Vibrational Response of Hydrogen-Bonded Interfacial Water is Dominated by Intramolecular Coupling

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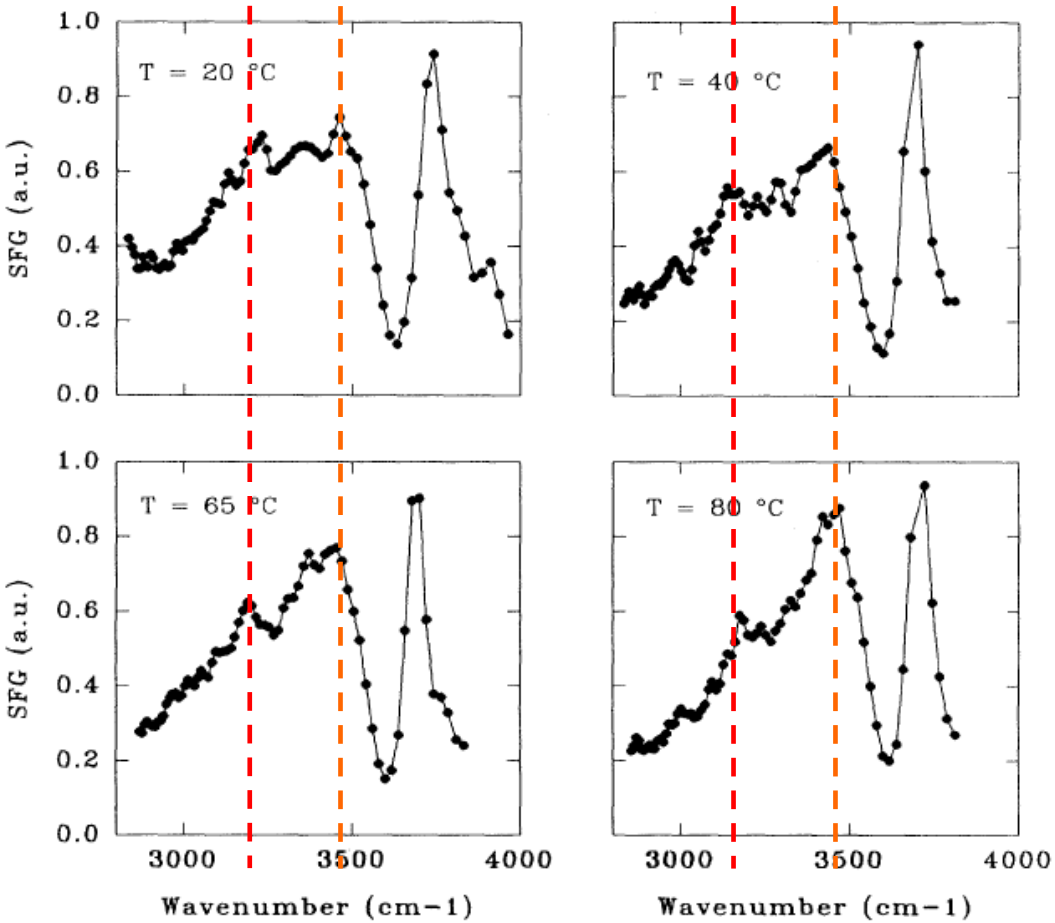
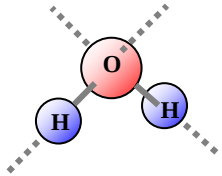
Using the surface-specific vibrational technique of vibrational sum-frequency generation, we reveal that the double-peaked structure in the vibrational spectrum of hydrogen-bonded interfacial water molecules originates from vibrational coupling between the stretch and bending overtone, rather than from structural effects. This is demonstrated by isotopic dilution experiments, which reveal a smooth transition from two peaks to one peak, as D_2O is converted into HDO. Our results show that the water interface is structurally more homogeneous than previously thought.

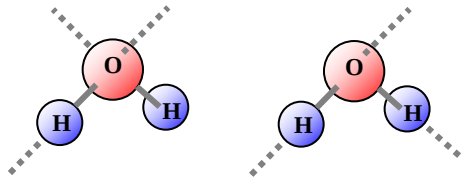
Introduction – model I (ice & water like)

ice like *v*OH water like *v*OH





ice like

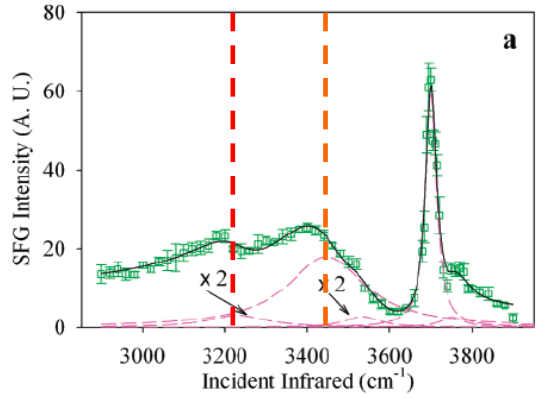


water like

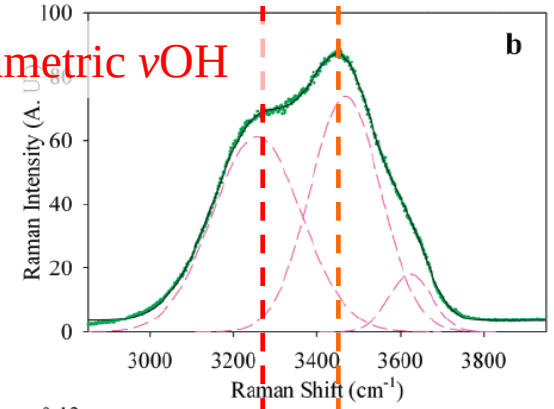
Du et al. Phys. Rev. Lett. **70**, 2313 (1993)

