

Theoretical study of the electronic structure of the KLi dimer

L. Miądowicz¹, P. Jasik² and J.E. Sienkiewicz²

¹Students' Scientific Group of Physics, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, ul. Gabriela Narutowicza 11/12, 80-233 Gdansk, Poland

²Department of Theoretical Physics and Quantum Informatics, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, ul. Gabriela Narutowicza 11/12, 80-233 Gdansk, Poland

Introduction

Homonuclear and heteronuclear alkali metal dimers and their ions have attracted attention of experimentalists and theoreticians for many years, mainly because they have got simple electronic structure (one or two valence-electron systems). It can serve as a convenient prototype for testing theoretical methods, which can be further applied to more complicated molecular systems. First useful theoretical calculations of the adiabatic potential energy curve for the ground state in the *KLi* dimer were presented by Müller *et al.* [1]. Next theoretical report describing 58 electronic states of *KLi* molecule using the non-empirical one-electron pseudopotentials, polarisation potentials and full-valence configuration interaction method were performed by Rousseau *et al.* [2]. The most important experimental works, where several excited states of *KLi* molecule were presented, were performed by Bednarska *et al.* [3, 4, 5], Pashov *et al.* [6], Jastrzębski *et al.* [7], Salami *et al.* [8] and Jędrzejewski-Szmeke *et al.* [9]. Our present calculations are based on the self-consistent-field configuration interaction (SCF CI) scheme which was used in our previous reports [10, 11].

Computational method

All calculations reported in this poster were performed by means of the MOLPRO program package [12]. The core electrons of *Li* and *K* atoms are represented by pseudopotentials ECP2SDF and ECP18SDF [13], respectively. The lithium basis for *s* and *p* orbitals, which comes with effective core potential ECP2SDF is enlarged by functions for *d*, *f* and *g* orbitals given by Feller [14] and assigned by CC-PV5Z. However the potassium basis for the *s*, *p*, *d* and *f* orbitals come from ECP10MDF basis set [15]. Additionally, our basis set was augmented by five *s* short range correlation functions for lithium (9996.402900, 1979.970927, 392.169555, 77.676373, 15.385230) and ten *s* functions for potassium (7530.969794, 2964.819792, 1167.201123, 459.508016, 172.607917, 99.254143, 21.788139, 14.810218, 2.080527, 1.452954), five *p* functions for lithium (2290.589942, 470.456384, 96.625417, 19.845562, 4.076012) and eight for potassium (3397.736070, 1268.042754, 473.236411, 176.612895, 61.230054, 23.722464, 10.891771, 3.954910), five *d* functions for lithium (13.495412, 7.115763, 3.751948, 1.978300, 1.043103) and four for potassium (25.549602, 10.052166, 3.954897, 1.680236) and in the end three *f* functions for lithium (3.566932, 2.242072, 1.409302) and one *f* function for potassium (1.680236). Also, we added to the basis a set of twenty six diffused functions: three *s* functions for *Li* (0.010159, 0.003894, 0.001493) and four for *K* (0.003496, 0.001615, 0.000746, 0.000344), three *p* functions for *Li* (0.007058, 0.002598, 0.000956) and four for *K* (0.001431, 0.000521, 0.000190, 0.000069), three *d* functions for *Li* (0.026579, 0.011581, 0.005046) and four for *K* (0.240858, 0.010789, 0.003932, 0.001433) and at last four *f* functions for *Li* (0.885847, 0.556818, 0.055000, 0.027500) and one for *K* (0.029604). We checked the quality of our basis set performing the CI calculations for the ground and several excited states of isolated lithium and potassium atoms. The calculated *KLi* adiabatic potentials correlate to the *Li(2s) + K(4s)* ground atomic asymptote and *Li(2s) + K(4p)*, *Li(2p) + K(4s)*, *Li(2s) + K(5s)*, *Li(2s) + K(3d)* and *Li(2s) + K(5p)* excited atomic asymptotes. The comparison of experimental and theoretical asymptotic energies for different states is shown in Table 1. We do not take into consideration in our calculations spin-orbit couplings (SO). The potential energy curves for *KLi* 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	Moore (exp.) [16]	Present work	Rousseau (theory) [2]
<i>Li(2s) + K(4p)</i>	13028	12997	13022
<i>Li(2p) + K(4s)</i>	14904	14911	14905
<i>Li(2s) + K(5s)</i>	21026	21009	21018
<i>Li(2s) + K(3d)</i>	21535	21526	21536
<i>Li(2s) + K(5p)</i>	24715	24714	24751

