

Ab initio potential energy surface and rotationally inelastic collisions of LiH ($X^1\Sigma^+$) with H. I. The ab initio evaluation of the potential energy surface

H. Berriche*, Chaker Tlili

Laboratoire de Physique et Chimie des Interfaces, Departement de Physique, Faculte des Sciences de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisia

Received 15 October 2003; accepted 26 January 2004

Abstract

In this work we present a study of the interaction between the hydrogen atom and the LiH ($X^1\Sigma^+$) molecule. The potential energy surface describing this interaction has been calculated very accurately for a fixed distance, that is the equilibrium distance of the LiH molecule and for a wide range of orientations and distances between the hydrogen atom and the center of mass of the LiH target system. The H–LiH system has been reduced to a system of only three electrons, those of valence, by replacing Li^+ ($1s^2$) by a pseudopotential. A large configuration interaction (CI) has been performed. The potential energy curves in terms of Jacobi coordinates $V(r_e = 3.014 \text{ a.u.}, R, \gamma)$, show the strong anisotropy of interaction potential. We note the presence of a double well for the angles around 11° . An analytical fitting of the potential energy surface has been realized in order to produce the long range interaction and to calculate the state-to-state rotational cross sections. © 2004 Elsevier B.V. All rights reserved.

Keywords: Configuration interaction; Potential energy surface; Anisotropy

1. Introduction

An additional attention has been given to Li, Li^+ , Li, LiH^+ and LiH systems due to their abundances in the interstellar medium. In one of the preliminary studies [1] on the abundances of LiH it was suggested that a large fraction of the primordial lithium might be incorporated into LiH. The consequences and effects of the presence of LiH in the early universe have therefore been explored by various works [2–4].

The LiH^+ and LiH species can be formed through radiative association, associative detachment or transfer reaction [5,6]. It is known that the relative abundance of LiH^+ is predicted to be 10% of that for neutral LiH for small redshift values, while becoming much smaller as the redshift increases.

The possibility of forming the LiH molecule in excited nuclear states is related to the efficiency of collisional transfers from the most abundant species in the interstellar

medium [7] and specially through collisions of LiH with H, H^+ , He and He^+ . That is, the evaluating of the interaction forces between LiH as a target and H as a projectile, and with a good accuracy, remain an important step for the calculation of excitation efficiency of that molecule at the temperature of relevance for the interstellar medium.

Many works have been done [8–10] to study the possibility of forming the LiH in excited rotational levels by collision with the He atom. Having an odd number of electrons, and presenting a strongly interacting system, the H–LiH presents a benchmark system for theoretical studies for both intermolecular potentials and collision energy transfer. To this aim the present work focuses on the accurate evaluation of the interaction forces.

The next section describes the ab initio calculation method used to evaluate the potential interaction between the hydrogen and the LiH molecule. On the other hand Section 3 reports the results of the calculation and analysis the interesting and unusual feature of the strong interaction and anisotropy of the potential. Finally we summarize by the conclusion.

* Corresponding author. Tel.: +216-73-500-276; fax: +216-73-500-278.
E-mail addresses: hamidberriche@yahoo.fr, hamid.berriche@fsm.rnu.tn (H. Berriche).

2. Theoretical method

In this work the Li atom is treated through a one electron pseudopotential proposed by Barthelat et al. [11] and used in many previous works [12–15]. In addition we account the core valence correlation by the use of the operatorial formulation of Müller, Flesh, and Meyer [16] where the core polarization potential is written:

$$V_{\text{CPP}} = -\frac{1}{2} \sum_{\lambda} \alpha_{\lambda} f_{\lambda} f \quad (1)$$

The summation runs over all the polarizable cores λ with a dipole polarizability α_{λ} . f_{λ} is the electric field created on center λ produced by valence electrons and all other cores, modified by a cutoff function F with an l -dependent adjustable parameter according to the formulation of Foucrault, Millie, and Daudey [17].