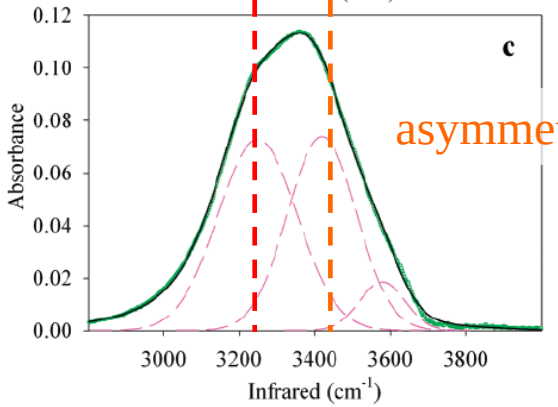
SMOS Soft-Matter Optical Spectroscopy

Introduction – model I (OH symmetric & asymmetric)

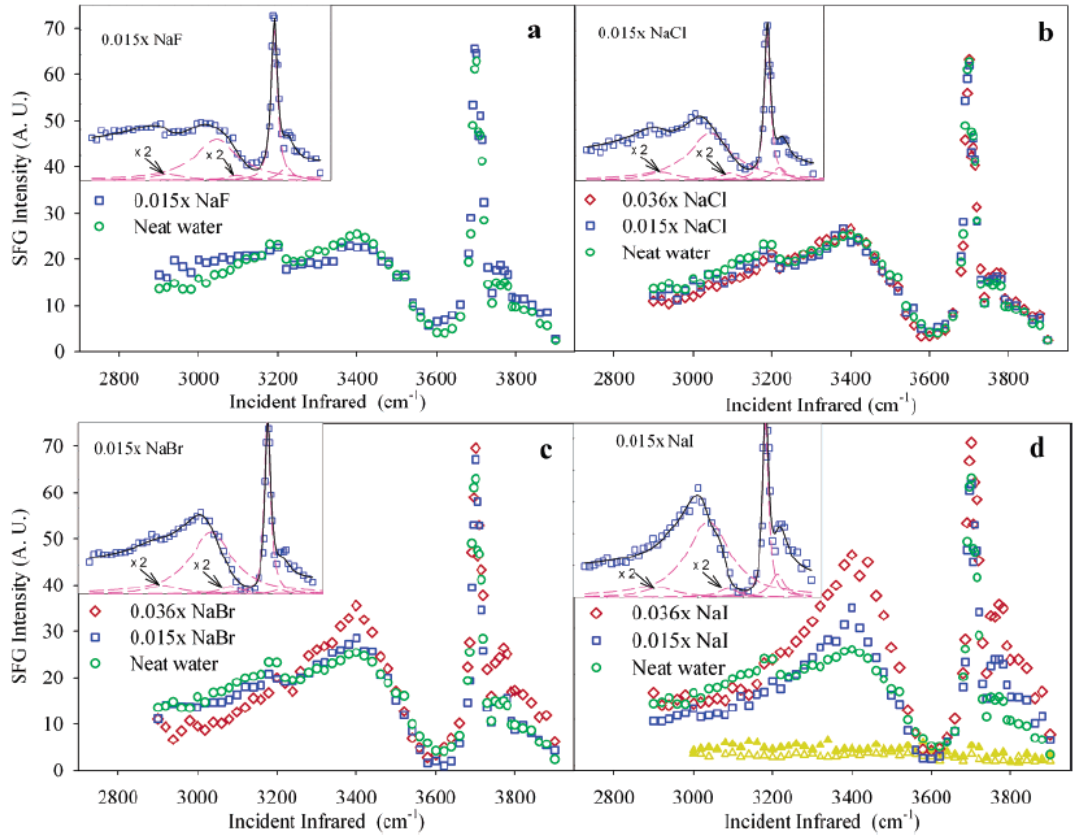


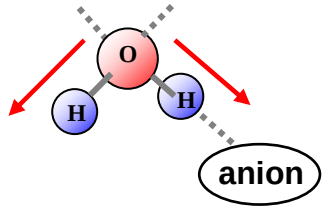
symmetric *v*OH

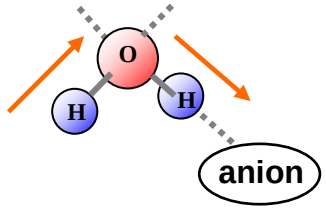




asymmetric *v*OH



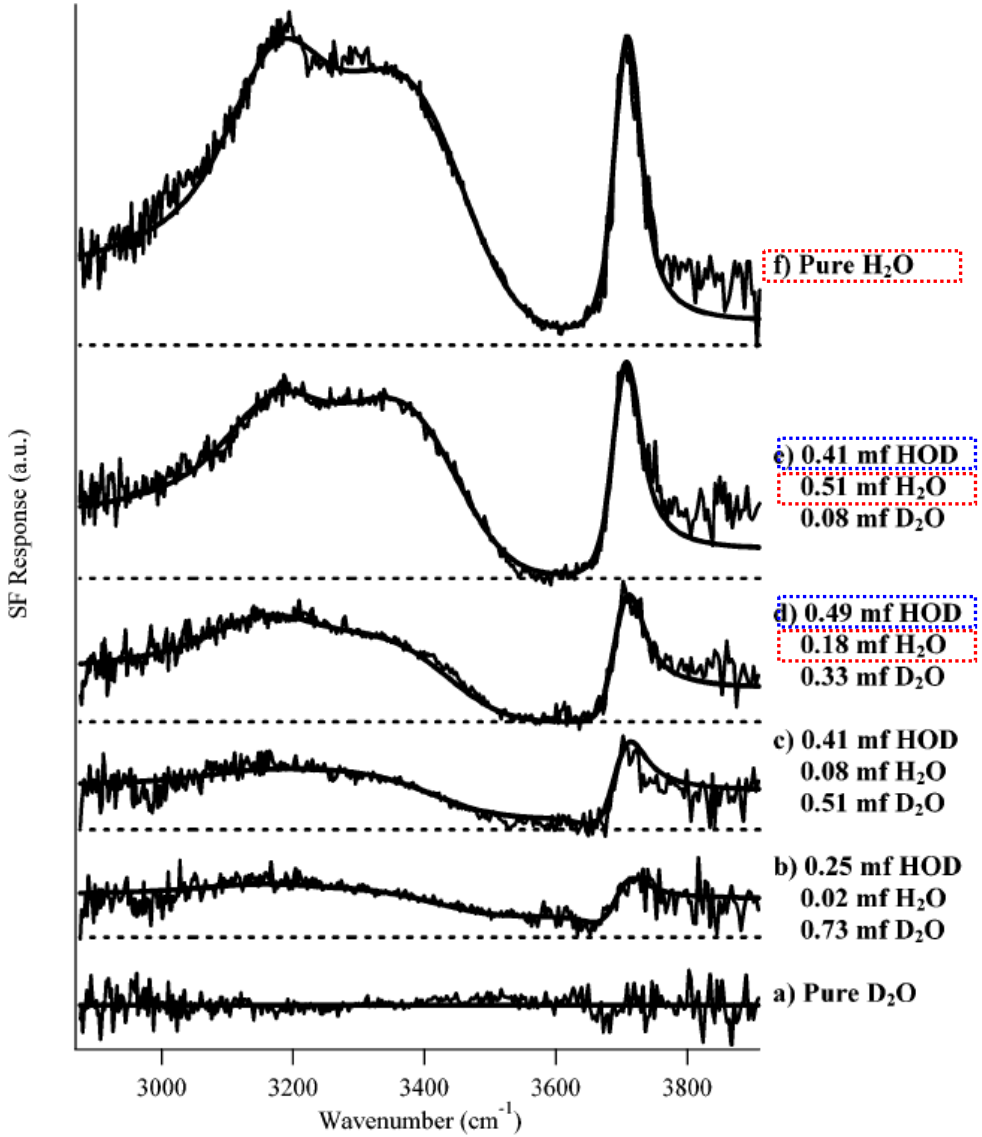


