

# Temperature Effects on the Absorption Spectra of Li in Solid H<sub>2</sub> Under High Pressure: A Path Integral Monte Carlo Study

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*The temperature dependence (5–45 K) of the absorption spectra of a Li atom doped in solid hydrogen at  $P = 1.2$  GPa is investigated using the path integral Monte Carlo (PIMC) method with a constant pressure ensemble. Higher temperature in our research range does not cause rearrangement of the trapping site structures. The significantly broadening and spreading of the three component absorptions with increasing temperature are observed. For the trapping site structures belonging to lower symmetry point groups, the singlet to doublet splitting decreases as temperature gets larger. An insight on the temperature-induced behaviors of the Li absorption spectrum in the doped system has been made by using the simulated results.*

## I. INTRODUCTION

The trapping and attachment of light alkali atom in quantum matrices has attracted considerable attention recently. These issues are of interest for their scientific importance in understanding the behavior of energetic species in cryogenic environments, and also for potential technological applications. The addition of a small amount of light atoms, such as lithium, into solid hydrogen is believed to improve chemical performance as a propellant for rocket propulsion.<sup>1</sup> Recent experiments have shown that Li atoms can be metastably trapped in both solid hydrogen and deuterium at  $T \leq 5$  K.<sup>2</sup>

The theoretical researches on the doped system of lithium in solid H<sub>2</sub> have previously been made by many investigators.<sup>3–8</sup> Both the Li atomic absorption spectrum and the dynamic behavior of Li atom at zero pressure

and a fixed temperature have been studied. In our previous work,<sup>9</sup> we have investigated the effects of pressure on the trapping site structures and absorption spectra of Li in solid H<sub>2</sub>. However, to our knowledge, the temperature effects on the system of Li atom doped in solid H<sub>2</sub> are unclear. It is of interest to understand how the doped system responds to these thermal perturbations. Accurate measurements of Li absorption spectrum can provide a powerful means to probe the local structures of the Li trapping sites.<sup>4</sup> Unfortunately, the experimental measurements on temperature dependence of Li absorption spectrum have not been reported so far. Therefore, in order to better understand the temperature-induced properties of the doped system, theoretical research is necessary to characterize the trapping sites and local environments of dopant atoms. In this paper, following the theory in treating the system of Li in solid H<sub>2</sub> outlined in Ref. 4, we calculate the absorption spectra of a lithium atom trapping in solid *para*-hydrogen at  $P = 1.2$  GPa and temperatures ranging from 5 to 45 K using quantum constant pressure PIMC simulations that was developed by Cui *et al.*<sup>10</sup> (By default, H<sub>2</sub> in this paper refers to *para*-H<sub>2</sub>.)

## II. THEORY

With the pairwise interaction, ground state system of a Li atom doped in solid hydrogen is described by the Hamiltonian:

$$\begin{aligned}
 H &= T + V, \\
 T &= -\frac{\hbar^2}{2m_1} \sum_{i=1}^{N-n_v} \nabla^2 R_i - \frac{\hbar^2}{2m_2} \nabla^2 R_{\text{Li}}, \\
 V &= \sum_{i=1}^{N-n_v} V_{\text{Li-H}_2}^g(|R_{\text{Li}} - R_i|) + \frac{1}{2} \sum_{i \neq j}^{N-n_v} V_{\text{H}_2\text{-H}_2}(|R_i - R_j|),
 \end{aligned} \tag{1}$$

where  $m_1$  and  $R_i$  are the hydrogen molecular mass and the center-of-mass position vector of  $i$ th hydrogen molecule, respectively.  $R_{\text{Li}}$  and  $m_2$  are the position vector and the atomic mass of lithium, respectively.  $V_{\text{H}_2\text{-H}_2}(|R_i - R_j|)$  is the interaction potential between the two H<sub>2</sub> molecules.  $V_{\text{Li-H}_2}^g(|R_{\text{Li}} - R_i|)$  is the ground state pairwise interaction potential between a lithium atom and  $i$ th hydrogen molecule.  $n_v$  is the number of H<sub>2</sub> molecules which have been replaced out of the simulation cell by introducing a lithium impurity.

