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Pressure-induced behaviours of 2p energy levels of lithium in a H₂ crystal field

Y M Ma, T Cui and G T Zou

National Laboratory of Superhard Materials, Jilin University, Chanchun 130023, China

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Abstract

Pressure-induced behaviours of 2p energy levels of lithium in solid H₂ are investigated by using the path integral Monte Carlo method with a constant-pressure ensemble (*NPT*). For the doped solid where a Li atom replaces one H₂ molecule, the splittings between the three degenerate energy levels of the Li atomic 2p excited state are equal. For the doped solid where a Li atom replaces two H₂ molecules, a novel different split of the three 2p energy levels is observed. An increase in pressure results in a significant shift of the individual 2p energy levels of the Li atom. The centroid of the 2p energy levels takes on a fascinating pressure dependence in which, with increasing pressure, the centroid of the 2p energy levels shifts towards higher energy below a turning pressure (P_t), arrives at the highest energy at P_t , then shifts towards lower energy above P_t .

1. Introduction

The addition of a small content of light atoms, such as lithium, to solid hydrogen is believed to improve its chemical performance as a propellant for rocket propulsion [1]. Investigation of this issue is also motivated by its potential scientific importance in explaining how the energetic species respond to cryogenic environments. The absorption spectrum of Li doped into molecular H₂ at zero pressure has been studied both experimentally and theoretically [2–4]. Recently, the pressure-induced behaviours of the system of Li in solid H₂ have been extensively investigated by using path integral Monte Carlo (PIMC) calculations [5].

However, to our knowledge, the pressure-induced behaviours of the energy levels of lithium in solid H₂ have never been reported. It is of interest physically to understand how the energy levels of Li in solid H₂ respond to pressure.

2. Path integral Monte Carlo calculations

96 H₂ molecules are placed at the ideal hcp lattice sites initially. The simulated cell is determined by two basis vectors (*a* and *b*) forming a 60° angle and the third one (*c*)

perpendicular to both \mathbf{a} and \mathbf{b} . The Li dopant is introduced into the simulation cell by replacing n_v nearest-neighbour H_2 molecules, and leaving only $N - n_v$ H_2 molecules in the simulation cell. At the start of the simulation, the lithium atom is placed at a reference ‘site’:

$$S_{\text{Li}} = \sum_{i=1}^{n_v} S_i / n_v$$

where i runs over the lattice sites of the replaced H_2 molecules. The trapping sites $n_v = 1$ and 2 are studied in this calculation. In order to minimize surface and finite-size errors, periodic boundary conditions are used in all three spatial dimensions. The interactions are evaluated making use of the periodicity and the ‘minimum image’ method [6], and the cut-off length is chosen to be equal to half of the shortest simulation cell side. A cut-off correction to the potential energy is performed by assuming that beyond the cut-off length the solid is a continuous and uniform medium.

The Metropolis scheme for the NPT ensemble is implemented by generating a Markov chain of states which has a limiting distribution proportional to [6]

$$\exp(-\beta PV - \beta E(s) + (N - n_v + 1) \ln V). \quad (1)$$

The number of ‘beads’ of the path integral is chosen as 50 at $T = 5$ K in this calculation. Each Monte Carlo step consists of an attempted Metropolis move for every bead, with the i th particle move incurring random displacement of R_i . To enhance sampling efficiency, the whole path for each particle also undergoes a random displacement at each MC step: i.e., every bead of the path is moved in the same way with identical values of ΔR . This corresponds to a simplified multilevel sampling [7]. One Metropolis move of the simulation cell is attempted every ten MC steps during the simulation. About 1500 MC steps are required for equilibration. After equilibration, statistical averages are collected every two steps.

The semiclassical line shape for electronic transitions in a condensed phase system is given as follows, as derived by Lax [8] using the semiclassical Franck–Condon principle:

$$I(\omega) \propto \int |M_{fi}(Q)|^2 P_i(Q) \delta(\Delta E(Q) - \hbar\omega), \quad (2)$$

with

$$\Delta E(Q) = E_f(Q) - E_i(Q), \quad (3)$$

where: $M_{fi}(Q)$ is the electronic transition dipole moment connecting the initial state i and the final state f ; $P_i(Q)$ is the quantum statistical mechanical thermal probability distribution for the initial electronic state; $E_i(Q)$ and $E_f(Q)$ are the energies of the system at configuration Q in the initial and final electronic states, respectively. For more details on the $E_i(Q)$ and $E_f(Q)$, see [9]. A finite-energy bin width is used instead of a delta function to calculate the absorption spectrum of a Li atom doped into solid hydrogen.