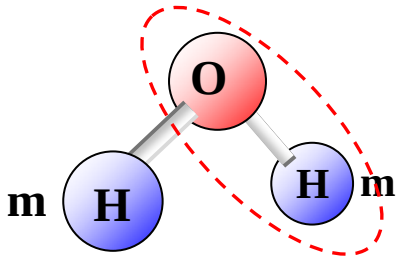


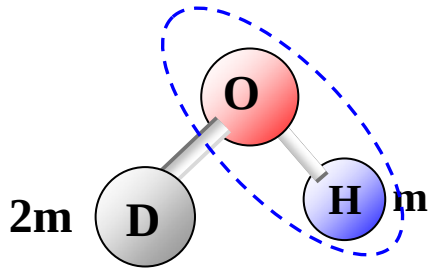
Raymond et al. J. Phys. Chem. B **108**, 5051 (2004)

Soft-Matter Optical Spectroscopy

Introduction – model I (ice & water like)

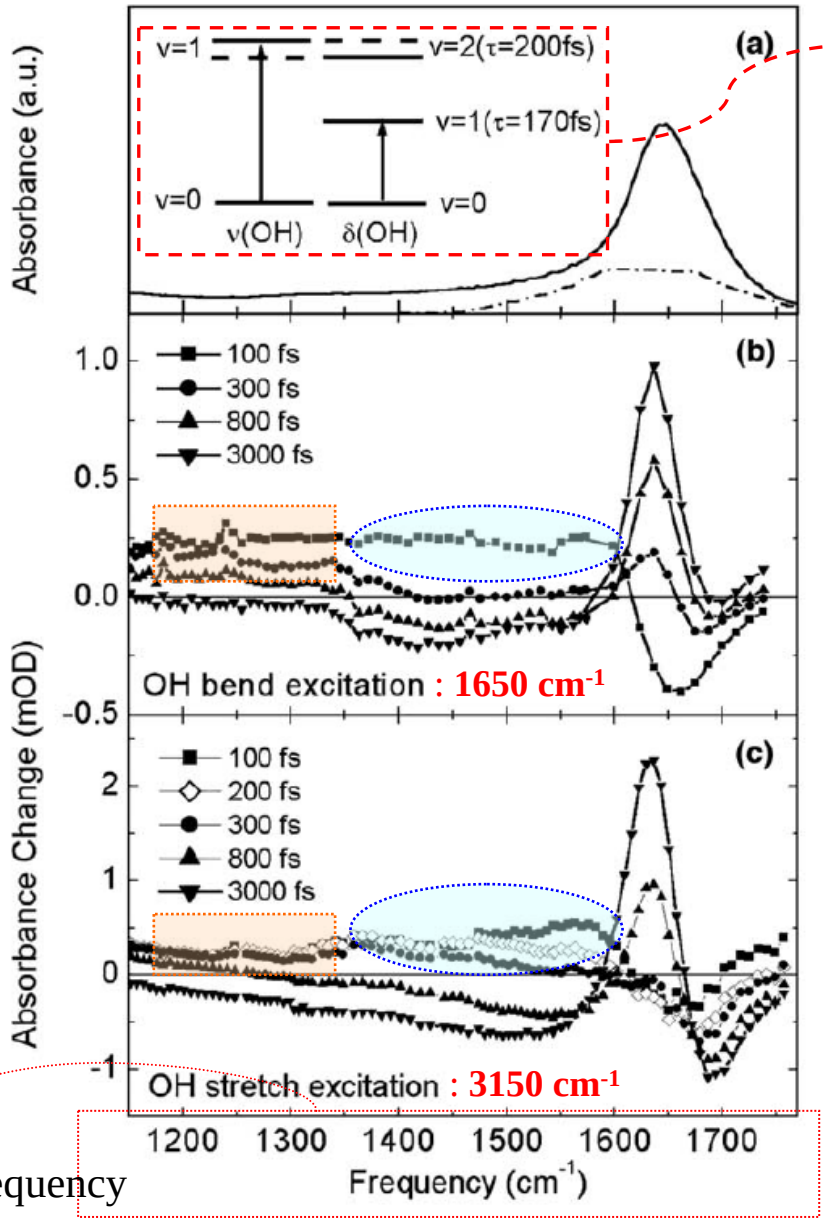






Raymond et al. J. Phys. Chem. B **107**, 546 (2003)