Calculations of the adiabatic potential energy curves are performed for the internuclear separation *R* in the range from 3 *a*₀ to 70 *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. 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 (*a*₀) and *D*_e (*cm*⁻¹) for the ground and excited states of *KLi* molecule.

State	<i>R</i> _e	<i>D</i> _e
$1^1\Sigma^+$		
Exp.[5, 6]	6.27	6216
Theory[1]	6.29	6138
Theory[2]	6.20	6220
Present work	6.25	6366
$2^1\Sigma^+$		
Theory[2]	7.40	7186
Present work	7.50	7241
$3^1\Sigma^+$		
Exp.[5, 6]	7.92	3619
Theory[2]	7.80	3477
Present work	7.75	3640
$1^3\Sigma^+$		
Theory[2]	9.40	273
Present work	9.25	299
$2^3\Sigma^+$		
Theory[2]	7.40	4309
Present work	7.25	4381
$1^1\Pi$		
Exp.[5, 6]	7.02	1686
Theory[2]	7.10	1517
Present work	7.00	1711
$2^1\Pi$		
Theory[2]	7.60	1584
Present work	7.50	1683

Contact with authors

Łukasz Miądowicz e-mail: Lmiadowicz@gmail.com
 Patryk Jasik e-mail: p.jasik@mif.pg.gda.pl
 Józef E. Sienkiewicz e-mail: jes@mif.pg.gda.pl

