NONADIABATIC COUPLING IN THE Li_2–Li_2^+ SYSTEM

Jan VOJTÍK, Alena KRTKOVÁ and Rudolf POLÁK

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2*

Nonadiabatic coupling between the lowest two doublet potential energy surfaces of the Li_2-Li_2^+ system is calculated using the semiempirical VB technique of diatomics-in-molecules (DIM). Location of nonadiabatic region in the configuration space and basic characteristics of the system in nonadiabatic and asymptotic regions are used to discuss the influence of the nonadiabatic effects on the behaviour of the Li_2-Li_2^+ system under chemical conditions.

In our recent papers[1,2] we have reported theoretical investigation of nonadiabatic interactions in the Li-Li_2^+ system. The main result of this study was that nonadiabatic effects in this system can become significant under conditions which can be regarded as chemical, *i.e.*, in situations corresponding to initial inner and translational states of the system which become populated at temperatures $700-800°K$. In this respect, there is a difference between the Li-Li_2^+ system and the H^+-H_2 one, where the breakdown of the Born–Oppenheimer approximation can only take place under special conditions in crossed beam experiments.

There is the same symmetry cause of nonadiabatic behaviour in both H^+-H_2 and Li-Li_2^+ and, hence, the above difference between the systems mainly stems from the difference in the position and size of the regions of significant nonadiabatic coupling and, also, from the difference in the vibrational levels of the H_2 and Li_2^+ diatomic collision partners. Accordingly, much of the peculiarity of the Li-Li_2^+ system with regard to its nonadiabatic behaviour seems to be more or less connected with the fact that, unlike in the H^+-H_2 system, the interactions in the Li-Li_2^+ system are rather weak and of a long range nature. Although some insight into the related problems has already been gained, the results indicated that it would be of interest to extend study to other systems with interactions of this type.

The purpose of the present communication is to report DIM calculations of nonadiabatic coupling in the Li_2-Li_2^+ system, where the interactions are also weak and of a long-range nature and where the existence of nonadiabatic coupling between the lowest doublet states is connected with symmetry properties of the system in the asymptotic region.

THEORETICAL

The necessary quantities, *i.e.*, the lowest doublet potential energy surfaces (PES's) for the Li_2-Li_2^+ system and the nonadiabatic coupling matrix elements were computed using the semiempirical version of the DIM method[3-6] which has proved to be quite successful in theoretical study of gas-phase reactions[7-9], adsorbate-cluster interactions[10-12] and chemiionization proces-

ses[13-15]. The approximations to the true adiabatic PES's and the corresponding eigenvectors were obtained by the diagonalization of the DIM Hamiltonian matrix

$$H = \sum_{K>L=1}^{4} \sum^{3} T_{(KL)} h^{(KL)} T_{(KL)}^{+} - 2 \sum_{K=1}^{4} h^{(K)} \qquad (1)$$

referring to a DIM basis which arises by taking the $Li(^2S)$ ground state and the ionized $Li^+(^1S)$ state on each nuclear centre[16,17]. The resulting polyatomic VB structures lead to 8-dimensional spin-adapted DIM basis[17]. As our basis includes only S-type states, there are no directional properties to consider in the construction of the diatomic transformation matrices $T_{(KL)}$. These matrices are independent of a geometrical configuration of the system and were obtained by the direct diagonalization approach[18].

The atomic contributions $h^{(K)}$ to the polyatomic Hamiltonian matrix were evaluated under the usual assumption that the DIM basis functions are formed from the eigenstates of the atomic Hamiltonians. As in the Li_3^+ calculations[1], the diatomic fragment matrices $h^{(KL)}$ are found to be diagonal. In evaluating these matrix elements, the necessary $^1\Sigma_g^+$ and $^3\Sigma_u^+$ PEC's of Li_2 were taken from the work of Pickup[16]. The PEC's are shown in Fig. 1, the Li_2 and Li_2^+ potentials being drawn with the same asymptote. In order to vizualize the nature of the interactions in the Li_2–Li_2^+ system, the right panel of the figure shows the corresponding H_2 and H_2^+ PEC's from ref.[19], for comparison.

