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Model study of the relaxation accompanying adsorption of atomic hydrogen on the Li(100) cluster surface*

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Relaxation effects in the (4, 1, 4) and (5, 4) Li_9 clusters induced by interaction with H are studied using the diatomics-in-molecules method. Total electronic energies for the clusters are determined as functions of the Li–Li bond lengths, both in the absence and in the presence of hydrogen adsorbed in a position of C_{4v} symmetry. Two models of cluster relaxation are considered, differing in which part of the cluster is allowed to relax. The calculations reveal that hydrogen adsorbed on the (100) cluster surface causes quite a significant contraction of the metal atoms. The effect of the cluster relaxation on the nonadiabatic coupling between the lowest two Born–Oppenheimer states of the hydrogen–cluster system is discussed.

Key words: Lithium clusters — Relaxation effects — Nonadiabatic effects

1. Introduction

In our earlier papers [1, 2] we reported results of theoretical study of adsorption of hydrogen atom on the (100) surface of Li_9 clusters. The interaction energy of the Li_9–H systems and nonadiabatic coupling between the lowest electronic states were calculated by the diatomics-in-molecules (DIM) method [3–6] which has proved to be very useful in theoretical descriptions of gas-phase collisions [7–9] and chemi-ionization processes [10–12]. The DIM binding energies and corresponding equilibrium distances obtained for different binding sites on the Li_9 cluster surface led to a picture of the cluster–hydrogen atom interaction, the main features of which are in a good agreement with those deduced by Beckmann and

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

Koutecký [13, 14] from their more sophisticated (and laborious) MRD-CI [15] calculations. Further, though the Li_9 clusters are admittedly rather small to model many properties of lithium metal [16–19], our results are consistent with the basic trends obtained by Hjelmberg [20] for hydrogen interacting with a jellium model of the Na(100) surface. On the positive side, the small cluster size (and the method used) made it possible to shed some light on the role of the excited electronic states in the adsorption of atomic hydrogen on the (100) lithium cluster surface.

There are several ways in which the models of adatom–cluster interactions can be improved. The most obvious one consists in increasing the cluster size. However, in view of our previous results, it appears sensible to follow another line, namely to keep the cluster size small and improve the description of some geometrical aspects of the hydrogen–cluster interaction. One can expect that this type of approach will be helpful in assessing the effect of changes in geometry on the nonadiabatic behaviour of the adatom–cluster systems.

In the present communication, we follow the latter line: By use of the DIM method, we study the Li_9 cluster model of the relaxation due to adsorption of atomic hydrogen on the (100) surface of lithium clusters. Our interest is primarily in the change in the equilibrium Li–Li bond lengths that accompanies the Li_9–H interaction. Attention is also paid to the effect of the cluster relaxation on the nonadiabatic coupling between the lowest electronic states of the Li_9H systems.

2. Model and method

Two different Li_9 clusters which are sections of the body-centred cubic (bcc) lithium lattice were used, namely (4, 1, 4) and (5, 4). For the (5, 4) cluster, *A*-site (atop) adsorption was considered. In the Li_9(4, 1, 4) case, we were interested in two normal approaches of H to the cluster surface: a *C* (centred)-site approach and an approach to a point on the surface which lies at a distance of 0.4 Å from the *C* site (see Fig. 1). In the following, this point on the cluster surface will be referred to as an *N* site.

