Molecular dynamics simulation based on the multi-component molecular orbital method : Application to H_50_2^+, D_50_2^+, and T_50_2^+

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Molecular dynamics simulation based on the multi-component molecular orbital method: Application to $H_5O_2^+$, $D_5O_2^+$, and $T_5O_2^+$

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Abstract

We propose a molecular dynamics (MD) method based on the multi-component molecular orbital (MC_MO) method, which takes into account the quantum effect of proton directly, for the detailed analyses of proton transfer in hydrogen bonding system. The MC_MO based MD (MC_MO-MD) method is applied to the basic structures, $H_5O_2^+$ (called "Zundel ion"), and its isotopomers ($D_5O_2^+$ and $T_5O_2^+$). We clearly demonstrate the geometrical difference of hydrogen bonded O⋯O distance induced by H/D/T isotope effect because the O⋯O in H-compound was longer than that in D- or T-compound. We also find the strong relation between stretching vibration of O⋯O and the distribution of hydrogen bonded protonic wavefunction because the protonic wavefunction tends to delocalize when the O⋯O distance becomes short during the dynamics. Our proposed MC_MO-MD simulation is expected as a powerful tool to analyze the proton dynamics in hydrogen bonding systems.

Keywords

molecular dynamics, nuclear quantum effect, MC_MO method, hydrogen bond, isotope effect

1. Introduction

Proton transfer reaction is ubiquitous as a basic process in the nature. Water mediates the proton transfer through water bridges in acid-base reactions in protein [1–3] and the proton transfer through water in membrane, such as Nafion, of polymer electrolyte fuel cell (PEFC) [4,5]. Although the proton transfer in aqueous environment is one of the most fundamental chemical reactions, details in many molecular behavior remain elusive. The H/D substitution is also widely used to characterize the proton transfer reaction. In fact, H/D isotope effect on amide bonds has been used to probe the relative contribution of hydrogen bonds to protein stability [6,7]. Interaction between a solvent and biomolecules is one the primary factors controlling protein folding and stability [8]. In addition, to obtain new insight for the hydronium ion in hydrated Nafion membranes, contract variation was analyzed by the use of several H_2O/D_2O mixtures [9]. Estimates of the effects of water concerning the proton transfer have been studied by using H_2O and D_2O [10,11]. Since the proton transfer via hydrogen bond is the result of a sensitive balance between intramolecular and hydration interaction, D_2O may alter the conformation and dynamics of hydrogen bonds in water. The H/D isotope effect is experimentally known as the Ubbelohde effect (i.e., deuterium forms weaker hydrogen bond than hydrogen) [12]. Because the solvent properties of D_2O differ from those of H_2O, it is expected to affect the proton transfer mechanism and stability during the dynamics.

To express the stability and proton transfer by autoionization of water molecule or acidic (basic) substrate in the aqueous solution, two fundamental structures, $H_3O_2^-$ and $H_5O_2^+$, involved in the proton transfer process are studied by experimental and theoretical approaches [13–36]. The deuterated species, $D_3O_2^-$ and $D_5O_2^+$, are also focused on the structures and vibrational spectra [37–44]. The bridging proton in $H_3O_2^-$ and $H_5O_2^+$ is located between two oxygen atoms. Tuckerman and co-workers carried out path integral molecular dynamics (PIMD) calculations to explore the quantum nature of hydrogen bonded systems [15]. Because their result suggested that hydrogen bonded proton is near the center of two oxygen atom, the nuclear quantum effect is quite important in these systems. In addition, Suzuki and co-worker reported the temperature dependence of a hydrogen bonded structure by using the PIMD [35].