The nonadiabatic coupling vector

$$c_{ji} = \langle \psi_j \mid \nabla \psi_i \rangle \qquad (2)$$

associated with the transitions between the adiabatic states ψ_i and ψ_j is approximated by the expression[20]

$$c_{ji} = C_j^+ (\nabla H) C_i / (E_i - E_j), \qquad (3)$$

where E_i is the DIM approximation to the adiabatic PES and C_i is the corresponding eigenvector of the polyatomic Hamiltonian matrix. The matrix ∇H is given by

$$\nabla H = \sum_{K>L=1}^{4} \sum^{3} T_{(KL)} (\nabla h^{(KL)}) T_{(KL)}^{+}, \qquad (4)$$

where $\nabla h^{(KL)}$ are the (diagonal) matrices consisting of the gradients of the diatomic fragment PEC's, and the transformation matrices $T_{(KL)}$ are those of Eq. (1). Note that in writing Eq. (4), use is being made of the fact that the $T_{(KL)}$ matrices are, in the DIM basis chosen, geometry independent.

Nature of Nonadiabatic Effects in the Li_2^+–Li_2 System

The Li_4^+ system has six internal degrees of freedom. As the corresponding variables we take here the six internuclear distances (ID's) $R_{12}, R_{13}, ..., R_{34}$. In the region of the configuration space we are mainly interested in, the system can be regarded as Li_2^+ interacting with Li_2. Accordingly, the ID's R_{12} and R_{34} are reserved for these diatomic fragments and the separation between the centres of these fragments is denoted by d.

Let us first turn our attention to the lower two eigenenergies of the Hamiltonian matrix (1) in the asymptotic region where $d \to \infty$, but the ID's R_{12} and R_{34} remain finite. Taking into account the form of the Hamiltonian matrix (1), the fact that the $h^{(\mathrm{KL})}$ matrices are diagonal and the way in which these diagonal elements are evaluated, it is easy to show[21] that the two energies of the Li_4^+ system in this region are

$$E_1^d = E_1^+(R_{12}) + E_1^0(R_{34}), \tag{5}$$

$$E_2^d = E_1^0(R_{12}) + E_1^+(R_{34}). \tag{6}$$

Here, E_1^+ stands for the energy of the lowest $^2\Sigma_g^+$ Li_2^+ state, and E_1^0 denotes the ground state (GS) PEC of Li_2. Both these potentials enter the DIM Hamiltonian matrix as input data and are, with the same asymptote, drawn in Fig. 1. It should be noted that the energy expressions (5) and (6) reflect the fact that in this asymptotic region the Li_2^+ and Li_2 fragments do not interact with each other. Hence, the electronic energy of the system is determined by the ID's R_{12} and R_{34} and by the location of the positive charge.

Suppose the $Li_2^+ + Li_2$ system enters the asymptotic region with an electronic configuration corresponding to the potential energy E_1^d, and adopt, as has now become a standard[22,23], a semiclassical model for the description of the nuclear motion. During the motion of the system the ID's $R_{12}, \ldots, R_{34}$ will be changed. However,
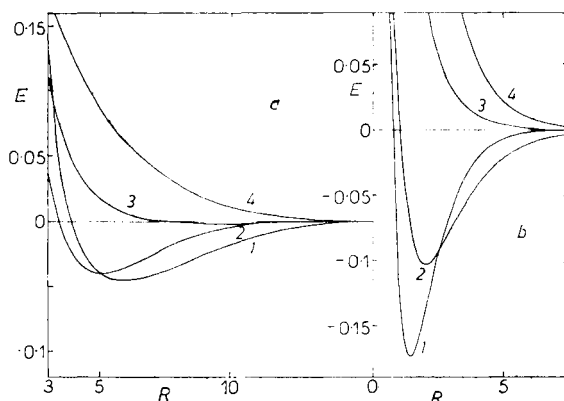

