jh200004-NAH

分子性結晶における水素ダイナミクスと同位体効果の起源解明

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Abstract

Nuclear Quantum Effect (NQE), such as zero-point vibrational energy, tunneling, and its H/D isotope effect, is quite important in various systems from small molecules to material or biochemical complex species. Especially, in the case of "Low Barrier Hydrogen Bonding (LBHB) systems", NQE of proton (or deuteron) is indispensable. To elucidate such hydrogen-functional mechanism, we will develop some ab initio approaches for multi-component systems including both electrons and nuclei quantum-mechanically: (I) Multi-component density functional theory (MC_DFT) and (II) *ab initio* path integral molecular dynamics (PIMD) methods.

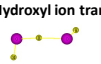
What is LBHB (Low Barrier Hydrogen Bonding) ?

•HB patterns by Jefferey [1]

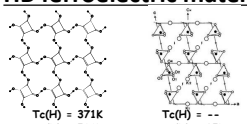
	Weak	Medium	Strong
HB Strength (kcal/mol)	< 4	4 - 15	15 - 40 (Ionic HB)
Example (X-H…A)	C-H……O	O-H….O	O-H…O⁻ F-H-F⁻
Geometric Isotope Effect (R_{XA})	Longer	Longer	?? LBHB	Shorter

[1] G. A. Jefferey, An Introduction to Hydrogen Bonding, (Oxford University Press 1997).

•Zundel structure of $H_3O_2^-$
Hydroxyl ion transfer in aqueous solution



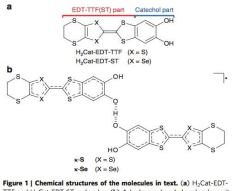
•HB ferroelectric materials



The Tc increases (more than 100K) by deuteration!

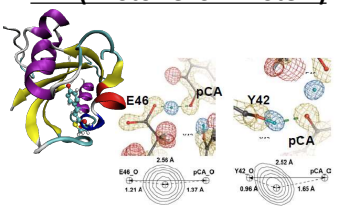
Where is LBHB?

•$H_3(Cat\text{-}EDT\text{-}TTF)_2$



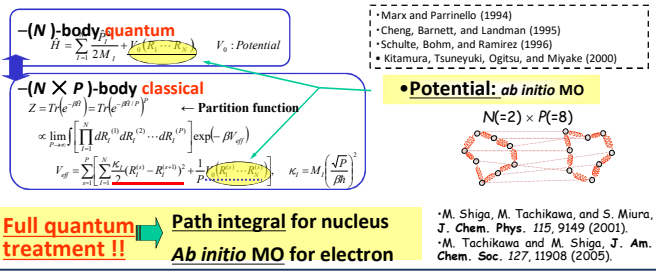
The phase transition is found only for κ-D

•PYP (Photo Yellow Protein)



The formation of LBHB is found in PYP by neutron crystallography

ab initio PIMD



- Marx and Parrinello (1994)
- Cheng, Barnett, and Landman (1995)
- Schulte, Bohm, and Ramirez (1996)
- Kitamura, Tsuneyuki, Ogitsu, and Miyake (2000)

- M. Shiga, M. Tachikawa, and S. Miura, *J. Chem. Phys.* *115*, 9149 (2001).
- M. Tachikawa and M. Shiga, *J. Am. Chem. Soc.* *127*, 11908 (2005).

ab initio MC_DFT

- Hamiltonian for Multi-Component system

(Electron: N, Classical nuclei: M, Quantum nuclei: L)

$$\hat{H}_{(e+p)} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} - \sum_{a=1}^{L}\frac{1}{2m_a}\nabla_a^2 - \sum_{i=1}^{N}\sum_{a=1}^{L}\frac{1}{r_{ia}} + \sum_{a=1}^{L}\sum_{A=1}^{M}\frac{Z_A}{r_{aA}} + \sum_{a=1}^{L}\sum_{b>a}^{L}\frac{1}{r_{ab}}$$

↑Conventional DFT ↑Quantum nuclei

- Kohn-Sham (KS) eq. for MC_DFT

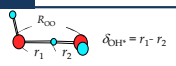
$$f_{e,p}^{(\mathrm{KS})}\phi_i = \varepsilon_i^{e,p}\phi_i^{e,p}$$

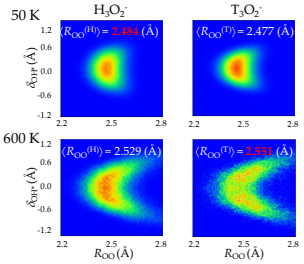
KS operator for MC_DFT

$$\text{Electron: } f_e^{(\mathrm{KS})} = h_e + \sum_e^N J_e - \sum_p^M J_p + V_{\mathrm{XC}(e-e)}, \qquad \text{Quantum nuclei: } f_p^{(\mathrm{KS})} = h_p + \sum_p^N J_p - \sum_e^M J_e$$

Nuclear quantum effect on $H_3O_2^-$

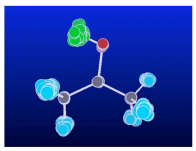
- **2D distribution with respect to δ_{OH^*} and R_{OO} [3]**

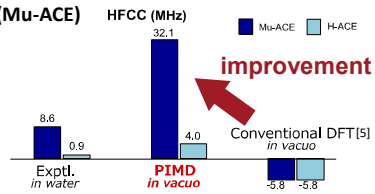




- At 50K, average OO bond length of $T_3O_2^-$ is shorter than that of $H_3O_2^-$ due to the anharmonicity of the potential, which is a similar result of QMC.
- At 600K, average OO bond length of $T_3O_2^-$ is longer than that of $H_3O_2^-$, which is a similar result of our previous PIMD.

