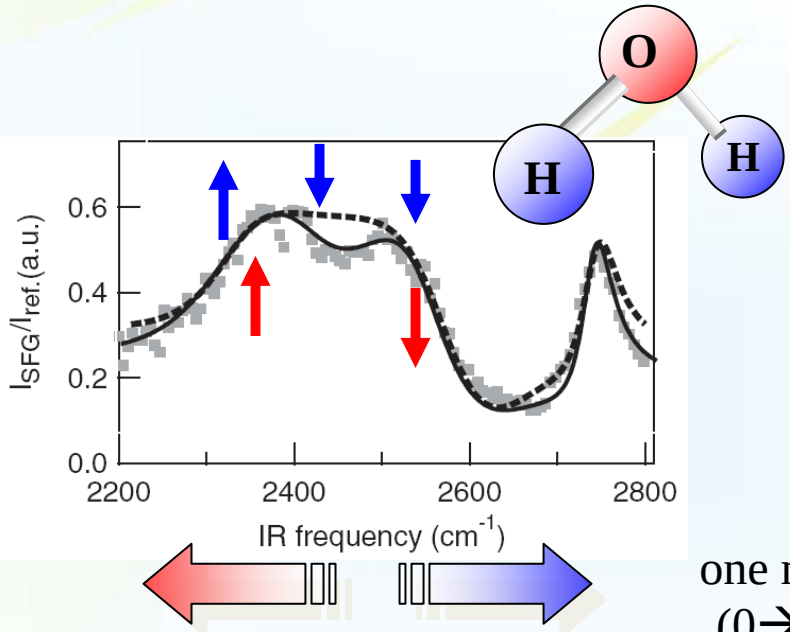
Interfacial water studied by sum-frequency generation

ice like &
water like



one more peak : overtone (0→ 2 transition) of the bending mode

발표자 : Yoonnam Jeon (28th Aug 2009)

Introduction – history

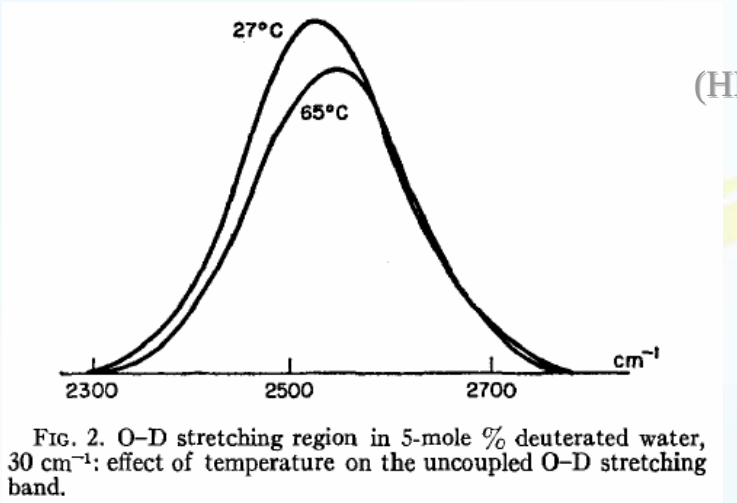
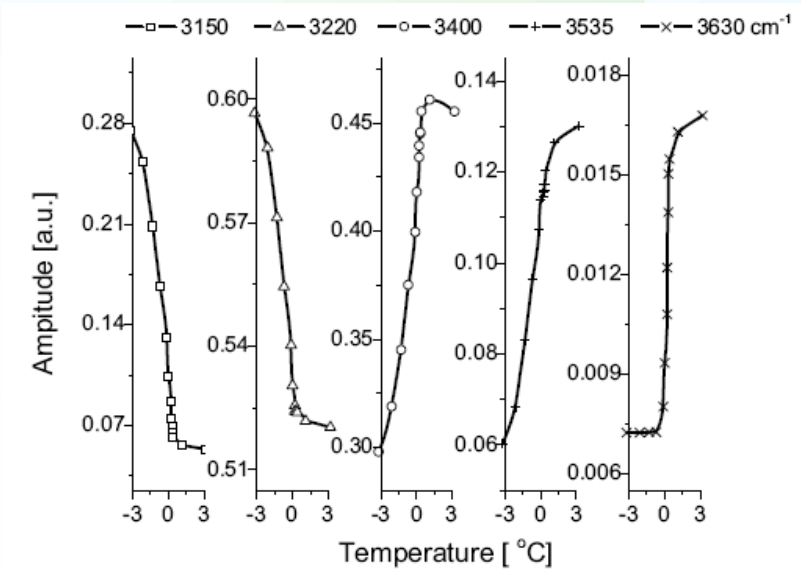


FIG. 2. O–D stretching region in 5-mole % deuterated water, 30 cm^{-1}: effect of temperature on the uncoupled O–D stretching band.