FIG. 1

Potential energy curves for the diatomics a) $Li_2^+(^2\Sigma_g^+)$, 1; $Li_2(^1\Sigma_g^+)$, 2; $Li_2(^3\Sigma_u^+)$, 3; $Li_2^+(^2\Sigma_u^+)$, 4 b) $H_2(^1\Sigma_g^+)$, 1; $H_2^+(^2\Sigma_g^+)$, 2; $H_2^+(^2\Sigma_u^+)$, 3; $H_2(^3\Sigma_u^+)$, 4. Distances and energies are expressed as relative quantities $R = R'/R_0$ and $E = E'/E_0$, where the quantities R' and E' are given in SI units and $R_0 = 0.052917$ nm and $E_0 = 4.35942 . 10^{-18}$ J, throughout the paper. In the text these quantities will be referred to as atomic units (a.u.)

it is intuitively clear (and will be shown below) that if the distance d remains very large (asymptotic region), no charge transfer between the fragments can take place. Hence, the system will remain governed by the PES E_1^d. Similarly, if the system starts its motion in the asymptotic region being governed by the surface E_2^d, it will evolve in this region on this surface.

As already noted, in the asymptotic region, E_1^d and E_2^d are the eigenenergies of the Hamiltonian matrix (1). If their order in this region were not altered with changes of R_{12} and R_{34}, each of these energies would (in this region) represent permanently one of the lowest doublet adiabatic energies of the electronic Born–Oppenheimer Hamiltonian of the system. However, it can be seen from Eqs (5) and (6) and Fig. 1 that this is not the case and that for physically reasonable choices of R_{12} and R_{34} the GS (adiabatic) energy E_1 is given by

$$E_1 = E_1^d, \quad R_{12} \gtreqqless R_{34}, \tag{7}$$

$$E_1 = E_2^d, \quad R_{12} \lesseqqgtr R_{34}.$$

Analogously, for the first excited doublet adiabatic PES in the asymptotic region, we get

$$E_2 = E_2^d, \quad R_{12} \gtreqqless R_{34}, \tag{8}$$

$$E_2 = E_1^d, \quad R_{12} \lesseqqgtr R_{34}.$$

Of course, $E_1 \leqq E_2$ and the adiabatic PES's become degenerate in geometries

$$R_{12} = R_{34}, \quad d \to \infty. \tag{9}$$

In these geometrical configurations, the surfaces E_1^d and E_2^d, which are called diabatic, cross. The situation is, as expected, similar to that in the case of the H$_4^+$ system[21].

Let us now discuss a semiclassical picture of the dynamics of the Li$_2$–Li$_2^+$ system in the asymptotic region. If the Li$_2$ and Li$_2^+$ fragments are vibrationally excited, the system can reach the region of the configuration space defined by Eq. (9). However, as we already know, the system will retain its electronic configuration when passing through this region. Put another way, the vibrational motion of the partners will, at configurations (9), produce breakdown of the Born–Oppenheimer approximation and induce nonadiabatic transitions between the adiabatic electronic states ψ_1 and ψ_2 corresponding to the energies E_1 and E_2, respectively.

As the diatomic fragments are being brought together, the interaction between Li$_2$ and Li$_2^+$ gradually modifies the mutual arrangement of the lowest two doublet adiabatic PES's around the configurations $R_{12} = R_{34}$. Though the degeneracy of the PES's E_1 and E_2 is removed, there is a region of significant nonadiabatic

coupling located around the crossing seam given by

$$R_{12} = R_{34} , \quad d \geqq b . \tag{10}$$

The parameter b appearing in (10) can be expected to depend on both $R = R_{12} = R_{34}$ and the mutual orientation of the fragments. It is also clear that this parameter essentially takes on values reflecting situations when the Li_2–Li_2^+ interaction is still rather weak.

The crossing seam is a plane in the configuration space and it is necessary to know which part of this plane can be reached by the Li_2–Li_2^+ system under chemical conditions. In the asymptotic and near-asymptotic geometries, the energetically accessible region of the configuration space is essentially determined by the PEC's for the Li_2 and Li_2^+ fragments which determine both the lowest two adiabatic PES's of Li_2–Li_2^+ and the vibrational energies of the fragments. The Li_2 and Li_2^+ levels, consistent with the present DIM model for Li_2–Li_2^+, were obtained by solving the appropriate one-dimensional Schrödinger equations with the potentials of ref.[16]. The numerical procedure used was that developed by Tobin and Hinze[24], the levels obtained are listed in Table 1. Also given in this table are the positions of the corresponding outer turning points from the Li_2 classical vibrational motion and of the inner turning points for Li_2^+. It is evident from the information given in this table that the part of the crossing seam which is most relevant for the present discussion can be given by $R = R_{12} = R_{34} \in \langle 5 \cdot 0; 6 \cdot 0 \rangle$ a.u. $(1 \text{a.u.} = 0 \cdot 052917 \text{ nm})$.

