Chemical Physics Letters 674 (2017) 168–172

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Editor's choice

Multicomponent DFT study of geometrical H/D isotope effect on hydrogen-bonded organic conductor, κ-H_3(Cat EDT-ST)$_2$

Kaichi Yamamoto [a], Yusuke Kanematsu [b], Umpei Nagashima [c], Akira Ueda [d], Hatsumi Mori [d], Masanori Tachikawa [a,*]

[a] Graduate School of Nanobioscience, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama-City, Kanagawa 236-0027, Japan
[b] Faculty of Information Sciences, Hiroshima City University, 3-4-1, Ozuka-Higashi, Asa-Minami-Ku, Hiroshima 731-3194, Japan
[c] Foundation for Computational Science (FOCUS), 7-1-28, Minatojimaminamimachi, Chuo-ku, Kobe 650-0047, Japan
[d] The Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan

ARTICLE INFO

Article history:
Received 24 January 2017
In final form 22 February 2017
Available online 24 February 2017

Keywords:
Multicomponent density functional theory
Geometrical isotope effect
Hydrogen-bond
π-electron system
Nuclear quantum effect

ABSTRACT

We theoretically investigated a significant contraction of the hydrogen-bonding O···O distance upon H/D substitution in our recently developed purely organic crystals, κ-H_3(Cat-EDT-ST)$_2$ (H-ST) and its isotopologue κ-D_3(Cat-EDT-ST)$_2$ (D-ST), having π-electron systems coupled with hydrogen-bonding fluctuation. The origin of this geometrical H/D isotope effect was elucidated by using the multicomponent DFT method, which takes the H/D nuclear quantum effect into account. The optimized O···O distance in H-ST was found to be longer than that in D-ST due to the anharmonicity of the potential energy curve along the O—H bond direction, which was in reasonable agreement with the experimental trend.

1. Introduction

Isotopic substitution of hydrogen by deuterium sometimes causes small but interesting changes on molecular structures [1–7], phase transition temperatures of hydrogen-bonds [8–13], and some physical properties [14–18], which are well known as H/D isotope effects [1–20]. Especially, the geometrical isotope effect (GIE) by the deuteration is known to be significant for hydrogen-bonding (H-bonding) systems. It was also reported that the nuclear quantum effect and the potential anharmonicity strongly affected GIEs on the distance between the heavy atoms of H-bonding systems [21,22].

One of the most famous examples of GIE in H-bonding systems is observed in tetragonal H-bonded ferroelectric KH_2PO_4 (KDP)-type crystals, in which the distance between the H-bonded oxygen atoms is extended by 9.7×10^{-3} Å by the deuteration [2]. A similar elongation of the H-bonded distance was also observed for other KDP-type crystals such as RbH_2PO_4, KH_2AsO_4, and $NH_4H_2PO_4$ [6]. Another example of GIE was reported for ionic water clusters of $H_5O_2^+$ and $H_3O_2^-$ by *ab initio* path integral molecular dynamics (PIMD) method [22], which enabled the molecular simulation with incorporating the nuclear quantum effect. The PIMD simulation demonstrated that the deuteration of $H_3O_2^-$ resulted in the elongation of the average O···O distance as with typical cases mentioned above, while that of $H_5O_2^+$ resulted in the contraction. Such opposite GIEs were associated with the difference of the shapes of potential energy surfaces (PESs); the PES of $H_3O_2^-$ had double minima where the equilibrium H-bonding geometry was asymmetric [O—H···O], while the PES of $H_5O_2^+$ had a single minimum with symmetric [O···H···O] equilibrium geometry.

Theoretically, the H/D isotope effect is attributed to the difference of the quantum fluctuations between hydrogen and deuterium, which are not taken into account in the conventional classical molecular dynamics. Therefore, to theoretically analyze GIEs in H-bonding systems, it is indispensable to incorporate quantum effects of hydrogen nuclei by using adequate computational methods such as PIMD [22–26], multi-component molecular orbital of density functional theory schemes [27–32], and some other methods based on the vibrational Schrödinger equation [33–38].

