

Adiabatic potentials of single ionized diatomic potassium molecule

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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. The first useful theoretical calculations on K_2^+ using the Hellmann-type pseudopotential method were performed by Valance [1]. For the first time full *ab initio* calculations were presented by Jeung *et al.* [2] and later by Montagnani [3]. Next, Nemukhin *et al.* [4] and Henriot *et al.* [5, 6] performed model potential calculations where they obtained several lowest lying states of K_2^+ molecule. In 90' a few new theoretical methods were used to obtain adiabatic potential energy curves for the potassium dimer. For example, the Fock space open-shell coupled cluster method was used by Ilyabaev *et al.* [7] and the generalized Heitler-London theory was used by Johann *et al.* [8]. The last theoretical results were presented by Magnier *et al.* [9, 10] where authors calculated adiabatic potential energy curves for ground and numerous excited states of potassium ion dimer. The most important experimental works where only ground state of K_2^+ molecule was taken into account were performed by Leutwyler *et al.* [11], Broyer *et al.* [12] and Stwalley *et al.* [13]. Our present calculations are based on the self-consistent-field configuration interaction (SCF CI) scheme which was used in our previous reports [14, 15].

Computational method

All calculations reported in this poster were performed by means of the MOLPRO program package [16]. The core electrons of K atoms are represented by pseudopotential ECP18SDF [17]. The basis for the s , p , d and f orbitals come from ECP10MDF basis set [18]. Additionally, our basis set was augmented by twelve s short range correlation functions (7530.969794, 2964.819792, 1167.201123, 459.508016, 172.607917, 99.254143, 21.788139, 14.810218, 12.123897, 2.575419, 2.080527, 1.452954), nine p functions (3397.736070, 1268.042754, 473.236411, 176.612895, 61.230054, 23.722464, 10.891771, 3.954910, 1.714952), four d functions (25.549602, 10.052166, 3.954897, 1.680236) and one f function (1.680236). Also, we added to the basis a set of eighteen diffuse functions: seven s functions (0.191032, 0.138106, 0.124861, 0.003496, 0.001615, 0.000746, 0.000344), six p functions (0.588121, 0.240857, 0.001431, 0.000521, 0.000190, 0.000069), four d functions (0.240858, 0.010789, 0.003932, 0.001433) and one f function (0.029604). We checked the quality of our basis set performing the CI calculations for the ground and several excited states of isolated potassium atom. The calculated K_2^+ adiabatic potentials correlate to the ($4s$) ground atomic asymptote and ($4p$), ($5s$), ($3d$), ($5p$), ($4d$) and ($6s$) 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 the spin-orbit couplings (SO) in our calculations. The potential energy curves for K_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	Moore (exp.) [19]	Present work	Magnier (theory) [9]
$K^+ + K(4p)$	13028	12999	13078
$K^+ + K(5s)$	21026	21011	20980
$K^+ + K(3d)$	21535	21529	21575
$K^+ + K(5p)$	24715	24715	24670
$K^+ + K(4d)$	27397	27399	27366
$K^+ + K(6s)$	27450	27443	27424

Calculations of the adiabatic potential energy curves are performed for the internuclear separation R in the range from $4.75a_0$ to $190a_0$ 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 K_2^+ molecule.

State	R_e	D_e
$1^2\Sigma_g^+$		
Exp.[11]	8.31	6444
Exp.[12]	8.31	6670
Exp.[13]		6669
Theory[1]	7.90	8296
Theory[5]	8.47	6690
Theory[7]	8.60	6574
Theory[9]	8.30	6685
Present work	8.40	6753
$2^2\Sigma_g^+$		
Theory[9]	16.00	3048
Present work	15.98	3096
$3^2\Sigma_g^+$		
Theory[9]	26.25	2233
Present work	25.91	2176
$4^2\Sigma_g^+$		
Theory[9]	19.25	587
Present work	18.98	503
$5^2\Sigma_g^+$		
Theory[9]	39.50	1202
Present work	39.97	1121
$1^2\Sigma_u^+$		
Theory[7]	22.30	110
Theory[9]	22.55	80
Present work	21.91	83
$2^2\Sigma_u^+$		
Theory[9]	30.25	188
Present work	29.68	202
$3^2\Sigma_u^+$		
Theory[9]	41.75	138
Present work	44.35	134
$4^2\Sigma_u^+$		
Theory[9]	49.25	73
Present work	44.99	39

