10 August 2001

ELSEVIER

Chemical Physics Letters 343 (2001) 604–612

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Isotope effects on the absorption spectrum of Li in solid hydrogens under high pressures

Y.M. Ma [a,b,*], T. Cui [a], G.T. Zou [a]

[a] *National Lab of Superhard Materials, Jilin University, Changchun 130023, China*
[b] *Laboratory of Excited State Processes and Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130021, P.R. China*

Received 3 April 2001; in final form 13 June 2001

Abstract

The isotope effects on the absorption spectrum of Li in solid hydrogens at $T = 5$ K and different pressures are extensively studied. At a lower pressure, the difference in Li atomic absorption spectra between the Li/D_2 and the Li/H_2 systems is significant, while becomes less remarkable with the increase in pressure. The zero-point motion from H_2 molecules influences the Li absorption spectrum in both a direct and an indirect way. Although the direct and indirect effects on the absorption spectrum from the quantum motion cancel partly, eventually the indirect effect dominates the variations of the Li absorption spectrum. © 2001 Elsevier Science B.V. All rights reserved.

1. 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 [1]. Recent experiments have shown that Li atoms can be metastably trapped in both solid hydrogen and deuterium at $T \leqslant 5$ K [2].

The theoretical research on the doped system of lithium in solid H_2 has previously been made by many investigators. Scharf et al. [3,4] performed the first quantum calculation of a lithium impurity in *para*-hydrogen at zero-pressure by using Path-integral Monte Carlo (PIMC) simulation. Cheng and Birgitta [5] performed another calculation on the absorption spectrum of Li atom in solid H_2 at zero-temperature and zero-pressure by using both variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) simulations. In our previous papers, both the pressure [6] and temperature [7] dependencies of the absorption spectra of Li in solid H_2 for various trapping sites are extensively investigated by using PIMC calculation. The dynamic behaviors of a Li atom in hydrogen clusters and a hydrogen slab, and two or more lithium impurities in solid hydrogen have been investigated by means of molecular dynamics (MD) simulation [8–11].

* Corresponding author. Fax: +86-431-892-0398.
E-mail address: ymma66@mail.jl.cn (Y.M. Ma).

0009-2614/01/$ - see front matter
PII: S0009-2614(01)00767-9

Although, as far as most properties are concerned, solid H_2 and D_2 are quite similar [12], they also show striking differences in several aspects. (1) There appears to be a significant isotope effect on the orientational-ordering transformation in the molecular solid, on the basis of phonon and roton measurements carried out below 100 GPa [13]. The ordering transformation occurs at significantly lower pressures in D_2 than in H_2. (2) There is also a pronounced isotope effect on the Raman-active vibron [14–17], deriving probably from the higher anharmonicity of hydrogen due to its larger zero-point motion. (3) A large isotope effect on the melting behavior of *para*-hydrogen in small clusters has been observed by Scharf et al. [18]. (4) Remarkable differences in some NMR behaviors of solid H_2 and D_2 have also been observed. For a review of these NMR properties see [19].

Scharf et al. [3,4] has calculated the absorption spectrum of Li atom in both solid hydrogen and deuterium at zero-pressure and $T = 4$ K. The results show that the difference between the Li/H_2 spectrum and the Li/D_2 one is significant. However, to our knowledge, the isotope effects on the absorption spectrum of Li atom in doped solid hydrogens under pressure is still open. It is of interest to understand how the doped system responds to the isotope matrix under pressure. In this Letter, following the theory in treating the system of Li in solid H_2 outlined in [5], we calculate the absorption spectra of a lithium atom trapping in both solid *para*-hydrogen and solid *ortho*-deuterium under pressure at $T = 5$ K using quantum constant pressure PIMC simulations. (By default, H_2 and D_2 in this paper refer to *para*-hydrogen and *ortho*-deuterium, respectively).

2. Path integral Monte Carlo calculations

In order to study the matrix mass effect on properties of lithium doped in the doped system under pressure, the technique of the constant pressure path integral Monte Carlo used in the present work was developed by Cui et al. [20] to study the pure solid hydrogen system. We have applied it to the Li/H_2 doped system [6].

The Metropolis scheme for NPT ensemble is implemented by generating a Markov chain of states which has a limiting distribution proportional to [21].