Results

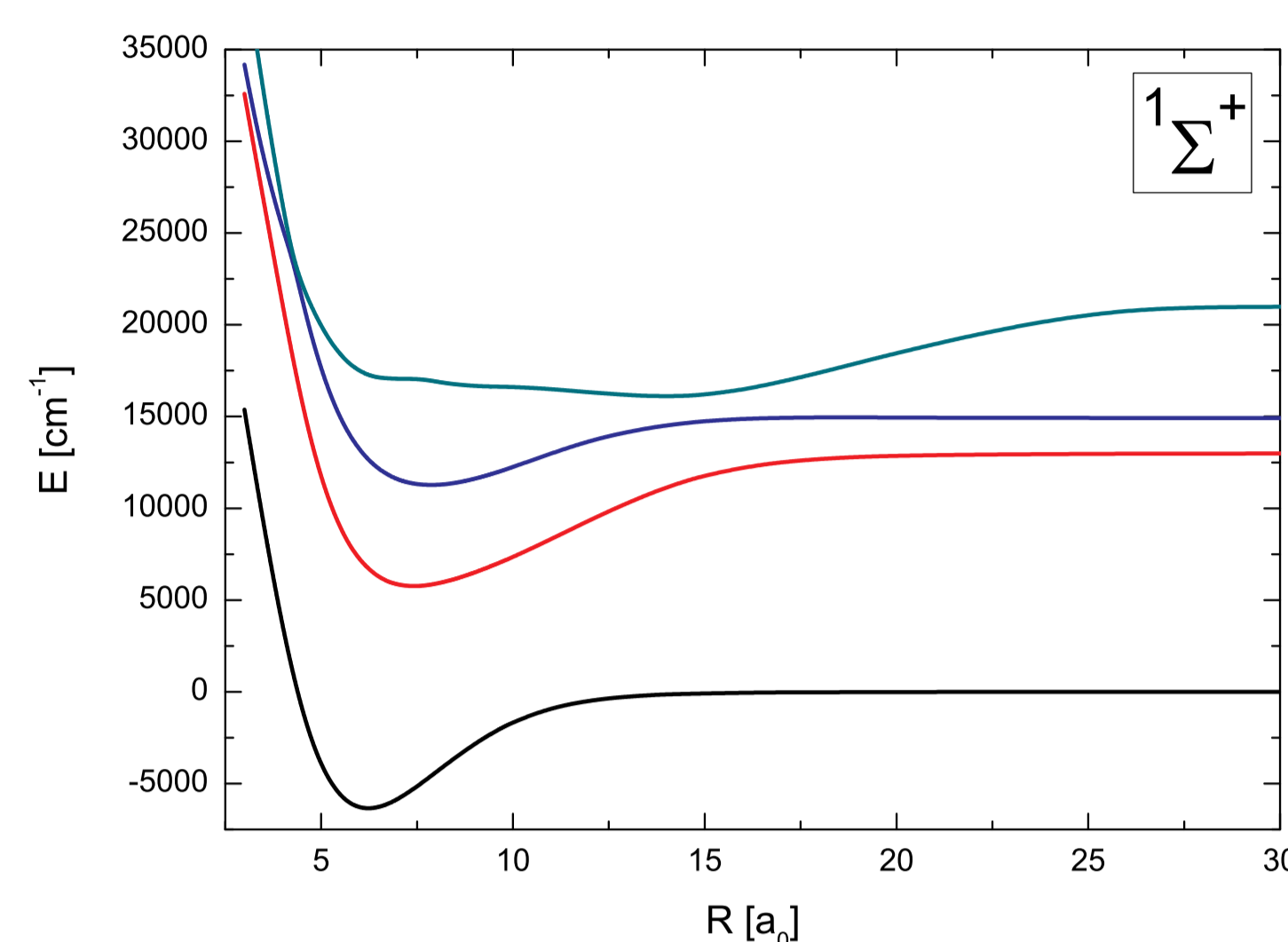


Fig. 1. Adiabatic potential energy curves for the ground and 3 excited states in the symmetry $1^1\Sigma^+$ of the *KLi* molecule correlating to the *Li(2s) + K(4s)*, *Li(2s) + K(4p)*, *Li(2p) + K(4s)* and *Li(2s) + K(5s)* asymptotes.

