

Nonadiabatic effects in the interaction of atomic hydrogen with a lithium metal cluster

^aJ. VOJTÍK and ^bJ. FIŠER

^a*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, CS-182 23 Prague*

^b*Department of Physical Chemistry, Faculty of Natural Sciences,
Charles University, CS-128 40 Prague*

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Dedicated to Professor L. Valko, DrSc., in honour of his 60th birthday

The effect of change of the adsorption site position on mutual arrangement and nonadiabatic coupling between the two lowest singlet potential energy surfaces of the $\text{Li}_9(4,1,4)\text{—H}$ system is studied for a normal approach of hydrogen to the cluster surface. The potentials and nonadiabatic coupling elements are obtained using the diatomics-in-molecules method. The changes in the extent of nonadiabatic behaviour of the system caused by changes of the position of the adsorption site are predicted to be quite pronounced.

Для системы $\text{Li}_9(4,1,4)\text{—H}$ изучался эффект сдвига центра адсорпции на взаимное положение и неадиабатическую связь между двумя самыми низкими синглетными поверхностями как результат перпендикулярного приближения водорода к поверхности кластера. Потенциалы и элементы неадиабатической связи были определены при помощи метода ДИМ. Изменения неадиабатического поведения системы вызванные сдвигом центра адсорпции предвидятся сравнительно глубокие.

In our previous papers [1—3] we have studied interaction of atomic hydrogen with the (100) surfaces of Li_9 clusters. The energy of the $\text{Li}_9\text{—H}$ systems was calculated by the semiempirical valence bond method of diatomics-in-molecules (DIM) [4—7] which is currently often employed to produce potential energy surfaces for theoretical study of various types of elementary processes in the gas phase [8—12]. One of the reasons for our having used the DIM model for these systems was that the DIM scheme yields excited state potential energy surfaces in addition to the ground state ones, and is also considered to be quite successful in providing information about the nonadiabatic interactions between the Born—Oppenheimer electronic states of polyatomic collision systems [13, 14].

The ground and singlet excited state potential energy curves (PEC's) obtained in our work for normal approach of the hydrogen atom to some Li_9 cluster surface sites were found to intersect or avoid crossing, thus indicating possible nonadiabatic character of the adsorption process. An intersection of

the ground and excited state PEC's for $\text{Li}_n\text{—H}$ systems has also been reported by *Beckmann* and *Koutecký* [15] and *Pacchioni et al.* [16] who used in their calculations a more sophisticated *ab initio* approach, namely the multi-reference double-excitation configuration interaction method [17, 18].

In both these studies, the crossing of the $\text{Li}_n\text{—H}$ PEC's was connected with a nontrivial spatial symmetry exhibited by the system during the normal approach of the hydrogen atom to the cluster surface — the curves found intersecting each other represent electronic states of different spatial symmetry [19].

The most important information which is deduced from PEC's corresponding to a normal approach of an atom to an adsorption site on the surface are the binding energy and the equilibrium distance. If only the ground state PEC is available, or the ground state PEC is found to neither intersect nor avoid crossing with the excited state PEC's, the above quantities are readily determined from the lowest-lying PEC. When the crossing or avoided crossing is present, however, the situation is not so clear-cut. In order to overcome this difficulty in a consistent way, we have adopted [2] the approach according to which the surface site is assigned every adsorption energy (and the associated adatom—surface distance), which corresponds to a minimum on either the ground or excited state PEC, provided that both the electronic structure and the nuclear configuration corresponding to this minimum are accessible by the system through a normal approach of the adatom to the surface. When applied to the above-mentioned situations where, due to the nontrivial spatial symmetry of the adatom—cluster system, the PEC's are intersecting, the model leads to only a single binding energy (and equilibrium distance), namely that corresponds to the PEC which asymptotically correlates with the ground state of the adatom—cluster system but, in the region of the equilibrium $\text{Li}_0\text{—H}$ distance, corresponds to an excited state. A small change in the adsorption site position breaks the spatial symmetry of the atom—cluster system, results in PEC's avoiding (*cf.* Refs. [1—3]) and thereby leads to a situation where more electronic structures can be acquired by the system through a normal approach of the atom to the surface. As a consequence, more binding energies are then to be considered for the adsorption site under question.

A crude theoretical picture of the adsorption on the cluster is usually based on the PEC's for a few adsorption sites which often exhibit nontrivial spatial symmetry. Hence, an information on the changes in the behaviour of the system caused by changes in the adsorption site position appears to be desirable, if only because it could be helpful in getting an idea about the validity of a model of adsorption based on the PEC's associated with a few interaction sites with spatial symmetry.

