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Path-integral molecular dynamics simulations of hydrated hydrogen chloride cluster $HCl(H_2O)_4$ on a semiempirical potential energy surface

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ABSTRACT

Path-integral molecular dynamics simulations for the $HCl(H_2O)_4$ cluster have been performed on the ground-state potential energy surface directly obtained on-the-fly from semiempirical PM3-MAIS molecular orbital calculations. It is found that the $HCl(H_2O)_4$ cluster has structural rearrangement above the temperature of 300 K showing a liquid-like behavior. Quantum mechanical fluctuation of hydrogen nuclei plays a significant role in structural arrangement processes in this cluster.

1. Introduction

Properties of $HCl(H_2O)_n$ clusters have extensively been studied from both experimental [1–6] and theoretical sides [7–29] in the past decade. This is largely because $HCl(H_2O)_n$ clusters are playing a key role in ozone depletion cycles in polar stratospheric clouds above Antarctica. It is generally accepted that ozone depletion processes are initialized by HCl dissociation on ice surface or in small water clusters [30–33]. In addition to this atmospheric context, microscopic understanding of the solvation and dissociation phenomena of strong acids in water systems has previously been the subject of fundamental interest. In particular, an important question is to understand how many water molecules are required to cause ionic dissociation of the HCl molecule in water environment.

Many theoretical studies have been carried out for small $HCl(H_2O)_n$ clusters [1,7–29]. Most of those studies were performed using electronic structure approaches including ab initio molecular orbital (MO) method and density-functional theory (DFT) method. For example, Packer and Clary [10] have done ab initio MP2-level calculations for the $HCl(H_2O)_n$ clusters up to $n = 3$ and found that ionic dissociation processes are not important in these small clusters. Re et al. [15] have performed systematic DFT calculations for $HCl(H_2O)_n$ ($n = 1–5$) clusters. They have reported that, in the case of $n = 4$ cluster, proton nontransferred (undissociated) and proton transferred (dissociated) zwitterionic structures have nearly similar potential energies. In the case of $n = 5$, they have shown that clusters have completely dissociated forms. Recently, Odde et al. [23] have carried out more systematic calculations for $HX(H_2O)_n$ clusters (X = F, Cl, Br, and I) up to $n = 6$ using B3LYP and MP2 levels of theory. They have theoretically shown that dissociated and undissociated clusters give very different vibrational spectra. All these previous electronic structure studies indicate that as least four water molecules are necessary to form stable structures in which positive and negative ions coexist in the cluster.

In addition to these ‘static’ electronic structure studies mentioned above, some classical molecular dynamics studies on $HCl(H_2O)_n$ clusters have been performed. Very recently, Masia et al. [27] have reported results of Car–Parinello molecular dynamics simulations [34] for deuterated $DCl(D_2O)_n$ clusters ($n = 1–6$) with a focus on autodissociation phenomenon of HCl acids as a function of the microsolvation environmental size. They have also discussed the relation between dynamical structures and infrared vibrational spectra in detail. A very similar study but for $HCl(H_2O)_6$ clusters have been independently done by Ndongmouo et al. [28] emphasizing the importance of temperature on the thermodynamics stability of various structures.

In this work we focus on the role of quantum mechanical nature of nuclei in a $HCl(H_2O)_4$ cluster using path-integral molecular dynamics (PIMD) method [35]. In the path-integral formalism, the quantum mechanical character of nuclei is described by a cyclic chain polymer composed of classical quasiparticles which are

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frequently called beads. Thermal equilibrium averages are computed from time averages over fictitious molecular dynamics trajectories generated from normal-mode equations of motion combined with a thermostat approach [36–41]. In our previous research, the PIMD approach combined with the ab initio electronic structure method and the corresponding computer code have been established [42–44]. This method generates the PIMD trajectory calculating potential energy and its derivatives on-the-fly using ab initio electronic structure codes such as the Gaussian program package [45]. Due to recent advances in computer power as well as in parallelizing techniques, ab initio (or first-principles) PIMD calculations are becoming feasible; however, it is still very expensive to use ab initio PIMD method to study the present $HCl(H_2O)_4$ system especially for the temperature range that structural rearrangement is important.

We have then decided to implement the semiempirical PM3-MAIS (Method Adapted for Intermolecular Studies) method, which has recently been developed by Bernal-Uruchurtu and Ruiz-López [46–49], into our code. In the PM3-MAIS method, only the core–core interaction terms in the semiempirical PM3 Hamiltonian [50] are modified so as to accurately reproduce interaction potential energies especially for hydrogen-bonded systems. In their most recent paper [49], numerical parameters used in the PM3-MAIS calculations have been developed to describe HCl dissociation in water clusters. Although the PM3-MAIS method predicts a slightly overestimated HCl acidity in water environment, they found that the overall agreement with previous ab initio MO as well as DFT calculations is satisfying. Therefore, it is quite encouraging for us to employ the PM3-MAIS method in the present PIMD simulations from the viewpoint of computational efficiency.