The H<sub>2</sub> molecules are treated as spherical particles. The Hemley-corrected SG potential<sup>11</sup> is used to represent the intermolecular interaction between two H<sub>2</sub> molecules, while the Li-H<sub>2</sub> interactions potentials with the Li atom in both ground and excited state used here were developed by

Cheng *et al.*,<sup>4</sup> through fitting to a new, more complete set of data from Konowalow.<sup>12</sup>

### A. Constant Pressure Path-Integral Monte Carlo

The technique of the constant pressure path integral Monte Carlo, which we employ in the present work, was developed in Ref. 10. 96 H<sub>2</sub> 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 (a) and (b). This choice, with the appropriate length ratio  $a : b : c = 1 : 1 : \sqrt{6}/2$ , has the advantage of accommodating both the fcc and hcp lattice structures.<sup>10</sup> The Li dopant is introduced into the simulation cell by replacing  $n_v$  nearest-neighbor H<sub>2</sub> molecules, and leaving only  $(N - n_v)$  H<sub>2</sub> molecules in the simulation cell. 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<sub>2</sub> molecules. The schematic representation of the lithium trapping sites in solid hydrogen studied here is presented in Fig. 1.

The partition number of path integral for different temperatures used in the calculations is listed in Table I. It has been tested that when  $MT$  is larger than 600 the variations of Li absorption spectrum with  $MT$  are negligible.

### B. Absorption Line Shape

The semiclassical line shape for electronic transitions in a condensed phase system is shown as follows, as derived by Lax<sup>13</sup> using 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 between 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. A finite energy bin width is used instead of a delta function to calculate the absorption spectrum of a Li atom doped

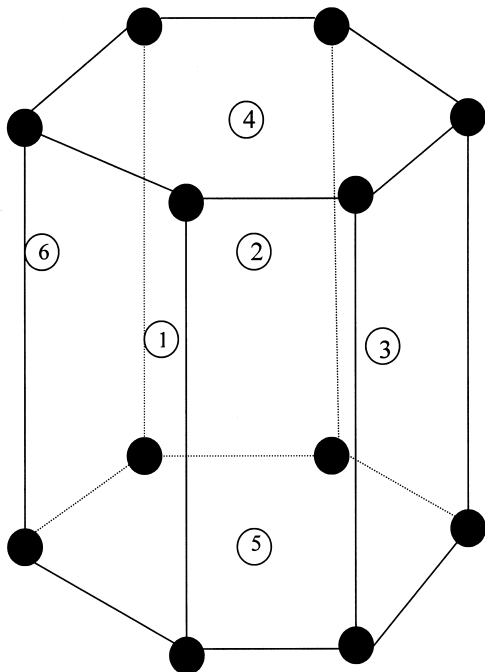


Fig. 1. A schematic representation of the Li trapping sites in solid  $\text{H}_2$  with a hcp lattice. The trapping sites are constructed by removing  $n_v = 1-6$  molecules as shown, and placing the Li atom at the center of the  $n_v$  sites.

in solid hydrogen. The treatments of the energies of the initial and final electronic states for a given configuration  $Q$  have been described in details elsewhere.<sup>4</sup>

### C. Centroid Spectral Shifts

A Li atom experiences a spherically averaged potential in both ground and excited states deriving from an isotropic  $\text{H}_2$  matrix and the spherical

TABLE I  
Partition Number  $M$  Used in the PIMC Calculations

$T$ (K)	5	15	25	35	45
$M$	50	40	30	20	15

average of all configuration can be represented by a radial correlation function, so the centroid shift of the spectral line can be obtained approximately by:<sup>4</sup>

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

Here  $g_{\text{Li-H}_2}(R)$  is the pair distribution function between Li atom and  $\text{H}_2$  molecules, which is normalized according to  $4\pi\rho \int_0^\omega R^2 g_{\text{Li-H}_2}(R) dR = 1$ .  $V_{\text{shift}}(R)$  is the average of the energy difference for any configuration between the spherically averaged excited state  $\text{Li}^*\text{-H}_2$  interaction and the ground state  $\text{Li-H}_2$  interaction.