Introduction – model II (overtone with bending mode)



have been reported

below 1350 cm^{-1} : transient absorption

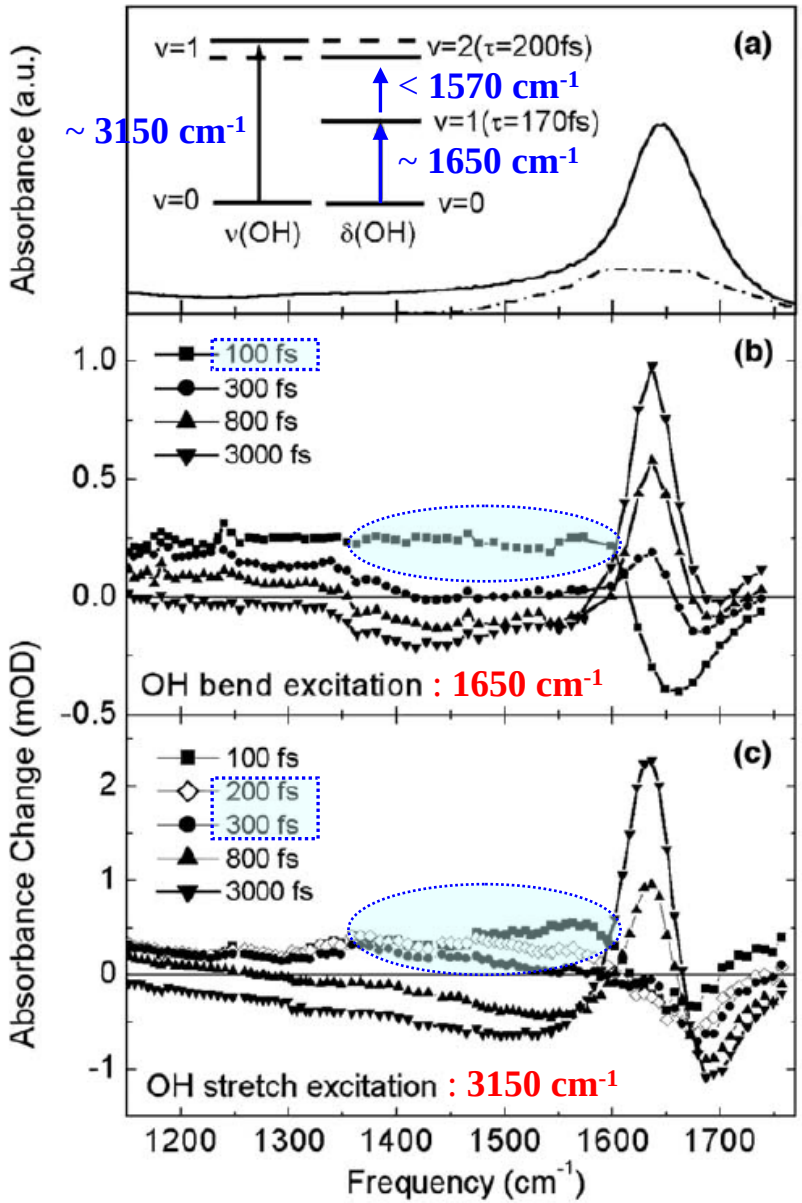
below 1570 cm^{-1} : broadband bleaching

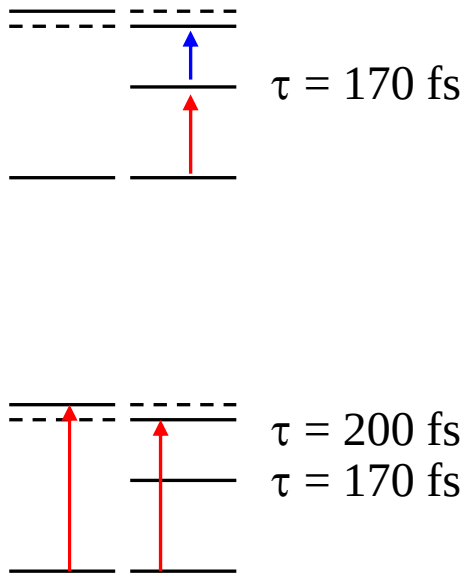
$\Delta A = -\log(T/T_0)$

Ashihara et al. Chem. Phys. Lett. **424**, 66 (2006)

