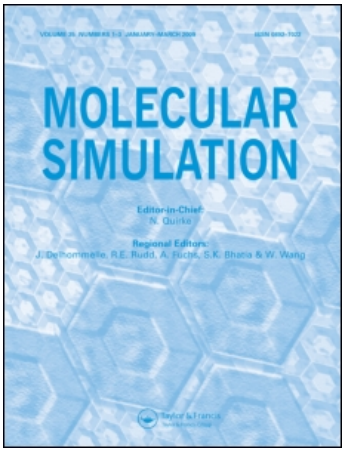

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H / D isotope effect on the dihydrogen bond by *ab initio* path integral molecular dynamics simulation

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H/D isotope effect on the dihydrogen bond by *ab initio* path integral molecular dynamics simulation

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We have performed *ab initio* path integral molecular dynamics (PIMD) simulation for the isotopomers of $C_2H_2\cdots HLi$ cluster to discuss the thermal, quantum, and isotope effects on the average geometries, which are compared with classical MD and equilibrium geometries. The $\pi\cdots$lithium bonding with T-shape geometry is more stable than the dihydrogen bonded linear geometry by both PIMD, classical MD, and equilibrium geometry. Our *ab initio* PIMD simulation has clearly demonstrated the H/D isotope effect on intermolecular fluctuation, that is, the out-of-plane and in-plane fluctuations are characterized for LiH and LiD moieties, respectively.

Keywords: Dihydrogen bonding; Lithium bonding; Path integral molecular dynamics; H/D isotope effect; Quantum effect

1. Introduction

There are several types of intermolecular forces, such as hydrogen bonding and a bonding between hydrogen and π-electrons in aromatic compounds called an XH—π hydrogen bonding [1,2]. Another example is a bonding between positively charged and negatively charged hydrogen atoms, called a dihydrogen bonding [3]. We have already studied a dihydrogen bonded cation system $NH_4^+\cdots BeH_2$ [4]. It was found that the dihydrogen bonded distance $H^{\delta+}\cdots H^{\delta-}$ is unusually short while O—H distance is unusually large [5], and the charge transfer between donor and acceptor is increased as the dihydrogen bond distances get shorter. Recently, a new type of dihydrogen bonded system including carbon and lithium atoms, such as C—H donor and Li—H acceptor has been found [6,7]. Patwari *et al.* [8,9] have investigated the C—H$\cdots$H—B dihydrogen bonded systems for acetylenes with borane-trimethylamine and borane-trimethylamine dimer using MP2 and B3LYP methods. These results demonstrate the importance of electron correlation.

On the other hand, intermolecular interaction including lithium atom is interested. Such lithium bonding plays an important role for further improvement of lithium-ion battery [10]. Salai *et al.* [11] have investigated $H_2CY\cdots LiF$ (Y = O, S) complexes theoretically choosing ten possible orientations, where the most stable form was a structure with strong lithium bonding interaction rather than that with hydrogen bonding interaction. Furthermore, π-lithium bonding is the most stable structure in LiF complexes with benzene, ethylene, and acetylene [12].

In this paper, we focus on the system $C_2H_2\cdots HLi$, which has been reported as dihydrogen bonded system [13]. In most of the previous studies, however, such intermolecular interactions are discussed in the equilibrium geometry, where the effects of quantum zero-point vibration and thermal activation are neglected. Thus, we have performed *ab initio* path integral molecular dynamics (PIMD) simulation for the isotopomers of $C_2H_2\cdots HLi$ species to discuss the thermal, quantum, and isotope effects on the average structure.

2. Computational method

The geometries of $C_2H_2\cdots HLi$ have been optimized by conventional molecular orbital (MO) method using the second-order Møller–Plesset perturbation theory (MP2) with 6-31++G** basis set. The *ab initio* PIMD

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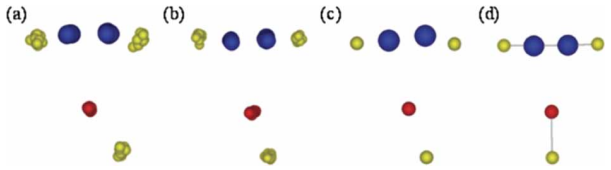

