Structures of H$_2$ layers on LiF(001)

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Abstract

Perturbation theory calculations of the rotational motion of a hydrogen molecule rotates at the center of a $p$-type unit cell are reported. These calculations show that the molecular axis of H$_2$ is azimuthally delocalized and hence it can be tunneled into classical forbidden region where the structures are indeed "c" type rather than "p" type. Thus estimating the quantum effects of those species will change the monolayer configurations into c-type structures and hence match the recently reported Helium Atom Scattering (HAS) results.

Keywords: Hydrogen; Quantum effects; Potential energy surface; Rotational motion; LiF.

Introduction

The adsorption of hydrogen molecules on LiF(001) has been of interest for some time and has recently come under investigation using Helium Atom Scattering (HAS) technique \cite{1} and Monte Carlo (MC) simulations \cite{2}. Although one of the simplest adsorbate–substrate systems imaginable for the study of gas–solid interactions, it has the additional possibility of exhibiting quantum effects, owing to the light mass of the adsorbate. The HAS study found evidence of a sequence of phase transitions c(2×2)→c(8×2) in the H$_2$/LiF system with coverage increases from 0.5 to 0.625\cite{1}. This sequence was recently confirmed using the Metropolis Monte Carlo simulation method \cite{2} in which the simulations yield structures that are consistent with recent HAS results \cite{1} in terms of coverage and stability, but disagree in terms of symmetry; the HAS work found “c” type structures whereas the MC simulations (without quantum considerations) yield a “p” type structures. Note here for a centered square or rectangular unit cell (c-type structure), an atom, ion, or molecule should exist at the center of the unit cell where it has the same symmetry (orientation) and environment as those at the corners; otherwise we have a p-type structure. However, Perturbation theory calculations that applied to solve the discrepancy in molecules symmetries over the surface were limited to a single molecule without considering the intermolecular forces among these molecules in the layer. Actually molecular interaction potentials of

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hydrogen is approximately determined for its ground para \((J = 0)\) state, while there are no potentials for all other rotational \((J > 0)\) states \(^{[2-5]}\).

In this paper, Perturbation theory calculations of a \(\text{H}_2\) molecule rotating in the presence of other hydrogen molecules, in a \(p\)-type unit cell, are reported. These calculations study the conversion of \(p\)-type structure into \(c\)-type structure by examining the motion of the molecule at the centre of the unit cell which represents a stringent test to our interaction potential model that published recently \(^{[2]}\).

**Interaction Potential**

The interaction potential that adopted in this study was described in details elsewhere \(^{[2, 6]}\). Briefly, the interactions between \(\text{H}_2\) molecules can be divided into three parts: electrostatic, repulsion and dispersion contributions. The electrostatic interactions are well modeled by assigning point dipoles to the hydrogen atomic sites so that the interaction energy between molecules may be calculated as the sum of dipole-dipole interactions. The values of the dipoles are chosen so as to reproduce the molecular quadrupole moment \(^{[7]}\) of \(\text{H}_2\) \((\Theta = 0.6177 \text{ D.Å})\) and are summarized in Table (1).

**Table (1):** The electrostatic parameters model of the hydrogen molecule. The positions of the H atoms are given with respect to the molecular center of mass. The two point dipoles are directed along the \(\text{H}_2\) bond axis away from the center of mass. The quadrupole polarizability of \(\text{H}_2\) molecule \(^{[13]}\) is 0.711 Å\(^5\).

<table>
<thead>
<tr>
<th></th>
<th>(\text{H}_a) atom</th>
<th>(\text{H}_b) atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>position (Å)</td>
<td>0.37</td>
<td>-0.37</td>
</tr>
<tr>
<td>point dipole (D)</td>
<td>0.4174</td>
<td>-0.4174</td>
</tr>
<tr>
<td>atomic polarizability (\perp) (Å(^3))</td>
<td>0.3504</td>
<td>0.3504</td>
</tr>
<tr>
<td>atomic polarizability (\parallel) (Å(^3))</td>
<td>0.5018</td>
<td>0.5018</td>
</tr>
</tbody>
</table>

Classical pair potentials were applied to model the repulsion-dispersion interaction between the hydrogen atomic sites on different molecules within the layer using the Buckingham formula, \(U(r) = A \exp(-\beta \cdot r) - C_6 / r^6\), where \(r\) is the internuclear distance between hydrogen atoms, \(C_6\) is the London dispersion coefficient, and the parameters \(A\), and \(\beta\), characterize the strength and inverse range of the repulsion interaction. The values of these parameters are taken from Ref. 2.