Results

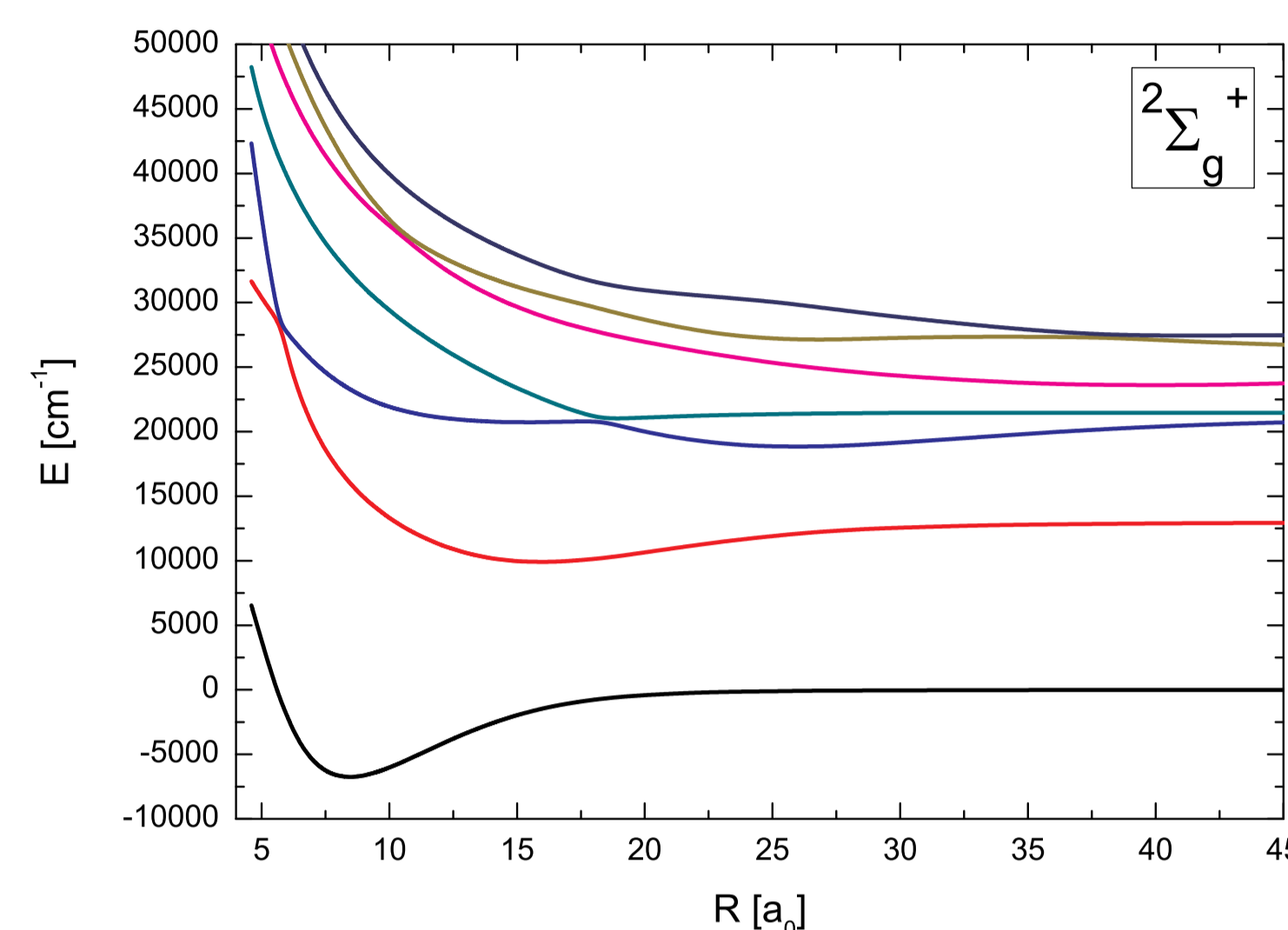


Fig. 1. Adiabatic potential energy curves for the ground and 6 excited states in the symmetry $2^2\Sigma_g^+$ of the K_2^+ molecule correlating to the $K^+ + K(4s)$, $K^+ + K(4p)$, $K^+ + K(5s)$, $K^+ + K(3d)$, $K^+ + K(5p)$, $K^+ + K(4d)$ and $K^+ + K(6s)$ asymptotes.