Figure 1. Representative snapshots for (a) $C_2H_2\cdots$HLi in *ab initio* PIMD, (b) $C_2D_2\cdots$DLi in *ab initio* PIMD, and (c) $C_2H_2\cdots$HLi in classical MD. Schematic illustration of $C_2H_2\cdots$HLi by (d) conventional MO.

simulation was done in essentially the same way as in our previous works [14–16]. The *ab initio* PIMD program code is developed based on velocity-Verlet time integrator with multiple time step algorithm and massive Nosé–Hoover chain thermostat algorithm [17,18] using normal mode coordinates. The Born–Oppenheimer potential and forces were calculated by MP2/6-31++G** level using GAUSSIAN 03 code [19]. The PIMD calculation was carried out at temperature $T = 300$ K with the imaginary time slices $P = 16$ (i.e. number of beads), the step size $\Delta t = 0.1$ fs, and the chain length parameter $L = 4$. The 16-CPU Pentium-IV (3.0 GHz) parallel computer cluster was used with MPI library for our *ab initio* PIMD code. In addition, the *ab initio* classical MD simulation has been performed by setting $P = 1$. In the classical simulation, the distribution of molecular configuration obeys classical Boltzmann–Gibbs statistics. The sampling was done for 40,000 and 280,000 time steps after thermal equilibration run of 10,000 and 20,000 steps, respectively. By comparing quantum and classical simulations, we can discuss the contribution due to quantization of nuclear degrees of freedom. Figure 1(a),(b) show the representative snapshots of the *ab initio* PIMD simulation for $C_2H_2\cdots$HLi and $C_2D_2\cdots$DLi, respectively. Also, figure 1 (c) is the snapshot in the classical MD, and the equilibrium geometry is shown in figure 1(d).

3. Results and discussion

Figure 2 shows the relative energies (ΔE (kcal/mol)) of some configurations for $C_2H_2\cdots$HLi by conventional MO method. The geometry with $\pi\cdots$lithium bonding (III) has been stabilized than that with dihydrogen bonding (I). The average geometries with PIMD are bent from the

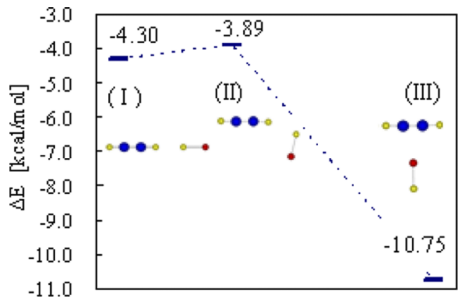

Figure 2. The relative energies (ΔE (kcal/mol)) for $C_2H_2\cdots$HLi by MP2/6-31++G** level of calculation.

Table 1. The geometrical results of intramolecular and intermolecular distances in LiH, C_2H_2, $C_2H_2\cdots$HLi and their isotopomers [Å].

		PIMD(H)	*PIMD(D)*	*Classical*	*Equilibrium*
LiH	$\langle R_{LiH}\rangle$	1.650	1.646	1.637	1.625
	ΔR_{LiH}	0.115	0.101	0.064	–
C_2H_2	$\langle R_{CC}\rangle$	1.230	1.229	1.225	1.221
	ΔR_{CC}	0.035	0.037	0.016	–
	$\langle R_{CH}\rangle$	1.080	1.077	1.067	1.064
	ΔR_{CH}	0.069	0.061	0.025	–
$C_2H_2\cdots$HLi	$\langle R_{LiH}\rangle$	1.653	1.653	1.641	1.627
	ΔR_{LiH}	0.113	0.117	0.065	–
	$\langle R_{CC}\rangle$	1.231	1.231	1.227	1.223
	ΔR_{CC}	0.035	0.035	0.017	–
	$\langle R_{CH}\rangle$	1.083	1.080	1.070	1.067
	ΔR_{CH}	0.068	0.061	0.026	–
	$\langle R_{\pi Li}\rangle$	2.377	2.400	2.418	2.347
	$\Delta R_{\pi Li}$	0.083	0.125	0.143	–
	$\langle \theta_{\pi LiH}\rangle$	151.5	149.2	146.2	180.0
	$\Delta\theta_{\pi LiH}$	14.3	13.9	17.0	–

equilibrium geometry of (III) due to the fluctuations by thermal and quantum effects as shown in figure 1.