The purpose of this communication is to present results relevant to an

assessment of the situation arising in a normal approach of the hydrogen atom to adsorption sites of the $\text{Li}_9(4,1,4)$ cluster which lie close to the central position on this cluster surface.

Model and method

The $\text{Li}_9(4,1,4)$ cluster used in the present calculations is shown in Fig. 1, together with the coordinates of an adsorption site. The nearest-neighbour Li—Li separation in the cluster is, in accordance with our previous work [1—3], taken to be 349.5 pm.

The DIM model used to obtain approximations to the true singlet atom—cluster PEC's is precisely the same as in our previous calculations. The nonadiabatic transition probability P_{12} between the two lowest adiabatic singlet states of the Li_9 —H system caused by a normal approach of hydrogen to the cluster surface is estimated according to the following approximate expression [20, 21]

$$\bar{P}_{12} \approx \exp \{ -|(E_2 - E_1)/\mathbf{v}_1^{(n)} \cdot \mathbf{d}_{21}^{(n)}| \} \quad (1)$$

Here, $\mathbf{v}_1^{(n)}$ is the normal component of the relative H— Li_9 velocity vector associated with the adiabatic surface E_1 and $\mathbf{d}_{21}^{(n)}$ is the normal component of the nonadiabatic coupling vector

$$\mathbf{d}_{21} = -i\hbar \langle \Psi_2 | \nabla | \Psi_1 \rangle \quad (2)$$

E_i and Ψ_i are the corresponding eigenvalue and eigenfunction, respectively, of the Born—Oppenheimer electronic Hamiltonian of the system. The normal component of the coupling vector (2) is approximated by the usual DIM expression [14]

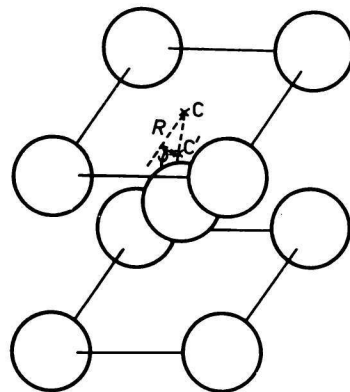


Fig. 1. The (4,1,4) lithium cluster and the polar coordinates of an adsorption site C' .

$$d_{21}^{(n)} = -i\hbar[C_2^\dagger(\partial H/\partial r)C_1]/(E_2 - E_1) \quad (3)$$

where r is the (normal) separation between H and the cluster surface, $\partial H/\partial r$ is a matrix formed by the derivatives of the individual elements of the DIM Hamiltonian matrix for the $\text{Li}_9\text{--H}$ system (*cf.* Ref. [2]) and C_i is a column matrix of the expansion coefficient of Ψ_i in the DIM basis.

Results and discussion

In Fig. 2 we show the two lowest singlet PEC's corresponding to the normal approach of H atom to the binding position C' with polar coordinates $R = 10$ pm, $\varphi = 0.1\pi$ (*cf.* Fig. 1), *i.e.* to a normal approach which is only slightly different from the C_{4c} one ($R = 0.0$ pm). Because of this slight difference, the overall shape of the resulting PEC's is not substantially different from the corresponding PEC's associated with the C_{4c} approach. However, as the $\text{Li}_9\text{--H}$ system does not possess any nontrivial spatial symmetry, the PEC's do not cross but only avoid crossing. This occurs at the $\text{Li}_9\text{--H}$ separation of 89.5 pm where the $(E_2 - E_1)/E_h$ difference reaches its minimum of 4.74×10^{-4} and the normal component of the nonadiabatic coupling vector $d_{21}^{(n)}$ (*cf.* eqn (3)) takes on the (maximum) value of 18.842 a.u. If we want to get an idea of how the $\text{Li}_9\text{--H}$ system will behave during its normal passage through the avoided crossing region, we have to evaluate the expression (1). Taking into account the potential energy of the system at the avoided crossing point relative to the asymptotic