The interaction between a hydrogen molecule and the ions of the surface is calculated as a sum of classical electrostatic interactions, plus contributions arising from repulsion and dispersion interactions. Using the electrostatic model of a hydrogen molecule described above, the two point dipoles \(\vec{\mu}_i\), located on atomic H sites at
positions \( r_i \), will interact with the electric field \( \vec{E}(r_i) \) generated at the surface by the substrate. Furthermore, this electric field will also interact with dipole moments induced on the atomic sites of the molecules by the electric field itself. The electrostatic plus induction interaction energy between a hydrogen molecule and the substrate may be calculated using the following formula,

\[
V_{\text{elec}}^{\text{int}} = \sum_{i=1}^{2} \left( -\vec{E}(r_i) \cdot \vec{\mu}_i - \frac{1}{2} \alpha_i^\perp \vec{E}_i^2(r_i) - \frac{1}{2} \alpha_i^\parallel \vec{E}_i^2(r_i) \right) \quad (1)
\]

where the sum is over the two atomic sites of hydrogen molecule and the induction energy is proportional to the atomic polarizabilities perpendicular \( \alpha_i^\perp \) and parallel \( \alpha_i^\parallel \) to the molecular axis. The values for the dipoles and polarizabilities are listed in Table (1).

The short range repulsion as well as the long range dispersion interactions have been calculated as a pair-wise two body summation of the interaction between the atoms of the \( \text{H}_2 \) molecules and the ions of the surface using the Tang-Toennies potential formula \[8\],

\[
V_{\text{vdW}}^{\text{int}}(r_{ij}) = A_{ij} \cdot \exp(-\beta_{ij} \cdot r_{ij}) - \sum_{n=3}^{5} \left( f_{2n}(r_{ij}) \frac{C_{2n}^{ij}}{(r_{ij})^{2n}} \right) \quad (2)
\]

where, \( A_{ij} \) and \( \beta_{ij} \) are the Born-Mayer parameters, and the \( C_{2n}^{ij} \) dispersion coefficients represent the strength of mutually induced attractive forces due to electron correlations. The \( f_{2n}(r_{ij}) \) are damping functions are given by;

\[
f_{2n}(r_{ij}) = 1 - \left[ \sum_{k=0}^{2n} \frac{(\beta_{ij} \cdot r_{ij})^k}{k!} \right] \cdot \exp(-\beta_{ij} \cdot r_{ij}) \quad (3)
\]

The parameters and coefficients that characterize the interaction potential between the surface and the \( \text{H}_2 \) molecules are also taken from Ref. 2. This potential was recently applied and yielded a reasonable description of the adsorption potential of molecular \( \text{H}_2 \) on \( \text{LiF}(001) \) \[2\].

**Rotational State Calculations**

Monte Carlo (MC) simulations results of \( \text{H}_2 \) molecules adsorbed on a \( \text{LiF}(001) \) surface have shown that a series of commensurate structure of \( p(n \times 2) \) type are exist, in disagreement with the recent HAS findings. Quantum mechanical delocalization of the hydrogen molecules’ axes will change the symmetry of the ad-layer structure from \( p(n \times 2) \) to \( c(n \times 2) \). Therefore, the nature of the rotational state of an adsorbed hydrogen molecule rotating in the plane of the layer was investigated to see if delocalization would occur. For simplicity the creation of the interaction potential of a rotating
hydrogen molecule, described as a rigid rotor, in the presence of the surface electric field and other hydrogen molecules located at the corner of the \( p(2\times2) \) unit cell is performed.