Recently, Mori et al. have newly developed the H-bonded molecular-unit-based organic conductor crystal, κ-H_3(Cat-EDT-ST)$_2$ (abbreviated as H-ST), whose novelty lies in the fusion of short H-bonds and stacked π-electron systems [39]. H-ST consists of two crystallographically equivalent catechol-fused diselenadithiafulvalene (Cat-EDT-ST) skeletons linked by a symmetric anionic $[O\cdots H\cdots O]^{-1}$-type strong H-bond, as shown in Fig. 1a). Subsequently, the deuterated isotopologue of H-ST, that is κ-D_3(Cat-EDT-ST)$_2$

---

* Corresponding author.
E-mail address: tachi@yokohama-cu.ac.jp (M. Tachikawa).

http://dx.doi.org/10.1016/j.cplett.2017.02.073
0009-2614/

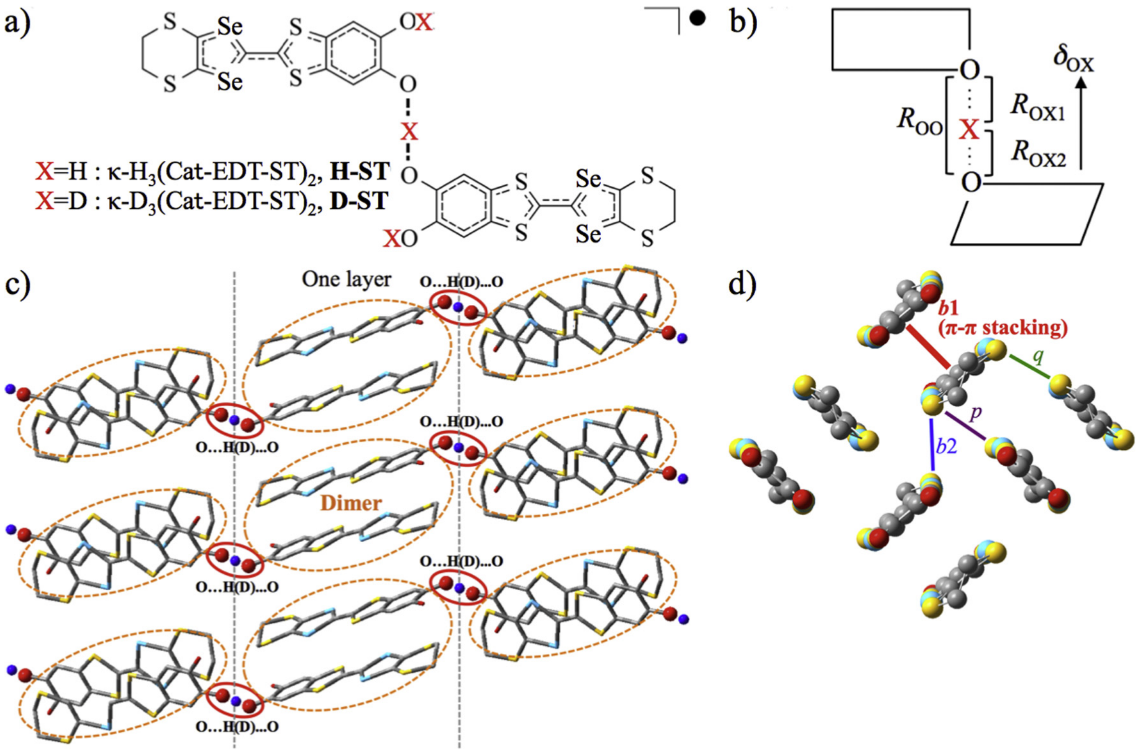

Fig. 1. (a) Molecular structure of H(D)-ST [39,40] and (b) its schematic illustration and the definition of H-bonding geometrical parameters. (c) The arrangement of H(D)-ST unit. Two units forms a π-dimer (dashed circle) and the neighboring dimers are connected by H-bond [O—H(D)—O]. (d) View of the 2D crystal structure in the layer shown in (c). There are four kind of inter-molecular interactions in the two-dimensional layer, namely, b1 (face-to-face π-π stacking), b2, p, and q [39,40]. All hydrogen atoms are omitted for simplicity of the figure. The unit structures of the H(D)-ST with the hydrogen atoms observed in refs. 39 and 40 are shown in the Supporting Information.

