

Car-Parrinello Molecular Dynamics Study for the Isotope Effect on OH Vibration in Ice Ih

Yeohoon Yoon^a

Frick Laboratory, Department of Chemistry, Princeton University, Princeton, NJ 08544 USA. E-mail: yeohoon.yoon@pnml.gov
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The stretching vibration of OH of ice Ih is studied by Car-Parrinello molecular dynamics in regarding the effect of mixed H/D contamination while the vibrational spectrum is considered by velocity-velocity autocorrelations of the sampled ensemble. When hydrogen atoms are immersed randomly into the deuterated ice, a typical vibrational frequency of OH stretching mode is observed to be similar to that from the pure H₂O ice. When focusing on the correlation of isolated neighboring OH stretching, a narrower and blue shifted peak is observed at the high frequency range as a result of the screening from the complex many body correlations by D₂O environment. It is also specifically related to the symmetric intermolecular correlations between neighboring OH stretching modes. More enhanced high frequency range can be explained by the expansion of such two body correlations to collective many body correlations among all possible OH stretching modes. This contribution becomes important when it involves in chemical interactions via excitation of such vibrational states.

Key Words : Ice, Isotope effect, Car-Parrinello molecular dynamics (CPMD), Vibrational spectrum

Introduction

Water has been extensively studied due to its ambient existence in nature particularly concerning possible involvement in chemical interactions in aqueous solution and at the interface of liquid/solid water.^{1,2} The interpretation of its vibrational spectrum can provide important information on the role of water molecules during such kind of chemical interactions through the channel accompanying the excitation of the corresponding vibrational state. For the fundamental understanding of the water vibration, the crystalline ice has been focused on while there is a difficulty with more complex liquid phase due to the strong hydrogen bonding nature. It is well known that the vibrational spectrum of water as well as ice has three main ranges of peaks with liberation, bending and stretching modes. Since the stretching mode is in high frequency range relevant to the ambient thermal interaction with 3000-3500 cm⁻¹ and sensitive to the hydrogen bonds related to the local molecular structure, many efforts are taken to interpret the physical origin of this mode for a long time.^{4,5} However, there are still unclear features in the inhomogeneous broadness of this range including the possible bending overtone. Particularly for the common crystalline ice Ih, it has been agreed that the intermolecular vibrational coupling contributes many features in this range and makes the situation complicated.⁶ In addition, dynamic correlations among the dipole moments are also able to generate more complex nature while static one has been mainly focused on so far.⁷

In order to simplify the problem by complex and dynamic

correlation, one can investigate isotope diluted water, *i.e.* HDO in either H₂O or D₂O. Consideration of the isotope effect with mixed light hydrogen and deuterium is supposed to provide clearer physical origin of the vibration while naturally generated OH/OD vibration is decoupled so the vibrational excitation remains local and represents the local environment. There are many experimental studies^{8,9} particularly by nonlinear spectroscopy with its ability to extract homogeneous character from the inhomogeneous broadening of the signal. Concerns on the ice surface also address such broadening and peak shifting by sum-frequency vibrational spectroscopy.¹⁰ Some theoretical approaches^{11,12} show that the mixed isotope ice generates basically narrower peak due to less disorder, yet it is still in the investigation for the inhomogeneous range including the shoulder peak in the high frequency range.

Motivated by the scheme using isotope effects, the same approach is applied theoretically to the bulk ice Ih in the present study. As a crystalline structure, ice Ih is adopted since it is ordinary form in most biospheres and stable under ambient pressure within the temperature range of 72 K to 273 K.¹³ In this structure, the proton is disordered obeying ice rule in which two each hydrogen atoms must occupy one among two chemical bonding and two hydrogen bonding positions next to oxygen atom.² The correlation of OH vibration between two different available positions will show different feature in the spectrum. In addition, the crystalline structure is able to generate clearer feature with ordered hydrogen bond network. Once such a feature is interpreted precisely, the resulting essential information can be provided further for more complex environments such as liquid water or the interface of water/ice.

^aCurrent Address: Fundamental and Computational Directorate, Pacific Northwest National Laboratory, Richland WA 99352, USA.