Our calculations use perturbation theory applied to the time independent Schrödinger equation for a rigid rotor. The Hamiltonian, \( \hat{\mathcal{H}} = \hat{\mathcal{H}}^0 + \hat{\mathcal{H}}^1 \), which describes the motion of the molecular axis near the surface and in the plane of the layer has the form:

\[
\hat{\mathcal{H}} = \frac{-\hbar^2}{2\cdot I} \frac{\partial^2}{\partial \varphi^2} + V(\varphi)
\]

where, \( I \) is the moment of inertia of \( \text{H}_2 \) molecule and is given by \( \mu \cdot r^2 \) (\( \mu \) is the reduced mass of the \( \text{H}_2 \) molecule with a value of \( 8.368 \times 10^{-28} \) kg, and \( r \) is its bond length, which has a value of 0.74 Å \[9\]). The first and second terms in equation 4 represent the unperturbed Hamiltonian of an \( \text{H}_2 \) molecule rotating freely in a plane, and the perturbed Hamiltonian operator respectively.

The Schrödinger equation describing the rotational motion of the central molecular \( \text{H}_2 \) in a \( p(2\times2) \) unit cell can be written as:

\[
\left( -\frac{\hbar^2}{2\cdot I} \frac{\partial^2}{\partial \varphi^2} + V(\varphi) \right) \psi_n = E_n \psi_n
\]

where, \( \psi_n \) is the rotational wave function of \( \text{H}_2 \). If the perturbation term is set to zero the wave function is given by: \( \psi_n = \frac{1}{\sqrt{2\cdot \pi}} \exp(in\varphi) \) and characterized by a quantum number \( n=0, \pm 1, \pm 2 \ldots \) whose sign designates the direction of rotation. \( E_n \) is the rotational energy of \( \text{H}_2 \) molecule in state \( n \).

By applying the time-independent Perturbation Theory (PT) technique to the second order correction level for a rotating adsorbed \( \text{H}_2 \), the azimuthal rotational energy \( E_n \) can be calculated using the formula below,

\[
E_n = \langle \psi_n | \hat{\mathcal{H}} | \psi_n \rangle + \langle \psi_n | \hat{\mathcal{H}} | \psi_n \rangle + \sum_{i \neq n} \frac{|\langle \psi_n | \hat{\mathcal{H}} | \psi_i \rangle|^2}{E_n^o - E_i^o} \tag{6}
\]

The probability density \( \psi_0^* \cdot \psi_0 \) was calculated by determining the corrected ground rotational wave function of the adsorbed \( \text{H}_2 \) molecule using the PT technique (second order correction) and orthonormal condition. The ground state wave function may be calculated using the following formula \[10\],
where,

\[ \psi_{n=0} \approx \psi_{n=0}^{(0)} + \psi_{n=0}^{(1)} + \psi_{n=0}^{(2)} \]

(7)

\[ \psi_{n=0}^{(0)} = \frac{1}{\sqrt{2 \pi}} \cdot \exp(i n \varphi) \]

\[ \psi_{n=0}^{(1)} = \sum_{m \neq n} \left\langle \psi_{m}^{(o)} \right| \hat{H} \left| \psi_{n}^{(o)} \right\rangle \cdot \psi_{m}^{(o)} \]

\[ \psi_{n=0}^{(2)} = \sum_{k \neq n} \left[ \sum_{m \neq n} \left\langle \psi_{k}^{(o)} \right| \hat{H} \left| \psi_{n}^{(o)} \right\rangle \cdot \left\langle \psi_{m}^{(o)} \right| \hat{H} \left| \psi_{n}^{(o)} \right\rangle \right] \cdot \psi_{k}^{(o)} - \frac{1}{2} \sum_{m \neq n} \left\langle \psi_{m}^{(o)} \right| \hat{H} \left| \psi_{n}^{(o)} \right\rangle \cdot \psi_{m}^{(o)} \]

(8)