Crossing Seam Characteristics

According to what has been said above, the Li_2–Li_2^+ distance b which determines the position of the crossing seam (10) is closely connected with the lower bound of those Li_2–Li_2^+ distances where the interaction between the two fragments becomes sufficiently weak.

In Fig. 2 we show a cut through the $C_{21} = |c_{21}|$ surface for nonplanar C_{2v} configurations of Li_2–Li_2^+ with $R_{12} = 5 \cdot 0$ a.u. and d kept fixed at 12 a.u. Also shown in this figure are the corresponding cuts through the lowest two adiabatic PEC's. Note that the energy of Li^+ is taken to be zero, so the energy of the separated atoms (ion) region is $-0 \cdot 5946$ a.u. It should also be remarked that the minimum in the asymptotic Li_2–Li_2^+ region, located at

$$R_{12} = 5 \cdot 0513 \text{ a.u.} , \quad R_{34} = 5 \cdot 8526 \text{ a.u.} , \quad d \to \infty \tag{11}$$

is $-0 \cdot 6804$ a.u.

There are two regions of avoided crossing between the lowest adiabatic potentials given in Fig. 2. However, the GS adiabatic energy of the system at the configuration with the more pronounced nonadiabatic coupling is so high that the configuration

is far from being energetically accessible by the system. Unlike this maximum on the $C_{21}(R_{34})$ curve, the position of the second maximum is seen to be in accord with the symmetry-based condition $R_{34} = R_{12}$ deduced above. Further, the direction defined by the coupling vector at this point is consistent with the fact that possible nona-diabatic behaviour of the system would be connected with the vibrational motion of the fragments. On the other hand, the region of nonadiabatic coupling is still rather diffuse, the maximum value of C_{21} rather small and the energy difference $E_2 - E_1$ at the avoided crossing is still rather large, In order to see how these facts will manifest itself in the nonadiabatic behaviour of the system, we have to consider the corresponding nonadiabatic transition probability P_{12}. A rough estimate of this probability is obtained from the expression[25,26]

$$P_{12} \approx \exp\left(- \left|(E_2 - E_1)/\mathbf{v} . \mathbf{d}_{21}\right|\right). \tag{12}$$

Here, $\mathbf{v}$ is the relative nuclear velocity vector corresponding to the adiabatic PEC E_1, E_2 are the adiabatic energies and
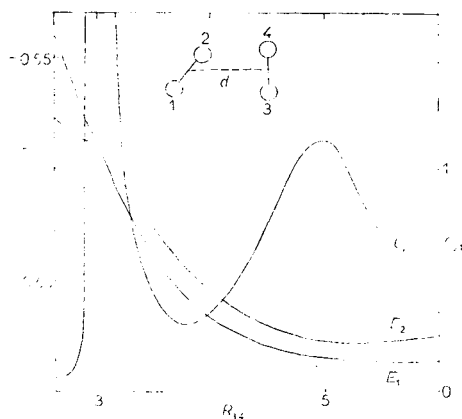
$$\mathbf{d}_{21} = -i\hbar\mathbf{c}_{21}, \tag{13}$$

FIG. 2

Cut through the lowest two adiabatic doublet PES's for nonplanar C_{2v} con-figurations of Li_2–Li_2^+ with $R_{12} = 5\cdot0$ a.u. and $d = 12\cdot0$ a.u. C_{21} is the magnitude of the nonadiabatic coupling vector $\mathbf{c}_{21}$

FIG. 3

The magnitude C_{21} of the nonadiabatic coupling vector as a function of the Li–Li internuclear separation R_{34} for different nonplanar C_{2v} configurations of the Li_2–Li_2^+ system with $d = 12\cdot0$ a.u. For the n-th curve R_{12} is kept fixed at $(4\cdot2 + 0\cdot2n)$ a.u.

where c_{21} is the nonadiabatic coupling vector (3). Taking into account that the vector c_{21} is essentially perpedicular to the plane $R_{12} = R_{34}$ and assuming that the relative velocity corresponding to vibrational motion of the Li_2 and Li_2^+ fragments will not typically exceed 10^{-3} a.u. during chemical scattering of the collision partners, we find that an upper bound to the nonadiabatic transition probabilities P_{12} at the point of the crossing seam found in Fig. 2 is of the order of 10^{-2}.