One of the effective techniques to treat the proton transfer dynamics in hydrogen bonds is *ab initio* molecular dynamics (MD) method [45–47]. The *ab initio* MD permits hydrogen bond breaking and forming events by the proton transfer during the simulation. It is expected that the *ab initio* MD including nuclear quantum effect directly gives useful and important information concerning the proton transfer dynamics. It is however difficult to treat the nuclear quantum effect during *ab initio* MD simulation because the conventional electronic structure calculation to obtain the force for each nucleus is based on the Born-Oppenheimer (BO) approximation. As a non-BO approach, the multi-component molecular orbital (MC_MO) method has been proposed and applied to a variety of system [48–54]. Similar approaches based on non-BO treatment have been developed by several groups [55,56]. Although these methods are fundamentally similar concept, the description of nuclear orbital, which is usually used Gaussian-type function (GTF), is different. Since the orbital exponent and center values in nuclear GTF are given as constants in related methods, the MC_MO method is possible to optimize the orbital exponent and center values in nuclear GTF under the given molecular system. So, flexible and adequate description is possible for the nuclear wavefunction by using MC_MO method. The MC_MO method enables to analyze the nuclear quantum effect, such as proton and deuteron, in molecular system because this method determines both electronic and nuclear wavefunctions simultaneously and directly. We have already found that the MC_MO method has great success in analyses of the geometrical isotope effect (GIE) and kinetic isotope effect (KIE) induced by the H/D substitution [52,54]. It is expected that the *ab initio* MD with MC_MO method gives the new insight and knowledge for proton transfer dynamics.

In this paper, we proposed the MD approach based on the MC_MO method (MC_MO-MD) to treat nuclear quantum effect directly during the simulation. The $H_5O_2^+$ is used to show the efficiency of our proposed method. The most stable structure of $H_5O_2^+$ was first determined by using MC_MO method. Geometrical changes of hydrogen bonded $O\cdots O$ distance and the position of hydrogen bonded proton in $H_5O_2^+$ were carefully analyzed during the dynamics. The isotopomers, $D_5O_2^+$ and $T_5O_2^+$, were also calculated by using the MC_MO-MD method to analyze the H/D/T isotope effect. We finally analyzed the relationship of the change between $O\cdots O$ stretching vibration and distribution of hydrogen bonded nuclear wavefunction.

2. Computational Method

To analyze the motion of proton in hydrogen bonding system, we used Zundel ion, $H_5O_2^+$, and its isotopomers, $D_5O_2^+$ and $T_5O_2^+$. Hydrogen bonded proton, deuteron, and triton as well as the electrons are treated as quantum waves under the field of nuclear point charges. The single s-type ([1s]) GTF, $\exp\{-\alpha(r-R)^2\}$, was employed for basis functions of proton, deuteron, and triton. The position of the proton, deuteron, and triton treated as quantum waves was regarded as the GTF center of the [1s] GTF for proton, deuteron, and triton, respectively. For the detailed analysis of quantum behavior of proton, deuteron, and triton, the exponent (α) value in GTF for proton, deuteron, and triton was optimized. We performed the MD calculation based on the MC_MO under the second-order Møllet-Plesset (MP2) perturbation theory with 6-31G(*d*,*p*) basis set for electronic part. The MC_MO-MD simulations were performed for 2000 steps for all molecular systems with a time step of 1.0 fs (total 2.0 ps). The kinetic energy of 0.0010 a.u., which corresponds to the temperature of about 315 K, was assigned as the initial condition for each atom while the directions of the initial velocity were assigned randomly. The position of hydrogen bonded proton (deuteron and triton), which is treated as quantum wave, was optimized every step of the MD simulation under the fixed nuclear point charges. Then, the position of atoms treated as point charges was determined by the use of force obtained by MC_MO calculation after the optimization of hydrogen bonded proton (deuteron and triton), which is treated as quantum wave.

3. Results and Discussion

We first focused on the hydrogen bonds in the most stable structure of $H_5O_2^+$. The optimized structures of $H_5O_2^+$ under the MP2 level of theory with 6-31G(*d*,*p*) by using the conventional MO and MC_MO methods are shown in Fig. 1. The most stable structures of $H_5O_2^+$ obtained by the both conventional MO and MC_MO methods was that the hydrogen bonded proton is located at the center of two oxygen atoms. The O···H bond distance obtained by MC_MO calculation was longer than that obtained by conventional MO. This result indicates that the direct quantum treatment of proton by using wavefunction enables to flexibly describe the O···H bond structure due to the anharmonicity of the potential. The difference between conventional MO and MC_MO calculations shows similar tend obtained by Tuckerman et al [15]. The O···D bond distance in deuterated $D_5O_2^+$ was 0.0051 Å shorter than O···H. The result obtained MC_MO calculation is same as the previous report obtained by path integral MD simulation concerning the H/D isotope effect of $H_5O_2^+$ and $D_5O_2^+$. The α values in [1s] GTFs of hydrogen bonded proton and deuteron in $H_5O_2^+$ and $D_5O_2^+$ were 18.55 and 27.49, respectively. This difference indicates that the deuteronic wavefunction is localized than the protonic one. The difference of wavefunction distributions between proton and deuteron reflects to the difference of O···H and O···D bond distances. The O···T bond distance in $T_5O_2^+$ was the shortest in our MC_MO calculations.