Following Cox and Bauschlicher [21, 22], the cluster relaxation (due to the interaction with a hydrogen atom) was studied at the equilibrium H-cluster separation, the starting cluster geometry being characterized by that uniform

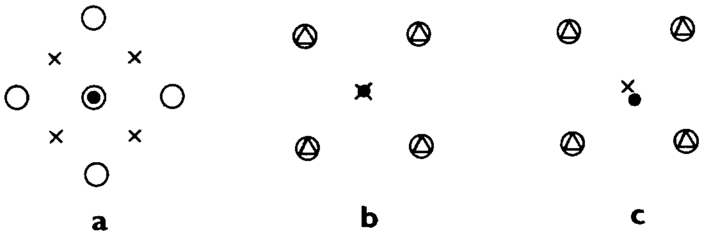


Fig. 1a–c. Three Li_9–H models: **a** (5, 4) cluster (*A*-site approach); **b** (4, 1, 4) cluster, *C*-site approach; **c** (4, 1, 4) cluster, *N*-site approach; ○ represents the surface atom, × represents the second layer, △ represents the third layer, ● denotes binding position of the hydrogen atom

Li-Li bond length which corresponds to the minimum electronic energy of the bare metal cluster.

According to our earlier calculations on the Li_9H systems [1, 2] a normal approach of hydrogen to the C site on the $Li_9(4,1,4)$ surface and also to those surface positions lying close to the C site is accompanied by a breakdown of the Born-Oppenheimer approximation. Because of this, the behaviour of the system in this case is more complicated than in the standard one, and it appears desirable to get an idea about how the relaxation effects can influence the nonadiabatic behaviour of the $Li_9(4,1,4)$-H system. Due to the C_{4v} symmetry of the Li_9H system, a perpendicular approach of H to the C site of the $Li_9(4,1,4)$ cluster represents a limiting case in which the relaxation has no effect on the nonadiabatic behaviour of the system. This is the reason why these effects are studied with the normal approach of H to the N site of the $Li_9(4,1,4)$ cluster chosen in such a way that the Li_9H system does not possess any nontrivial spatial symmetry.

The electronic energies of the lowest singlet states of each Li_9H system were obtained by diagonalization of the DIM Hamiltonian matrix

$$H = \sum_{K>L=1}^{10}\sum^{9} V_{(KL)} h^{(KL)} V^{\dagger}_{(KL)} - 8 \sum_{K=1}^{10} h^{(K)} \tag{1}$$

referring to the basis of the valence-bond (VB) type functions discussed in [2, 23]. The unitary transformation matrices $V_{(KL)}$ were constructed by the direct diagonalization approach [23, 24]. The atomic contributions $h^{(K)}$ to the polyatomic Hamiltonian matrix were obtained by assuming that the DIM basis functions are formed from the eigenstates of the atomic Hamiltonians. Within the present DIM model the diatomic fragment matrices $h^{(KL)}$ are known to be diagonal [2]. In evaluating these elements for the Li_2 fragment contributions to the polyatomic Hamiltonian matrix, the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ potential energy curves (PECs) were taken from the work of Pickup [25]. In the LiH fragments, the $^1\Sigma^+$ and $^3\Sigma^+$ PECs used are those based on the MCSCF results of Docken and Hinze [26].

3. Results and discussion

3.1. Cluster relaxation

As indicated in the preceding section, the first step of our model study of the cluster relaxation consisted of the determination of those values of the cluster lattice parameter ($r_{\text{Li-Li}}$) which lead to the minimum total energy of the clusters. For the $Li_9(4,1,4)$ cluster, the minimum energy was reached at $r^0_{\text{Li-Li}} = 3.278$ Å. In the $Li_9(5,4)$ case, the optimum value of the $r_{\text{Li-Li}}$ parameter was determined to be 3.441 Å, which is only slightly smaller than the bulk lattice parameter, 3.491 Å, used in our previous studies [1, 2]. It should be perhaps noted that when the $r_{\text{Li-Li}}$ parameter was optimized simultaneously in both layers of the (5, 4) cluster while keeping the distance between the two layers fixed at its bulk value, we obtained the value $r^0_{\text{Li-Li}} = 3.448$ Å.