SMOS Soft-Matter Optical Spectroscopy

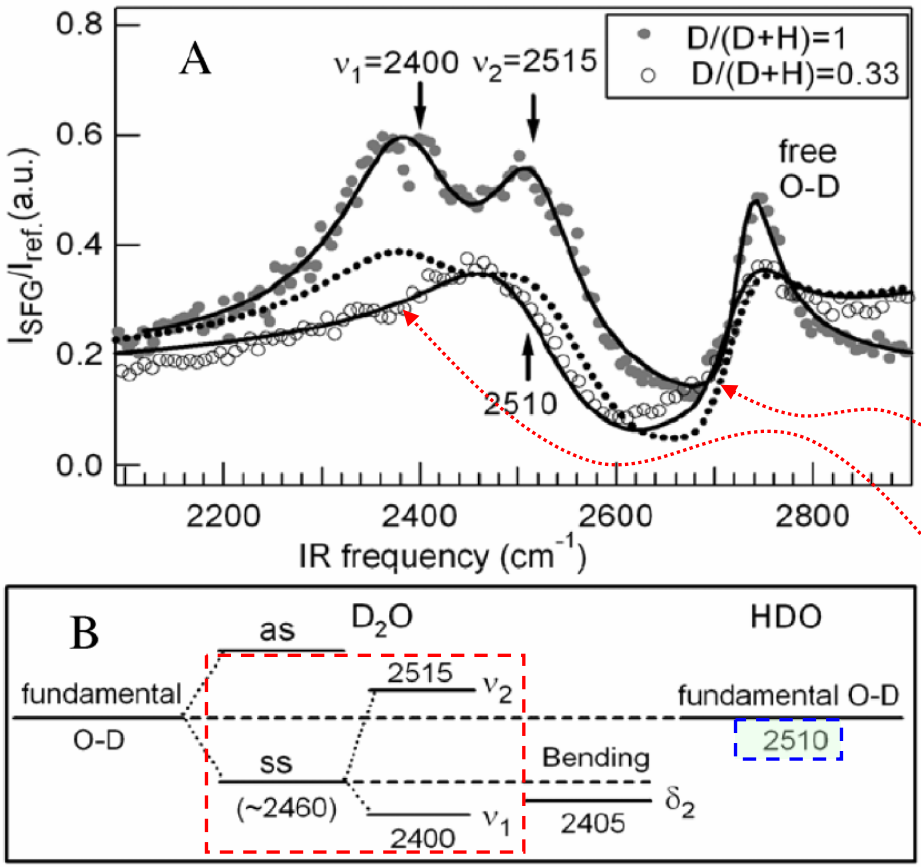
Introduction – model II (overtone with bending mode)





Ashihara et al. Chem. Phys. Lett. **424**, 66 (2006)

OD vibration modes



The **O-D**, rather than the O-H, stretch vibrations are probed, as our tunable infrared source works more effectively in this frequency range.

simulated data for the 'icelike' and 'waterlike' hypothesis

D/(D+H)=0.33

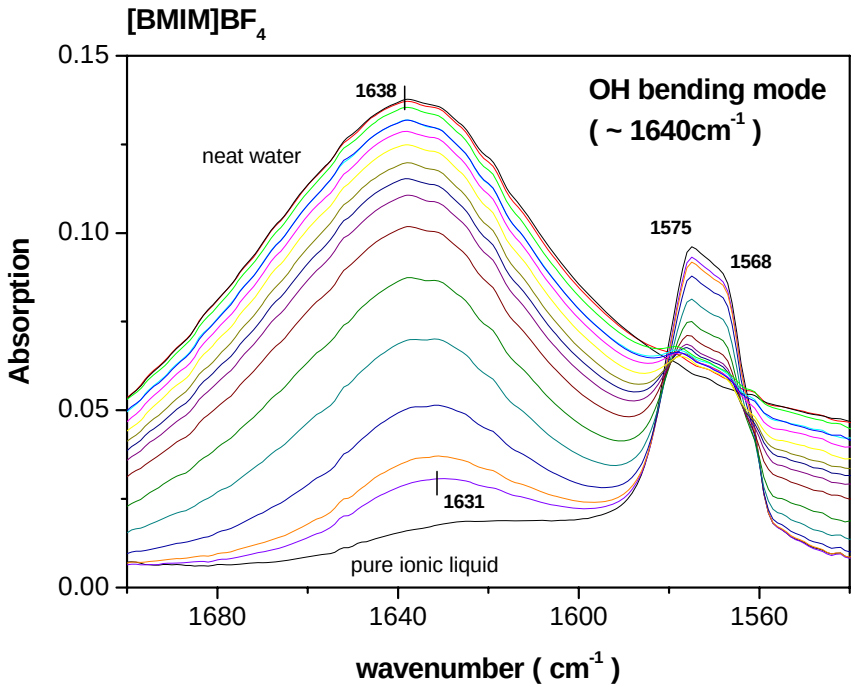
n (HDO) ~ 4 * n (D_2O)

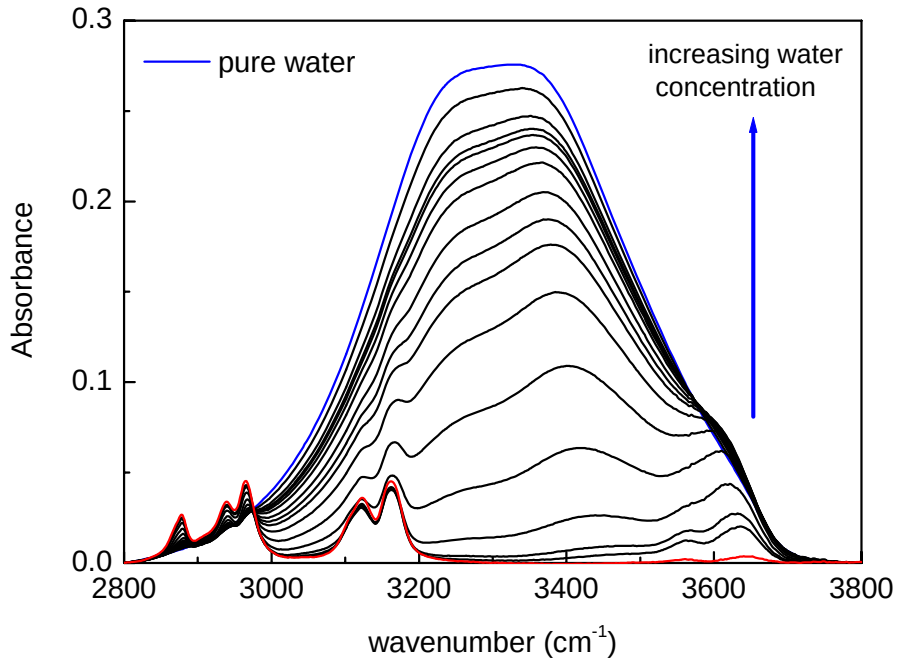
$I_{\nu OD}$ **(HDO)** >> $I_{\nu OD}$ (D_2O)

