotes.

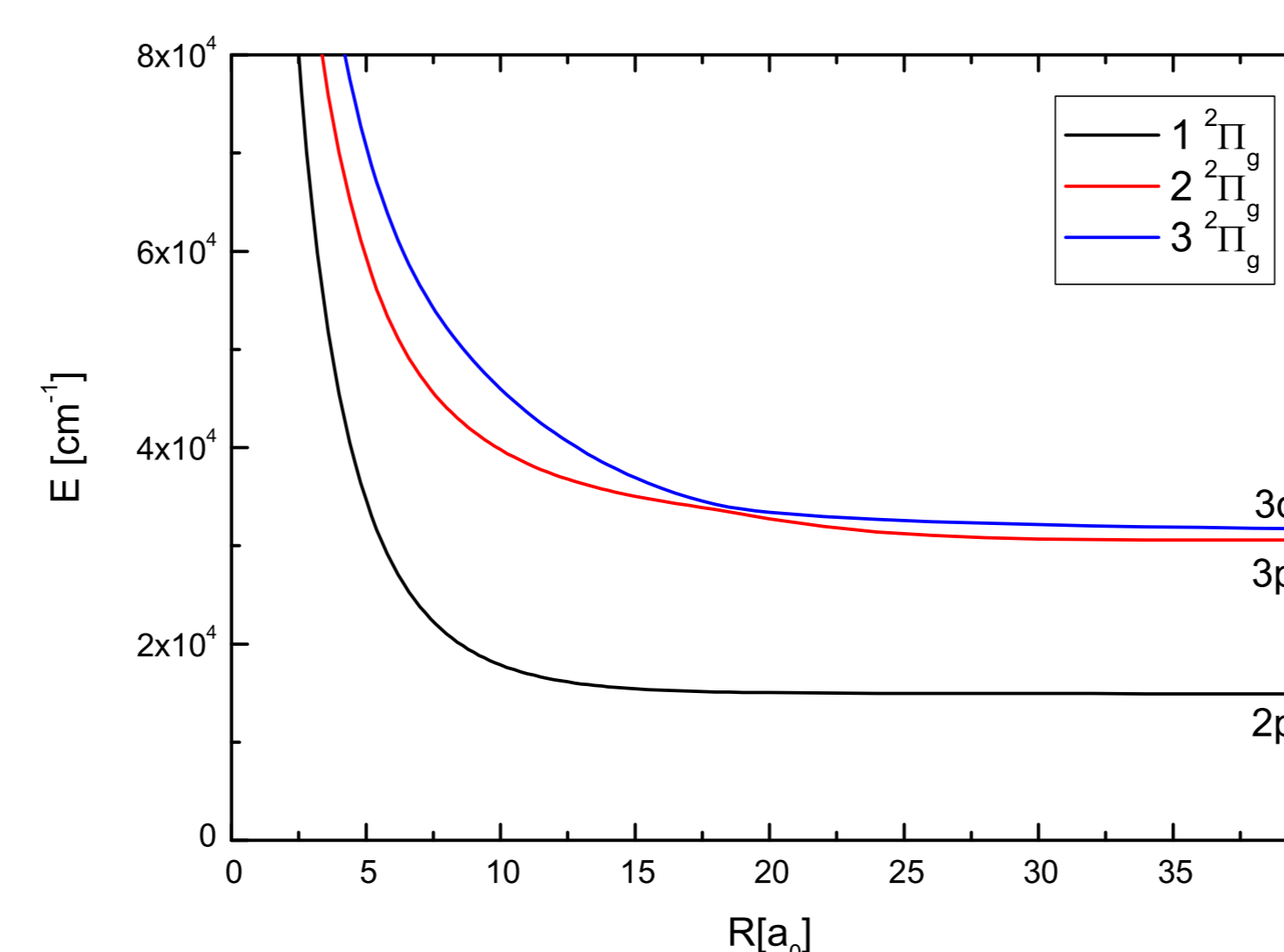


Fig. 4. Adiabatic potential energy curves for 3 excited states in the symmetry $2^2\Pi_g$ of the Li_2^+ molecule correlating to the $Li^+ + Li(2p)$, $Li^+ + Li(3p)$ and $Li^+ + Li(3d)$ asymptotes.