We performed MD simulation based on the MC_MO method for $H_5O_2^+$, $D_5O_2^+$, and $T_5O_2^+$. The calculated results for $H_5O_2^+$, $D_5O_2^+$, and $T_5O_2^+$ are shown in Table 1. The ΔR in Table was estimated by following equation,

$$\Delta R = \mathrm{Abs}(R(O1\text{-}X^*) - R(O2\text{-}X^*)). \quad (1)$$

The symbol of X indicates H, D, or T. The maximum value of O···O distance was obtained by the $H_5O_2^+$ case, while the minimum value of O···O distance was obtained by the $T_5O_2^+$. This result indicates that the O···T bond in $T_5O_2^+$ is stronger than O···H in $H_5O_2^+$. We could clearly found the geometrical difference induced by H/D isotope effect because the average value of O···O distance in $H_5O_2^+$ was about 0.011 and 0.016 Å longer than those in $D_3O_2^-$ and $T_5O_2^+$. It is difficult to obtain such a geometrical difference by using the conventional *ab initio* MD simulation, although only the difference of total energy between $H_3O_2^-$ and $D_3O_2^-$ or $T_5O_2^+$ was expressed by the difference zero-point vibrational energy (ZPVE) between proton and deuteron. This result indicates that the different behavior of H/D/T isotopes is not adequately described by the only the treatment of the mass difference in conventional *ab initio* MD. The hydrogen bonded proton was almost located at the center of two oxygen atoms because the average of ΔR for $H_5O_2^+$ was about 0.03

Å. The total energy of $T_5O_2^+$ was larger than that of $H_5O_2^+$ and $D_5O_2^+$ due to the difference of nuclear kinetic energy. The analyses of vibrational frequencies and energy profiles are possible as well as the geometrical changes by using this method. It is expected that this method enables us to analyze the proton transfer reaction mechanism with the dynamics in detail.

In this study, we could not obtain enough result concerning the proton transfer reaction mechanisms because the $H_5O_2^+$ and its isotopomers have symmetrical structure. It is expected that we analyze the dynamics of proton transfer reaction mechanisms with nuclear quantum effect by applying the MC_MO-MD method to asymmetrical molecular systems. In addition, mixed isotopomers, such as $[H_2ODOH_2]^+$, $[D_2OHOD_2]^+$, and $[H_2OHOD_2]^+$, are interesting systems to be analyzed in the near future.

The α values in [1s] GTF for proton, deuteron, and triton is shown in Table 2. The wavefunction of triton was localized the most because the α value is the largest in comparison with both $H_3O_2^-$ and $D_3O_2^-$ systems. The values of half width for proton, deuteron, and triton were 0.16, 0.13, and 0.12, respectively. This value is one of the indexes to understand the distribution of wavefunction of proton, deuteron, and triton.

Finally, we focused on the relationship of the $O{\cdots}O$ distance, ΔR, and distribution of nuclear wavefunction. We show in Fig. 2 the trajectories of $O{\cdots}O$ distance, ΔR, and α value in [1s] GTF of $H_5O_2^+$, $D_5O_2^+$, and $T_5O_2^+$ from 500 to 1000 steps during the MC_MO-MD simulation. When the $O{\cdots}O$ distance became long, the protonic wavefunction tends to delocalize because the α value in [1s] GTF became small. Contrarily, when the $O{\cdots}O$ distance became short, the protonic wavefunction tends to localize because the α value in [1s] GTF became large. This result indicates the close connection between the stretching vibration of $O{\cdots}O$ and the wavefunction distribution of hydrogen bonded proton. We obtained the same tendency in the case of deuterated and tritiated species. In addition, the hydrogen bonded proton, deuteron, and triton is almost located at the center of two oxygen atoms during the MD simulation in the case of $H_5O_2^+$ and its isotopomers. The MC_MO-MD simulation, which takes into account the nuclear quantum effect directly, is powerful tool to analyze the proton dynamics, such as proton transfer, in hydrogen bond system.