Models and Computational Details

The principal approach to obtain a vibrational spectrum is computing velocity-velocity autocorrelation function from the molecular dynamics sampling.¹⁴ In the present study, Car-Parrinello molecular dynamics (CPMD)¹⁵ is performed to sample the ensemble using CPMD program package.¹⁶ For the electronic potential calculation in CPMD scheme, Perdew-Burke-Ernzerhof (PBE) functional¹⁷ is used for the exchange-correlation functional within the density functional theory (DFT) formalism. The plane wave is used with a cutoff of 85 Ry for the description of valence electrons, while Troullier-Martins normconserving pseudopotential¹⁸ is adopted for the core electrons. Only Γ -point is used for Brillouin-zone sampling. During the time evolution of the system within CPMD scheme, the electronic fictitious mass (μ) is assigned to 85 a.u. which is very small relative to most of previous simulations so that more accurate description of the dynamics is feasible by minimizing possible intrinsic red shift commonly coming from CPMD scheme. Note that the influence of fictitious electron dynamics depending on the value of μ on the nuclear dynamics decreases by the frequency separation of electronic and nucleic motion.¹⁹ Then CPMD is performed with a small time step of 1.5 a.u. (~ 0.036 fs) while the temperature is controlled by stochastic thermostat to obtain equilibration.²⁰ This thermostat allows one to minimize the time to reach equilibrium and to generate independent configurations. For the sampling of the equilibrated ensemble, microcanonical (NVE) ensemble is considered by removing the thermostat and the resulting average temperature is 250 K. From the ensemble sampled during around 10 ps for each trajectory, velocity-velocity autocorrelation function is obtained by

$$C(\tau) = \langle v(0) \cdot v(\tau) \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N v_i(\tau + t_0) \cdot v_i(t_0) \right\rangle,$$

where $v_i(\tau)$ is the velocity of the i th particle at time τ , N is the number of particles. Then the vibrational spectrum can be generated by the Fourier transformation of this function,

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt e^{i\omega t} C(t).$$

When it is compared to the infrared (IR) spectrum, the quantum correction is applied with a Kubo prefactor.²¹

The ice *Ih* model system is prepared in the orthorhombic simulation cell whose dimension is $13.6 \text{ \AA} \times 15.7 \text{ \AA} \times 14.8 \text{ \AA}$ with 96 water molecules. Defect free lattice structure is assumed and a possible proton disorder is considered so as overall dipole through the simulation cell to be minimized. Each of water molecules can be H_2O , HDO or D_2O depending on the interested configurations by randomly placing deuterium or light hydrogen.

Results and Discussion

Pure H_2O Ice *Ih*. At first, the spectrum of pure H_2O ice *Ih* is obtained to confirm the consistency of current simulation

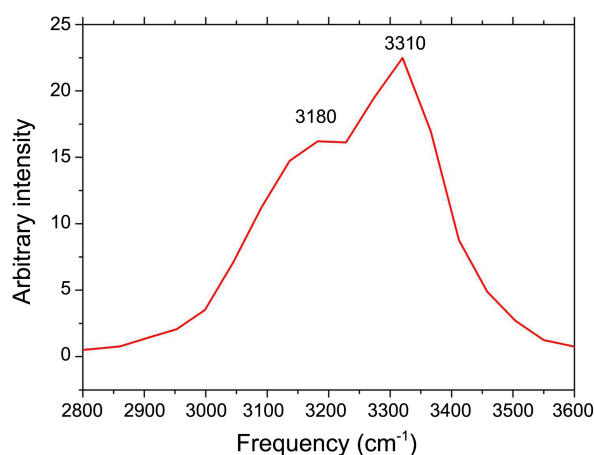


Figure 1. The calculated vibrational spectrum of pure H_2O ice in the OH stretching range.

scheme to other experimental results. Figure 1 shows the spectrum obtained by the present simulation in the range of OH stretching mode and it can be compared to the experiment, for instance, as reported by Bergen *et al.* (Figure 3 therein)⁵ as a reference. The overall peak position is blue shifted about $50\text{--}80 \text{ cm}^{-1}$ which may come from the intrinsic error of CPMD scheme and the used functional form within DFT formalism. Nonetheless, the overall shape and feature are similar to each other. The observed peak is broad but the positions of this peak can be distinguished mainly by two in this range; one is at $\sim 3180 \text{ cm}^{-1}$ and the other is at $\sim 3310 \text{ cm}^{-1}$. These two features correspond to intramolecular in phase symmetric and antisymmetric stretching modes broadened by the intermolecular interactions and possibly the overtone of bending mode. A similar splitting can be observed as well in the isolated water molecule in the gas phase. In this case, symmetric mode is at $\sim 3720 \text{ cm}^{-1}$ and antisymmetric mode is at $\sim 3850 \text{ cm}^{-1}$. There is a blue shift of 70 cm^{-1} going from experiment to theory in the isolated molecule.²² When considering the amount of splitting, it becomes $\sim 130 \text{ cm}^{-1}$ in theory and slightly larger than the experiment⁵ by 50 cm^{-1} . This splitting is similarly overestimated compared to the experiment both in molecular and condensed phases.