### III. RESULTS AND DISCUSSION

The spherically averaged pair distribution functions,  $g_{\text{Li-H}_2}(R)$  for  $n_v = 1, 2, 4, 5,$  and  $6$  at  $P = 1.2$  GPa and  $T = 5$  K, which characterize the structural information around Li atom in the doped system, are presented in Figs. 2(a)–(e). The difference in the line shapes of  $g_{\text{Li-H}_2}(R)$  for various trapping sites indicates the difference in the locally structural symmetries around the dopant. The simulated  $g_{\text{Li-H}_2}(R)$  for various trapping sites (not shown) has negligible changes with increasing temperature up to 45 K at  $P = 1.2$  GPa, revealing that application of temperature does not rearrange the local structure around the dopant for various trapping sites under study. The pair distribution function,  $g_{\text{H}_2\text{-H}_2}(R)$  for  $n_v = 1$  at  $P = 1.2$  GPa and  $T = 5$  K, which characterize the structural information on the radial  $\text{H}_2$  molecules distribution, is presented in Fig. 2(f). For other trapping sites,  $g_{\text{H}_2\text{-H}_2}(R)$  is almost identical with  $n_v = 1$  one under the same pressure and temperature condition, indicating that the difference in the radial  $\text{H}_2$  molecule distribution for different selected vacancy is small. Also,  $g_{\text{H}_2\text{-H}_2}(R)$  has a negligible change with increasing temperature from 5 to 45 K.

The calculated spectra of Li in solid  $\text{H}_2$  with hcp lattice for  $n_v = 1$  at  $P = 1.2$  GPa and different temperatures are presented in Fig. 3. The trapping site structures around Li atom for  $n_v = 1$  corresponding to  $\text{D}_{6h}$  symmetrical point group at  $P = 1.2$  GPa and  $T = 5$  K,<sup>9</sup> give a highly symmetrical triplet absorption pattern as shown in Fig. 3(a). The spectrum shows a clearly blue shift relative to the gas phase value. With increasing temperature, the various spectra for this case show similar triplet absorption line shape, except for a general increase in the spectral half-width of the three components. It should be pointed out that the first peak has a decreasing blue shift with temperature, while an increasing blue shift with temperature is observed for the second and third peaks as evidenced in Fig. 8(a). Note