Table 1 shows the geometrical results for LiH and C_2H_2 monomers, $C_2H_2\cdots$HLi cluster, and their isotopomers, in the *ab initio* PIMD, classical MD, and equilibrium structure. The abbreviations "H" and "D" are used for the H-species (LiH, C_2H_2, and $C_2H_2\cdots$HLi) and for the D-species (LiD, C_2D_2, and $C_2D_2\cdots$DLi), respectively. Table 1 shows the average bond lengths for LiH (R_{LiH}), C—C (R_{CC}), CH (R_{CH}), $\pi\cdots$Li ($R_{\pi Li}$), angle for $\pi\cdots$Li—H ($\theta_{\pi LiH}$), and their dispersion values, where π is defined as the position at the middle point between two carbons.

In Table 1, the average values of Li—H, C—C, and C—H bond lengths in classical MD are larger than that of equilibrium structure. These elongations are due to the thermal effect under the anharmonic potential. The average values for bond lengths in PIMD are also larger than that in classical MD due to the quantum effect. For a similar reason, the dispersion values in PIMD are also larger than that in classical MD. On the other hand, seeing the intermolecular $\pi\cdots$Li distance and $\pi\cdots$Li—H angle, the average value of $R_{\pi Li}$ in classical MD is largest in all simulations. In term of H/D isotope effect, the $\langle R_{\pi Li}\rangle$ of D-species in PIMD is larger than that of H-species in PIMD. For the $\pi\cdots$Li—D bond angle, the average structure is bending comparing with T-shape equilibrium geometry, due to fluctuation by quantum and thermal effects. The average values for $\pi\cdots$Li—D bond angle of D-species in PIMD are slightly smaller than that of H-species in PIMD, while the average value for $\pi\cdots$Li—H bond angle in classical MD is smallest in all simulation.

To elucidate such fluctuation of intermolecular bending between C_2H_2 and LiH molecules, we show the two dimensional distribution of $(\theta_{\pi LiH}, R_{HH})$ and $(\theta_{\pi LiH}, \phi_{C\pi LiH})$ in figures 3 and 4, respectively, where the $\phi_{C\pi LiH}$ is the dihedral angle of C—π—Li—H. In figure 3, the distribution is localized on the region nearby equilibrium geometry at $(\theta_{\pi LiH}, R_{HH}) = (180°, 4.3\,Å)$ for both quantum and classical simulations, which indicates that this system mainly has the $\pi\cdots$Li bonded geometry. Next, we focus on the dihedral angle of $\phi_{C\pi LiH}$. Figure 4

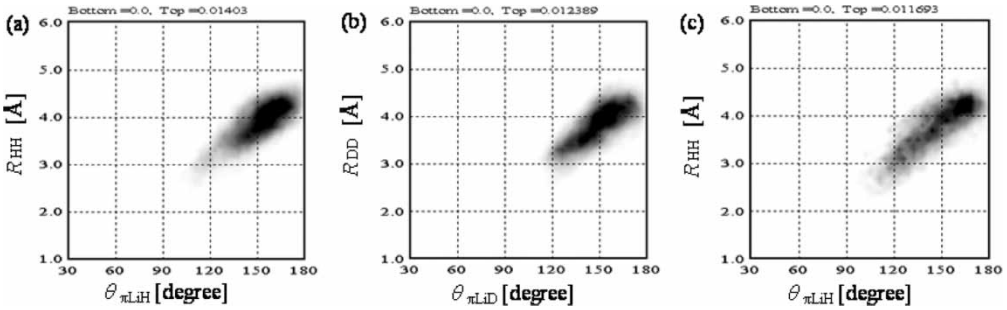

Figure 3. Two-dimensional distribution of $\theta_{\pi LiH}$ and R_{HH}: (a) $C_2H_2\cdots HLi$ in *ab initio* PIMD; (b) $C_2D_2\cdots DLi$ in *ab initio* PIMD; and (c) $C_2H_2\cdots HLi$ classical MD.

