Abstract

We report results of Car–Parrinello molecular dynamics simulations showing the effect of surface trapped electrons on the dynamics of HCl adsorbed ice surfaces. It is found that the existence of excess electrons can lead to extensive changes in structural and electronic properties of ice surfaces, which provide better environments for proton transfer. The results of simulations show rapid exchanging mechanism of the proton under such environment, suggesting the importance of interlayer proton transfer in the heterogeneous reaction of HCl adsorbed ice surfaces.

1. Introduction

Since the discovery of the ozone hole, heterogeneous processes have been recognized as playing an essential role in the chemistry of the stratosphere [1]. Ice particles are known to affect the chemistry involved with the ozone hole, by providing surfaces on which heterogeneous reactions may proceed. For example, it has been shown experimentally that reaction of HCl with ClONO2 might proceed very rapidly on ice surfaces and that photolysed Cl atoms could destroy ozone in a catalytic cycle [2].

One of the fundamental issues for reaction dynamics on ice surfaces concerns the character of species resulting from the adsorption of acids. They may exist as ions after undergoing complete dissociation or as molecular species subject to partial dissociation. Kang et al. [3] showed by Cs+ scattering experiments that HCl exists as molecular species at lower temperatures, while at the temperatures higher than 140 K complete dissociation is possible. At intermediate temperatures, molecular HCl and partially dissociated HCl coexist. Another experimental study by Devlin et al. [4] emphasized the role of a hydrogen bond network in stabilizing dissociated ions on an ice surface. Chloride ions can be stabilized by coordination with three hydrogens including two dangling hydrogen atoms. A theoretical study by Mantz et al. [5] also showed that HCl dissociation occurs when it is located around two dangling hydrogens. The coordination environment allows proton transport through hydrogen bond networks, which may facilitate HCl dissociation or subsequent reactions on an ice surface. The main focus of the present study is to examine the possible role of proton transfer in the reaction dynamics of HCl adsorbed on ice surfaces.

Heterogeneous processes in ice stratospheric clouds can be influenced by excess electrons produced by cosmic rays. Local trapping of excess electrons at the surface of ice has recently been studied experimentally and theoretically [6,7]. A theoretical study by Baletto et al. [7] showed that excess electrons induce a structural reorganization of the ice surface on a time scale of a picosecond. We will examine the effect of such excess electrons on the properties and reactivities of adsorbed HCl.

In the present study, we have performed Car–Parrinello molecular dynamics (CPMD) simulations [8] for model hexagonal ice (Ih). CPMD provides a consistent treatment for bond formation and breaking and a dynamical treatment for solvating effects at finite temperatures. We exam-
ined the nature of electronic properties of HCl on an ice surface and the role of proton transfer.

2. Model system and simulation details

We have considered ice Ih basal (0001) face as a model ice surface, which is thought to be relevant under polar stratospheric conditions. A defect free periodic ice slab is constructed with 32 water molecules for the model system. The positions of oxygen atoms are determined from X-ray diffraction data [9] and the hydrogen atoms are placed according to the Bernal–Fowler’s ice rule such that the total dipole moment is to be zero [10,11]. An infinite surface was modeled by repeating the cell in the directions parallel to the surface and allowing sufficiently large vacuum space in the perpendicular direction. With 32 water molecules, four layers were constructed in a hexagonal simulation cell with dimension of 9.046 Å × 20.76 Å, and the positions of oxygen atoms in the lowest layer are fixed during the molecular dynamics simulation to mimic infinite ice layers. Some stable sites of HCl adsorption were suggested by the previous work by Mantz et al. [5]. They studied three possible positions of adsorbed HCl. In one of the cases, HCl is assumed to interact with two dangling OH, resulting triply coordinated Cl by neighboring hydrogen atoms. It is known that the condition for HCl dissociation is closely related to the coordination of the Cl atom to neighboring hydrogen atoms, which was also confirmed by our preliminary calculations. In the present work, HCl molecule is initially placed on the sites which can allow triple coordination.

We used CPMD code [12] to perform optimization of wavefunctions and Car–Parrinello molecular dynamics simulations using the Becke–Lee–Yang–Parr (BLYP) functional [13,14] with a planewave cutoff of 80.0 Ry and Troullier– Martins pseudopotentials [15]. For Brillouin-zone sampling, only the Γ-point is used. MD simulations are performed through 11.6 ps with a time step of 0.125 fs. In order to use larger time steps, deuterium mass was assigned to the hydrogen nuclei. In order to model stratospheric conditions, the temperature was set to 190 K, while the lower temperature (100 K) was also considered for comparison. Temperatures are controlled using a Nosé–Hoover thermostat [16].

When excess electron is introduced in the system, consideration of spin polarization would be important. In order to include the effect of spin polarization, local spin density (LSD) approximation may be adopted for optimization. Preliminary CPMD simulations indicated that results with LSD approximation did not show any qualitative difference from those without LSD approximation, at least for our purposes. In the present work, we performed calculations without local spin density approximation.

3. Results and discussion

We performed Car–Parrinello molecular dynamics simulations of ice surfaces containing adsorbed HCl molecules. We examined whether HCl dissociates or not. Fig. 1 shows the time evolution of the distance between chlorine and three neighboring hydrogens, observed from one of the simulated trajectories. In the case of a pure ice surface, the chlorine atom seems to be shared by neighboring hydrogens, which may represent a pre-state to dissociation or further reaction. We also examined the behavior of an adsorbed HCl molecule on the ice surface when the excess electron is added. With an excess electron, the sharing of the chlorine atom between the hydrogen from HCl and other dangling hydrogens is more extensive. These results suggest that the existence of this excess electron leads to better coordination or microsolvation of the chlorine atom, providing better environment for proton transport.