fitting parameters

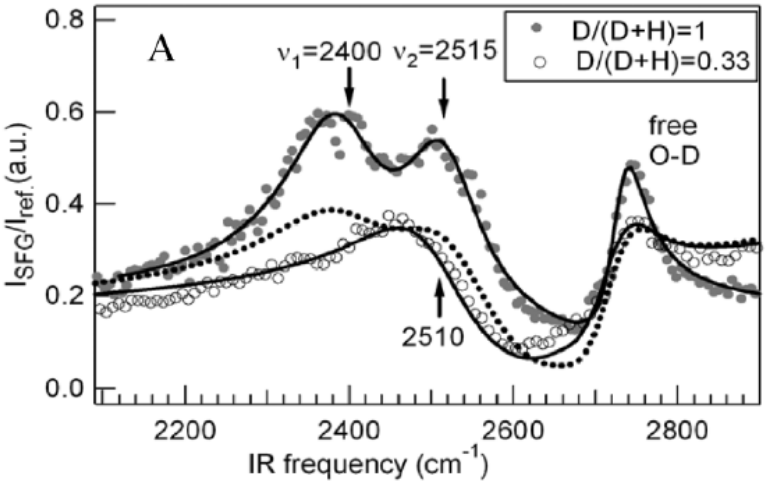
	ω_i	Γ_i
ν_1	2400	140
ν_2	2515	120

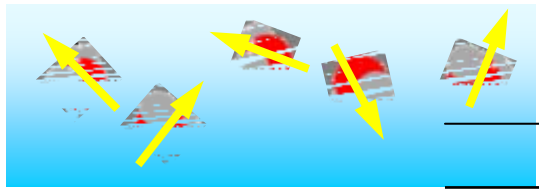
Introduction



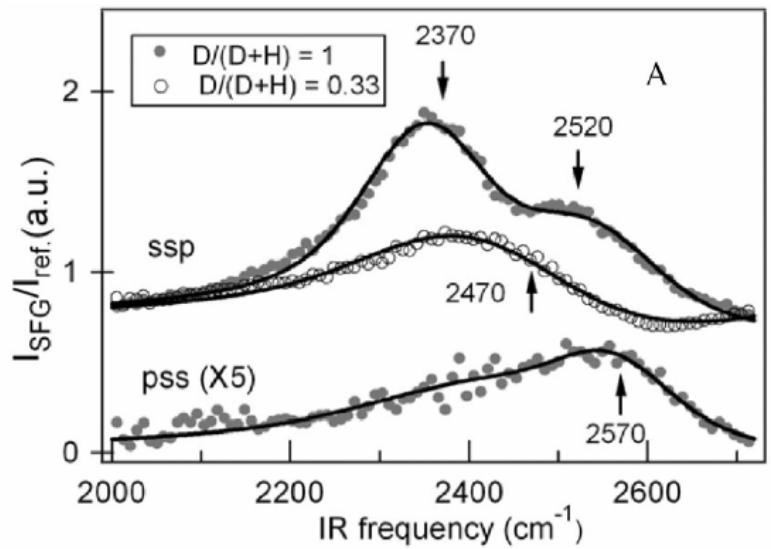


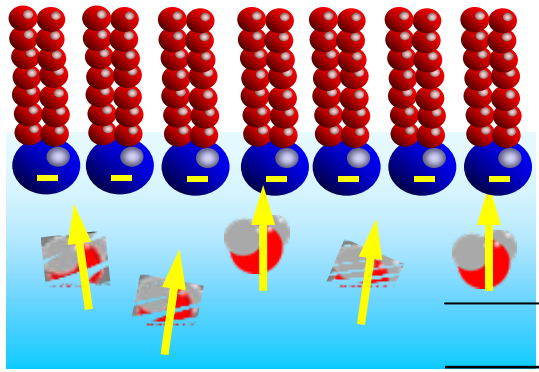
OD vibration modes





	ω_i	Γ_i
ν_1 (D_2O)	**2400**	**140**
ν_2 (D_2O)	**2515**	**120**
ν (HDO)	**2510**	**140**





interaction
→ red shift
→ broaden

	ω_i	Γ_i
ν_1 (D_2O)	**2370**	**140**
ν_2 (D_2O)	**2520**	**180**
ν (HDO)	**2470**	**240**