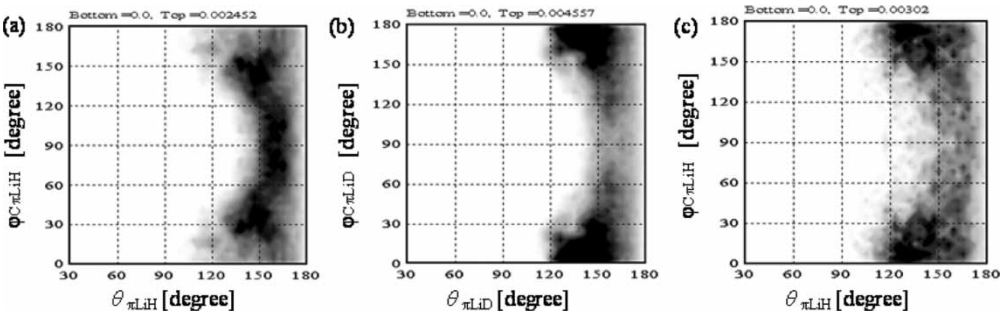

Figure 4. Two-dimensional distribution of $\theta_{\pi LiH}$ and $\phi_{C\pi LiH}$: (a) $C_2H_2\cdots HLi$ in *ab initio* PIMD; (b) $C_2D_2\cdots DLi$ in *ab initio* PIMD; and (c) $C_2H_2\cdots HLi$ classical MD.

(a) shows that the distribution of $\phi_{C\pi LiH}$ direction in H-species is delocalized overall, while figure 4(b),(c) show that on $\phi_{C\pi LiH} = 0^\circ$ and 180° by the deuteron substitutions and classical MD. These results mean that the out-of-plane fluctuation is characterized for light hydrogen systems, while in-plane fluctuation is characterized for heavy hydrogen and classical systems. The stable structures are found at $\phi_{C\pi LiH} = 0$ and 180°, i.e. in-plane geometry, while the transition structure is at $\phi_{C\pi LiH} = 90^\circ$. To see such H/D isotope and quantum effects, we show the two dimensional potential energy surface of $\theta_{\pi LiH}$ and $\phi_{C\pi LiH}$ for $C_2H_2\cdots HLi$ in figure 5. Certainly, the distributions along potential energy surface have been obtained in PIMD and classical MD. The localization of the distributions for D-species and classical MD is due to contributions of multi-dimensional coordinates, such as $\theta_{\pi LiH}$, $\phi_{C\pi LiH}$, and $R_{\pi Li}$.

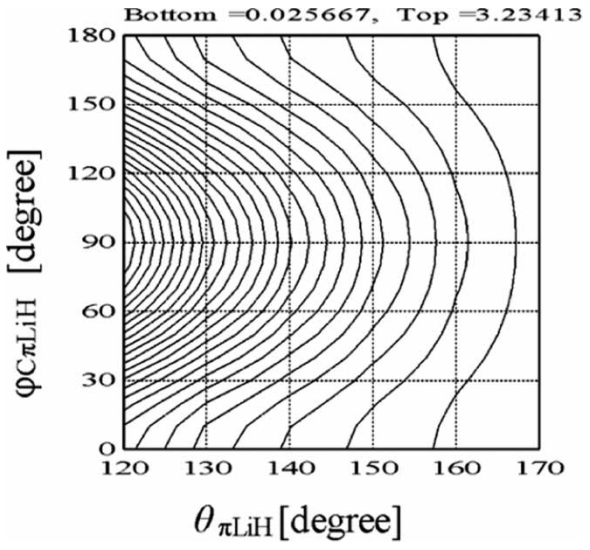

Figure 5. The two dimensional potential energy surface of $\theta_{\pi LiH}$ and $\phi_{C\pi LiH}$ for $C_2H_2\cdots HLi$.

4. Conclusions

We have calculated the dihydrogen bonded systems of $C_2H_2\cdots HLi$ by *ab initio* MO and *ab initio* path integral molecular dynamics method. We have found that the $\pi\cdots Li$ bonding with T-shape geometry is more stable than dihydrogen bonded linear geometry. By using *ab initio* PIMD, we have found the H/D isotope and quantum effects that the $\pi\cdots Li$ bond length of H-species is shorter than those of D-species and classical MD. Additionally, the fluctuation of LiH molecule in H-species ($C_2H_2\cdots HLi$) is out-of-plane, while those in D-species ($C_2D_2\cdots DLi$) and classical MD are in-plane. Another alkali hydride clusters are now in progress.