The Hemley-corrected SG [10, 11] potential was used to represent the intermolecular interaction between two matrix molecules, while the Cheng potential [4], through a fitting to new *ab initio* data for the Li/ H_2 system [12], was used for the Li– H_2 pair interaction potentials with the Li atom in both ground and excited states in this calculation.

A Li atom experiences a spherically averaged potential in both ground and excited states, deriving from the isotropic H_2 matrix, and the spherical average over all configurations can be represented by a radial correlation function, so the centroid shift of the whole 2p energy level relative to the 2s energy level of the Li atom can be obtained approximately from [4]

$$\hbar\omega_{\text{shift}} = 4\pi\rho \int_0^\infty R^2 g_{\text{Li-H}_2}(R) V_{\text{shift}}(R) dR. \quad (4)$$

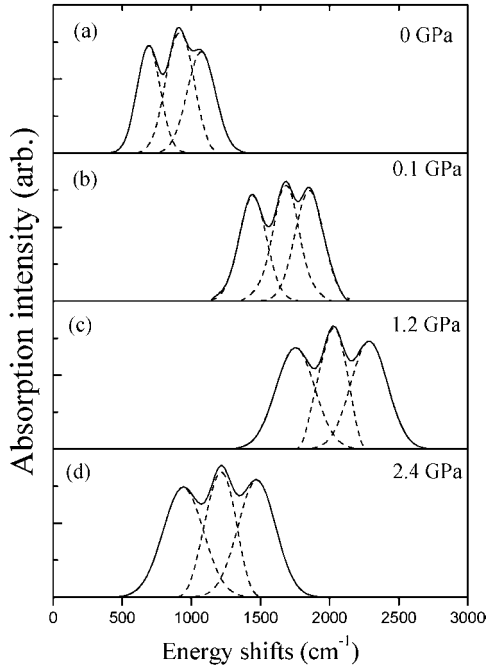


Figure 1. The Li absorption spectra where a Li atom replaces one H₂ molecule in solid H₂ with a hcp lattice at $T = 5$ K and 0.02 (a), 0.1 (b), 1.2 (c), and 2.4 GPa (d); the dashed curves are the individual underlying components.

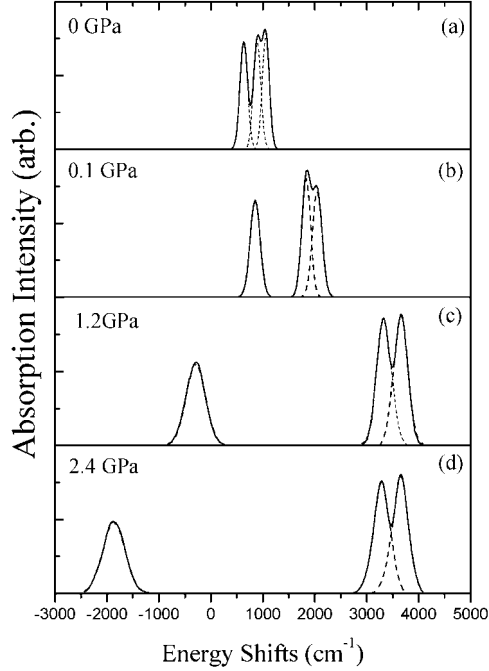


Figure 2. The Li absorption spectra where a Li atom replaces two H₂ molecules in solid H₂ with a hcp lattice at $T = 5$ K and 0.02 (a), 0.1 (b), 1.2 (c), and 2.4 GPa (d); the dashed curves are the individual underlying components.

Here $g_{\text{Li-H}_2}(R)$ is the pair distribution function for the Li atom and H₂ molecules, which is normalized according to $4\pi\rho \int_0^\infty R^2 g_{\text{Li-H}_2}(R) dR = 1$. $V_{\text{shift}}(R)$ takes the form

$$V_{\text{shift}}(R) = \frac{1}{3}[V_{B\Sigma}(R) + 2V_{A\Pi}(R)] - V_{X\Sigma}(R). \quad (5)$$

Here, $V_{X\Sigma}(R)$ is the ground state Li-H₂ pair interaction; $V_{B\Sigma}(R)$ and $V_{A\Pi}(R)$ are the excited state Li-H₂ pair potentials [4].