Next we calculated the PECs corresponding to a normal approach of the hydrogen atom to the cluster surfaces. During the approach, the cluster lattice parameter was kept fixed at the optimum value given above. The resulting PECs for both the *A*-site and *C*-site adsorption are shown in Fig. 2. In the case of the (5, 4) cluster, the lowest two PECs are practically the same as those corresponding to the cluster with the bulk lattice parameter 3.491 Å. As the present Li-Li distance is only slightly decreased (3.441 Å), this high degree of similarity - leading to an unchanged adatom-surface equilibrium separation $r_e = 1.59$ Å, and practically the same binding energy - is not surprising.

In the $Li_9(4, 1, 4)$-H *C*-site case, the change in the $r^0_{\text{Li-Li}}$ parameter (to 3.287 Å) is more significant. In spite of this, the mutual arrangement of the lowest PECs for the *C*-site adsorption remains unchanged, while the PEC that represents the ground state in the asymptotic region (B_1) is intersected by the curve corresponding to a state of different (A_1) symmetry. Thus, due to the breakdown of the Born-Oppenheimer approximation, there are two local minima on the PECs (and two Li_9-H equilibrium separations) to consider in the third step of the procedure for study of the cluster relaxation in the $Li_9(4, 1, 4)$ case.

A word needs to be said here about our considering both these equilibrium separations: First, if one limits oneself to a normal approach of the hydrogen atom to the *C* site of the (4, 1, 4) cluster surface, i.e., if one strictly follows the model of adsorption of hydrogen on clusters discussed in our previous paper [2], one ends up with the minimum on the B_1 PEC located at the adsorption bond length $r_e = 0.49$ Å. The reason for this is that when the hydrogen approach is perpendicular to a *C* site, the C_{4v} symmetry of Li_9-H is conserved and the transition probability from the lowest B_1 state to the A_1 one is, by symmetry, equal to zero regardless of whether the two PECs approach each other or even cross at some Li_9-H separations. If the restriction of a normal approach of H to

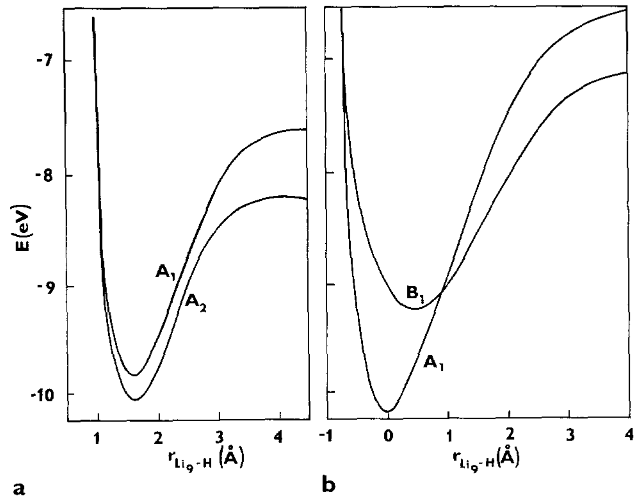
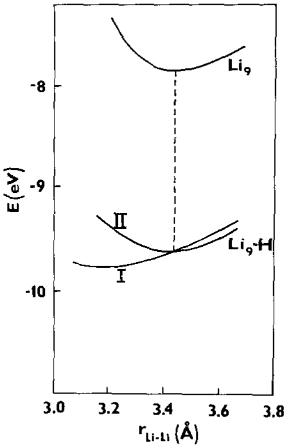


Fig. 2a, b. Potential energy curves for H interacting with the (100) surface of the Li_9 clusters: **a** (5, 4) cluster, *A*-site approach; **b** (4, 1, 4) cluster, *C*-site approach the cluster surface is released, however, the situation is different. In this case, cuts through the lowest two singlet potential energy surfaces corresponding to a general approach of H to the cluster surface will avoid crossing. As a consequence, the $Li_9(4,1,4)$-H cluster can reach the C_{4v} geometry with hydrogen just on the cluster surface ($r_e = 0.00$ Å) in an electronic state corresponding to the A_1 PEC.