$$f_{\lambda} = \sum_i \frac{\vec{r}_{i\lambda}}{r_{i\lambda}} F(r_{i\lambda}, \rho_{\lambda}) - \sum_{\lambda' \neq \lambda} \frac{\vec{R}_{\lambda'\lambda}}{R_{\lambda'\lambda}^3} Z_{\lambda'} \quad (2)$$

Where $r_{i\lambda}$ is a core–electron vector and $R_{\lambda'\lambda}$ is a core–core vector. $F(r_{i\lambda}, \rho_{\lambda})$ is the cutoff operator, expressed following the Foucrault formalism

$$F(r_{i\lambda}, \rho_{\lambda}) = \begin{cases} 0, & r_{i\lambda} < \rho_{\lambda} \\ 1, & r_{i\lambda} > \rho_{\lambda} \end{cases} \quad (3)$$

which has a physical meaning of excluding the valence electrons from the core region for calculating the electric field. The cutoff radius is taken to be a function of l as following:

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} F_l(r_{i\lambda}, \rho_{\lambda}^l) |lm\lambda\rangle \langle lm\lambda|, \quad (4)$$

where $|lm\lambda\rangle$ is the spherical harmonic centered on λ . In Muller et al. formalism this cutoff function is unique for a given atom, generally adjusted to reproduce the first ionization potential. The cutoff radii (in bohr) used for the Li atom and for s, p, d, and f orbitals are, respectively, 1.434, 0.982, 0.6, and 0.4. We used for Li and H the same basis sets of gaussian-type orbitals (GTO's) as in our previous works [12–15]. The core dipole polarizability of Li is $0.1915 a_0^3$. The accuracy of this method and basis sets used in this work can be judged from the comparison of previous works on LiH, LiH^+ , LiNa^+ with numerous experimental and theoretical works. For these systems we produced exact potential energy in the basis set as we performed a full configuration interaction (CI) according to the number of electrons does not exceed two. For the LiH_2 system, a three active electrons CI are performed through the CIPSI [18] algorithm (CI by perturbation of a multiconfiguration wavefunction selected iteratively) corresponding to the standard chain of programs from Toulouse, involving single, double and triplet determinants.

3. Potential energy surfaces (PES)

3.1. Potential energy curves analysis

The potential energy curves, in terms of Jacobi coordinates $V(r_e = 3.014 \text{ a.u.}, R, \gamma)$, were carried out for 12 angles and a fixed distance for the LiH molecule corresponding to the equilibrium distance. The distance R is the separation between the H atom and the center-of-mass of the LiH molecule, and γ is the angle between R and the LiH internuclear axis.

Fig. 1 presents the potential energy curves of the H–LiH interactions for an angle γ lower than 90° . First, we notice that all these curves are attractive since they present minimums of lower energy relative to the asymptotic limit. The spectroscopic constants corresponding to: the equilibrium position (R_e), the depth of the well (D_e), and the asymptotic limit calculated at 200 a.u. are given by Table 1. Second, we remark that the equilibrium distance and the depth of the well depend on the angle γ showing the strong anisotropy of the system. These curves present some barriers between 5 and 7 a.u. We can explain the origin of such barriers through the charge distributions of Mulliken obtained in the SCF calculation level (see Fig. 2). We note that for R lower than 6 a.u., there is a transfer of charge between the three atoms, which allows us to conclude that in this region our system behaves as being three charges in