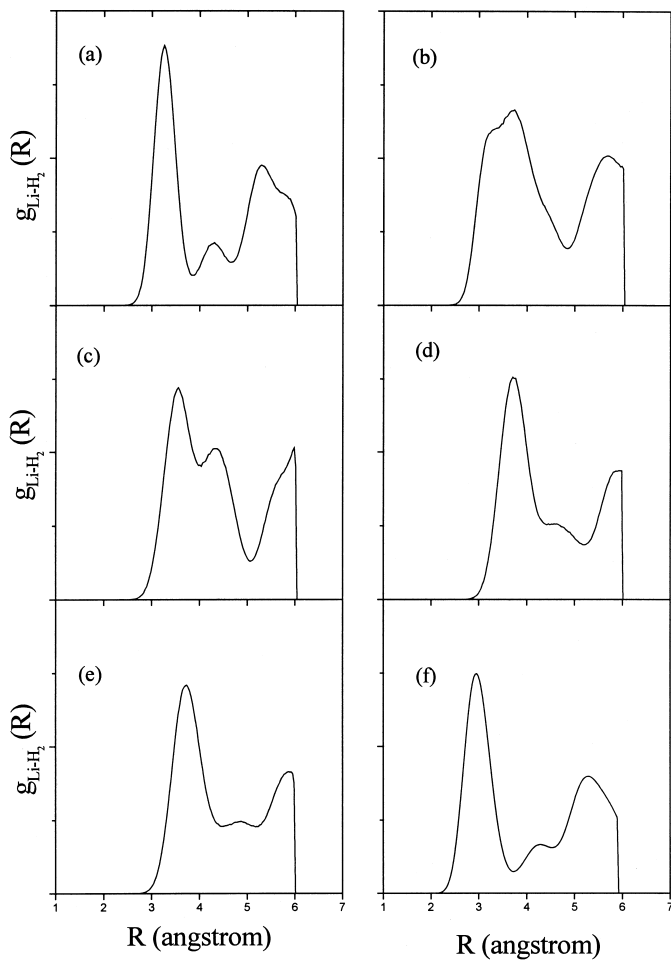


Fig. 2. (a)–(e) are the Li–H<sub>2</sub> pair distribution function for the doped solid with the Li atom replacing one, two, four, five, and six molecules, respectively, in hcp lattice at  $T = 5$  K and  $P = 1.2$  GPa. (f) shows the H<sub>2</sub>–H<sub>2</sub> pair distribution function for the system with the Li atom replacing one molecule in hcp lattice at  $T = 5$  K and  $P = 1.2$  GPa. For  $n_v = 2, 4, 5,$  and  $6$  cases, the H<sub>2</sub>–H<sub>2</sub> pair distribution functions are almost identical with that of  $n_v = 1$ .

that although the centroid spectral shift (CSS) calculated by using Eq. (4), shows very little dependence on temperature by comparing with that of the three components themselves, a linear decrease in blue shift with a slope of  $-0.78 \text{ cm}^{-1}/\text{K}$  is observed from Fig. 8(f) in this calculation. The blue-shifted decrease for the CSS may not be amenable to the experiments, resulting

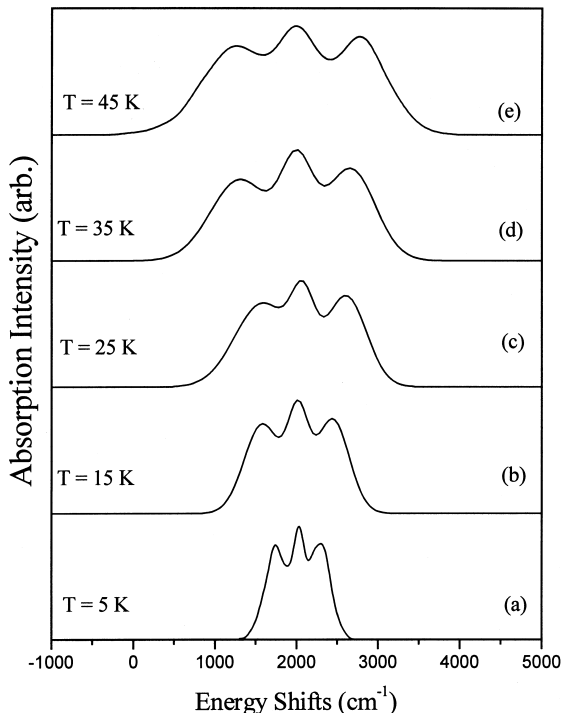


Fig. 3. Temperature dependence of the simulated absorption spectrum of a Li atom in solid  $H_2$  for  $n_v = 1$  at  $P = 1.2$  GPa. (a)–(e) show the spectra calculated for  $T = 5$ –45 K, in 10 K increments.

from the very small magnitude of the decrease. These results are quite similar to the results of Na/Ar doped system.<sup>14</sup> The trapping site structures belonging to the same symmetry point group at different temperatures and a fixed pressure is responsible for the similar highly symmetrical triplet absorption line shape, i.e., higher temperature does not rearrange the trapping site structure, in agreement with the results of  $g_{Li-H_2}(R)$  as described above, while the strongly increased thermal fluctuations from the trapping site structure contribute to an increase in spectral half-width and the individual shifts of the three components with temperature. The temperature dependencies of three individual peak energies for  $n_v = 1$  are presented in Fig. 6(a). It is clear that the separations between the components of the triplet for this case show an increased tendency with increasing temperature.

