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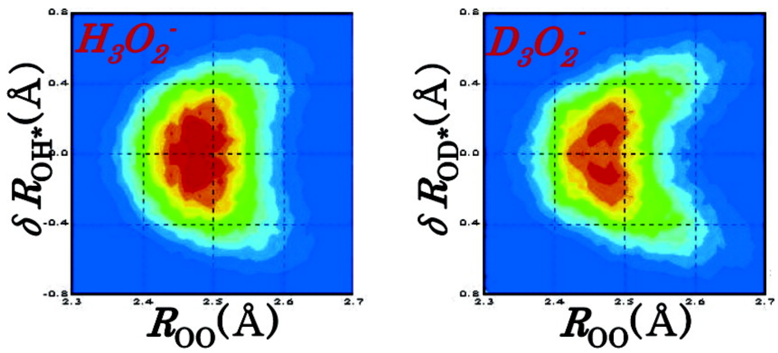

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Geometrical H/D Isotope Effect on Hydrogen Bonds in Charged Water Clusters

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The isotope substitution of shared hydrogen has a subtle effect on the geometry, but it will sometimes have large influence on some properties of hydrogen-bonded systems. For example, it is believed that the large isotope effect in the phase transition temperature of hydrogen-bonded ferroelectric crystals such as potassium dihydrogen phosphate (KDP) is due to a small structural modification of the crystal by deuterization.[1] In the neutral liquid water, it is known that the geometrical isotope effect is small, but it is measurable by the synchrotron X-ray experiments[2] and a recent ab initio simulation.[3]

There have been a number of reports on the protonated and hydroxylated water clusters such as $H_5O_2^+$ and $H_3O_2^-$ ions[4] since they are representative species in proton- or hydroxy-transfer processes of aqueous solutions.[5] In fact, the equilibrium structures[6] and vibrational spectrum[7] for these species are investigated from both experiment and theory. However, the isotope effect has not been reported in detail thus far, partly because these species have highly anharmonic motions that allow large-amplitude fluctuation in the geometries.[8]

The main subject of the present study is to address whether the geometrical isotope effect exists also for the hydrogen bonds in aqueous solutions or water clusters with acidity or basicity. We note that the interatomic forces are independent of the atomic masses and therefore the thermal distributions on the geometries of isotopomers are the same if the nuclei are treated classically. In this sense, the geometrical isotope effect is a purely quantum effect of nuclei.

Here, we study the isotope effect of $H_5O_2^+$ and $H_3O_2^-$ ions at the room temperature 300 K by ab initio path integral molecular dynamics (PIMD) simulation.[9] In this approach, the quantum nuclear distribution is obtained from the molecular dynamics for cyclic bead chains of atoms on the Born−Oppenheimer hypersurface, which is solved on the fly by ab initio quantum chemical calculation. In the present case, the ab initio calculation is performed based on the second-order Moller−Plesset perturbation theory (MP2) and 6-31+G** basis set by the Gaussian98[10] program package, since it is quantitative within kcal/mol accuracy for these hydrogen-bonded systems. Previously, we have confirmed that the barrier height of the pyramidal H_3O^+ ion has an accuracy of more than 90% at this level.[9] In this work, the ab initio PIMD run has been performed for 60 000 steps (6 ps) with the step size of 0.1 fs and $P = 24$.

In Figure 1, we show some representative snapshots from the PIMD simulation. We can see that these ionic species have a linear hydrogen bonding, sharing the hydrogen by two oxygens, O···H(D)···O, where the protons/deuterons are broadly distributed as a result of thermal and quantum fluctuations. The quantum statistical averages of molecular configurations are taken respectively for $H_5O_2^+$ and $H_3O_2^-$, and their isotopomers by running the independent PIMD simulations. For clarity, we label the shared proton and deuteron as “H*” and “D*”. Figure 2 shows the distribution of the OH*/OD* bond lengths.