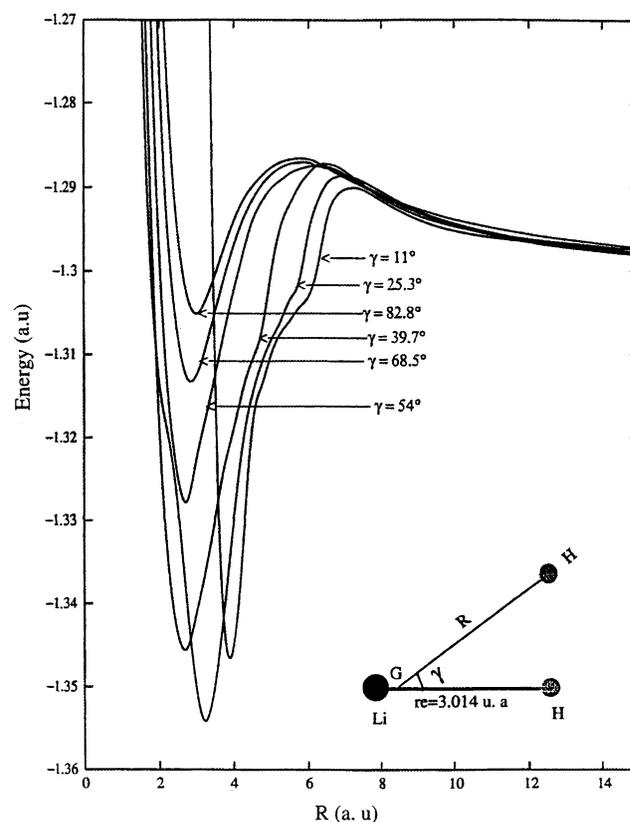


Fig. 1. Orientational features of the rigid-rotor potential energy surfaces for $\gamma < 90^\circ$.

Table 1
Equilibrium distance, well depth and dissociation energy limit for each orientation of the H–LiH interaction

γ	Re (a.u.)	De (cm ⁻¹)	V(R, γ) at R = 200 a.u.
11.0°	1.59	Repulsive	-1.299826
	3.9	10231	
25.3	3.23	11937	-1.299824
39.7	2.66	10101	-1.299825
54.0	2.67	6239	-1.299832
68.5	2.86	2939	-1.299832
82.8	2.98	1159	-1.299832
97.2	3.11	Repulsive	-1.299822
111.6	3.29	Repulsive	-1.299822
126.0	3.58	Repulsive	-1.299826
140.3	4.57	Repulsive	-1.299830
154.7	4.36	Repulsive	-1.299831
169.8	4.52	Repulsive	-1.299836

interaction. On the other hand, for R larger than 6 a.u. the system behaves as being a polar molecule, LiH, in interaction with a neutral atom.

Fig. 3 presents the potential energy curves for an angle γ higher than 90°. These last curves are repulsive and have unusual shape. For the small distances, the curves are repulsive. For the intermediate distances, the curves present minimums of energy that are unstable positions. From 6 to 8 a.u., we notice the apparition of the potential energy barriers that continues to decrease until the asymptotic limit.

When R reaches theoretically infinite value, the energy of the H–LiH is -1.288779 a.u. The results that we have obtained by the ab initio calculation at $R = 200$ a.u. for the different orientations differ from the theoretical one by less than 10^{-5} a.u.

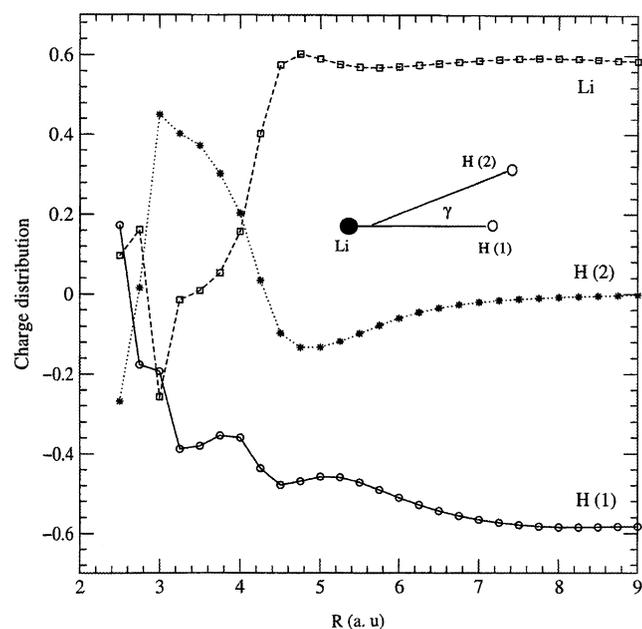


Fig. 2. Charge distribution on Li and H atoms as a function of R and for a fixed angle $\gamma = 25.3^\circ$.

