Electronic and Nuclear Contributions to Vibrational Stark Shifts of Hydroxyl Stretching Frequencies of Water Clusters

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ABSTRACT: In spite of the importance of vibrational Stark effect (VSE) and many attempts, origin of VSE is still unclear in molecular level. Here, we studied on origin of VSE of hydroxyl stretching vibration in small water clusters (monomer, dimer, and tetramer) assuming that VSE can be separated by nuclear and electronic contribution. We calculated total Stark tuning rate (Δμtot) and its nuclear contribution (Δμgeom) by using the ab initio method, then the electronic contribution (Δμelec) was simply obtained by the difference, Δμtot − Δμgeom. In all cases, the nuclear contribution has dominant contribution to VSE. The hydroxyl stretching mode with neighboring hydrogen acceptor showed larger Δμgeom than that of dangling bonds. Furthermore, the calculated Δμgeom became larger in larger cluster due to the hydrogen bond network. The comparison between Stark tuning rates including and excluding anharmonicity supports the importance of potential anharmonicity in VSE, as previously reported. Interestingly, a good linear relationship is observed between the hydroxyl stretch frequency (ν) and Stark tuning rate (Δν/ΔF) for water. The effective Stark tuning rate (Δν/ΔF) showed a good linear relationship with atomic charge derived by electronic perturbation (Δμelec) and change of that (Δ(Δμelec)), respectively.

INTRODUCTION

Electric field can change the electron density and induce dipole moment of a molecule and perturb the polarization in the molecule. Such an effect, what is called, Stark effect, has been experimentally applied to probe the electronic structure of molecules, the band structure of semiconductors, and to understand complicated dynamics of biological systems.1–5 In particular, the Stark effect is an important contributor to complicated vibrational spectra in condensed phase. Inhomogeneous broadening of IR spectra in condensed phase is known to be largely generated by the Stark shift of vibrational frequencies mostly due to the influence of local fields in the media.6–8 To measure the vibrational Stark effect (VSE), strong electric fields (>10⁶ V/m) should be applied, which may cause inherent spectral broadening due to the perturbation in local fields.9

The VSE has been used as a method to recognize the molecular species† and investigate local electrostatic information of biological molecular systems2,6,13 or liquid solutions.3,8,14 Several methods utilizing the VSE to investigate physical nature have been highlighted.3,10 Moreover, the VSE can be referred to explain a role of electrostatics in many biomolecular systems15,16 and understand important fundamentals about chemical bonding and anharmonicity.17 The VSE of vibrations of water in condensed phases is an important subject of physical chemistry research, but its understanding is complicated by the inherent complexity of vibrational spectrum of condensed-phase water. Very limited studies have been conducted to precisely measure the VSE of hydroxyl stretching mode of water in liquid and solid phases with spectroscopy under conditions that discriminate the effect of intermolecular vibrational coupling. Recently, Kang and co-workers reported a technique that can measure the VSE of condensed molecular films under the influence of an extraordinarily strong electric field.18 Using the technique, Kang and co-workers investigated the VSE of acetonitrile,18 acetone,19 water,20 and carbon monoxide21 in condensed phase.

Many studies have been attempted to understand the origin of VSE for years by various analyses, theoretical methods,21,22 Stark spectroscopy,27–29 and electroabsorption responses.30,31 For example, comparing the local fields in various configurations during the molecular dynamics simulations and their vibrational frequencies calculated by the quantum chemical method, the VSE has a linear relationship with local field strength.32 Local field is the sum of external

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applied electric field and the internal electric field that is generated from the other molecular environment. However, in our recent study for water clusters, the variation of internal field ($\Delta F_{\text{int}}$) was smaller than the applied external field ($F_{\text{ext}}$). Thus, there must be more complicated origin on the VSE in water clusters. Additional difficulty exists in investigating the VSE of hydroxyl stretching vibrations due to inherent complexity of the vibrations of water. It was also reported that the potential anharmonicity is one of origin of VSE from the comparison of potential curves under the influence of applied electric field. However, these studies are not enough to grasp the origin of VSE. In this regard, it is very interesting to understand the origin of VSE in depth. The applied electric field can change the electronic polarization, which is responsible for the VSE. Then, this electronic polarization can be obtained by purely electronic (without change of geometry) or purely nuclear influence. In this study, we defined these influences as electronic and geometric effects, respectively. It is scientifically interesting to separate the contribution of VSE into purely electronic and geometric (nuclear) terms. Because the hydroxyl stretching vibration mode showed a uniquely large magnitude of VSE than that of CO or CN, here, we try to pinpoint the origin of VSE of hydroxyl stretching vibration in water clusters (monomer, dimer, and tetramer) by partitioning into electronic and geometric contributions.