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

The number of 'beads' of the path integral is chosen as 50 at $T = 5$ K in this calculation as in our previous work [6]. Each Monte Carlo step consists of an attempted Metropolis move for every bead, with ith particle move incurring random displacement in R_i. To enhance sampling efficiency, the whole path for each particle also gets a random displacement at each MC step: i.e. every bead of the path is moved in the same way with identical ΔR. This corresponds to a simplified multilevel sampling [22]. 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 from every two steps, to a total of about 10 000 data points. Other details of the PIMC technique can be found in [6].

96 H_2 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 [20]. The Li dopant is introduced into the simulation cell by replacing n_v nearest-neighbor 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' $S_{Li} = \sum_{i=1}^{n_v} S_i/n_v$, where i runs over the lattice sites of the replaced H_2 molecules. In order to minimize surface and finite size errors, the periodic boundary condition is used in all three spatial dimensions. The interactions are evaluated making use of the periodicity and the 'minimum image' method [21], and the cutoff length is chosen to be equal to half of the shortest simulation cell side. Cutoff correction to the potential energy is performed by assuming that beyond the cutoff length the sold is a continuous and uniform medium.

There are two kinds of Li absorption spectra in the doped solids for various trapping sites n_v from 1 to 6 at $T = 5$ K and a given pressure [6]: one kind is the highly symmetrical triplet absorption line shape for $n_v = 1$ and 4 trapping sites; the other one is the low symmetrical triplet (or singlet plus doublet) absorption feature for $n_v = 2,\ 3,\ 5$ and 6 trapping sites. Therefore, for simplicity, we study only two representative trapping sites $n_v = 2$ and 4 in this calculation.

The semiclassical line shape for electronic transitions in a condensed phase system is shown as follows, as derived by Lax [23] using semiclassical Franck–Condon principle

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

with

$$\Delta E(Q) = E_f(Q) - E_i(Q), \tag{3}$$

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. For more details of the $E_i(Q)$ and $E_f(Q)$ see [24]. A finite energy bin width is used instead of a delta function to calculate the absorption spectrum of a Li atom doped in solid hydrogen.

The Hemley-corrected SG [25,26] potential was used to represent the intermolecular interaction between two matrix molecules, while the Cheng potential [5], through fitting to a new ab initio data for the Li/H_2 system [27], was used for the $Li–H_2/D_2$ pair interaction potentials with the Li atom in both ground and excited state in this calculation. The ground state $Li–H_2/D_2$ pair interaction labeled as $V_{X\Sigma}(R)$, takes the form

$$V_{X\Sigma}(R) = e^{\alpha-\beta R-\gamma R^2} - f(R)\left\{\frac{C_6}{R^6} + \frac{C_8}{R^8}\right\}, \tag{4}$$

with

$$f(R) = \begin{cases} e^{-(1.28R_m/R-1)^2} & \text{If } R < 1.28R_m \\ 1 & \text{Otherwise} \end{cases}. \tag{5}$$

The parameters for the pair potential $V_{X\Sigma}(R)$ are listed in Table 1.

The excited state $Li^*–H_2/D_2$ pair potentials take two kinds [5]: $V_{B\Sigma}(R)$ and $V_{A\Pi}(R)$, which have the same form as the $V_{X\Sigma}(R)$ one. The parameter values are also listed in Table 1.

A Li atom experiences a spherically averaged potential in both ground and excited states deriving from an isotropic D_2 (or H_2) matrix and the spherical 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 [5].

$$\hbar\omega_{shift} = 4\pi\rho \int_0^\infty R^2 g_{Li–H_2}(R) V_{shift}(R)\, dR. \tag{6}$$

Here $g_{Li–H_2}(R)$ is the pair distribution function between Li atom and H_2 molecules, which is normalized according to

$$4\pi\rho \int_0^\infty R^2 g_{Li–H_2}(R)\, dR = 1.$$

$V_{shift}(R)$ takes the form

$$V_{shift}(R) = \frac{1}{3}[V_{B\Sigma}(R) + 2V_{A\Pi}(R)] - V_{X\Sigma}(R). \tag{7}$$