Deuterated Ice Containing Dilutely Mixed with Hydrogen Atoms. In order to observe the isotope effect of OH stretching mode, light hydrogen atoms are immersed into a deuterated ice dilutely by replacing some deuterium atoms with light hydrogen atoms in random position. As a result for the current study, the model system is prepared with 87 D_2O molecules and 9 HDO molecules. This corresponds to 5% hydrogen concentration and it is disregarded if H_2O molecule is generated within random manner. The resulting spectrum does not look far from that of pure H_2O ice in general (not shown). However, somewhat different substructural feature is observed particularly near the high frequency range around $\sim 3300 \text{ cm}^{-1}$ because some unknown correlated state is dominantly populated within stretching mode range in this HDO/ D_2O ice crystal. In other words, there should be some other contributions in order to make such kind of substructure besides typically assigned intra-

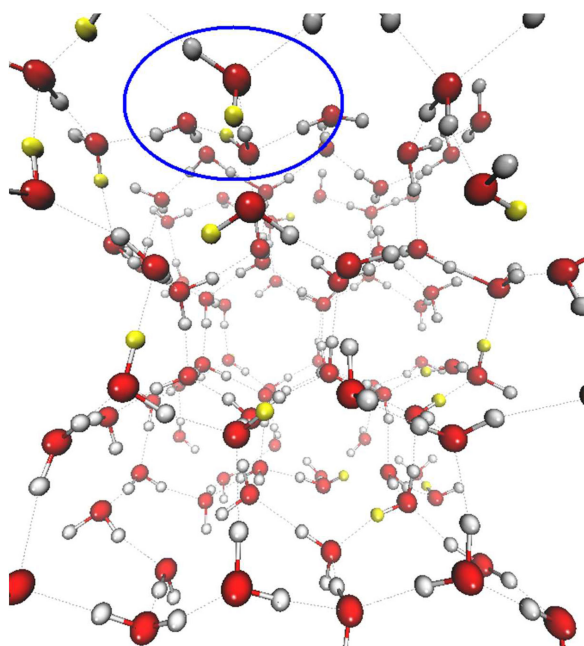


Figure 2. A model structure of ice Ih with 96 water molecules with randomly immersed hydrogen atoms (yellow) instead of deuterium (white). Red balls represent oxygen atoms. A dimer of HDO can be seen in the region with blue ellipse.

molecular antisymmetric OH stretching, and the intermolecular correlation can be considered as one candidate. Since there are only small number of hydrogen atoms in the HDO/D₂O ice, such correlation can be generated only when there is another HDO next to HDO in consideration. On the other hand, the long range correlation via hydrogen bond network is excluded since this dimer is screened by D₂O environment from another possible HDO assuming very dilute model. In order to confirm this hypothesis, several model systems are considered while hydrogen atoms are positioned differently in random way and similar features are observed in different models. Figure 2 shows one representative configuration of HDO molecules in D₂O ice which is one of the randomly created models. The resulting spectrum is complex so as it hard to be interpreted by combination of many independent OH vibrations from different HDO molecules.

Having observed the dominant contribution by the correlation of the neighboring intermolecular OH vibrations, another model configuration is constructed by artificially generating only isolated HDO-HDO dimer units surrounded by the D₂O environment (the region within eclipse in Figure 2) with the same total concentration of hydrogen atoms, *i.e.* 5%, in the deuterated ice as before. By doing so, other possible complex correlations can be excluded so as to minimize inhomogeneous broad features of the peak. Additionally, more intense features reflecting sole HDO-HDO correlation should be observed while complex substructures are disappeared as shown in Figure 3. In this case, the coupled vibrations are observed from ~ 3225 cm⁻¹ to ~ 3315 cm⁻¹ and this coupling is constructed by two OH groups belong to either of two neighboring HDO dimer isolated by D₂O environment. Reminding of typical pure H₂O ice spec-