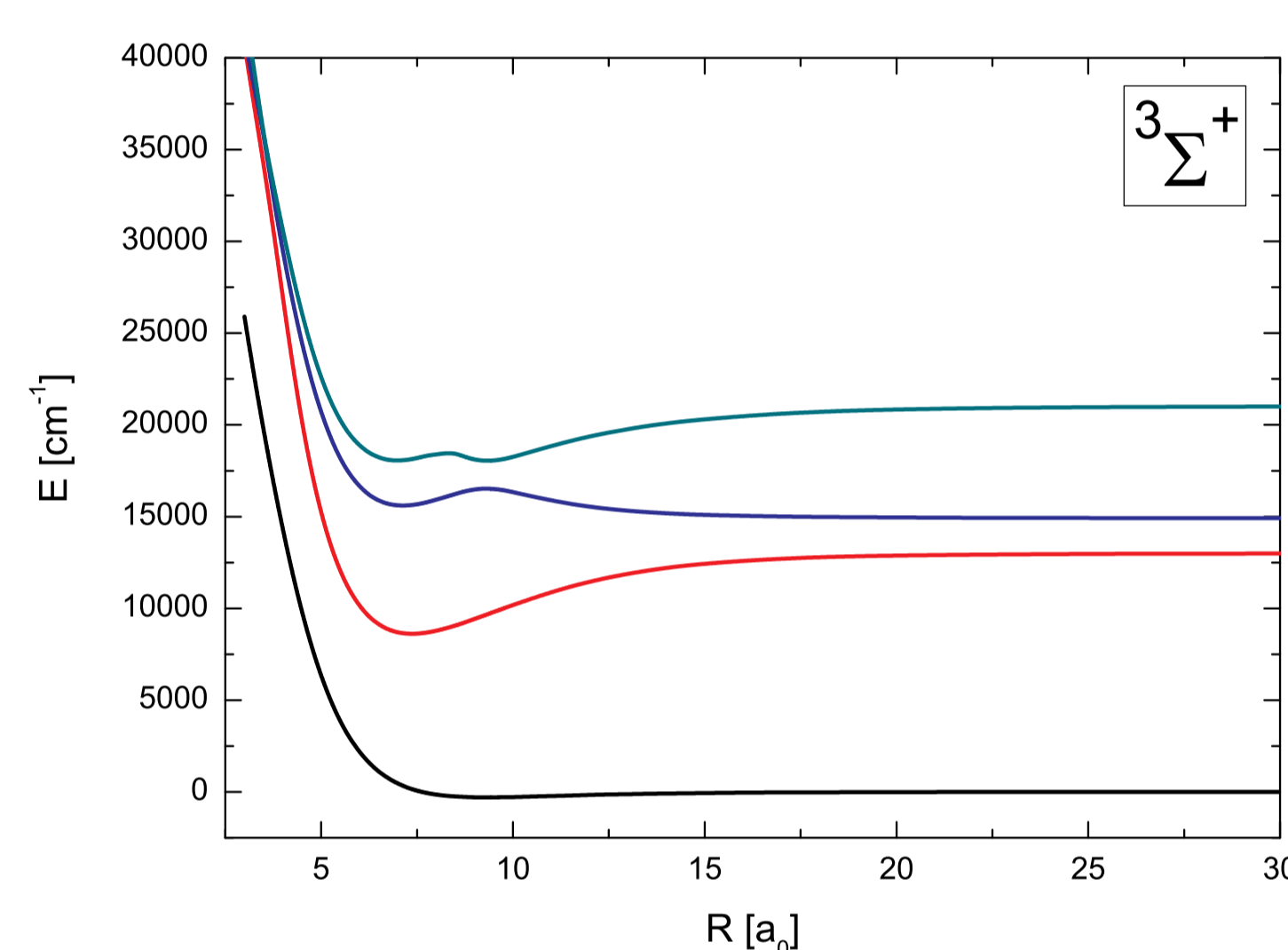


Fig. 2. Adiabatic potential energy curves for 4 excited states in the symmetry $3^1\Sigma^+$ of the *KLi* molecule correlating to the *Li(2s) + K(4s)*, *Li(2s) + K(4p)*, *Li(2p) + K(4s)* and *Li(2s) + K(5s)* asymptotes.