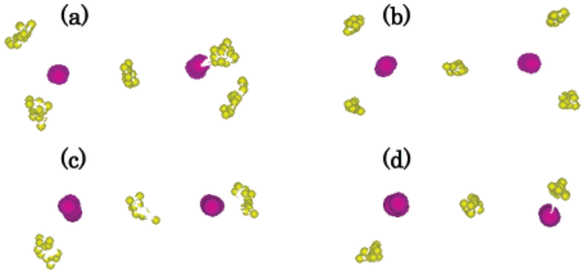

Figure 1. Representative snapshots in ab initio path integral molecular dynamics at 300 K for (a) $H_5O_2^+$, (b) $D_5O_2^+$, (c) $H_3O_2^-$, and (d) $D_3O_2^-$.

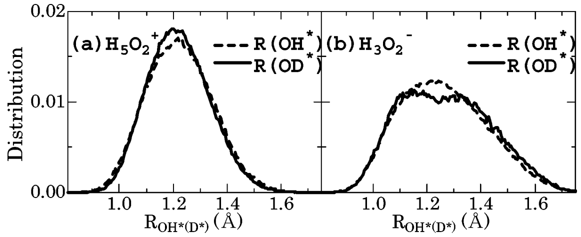

Figure 2. Distribution of OH*(OD*) bond length $R_{OH(D)*}$ in (a) $H(D)_5O_2^+$ and (b) $H(D)_3O_2^-$. (a) The average OH(D)* bond lengths of $H_5O_2^+$ and $D_5O_2^+$ are 1.224 and 1.220 Å, while the equilibrium one is 1.194 Å. (b) The average OH(D)* bond lengths of $H_3O_2^-$ and $D_3O_2^-$ are 1.261 and 1.262 Å, while the R_{OD*} distribution has two weak peaks at 1.15 and 1.35 Å. The equilibrium OH* bond lengths are 1.398 and 1.095 Å.

In the case of the cation, the average OH* bond length of $H_5O_2^+$ (1.224 Å), is longer than the $D_5O_2^+$ counterpart (1.220 Å). This bond length shift is similar to the case of the H_2O molecule and the H_3O^+ ion,[9] where the hydrogen is on a single-potential well. This can be explained from the difference of quantum zero-point fluctuation between the isotopomers on an anharmonic potential surface as to the OH* bonds. In fact, the shared proton of $H_5O_2^+$ ion has a single potential minimum located at the center of two oxygens in the equilibrium structure.[6] As shown in Figure 2a, the fluctuation of the R_{OH*} bond in $H_5O_2^+$ (the root-mean-square displacement of the OH* bond is $\Delta R_{OH*} = 0.122$ Å) is slightly larger than that of R_{OD*} in deuterated $D_5O_2^+$ ($\Delta R_{OD*} = 0.114$ Å). Then, the quantum fluctuation induces the anharmonic motion making the OH*(OD*) bonds stretch from the equilibrium position. The OO bonds stretch as the OH*(OD*) bonds stretch. In fact, the average OO bond distance of $H_5O_2^+$ (2.422 Å) is longer than that of $D_5O_2^+$ (2.418 Å). In this way, the two oxygens are subject to the repulsive force by the nuclear quantum effect of the shared proton/deuteron, which acts stronger in $H_5O_2^+$ than in $D_5O_2^+$.

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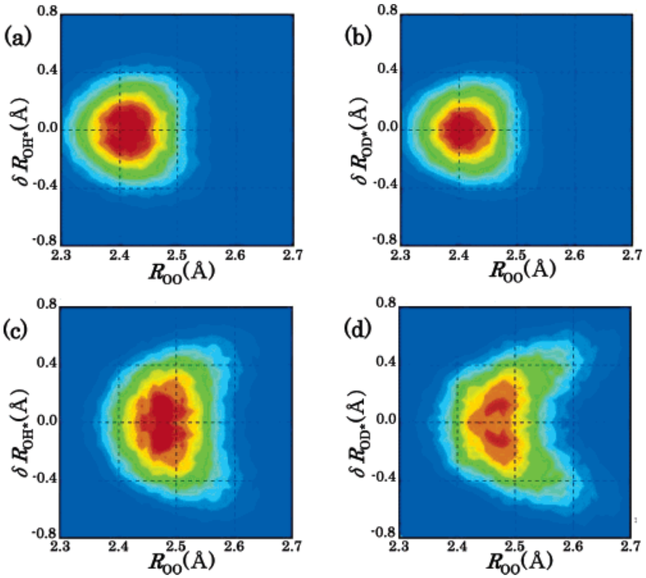