In the third step of this procedure, the hydrogen-metal bond length was kept fixed at its equilibrium value and the total energy was minimized with respect to variation in the Li-Li bond lengths in the cluster. For both the clusters, two models of relaxation preserving the C_{4v} symmetry were employed: In the first model (denoted by I), only the surface layer's parameter was changed (surface relaxation), in the other model (II) the cluster lattice parameter was varied uniformly in the whole cluster. This step of the procedure is illustrated by Figs. 3 and 4 in which the total energy of the Li_9 and Li_9H systems (with respect to the energy of the ground state separated atom region) is shown as a function of the Li-Li bond lengths. It should be remarked that additional variation of the hydrogen-cluster distance did not lead to any decrease in the electronic energy of the systems, thus indicating that the procedure we used for the study of the cluster relaxation is, in the present situation, sound.

The results of the lithium cluster relaxation are summarized in Table 1. One of the main results of these calculations is that hydrogen adsorbed on the (100)



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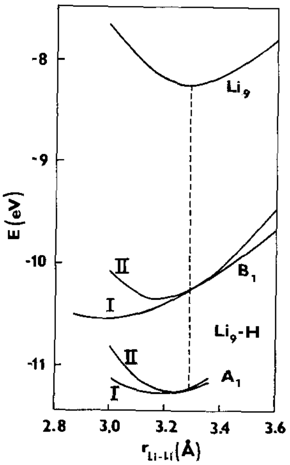

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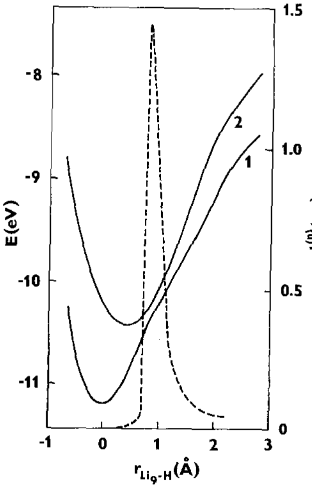

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Fig. 3. The total energy of the $Li_9(5,4)$ and the $Li_9(5,4)$-H clusters as functions of the Li-Li bond length. *Curve I*: model I (surface relaxation). *Curve II*: model II (Li-Li bond length varied uniformly in the whole cluster)

Fig. 4. The total energy of the $Li_9(4,1,4)$ and the $Li_9(4,1,4)$-H clusters as functions of the Li-Li bond length. *Curve I*: model I, *curve II*: model II

Fig. 5. *Solid lines* correspond to potential energy curves for H approaching the position N lying at a distance of 0.4 Å from the C site. The *dashed line* represents the normal component $d_{21}^{(n)}$ of the nonadiabatic coupling vector as a function of the adatom-surface distance

cluster surface causes a significant contraction of the Li-Li nearest neighbour distance.

In the case of the (4, 1, 4) cluster and for both the electronic states, the contraction of the Li-Li bond lengths in model I (10.3% and 3.2% in the state B_1 and A_1, respectively) is considerably larger than that in model II (3.2% and 1.6%). As far as the relative changes in binding energy accompanying relaxation are concerned, our calculation gives the largest value of 11.3% for the state B_1 with relaxation limited to the uppermost layer. In contrast, the value of 0.3% was obtained within both models for the ground state A_1.

In the $Li_9(5, 4)$ cluster, the difference between the two models of relaxation is even more prominent. The reduction of the Li-Li distance is 8.4% (model I) and 0.5% (model II). These results may be compared with the changes induced by hydrogen adsorbed in the atop position (C_{3v} symmetry) on the $Be_{10}(7, 3)$ cluster [21] (*ab initio* MO SCF calculations). When the nearest neighbour distance in both beryllium layers was varied simultaneously, the reduction was 0.3% but when only the surface layer's parameter was changed, the shortening was 0.7%. The great difference from the present value of 8.4% may be connected with the fact that in the $Li_9(5, 4)$ cluster, the number of the surface atoms lying in the neighbourhood of the *A* position is different from that in the $Be_{10}(7, 3)$ cluster. It should also be noted that while the electronic structure of the Li_9 cluster is of an open-shell type, the Be_{10} cluster has a closed-shell electronic configuration. It is interesting to note that the MRD-CI calculations of the geometrical relaxation of the $Be_7(7, 0)$ cluster have shown [27] that the contraction of the Be-Be bond lengths is of the same order of magnitude as that found by Cox and Bauschlicher in Be_{15}-H, and larger than that of Be_{10}-H [21].