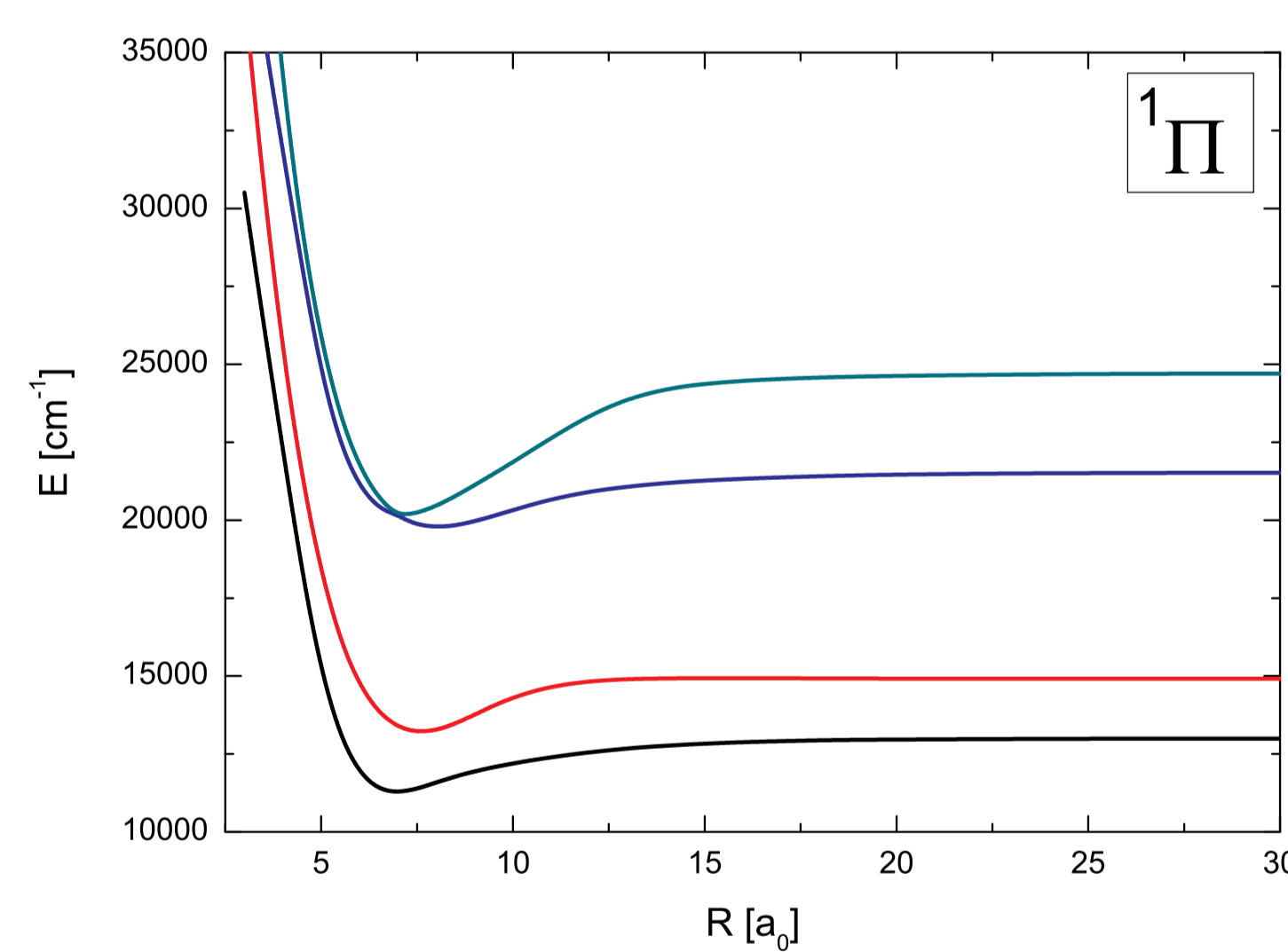


Fig. 3. Adiabatic potential energy curves for 4 excited states in the symmetry $1^1\Pi$ of the *KLi* molecule correlating to the *Li(2s) + K(4p)*, *Li(2p) + K(4s)*, *Li(2s) + K(3d)* and *Li(2s) + K(5p)* asymptotes.