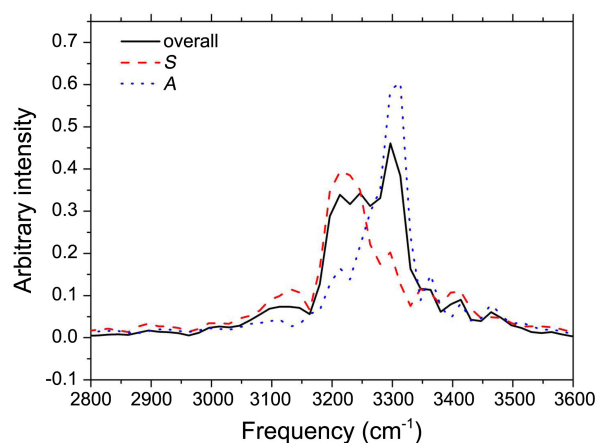


Figure 3. The stretching mode of isolated HDO contained deuterated ice (black solid line) and decomposed signal to symmetric (red dashed line) and antisymmetric (blue dotted line) modes.

trum, the splitting in this range is about 130 cm⁻¹ and it is mainly due to the different intramolecular correlation. However, the splitting of current model becomes 40 cm⁻¹ narrower than that of pure H₂O ice. In fact, this decreasing can be explained that there is lack of the intramolecular correlations since they are artificially undermined in the current model. Therefore, the only possible correlation of OH stretching should be accompanied by another OH stretching from the neighboring HDO molecule. In this reason, it is considered the contribution of the intermolecular symmetric and antisymmetric modes from two different HDO next to each other with their OH stretching modes. Here the symmetric (antisymmetric) mode is assigned when both OH stretching modes from the different HDO molecule are symmetric (antisymmetric) in phase. If those two modes are decomposed from the overall spectrum with current model, the origin of two different peaks fit very well to the original substructure of overall spectrum as shown in Figure 3. Since the population of symmetric mode of neighboring OH stretching is larger, it should be appeared dominantly in the overall spectrum. In the meantime, the average peak position is blue shifted by around 30 cm⁻¹ which is qualitatively in good agreement with previous experiments for both bulk and surface of ice Ih.^{9,10}

So far, it is examined that the intermolecular correlation contributes to the inhomogeneous broadening in the high frequency range. Nonetheless, it is still necessary to confirm the possibility of such contribution in the presence of other H₂O molecules as well. In this condition, the screening of long range correlations by D₂O environment is removed while the role of many body correlations may become important. The resulting spectrum basically resembles that of pure H₂O ice as shown in Figure 4, but some different features are able to be pointed out at the same time. In general, there are more substructures which come from enhanced intermolecular correlations, and a blue shift is observed as well from the high frequency peak. If overall peak is tried to be simply decomposed by the intramolecular correlation with symmetric and antisymmetric modes, a clear separation can

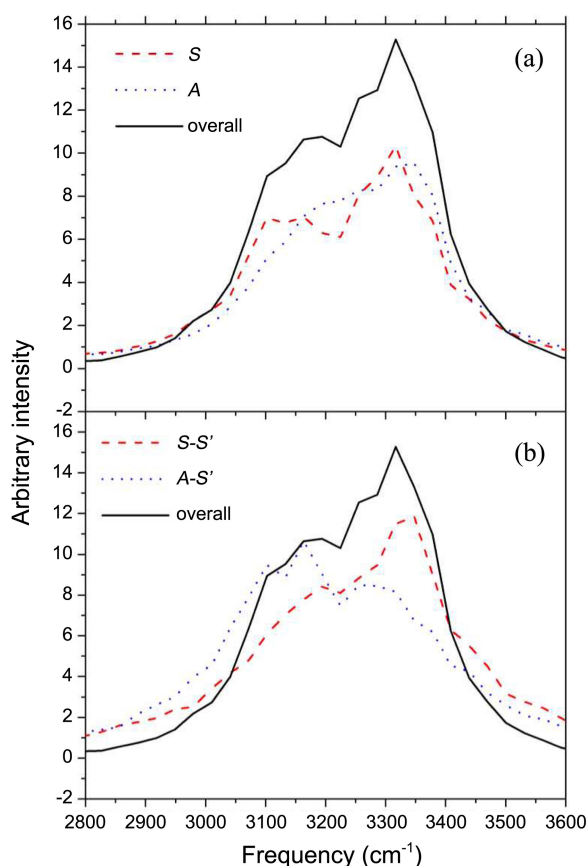


Figure 4. (a) Stretching mode range of hydrogen immersed deuterated ice (black solid line) and decomposed ones by intramolecular S (red dash line) and A (blue dotted line) modes. (b) Same as (a) with an intramolecular correlation A (red dashed line) and S (blue dotted line) coupled to the collective intermolecular correlation with S' .