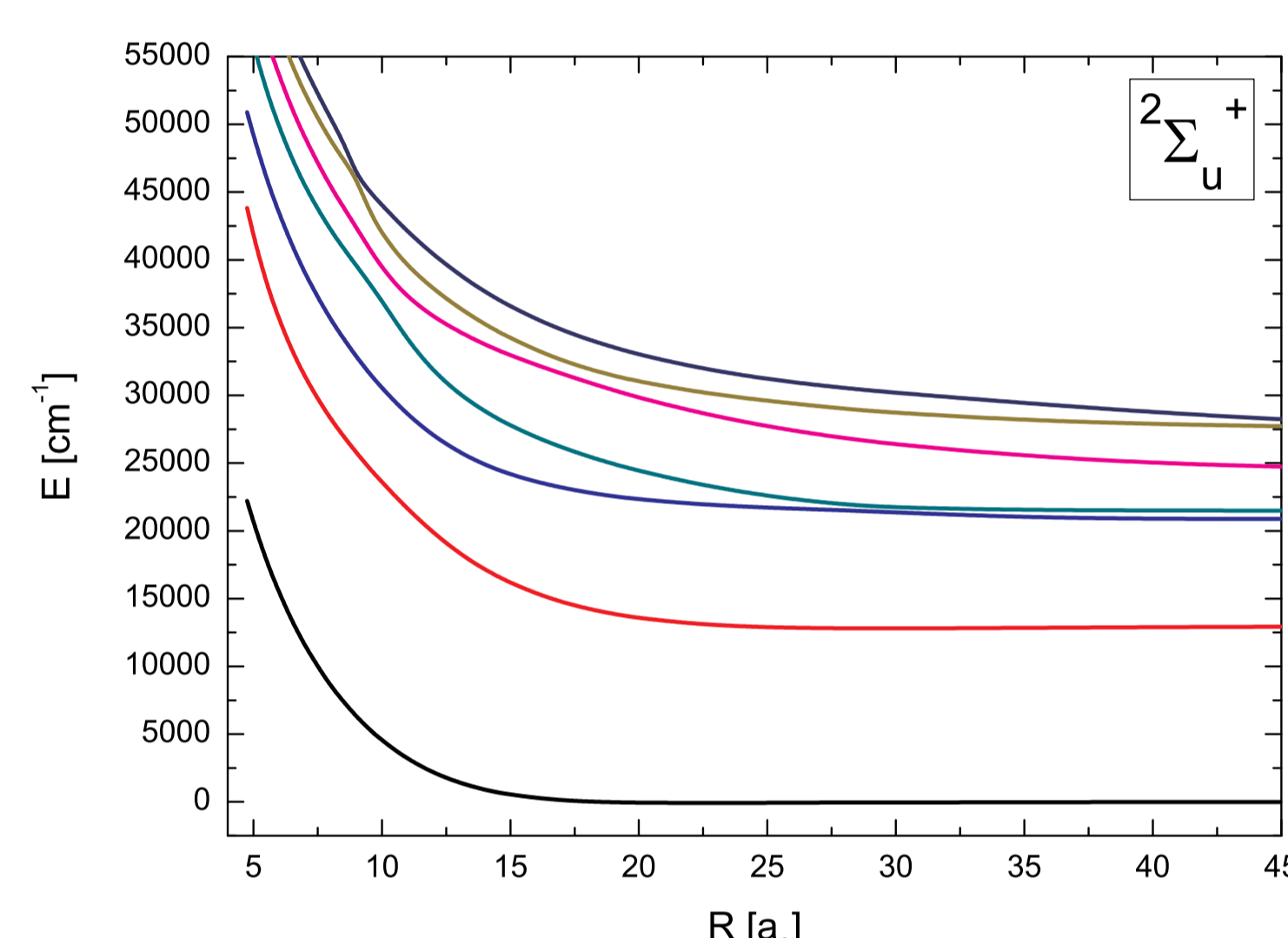


Fig. 2. Adiabatic potential energy curves for 7 excited states in the symmetry $2^2\Sigma_u^+$ of the K_2^+ molecule correlating to the $K^+ + K(4s)$, $K^+ + K(4p)$, $K^+ + K(5s)$, $K^+ + K(3d)$, $K^+ + K(5p)$, $K^+ + K(4d)$ and $K^+ + K(6s)$ asymptotes.