Table 1. Optimized bond lengths, binding energies and changes due to cluster relaxation

Cluster	Electronic state	Model	$r^0_{\text{Li-Li}}$ (Å)	r_e (Å)[a]	Contraction of the Li-Li bond lengths (%)	E_b (*eV*)		Relative change in binding energy (%)
						Unrelaxed cluster	Relaxed cluster	
$Li_9(4, 1, 4)$			3.287					
$Li_9(4, 1, 4)$-H	A_1	I	3.172	0.00	3.5	2.98	2.99	0.3
		II	3.233		1.6		2.99	0.3
	B_1	I	2.950	0.49	10.3	2.04	2.27	11.3
		II	3.182		3.2		2.10	2.9
$Li_9(5, 4)$			3.441					
$Li_9(5, 4)$-H	A_2	I	3.152	1.59	8.4	1.74	1.92	10.3
		II	3.423		0.5		1.75	0.6

[a] r_e is the distance of hydrogen from the cluster surface

3.2. *The effect of the cluster relaxation on the nonadiabatic behaviour of the $Li_9(4, 1, 4)$–H system*

In Fig. 5 we show the two lowest PECs corresponding to a normal approach of H to the N site of the $Li_9(4,1,4)$ cluster surface considered in Sect. 2. The $r_{\text{Li-Li}}$ parameter was taken to be 3.287 Å (optimum value for the bare cluster). Besides the two PECs, the figure also shows the magnitude of the normal component of the nonadiabatic coupling vector

$$d_{21}^{(n)} = -i\hbar\langle\psi_2|\frac{\partial}{\partial r}|\psi_1\rangle \tag{2}$$

between the lowest two singlet adiabatic states. In Eq. (2), r is the distance from H to the cluster surface and ψ_i are the eigenfunctions of the Born-Oppenheimer electronic Hamiltonian of the Li_9H system. As usual in the DIM scheme [28], $d_{21}^{(n)}$ is approximated by the expression

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

where $\partial H/\partial r$ is obtained by differentiating each of the matrix elements of Eq. (1), C_i is the column matrix of the expansion coefficients of ψ_i in the DIM basis and E_i is the corresponding eigenvalue of H.

In accordance with a semi-classical description of the nonadiabatic behaviour of polyatomic systems [29], the quantity $d_{21}^{(n)}$ can be used to estimate the probability P_{12} of the nonadiabatic transition between the first two singlet adiabatic states of the Li_9–H systems; this transition is caused by a passage of the system through the nonadiabatic region during a normal approach of H to the N site of the $Li_9(4,1,4)$ cluster surface. A rough estimate of the transition probability can be obtained from the expression [30, 31]

$$P_{12} \approx \exp\{-|(E_2 - E_1)/v_1^{(n)} d_{21}^{(n)}|\}. \tag{4}$$

Here, $v_1^{(n)}$ is the normal component of the nuclear velocity vector appropriate to the adiabatic surface E_1, and the other quantities have the meaning mentioned above. Using the difference between the values of E_1 in the avoided crossing and in the Li_9–H asymptotic regions ($E_1^{\text{as}} = -0.3030$ a.u.) to assess $v_1^{(n)}$, and taking into account the values of $d_{21}^{(n)}$ and $E_2 - E_1$ at the avoided crossing point (see Table 2), the probability P_{12} may be estimated to be ≈ 0.65.