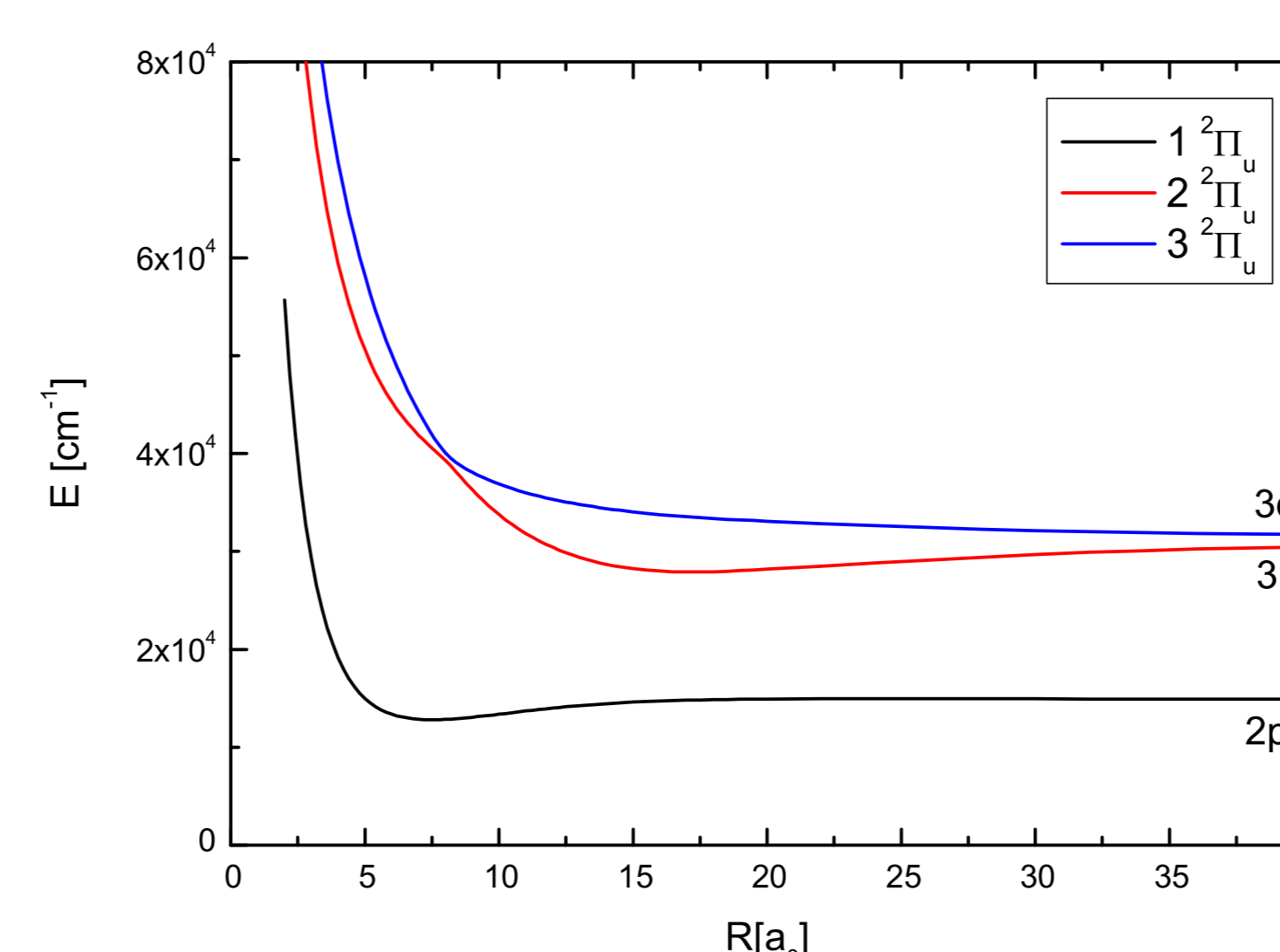


Fig. 5. Adiabatic potential energy curves for 3 excited states in the symmetry $2^2\Pi_u$ of the Li_2^+ molecule correlating to the $Li^+ + Li(2p)$, $Li^+ + Li(3p)$ and $Li^+ + Li(3d)$ asymptotes.