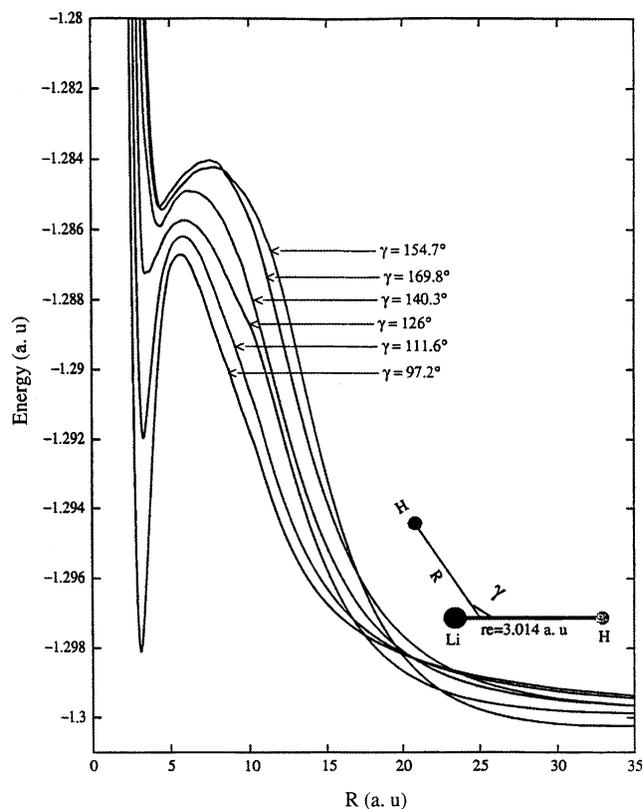


Fig. 3. Orientational features of the rigid-rotor potential energy surfaces for $\gamma > 90^\circ$.

The analysis of the potential energy surface shows that the geometry exhibiting the deepest well, except the colinear H–LiH system, is obtained for an orientation around $\gamma = 25^\circ$ with $D_e = 11937$ cm⁻¹ at $R_e = 3.23$ a.u. This large value of D_e shows the clear chemical nature of the bonding energy. From Fig. 2 we can understand the origin of the deep well. We remark that, at the equilibrium distance, negative charges are on the Li and H atoms (of the LiH target) and a positive charge on the H projectile. This leads to a formation of H₂ ionic system (H⁺H⁻), which minimize the energy at its maximum and explain the origin of the deepest well obtained for this angle.

In an earlier paper [19], that deals with the same problem, the authors have calculated the potential energy surfaces for the H–LiH interaction for 14 angles and a dense grid from 1 to 11.75 a.u. and for five intermolecular distances of the diatomic molecule between the turning points of $v = 4$ vibrational level. They have used the coupled cluster method where the two core electrons of the Li were fixed in the SCF molecular orbital and the correlation between the three valence electrons was considered by including all single, all double and triple excited configurations. In their Fig. 2 they report the potential for several fixed angles and for a fixed distance $r_e = 3.014$ a.u. which is the equilibrium distance of the LiH molecule. The figures were plotted between 0.5 and 4.0 Å. It seems that we obtain the same behaviour especially for the small angle where the potential

exhibits two minima one located near the target hydrogen atom corresponding to the formation of H_2 and the other one near the Li atom corresponding to the formation of the LiH molecule in which the H atom comes from the projectile. The two wells are located around 1.59 and 3.9 a.u. showing a very good agreement between the two works. The absolute minima of the surface was found to correspond to a geometry in which the approaching angle γ of the impinging H atom is around 20° and where the distance R is such that the distance between the two hydrogen atoms is around 1.4 a.u., which is the equilibrium distance of the H_2 molecule. Also we observe the presence of the cusp in the short-range region and for small angles. Our value for the difference between the energy of the absolute minima and the asymptotic energy of the dissociated system LiH (at r_e) + H is around 1.5 eV, which is lower than the value given in the work of Gianturco et al. [19] (2.068 eV).

