

## Study of Nonadiabatic Effects in the Li–Li<sub>2</sub><sup>+</sup> System. Location of Nonadiabatic Regions

Jan Vojtík, Alena Krtková and Rudolf Polák

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, CS-12138 Prague, Czechoslovakia

Nonadiabatic coupling between the lowest two singlet potential energy surfaces of the Li–Li<sub>2</sub><sup>+</sup> system is calculated using the diatomics-in-molecules method. Location of nonadiabatic regions in the configuration space of Li–Li<sub>2</sub><sup>+</sup> and their analysis is used to estimate those inner and translational states of the reactants which can lead to nonadiabatic behavior.

**Key words:** Nonadiabatic coupling—crude chemical model

### 1. Introduction

In our recent paper [1] we have embarked on the study of nonadiabatic effects in the Li–Li<sub>2</sub><sup>+</sup> system. In this system, the reaction  $\text{Li} + \text{Li}_2^+ \rightarrow \text{Li}_3^+$  is known to take place, and our main objective has been to explore whether or not the system can behave nonadiabatically as the reactants approach each other. To this end, typical ground-state minimum energy paths for this reaction were constructed and nonadiabatic transition probabilities between the lowest singlet states, corresponding to an idealized motion of the system along these pathways, were estimated. This approach to the Li–Li<sub>2</sub><sup>+</sup> system did not indicate any breakdowns in the Born–Oppenheimer approximation.

It is now of interest that symmetry considerations analogous to those of Preston and Tully [2] do predict nonadiabatic behavior of the Li–Li<sub>2</sub><sup>+</sup> system. One must of course take into account that symmetry arguments such as these, being qualitative, do not specify the conditions under which nonadiabatic behavior of the system occurs, and need not necessarily imply the failure of the crude chemical approach of Ref. [1] to give a physically meaningful picture of the behavior of

the Li-Li<sub>2</sub><sup>+</sup> system under chemical conditions. A detailed analysis of the H<sup>+</sup>-H<sub>2</sub> system [3] may serve to illustrate this fact.

The study of Li-Li<sub>2</sub><sup>+</sup> was based on the diatomics-in-molecules (DIM) calculation of the necessary quantities. A proper minimal basis DIM treatment of Li<sub>3</sub><sup>+</sup>, which can be considered to be physically relevant, is based on only three spin adapted polyatomic structures. It is therefore possible to supplement our previous calculation by a more extensive study of the lowest singlet potential energy surfaces (PES's), including the location and analysis of the nonadiabatic regions in the whole configuration space of the system.

In this communication we report such calculations. Using the results obtained, we estimate those inner and translational states of the reactants which can lead to non-adiabatic behavior of Li-Li<sub>2</sub><sup>+</sup>, and try to shed some light on the validity of the crude chemical approach in this particular case.

## 2. Calculation

The DIM model we used to perform the calculations for the lowest Born-Oppenheimer electronic singlet states of the Li<sub>3</sub><sup>+</sup> system was described in some detail in our previous communications [1, 4]. In view of this, we here only mention those features of the model which pertain to the present study. The approximations to the true potential energy surfaces are obtained from the diagonalization of the matrix

$$\mathbf{H} = \sum_{K>L}^3 \sum_{L=1}^2 \mathbf{T}_{(KL)} \mathbf{h}^{(KL)} \mathbf{T}_{(KL)}^+ - \sum_{K=1}^3 \mathbf{h}^{(K)} \quad (1)$$

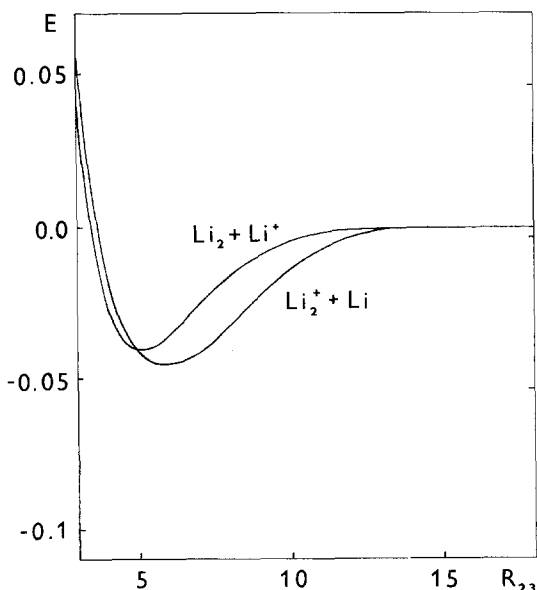


Fig. 1. Potential energy curves for the ground states of Li<sub>2</sub><sup>+</sup> and Li<sub>2</sub> drawn with same asymptote, showing crossing at  $R = 4.986$  a.u. Energy is in a.u.