All states

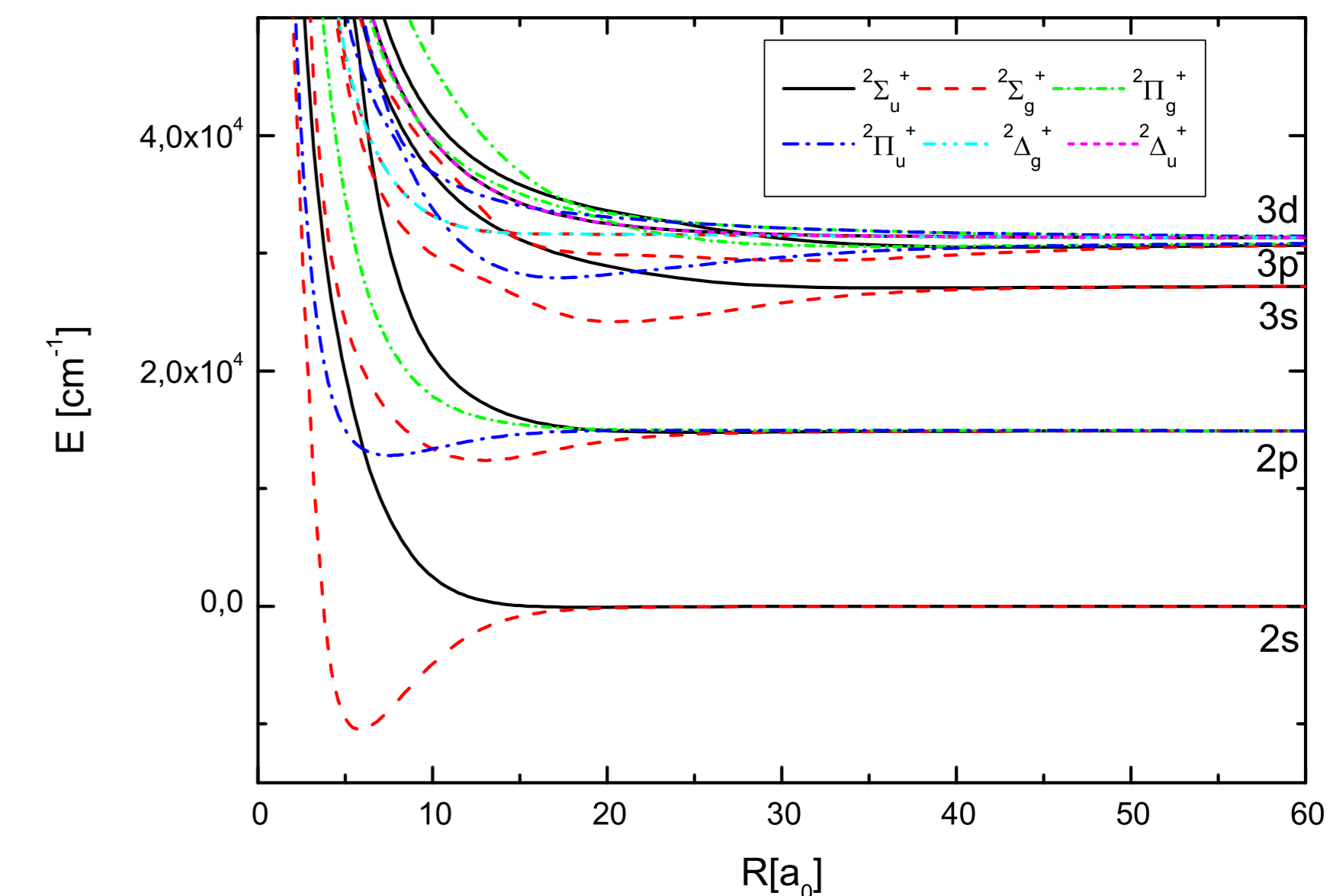


Fig. 6. Adiabatic potential energy curves for all calculated by us states of the Li_2^+ molecule correlating to the $Li^+ + Li(2s)$, $Li^+ + Li(2p)$, $Li^+ + Li(3s)$, $Li^+ + Li(3p)$ and $Li^+ + Li(3d)$ asymptotes.

Conclusion

We have calculated the adiabatic potential energy curves of the lithium ion dimer using CASSCF/MRCI method. Comparisons with available low-lying theoretical and experimental curves provide almost perfect agreement. For the first time we present spectroscopic parameters for three states $3^2\Sigma_g^+$, $4^2\Sigma_g^+$ and $2^2\Pi_g$ previously known as repulsive potentials (Table 2). We obtained these adiabatic potential energy curves with minima, because all our states were calculated for large internuclear separations R (up to $100 a_0$). All of our new minima are very shallow and very wide: $3^2\Sigma_g^+ - R_e = 19.492 a_0$ and $D_e = 162 cm^{-1}$; $4^2\Sigma_g^+ - R_e = 23 a_0$ and $D_e = 383.5 cm^{-1}$; $2^2\Pi_g - R_e = 19.144 a_0$ and $D_e = 349 cm^{-1}$. In Fig. 7. we present these minima near their equilibrium positions which are lain in the large distance on the internuclear separations scale.