So far, $HCl(H_2O)_4$ cluster has been studied by molecular dynamics without taking account of nuclear quantum effect where nuclei have been assumed to be classical point charges (“classical simulation”, hereafter). In this paper, we use the PIMD method (“quantum simulation”, hereafter) to investigate the possible role of quantum mechanical fluctuations in proton-transfer processes and hydrogen-bond rearrangement processes in the $HCl(H_2O)_4$ cluster. The PIMD simulations are carried out for different temperatures ranging from 100 K to 300 K. Comparing the results for quantum and classical simulations, we indeed found quantum description has strong influence on the structure of the $HCl(H_2O)_4$ cluster.

2. Computational method

Before starting PIMD simulations, it is important to understand the features of the ground-state potential energy surface of the $HCl(H_2O)_4$ cluster. To this end, we have implemented the PM3-MAIS core–core functions of the $HCl–H_2O$ system [49] into the semiempirical part of the Gaussian03 ab initio package program [45]. This modification has then been combined with the GRRM computer code based on scaled hypersphere search (SHS) algorithm developed by Maeda and Ohno [51–53]. The SHS method can automatically search for various isomers from a given equilibrium structure using an uphill-walking technique. Using this technique, many low-lying isomers on the potential energy surface have been explored. Another important feature of the GRRM code is that transition-state structures can also be optimized with the SHS algorithm. Harmonic vibrational frequencies were then calculated in order to confirm whether the optimized stationary point geometry is a minimum or a saddle point on the potential energy surface. Subsequently, intrinsic reaction coordinates (IRC) calculations were performed to check whether the transition-state connects right isomers or not. After these computational processes, we can finally obtain a full topographical feature of the potential energy surface of the $HCl(H_2O)_4$ cluster.

A standard imaginary-time PIMD simulation [36–41] has been performed to calculate thermal equilibrium structures of the $HCl(H_2O)_4$ cluster on the PM3-MAIS potential energy surface. In the path-integral formalism, the quantum mechanical character of nuclei is described by a cyclic polymer chain consisting of classical quasiparticles. Thermal equilibrium averages are computed from time averages over fictitious molecular dynamics trajectories generated from the equation-of-motions described in the normal-mode coordinate representation. The system temperature was controlled with a massive Nóse–Hoover chain technique. Apart from the semiempirical PM3-MAIS parameters, the only important assumptions made here are Born–Oppenheimer approximation and neglect of the exchange between hydrogen nuclei, which should work well in the present system. Potential energy and gradient values were directly calculated using the MOPAC2007 code [54] including the PM3-MAIS modification. The PIMD run was performed with 30–100 beads in the temperature range of $T = 100$–300 K. For example, we found that 100 beads are necessary at $T = 100$ K in order to obtain numerically converged results. With time increment $\Delta t = 5$ a.u., the total time steps were ranged 10^5–10^6. The Nóse–Hoover thermostat of length 4 combined with the velocity Verlet algorithm was used to control the system temperature. The details of our computational method are also described in Refs. [42–44].

3. Results and discussion

3.1. Static calculation

Before presenting the results of PIMD simulations, it should be important to present important features of the ground-state potential energy surface of the $HCl(H_2O)_4$ cluster system at the semiempirical PM3-MAIS level. By using the SHS algorithm [51–53], 18 isomers (see Fig. 1) of the $HCl(H_2O)_4$ cluster were located. In addition, 34 transition-state structures (not shown) were automatically located at the same time. Harmonic vibrational frequencies for the optimized geometries were computed to characterize them as either minima or saddle points of the potential energy surface. The geometries of these isomers are listed in Fig. 1 along with the relative energies without and with zero-point energy correction. These isomers can be categorized into several groups of structures as explained below.

The lowest-energy isomer EQ0 has a five-membered-ring structure with the HCl molecule being fully dissociated. Also, the Zundel-type $H_5O_2^+$ structure is also seen in EQ0. It is interesting to note that EQ2, EQ3, EQ6, and EQ11 have a very similar cyclic structure to EQ0, but have different structures in the direction of dangling hydrogen atoms. This means that isomeric interchange among EQ0, EQ2, EQ3, EQ6, and EQ11 structures can be presumably possible by rotation of water molecules.

The second lowest isomer EQ1 has a solvent-separated zwitterionic form, where the H_3O^+ moiety is bound through three hydrogen-bonds to three water molecules. The negative Cl^- ion is also bound by these three water molecules through hydrogen-bonds. Thus, there are a total of six hydrogen-bonds in this cluster to form the stable structure. EQ5 and EQ7 have a similar structure to EQ1 but have different dangling hydrogen atom structures. Thus, isomeric interchange can easily be possible by rotation of water molecules bridging H_3O^+ and Cl^-.

Isomer EQ4 has a four-membered ring structure, where the HCl molecule is fully dissociated, due to an elongated HCl separation of 1.76 Å. Thus, H_3O^+ moiety is clearly seen in the ring. It is interesting to note that one water molecule is bound to the dangling hydrogen of H_3O^+ in this ring through a hydrogen-bond. Isomers EQ8, EQ9, EQ10 and EQ12 have a similar structure to EQ4 but with different