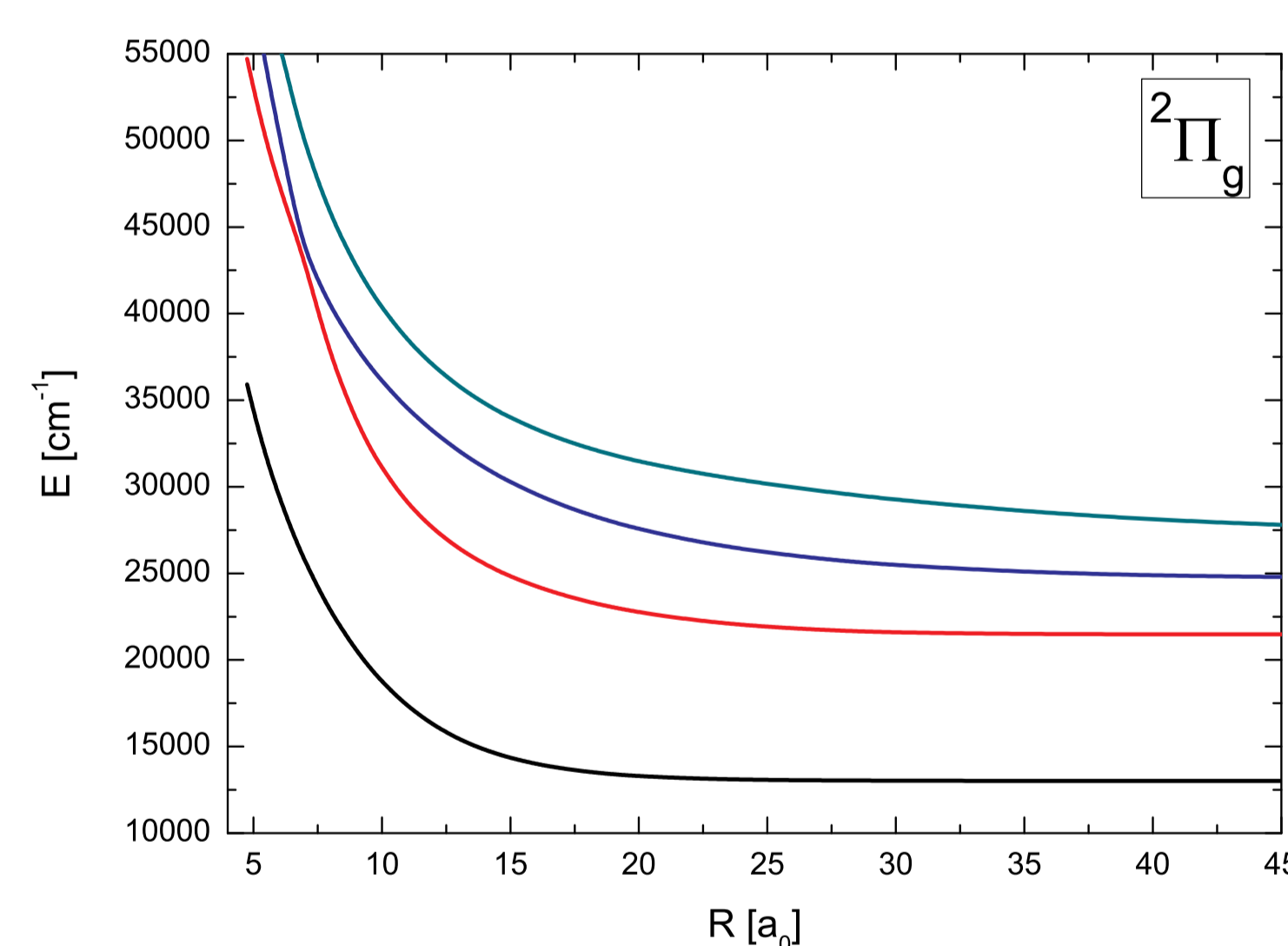


Fig. 3. Adiabatic potential energy curves for 4 excited states in the symmetry $2^2\Pi_g$ of the K_2^+ molecule correlating to the $K^+ + K(4p)$, $K^+ + K(3d)$, $K^+ + K(5p)$ and $K^+ + K(4d)$ asymptotes.