As already noted, it would be of interest to obtain some idea about how the quantities which determine the transition probability are affected by the cluster relaxation. To this end we have adopted essentially the same approach as in Sect. 3.1. In accordance with what has been said above, the $Li_9(4,1,4)$–H separation was fixed at the value ($r_c = 0.85$ Å) which maximized the magnitude of the normal component $d_{21}^{(n)}$ of the nonadiabatic coupling vector (3). The Li-Li separations in the cluster were then varied according to the two models discussed in Sect. 2.

The dependence of the pertinent characteristics of the system on the Li-Li bond lengths is shown in Fig. 6a, b. It is seen from this figure that with the $Li_9(4,1,4)$–H

Table 2. Properties of the $Li_9(4, 1, 4)$-H system at the avoided crossing Li_9-H separation, and their changes due to cluster relaxation

Model	Electronic state i	$r^0_{\mathrm{Li-Li}}$ (Å)	Contraction of the Li-Li bond lengths (%)	$E_2(r^0_{\mathrm{Li-Li}}) - E_1(r^0_{\mathrm{Li-Li}})$ (eV)	$E_1(r^0_{\mathrm{Li-Li}})$ (eV)	$d^{(n)}_{21}$ (a.u.)[a]	P_{12}[b]
Unrelaxed cluster		3.287	—	0.158	−10.36	1.44	0.65
I	1	3.025	8.0	0.242	−10.51	0.55	0.18
	2	3.120	5.1				
II	1	3.185	3.1	0.152	−10.43	1.45	0.67
	2	3.182	3.2				

[a] DIM approximation to the normal component of the nonadiabatic coupling vector

[b] Nonadiabatic transition probability estimate

separation fixed at the value corresponding to the separation of the avoided crossing, the difference between the pictures provided by the two models of relaxation are in some respects even more pronounced than was the case for the equilibrium Li_9-H separation.

In model II, the $E_2 - E_1$ difference is not substantially changed with the variation of $r_{\mathrm{Li-Li}}$. Taking into account that the normal component of the nonadiabatic coupling vector is evaluated using Eq. (3), one is not surprised to find that in the present case the relaxation has practically no effect on the quantity $d^{(n)}_{21}$ (see Table 2). This, together with the fact that the energy of the lowest adiabatic state at the avoided crossing point is not significantly lowered by the cluster relaxation, indicates that within this model, the extent of the nonadiabatic behaviour of the Li_9-H system is predicted not to be substantially different from that exhibited by the unrelaxed system. This is best seen from Eq. (4) which, when supplied with the pertinent values from Table 2, leads to $P_{12} = 0.67$, a value which is only slightly greater than the nonadiabatic transition probability in the unrelaxed case ($P_{12} = 0.65$).

Even a cursory examination of Table 2 reveals that when only the uppermost layer of the $Li_9(4, 1, 4)$ cluster is allowed to relax (model I), the situation is substantially different from both model II and the unrelaxed case. In fact, the transition probability is now assessed to be ≈ 0.18. The main reason for this decrease in P_{12} is that in this case, the variation of the lowest adiabatic energy of the $Li_9(4, 1, 4)$ system with the Li-Li bond length differs from that corresponding to the first excited singlet state.

Summarizing, we can conclude that chemisorption of hydrogen on the (100) Li_9 cluster surface is accompanied by a marked contraction of metal atoms. The relaxation depends on the model used, the cluster shape and the electronic state