which refers to a 3-dimensional spin-adapted DIM basis obtained by taking the <sup>2</sup>S ground state and the ionized Li<sup>+</sup>(<sup>1</sup>S) state on each nucleus. A unitary  $T_{(KL)}$  matrix transforms the set of primitive (unantisymmetrized) DIM basis functions to a new one which, after proper antisymmetrization, is symmetry adapted with respect to the normal constants of the motion of the corresponding Li-Li diatomic fragment  $KL$ . It happens that for each diatomic fragment, the  $T_{(KL)}$  transformation leads to functions of different symmetry, namely  ${}^1\Sigma_g^+(\text{Li}_2)$  and  ${}^2\Sigma_g^+, {}^2\Sigma_u^+(\text{Li}_2)$ . As a consequence, the  $\mathbf{h}^{(KL)}$  matrices of Eq. (1) are diagonal. The potential energy curves (PEC's) employed in evaluating the diagonal elements of the  $\mathbf{h}^{(KL)}$  matrices were taken from the work of Pickup [5] and are drawn (with the same asymptote) in Fig. 1. It can be seen from this figure that the  $\text{Li}_2^+({}^2\Sigma_g^+) + \text{Li}({}^2S^e)$  and the  $\text{Li}_2({}^1\Sigma_g^+) + \text{Li}^+({}^1S^e)$  curves intersect each other at the Li-Li fragment separation of 4.986 a.u.

### 3. Results and Discussion

As in our previous paper [1], the internuclear distances between the individual nuclei of the Li<sub>3</sub><sup>+</sup> system are designated as  $R_{12}$ ,  $R_{13}$  and  $R_{23}$ . Further, at those geometrical configurations, where the system can be regarded as a diatomic Li<sub>2</sub><sup>+</sup> (or Li<sub>2</sub>) interacting with Li (or Li<sup>+</sup>),  $R_{23}$  is reserved for the diatomic fragment internuclear separation. The distance from Li to the centre of Li<sub>2</sub><sup>+</sup> is denoted by  $d$ .

The PEC's of Fig. 1 correspond to a cut through the DIM singlet PES's for configurations  $R_{12} = R_{13} = \infty$ . It is seen that the lowest two adiabatic singlet PES's (to be denoted by  $E_1$  and  $E_2$ ) are degenerate in the asymptotic region at the Li-Li internuclear distance  $R_{23} = 4.986$  a.u., while the corresponding diabatic curves, namely the  $\text{Li} + \text{Li}_2^+$  and  $\text{Li}^+ + \text{Li}_2$  cross at this point.

Two, to a degree interconnected remarks are to be made here. First, this crossing is located not too far from the region of the configuration space given by  $R_{12} = R_{13} = \infty$ ,  $R_{23} = 5.853$  a.u., where the reactant system  $\text{Li} + \text{Li}_2^+$  reaches its minimum, and which corresponds to the initial limiting structures of the minimum energy paths for the reaction  $\text{Li} + \text{Li}_2^+ \rightarrow \text{Li}_3^+$ . The energy of the crossing point, relative to the reactant minimum energy, will be denoted by  $E_{C.P.}$  and is found to be  $4.99 \times 10^{-3}$  a.u. The second remark concerns the quasiclassical trajectory picture of the system in the (asymptotic) reactant region. If the Li<sub>2</sub><sup>+</sup> diatomic is in a sufficiently highly excited vibrational state, the  $\text{Li} + \text{Li}_2^+$  system (with asymptotically distant Li) will reach the crossing region. However, as will be shown below, if the distances  $R_{12}$  and  $R_{13}$  remain large enough, a motion of the system through the  $R_{23} = 4.986$  a.u. point will certainly cause transition between the adiabatic states, and the passage will proceed diabatically. The system will remain governed by the  $\text{Li} + \text{Li}_2^+$  curve and no charge transfer will take place.