In this work, both isotope molecules have been treated as spherical particles for three main reasons. First, it has the advantage of direct comparison of matrix H_2 and D_2 without worrying about the differences in intramolecular bond lengths, molecular polarizabilities, etc. [18]. Second, in our research range ($P = 0.02$–2.4 GPa and $T = 5$ K), either pure solid is in phase I, orienta-

Table 1
Parameter values (in atomic units) for the spherical interaction potentials between Li and H_2

Potential	α	β	γ	R_m	C_6	C_8
$V_{X\Sigma}$	−2.976	0.1612	0.05033	9.856	85.00	4050
$V_{B\Sigma}$	−1.858	0.2517	0.03424	37.8	85.00	0
$V_{A\Pi}$	−1.328	1.109	0.05295	4.79	85.00	305.0

tionally disorder phase, in which the molecules behave approximately as spherical particles. Third, it enabled us to relate our results to the previous study of Li/H_2 solid [6]. We also perform a classical simulation of lithium doped in solid H_2, to probe the quantum effect on the Li absorption spectrum.

3. Results and discussion

The absorption spectra of Li atom in solid D_2 for $n_v = 2$ at $T = 5$ K and different pressures are presented in Fig. 1. The spectra at different pressures show a singlet plus a doublet pattern. As the pressure gets larger, the splitting between the singlet and the doublet increases remarkably. An increase in pressure also results in an increase in spectral width. It should also be pointed out that a fascinating pressure dependency of the centroid spectral shift (CSS) calculated by the Eq. (6) is observed. The variation of the CSS with pressure is plotted in Fig. 4a (open up triangle) for this case. One observes that with the pressure increase, the CSS tends to have a increasing blue shift at a pressure range below a 'turning pressure', P_t (≈ 0.6 GPa), and tends to have a decreasing blue shift above P_t under study. The pressure dependency of Li atomic absorption spectrum in the Li/D_2 doped solid for $n_v = 2$ case is quite similar to that in the Li/H_2 solid [6].

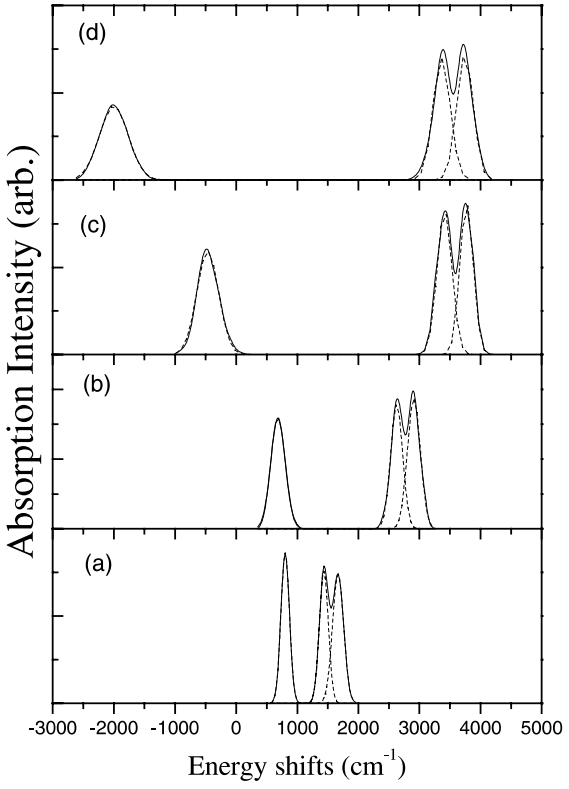

Fig. 1. Li absorption spectra for a Li atom replacing two D_2 molecules in solid D_2 with a hcp lattice at $T = 5$ K and $P = 0.02$ (a), 0.3 (b), 1.2 (c), and 2.4 GPa (d), respectively, the dashed curves are the individual underlying components.