Figures 4 and 5 show the simulated spectra of Li atom for  $n_v = 2$  and 6. The low symmetrical trapping site structures around dopant for  $n_v = 2$  and

6 at  $T = 5$  K and  $P = 1.2$  GPa corresponding to  $C_2$ , and  $C_3$  symmetry point group<sup>9</sup> respectively, determine the blue-shifted singlet plus doublet absorption line shapes as shown in Figs. 4(a) and 5(a). As the temperature gets larger, the various spectra for the two cases also show a significant increase in the spectral half-width of the three components, deriving from the largely increased thermal fluctuations from the trapping site structure. For  $n_v = 2$  case, One finds that the first and third peaks tend to have a increasing blue shift with temperature, while a decreasing blue shift with temperature is observed for the second peak as evidenced in Fig. 6(b). For  $n_v = 6$  case, the first and second peaks show a increasing blue shift with temperature, while an decreasing blue shift with temperature is observed for the third peak as shown in Fig. 6(e). For both cases, a very small magnitude of

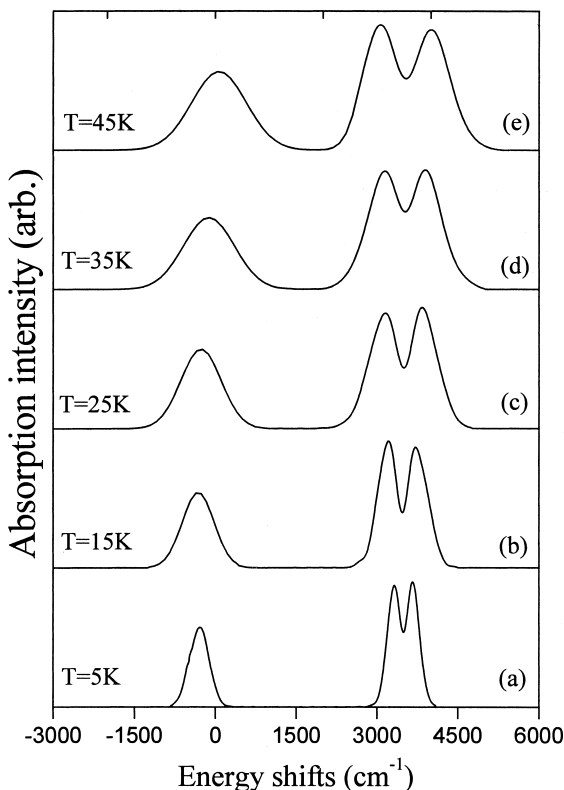


Fig. 4. Temperature dependence of the simulated absorption spectrum of a Li atom in solid  $H_2$  for  $n_v = 2$  at  $P = 1.2$  GPa. (a)–(e) show the spectra calculated for  $T = 5$ –45 K, in 10 K increments.



the linear blue-shifted decrease in CSS with the slopes of  $-0.78$  and  $-0.86$   $\text{cm}^{-1}/\text{K}$  for  $n_v = 2$  and  $6$ , respectively, as plotted in Fig. 6(f), is also observed, in agreement with the  $n_v = 1$  case. They are similar to the results simulated in Na/Ar doped system.<sup>14</sup> Note also that the splittings between the singlet and doublet decrease remarkably with increasing temperature, and for  $n_v = 6$  case, the absorption spectra convert to the low symmetrical triplet absorption feature at  $T = 15$  K, as shown in Fig. 5(b). For lower symmetrical trapping sites, at  $T = 5$  K, application of pressure results in a splitting in absorption spectrum from a low symmetrical triplet absorption line shape to a singlet plus doublet absorption pattern, and the singlet to doublet splitting increases with increasing pressure, deriving from the