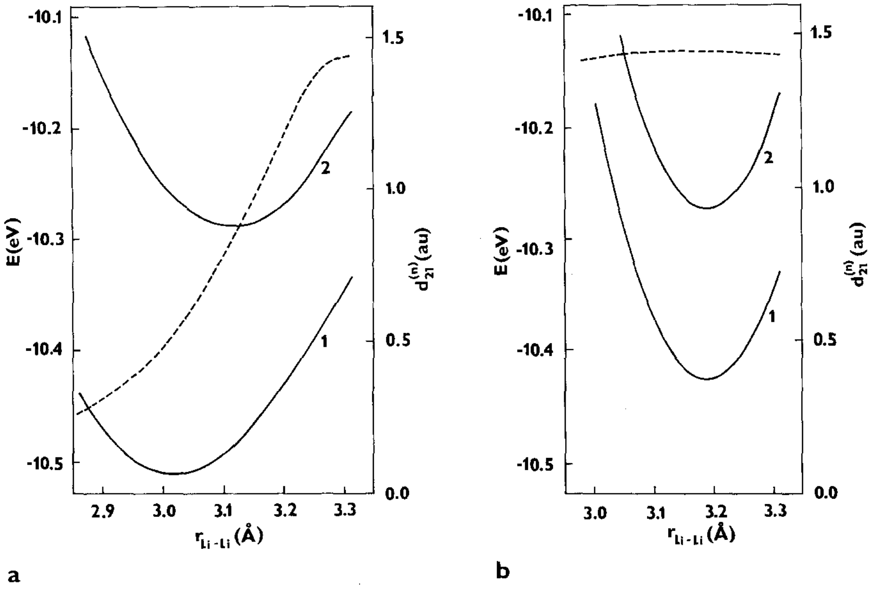

Fig. 6a, b. *Solid lines* correspond to the two lowest total energies of the $Li_9(4, 1, 4)$-H cluster, *N*-site adsorption. The *dashed lines* represent the normal component $d_{21}^{(n)}$ of the nonadiabatic coupling element as a function of the Li-Li bond length. The adatom-surface distance was 0.85 Å. **a** Model I; **b** model II

of the system. The contraction of the surface Li-Li bonds in model I (of about 3% and 8%) is more significant than that in model II. It is considerably larger than the shortening of the surface bond lengths in beryllium clusters [21] (1% or 2%). However, the contraction of the Li-Li bonds within model II is comparable in magnitude with the (uniform) reduction of the lattice parameter in both layers of beryllium ($Be_{10}(7, 3)$ and $Be_{15}(10, 5)$) [21] and nickel clusters ($Ni_{10}(7, 3)$) [22].

The effect of the cluster relaxation on the nonadiabatic behaviour of the $Li_9(4, 1, 4)$-H cluster is assessed for the *N*-site adsorption. The approximate semiclassical probability of the nonadiabatic transition between the two lowest electronic states remains practically the same during cluster relaxation within model II while it is significantly lowered by surface relaxation in model I. This finding seems to lend some support to the idea [1] that the nonadiabatic behaviour of the $Li_9(4, 1, 4)$-H system might be connected with changes in that part of the energy and wavefunction which corresponds to the Li_9 cluster.

In concluding this communication we would like to remark that the (4, 1, 4) and (5, 4) clusters which are sections of the bcc lattice probably do not represent local minima of the ground-state potential energy surface. Based on recent investigations [16-19], the geometry of small alkali metal clusters can deviate from that of the bulk. However, the use of the $Li_9(4, 1, 4)$ and (5, 4) clusters as models for the chemisorption sites on the (100) bcc metal surface made it possible to partially optimize the Li_9H systems under the C_{4v} symmetry constraint and estimate the relaxation effects during the adsorption process. It should be noted that these Li_9 cluster models cannot allow for both the small changes in the second nearest neighbour Li–Li distances and the work needed to distort the surrounding lattice. Therefore, the present calculations exaggerate the relaxation effects.

The recent experiments on small clusters have shown that the size needed to simulate many properties of the bulk metal is much larger than in our case. Hence, because of the cluster size and also the restrictions imposed on the way in which the clusters are allowed to relax, the present systems cannot be considered to model the adsorption induced changes in the lithium metal surface. However, the adatom-cluster calculations of this type can be helpful in obtaining an idea about local surface reconstruction due to the chemisorption of an atom upon a (100) surface of lithium.

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