However, it is obvious that, at a given pressure point both the CSS and the absorption spectral line shape in the Li/D_2 solid are remarkably different from those in the Li/H_2 solid. The comparison of the Li/H_2 quantum absorption spectra with the Li/D_2 one at $T = 5$ K under $P = 0.02$ and 1.2 GPa are shown in Fig. 3a,b. At $P = 0.02$ GPa, the spectrum in the Li/H_2 system shows a low symmetrical triplet absorption feature, while the Li/D_2 one shows a singlet plus doublet absorption line shape, as shown in Fig. 3a. For $n_v = 2$ case, the trapping site structure for both doped solids belongs to a lower symmetrical point group, which is responsible for the low symmetrical triplet pattern in the Li/H_2 system and the singlet plus doublet absorption feature in the Li/D_2 system [6]. Note that the difference in separation between the 'singlet' and the 'doublet' for both systems is significant and the CSS of the Li/D_2 spectrum is 1294 cm^{-1}, larger than the Li/H_2 one, 1102 cm^{-1}, at this pressure point. It should also be pointed out that the spectral width of the Li/D_2 spectrum is slightly larger than the Li/H_2 one, indicating that the spectral width is less sensitive to the isotope matrix than the CSS and the singlet to the doublet splitting are at a given condition. At $P = 1.2$ GPa, the differences in both absorption spectra are less remarkable than those at $P = 0.02$ GPa. The two spectra all show a singlet plus doublet absorption pattern as depicted in Fig. 3b, arising from the lower symmetrical trapping site structure too. The singlet to doublet splitting of the Li/D_2 spectrum is larger than that of the Li/H_2 one, similar to the case at $P = 0.02$ GPa. The differences in the CSS

for the two systems are also slightly noticeable. The variations of CSS for both spectra with pressure from 0.02 to 2.4 GPa are presented in Fig. 4a. The difference in CSS for the two spectra is significant at lower pressure, but less visible with the pressure increases up to 2.4 GPa.

Fig. 2 shows the absorption spectra of the Li/D_2 doped solid for $n_v = 4$. The spectrum for a given pressure shows a highly symmetrical 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. A significant CSS with increasing pressure is also observed as plotted in the Fig. 4b (open up triangle). The pressure response of the spectrum for this case agrees well with that in the Li/H_2 solid [6].

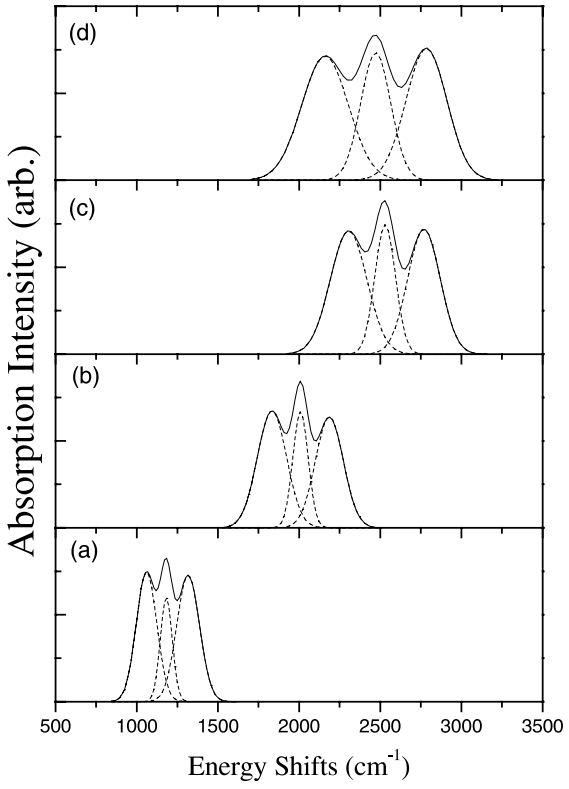

Fig. 2. Li absorption spectra for a Li atom replacing four D_2 molecules in solid D_2 with a hcp lattice at $T = 5$ K and $P = 0.02$ (a), 0.3 (b), 1.2 (c), and 2.4 GPa (d), respectively, the dashed curves are the individual underlying components.

The comparison of the Li/H_2 quantum absorption spectra with the Li/D_2 ones for $n_v = 4$ at $T = 5$ K under $P = 0.02$ and 1.2 GPa are presented in Fig. 3c,d. The spectra for both solids show a highly symmetrical triplet feature. The Li atomic trapping site structure belonging to higher symmetrical point group in both solids dominates these behaviors [6]. One observes that at both pressure points, the differences in the absorption pattern for the two systems are negligible, except for the differences in the spectral half-width and the CSS shown in Fig. 3c,d. The pressure dependences of the CSS for the two spectra are plotted in Fig. 4b. The difference in the CSS of two spectra gets smaller with increasing pressure quite similar to the $n_v = 2$ case.

