Effect of Electric Field on Condensed-Phase Molecular Systems. II. Stark Effect on the Hydroxyl Stretch Vibration of Ice

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14-11-2015
Electric fields play an important role in chemical reactions and influence various physical and chemical phenomena in nature.

Rate of reactions are influenced by the electric fields that are generated from local charge, dipole moment, polarizability of the reactant molecule and also by the fields from surrounding solvents in condensed phase.

Electric fields can shift the absorption frequencies of molecular vibrations by changing the dipole moment and polarizability of molecules associated with the vibrational transitions. This phenomenon, known as the vibrational Stark effect (VSE), is an important aspect of IR spectroscopy in condensed phases.

In this paper…how electric field affect –OH stretching frequency on condensed water surface…probed using VSE
The IR spectra of water ice is complicated by contributions from several factors.

The hydroxyl stretching frequency is sensitive to the local environment of ice because the local field varies with the proton-disordered arrangement of the lattice.

Intra, inter and lattice molecular vibrational coupling in ice tend to delocalize the vibrational modes.

This vibrational coupling effects are separated by using samples of diluted HDO in H₂O (or D₂O). The –OD (or –OH) in HOD, vibrational couplings are negligible in such system and the experimental line shape can directly reflect the local electric field.

The ice film capacitor method has been used to apply strong electric field to the sample.
Construction of ice film capacitor

HDO concentration was prepared by mixing liquid H\(_2\)O and D\(_2\)O in a \textbf{96.5:3.5} ratio at room temperature.

Voltage of the film measured by:
1. Kelvin probe
2. Vibrational Stark effect

DOI: 10.1021/acs.jpcc.5b01850
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Schematic of the experimental apparatus. A molecular film was condensed onto a Pt(111) crystal, which is located at the chamber center and maintained at low temperature by a liquid He cryostat. The molecular film was covered with an ice overlayer and subsequently charged by depositing Cs+ ions on the ice surface (see inset). The Kelvin work-function probe measured the voltage developed across the charged sample. The FT-IR spectrometer measured the molecular composition and orientation of the molecules in the sample. All the experiments were conducted under a UHV environment.
Equations concerning parallel plate capacitor

\[ V = \frac{Q}{C} = \frac{\sigma d}{\varepsilon_r \varepsilon_0} \]

- \( V \) - voltage across the film
- \( Q \) - surface charge of Cs\(^+\) ions
- \( C \) - capacitance of the film
- \( \sigma \) - surface charge density
- \( d \) - film thickness
- \( \varepsilon_r \) - dielectric constant of the sample
- \( \varepsilon_0 \) - vacuum permittivity

Electric field strength within the sample will be

\[ F = \frac{V}{d} = \frac{\sigma}{\varepsilon_r \varepsilon_0} \]

The voltage across the film was measured using a Kelvin probe.
The thickness of the ice using TPD measurements.
Kelvin Probe measures,
Contact Potential Difference (CPD) = $\varphi_{\text{probe}} - \varphi_{\text{sample}}$
ΔCPD, the difference of film voltages measured before and after Cs$^+$ deposition is what is important for the experiment.

Dividing ΔCPD with film thickness ($d$) gives the electric field strength ($F$) within the film, $F = \Delta \text{CPD}/d$.

The film thickness can be estimated by measuring the water coverage in TPD experiments and from the water monolayer coverage ($1.1 \times 10^{19}$ molecules m$^{-2}$ ML$^{-1}$) and the density of amorphous ice, assuming that the amorphous ice structure was isotropic.
**Stark Effect**

The **Stark effect** is the shifting and splitting of spectral lines of atoms and molecules due to presence of an external electric field.