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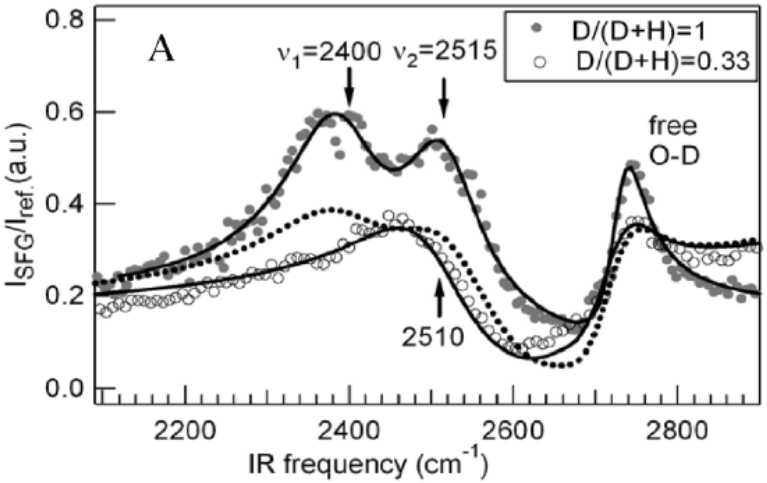
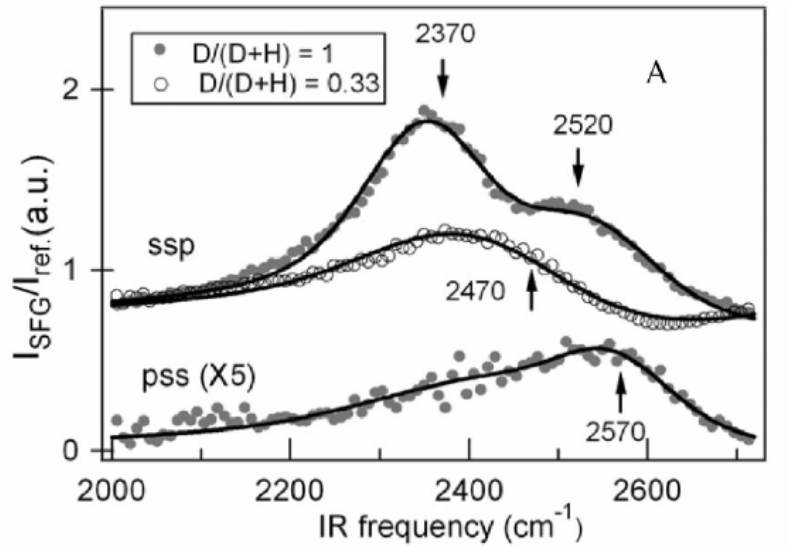
OD vibration modes



model I ("ice or water like")

- the structure of VSFG : should have remained identical
- overall spectrum : <u>only the amplitudes should have decreased</u> upon isotopic dilution



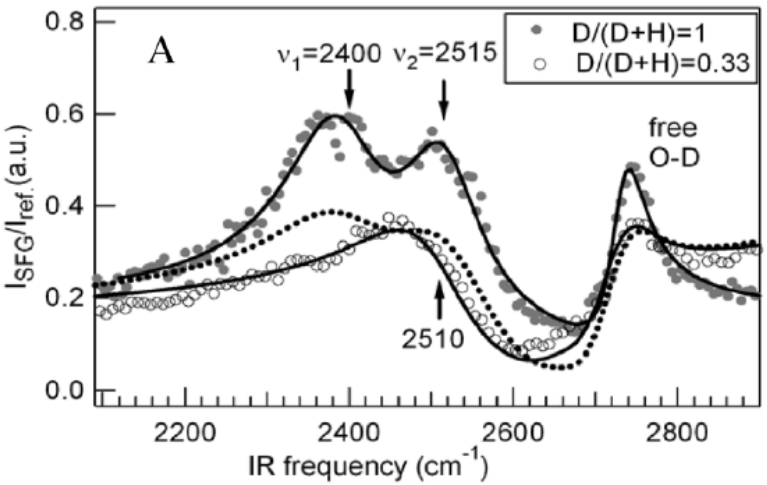
model II (ice & water like)

D_2O → HDO
: appearance of new spectral feature

↓ molecular symmetry is broken

two O-D stretch peaks of interfacial D_2O originate from **intramolecular coupling** (ex. ss & as)

OD vibration modes

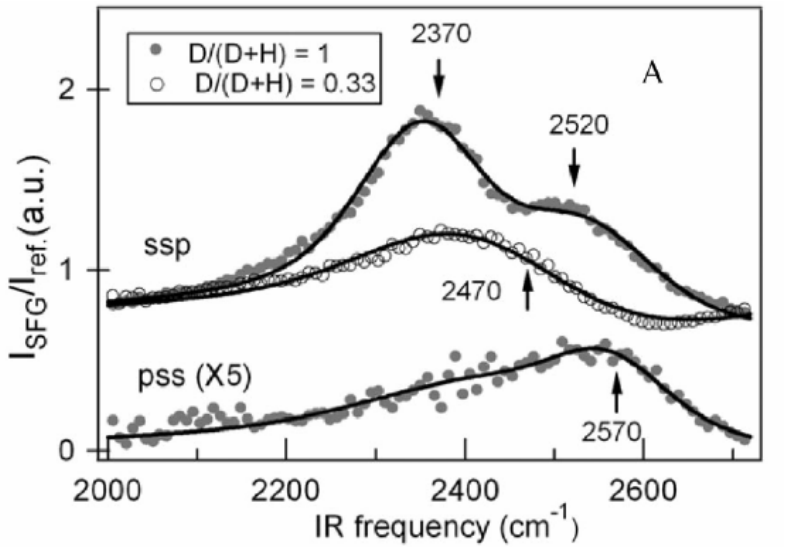


model I ("ss & as stretch OH")