Fig. 3 presents another $C_{21}(R_{34})$ curves for nonplanar C_{2v} configurations of the $Li–Li_2^+$ system with the distance $d = 12$ a.u. The fixed values of R_{12} were chosen from the interval $\langle 4\cdot4, 6\cdot0 \rangle$ a.u. Again, the curves indicate that the system could tend to behave nonadiabatically when passing, due to the vibrational motion of the diatomics, through some configurations. However, as in the previous case, a closer inspection of the situation reveals that for nonplanar C_{2v} configurations the distance $d \approx 12\cdot0$ a.u. between the centres of Li_2 and Li_2^+ must be taken as a boundary of the region of significant nonadiabatic coupling. It is pertinent to note that at this distance between the fragments, the nonadiabatic characteristics of the $H_2–H_2^+$ system could be regarded as those typical of the asymptotic region[27].

Consider now a nonplanar C_{2v} configuration with $d = 12\cdot0$ a.u., and given R_{12} and R_{34}. Denote by R_{min} the lowest of the distances R_{13}, R_{14}, R_{23} and R_{24}. If the configuration is changed without altering the parameters d, R_{12} and R_{34}, R_{min} will decrease. Accordingly, the behaviour of the $Li_2–Li_2^+$ system will become more influenced by the interaction between Li_2 and Li_2^+. The energy difference $E_2 - E_1$ will increase and the $Li_2–Li_2^+$ system will generally show less tendency to behave nonadiabatically at configurations with $R_{12} = R_{34}$. We can therefore conclude that the region of the configuration space where the vibrational motion of the Li_2 and Li_2^+ fragments can produce breakdown of the Born–Oppenheimer approximation is certainly limited to $d \geqq 12\cdot0$ a.u.

Another consequence of the above fact is that for configurations of the $Li_2–Li_2^+$ system different from the nonplanar C_{2v} arrangement, the boundary of the near-asymptotic region will occur at larger d. Fig. 4 serves to show that the main features of the $C_{21}(R_{34})$ dependences for planar C_{2v} geometries of the $Li_2–Li_2^+$ system with $d = 13$ a.u. are similar to those of Fig. 3 $\left(d = 12 \text{ a.u.} \right)$, thus illustrating the point just outlined.

Of primary importance are the values of the nonadiabatic coupling vector magnitude C_{21} and the energy difference $E_2 - E_1$ at the crossing seam. In Fig. 5 we show these quantities for D_{2d} configurations of $Li_2–Li_2^+$ with $R = R_{12} = R_{34} = 5\cdot5$ a.u. and $d \in \langle 13\cdot5, 17\cdot0 \rangle$ a.u. Note that, according to Table I, the part of the crossing seam just considered is accessible for the $Li_2–Li_2^+$ system under chemical conditions. It is seen from this figure and Eqs (12) and (13) that the changes with d of both the quantities lead to quite significant changes in the nonadiabatic transition probability. Indeed, assuming again that the relative velocity of the vibrational motion of the Li_2 and Li_2^+ fragments at the crossing seam is 10^{-3} a.u., a rough estimate

of the transition probability we get from Eqs (*12*) and (*13*) is 0·53 for $d = 13·5$ a.u., 0·91 for 14·50 a.u. and 0·99 for $d = 15·5$ a.u. It should be stressed that the magnitude of the coupling vector c_{21} at the points of the crossing seam with $d = 13·5$ a.u.