As described above, the pressure dependency of Li atomic absorption spectrum in the Li/D_2 doped solid for a selected trapping site is quite similar to that in the Li/H_2 solid. But it is clear that at a lower pressure point the behavior of the spectral line shape for a trapping site in the Li/D_2 solid are remarkably different from that in the Li/H_2 solid. The difference for the spectra between the Li/D_2 and the Li/H_2 doped systems becomes smaller with the increase in pressure.

The reason that causes the difference in the two absorption spectra for the Li/D_2 and the Li/H_2 systems at a given pressure should be ascribed to the difference in zero-point motion of H_2 and D_2 molecules. This quantum motion influences the absorption spectra in both a direct way and an indirect way. The direct way is that after the doped solid arrives at equilibrium, the quantum motion influences directly the absorption spectrum. The indirect way is that the zero-point motion influences the system density first, then acts on the spectra through density. The densities for $n_v = 2$ and 4 doped solid at $P = 0.02$ and 1.2 GPa are listed in Table 2. At a given pressure point the density of the Li/D_2 solid is larger than that of the Li/H_2 solid as expected, because stronger zero-point motion exists in the Li/H_2 system. At a lower pressure point $P = 0.02$ GPa, the difference of densities is larger, while smaller at $P = 1.2$ GPa, a larger pressure, due to the fact that the zero-point motion tends to converge with the increase of pressure. The density for a doped solid is related