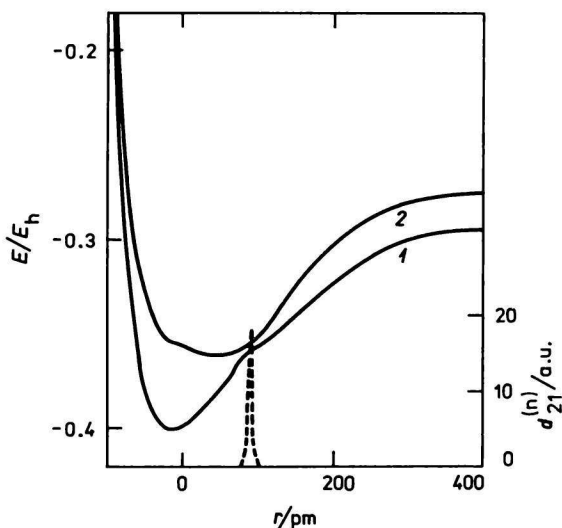


Fig. 2. The two lowest singlet potential energy curves (solid lines) corresponding to a normal approach of H to the $\varphi = 0.1\pi$, $R = 10$ pm adsorption site on the cluster surface. The dashed line represents the normal component $d_{21}^{(n)}$ of the nonadiabatic coupling vector between the corresponding adiabatic states.

$\text{Li}_9 + \text{H}$ configuration, the normal component of the H— Li_9 velocity can be estimated to be $1.26 \times 10^4 \text{ m s}^{-1}$ (5.75×10^{-3} a.u.). This, together with the above information about the avoided crossing point leads to the hopping probability $P_{12} = 0.996$. We can therefore conclude that within the present model, a normal passage of the system through the avoided crossing region of Fig. 2 will almost certainly lead to a surface hopping. As a result, for the Li_9 —H separations $r < 90$ pm, the idealized normal approach of H atom to this site on the Li_9 cluster surface is governed by the PEC representing the first excited adiabatic singlet state of the system. Accordingly, the binding position $R = 10$ pm, $\varphi = 0.1 \pi$ is assigned the equilibrium distance $r_e = 40$ pm and the interaction energy $E_c = -1.77$ eV, *i.e.* essentially the same values as those corresponding to the C_{4v} H— Li_9 approach (*cf.* Refs. [2, 3]). It should be stressed that the coincidence between the characteristics for both the binding positions considered is connected with two factors: First, except for the avoided crossing replacing the actual crossing, the relevant PEC's for the $R = 10$ pm, $\varphi = 0.1 \pi$ binding position are practically the same as those corresponding to the C_{4v} approach. Secondly, the nonadiabatic transition probability is very high, $P_{12} = 0.996$, the value practically identical with that for the C_{4v} approach where, by symmetry, the (formally) analogous quantity is equal to 1.

As already noted in the introduction, our main objective is to get an idea of how this probability changes with increasing separation R of the adsorption site to the central position on the cluster surface. To this end, we have computed the lowest singlet PEC's and the normal component $d_{21}^{(n)}$ of the coupling vector between the associated states, corresponding to normal approaches of H to a selected set of binding positions from the region $\varphi = 0.1 \pi$, $R \in \langle 5, 90 \rangle$ pm. The situation for the adsorption site $\varphi = 0.1 \pi$, $R = 40$ pm is illustrated by Fig. 3. A comparison of the PEC's of Fig. 3 with those corresponding to the $\varphi = 0.1 \pi$, $R = 10$ pm position (Fig. 2) reveals that the effect of the change in R on the PEC's is substantial only in the avoided crossing region. What is important in the present context is that for the $R = 40$ pm site, the two lowest singlet adiabatic curves do not get so close to each other as in the $R = 10$ pm case. Another important point is that in the avoided crossing region, the changes with decreasing Li_9 —H separation of the electronic structure of the system in the corresponding adiabatic states are, as reflected by the $d_{21}^{(n)}(r)$ dependence, not so pronounced as in the $R = 10$ pm case. Both these factors are responsible for decreased nonadiabatic transition probability P_{12} .

The main characteristics connected with the assessment of the transition probabilities for the binding positions from the region $\varphi = 0.1 \pi$, $R \in \langle 5, 90 \rangle$ pm are given in Table 1, and the dependence of the maximum value of the normal component of the nonadiabatic coupling vector $d_{21}^{(n)}$ on R , together with the variation of the resulting nonadiabatic transition probability estimate P_{12} with

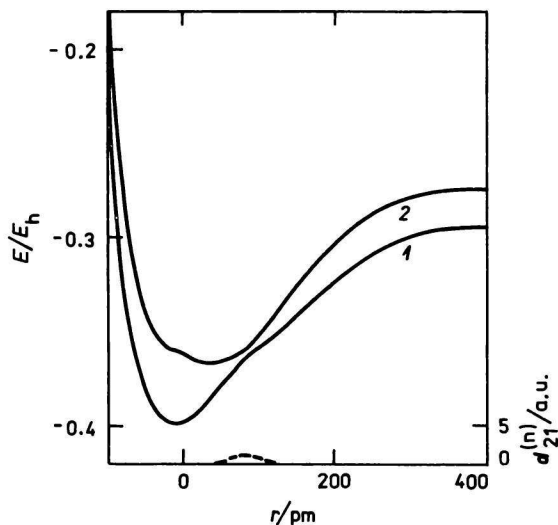


Fig. 3. The two lowest singlet potential energy curves (solid lines) associated with a normal approach of H to the $\varphi = 0.1\pi$, $R = 40$ pm adsorption site on the cluster surface. The dashed line represents the normal component $d_{21}^{(n)}$ of the nonadiabatic coupling vector between the corresponding adiabatic states.