In Fig. 2 we show a cut through the lowest two singlet adiabatic potentials which is analogous to that of Fig. 1 except that the distances  $R_{12}$  and  $R_{13}$  are now finite. Specifically, the slice corresponds to a linear configuration of the system with

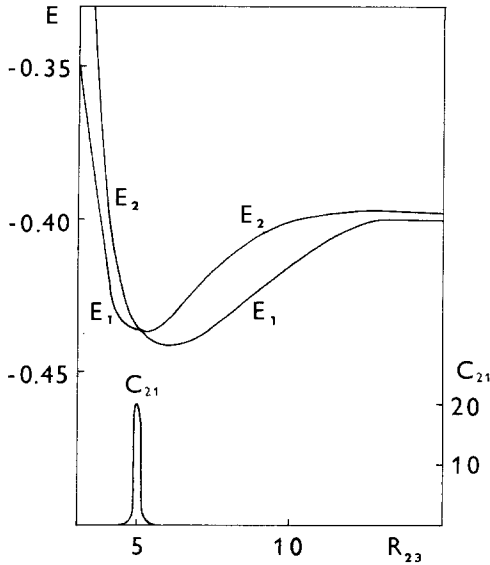


Fig. 2. Cut through the lowest two adiabatic singlet PES's of collinear  $(\text{Li-Li}_2)^+$  for configurations  $R_{13} > R_{12} = 15.5$  a.u.  $C_{21}$  is the magnitude of the nonadiabatic coupling vector  $c_{21}$  for the same geometries. Energies, distances and coupling strength are in a.u.

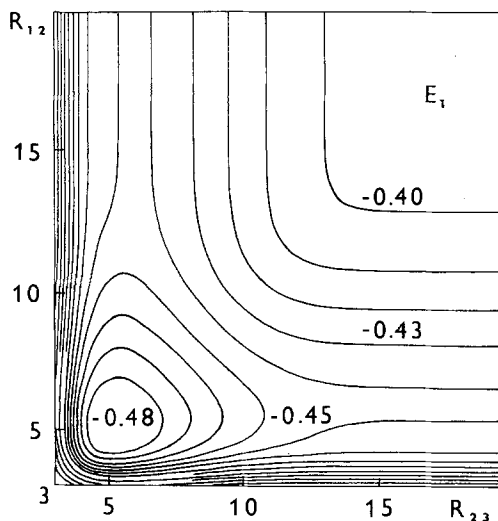
$R_{13} > R_{12} = 15.5$  a.u. The energy of  $\text{Li}^+$  is taken to be zero so that the energy of the separated  $\text{Li} + \text{Li} + \text{Li}^+$  regions is  $-0.39640$  a.u. The lower panel of the figure shows a cut through the surface of the magnitude of the DIM approximation to the nonadiabatic coupling vector [2]

$$c_{21} = \langle \Psi_2 | \nabla \Psi_1 \rangle \quad (2)$$

between the lowest singlet adiabatic states. It is seen from this figure that the shape of the adiabatic singlet curves is not influenced too much by the interaction with the third centre. In spite of this, the degeneracy is now removed, the smallest  $E_2 - E_1$  difference being  $3.16 \times 10^{-4}$  a.u. Another difference is that the quantity  $C_{21} \equiv |c_{21}|$  which was essentially a delta function in the asymptotic case is now finite. Note, however, that there is still one respect in which the situation is similar to the asymptotic case: For configurations with  $R_{23} \geq 4.986$  a.u., the lowest adiabatic potential curve corresponds to the electronic structure  $\text{Li-Li}_2^+$  while for  $R_{23} \leq 4.986$  a.u., the ground state DIM wave function is dominated by the electronic structure corresponding to  $\text{Li}^+-\text{Li}_2$ . Just the opposite holds for the first excited singlet state.