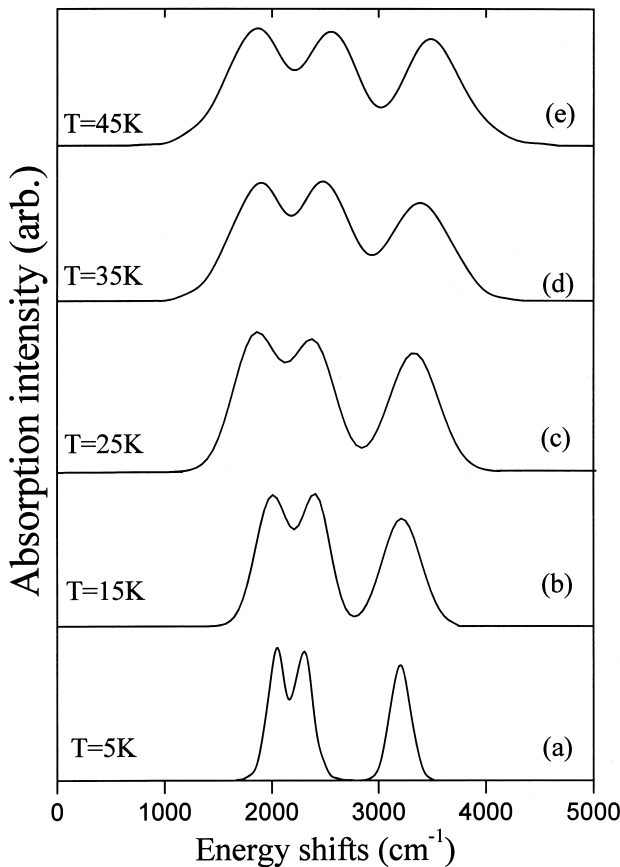


Fig. 5. Temperature dependence of the simulated absorption spectrum of a Li atom in solid  $\text{H}_2$  for  $n_v = 6$  at  $P = 1.2$  GPa. (a)–(e) show the spectra calculated for  $T = 5$ – $45$  K, in 10 K increments.