The Rotational Potential

Classically, it was found from the MC simulations that H\(_2\) molecules in its ground rotational state adopt \(p(2 \times 2)\) structure, but this is in disagreement with experiment results \([1]\). To examine the influence of the rotational motion of a layer of adsorbed H\(_2\) molecules on their configurations, a \(p(2 \times 2)\) configuration generated by the MC simulation was selected to perform PT calculations on a set of molecules in a \(p(2 \times 2)\) unit cell. As shown in Figure 2, the unit cell of the \(p(2 \times 2)\) structure contains two molecules aligned mutually perpendicular to each other in a tee configuration. We assume that the rotation of one of the molecules will allow us to compare the experimentally proposed \(c(2 \times 2)\) structure with the \(p(2 \times 2)\) structure from our MC simulation that published recently \([2]\). The molecules at the four corners of the unit cell are kept fixed with \(\varphi = 135^\circ\) while the molecule at the center of the unit cell is rotated freely in the plane of the \(p(2 \times 2)\) unit cell, where the azimuthal orientation \(\varphi\) of the H—H bond with respect to the x-axis was allowed to vary in the xy-plane* (see Figures 1 and 2). In this way, the rotational potential of the central molecule was generated and plotted as a function of \(\varphi\) as shown in Figure (3). It has two global minima at \(\varphi = 45^\circ\), and \(225^\circ\) where the two molecules form a \(p(2 \times 2)\) structure and two local minima at \(\varphi = 135^\circ\), and \(315^\circ\) where the two molecules form a \(c(2 \times 2)\) structure. This rotational potential was described exactly using the following formula,

\[ V(\varphi) = A_0 + A_1 \cdot \cos(4 \cdot \varphi) + A_2 \cdot \sin(2 \cdot \varphi) \]

(8)

* For \(p(2 \times 2)\) structure all the molecules lay flat \((\theta = 90^\circ)\) over Li\(^+\) site.
Figure (1): Schematic diagram of a $\text{H}_2$ molecule locates over LiF surface, where the mass center of $\text{H}_2$ (H atoms represented by gray solid circle) is on the top of F\textsuperscript{-} site. The molecular orientation with respect to the surface normal is given by $\theta$, the bond length is given by $r$, and the azimuthal orientation of the H—H bond with respect to the x-axis is given by $\phi$.

Figure (2): A schematic diagram represents the rotational motion of the central $\text{H}_2$ molecule in a $p(2\times2)$ unit cell. This kind of motion is restricted to the plane parallel to LiF(001) surface. Once, the molecule rotates (represented by gray circles) a 90° or 270° from its initial position, all the molecules arranged in a unit cell of $c(2\times2)$ symmetry.
The rotational potential described by equation (8) reflects the four-fold symmetry of the surface and the interaction between molecules within the unit cell. The values of the coefficients may be determined by fitting the above function to the potential energy of a hydrogen molecule rotating in a $p(2\times2)$ unit cell at the surface. The potential energy was calculated by fixing the molecular centre of mass at an equilibrium height of 2.82 Å directly above Li$^+$ sites, and rotating the molecule by increments of $5^\circ$ through all possible values of the azimuthal angle $\varphi$. Using a least squares fit program from MAPLE V.7 (Waterloo, Maple Inc., Maple Handbook (Maple V, release 4, 1996)), the coefficients were determined and are found to be $A_o = -0.7605$ kcal/mol, $A_1 = 0.0246$ kcal/mol, and $A_2 = -0.0312$ kcal/mol.

In order to include the quantum effect of these light molecules, we apply the time-independent perturbation theory method as described previously. The rotational potential is treated as a perturbing Hamiltonian ($\hat{H}'$) that includes the influence of the surface electric field as well as the interactions with the neighboring molecules on the motion of the central hydrogen molecule. Using equation (6), it is found that the rotational energy levels can be calculated using the following equation:

$$E_{n>0} = \frac{n^2 \cdot \hbar^2}{2 \cdot I} + A_o - \frac{I \cdot A_0^2}{16 \cdot \hbar^2} \cdot \frac{1}{n+2} - \frac{I \cdot A_1^2}{8 \cdot \hbar^2} \cdot \frac{1}{n+1}$$ (9)

The rotational energies for the first two levels ($n= 0, 1$) were calculated and presented in Table 2. By comparing these energies with the rotational potential, it was found that H$_2$ molecule in its ground state ($n= 0$) is close to the top of the rotational barrier and has a high probability of penetrating the barrier. On the other hand, H$_2$ in its first rotational state ($n=1$) is freely rotating because its rotational energy lies above the maximum of rotational potential curve (see Figure 3). If all molecules are free to rotate they are all azimuthally delocalised and hence there is no differences in molecular orientation from site to site. In this case the $p(2\times2)$ structure converts to a $c(2\times2)$ structure.