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References

[1] G.R. Desiraju, T. Steiner (Eds.), *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Chapter 3, Oxford (1999).
[2] P. Hobza, Z. Havlas. Blue-shifting hydrogen bonds. *Chem. Rev.*, **100**, 4253 (2000).
[3] R. Custelcean, J.E. Jackson. Dihydrogen bonding: structures, energetics, and dynamics. *Chem. Rev.*, **101**, 1963 (2001).
[4] A. Hayashi, M. Shiga, M. Tachikawa. *Ab initio* path integral molecular dynamics simulation study on the dihydrogen bond of $NH_4^+ \cdots BeH_2$. *Chem. Phys. Lett.*, **410**, 54 (2005).
[5] S.J. Grabowski, T.L. Robinson, J. Leszczynski. Strong dihydrogen bonds—*ab initio* and atom in molecules study. *Chem. Phys. Lett.*, **386**, 44 (2004).
[6] D. Hugas, S. Simon, M. Duran. MH···HX dihydrogen bond with M = Li, Na, and X = F, Cl, Br: a CP-corrected PES calculation and an AIM analysis. *Struct. Chem.*, **16**, 257 (2005).
[7] K.N. Robertson, O. Knop, T.S. Cameron. C—H···H—C interactions in organoammonium tetraphenylborates: another look at dihydrogen bonds. *Can. J. Chem.*, **81**, 727 (2003).
[8] P.C. Singh, G.N. Patwari. Theoretical investigation of C—H···H—B dihydrogen bonded complexes of acetylenes with borane-trimethylamine. *Chem. Phys. Lett.*, **419**, 5 (2006).
[9] P.C. Singh, N. Patwari. The C—H···H—B dihydrogen bonded borane-trimethylamine dimer: a computational study. *Chem. Phys. Lett.*, **419**, 265 (2006).
[10] Y. Wang, P.B. Balbuena. Adsorption and 2-dimensional association of lithium alkyl dicarbonates on the graphite surface through $O^- \cdots Li^+ \cdots \pi$ (arene) interactions. *J. Phys. Chem. B*, **107**, 5503 (2003).
[11] S. Salai Cheettu Ammal, P. Venuvanalingam, Sourav Pal. Lithium bonding interaction in $H_2CY \cdots LiH$ (Y = O, S) complexes: a theoretical probe. *J. Chem. Phys.*, **107**, 4329 (1997).
[12] S. Salai Cheettu Ammal, P. Venuvanalingam. π-Systems as lithium/hydrogen bond acceptors: some theoretical observations. *J. Chem. Phys.*, **109**, 9820 (1998).
[13] S.J. Grabowski, W.A. Sokalski, J. Lezczynski. Nature of $X—H^{+\delta} \cdots {}^{-\delta}H—Y$ dihydrogen bonds and $X—H \cdots \sigma$ interactions. *J. Phys. Chem. A*, **108**, 5823 (2004).
[14] M. Shiga, M. Tachikawa, S. Miura. A unified scheme for *ab initio* molecular orbital theory and path integral molecular dynamics. *J. Chem. Phys.*, **115**, 9149 (2001).
[15] M. Tachikawa, M. Shiga. Theoretical study on isotope and temperature effect in hydronium ion using *ab initio* path integral simulation. *J. Chem. Phys.*, **121**, 5985 (2004).
[16] M. Tachikawa, M. Shiga. Geometrical H/D Isotope effect on hydrogen bonds in charged water clusters. *J. Am. Chem. Soc.*, **127**, 11908 (2005).
[17] S. Nosé. A unified formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.*, **81**, 511 (1984).
[18] G.J. Martyna, M.L. Klein, M.E. Tuckerman. Nosé–Hoover chains: the canonicalensemble via continuous dynamics. *J. Chem. Phys.*, **97**, 2635 (1992).
[19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al. GAUSSIAN 03. Revision B.05, Gaussian, Inc., Pittsburgh PA (2003).