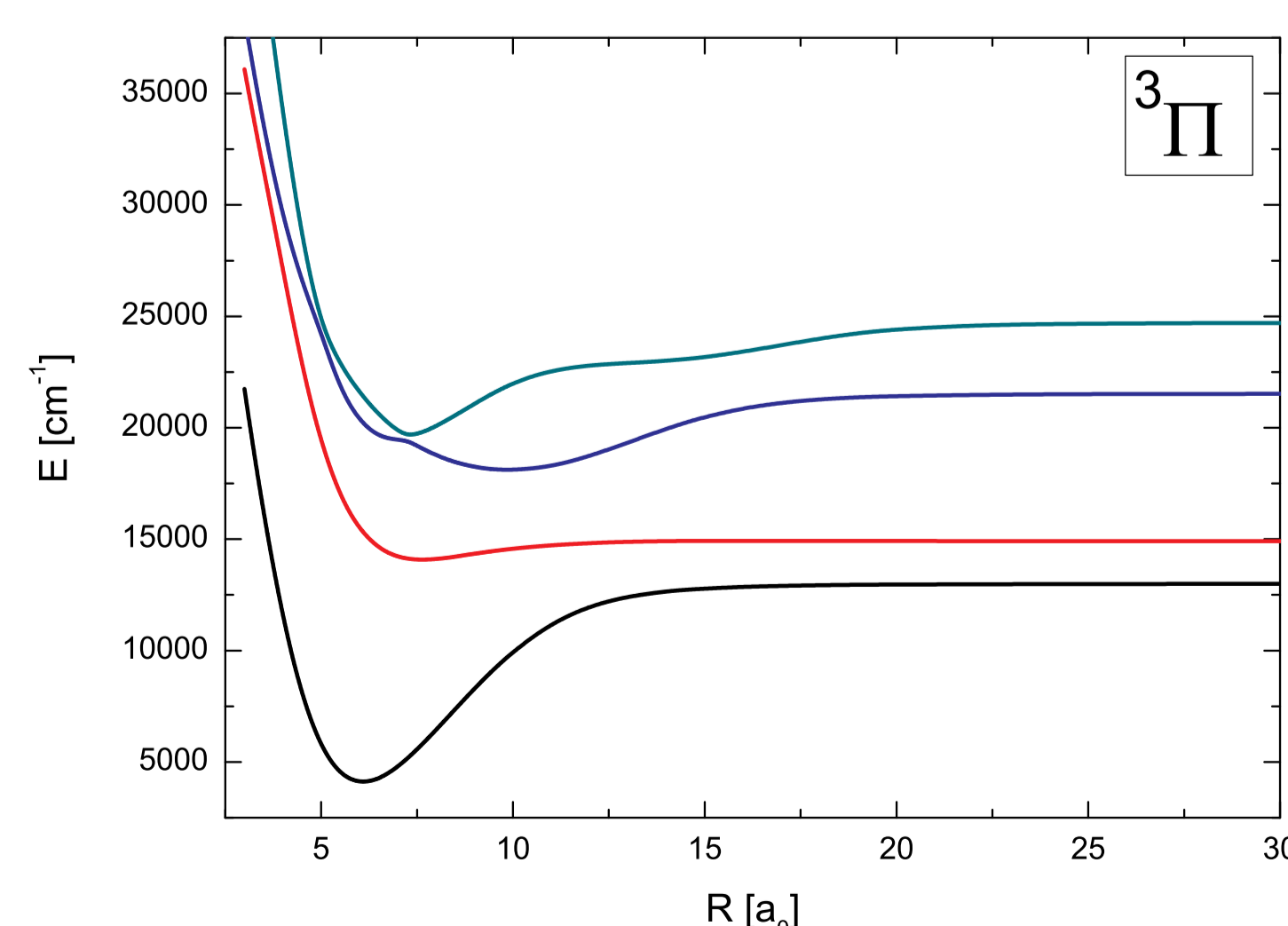


Fig. 4. Adiabatic potential energy curves for 4 excited states in the symmetry $3^1\Pi$ of the *KLi* molecule correlating to the *Li(2s) + K(4p)*, *Li(2p) + K(4s)*, *Li(2s) + K(3d)* and *Li(2s) + K(5p)* asymptotes.