TABLE I

Lowest vibrational levels and corresponding classical turning point internuclear distances for Li$_2$ and Li$_2^{+a}$

Level v	Li$_2$		Li$_2^+$	
	energy $(10^{-3}$ a.u.)	outer turning point (a.u.)	energy $(10^{-3}$ a.u.)	inner turning point (a.u.)
0	0·80	5·38	0·60	5·55
1	2·38	5·53	1·85	5·30
2	3·92	5·85	3·10	5·16
3	5·43	6·01	4·26	5·06

[a] The data correspond to ^{7}Li–^{7}Li isotopic variants of the diatomics subject to the potential energy curves taken from ref.[16].
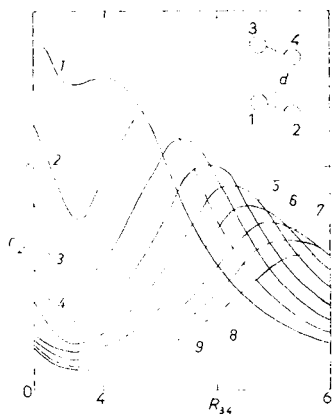

FIG. 4

The magnitude C_{21} of the nonadiabatic coupling vector c_{21} as a function of the Li–Li distance R_{34} for different planar C_{2v} geometries of Li$_2$–Li$_2^+$ with $d = 13·0$ a.u. For the n-th curve R_{12} is kept at $(4·2 + 0·2n)$ a.u.
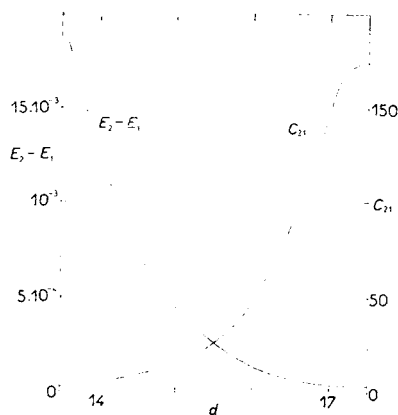

FIG. 5

The E_2–E_1 energy difference and the magnitude C_{21} of the nonadiabatic coupling vector as functions of the Li$_2$–Li$_2^+$ distance d. The arrangement of the nuclear centres corresponds to the part of the crossing seam with D_{2d} symmetry and R_{12} $(= R_{34}) = 5·5$ a.u.

is still rather small so that the relatively very high transition probabilities are mainly due to very small energy difference $E_2 - E_1$. In this respect, the situation here is similar to that in the $Li-Li_2^+$ system, and this kind of behaviour seems to be characteristic of such cases where the existence of the nonadiabatic coupling is connected with asymptotic properties of systems with rather weak and long-range interactions.

In Fig. 6 we show the behaviour of the magnitude of the nonadiabatic coupling vector $\mathbf{c}_{21}$ in the part of the crossing seam corresponding to nonplanar C_{2v} geometries and fixed $Li_2-Li_2^+$ distances selected from the region $\langle 13\cdot5, 17\cdot0 \rangle$ a.u. It is seen from this figure that for chemically most important configurations $R = R_{12} = R_{34} \approx$ $\approx 5\cdot5$ a.u., the C_{21} quantity increases steadilly with increasing d. For other relevant values of R, C_{21} is seen to remain finite. Taking into acount the changes with d of the energy difference $E_2 - E_1$, the beginning of the asymptotic region can be, for the purposes of the present paper, estimated to lie at $d \approx 17-20$ a.u.

Accordingly, for $d \geqq 20$ a.u. any passage of the $Li_2-Li_2^+$ system through the crossing seam is predicted to certainly induce transition between the lowest doublet adiabatic PES's. The system will behave diabatically in this region, retaining its electronic configuration. It is pertinent to note that this result is a more specific expression of the intuitive argument given in the first part of this section.

The existence of the crossing seam, its location in the configuration space and its accessibility by the system under quite moderate conditions indicate that a theoretical picture of collisions in the $Li_2-Li_2^+$ system cannot be based on a single GS adiabatic PES. A sophisticated theoretical description of the reaction would require a thorough study of the dynamics of the system by means of the quasiclassical trajectory approach including an application of the trajectory surface hopping model[28]. With the four- -centre $Li_2-Li_2^+$ system, the application of this approach is at present prohibitively expensive in terms of computer time.