In order to examine the effect of the electronic environment, we calculated the electron density during a molecular dynamics run. Electron density is rather uniformly distributed in the case of the pure ice surface. As observed by Baletto et al. [7], the presence of an excess electron can lead to structural rearrangement and redistribution of electron densities. It is observed that the electron density of the trapped electron is extended to the lower layers of the ice surface at 190 K. At 100 K, such surface reorganization due to the excess electron is not extensive. In the presence of an HCl molecule, the electron density around the oxygen atom where HCl is adsorbed is enhanced. When an excess electron is added to the system, such electron redistribution after HCl adsorption is extended to the second layer. It is noted that enhancement of structural and electronic reorganization of HCl adsorbed ice surface due to the presence of the excess electron can provide a favorable environment for facilitating proton transfer.

The dipole moment autocorrelation function can be used to examine the dynamical effects of interaction between HCl and ice surfaces. We obtained the dipole moment autocorrelation function for facilitating proton transfer.

![Fig. 1. Time evolution of the distance between chlorine and three neighboring hydrogen atoms for (a) pure ice surface and (b) ice surface with excess electron. Solid line represents the distance of the Cl atom from hydrogen atom originally belonged to HCl and dashed/dotted lines are the distances from the two dangling hydrogen atoms.](image-url)
moment using the Berry phase scheme [17,18] during the simulation and calculated a power spectrum from the Fourier transform of the dipole autocorrelation function with a prefactor of $\omega \cdot \tanh(\beta \omega / 2)$ where $\beta = 1/k_B T$ and $T$ is temperature [18]. Fig. 2 shows the power spectrum of HCl adsorbed ice surface system. The overall shape of the power spectrum for a pure ice surface is similar to liquid water. The peaks of the high frequency region represent stretching modes and the peaks in the middle range represent bending modes. The low frequency peaks can be attributed to intermolecular interactions [18,19]. When the HCl is adsorbed, the peaks corresponding to intermolecular interaction and stretching mode are red shifted while the bending mode peak show little changes. It can be concluded that the stretching motions and intermolecular interactions of water molecules on ice surface are mostly affected by the presence of partially dissociated proton from HCl. The low frequency peaks corresponding to the intermolecular interaction is affected most as a function of temperature. When the excess electron is added to the HCl adsorbed surface, the overall shape of the power spectrum is significantly changed, clearly suggesting extensive structural reorganization.

The interchange of hydrogen bond partners among water molecules in liquid water or ice can be done either by thermally-activated breaking or by infrequent but rapid switching events. Recently, Eaves et al. [20] showed that proton transfer occurs by infrequent but rapid hydrogen switching events. When one considers switching of hydrogen bond partners, the concept of non-hydrogen bonded configurations (NHB) between adjacent molecules can be used. In order to describe proton transfer through the

![Fig. 2. Power spectrums of dipole moment autocorrelation functions for (a) pure ice surface (dotted line) and HCl adsorbed ice surface (solid line) at 190 K; (b) HCl adsorbed ice surface at 100 K (dotted line) and 190 K (solid line); (c) HCl adsorbed ice surface at 190 K with (dotted line) and without (solid line) an excess electron.](image)

![Fig. 3. Time evolutions of the ratio of the distances between hydrogen and two neighboring oxygens for hydrogen bonding configuration (parameter $f$) in the upper layer of HCl adsorbed ice surfaces (a) without excess electron at 190 K; (b) with excess electron at 190 K; (c) without excess electron at 100 K; and (d) with excess electron at 100 K.](image)
hydrogen bond network, we introduced a parameter $f$, which is the ratio of the distances between hydrogen and two neighboring oxygens. For normal hydrogen bonding configurations, the two distances are 1.0 Å and 1.8 Å. The parameter $f$ can have a value of 0.56 or 1.8. The change between these two values represents a switching of the hydrogen bonding partner through NHB as a transition state, indicating proton transfer. We calculated the parameter $f$ for hydrogen bonds in three different regions. There are six possible hydrogen bonds in the upper and the second layers, respectively. The two layers are linked by three hydrogen bonds. Fig. 3 shows time evolution of parameter $f$ in the upper layer for the HCl adsorbed ice surface. It is found that complete proton transfer is observed on the surface layer when the excess electron is included. It can be argued that it is much easier for proton to transfer in the presence of excess electron in the system. In fact, during our simulations with excess electron, the intermediate NHB state with $f$ value of around 1.2 was not found, suggesting rapid switching mechanism during proton transfer.

4. Concluding remarks

In this letter, we report results of Car–Parrinello molecular dynamics simulations on HCl adsorbed ice surfaces. Our calculations showed partial dissociation of HCl on ice surfaces, where the chlorine atom was shared by neighboring hydrogens. Of particular interest is the effect of excess electrons on the dynamics and reactivity of ice surfaces. It is found that the existence of excess electrons can lead to extensive changes in the structural and electronic properties of ice surfaces, which provide better environments for proton transfer. The results of simulations show rapid exchanging mechanism of the proton under such environment, suggesting the importance of interlayer proton transfer in the heterogeneous reaction of HCl adsorbed ice surfaces.

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