ν_1 = 2400 cm^{-1} : ss mode
ν_2 = 2515 cm^{-1} : as mode

$m_D << m_O$

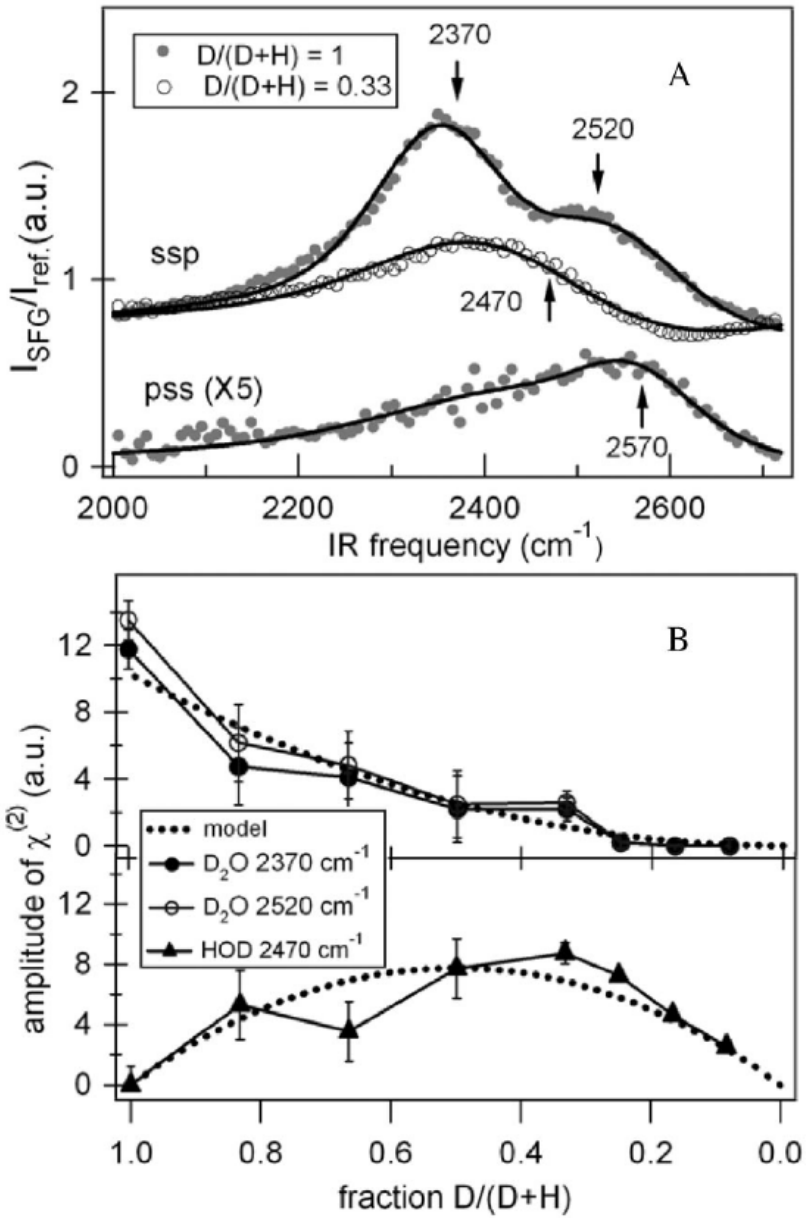
$\nu_{O\text{-}D}(HOD) = (\nu_1 + \nu_2)/2 = 2460\ cm^{-1}$



if ν_2 = 2460 cm^{-1} peak originates from the **as** mode

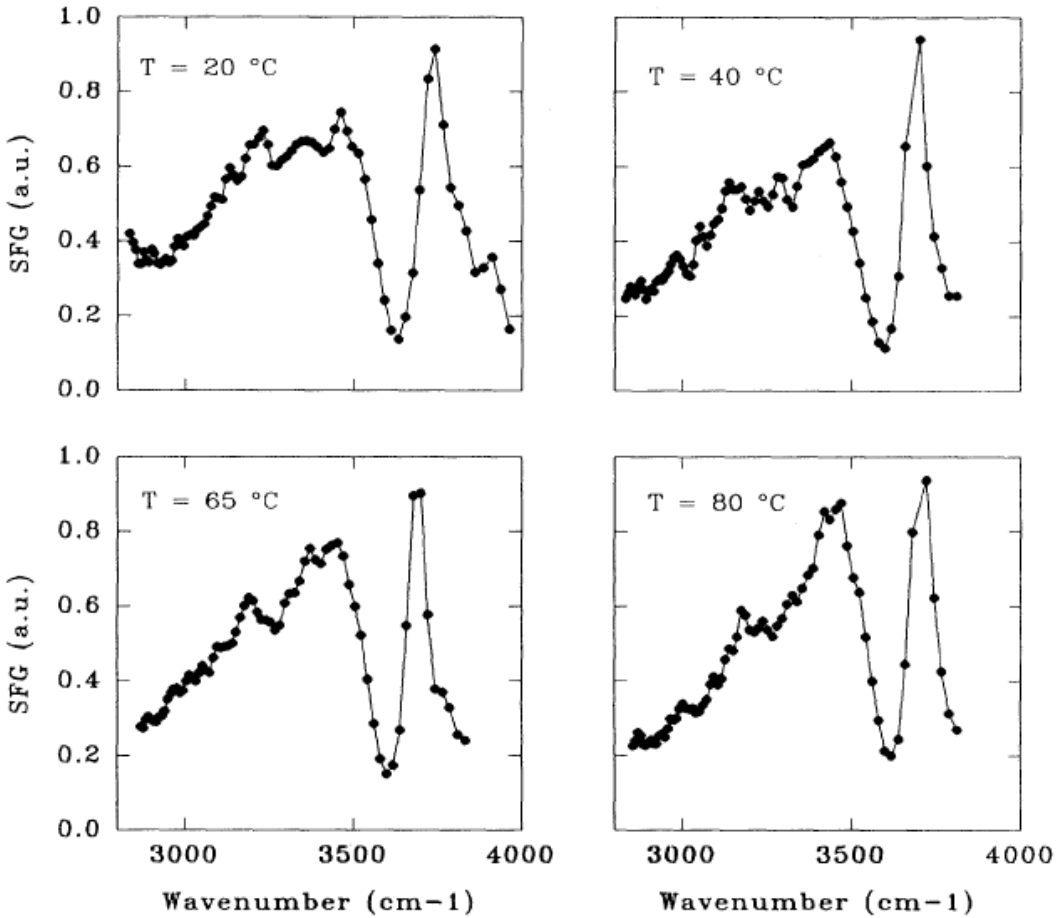
then it should appear more markedly in the *ppp* and *pss* spectra

OD vibration modes



OH vibration modes

Q. Do it well correspond with **temperature** dependence ?



Du et al. Phys. Rev. Lett. **70**, 2313 (1993)

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