Here it is seen in Vibrational spectrum hence **VIBRATIONAL STARK EFFECT (VSE)**

The other one is **Zeeman effect** the same due to an external magnetic field.

http://www.afs.enea.it/apruzzes/Spectr/Stark/strong.html
Figure 1. (upper) RAIR spectrum of crystalline ice composed of ∼7% HDO and ∼93% H2O measured in the absence of an external electric field. (lower) The field-on minus field-off difference spectrum, which corresponds to the absorbance difference (ΔA) of a sample in the presence and absence of applied field. The field strength was $1.8 \times 10^8$ V·m$^{-1}$. The difference spectrum is displayed on a magnified scale (×5).
Figure 2. (a) (upper) RAIR spectra showing spectral broadening of the ν(O–D) band of dilute HDO in HDO–ice with increasing applied electric field. (lower) The field-on minus field-off difference spectra for the absorbance spectra shown at the top. (b) Spectral broadening of the ν(O–H) band of dilute HDO in D2O–ice. The relative population of HDO in ice was ∼7% in both the samples.

Full width half maxima (FWHM) Changed from ~20 cm⁻¹ to ~37 cm⁻¹ due to the field

Stark effect appears as a spectral broadening rather than a shift in peak position because the chromophores are randomly oriented in the sample.

Crystalline ice sample ensures narrower inhomogeneous band broadening and also prohibits the re-orientation of water molecules under applied field, which may cause additional spectral changes.
Figure 3. Variation in the spectral width (fwhm) of ν(O–D) as the electric field strength was increased and decreased. The numbers within the plot indicate the field change sequence.

The reversibility of bandwidth behaviour indicates that the changes are due to an electronic effect (VSE) and not due to any structural change in the sample.
Figure 4. Spectral analysis of the ν(O–D) band of dilute HDO in H2O–ice using different models. The applied field strength is $1.8 \times 10^8$ V·m$^{-1}$. (a) The experimental difference spectrum (black) is fitted to the model developed by Andrews and Boxer (red).(23) (b) The experimental absorbance spectrum (black) is fitted to the results of the numerical simulations (red). The dotted curves represent the simulated absorbance for O–D oscillators with the polar angle with respect to the field direction between $\theta = 30^\circ \pm 10^\circ$ (blue), $\theta = 70^\circ \pm 10^\circ$ (orange), $\theta = 110^\circ \pm 10^\circ$ (orange), and $\theta = 150^\circ \pm 10^\circ$ (blue). These curves illustrate that the oscillators in the near-polar angles (blue) contribute a larger amount of absorbance to the spectrum than those in the near-equatorial angles (orange) due to the cos2(θ) factor (see text), although the number of oscillators in the near-polar solid angle is smaller than that in the near-equatorial solid angle.

- $\Delta \mu$ plays a dominant role in spectral broadening
- $\Delta \alpha$ term to spectral broadening is minor.
- $\Delta \alpha$ term reproduce the asymmetry in the ν(O–D) spectral shape appearing under the field.
- This simulation method looks more accurate than Andrews and Boxer method using second derivative spectra.

**Stark Tuning Rate ($\Delta \mu$)**

$$\Delta \nu \cong -\frac{1}{\hbar} \left( \Delta \mu \cdot F + \frac{1}{2} F \cdot \Delta \alpha \cdot F \right)$$

- Peak shift
- Stark tuning rate, represents the difference in dipole moments between the ground and excited states cm$^{-1}$/MV/cm$^{-1}$ or D
- Difference in polarizability

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Observations regarding the Stark tuning rates

- $\Delta \mu$ value of the hydroxyl stretching vibration of ice is over 10 times larger than that of typical chromophore groups of other frozen molecular solids
  $\Delta \mu(\text{C≡N of acetonitrile}) = 0.23-0.6 \text{ cm}^{-1}/(\text{MV} \cdot \text{cm}^{-1})$
  $\Delta \mu(\text{C≡O}) = 0.67 \text{ cm}^{-1}/(\text{MV} \cdot \text{cm}^{-1})$

- $\Delta \mu$ value of $\nu(\text{O–H})$ is 1.5–1.8 times larger than that of $\nu(\text{O–D})$ at the same field strength

- $\Delta \mu$ values decrease with increasing field

- In eq 1 it is assumed that $\Delta \mu$ is a constant for linear proportionality between $\Delta \nu$ and $F$ while in the present results, however, $\Delta \nu$ varies quite nonlinearly with $F$. 