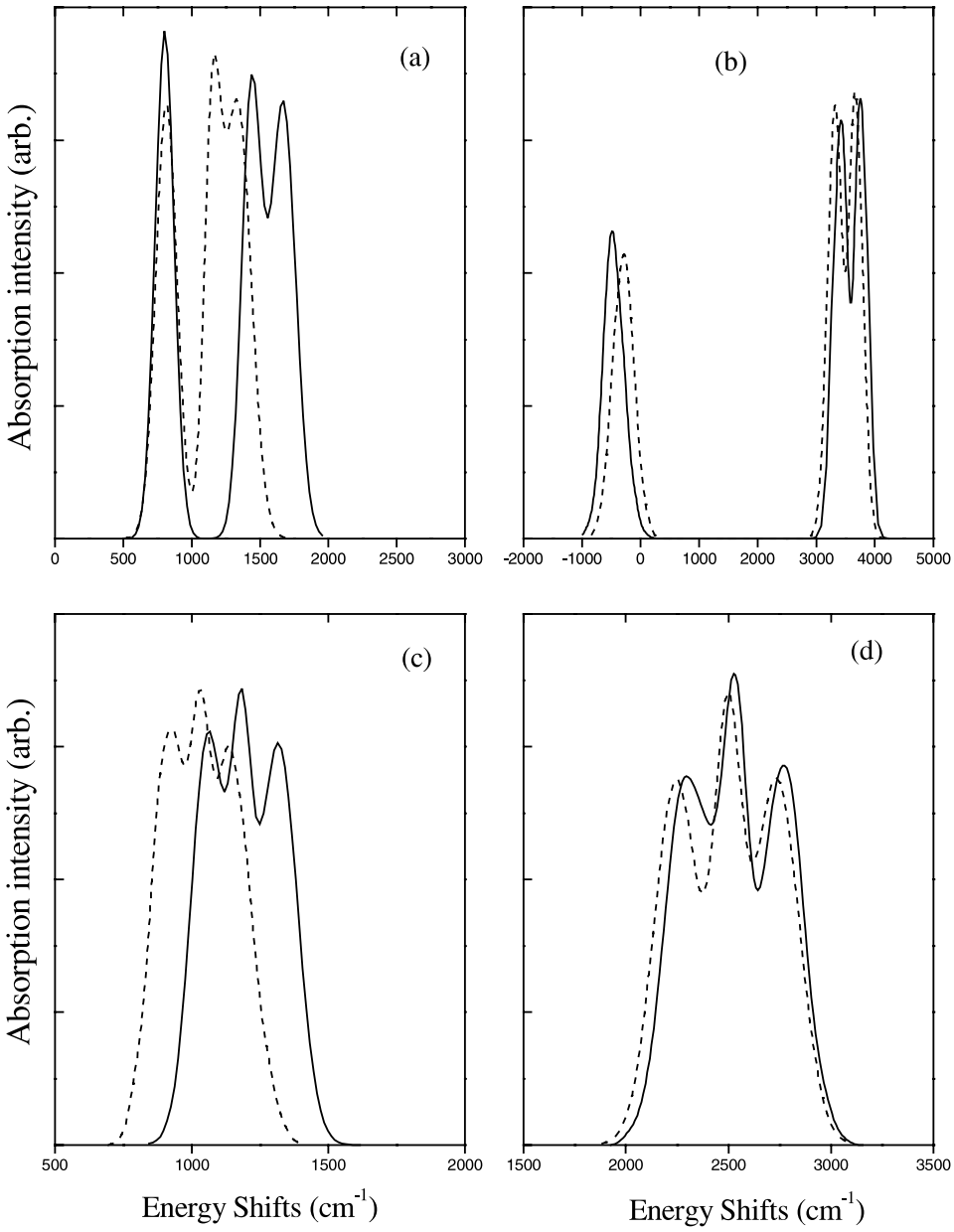

Fig. 3. The comparison of the Li absorption spectra in the Li/D_2 solid (solid line) with that in the Li/H_2 solid (dashed line) at $T = 5$ K. (a) is for $n_v = 2$ and $P = 0.02$ GPa; (b) is for $n_v = 2$ and $P = 1.2$ GPa; (c) is for $n_v = 4$ and $P = 0.02$ GPa; (d) is for $n_v = 4$ and $P = 1.2$ GPa.

to the compact behavior in the trapping site structure around the Li atom. The larger density indicates a more compact trapping site structure around the dopant. Therefore, the Li absorption spectrum for the Li/D_2 solid at a lower pressure is similar to the Li/H_2 spectrum at a higher pressure. In another word, at a given pressure the stronger zero-point motion in the Li/H_2 system makes its absorption spectrum similar to that of the Li/D_2 system at a lower pressure.

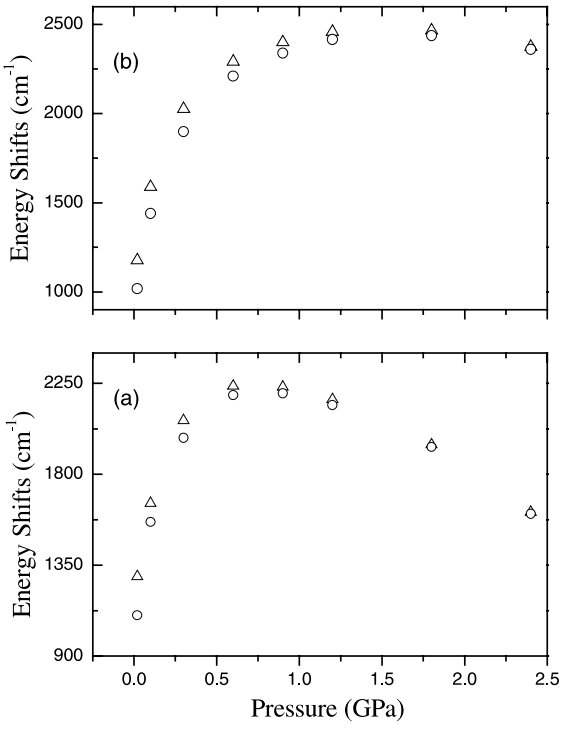

Fig. 4. The pressure dependency of the CSS in both the solid Li/D_2 (open up triangle) and the solid Li/H_2 (open circle) for $n_v = 2$ (a) and 4 (b) at $T = 5$ K.