- **Muoniated acetone radical (Mu-ACE)**

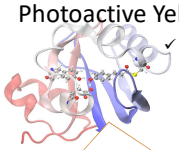




Our HFCC using PIMD qualitatively reproduced experimental HFCC.

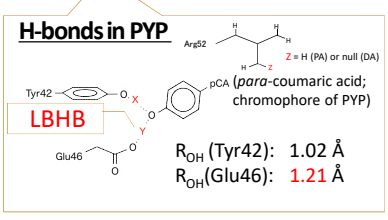
Nuclear quantum effect on PYP

Photoactive Yellow Protein (PYP)

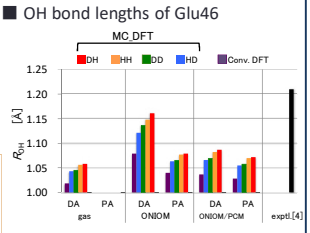


✓ Neutron crystallography demonstrated the formation of LBHB in PYP, which was assumed to play the important role in photosencing process.[4]

H-bonds in PYP

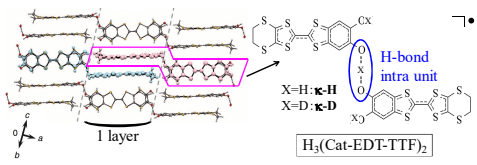


■ OH bond lengths of Glu46

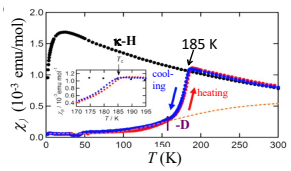


→The significant elongation of OH bond is possible when Arg52 is deprotonated.

Nuclear quantum effect on $H_3(Cat\text{-}EDT\text{-}TTF)_2$



Magnetic susceptibility[2]



X-ray structure[2]

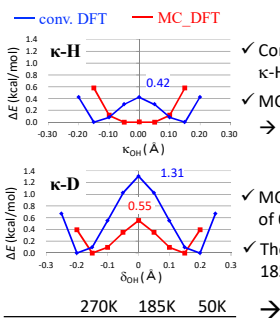
	High temp.	Low temp.
κ-H	d_{OO}=2.435 Å, d_{OH}=1.275 Å, center	d_{OO}=2.486 Å, d_{OH}=1.233 Å, center
κ-D	d_{OO}=2.501 Å, d_{OH}=1.265 Å, center	d_{OO}=2.501 Å, d_{OH}=1.017 Å, *off-center*

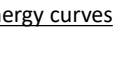
✓ Purely organic single-component conductor composed of only **κ-H(D)** has recently developed.
✓ **The phase transition is found only for κ-D.**

Geometry
- κ-H(D) has intra-unit hydrogen bond
- Molecular arrangement formed "κ-type"

Physical Property
- κ-H has lowest electrical resistivity at room temp. in purely organic single-component conductor.
- κ-D has specific temperature dependence in electric resistivity and magnetic susceptibility.

Comparison of the potential energy curves





✓ Conventional DFT provides **double-well** potential energy curves both for κ-H and κ-D.
✓ MC_DFT provides **single-well** effective PEC for κ-H.
→ Nuclear quantum effect decreases the proton-transfer barrier to locate the proton on **the center of the H-bond,** without dependence on the temperature.
✓ MC_DFT provides double-well effective PEC for κ-D with the barrier height of **0.55 kcal/mol, which corresponds to the thermal energy at 185 K.**
✓ The barrier height of 0.55 kcal/mol corresponds to the thermal energy at 185 K.

	270K	185K	50K
3/2 k_BT [kcal/mol]	0.81	0.55	0.15

→The localization of the deuteron on off-center can be the trigger of the phase transition.

[1] T. Isono, H. Kamo, A. Ueda, K. Takahashi, A. Nakao, R. Kumai, H. Nakao, K. Kobayashi, Y. Murakami and H. Mori, *Nat. Commun.* **2013,** 4, 1344 [2] A. Ueda, S. Yamada, T. Isono, H. Kamo, A.Nakao, R. Kumai, H. Nakao, Y. Murakami, . Yamamoto, Y. Nishio and Hatsumi Mori, *J. Am. Chem. Soc.* **2014**, 136, 12184–12192 [3] T. Udagawa, M. Tachikawa, *J. Chem. Phys.*, **2006**, 125, 244105 [4] S. Yamaguchi, H. Kamikubo, et al., *Proc. Natl. Acad. Sci.*, **106**, 440 (2009). [5] R. M. Macrae et al., *Physica B*, **326** 81 (2003).