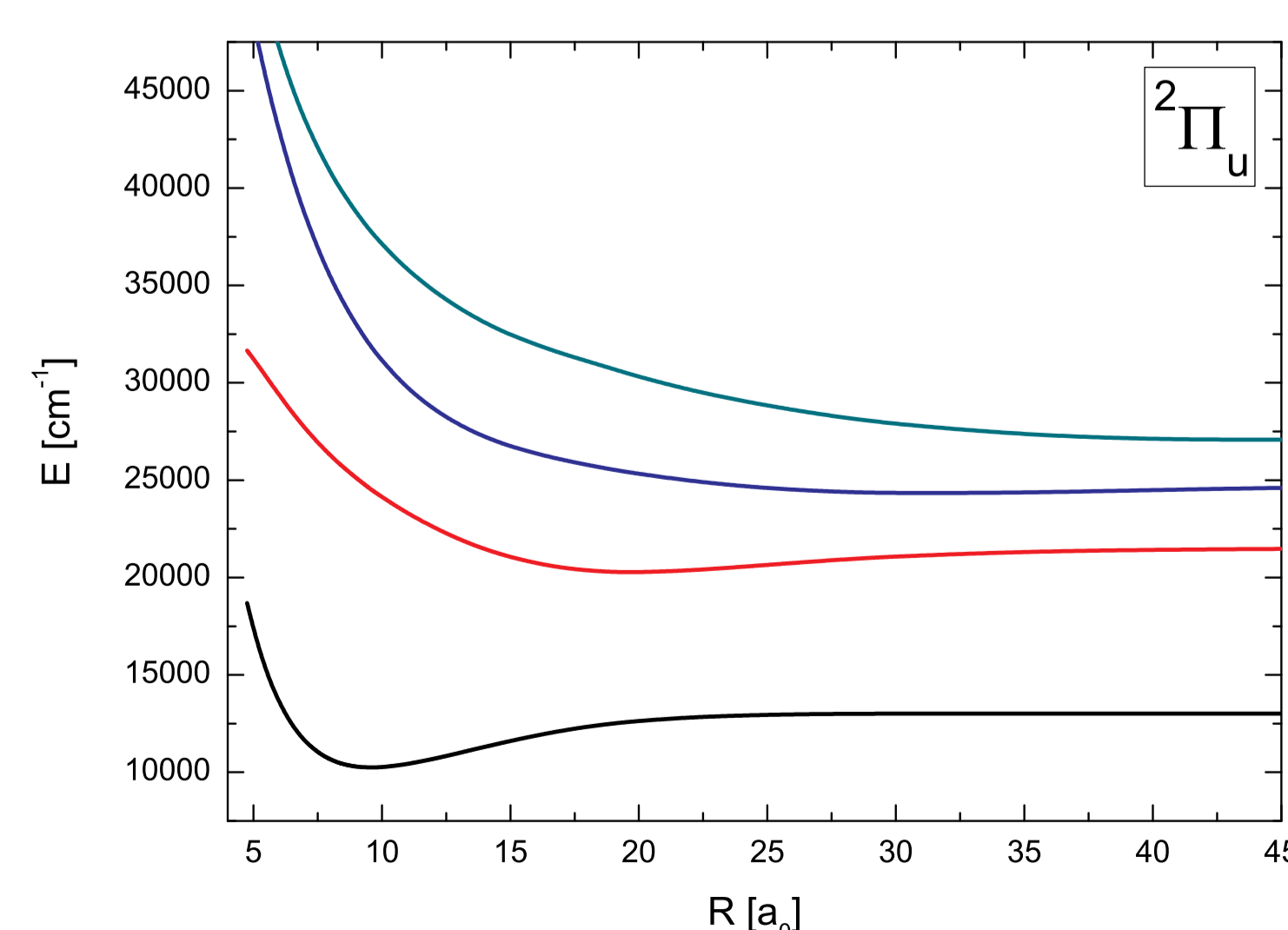


Fig. 4. Adiabatic potential energy curves for 4 excited states in the symmetry $2^2\Pi_u$ of the K_2^+ molecule correlating to the $K^+ + K(4p)$, $K^+ + K(3d)$, $K^+ + K(5p)$ and $K^+ + K(4d)$ asymptotes.