On the other hand, we do not want to conclude our discussion without relating the present results to the behaviour of the system during the course of the reaction $Li_2 + Li_2^+ \rightarrow Li_4^+$. In view of this, we consider an idealized motion of the system along a minimum energy path (MEP) for the above reaction. The MEP corresponds to nonplanar C_{2v} configuration of the system in the asymptotic region and was constructed in much the same way as in our previous study[1] of the reaction $Li +$ $+ Li_2^+ \rightarrow Li_3^+$. The initial limiting structure of the pathway corresponds to the GS minimum in the reactant $Li_2-Li_2^+$ region located at the configuration defined by Eqs (*11*). The resulting MEP along with the relevant cuts through the lowest two doublet PES's and the magnitude of the nonadiabatic coupling vector are presented in Fig. 7. The lower panel in the plot shows the relationships among the ID's R_{12}, R_{34} and the $Li_2-Li_2^+$ distance d along this pathway. It is seen from the figure that the MEP does not pass through the crossing seam (*10*) with $b = 12$ a.u. Consequently, nuclear motion corresponding to this MEP does not cause any breakdown of the Born-Oppenheimer approximation. On the other hand, there are regions of somewhat larger

values of the nonadiabatic coupling vector magnitude, appearing in those regions of the MEP where the ID's difference $R_{12} - R_{34}$ undergoes a relatively precipitous decrease. However, this occurs at such configurations where the $Li_2-Li_2^+$ distance is already rather small, the $Li_2-Li_2^+$ interaction and the energy difference $E_2 - E_1$ rather large so that the nonadiabatic transition probability $(cf., Eq (12))$ is negligible. The same general behaviour of the system was observed along other MEP's for the reaction $Li_2 + Li_2^+ \rightarrow Li_4^+$ we have studied.

Starting from a MEP, the first step toward more realistic picture of the reaction $Li_2 + Li_2^+ \rightarrow Li_4^+$ is to take into account the type of motion of the system which is complementary to that along the MEP, and corresponds to chemical conditions. It is clear form Fig. 7 and relatively very small vibrational energies of both Li_2 and Li_2^+ that, for asymptotic and near-asymptotic region, one should consider the vibrational motion of the reactants.

In the region given by $d \geq 20$ a.u. any passage of the system through the crossing seam due to the vibrational motion of the reactants will cause nonadiabatic transition $\psi_1 \rightarrow \psi_2$ but the next passage will lead to transition $\psi_2 \rightarrow \psi_1$, and so on. The system will be, in this region, governed by the diabatic PES E_1^d of Eq. (5) which, for configurations of the MEP, is identical with the adiabatic PES E_1. Thus, for $d \geq 20$ a.u., the behaviour of the system is well represented by the MEP.
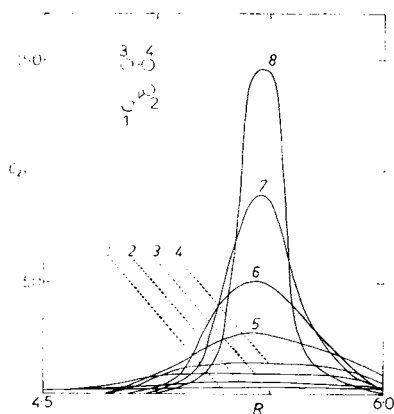

FIG. 6

The magnitude C_{21} of the nonadiabatic coupling vector as a function of the crossing seam geometry parameter $R = R_{12} = R_{34}$ for different D_{2d} configurations of the $Li_2-Li_2^+$ system. For the n-th curve d is kept at $(13\cdot0 + 0\cdot5\ n)$ a.u.
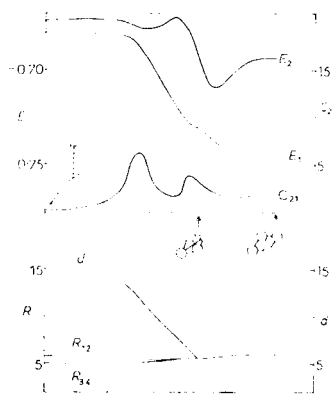
FIG. 7

Ground and first excited doublet PES's along the minimum energy path corresponding to the C_{2v} asymptotic structure of $Li_2 + Li_2^+$. C_{21} is the magnitude of the nonadiabatic coupling vector along this pathway. The remaining symbols are defined in the text

In the region 12 a.u. $\leq d \leq$ 20 a.u., the situation is different. Here, the nonadiabatic transition probability P_{12} at the crossing seam varies from 0 to 1 and a passage of the system through the crossing seam may, but need not induce nonadiabatic transition. As a consequence, the system can get trapped on the excited adiabatic surface for one or more vibrational periods of the collision partners. When this happens to be the case, the ground state MEP cannot be expected to provide even an idealized representation of the pertinent trajectory of the quasiclassical description of the system.