The curves shown in Figs. 1 and 2 indicate the core of the qualitative analogy in the nonadiabatic behavior of  $\text{Li-Li}_2^+$  and  $\text{H}^+-\text{H}_2$ . In both the systems there is a relatively narrow region of strong nonadiabatic interaction between the lowest surfaces, a crossing seam. Adopting the trajectory surface hopping model [3] in the present situation, we can note that an adiabatic passage of the system through this crossing seam is accompanied by a relatively precipitous change in the electronic configuration of the system - a charge transfer. On the other hand, when the vibrational motion of  $\text{Li}_2^+$ , colliding with Li, causes a nonadiabatic transition between the relevant surfaces, the electronic configuration of the system is essentially retained.

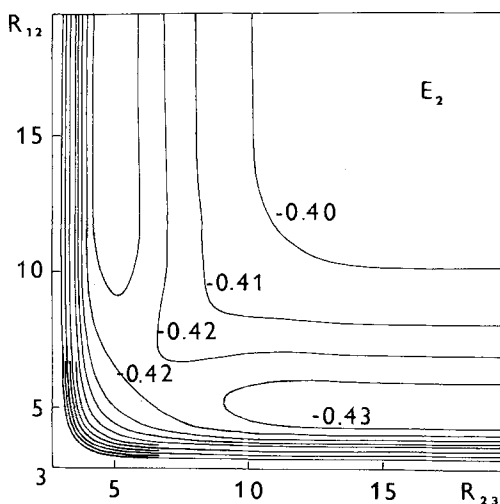
**Fig. 3.** Potential-energy contour plot (in a.u.) for the ground state (adiabatic) PES of collinear (Li-Li<sub>2</sub>)<sup>+</sup>. Distances are in a.u.



In Fig. 3 we show an equipotential contour plot for the lowest singlet PES  $E_1$  of the collinear (Li-Li<sub>2</sub>)<sup>+</sup> system. The minimum energy for linear geometries occurs for a  $D_{\infty h}$  configuration at  $R_{12} = R_{23} = R_{13}/2 = 5.166$  a.u. with an energy of  $E_1 = -0.49234$  a.u. This critical point on the ground state PES's was shown in our previous paper [1] to be a saddle point.

What is important in the present context is that in the region  $4.5 \text{ a.u.} \leq R_{23} \leq 8 \text{ a.u.}$ , the shape of the functional dependence on  $R_{23}$  of the ground state adiabatic PES is practically unchanged as  $R_{12}$  varies from infinity up to the value of about 14 a.u. This feature of the ground state PES was found to be maintained as the (Li-Li<sub>2</sub>)<sup>+</sup> approach angle changed from the  $C_{\infty v}$  approach to the  $C_{2v}$  one.

**Fig. 4.** Equipotential contour plot (in a.u.) of the lowest excited adiabatic singlet PES of collinear (Li-Li<sub>2</sub>)<sup>+</sup>. Distances are in a.u.



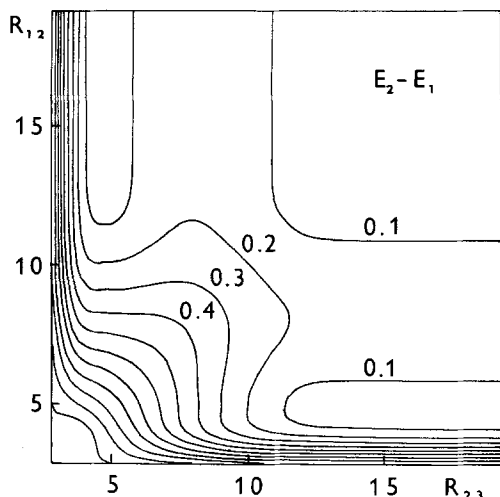


Fig. 5. The  $E_2 - E_1$  energy difference contour plot (in a.u.) of collinear  $(\text{Li-Li}_2)^+$ . Distances are in a.u.

Figs. 4 and 5 give contours of the first excited adiabatic singlet PES,  $E_2$ , and of the energy difference  $E_2 - E_1$  respectively, for collinear  $(\text{Li-Li}_2)^+$ . Fig. 4 illustrates our finding that the lowest excited singlet surface is repulsive in nature and, that, in the region  $4.5 \text{ a.u.} \leq R_{23} \leq 8 \text{ a.u.}$ , the variation of this potential energy with  $R_{23}$  is not significantly affected by changes in the  $(\text{Li-Li}_2)^+$  distance  $d$ , limited to the region  $\infty > d > 13 \text{ a.u.}$  Fig. 5 shows the behavior of the energy difference  $E_2 - E_1$  and gives a rough idea of the location of the crossing seam.