(abbreviated as D-ST), has also been developed [40]. The drastic deuterium isotope effect has been observed in the crystal structure and some physical properties. For instance, H-ST has shown a paramagnetic semiconducting behavior without transition, whereas D-ST has changed to a non-magnetic insulating state below 195 K, where the H-bonded dynamics-based phase transition has occurred.

Another interesting property of H-ST is the GIE on the H-bonding distance between two oxygen atoms (R_{OO}) in the high temperature phase. According to the X-ray crystal structure analysis (Fig. S3), R_{OO} of H-ST and D-ST at around room temperature were determined to be 2.509(8) and 2.497(6) Å, respectively [39,40]. Therefore, unlike typical GIEs, a small contraction in R_{OO} by the deuteration was observed in the H-ST. Recently, by using MC_DFT method [44], we revealed that face-to-face π-π stacking strongly affected the energy profile with respect to the hydrogen transfer in the H-bond of κ-X_3(Cat-EDT-TTF)$_2$ [X = H or D] [41–43], which is a Se/S substituted analogue of H(D)-ST. Importantly, we theoretically confirmed that hydrogen fluctuations in the H-bond and π-electron system were highly coupled each other [44]. From these reports, it was predicted that this H-bond–π-electron coupling, which was unprecedented for other H-bonding systems, caused such a specific GIE. However, no theoretical analysis has been performed to confirm it.

2. Computational method

We calculated the potential energy curves (PECs) of the 1-, 3-unit models of H(D)-ST by the conventional density functional theory (DFT). We also performed MC_DFT calculation to obtain the 'effective PECs' (eff-PECs) [30], which were effectively corrected by the hydrogen nuclear quantum effect, for these models of H(D)-ST. The detail of the MC_DFT methods can be found in the Supplementary Information and elsewhere [27–32]. In both the DFT and MC_DFT methods, a hybrid exchange-correlation functional of M05-2X [45] was employed without the spin restriction on molecular orbitals. We applied the 6-31++G(d,p) basis set for H-bonded three atoms [O···H···O] and the 6-31G(d) for the other atoms, and [1s] Gaussian-type functions (GTF) with exponents for quantum proton (24.1825 a.u.) and deuteron (35.6214 a.u.) optimized in the multicomponent HF scheme [46]. We assumed the spin multiplicity $S = n+1$ for $(\text{H-ST})_n$, according to the comparison of the energies of different spin states in κ-H_3(Cat-EDT-TTF)$_2$ at 50 K in the previous study [44]. We used the modified version of GAUSSIAN 09 program package, in which we have implemented our MC_DFT scheme.

3. Model systems

We treated several model systems based on the X-ray crystal structures of H-ST at 293 K and D-ST at 270 K [39,40]. Here, we introduce the model systems of H(D)-ST; 1-, 3-unit models. The 1-unit model is just a minimum molecular unit of the X-ray structure of the H(D)-ST as shown in Fig. 1a). The 3-unit model was constructed by picking out three molecules linked with the face-to-face π-π stacking from the X-ray structure, as shown in Fig. 2. Note that electron density of hydrogen atoms was experimentally observed by X-ray diffraction, and there were no missing atoms in the X-ray structures [39,40].

4. Results and discussion

4.1. Effective potential energy curves in the 1- and 3-unit models

H-ST and D-ST have a unique packing structure where the two-dimensional π-electron conducting layers shown in Fig. 1d) are