3. Results and discussion

Figure 1 shows the absorption spectra of the Li/H₂ doped solid for $n_v = 1$ [5]. The spectrum for a given pressure shows a high-symmetry triplet absorption pattern. The differences in spectral line shape at different pressures are negligible except for an increase in the spectral half-width with increasing pressure. The Li atomic trapping site structure belonging to a higher-symmetry point group, D_{6h} , at different pressures in the doped solid dominates these behaviours [5].

Figure 3(a) shows a schematic representation of the centroid shifts of the three individual energy levels for the 2p excited state of Li in solid H₂ with pressure, obtained by analysing the calculated absorption spectra shown in figure 1. The perturbation of H₂ molecules around the Li atom results in the degenerate energy levels of the 2p excited state of the Li atom splitting into three individual energy levels, $2p_{-1}$, $2p_0$, and $2p_1$, at zero pressure. For the $n_v = 1$ doped solid, the local structure around the dopant belongs to a higher-symmetry point group, D_{6h} . Therefore, the dopant is in a locally higher-symmetry crystal field from H₂ molecules. The higher-symmetry crystal field around the dopant acts equally on the three energy levels $2p_{-1}$,

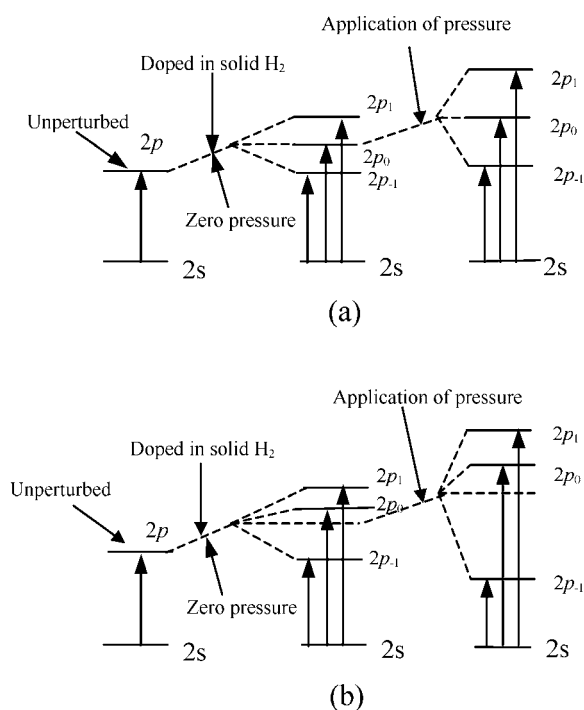


Figure 3. A schematic representation of the centroid shifts of the energy levels for the 2p excited state relative to the 2s state of Li in solid H₂ with pressure. (a) is for the higher-symmetry trapping site ($n_v = 1$); (b) is for the lower-symmetry trapping site ($n_v = 2$).

$2p_0$, and $2p_1$ for the 2p excited state of the Li atom, resulting in the three 2p energy levels splitting equally. With increasing pressure, the action of the crystal field on the three energy levels for the 2p excited state of the Li atom increases, resulting in an increase in the equal splittings between the three energy levels. These features contribute to the pressure dependence of the absorption spectrum as shown in figure 1. Also, with increasing pressure, a significant shift of the individual 2p energy levels is observed, as plotted in figure 4(a). The centroid of the whole 2p energy level calculated from equation (4) takes on a fascinating pressure dependence, in which the centroid of the whole 2p energy level shifts to higher energies below a turning pressure P_t (around 0.6 GPa corresponding to a 2116 cm^{-1} energy shift), arrives at the highest energy at P_t , then shifts towards lower energies above P_t , as shown in figure 5.

The absorption spectra of Li atoms in solid H₂ for $n_v = 2$ at $T = 5 \text{ K}$ and different pressures are presented in figure 2 [5]. One observes that the spectrum at zero pressure shows a triplet feature in which there is a large separation between the first and the second peak. As the pressure gets larger, the triplet is split into a singlet plus a doublet pattern. For this case, the trapping site structure around the dopant belonging to a lower-symmetry point group, C_2 , is responsible for the behaviours of the absorption spectrum under different pressures [5].