Sufficiently detailed information on the crossing seam requires knowledge of the functional dependence of the nonadiabatic coupling vector  $c_{21}$  of Eq. (2) on the variable  $R_{23}$ [2, 3]. For different  $(\text{Li-Li}_2)^+$  distances  $d$ , the quantity was evaluated using the approximate DIM expression [2]

$$c_{21} = C_2^+(\nabla H)C_1/(E_1 - E_2), \quad (3)$$

where  $C_1$  and  $C_2$  are the eigenvectors of the Hamiltonian matrix (1) and  $\nabla H$  stands for the matrix formed by the gradients of the individual elements of the DIM Hamiltonian matrix (1).

In Fig. 6 we show cuts through the  $C_{21} \equiv |c_{21}|$  surface corresponding to linear configurations of the  $(\text{Li-Li}_2)^+$  system with the  $R_{12}$  distance fixed at different values, selected from that region of the configuration space which was found interesting by inspection of Fig. 5. We see that the  $C_{21}(R_{23})$  curves fit the picture of the crossing seam indicated by Figs. 1 and 2, and also by Fig. 5. More information on the magnitude of the coupling vector, the adiabatic energies and on the behavior of other important quantities along the crossing seam corresponding to linear  $(\text{Li-Li}_2)^+$  configurations is given in Table 1. It should be remarked that the main features of the  $C_{21}(R_{23})$  dependence were found to be practically isotropic in the region of the configuration space of interest. Hence, for the purposes of the present paper, the location of the crossing seam can be simply

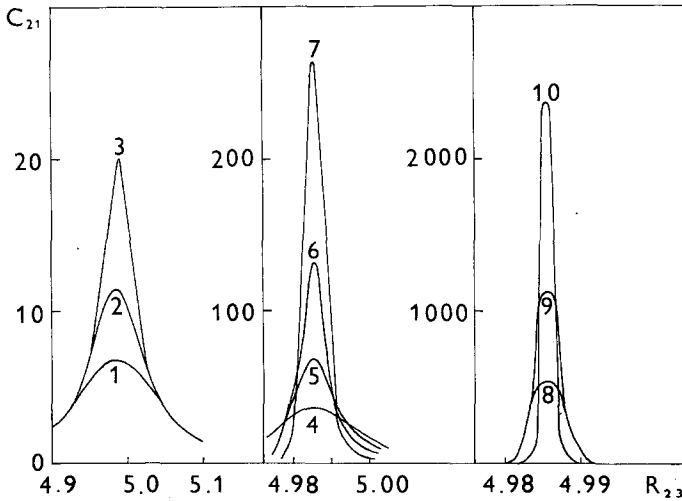


Fig. 6. The magnitude of the nonadiabatic coupling vector  $c_{21}$  as a function of the Li-Li internuclear separation  $R_{23}$  for different linear configurations of the  $(\text{Li-Li}_2)^+$  system. For  $n$ th curve, the  $R_{12}$  Li-Li distance is kept at  $14.0 + 0.5n$ . Distances and coupling strength are in a.u.

given by

$$R_{23} = 4.986 \text{ a.u.}, \quad d \geq 15 \text{ a.u.} \tag{4}$$

Note, however, that with decreasing  $d$ , the region of strong nonadiabatic coupling becomes diffuse and the magnitude of the coupling vector,  $C_{21}$ , at the crossing seam decreases. The main portion of this behavior of  $C_{21}$  along the crossing seam can be understood in terms of changes in the separation between the adiabatic

Table 1.  $(\text{Li-Li}_2)^+$  singlet crossing seam characterization for collinear geometries<sup>a</sup>.  $R_{23} = 4.986 \text{ a.u}$