Table 1

Characteristics of the $\text{Li}_9(4,1,4)\text{—H}$ system at the avoided-crossing points for a normal approach of H to the ($\varphi = 0.1\pi$, R) binding positions lying at a distance R from the C site

R/pm	r_{ac}/pm^a	$(E_2 - E_1)/10^{-3} E_h$	$d_{21}^{(n)}/\text{a.u.}^b$	P_{12}^c
5	89.9	0.121	74.306	1.00
10	89.5	0.474	18.842	0.996
15	89.2	1.034	8.514	0.98
20	88.2	1.761	4.945	0.94
25	87.1	2.620	3.269	0.87
30	85.9	3.569	2.354	0.78
35	84.3	4.582	1.800	0.66
40	82.6	5.625	1.437	0.53
45	80.6	6.683	1.184	0.40
50	78.4	7.735	1.001	0.30
55	76.1	8.765	0.863	0.21
60	73.5	9.770	0.757	0.14
70	68.1	11.65	0.603	0.06
80	62.4	13.34	0.498	0.02
90	56.5	14.82	0.422	0.00

a) Distance of the H atom from the cluster surface at the avoided-crossing point; b) normal component of the nonadiabatic coupling vector between the two lowest singlet adiabatic states; c) nonadiabatic transition probability estimate.

R is shown in Fig. 4. It is evident that for $R \in \langle 15, 80 \rangle$ pm the system ceases to be governed by a single (diabatic) PEC during an idealized normal approach of H to the Li_9 cluster surface. Accordingly, in this region of R , two couples of r_c and E_c are to be taken into account when considering the corresponding adsorption sites, and the quantity $1 - P_{12}$ may be taken as a measure of the degree to which the characteristics corresponding to the ground state adiabatic curve will apply in addition to those associated with the excited state PEC (with the probability P_{12}).

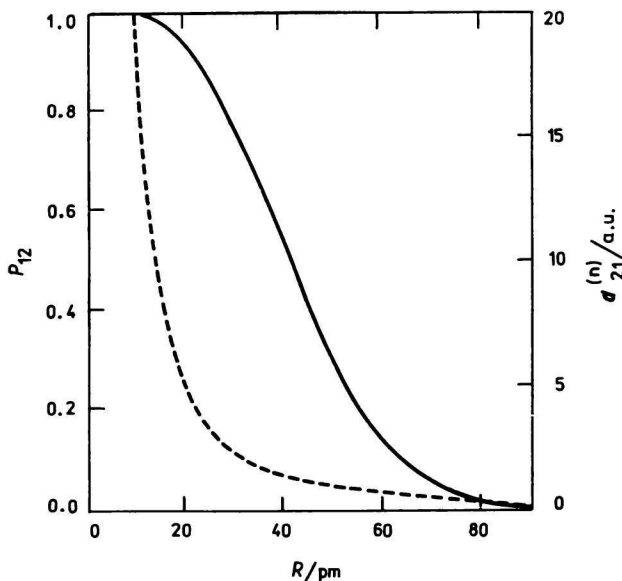


Fig. 4. The maximum value of the normal component of the nonadiabatic coupling vector $d_{21}^{(n)}$ (dashed line) and nonadiabatic transition probability P_{12} (solid line) as functions of the distance R of the adsorption site $\varphi = 0.1 \pi$, R from the C_{4v} binding position ($R = 0$).