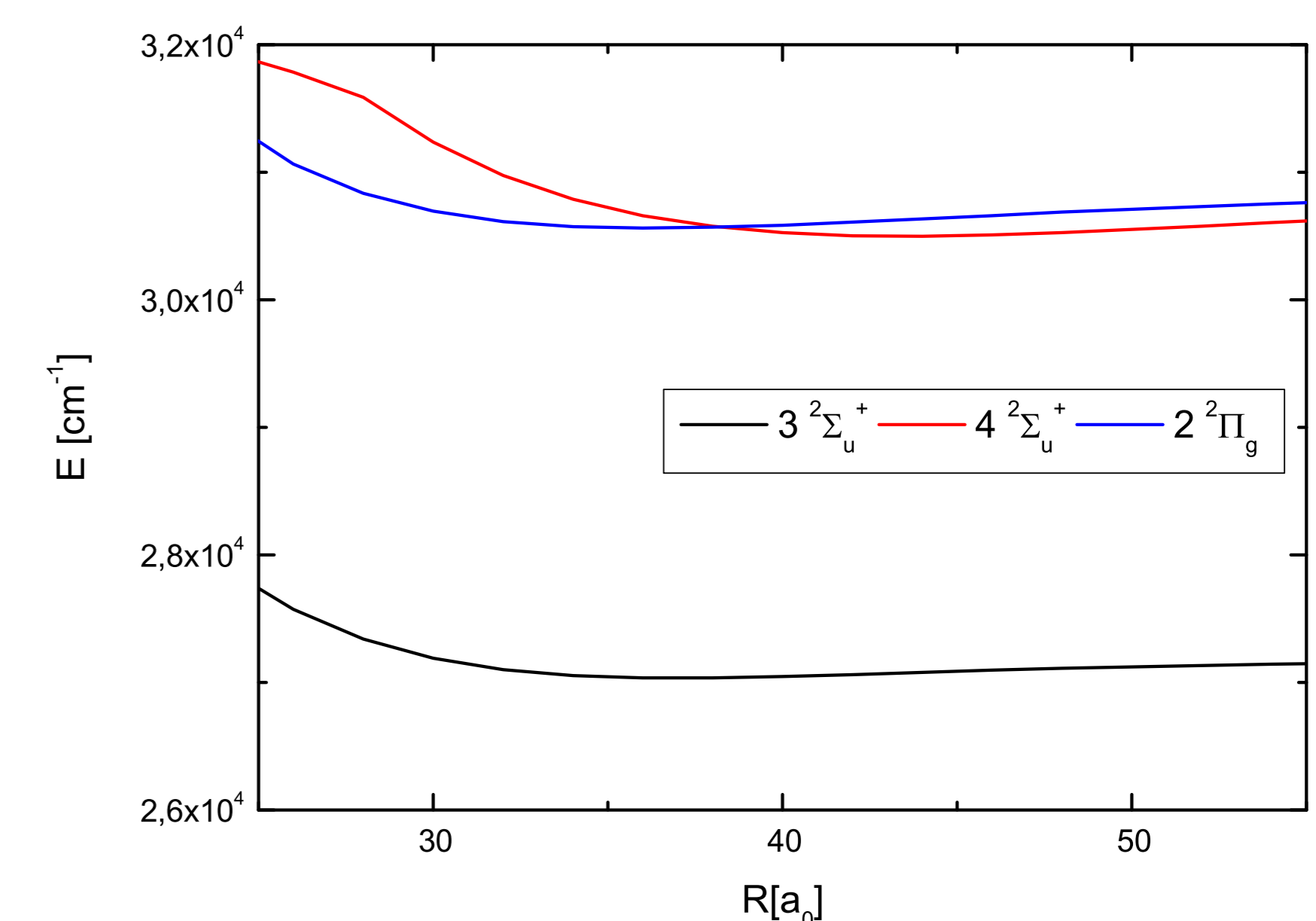


Fig. 7. Three states $3^2\Sigma_g^+$, $4^2\Sigma_g^+$ and $2^2\Pi_g$ with previously unknown minima near their equilibrium positions.

References

- References
- [1] D. D. Konowalow and M. E. Rosenkrantz, *Chem. Phys. Lett.* **61**, 489 (1979).
 - [2] I. Schmidt-Mink, W. Müller and W. Meyer, *Chem. Phys.* **92**, 263 (1985).
 - [3] S. Magnier, S. Rousseau, A. R. Allouche, G. Hadinger and M. Aubert-Frécon, *Chem. Phys.* **245**, 57 (1999).
 - [4] R. A. Bernheim, L. P. Gold and T. Tipton, *Chem. Phys.* **78**, 3635 (1983).
 - [5] R. A. Bernheim, L. P. Gold, T. Tipton and D. Konowalow, *Chem. Phys. Lett.* **105**, 201 (1984).
 - [6] M. W. McGeoch and R. E. Schlier, *Chem. Phys. Lett.* **99**, 347 (1983).
 - [7] P. Jasik and J. E. Sienkiewicz, *Chem. Phys.* **323**, 563 (2006).
 - [8] P. Jasik and J. E. Sienkiewicz, *SPIE Proceedings* **5849**, 82 (2005).
 - [9] MOLPRO is a package of *ab initio* programs written by H. J. Werner and P. J. Knowles with contributions from R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobson, F. Eckert, C. Hampel, G. Hetzer, T. Leininger, R. Lindh, A. W. Lloyd, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Peterson, R. Pitzer, P. Pulay, G. Rauhut, M. Schütz, H. Stoll, A. J. Stone and T. Thorsteinsson.
 - [10] P. Fuentealba, H. Preuss, H. Stoll and L. Von Szentpály, *Chem. Phys. Lett.* **89**, 418 (1982).
 - [11] P. O. Widmark, P. A. Malmqvist and B. O. Roos, *Theor. Chim. Acta* **77**, 291 (1990).
 - [12] S. Bashkin, J. O. Stoner Jr. Atomic energy levels and grotian diagrams, Vol. 1, North-Holland, Amsterdam, (1975).

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