3.2. The double well in the case of small angle

As shown in Fig. 4, the potential energy curve, obtained for $\gamma = 11^\circ$ presents two equilibrium positions. The first is unstable for $R = 1.59$ a.u. and the second is stable for $R = 3.93$ a.u. This can be explained by the fact that when we fix the angle γ around 11° and we vary the distance R , the variation of the R leads to two positions where

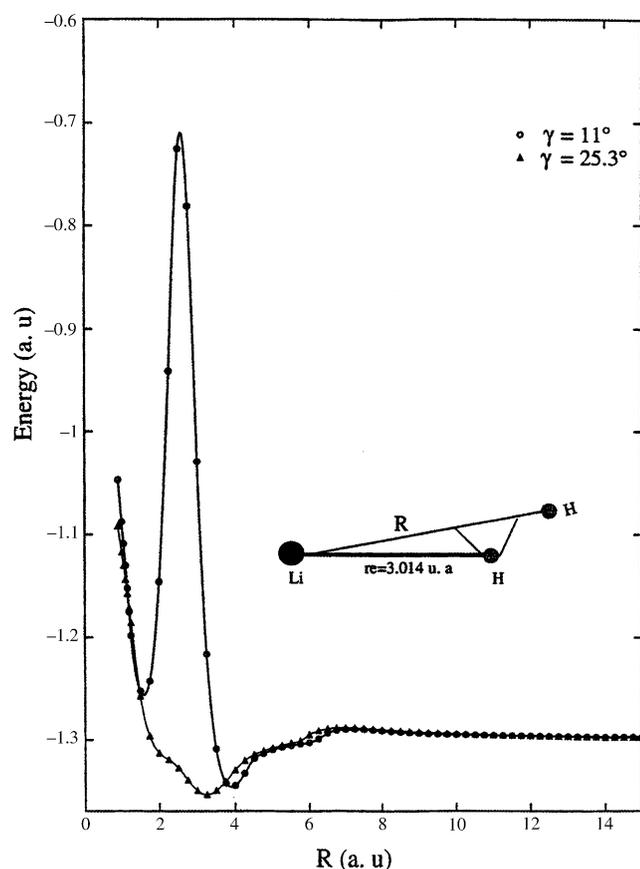


Fig. 4. The potential energy curve for $\gamma = 11^\circ$ and $\gamma = 25.3^\circ$.

the intermolecular distance between the two hydrogen atoms is around 1.40 a.u. which is the bonding distance of the H_2 molecule. The two positions of R are around two equilibrium distances ($R_e = 1.59$ and 3.93 a.u.). The second well is deeper than the first because of both the strong attraction between the hydrogen–hydrogen and hydrogen–lithium atoms (the equilibrium distance of LiH diatomic molecule is 3.014 a.u.). We note that when R varies between 1.59 and 3.90 a.u. the potential energy curve becomes very repulsive. This is due to the strong nuclear repulsion between the two hydrogen atoms. Furthermore, for very small angles (around $\gamma = 11^\circ$) the distance between the two hydrogen atoms becomes very short leading to a strong nuclear repulsion in the hamiltonian. In deed the cusp is localized in the region where the target hydrogen atom approaches directly the H side of the LiH molecule. The same behaviour was seen in the work of Gianturco et al. for the same angle and where the cusp for the angle $\gamma = 18^\circ$ was found to be less important and disappears for higher angles.