A schematic representation of the centroid shifts of the three individual energy levels for the 2p excited state of Li in solid H₂ with pressure obtained by analysing the calculated absorption spectra shown in figure 2 is presented in figure 3(b). For the $n_v = 2$ doped solid, the local structure around the dopant belongs to a lower-symmetry point group, C_2 . Therefore, the Li atom is in a lower-symmetry crystal field, in which there is a strongly preferred direction: along the asymmetrical axis of the trapping site structures. In this case, the strongly preferred

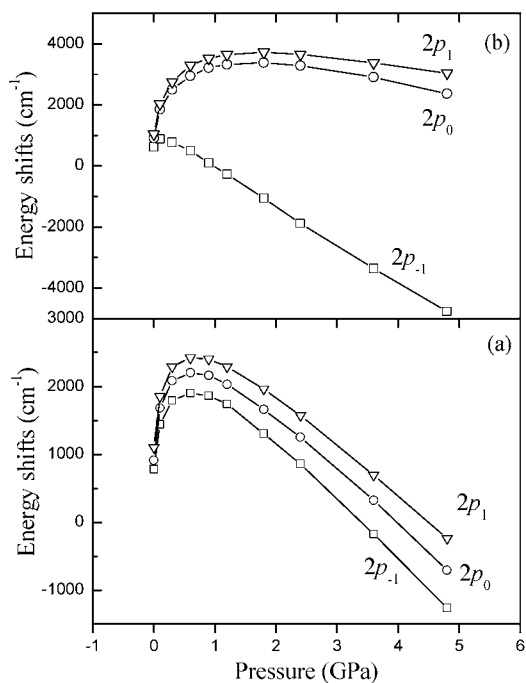


Figure 4. The pressure dependences of the centroid of the three individual 2p energy levels of Li in solid H₂ for $n_v = 1$ (a) and 2 (b).

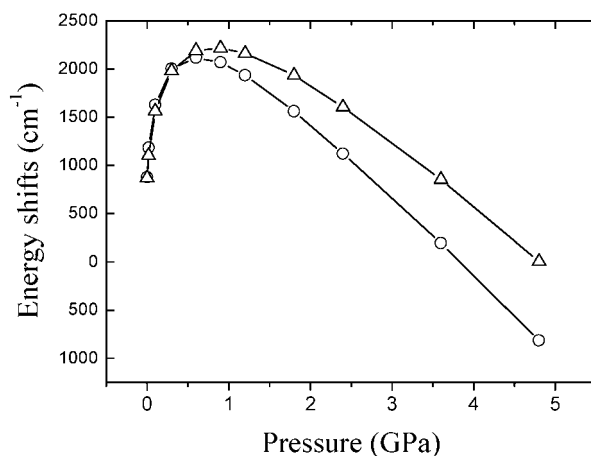


Figure 5. The pressure dependence of the centroid of the whole 2p energy level of Li in solid H₂ for $n_v = 1$ (open circles) and 2 (open triangles).

direction of the crystal field is along the direction of the 2p₋₁ energy level; therefore, the action from the crystal field on the Li atomic 2p₋₁ energy level is larger than those on the 2p₀ and 2p₁ energy levels of the Li atom, resulting in the novel different splittings of the three 2p energy levels. Note that the actions of the crystal field on the 2p₀ and 2p₁ energy levels of the Li atom are equal. Also the different splittings increase with increase in pressure due to the increased action of the lower-symmetry crystal field. These features are responsible for the

pressure-induced behaviours of the Li atomic absorption spectrum shown in figure 2. As the pressure gets larger, a significant shift of the individual 2p energy levels is observed as plotted in figure 4(b). The fascinating pressure dependence of the centroid of the whole 2p energy level is also depicted in figure 5. The turning pressure P_t is about 0.9 GPa, corresponding to an energy shift of 2216 cm^{-1} .

4. Conclusions

In general, the perturbation of H_2 molecules around Li atoms results in the degenerate energy levels of the 2p excited state of the Li atom splitting into three energy levels. However, two kinds of splitting are clearly observed.

- (a) For the $n_v = 1$ doped solid, the Li atom is in a locally higher-symmetry crystal field; the three energy levels for the 2p excited state of the Li atom split equally. With increasing pressure, an increase in the equal splittings between the three energy levels is observed. Also, with increasing pressure, the individual 2p energy levels show a significant shift (shown in figure 3(a)).
- (b) For the trapping site $n_v = 2$, the Li atom is in a locally lower-symmetry crystal field, in which there is a strongly preferred direction: along the asymmetrical axis; a novel different splitting of the three 2p energy levels is observed. The different splittings increase with increase in pressure due to the increased action of the lower-symmetry crystal field. As the pressure gets larger, a significant shift of the individual 2p energy levels is also observed.

Generally, for both doped solids under study, the centroid of the whole 2p energy level shows a fascinating pressure dependence, in which the centroid of the whole 2p energy level shifts towards higher energy below a turning pressure P_t , arrives at the highest energy at P_t , then shifts towards lower energy above P_t , as shown in figure 5.

Acknowledgments

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