Figure 5. Stark tuning rates of the $\nu(\text{O–H})$ and $\nu(\text{O–D})$ bands of ice measured at different field strengths.
Simulating VSE of water molecules in ice for three model systems: Monomer (HDO); w1, dimer (HDO)\textsubscript{2}; w2 and octamer (HDO)\textsubscript{8}; w8

Figure 6. Optimized geometries of (a) w1, (b) w2, and (c) w8 without an external electric field. The direction of external field (arrow) is drawn on the O–D bonds of interest (marked with a star).

W1----0.35 cm\textsuperscript{-1}/(MV.cm\textsuperscript{-1})
W2----0.69 cm\textsuperscript{-1}/(MV.cm\textsuperscript{-1})
W1----4.8 cm\textsuperscript{-1}/(MV.cm\textsuperscript{-1})
Experimental value is 
------6.4 cm\textsuperscript{-1}/(MV.cm\textsuperscript{-1})

Figure 7. Potential energy curve for O–D in (a) w1, (b) w2, and (c) w8 at applied field strengths of $-7.7 \times 10^0$, 0, and $7.7 \times 10^8$ V·m\textsuperscript{-1}.
Figure 8. Comparison of the potential energy curves of O–D for w1 (red), w2 (black), and w8 (blue) without an external field.

- Intermolecular H-bonding causes significantly larger changes in the potential energy curves compared to the changes caused by the external field.
- The energy of the potential energy curve is lowered for w2 and w8 compared to w1.
- Anharmonicity of the O-D vibrations is also increased for w8.
- The presence of a larger number of neighbouring water molecules can better stabilize the stretched O–D bond via the hydrogen bond network inside the water cluster.
- The enhanced anharmonicity of the O–D oscillator possibly induces greater changes in the difference of the dipole moments and polarizabilities.
Effect of Electric Field on Condensed-Phase Molecular Systems. I. Dipolar Polarization of Amorphous Solid Acetone

DOI: 10.1021/acs.jpcc.5b01849
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They have studied the VSE of the hydroxyl stretch vibration of a crystalline ice sample under strong direct current electric fields by monitoring the spectral changes of vibrationally decoupled O–H or O–D bands of dilute HOD in ice.

This experiment measures the VSE induced only by an applied electrostatic field in the absence of other frequency-shifting effects such as those associated with structural changes of chromophore environment under the electric field.

The major features of the spectral changes appearing under the field could be reproduced by a numerical analysis model that calculates the integrated absorption of a collection of Stark-shifted oscillators in RAIRS geometry.

The Stark tuning rate of the hydroxyl stretch vibration is estimated to be $\Delta \mu (\text{O–D}) = 6.4-12 \text{ cm}^{-1}/(\text{MV/cm})$ at $F = 1.8 \times 10^8$ to $6.4 \times 10^7 \text{ V} \cdot \text{m}^{-1}$ and $\Delta \mu (\text{O–H}) = 10-16 \text{ cm}^{-1}/(\text{MV} \cdot \text{cm}^{-1})$ at $F = 2.3 \times 10^8$ to $9.2 \times 10^7 \text{ V} \cdot \text{m}^{-1}$.
The $\Delta \mu$ value is not constant in these field strength ranges. Instead, $\Delta \mu$ decreases with increasing field strength when it is deduced from eq 1, which assumes that $\Delta \mu$ is linear proportionality coefficient between $\Delta \nu$ and $F$.

The isotopic effect on the Stark tuning rate is observed to be $\Delta \mu(\text{O-H})/\Delta \mu(\text{O-D}) = 1.5-1.8$.

The VSE of the hydroxyl stretch vibration of ice is uniquely large compared to the vibrations in other frozen molecular solids.

The large $\Delta \mu$ value of ice can be attributed to the extensive hydrogen-bonding network in water ice.

This interpretation is supported by quantum mechanical calculations of water cluster models, which illustrate that the intermolecular hydrogen bonding in water clusters increases the Stark shift of the hydroxyl stretch frequency.
Future perspective

Re-orienting a molecule with respect to field may help to have better interaction with a catalyst on ice surface

Thank you all....