Depending mainly on the initial values of the Monte Carlo variables corresponding to the vibrational motion of the collision partners, the trajectory of the system can begin to evolve on the excited adiabatic PES E_2 at any d from the region $\langle 12 \cdot 0;\ 20 \cdot 0 \rangle$ a.u.. As a consequence, one cannot expect to get a simple idealized picture of the situation in terms of one or few additional excited-state MEP's. Hence, a sufficiently detailed theoretical description of the nonadiabatic behaviour of the $Li_2 - Li_2^+$ system must wait for a thorough study of the dynamics of the collision process.

REFERENCES

 1. Vojtík J., Krtková A., Polák R.: Theor. Chim. Acta *63*, 235 (1983).
 2. Vojtík J., Krtková A., Polák R.: Theor. Chim. Acta *66*, 405 (1985).
 3. Ellison F. O.: J. Amer. Chem. Soc. *85*, 3540 (1963).
 4. Tully J. C.: J. Chem. Phys. *58*, 1396 (1973).
 5. Steiner E., Certain P. R., Kuntz P. J.: J. Chem. Phys. *59*, 47 (1973).
 6. Tully J. C., Truesdale C. M.: J. Chem. Phys. *65*, 1002 (1976).
 7. Kuntz P. J. in the book: *Atom-Molecule Collision Theory. A Guide for the Experimentalist* (R. B. Bernstein, Ed.), p. 79. Plenum Press, New York 1979.
 8. Tully J. C.: Advan. Chem. Phys. *42*, 63 (1980).
 9. Schneider F., Zülicke L.: Chem. Phys. Lett. *67*, 491 (1979).
10. Vojtík J., Fišer J., Polák R.: Chem. Phys. Lett. *80*, 569 (1981).
11. Vojtík J., Fišer J.: Surface Sci. *121*, 111 (1982).
12. Vojtík J., Šavrda J., Fišer J.: Chem. Phys. Lett. *97*, 397 (1983).
13. Vojtík J., Paidarová I.: Chem. Phys. Lett. *99*, 93 (1983).
14. Vojtík J., Paidarová I.: Chem. Phys. Lett. *103*, 305 (1984).
15. Paidarová I., Vojtík J.: Chem. Phys. *84*, 225 (1984).
16. Pickup B. T.: Proc. Roy. Soc. *A 333*, 69 (1973).
17. Polák R., Vojtík J., Schneider F.: Chem. Phys. Lett. *53*, 117 (1978).
18. Vojtík J., Paidarová I.: Chem. Phys. Lett. *91*, 280 (1982).
19. Pedersen L., Porter R. N.: J. Chem. Phys. *47*, 4751 (1967).
20. Preston R. K., Tully J. C.: J. Chem. Phys. *54*, 4297 (1971).
21. Stine J. R., Muckerman J. T.: J. Chem. Phys. *65*, 3975 (1976); *68*, 185 (1978).
22. Nikitin E. E. in the book: *Chemische Elementar Prozesse* (H. Hartmann, Ed.), p. 43. Springer, Berlin 1968.

23. Tully J. C. in the book: *Dynamics of Molecular Collisions* (W. H. Miller, Ed.), Part B, p. 217. Plenum Press, New York 1976.
24. Tobin F. L., Hinze J.: J. Chem. Phys. *63*, 1034 (1975).
25. Tully J. C.: J. Chem. Phys. *59*, 5122 (1971).
26. Faist M. B., Muckerman J. T.: J. Chem. Phys. *71*, 233 (1979).
27. Vojtík J., Polák R.: Chem. Phys. *42*, 177 (1979).
28. Tully J. C., Preston R. K.: J. Chem. Phys. *55*, 562 (1971).