Results

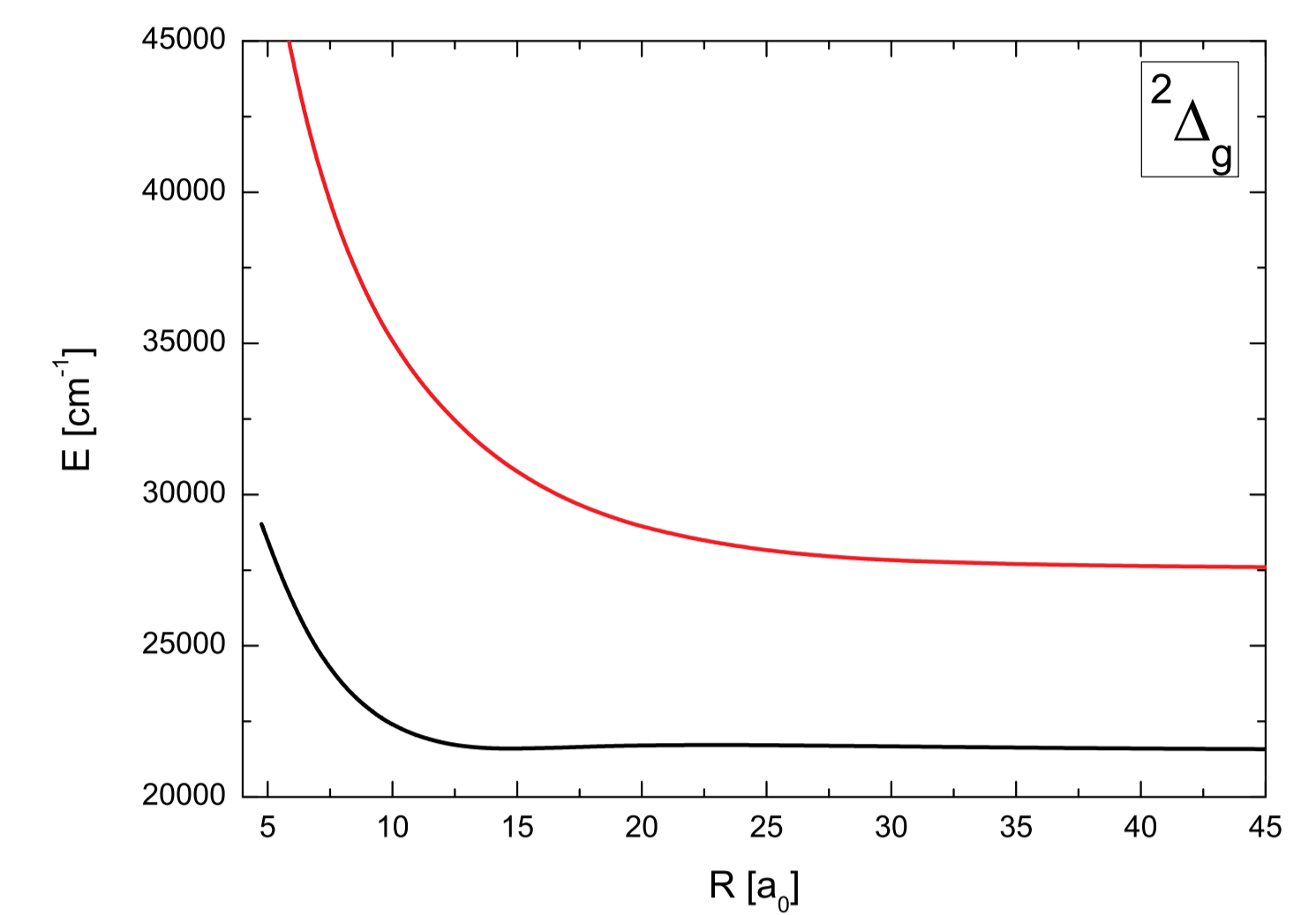


Fig. 5. Adiabatic potential energy curves for 2 excited states in the symmetry $2^2\Delta_g$ of the K_2^+ molecule correlating to the $K^+ + K(3d)$ and $K^+ + K(4d)$ asymptotes.