4. Conclusions

In this study, to perform the *ab initio* MD simulation taking into account the quantum effect of proton, we proposed an approximated MD approach based on the MC_MO method and applied to the $H_5O_2^+$, $D_5O_2^+$, and $T_5O_2^+$. The hydrogen bonded proton is almost located at the center of two oxygen atoms in all $H_5O_2^+$, $D_5O_2^+$, and $T_5O_2^+$ obtained by MC_MO calculation, while we found the difference of O···X (X = H, D, and T) bond due to the difference of nuclear quantum effect. The MC_MO-MD method is possible to express the geometrical difference induced by the H/D isotope effect because the average of O···O distance during the dynamics in T-compound is shorter than that in H- or D-compounds. In addition, the change of α value in [1s] GTF in protonic wavefunction was carefully analyzed. We have found the important relationship between the O···O distance and α value in [1s] GTF during the MD simulations. Our proposed MC_MO-MD simulation, which takes into account the nuclear quantum effect directly, is powerful tool to analyze the proton dynamics, such as proton transfer, in hydrogen bond system.

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Table 1. Calculated geometrical parameters (O···O and ΔR) and total energy for $H_5O_2^+$, $D_5O_2^+$, and $T_5O_2^+$ obtained by MC_MO-MD simulations.

	O···O [Å]	ΔR [Å]	Energy [a.u.]
$H_5O_2^+$			
Maximum	2.428	0.027	–152.35066
Minimum	2.368	0.000	–152.35136
Average	2.399	0.011	–152.35104
Standard deviation	0.020	0.006	0.00016
$D_5O_2^+$			
Maximum	2.409	0.032	–152.35950
Minimum	2.366	0.000	–152.36002
Average	2.388	0.014	–152.35978
Standard deviation	0.014	0.008	0.00012
$T_5O_2^+$			
Maximum	2.401	0.037	–152.36350
Minimum	2.365	0.000	–152.36404
Average	2.383	0.016	–152.36377
Standard deviation	0.012	0.009	0.00011

Table 2. Exponent (α) value in [1s] GTF of the proton, deuteron, and triton for $H_5O_2^+$, $D_5O_2^+$, and $T_5O_2^+$ obtained by MC_MO-MD simulations.

	$H_5O_2^+$	$D_5O_2^+$	$T_5O_2^+$
Maximum	18.87	27.79	34.83
Minimum	18.18	27.17	34.10
Average	18.50	27.48	34.39
Standard deviation	0.17	0.16	0.15
Half width	0.16	0.13	0.12

Figure Captions

Figure 1. Optimized structures of $H_5O_2^+$, $D_5O_2^+$, and $T_5O_2^+$ by using the MC_MO calculation under the MP2/6-31G(*d*,*p*) level of theory. Geometrical parameters of $H_5O_2^+$ obtained by conventional MO calculation are shown in parentheses. The symbol of X indicates H, D, or T.

Figure 2. Trajectories of $O \cdots O$ distance (upper), ΔR (middle), and optimized α value (lower) of $H_5O_2^+$, $D_5O_2^+$, and $T_5O_2^+$ during the MC_MO-MD simulations from 500 to 1000 steps.

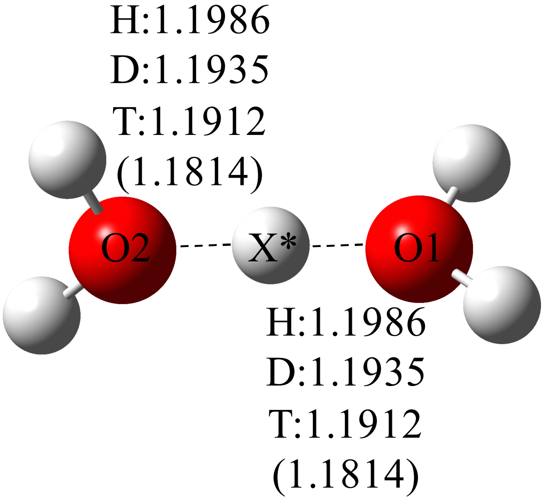

Figure. 1 Ishimoto et al.