Figure 3. Two-dimensional distribution of (R_{OO}, $\delta R_{OH(D)*}$) for (a) $H_5O_2^+$, (b) $D_5O_2^+$, (c) $H_3O_2^-$, and (d) $D_3O_2^-$. The peak positions (R_{OO}, $\delta R_{OH(D)*}$) are around (2.42, 0.00) and (2.41, 0.00) for (a) $H_5O_2^+$ and (b) $D_5O_2^+$, while around (2.47, 0.00) and (2.48, ±0.15) for (c) $H_3O_2^-$, and (d) $D_3O_2^-$, respectively.

On the other hand, the geometric isotope effect is found differently in the $H_3O_2^-$ anion. First, the average OH*/OD* bond lengths, 1.261 and 1.262 Å, are almost the same for $H_3O_2^-$ and $D_3O_2^-$ ions. The potential surface of $H_3O_2^-$ has a double minima in which the structure is asymmetric.[6] The two different R_{OH*} equilibrium bond lengths (1.398 and 1.095 Å) indicate that the shared hydrogen has two positions on either oxygen side. Thus, the average bond lengths of R_{OH*} and R_{OD*} are between these two positions. However, Figure 2b shows the clear difference between the radial distributions of R_{OH*} and R_{OD*}. While the R_{OD*} distribution has two weak peaks at 1.15 and 1.35 Å, the R_{OH*} distribution has only one peak at the central position 1.26 Å. Second, the average bond length $\langle R_{OO}\rangle$ of $D_3O_2^-$ (2.504 Å) becomes longer than that of $H_3O_2^-$ (2.498 Å). This implies that the nuclear quantum effect works as an attractive force between the oxygen atoms, in contrast to the $H_5O_2^+$ case.

In Figure 3, the geometrical distributions are shown in more detail as two-dimensional contours with respect to R_{OO} and anti-symmetric stretching coordinates δR_{OH*} ($= R_{OaH*} - R_{ObH*}$). Contrary to the $H_5O_2^+$ case, two internal coordinates of R_{OO} and δR_{OH*} in $H_3O_2^-$ are strongly correlated each other. The peak positions (R_{OO}, δR_{OH*}) are found to be very close between $H_5O_2^+$ and $D_5O_2^+$ [around (2.42, 0.00) and (2.41, 0.00), respectively], while they differ substantially between $H_3O_2^-$ and $D_3O_2^-$ [around (2.47, 0.00) and (2.48, ±0.15), respectively]. In the case of $H_3O_2^-$ and $D_3O_2^-$, there is a potential minimum at (2.49, 0.30). However, in $H_3O_2^-$, the proton is highly delocalized by quantum effect, and these minimum structures are washed out. This is because the potential barrier between these minima is very low. By contrast, the quantum effect in $D_3O_2^-$ is not strong enough to completely wash out the minimum structures, and the double peaks in the distributions show that the delocalization of the deuteron in $D_3O_2^-$ is limited. Here, a large contribution to proton delocalization in $H_3O_2^-$ comes from the quantum effect.[4]

At this point, we discuss an unusual isotope effect wherein the R_{OO} bond length is smaller in $H_3O_2^-$ and $D_3O_2^-$. This is hard to explain from the potential anharmonicity of the OH* bond. Thus, we deal with this problem from a different point of view using the idea in the field of the hydrogen-bonded crystals. This is known as the "Ubbelohde effect",[11] which represents the lattice expansion of crystals as a result of the D substitution of O···H···O-type hydrogen bonds. The explanation of this effect is based on assumption that proton/deuteron mediates the attractive interaction of two oxygen. Chemically, the resonance of O···H−O and O−H···O is more likely to occur and the oxygens are more attractive by proton rather than by deuteron, because the proton can delocalize better than the deuteron. We consider that this idea can be used for the geometrical shift of $H_3O_2^-$ and $D_3O_2^-$ anions, since we have seen that proton is indeed more delocalized than deuteron in these systems. We note that the drastic difference in the delocalization can be realized under a relevant potential barrier at which the proton can exchange the hydrogen bonds easily while the deuteron cannot.