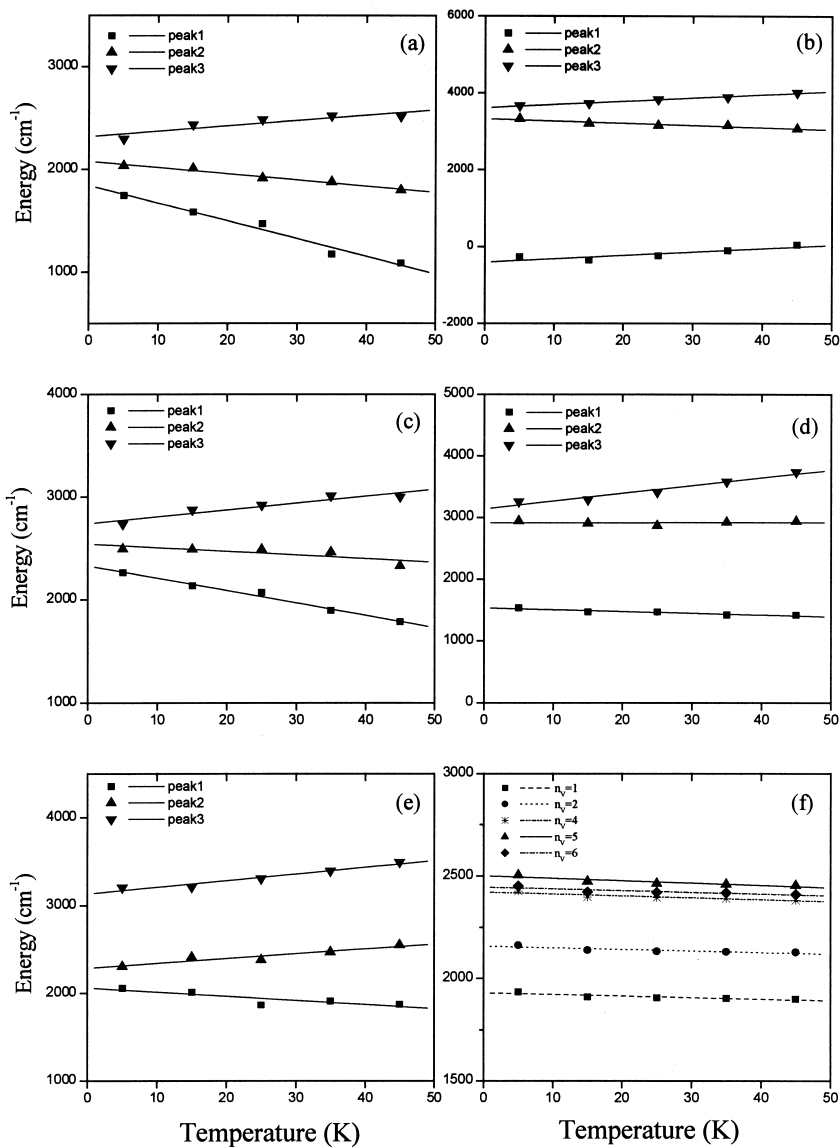


Fig. 6. (a)–(e) are the three individual peak energies of Li absorption spectra as functions of temperature for  $n_v = 1, 2, 4, 5$ , and  $6$ , respectively, at  $P = 1.2$  GPa. (f) shows the temperature dependence of centroid spectral shift (CSS) for various trapping sites at  $P = 1.2$  GPa.

decreased Li-H<sub>2</sub> separation along the asymmetrical axis which dominates the singlet to doublet splitting.<sup>9</sup> Thus, for the lower symmetrical trapping sites, the Li-H<sub>2</sub> separation along the asymmetrical axis may be increased with an increase in temperature. This fact may contribute to the temperature-induced decrease in singlet to doublet splitting of Li absorption spectrum. It should be pointed out that for the lower symmetrical trapping site structures, higher temperature also could not rearrange the trapping site structure. This conclusion is supported by the similar absorption line shapes at different temperatures and  $P = 1.2$  GPa, except for the difference in the singlet to doublet splittings with the different Li-H<sub>2</sub> separations along the asymmetrical axis. The temperature effects on the individual peak energies for the two cases are shown in Figs. 6(b) and (e). One observes that an increase in temperature results in an increase of the separation within the doublet.

## V. CONCLUSIONS

In this paper, following the theory in treating the system of Li in solid H<sub>2</sub> outlined in Ref. 4, we have performed quantum constant pressure PIMC calculations on a Li atom trapped in solid hydrogen with hcp phase at  $P = 1.2$  GPa and temperatures ranging from 5 to 45 K. It is found that application of temperature could not rearrange the local structure around the Li atom. With increasing temperature, the significantly broadening and spreading of the three component absorptions are observed clearly. The blue-shifted decrease for the CSS obtained in this calculation similar to that in Na/Ar system<sup>14</sup> may not be amenable to the experiments, resulting from the very small magnitude of the decrease.

An insight on the temperature-induced spectral behaviors for various trapping sites can be made as follows. (1) For the trapping site structure belonging to a higher symmetry point group (i.e., D<sub>6h</sub>), which dominates the highly symmetrical triplet absorption pattern, the splitting of the degeneracy of the excited Li\* atom 2P state are largely due to the thermal fluctuations away from the trapping site structure. This conclusion is further supported by the results of these highly symmetrical trapping sites at higher temperature, which show an increase in the peak splittings with temperature. With increasing temperature, the largely increased electron-phonon coupling may contribute to an increase in spectral half-width and the individual shifts of the three components with temperature. (2) For the trapping site structure belonging to a lower symmetry point group (i.e., C<sub>1</sub> or C<sub>3</sub>), which determines the singlet plus doublet absorption feature, the thermal fluctuations contribute largely to the splitting within the doublet as evidenced in Figs. 6(b) and (e). The singlet to doublet splittings decrease

with increasing temperature, arising from the increased Li-H<sub>2</sub> separation along the asymmetrical axis. The increased thermal perturbation of H<sub>2</sub> on Li atom is also responsible for an increase in spectral half-width and the individual shifts of the three components with temperature.

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