Results

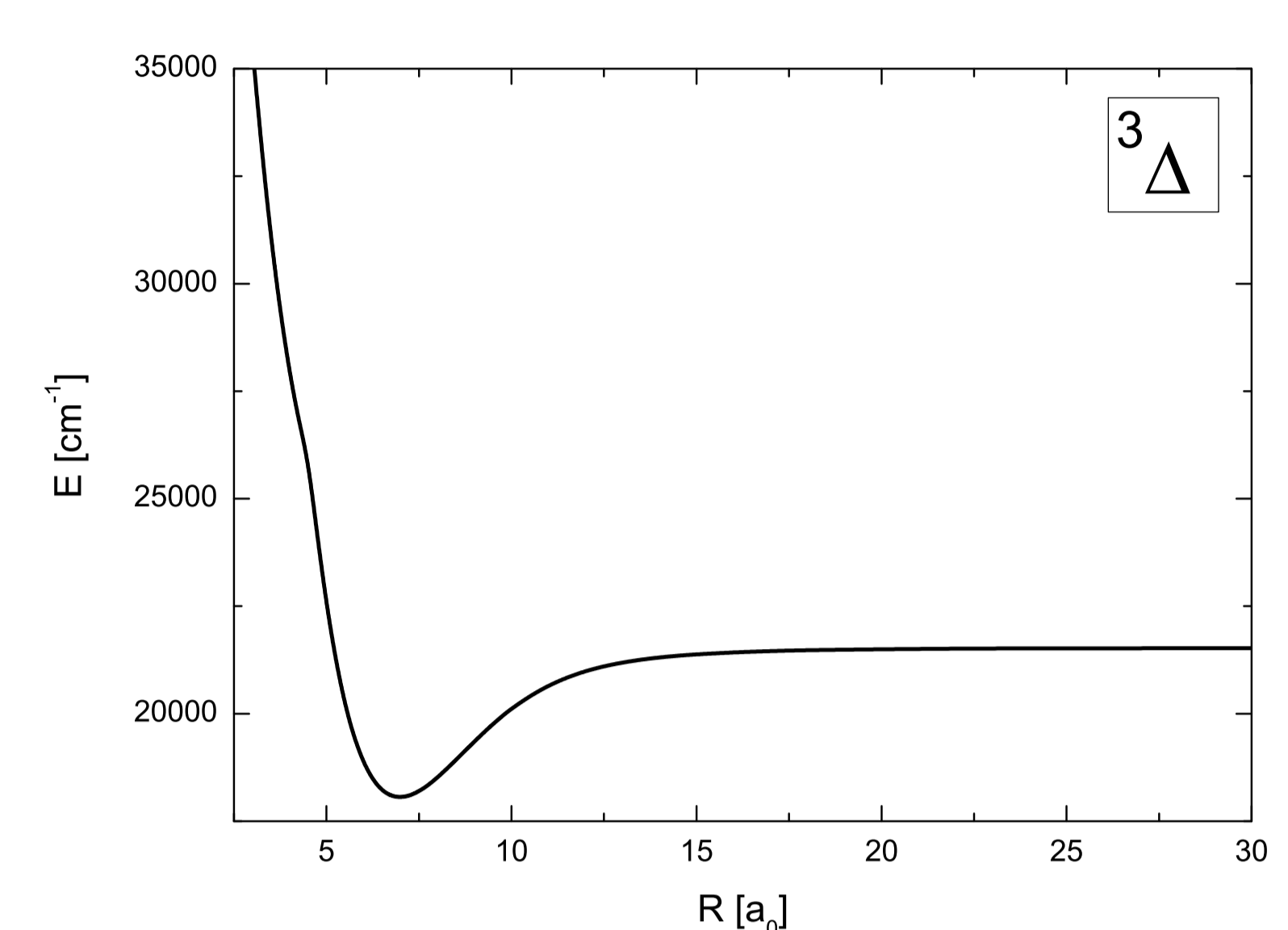


Fig. 5. Adiabatic potential energy curves for 1 excited state in the symmetry $3^1\Delta$ of the *KLi* molecule correlating to the *Li(2s) + K(3d)* asymptote.