# COMPUTATIONAL DETAILS

In this study, we performed the geometry optimization for $(\text{H}_2\text{O})_n$ $n = 1, 2, 4$ (denoted as w1, w2, w4, respectively) and calculated the hydroxyl stretching frequencies. It is known that the induced frequency shift by the electric field is larger when the electric field is applied parallel to bond direction rather than orthogonal to hydroxyl stretching vibration. Thus, we only considered the parallel electric field from 0 to $7.71 \times 10^8$ V/m whose direction is from hydrogen to oxygen in hydroxyl bond. To prevent the targeted hydroxyl stretching vibration from coupling with others, we substituted deuterium for hydrogen in target bond (expressed as O$\cdots$D bond), as done in previous studies. There exist only one type of hydroxyl bond in water monomer, three in dimer, and two in tetramer, which were denoted as w1, w2-b, w2-d, w2-d2, w4-b, and w4-d, respectively (Figure 1) where b and d mean hydrogen bond and dangling bond, respectively. In this study, all calculations were done at the second-order Møller–Plesset (MP2) perturbation theory with augmented correlation-consistent polarized valence double-$\zeta$ (aug-cc-pVDZ) basis set. The vibrational frequencies were calculated with and without the consideration of anharmonicity. All of the calculations were performed with Gaussian 09 program.

## RESULTS AND DISCUSSION

The VSE can originate from changes in both nuclear coordinates and electron distribution of molecules under the influence of an applied electric field, and is often quantified by Stark tuning rate ($\mu = \Delta \nu / \Delta F$) defined as the amount of frequency shift with respect to the field strength applied. Therefore, the positive and negative Stark tuning rates of a specific stretching mode mean the increase and decrease of the relevant bond strength due to an applied electric field. The total Stark tuning rate ($\Delta \mu_{\text{tot}}$) can be obtained as the sum of the nuclear contribution ($\Delta \mu_{\text{geom}}$) and the electronic one ($\Delta \mu_{\text{elec}}$). Thus, we can calculate $\Delta \mu_{\text{geom}}$ and $\Delta \mu_{\text{elec}}$ according to the following procedure. We first optimize the geometry at each applied electric field. The calculated frequencies at this geometry under the electric field give $\Delta \mu_{\text{elec}}$, whereas those at the same geometry without electric field give $\Delta \mu_{\text{geom}}$. Finally, $\Delta \mu_{\text{elec}}$ can be easily obtained as $\Delta \mu_{\text{tot}} - \Delta \mu_{\text{geom}}$. These are illustrated in Scheme 1.

![Figure 1. Water clusters; (a) monomer, w1; (b) dimer, w2; and (c) tetramer, w4.](Image)

The calculated $\Delta \mu_{\text{geom}}$, $\Delta \mu_{\text{elec}}$, and $\Delta \mu_{\text{tot}}$ for water clusters obtained using anharmonic (including anharmonicity) and harmonic (excluding anharmonicity) frequencies are shown in Figure 2. For all kinds of O$\cdots$D bonds, $\Delta \mu_{\text{geom}}$ is substantially larger than $\Delta \mu_{\text{elec}}$, namely the geometric effect is major origin of VSE. In larger cluster, intermolecular hydrogen bond network can play an important role. To check this influence of hydrogen bonding on cluster size, we compared $\Delta \mu_{\text{tot}}$ for w1, w2-b, and w4-b. It is clear from Figure 2a that $\Delta \mu_{\text{geom}}$ and $\Delta \mu_{\text{tot}}$ values become larger as the cluster size increases, which is consistent with our previous report based on the vibrational frequencies obtained from Morse potential fitting under the influence of external electric field. The calculated $\Delta \mu_{\text{tot}}$ value of water...
tetramer is about 2.7 cm\(^{-1}/(10^8 \text{ V/m})\), which is comparable to that of bulk ice (6–12 cm\(^{-1}/(10^8 \text{ V/m})\)).\(^{19}\)

As shown in Figure 2b, if the anharmonicity is excluded, the calculated \(\Delta \mu_{\text{elec}}\) of dangling bonds would be negligible. But considering anharmonicity, the calculated \(\Delta \mu_{\text{elec}}\) for \(w_2-d_2\) significantly increased, which makes us possible to assume that the potential energy curve for the hydroxyl stretching becomes narrower under the external electric field along \(w_2-d_2\) due to the increased electronic contribution. This tendency in potential curve of hydroxyl stretching results in the decrease of anharmonic characteristics, hence the increase of \(\Delta \mu_{\text{elec}}\). On the other hand, the calculated \(\Delta \mu_{\text{geom}}\) for \(w_2-b\) decreased substantially by considering anharmonicity. This is because the anharmonic potential curve for the hydroxyl stretching becomes less narrowed than the harmonic potential curve under the influence of external electric field, which makes \(\Delta \mu_{\text{geom}}\) with anharmonicity smaller than that without anharmonicity. In this case, the narrowing of anharmonic potential energy curve for the hydroxyl stretching compared with harmonic potential is due to the nuclear motions. Interestingly, \(w_2-b\) and \(w_2-d_2\) showed considerable change of geometry when the electric field was applied along those bonds (Supporting Information). This is related with the induced dipole moment in the system by the external electric field along the specified bonds (\(w_2-b\) and \(w_2-d_2\)). When the dipole moment of a system aligns harmoniously with the external electric field, the system can be stabilized. Practically Kim and co-workers reported that the water molecules are along the same direction of external electric field in water cluster.\(^{35}\)

Consistently with this, the geometry of water dimer showed harmonious alignment with the direction of external electric field along \(w_2-b\) and \(w_2-d_2\). However, the dipole moment of water dimer is already parallel to the direction of electric field along \(w_2-d_1\), thus the geometry change is little under the influence of external electric field. On the other hand, the geometry change of water tetramer under the influence of electric field is very small due to the small dipole moment of water tetramer.