$R_{12}$	$E_1$	$E_2 - E_1$	$C_{21}^b$	$\xi_{12}^{(4)c}$	$P_{12}^{(4)d}$	$P_{12}^{(5)}$
12.5	-0.44022	$5.30 \times 10^{-3}$	1.21	$6.16 \times 10^{-2}$	0	0.001
13.0	-0.43923	$3.62 \times 10^{-3}$	1.76	$1.31 \times 10^{-2}$	0	0.043
13.5	-0.43837	$2.39 \times 10^{-3}$	2.66	$3.01 \times 10^{-1}$	0.036	0.251
14.0	-0.43777	$1.53 \times 10^{-3}$	4.18	$7.38 \times 10^{-1}$	0.258	0.570
14.5	-0.43737	$9.39 \times 10^{-4}$	6.80	$1.96 \times 10^0$	0.600	0.809
15.0	-0.43712	$5.55 \times 10^{-4}$	11.50	$5.60 \times 10^0$	0.836	0.928
15.5	-0.43697	$3.16 \times 10^{-4}$	20.18	$1.72 \times 10^1$	0.943	0.976
16.0	-0.43689	$1.74 \times 10^{-4}$	36.68	$5.69 \times 10^1$	0.982	0.993
16.5	-0.43685	$9.24 \times 10^{-5}$	68.84	$2.01 \times 10^2$	0.995	0.998
17.0	-0.43683	$4.76 \times 10^{-5}$	133.10	$7.55 \times 10^2$	0.999	0.999
17.5	-0.43682	$2.38 \times 10^{-5}$	264.10	$3.00 \times 10^3$	1.000	1.000

<sup>a</sup> Distances and energies are given in a.u..

<sup>b</sup> Magnitude (in a.u.) of the nonadiabatic coupling vector, Eq. (3).

<sup>c</sup> The Massey parameter (in a.u.), obtained from Eq. (6) with the nuclear velocity vector of the magnitude of  $2.7 \times 10^{-4}$  a.u., corresponding to the 4th vibrational level of  $\text{Li}_2^+$ .

<sup>d</sup> Nonadiabatic transition probability estimate as calculated from Eq. (5)

potential surfaces (cf. Ref. [6] and [7]). Another important point is that in analogy with the  $\text{H}^+-\text{H}_2$  system, the vector  $\mathbf{c}_{21}$  is found to be practically normal to the crossing seam plane, which justifies (cf. Ref. [3]) our having connected the nonadiabatic behavior of the  $\text{Li}-\text{Li}_2^+$  system with the  $\text{Li}_2^+$  vibrational motion.

We are now in the position of being able to start discussing the conditions under which the nonadiabatic coupling between the lowest surfaces can be expected to influence the behavior of the  $\text{Li}-\text{Li}_2^+$  system. The argument which follows is semiquantitative and is based on the classical trajectory approach to the description of the dynamics of the system.

Within the classical trajectory approach, the vibrational motion of the  $\text{Li}_2^+$  collision partner is, aside from the Monte Carlo variable corresponding to the vibrational phase, determined by the  $\text{Li}_2^+$  vibrational energies. The  $\text{Li}_2^+$  levels which are consistent with the present DIM model are those obtained by solving the one-dimensional Schrödinger equation for a particle (of the mass equal to the reduced mass of the  $\text{Li}-\text{Li}^+$  pair) subject to the  $^2\Sigma_g^+$  generalized Morse potential of Ref. [5]. The pertinent levels were determined using the algorithm devised by Tobin and Hinze [8]; and are given (for three different isotopic variants of  $\text{Li}_2^+$ ) in Table 2.

In the light of the above results, these vibrational levels are to be compared with the energy of the crossing point  $E_{C.P.} = 4.99 \times 10^{-3}$  a.u. This energy is greater than the lowest  $\text{Li}_2^+(^2\Sigma_g^+)$  vibrational levels up to  $v=3$ , but lower than the levels corresponding to  $v \geq 4$ . We thus see that for  $d \geq 15$  a.u. the  $\text{Li}-\text{Li}_2^+$  system with the  $\text{Li}_2^+$  collision partner in at least the fourth vibrational state will certainly pass through the crossing seam (4). In order to get an idea about the extent of the nonadiabatic behavior of the system during its passage through the crossing seam, we have to possess knowledge of the probability  $P_{12}$  of the nonadiabatic transition between the corresponding adiabatic states. A rough estimate of this probability can be obtained from the expression [9, 10]

$$P_{12} \approx \exp(-1/\xi_{21}), \quad (5)$$

where  $\xi_{21}$  is the Massey parameter given by

$$\xi_{21} = |\mathbf{v} \cdot (-i\hbar\mathbf{c}_{21}) / (E_2 - E_1)| \quad (6)$$