In summary, the results of ab initio path integral simulations have shown that the geometrical isotope effects for an $H_5O_2^+$ cation and an $H_3O_2^-$ anion are different from each other. By deuterization, the hydrogen bond is shortened in $H_5O_2^+$ while it is stretched in $H_3O_2^-$. We consider that there are two competing origins of the isotope shift. One comes from the difference of zero-point vibrations of the shared proton and deuteron which act as repulsive force between oxygens, and the other, which might be more interesting, comes from the difference of delocalization of the shared proton and deuteron which acts as an attractive force between oxygens. The former repulsion is dominant in the case of $H_5O_2^+$, where the shared hydrogen is in the single potential well between oxygens. However, the latter attraction becomes important in the case of $H_3O_2^-$ where the hydrogen is inclined to sit on either side of the double potential minima (nearer to one oxygen). In this case, the deuterization can localize on the shared deuteron, loosen the hydrogen bond, and as a result, lengthen the oxygen−oxygen distance.

Supporting Information Available: Complete ref 10. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Blinc, R. *J. Phys. Chem. Solids* **1960**, *13*, 204. (b) McMahon, M. I.; Nelmes, R. J.; Kuhs, W. F.; Derwarth, R.; Piltz, R. O.; Tun, Z. *Nature* **1990**, *348*, 317.
(2) (a) Tomberli, B.; Benmore, C. J.; Egelstaff, P. A.; Neuefeind, J.; Honkimaki, V. *J. Phys. Condens. Matter* **2000**, *12*, 2597. (b) Badyal, Y. S.; Price, D. L.; Saboungi, M. L.; Haeffner, D. R.; Shastri, S. D. *J. Chem. Phys.* **2002**, *116*, 10833.
(3) Chen, B.; Ivanov, I.; Klein, M. L.; Parrinello, M. *Phys. Rev. Lett.* **2003**, *91*, 215503.
(4) (a) Tuckerman, M. E.; Marx, D.; Klein, M. L.; Parrinello, M. *Science* **1997**, *275*, 817. (b) Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. *Nature* **1999**, *397*, 601. (c) Tuckerman, M. E.; Marx, D.; Parrinello, M. *Nature* **2002**, *417*, 926.
(5) (a) Agmon, N. *Isr. J. Chem.* **1999**, *39*, 493. (b) Agmon, N. *Chem. Phys. Lett.* **2000**, *319*, 247.
(6) (a) Auer, A. A.; Helgaker, T.; Klopper, W. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2235. (b) Samson, C. C. M.; Klopper, W. *J. Mol. Struct. (THEOCHEM)* **2002**, *586*, 201.
(7) (a) Asmis, K. R.; Pivonka, N. L.; Santambrogio, G.; Brummer, M.; Kaposta, C.; Neumark, D. M.; Woste, L. *Science* **2003**, *299*, 1375. (b) Robertson, W. H.; Diken, E. G.; Price, E. A.; Shin, J.-W.; Johnson, M. A. *Science* **2003**, *299*, 1367. (c) Diken, E. G.; Headrick, J. M.; Roscioli, J. R.; Bopp, J. C.; Johnson, M. A.; McCoy, A. B. *J. Phys. Chem. A* **2005**, *109*, 1487.
(8) (a) Dai, J.; Bacic, Z.; Huang, X.; Carter, S.; Bowman, J. M. *J. Chem. Phys.* **2003**, *119*, 6571. (b) Huang, X.; Braams, B. J.; Carter, S.; Bowman, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 5042.
(9) (a) Shiga, M.; Tachikawa, M.; Miura, S. *J. Chem. Phys.* **2001**, *115*, 9149. (b) Tachikawa, M.; Shiga, M. *J. Chem. Phys.* **2004**, *121*, 5985.
(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
(11) Ubbelohde, A. R.; Gallagher, K. J. *Acta Crystallogr.* **1955**, *8*, 71.

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