hardly be achieved as shown in Figure 4(a) whereas it is possible in the case of pure H_2O . It is because both modes from the intramolecular correlation are extended over the entire spectral range and they overlap very strongly with each other so that it is essentially impossible to distinguish based on the spectral shape and range. Concerning experimental data, however, this broad peak may not what is probed in optical experiments in which the electric field is spatially uniform over hundreds of nanometers. In that case, the peak can be represented by only the intramolecular modes which are coherent over the entire supercell. For a crystalline system, that would correspond to the consideration of mode with crystal momentum $k = 0$. In the present case, a translational invariance is satisfied for the lattice vectors of the supercell. Therefore, as considered with isolated HDO model, we can make a hypothesis that the substructure observed at the high frequency range is constructed as a result of the collective many body correlations of the OH stretching modes from the neighboring OH in both intra- and intermolecular correlations through the hydrogen bond network. For the confirmation of this hypothesis, another way of decomposition is considered. Suppose one molecule of a dimer has decomposed by intramolecular symmetric

and antisymmetric modes, and then the OH stretching of the other molecule is projected to the phase which is aligned as the same coordinates of the intramolecular stretching phase from the first molecule. Here the intramolecular correlation modes are denoted simply by S and A , and the projected intermolecular correlation modes are denoted by S' and A' . Then four combinations of decomposed factors are available as $S-S'$, $S-A'$, $A-S'$, $A-A'$. For example, $S-S'$ means that two OH stretching correlation from the different molecules is symmetric in phase during the intramolecular correlation in the reference molecule is also symmetric. When considering all intramolecular S and A modes but having symmetric correlation (S') between neighboring molecules in the supercell, Figure 4(b) can be obtained. The other combinations of correlation are excluded from the consideration since they present the overlapped inhomogeneous feature over the entire spectral range. This particular condition reflects extended symmetric correlation among all pairs of neighboring molecules in the supercell. Now one can clearly see that the mode with $S-S'$ character is located around $\sim 3150 \text{ cm}^{-1}$ while mode with $A-S'$ character is around $3300\text{--}3350 \text{ cm}^{-1}$. Although there is still some overlap, two different modes can be distinguished with sufficiently different spectral shape. As a result, collective symmetric (S') vibration of OH throughout the supercell can be concluded to be an important factor contributing to the blue shift and enhanced intensity at the high frequency range. Note that $S-S'$ assigning lower frequency peak is rather broad with an inhomogeneity in this range, whereas $A-S'$ assigning high frequency peak is blue shifted and observed as relatively sharper peak which represents more homogeneous contribution by this correlation.

Concluding Remarks

The purpose of the present study is to investigate the fine substructure of OH stretching mode using isotope effect with dilute hydrogen immersed D_2O ice crystal. Basically the intramolecular correlation gives a similar feature as the pure H_2O ice spectrum. On the other hand, the intermolecular correlation contributes to the blue shift and the broadening of the OH stretching peak which is consistent with the previous experiments.^{9,10}

The broad inhomogeneity is originated from the enhanced intermolecular OH stretching correlation as proposed in the following. The lower frequency of OH stretching mode is less populated while the higher frequency peak is observed more dominantly. As a result, the average peak position over the OH stretching range is blue shifted comparing to the pure H_2O spectrum. In addition, the collective symmetry among many body OH stretching correlations throughout the supercell is proposed to be an important contributor in this vibrational frequency range. While most optical spectroscopy may response stronger with a symmetric intramolecular coherence, the intermolecular mode itself is also symmetry sensitive within this coherence and the collective symmetric mode mainly contributes to the high frequency peak at the same time with a blue shift. This collective

correlation effect is worth considering as an application to the chemical interactions at the interface of solutes in solution and at the water/ice surface.

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