For $\gamma = 25.3^\circ$, we can get two positions for which the distance between the two hydrogen atoms equals 1.40 a.u. but the distance that separates the two positions is very small. Thus, we don't obtain a double well for this angle and also for higher orientations.

3.3. Asymptotic behavior and the analytical representation of the potential

At short distances (for $R < 2.25$ a.u.) and for all γ orientations the potential energy curves are repulsive, except for $\gamma = 11^\circ$ where the potential exhibits a well at shorter distance than 2.25 a.u. In This region, we interpolated them by the analytic form proposed by Heiler and London [20]:

$$V(R) = A e^{-BR} \quad (5)$$

Concerning the curve describing the interaction of $\gamma = 11^\circ$, this interpolation has been achieved for distances lower than the first minimum position ($R < 1.59$ a.u.). We notice that in the region $2.25 < R < 6$ a.u. there is an elementary transfer of charge between the three atoms. In fact this charge distribution can help us to understand the behavior of the potential energy curves. The corresponding well to $\gamma = 25.3^\circ$ is the deepest one. From this angle the well depth (D_e) decreases as well as γ increases. In fact the angle $\gamma = 25.3^\circ$ is a particular one, permitting a large contribution of the attraction between LiH and H_2 systems and minimizing (at its maximum) the energy of LiH₂. For the angle $\gamma = 11^\circ$, the contribution of LiH is more important than that of H_2 . From $R = 6$ a.u. we notice a stability in the distributions of the atomic charges. The Li is charged positively, the first atom of hydrogen is charged negatively whereas the second atom of hydrogen is neutral. In fact from this distance, we can model our system by an interaction between a dipole (Li^+H^-)

and a neutral hydrogen atom. Finally, at large distances, our system is equivalent to an interaction between a dipole and a neutral entity. Therefore, the contributions in this region are of electrostatic type, polarization and scattering. For a dynamic study, it is necessary to have an analytic form. Therefore, we interpolate the curves on a grid more dense and going beyond 200 a.u. Using the fact that in this region the types of strengths of interaction are of electrostatic, polarization and diffusion types, we express our potential following the analytical form

$$V(R, \gamma) = -\frac{C_3^{\text{el}}}{R^3} - \frac{C_4}{R^4} - \frac{C_6}{R^6} - \frac{C_8}{R^8} \quad (6)$$

We notice that the difference between the ab initio calculated points and the points found by the analytical expression varies between 10^{-4} and 10^{-6} a.u.

One of the standard indicators for the orientational anisotropy in the RR (rigid rotor) interactions, is given by the familiar multipolar expansion

$$V_{\text{RR}}(R, \gamma) = \sum_{\lambda=0}^{\lambda_{\text{max}}} V_{\lambda}^{\text{RR}}(R) P_{\lambda}(\cos \gamma) \quad (7)$$

Where R is the separation between the H atom and the center-of-mass of the LiH molecule, and γ is the angle between R and the LiH internuclear axis.

Furthermore, in the standard close-coupling formulation of atom–rigid rotor collisions, the determination of the required matrix elements of the potential is facilitated by the usual expansion in Legendre polynomials.

Fig. 5 imports $V_{\lambda}(R)$ the multipolar functions from $\lambda = 0$ to $\lambda = 11$. Most of the $V_{\lambda}(R)$ exhibit attractive wells,