**Table (2):** Rotational energy levels of an adsorbed H$_2$ molecule, rotates at the center of $p(2\times2)$ unit cell, calculated by using PT second order correction level. The values are in Kcal/mol unit.

<table>
<thead>
<tr>
<th>Rotational state</th>
<th>$E_n$ (No molecular interaction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n = 0$</td>
<td>-0.761</td>
</tr>
<tr>
<td>$n = 1$</td>
<td>-0.586</td>
</tr>
<tr>
<td></td>
<td>-0.663</td>
</tr>
<tr>
<td></td>
<td>-0.489</td>
</tr>
</tbody>
</table>
In the case of $n=0$ rotational level, it is necessary to calculate the rotational ground state distribution to determine whether a similar situation holds. Calculating the quantum probability function of $H_2$ in its rotational ground state, $\psi_0^* \cdot \psi_0$, solves this issue, and predicts that $H_2$ in its ground state is azimuthally delocalized as described below.

The corrected wave functions to the second order level have been calculated, according to PT, using equation (7). The contributions to the perturbed ground state wave function up to second order are:

$$
\psi_{n=0}^{(0)} = \frac{1}{\sqrt{2 \cdot \pi}}
$$

$$
\psi_{n=0}^{(1)} = -\frac{1}{\sqrt{2 \cdot \pi}} \left[ \frac{I \cdot A_1 \cdot \pi^2}{2 \cdot h^2} \cdot \cos(4 \cdot \phi) + \frac{2 \cdot A_2 \cdot I \cdot \pi^2}{h^2} \cdot \sin(2 \cdot \phi) \right]
$$

$$
\psi_{n=0}^{(2)} = \frac{1}{\sqrt{2 \cdot \pi}} \left( \frac{A_1^2 \cdot I^2 \cdot \pi^4}{32 \cdot h^4} \cdot \cos(8 \cdot \phi) + \frac{5 \cdot A_1 \cdot A_2 \cdot I^2 \cdot \pi^4}{18 \cdot h^4} \cdot \sin(6 \cdot \phi) - \frac{(A_1^2 + 8 \cdot A_2^2) \cdot I^2 \cdot \pi^4}{16 \cdot h^4} \cdot \cos(4 \cdot \phi) - \frac{5 \cdot A_1 \cdot A_2 \cdot I^2 \cdot \pi^4}{2 \cdot h^4} \cdot \sin(2 \cdot \phi) + \frac{A_2^2 \cdot I^2 \cdot \pi^4}{h^4} \cdot \cos(2 \cdot \phi) \right)
$$
By substituting the values of these terms into equation (7), the perturbed rotational wave function of hydrogen molecule in its ground state (n=0) may be written as follows,

\[
\psi_{n=0} \approx \frac{1}{\sqrt{2\pi}} (1-1.1311 \times 10^{-3} \cdot \cos(4\cdot \varphi) + 4.4798 \times 10^{-2} \cdot \sin(2\cdot \varphi) + 9.705 \times 10^{-8} \cdot \cos(8\cdot \varphi) \\
-1.0941 \times 10^{-5} \cdot \sin(6\cdot \varphi) + 4.9953 \times 10^{-4} \cdot \cos(2\cdot \varphi))
\]

The quantum probability density has been calculated and plotted as a function of \(\varphi\) as shown in Figure 4. It was found that on average: the probability of finding the H\(_2\) molecule at all angles equal 0.159 which indicates that hydrogen molecule is largely azimuthally delocalized. There is a small residual preference for an orientation in the \(\varphi = 45^\circ\) and \(225^\circ\) directions. However, if the molecules at the corners of the unit cell are averaged over the same orientational distribution as the central molecule then one would expect a fourfold azimuthal distribution as in the case of a single molecule \([2]\). Consequently, the hydrogen molecules, in state n=0, of \(p(2 \times 2)\) layer actually forms a \(c(2 \times 2)\) structure. The same argument may be used in the n=1 case to ensure that residual azimuthal preferences have the four-fold symmetry required by the \(c(2 \times 2)\) structure. These calculations show that the MC simulations are consistent with the HAS experimental results \([2]\).