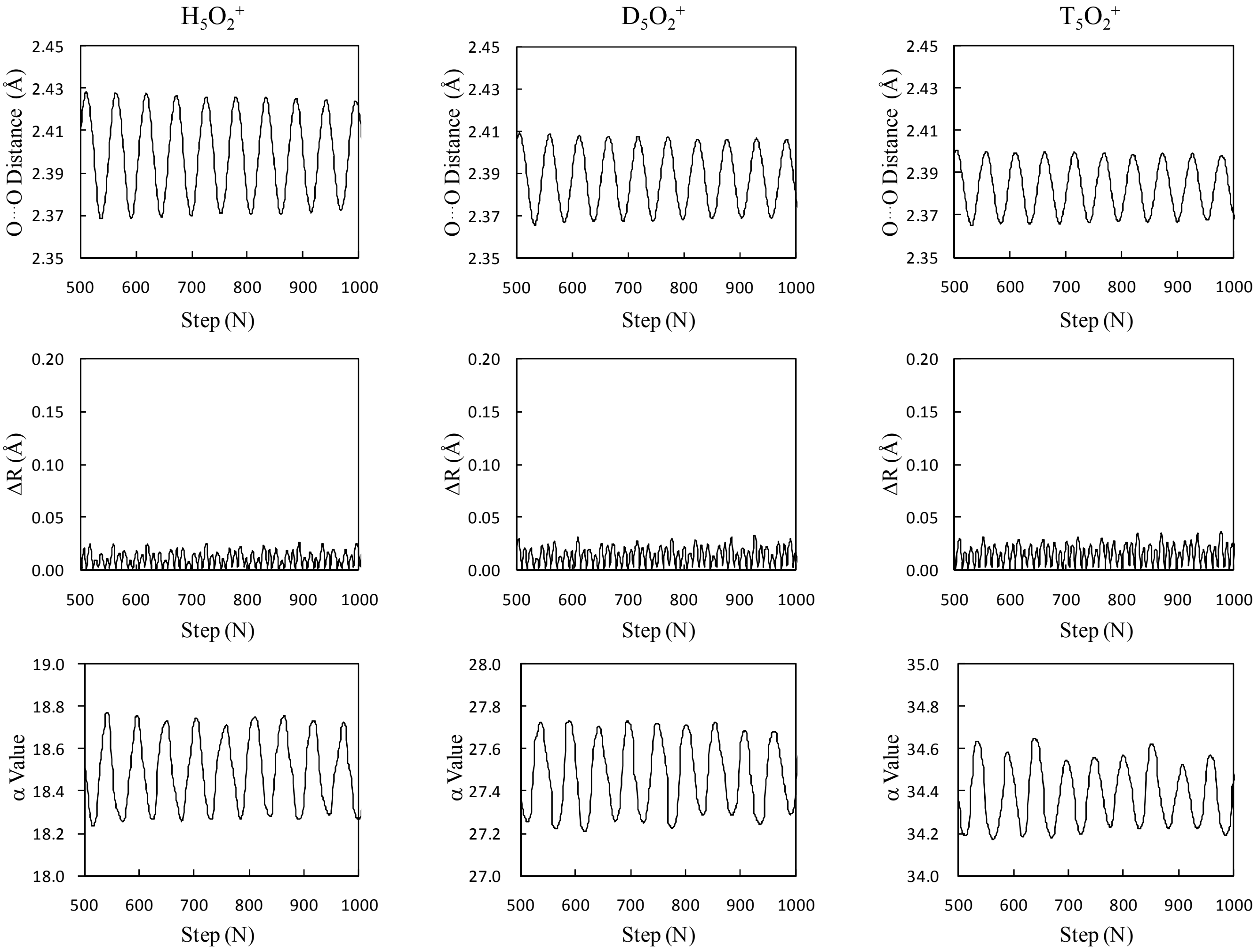

Figure. 2 Ishimoto et al.