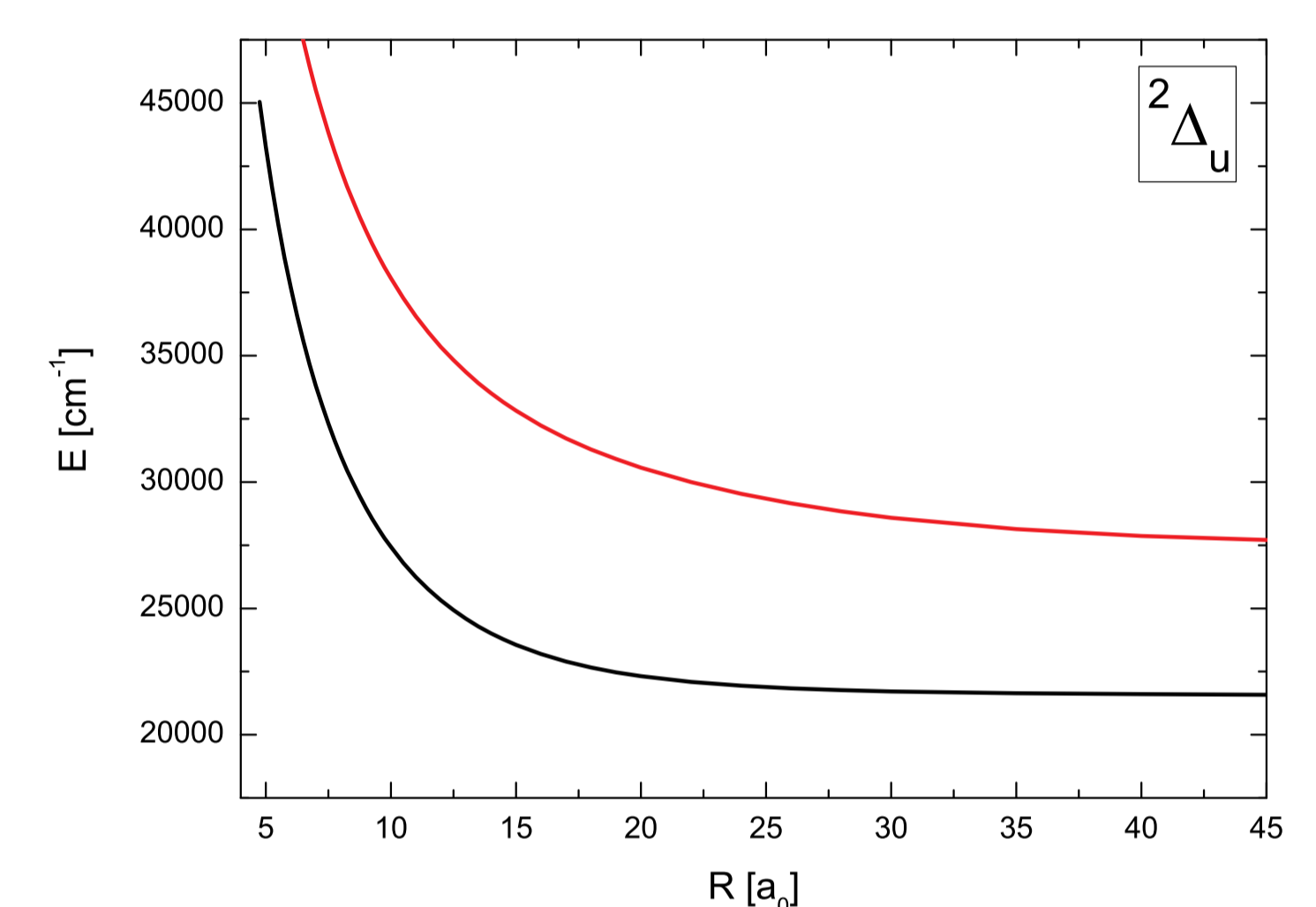


Fig. 6. Adiabatic potential energy curves for 2 excited states in the symmetry $2^2\Delta_u$ of the K_2^+ molecule correlating to the $K^+ + K(3d)$ and $K^+ + K(4d)$ asymptotes.

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