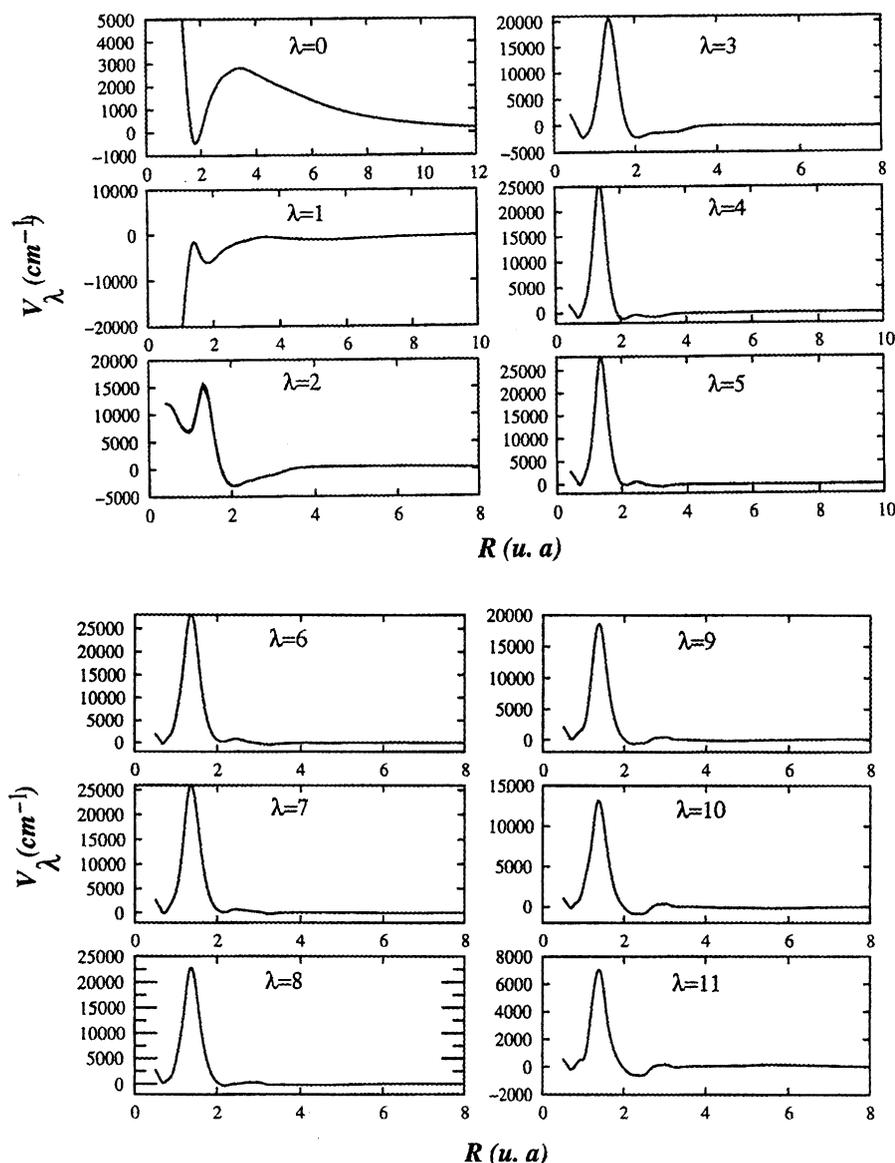


Fig. 5. Multipolar coefficients from Eq. (7) for $\lambda = 0 - 11$.

and present a particular feature similar to that of the potential energy curve associated to $\gamma = 11^\circ$. The V_2 has a similar feature to the potential energy curve associated to the angle $\gamma = 11^\circ$ with two minimums. The higher multipolar functions V_l present also two minimums separated by a higher barrier attending its maximum (more than 25000 cm^{-1}) for $\lambda = 6$. This last (V_6) presents the deepest well. Finally this particular behavior and especially for $\lambda = 1$, shows the strong anisotropy of the potential and the chemical ‘bonding’ nature of the interaction in H–LiH system. Our presented V_l are in very good agreement with the work of Gianturco et al. In both works the peak appears at a distance close to the r_e (the equilibrium distance of the LiH diatomic molecule) and the deep HH well is well described by the first few terms.