**Table 2.** Vibrational levels (in  $10^{-3}$  a.u.) for different isotopic variants of  $\text{Li}_2^+$

Level $v$	Isotopic variant		
	$(^7\text{Li}-^7\text{Li})^+$	$(^7\text{Li}-^6\text{Li})^+$	$(^6\text{Li}-^6\text{Li})^+$
0	0.60	0.62	0.64
1	1.78	1.85	1.92
2	2.94	3.10	3.18
3	4.09	4.26	4.41
4	5.22	5.44	5.64
5	6.34	6.60	6.84



Here  $\mathbf{v}$  is the relative nuclear velocity vector corresponding to the adiabatic PEC. The nonadiabatic coupling vector  $\mathbf{c}_{21}$  was evaluated through the approximate DIM expression (3). The values of the magnitude of this vector, which is essentially equal to its  $R_{23}$  component, are given, for selected points on the crossing seam, in Table 1.

What remains to be guessed is the  $R_{23}$  component of the nuclear relative velocity vector at points along the crossing seam. According to our information on the general shape of both the adiabatic singlet PES's in the pertinent region of the configuration space, the value of the relevant component of  $\mathbf{v}$  corresponding to the  $v$ -th ( $v \geq 4$ ) vibrational state of Li<sub>2</sub><sup>+</sup> can be roughly estimated from the difference between the vibrational level,  $E_v$ , and the energy of the crossing seam in the asymptotic region,  $E_{C.P.}$ . In this way, the velocity component associated with the fourth vibrational state can be roughly estimated as  $2.7 \times 10^{-4}$  a.u. The corresponding nonadiabatic transition probabilities  $P_{12}^{(4)}$  obtained from (5) and (6) for linear configurations of the Li-Li<sub>2</sub><sup>+</sup> system are given in Table 1. Also given in this table are the probabilities  $P_{12}^{(5)}$  related to the fifth vibrational state of Li<sub>2</sub><sup>+</sup>.

According to these transition probability estimates, there is a region of the configuration space given approximately by  $16 \text{ a.u.} \leq d \leq 19.5 \text{ a.u.}$  where a passage of the system through the crossing seam can, but need not cause nonadiabatic transition between the two adiabatic singlet states. As a consequence, if the system with Li<sub>2</sub><sup>+</sup> in at least the fourth vibrational state enters this region, there is a nonvanishing probability that the system can begin to evolve on the first excited adiabatic singlet PES. As indicated above, this surface is repulsive in nature so that the system can reach the asymptotic region being governed by the diabatic surface corresponding to the electronic configuration Li<sup>+</sup>-Li<sub>2</sub>. This outcome of the Li-Li<sub>2</sub><sup>+</sup> collisions is not predicted by the approach of Ref. [1].

The vibrational energy which the Li<sub>2</sub><sup>+</sup> collision partner has to have to reach the crossing seam is (for the <sup>7</sup>Li-<sup>7</sup>Li isotopic variant)  $5.22 \times 10^{-3}$  a.u., i.e.  $4.62 \times 10^{-3}$  a.u. above the zero vibrational level,  $3.44 \times 10^{-3}$  a.u. above the first level, etc. These values are more than one order of magnitude lower than those reported [2] for the charge transfer reaction  $\text{H}^+ + \text{H}_2 \rightarrow \text{H} + \text{H}_2^+$ . In fact, the values are so small that even at temperatures 700-800°K, the fraction of the Li<sub>2</sub><sup>+</sup> fragments, which are initially in at least the 4-th vibrational state or can get excited to this state through a conversion of the (Li-Li<sub>2</sub>)<sup>+</sup> relative kinetic energy to the Li<sub>2</sub><sup>+</sup> vibrational energy, can by no means be neglected. We thus see that even under conditions which can be still regarded as "chemical", the reaction channel  $\text{Li} + \text{Li}_2^+ \rightarrow \text{Li}^+ + \text{Li}_2$  can become open. This result contradicts the picture of the Li-Li<sub>2</sub><sup>+</sup> collision events provided by the crude chemical approach of Ref. [1]. The quantitative aspect of this conclusion will have to be estimated on the basis of a thorough dynamical treatment of the system.

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