The two lowest singlet adiabatic PEC's for the binding position $\varphi = 0.1 \pi$, $R = 90$ pm are shown in Fig. 5. In this case, the nonadiabatic coupling vector d_{21} is very small and is not shown in the figure. The characteristics of Table 1 for this H— Li_9 approach are seen to demonstrate that for this binding position, the present model does not predict any breakdown of the Born—Oppenheimer approximation induced by a normal approach of the hydrogen atom to the Li_9 cluster surface. Thus, we arrive at the standard situation in which the binding energy and the equilibrium Li_9 —H separation are deduced from a single ground state PEC. The resulting adsorption characteristics are $r_c = -30$ pm; $E_c = -2.86$ eV. These values are not substantially different from those corre-

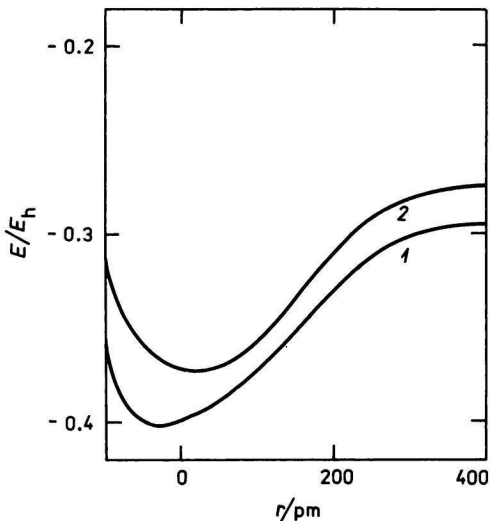


Fig. 5. The two lowest singlet PEC's corresponding to a normal approach of H to the $\varphi = 0.1\pi$, $R = 90$ pm adsorption site on the cluster surface.

sponding to the ground state PEC associated with the C_{4v} approach (and to a normal approach of H to the $\varphi = 0.1\pi$, $R = 10$ pm adsorption site). Hence, the changes in the picture of the adsorption in the Li_9 -H system are seen to be mainly caused by the decrease in the extent of the nonadiabatic behaviour of the system as reflected by the quantity P_{12} .

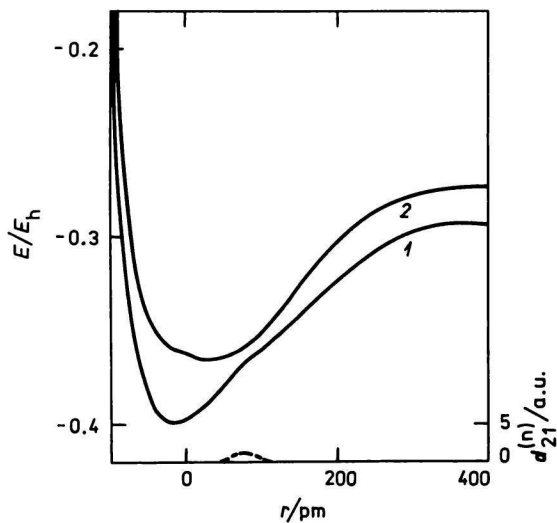


Fig. 6. The two lowest singlet PEC's (solid lines) associated with a normal approach of H to the $\varphi = 0.3\pi$, $R = 40$ pm adsorption site on the cluster surface. The dashed line represents the normal component $d_{21}^{(n)}$ of the nonadiabatic coupling vector between the corresponding adiabatic states.

In Fig. 6 we give the PEC's representing the two lowest singlet adiabatic states (and the normal component of the nonadiabatic coupling vector between these states) which correspond to a normal approach of H to the $\varphi = 0.3\pi$, $R = 40$ pm binding position on the Li_9 cluster surface. This figure serves to illustrate that in the region of R considered, the main features of the two lowest single Li_9 —H potentials, as well as of the nonadiabatic coupling between them were found to be practically independent of the coordinate φ of the adsorption site. As a consequence, for all $\varphi \in \langle 0, \pi/2 \rangle$, we got $P_{12}(R)$ dependences which are not markedly different.

In concluding this communication, we note that the potential energy of the system in the avoided crossing region is predicted to be quite low compared with that in the $\text{Li}_9 + \text{H}$ asymptotic configuration. However, due to the approximate character of our DIM model, the present assessment of these energy differences between the pertinent regions cannot be considered to be highly quantitative. In the light of the results of Beckmann and Koutecký [15] and Pacchioni *et al.* [16] cited above, this difference appears to be almost certainly overestimated in our calculations. This, together with eqn (I) makes us inclined to feel that in the case of cluster—adatom systems exhibiting nonadiabatic behaviour of the type studied here, the change of the nonadiabatic transition probability with a change of the position of the adsorption site can be expected to be more pronounced than the one reported here.

While the quantitative aspect of this conclusion will have to be estimated on the basis of more sophisticated calculations, the present results seem to indicate again (*cf.* Refs. [2, 22]) that excited states may play an important role in adsorbate—substrate interactions and that theoretical studies of adsorption and catalytic processes based on the cluster models should not ignore possible nonadiabatic behaviour of the pertinent systems.

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