As shown in Figure 3a, the nuclear contribution of the calculated frequencies (\(\nu_{\text{geom}}\)) for O–D bond lengths shows a good linear relationship. Furthermore, the nuclear contribution of the Stark tuning rate (\(\Delta \mu_{\text{geom}}\)) and the change of O–D bond lengths (\(\Delta d_{\text{OD}}\)) (b) for \(w_1\), \(w_2-b\), \(w_2-d_1\), \(w_2-d_2\), \(w_4-b\), and \(w_4-d\).
(\(\Delta q_{\text{elec,LD}}\)) had similar tendency except for the sign. Therefore, we used charge difference values between oxygen and deuterium (\(\Delta q_{\text{pol,LD}} - \Delta q_{\text{pol,O}}\)), as shown in Figure 4a to consider both atomic charges. Interestingly, the linear relationship between \(\Delta q_{\text{pol,LD}} - \Delta q_{\text{pol,O}}\) had size dependency, unlike relation of \(\Delta q_{\text{elec,LD}}\) and O–D bond length. It may be related with more hydrogen bond networking in w2 cluster. In Figure 4b, we could confirm, although there is a slight deviation, the \(\Delta q_{\text{elec,LD}}\) had a linear relationship to the change of charge difference (\(\Delta (\Delta q_{\text{pol,LD}} - \Delta q_{\text{pol,O}})\)).

The local field at a certain position of a molecule is an actual field inside the medium that is contributed by the external field (\(F_{\text{ext}}\)) as well as the internal field (\(F_{\text{int}}\)) generated by the surrounding molecules. The local and internal fields were obtained at the center of charge between oxygen and deuterium. Although the internal field strength was larger than external one (\(|F_{\text{int}}| > |F_{\text{ext}}|\)), the change in internal field upon the change of external field showed different relationships depending on cluster size. In w4, the change of internal field (\(|\Delta F_{\text{int}}|; 8.31 \times 10^8 \text{ V/m}\)) was larger than the change of applied external field. These results implicate that the internal field influence on Stark tuning rate is size-dependent. It might be because the change of internal field (\(\Delta F_{\text{int}}\)) is significantly influenced for small clusters by external field. In large clusters, such changes are somewhat canceled by more surrounding molecules. From the size dependency, it is expected that the large clusters and bulk ice, the Stark tuning rate may be more influenced by the external electric field than the internal field.

## CONCLUSIONS

We calculated Stark tuning rate of hydroxyl stretching modes of w1, w2, and w4 using the ab initio method. The calculated Stark tuning rates were partitioned by origin of VSE: geometric and electronic effects. The results illustrated that contribution of geometric effect is larger than that of electronic effect. We found larger \(\Delta \mu_{\text{geom}}\) and \(\Delta \mu_{\text{elec}}\) values in larger sized cluster due to intermolecular hydrogen bond network in larger cluster. From the comparison of Stark tuning rates including and excluding anharmonicity, we could confirm that anharmonicity had a greater effect on Stark tuning rate only in specific bonds. The \(\Delta \mu_{\text{geom}}\) of w2-b and \(\Delta \mu_{\text{elec}}\) of w2-d2 showed significant decrease and increase, respectively, by considering anharmonicity. The changes of molecular arrangement and dipole moment were also observed only in these two bonds by applied electric field. Among the structural factors, the bond length was a good indicator for the geometric contribution of Stark tuning rate, with a linear relationship between the O–D stretching frequency and bond length. For electronic effect, the atomic charges of oxygen and deuterium showed a good linear relationship with electronic contribution of Stark tuning rate and showed size dependency in relation with \(\nu_{\text{elec}}\). Finally, we compared the local field induced by external field and confirmed that the influence of internal field on Stark tuning rate has size dependency. Our consideration of the electronic and nuclear contributions separately to VSE is the first trial to understand the origin of VSE more deeply and may give a new insight for the utilization of VSE.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b03936.

Change of molecular arrangement and dipole moment under the external electric fields (Figure S1); dipole moments of water dimer under the external electric fields (Table S1); relationships of the electronic contribution of calculated frequencies (\(\nu_{\text{elec}}\))/Stark tuning rate (\(\Delta \mu_{\text{elec}}\)) with the variation of atomic charges of O and D (\(\Delta (\Delta q_{\text{elec,LD}})/\mu_{\text{geom}}\)) the difference in the charge variation (\(\Delta q_{\text{elec,LD}}\)) Figure S2 (PDF).

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