![Figure (4): The probability density, \(\Psi_0^* \cdot \Psi_0\), as a function of azimuthal angle (\(\varphi\)) for a single H\(_2\) molecule rotates at the center of the unit cell of \(p(2 \times 2)\) layer over the LiF(001) surface.](image)

The reported plots of the monolayer configurations implicitly showed the orientation of the hydrogen molecules axes by representing the molecule as two circles
centered on each of the hydrogen atoms \[^2\]. The quantum calculations show that the axes are azimuthally delocalized and so the molecules are freely rotating in the plane of the layer. Thus, the hydrogen molecule could alternatively be represented by a single circle centered on the molecular centre of mass. As a result, the hydrogen molecules are arranged in a \( c(n \times 2) \) structure as shown in Figure 5. In all cases, the unit cells are obviously \( c \)-type.

![Figure 5](image-url)

**Figure (5):** The LiF(001) surface covered with 160 \( H_2 \) molecules. The (+) symbol represents a \( Li^+ \) ion and the (-) symbol represents a \( F^- \) ion. The hydrogen molecules that lie over \( Li^+ \) sites are shown as light gray circles; while for \( H_2 \) molecules whose center of mass lies between the cationic \( Li^+ \) and the anionic \( F^- \) sites represent as gray circles. The \( c(n \times 2) \) unit cells are shown in solid lines.

For a single hydrogen molecule rotating azimuthally on the surface at the top of \( Li^+ \) cationic site, the rotational potential was exactly represented using the form,\[ V(\varphi) = A_o + A_1 \cdot \cos(4 \cdot \varphi) , \]where \( A_o = -0.6634 \) kcal/mol, and \( A_1 = 0.0063 \) kcal/mol.

Using eq. 6, the perturbation theory treatment yields the rotational energy levels, namely
\[ E_{n>0} = \frac{n^2 \cdot \hbar^2}{2 \cdot I} + A_o - \frac{I \cdot A^2_1}{16 \cdot \hbar^2} \cdot \frac{1}{n + 2} \] \[ (10) \]
The values of the rotational energies for the first two levels are calculated using the above formula and are listed in Table (2). The energy of a hydrogen molecule rotating on the center of a \( p(2 \times 2) \) unit cell is greater than that of a single molecule on the surface owing to the net attraction between molecules within the layer.

**Conclusions**

Our perturbation theory calculations of rotational states of a hydrogen molecule in a monolayer shows that the structure conversion of \( p(n \times 2) \) to \( c(n \times 2) \) symmetries is indeed possible; in particular, quantum mechanical delocalization of the hydrogen molecular axes eliminates azimuthal differences between molecules in the layer and hence those molecules exhibit a cylindrical distribution from site to site in a unit cell of \( c(n \times 2) \) structure.

PT calculations show that the intermolecular forces between hydrogen molecules in adsorbed phase is weak and has little effects on their rotational states as compared with PT calculations of a single molecule over the surface \(^2\). Therefore, those calculations support the previous MC simulation results and match completely the HAS findings. It is worthwhile to mention here that interaction potential of \( \text{H}_2 \) molecules in different rotational states is not known, since these molecules in adsorbed phase represent a model of quantum solid where the molecules localized at their lattice sites but freely rotating even at 0 K \(^{11, 12}\). This represents a big problem to do the simulation in a complete way and unfortunately, path-integral MC of those quantum species is very expensive calculations and also limited to a few molecules. Hopefully, in the near future we will find a way to determine a practical quantum potential of those species and reapply it to those kinds of systems.

**Acknowledgments**

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**References**

[1] Private communication with Toennies J. P. and Treager F.