Table 2
The densities of the Li/H_2 and Li/D_2 systems for $n_v = 2$ and 4 at $T = 5$ K and $P = 0.02$ and 1.2 GPa, respectively

Pressure (GPa)	n_v	Density for the doped solid ($10^{-2} \times$ Å^{-3})	
		Li/H_2	Li/D_2
0.02	2	2.626	2.906
0.02	4	2.683	2.967
1.2	2	5.201	5.283
1.2	4	5.291	5.370

For understanding how the zero-point motion acts on the absorption spectrum directly, we also performed a 'classical simulation' in which the H_2 molecules are treated as particles without any quantum motions. We make a comparison between the Li/H_2 quantum absorption spectrum (QAS) and the 'classical' absorption spectrum (CAS) at the same density. Fig. 5a,b show the results of the QAS and the CAS for $n_v = 2$ and 4 at $T = 5$ K and $P = 0.02$ GPa, respectively. The difference between QAS and CAS indicates that the zero-point motion plays an important role in determining of absorption spectrum, but in an opposite way to the indirect effect as shown in Fig. 5. For the lower symmetrical trapping site ($n_v = 2$), the larger the zero-point motion, the larger the singlet to doublet splitting, the spectral half-width and the CSS. For the higher symmetrical trapping site ($n_v = 4$), the quantum effect results in an increase in the spectral half-width and the CSS.

In a quantum solid, the indirect effect from the zero-point motion on the absorption spectrum is larger than the direct effect, determining the properties of the absorption spectra eventually at a pressure after canceled each other partly, i.e., the compact behavior in trapping site structure around the Li atom dominates the variations of the Li absorption spectrum.

4. Conclusions

In this Letter, following the theory in treating the system of Li in solid H_2 outlined in [5], we have performed quantum constant pressure PIMC calculations on a Li atom trapped in solid deuterium with a hcp phase at $T = 5$ K and different pressures ranging from 0.02 to 2.4 GPa. The isotope effects on the absorption spectrum are extensively investigated.

We can make an insight to the difference between the Li/H_2 spectrum and the Li/D_2 spectrum at a given pressure. For the trapping sites belonging to lower symmetrical point groups ($n_v = 2$), the lower symmetrical trapping site structures around the Li atom are responsible for the low symmetrical triplet absorption feature or the singlet plus the doublet absorption pattern. The compact behavior in trapping site structure dominates the behavior of the spectral half-width, the CSS and the singlet to doublet splitting in spite of the cancellation from the direct effect of the zero-point motion. For the trapping sites belonging to higher symmetrical point groups ($n_v = 4$), the higher symmetrical trapping site structures around the Li atom contribute to the highly

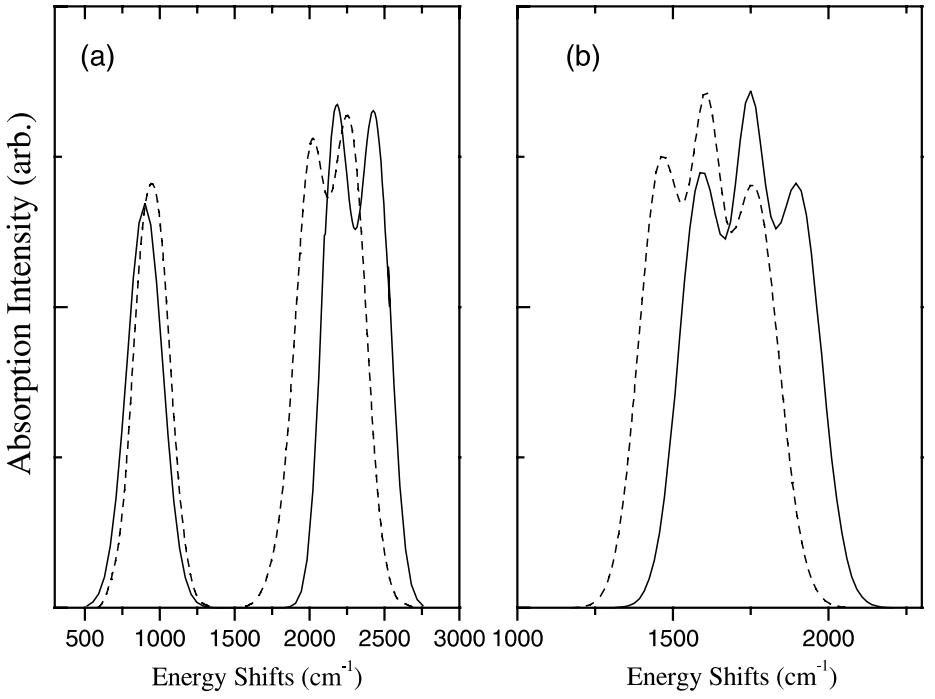

Fig. 5. The comparison between the classical reference Li/H_2 absorption spectrum (dashed line) and the quantum Li/H_2 absorption spectrum (solid line) with same density for $n_v = 2$ (a) and 4 (b) at $T = 5$ K and $P = 0.02$ GPa.

symmetrical triplet absorption line shape, the compact behavior in trapping site structure dominates the behavior of the spectral half-width and the CSS against the direct effect of the molecular zero-point motion.