Comparisons

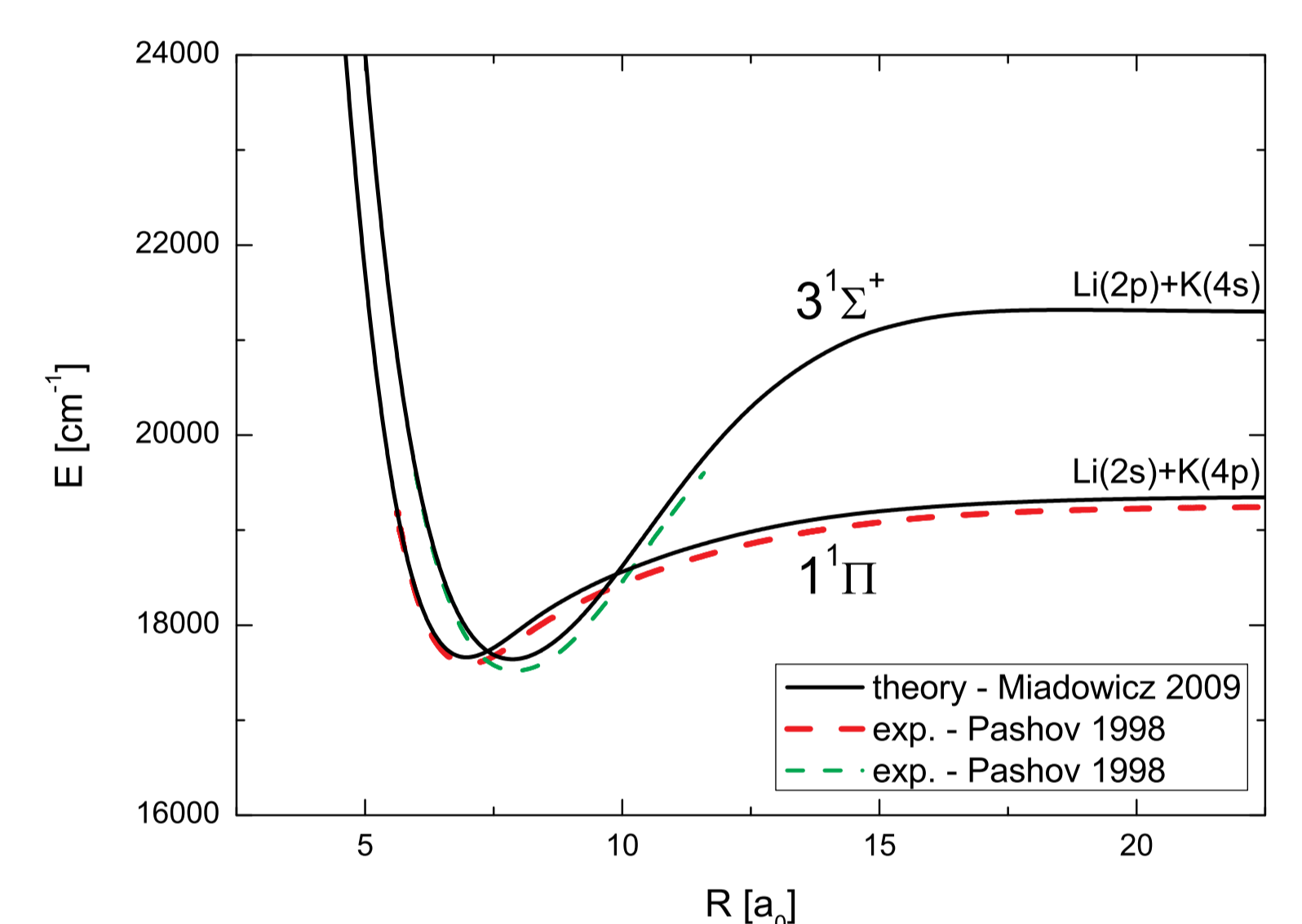


Fig. 7. Comparison of the $1^1\Pi$ and $3^1\Sigma^+$ states correlating, respectively, to *Li(2s) + K(4p)* and *Li(2p) + K(4s)* asymptotes with experimental results obtained by Pashov *et al.* [6].

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Acknowledgments

This scientific work is partially financed by the COST Action CM0702 - Chemistry with Ultrashort Pulses and Free-Electron Lasers: Looking for Control Strategies Through Exact Computations (CUSPEL).