4. Conclusion

In this work we have evaluated and detailed the full potential energy surface of the LiH molecule (considered as a rigid rotor) interacting with the hydrogen atoms. We have used the pseudopotential techniques by replacing the lithium atom core Li^+ by a pseudopotential. The H–LiH system is reduced to only three electrons system making a possible large CI calculation. The potential energy surface is used to study the inelastic rotational collisional process and will be presented in the next paper. The highly polar nature of LiH molecule is seen to affect the orientational anisotropy of the RR potential energy. Thus the potential energy curves present unusual feature and exhibit deep wells at small intermolecular distance showing the chemical nature of the bonding energy. It seems that the deepest well is associated to the orientation $\gamma = 25.3^\circ$. We assume that this well is due to the double bonding interaction between H–H and H–Li. Both systems are very attractive. We have also discovered

that small orientation potential energy curves, in particular for $\gamma = 11^\circ$, exhibit two minima separated by a high barrier. Our potential energy surface is in very good agreement with the Gianturco et al. coupled cluster calculated surface. It will be used, first to calculate the state-to-state rotational cross section, and then generalized later for a full dynamic study.

References

- [1] S. Lepp, J.M. Shull, *Astrophys. J.* 280 (1984) 465.
- [2] F. Palla, E.E. Salpeter, S.W. Stahler, *Astrophys. J.* 271 (1983) 632.
- [3] R. Maoli, F. Melchiorri, D. Tosti, *Astrophys. J.* 424 (1994) 372.
- [4] P. De Bernardis, V. Dubrovich, P. Encrenaz, R. Maoli, S. Masi, G. Mastrantonio, B. Melchiorri, F. Melchiorri, M. Signore, P.E. Tanzilli, *Astron. Astrophys.* 269 (1993) 1.
- [5] F.A. Gianturco, G. Gori Giorgi, H. Berriche, F. X. Gadea, *Astron. Astrophys. Suppl. Ser.* 117 (1996) 377.
- [6] P.C. Stancil, S. Leep, A. Dalgarno, *Astrophys. J.* 458 (1996) 401.
- [7] W.V. Wagoner, W.A. Fowler, F. Hoyle, *Astrophys. J.* 148 (1967) 3.
- [8] F.A. Gianturco, S. Kumar, S.K. Pathak, M. Raimondi, M. Sironi, J. Gerratt, D.L. Cooper, *Chem. Phys.* 215 (1997) 227.
- [9] F.A. Gianturco, S. Kumar, S.K. Pathak, M. Raimondi, M. Sironi, *Chem. Phys.* 215 (1997) 239.
- [10] B.K. Taylor, R.J. Hinde, *J. Chem. Phys.* 111 (1999) 973.
- [11] Ph. Durand, J.C. Barthelat, *Theor. Chim. Acta* 38 (1975) 283. J.C. Barthelat, Ph. Durand, *Gazz. Chim. Ital.* 108 (1978) 225.
- [12] H. Berriche, Ph. D. Thesis from the Paul Sabatier University, 1995 (unpublished).
- [13] H. Berriche, F.X. Gadea, *Chem. Phys.* 191 (1995) 119.
- [14] M.B. El Hadj Rhouma, H. Berriche, Z.B. Lakhdar, F. Spiegelman, *J. Chem. Phys.* 116 (2002) 1839.
- [15] H. Berriche, *J. Mol. Struct.:Theochem* 663 (2003) 101.
- [16] W. Müller, J. Flesh, W. Meyer, *J. Chem. Phys.* 80 (1984) 3297.
- [17] M. Foucrault, Ph. Millié, J.P. Daudey, *J. Chem. Phys.* 96 (1992) 1257.
- [18] B. Huron, P. Rancurel, J.P. Malrieu, *Chem. Phys.* 58 (1973) 5475.
- [19] E. Bodo, F.A. Gianturco, R. Martinazzo, M. Raimondi, *Eur. Phys. J. D* 15 (2001) 321.
- [20] N. Heiler, F. London, *Z. Phys.* 44 (1927) 1346.