At lower pressures, the difference in solid density for both doped solids is larger, so the difference in absorption spectrum for the two-doped solid is significant. Due to the fact that the molecular zero-point motion tends to converge, the difference in solid densities for the two doped solids decreases with increasing pressure as listed in Table 2. Therefore, as the pressure gets larger, the difference in absorption spectrum becomes less remarkable.

Acknowledgements

The research was supported by the Chinese National Foundation for Doctoral Education, No. 98018309 and Scientific Research Foundation for Returned Oversees Chinese Scholars, No. (1997) 832, State Education Department.

References

[1] T.L. Thompson (Ed.), in: The Proceedings of the High Energy Density Matter (HEDM) Conference, 1993.
[2] M.E. Fajardo, J. Chem. Phys. 98 (1993) 110.
[3] D. Scharf, G.J. Martyna, M.L. Klein, J. Chem. Phys. 99 (1993) 8997.
[4] D. Scharf, G.J. Martyna, D. Li, G.A. Voth, M.L. Klein, J. Chem. Phys. 99 (1993) 9013.
[5] E. Cheng, K. Birgitta Whaley, J. Chem. Phys. 104 (1996) 3155.
[6] Y.M. Ma, T. Cui, G.T. Zou, J. Chem. Phys. 114 (2001) 3092.
[7] Y.M. Ma, T. Cui, G.T. Zou, J. Low Temp. Phys., in press.
[8] K. Kinugawa, P.B. Moore, M.L. Klein, J. Chem. Phys. 106 (1997) 1154.
[9] K. Kinugawa, P.B. Moore, M.L. Klein, J. Chem. Phys. 109 (1998) 610.
[10] S. Jang, G.A. Voth, J. Chem. Phys. 108 (1998) 4098.

[11] S. Jang, S. Jang, G.A. Voth, J. Phys. Chem. A 103 (1999) 9512.
[12] I.F. Silvera, Rev. Mod. Phys. 52 (1980) 393.
[13] I.F. Silvera, R.J. Wijingaarden, Phys. Rev. Lett. 47 (1981) 39.
[14] S.K. Sharma, H.K. Mao, P.M. Bell, Phys. Rev. Lett. 44 (1980) 886.
[15] R.J. Wijingaarden, A. Lagendijk, I.F. Silvera, Phys. Rev. B 26 (1982) 4957.
[16] H.K. Mao, P.M. Bell, R.J. Hemley, Phys. Rev. Lett. 55 (1985) 99.
[17] R.J. Hemley, H.K. Mao, Phys. Rev. Lett. 63 (1989) 1393.
[18] D. Scharf, G.J. Margyna, M.L. Klein, Chem. Phys. Lett. 197 (1992) 231.
[19] A.B. Harris, H. Meyer, X. Qin, Phys. Rev. B 49 (1994) 3844.
[20] T. Cui, E. Cheng, B.J. Alder, K.B. Whaley, Phys. Rev. B 55 (1997) 12 253.
[21] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Clarendon Press, Oxford, 1987.
[22] D.M. Ceperley, Rev. Mod. Phys. 67 (1995) 279.
[23] M. Lax, J. Chem. Phys. 20 (1952) 1752.
[24] J.A. Boatz, M.E. Fajardo, J. Chem. Phys. 101 (1994) 3472.
[25] R.J. Hemley, H.K. Mao, L.W. Finger, A.P. Jephcoat, R.M. Hazen, C.S. Zha, Phys. Rev. B 42 (1990) 6458.
[26] T.S. Duffy, W.L. Vos, C.S. Zha, R.J. Hemley, H.K. Mao, Science 263 (1994) 1590.
[27] D.D. Konowalow, in: T.L. Thompson (Ed.), Proceedings of the High Energy Density Matter (HEDM) Conference, 1993 (unpublished).