(HDO exp. with Raman)

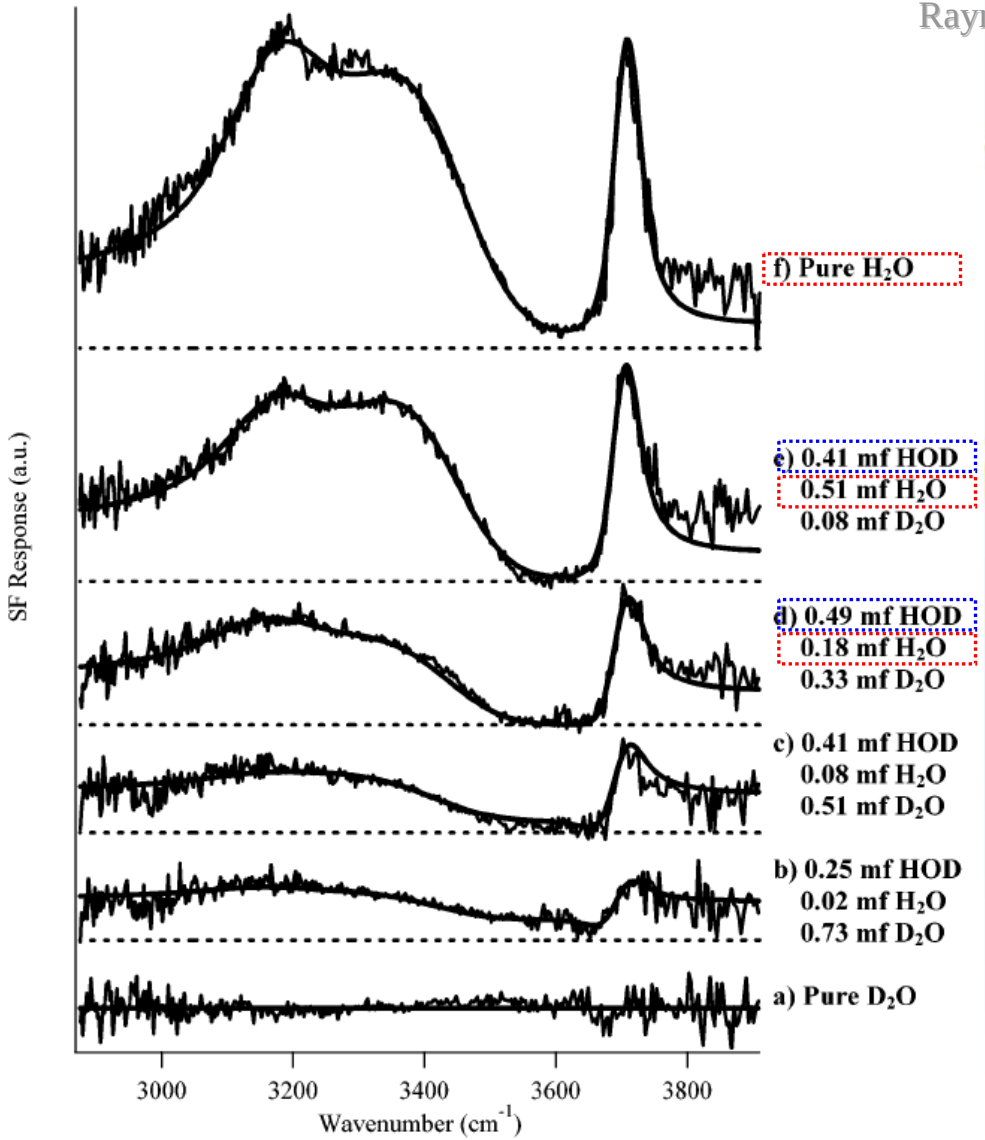
Wall and Hornig. J. Chem. Phys. **43**, 2079 (1965)

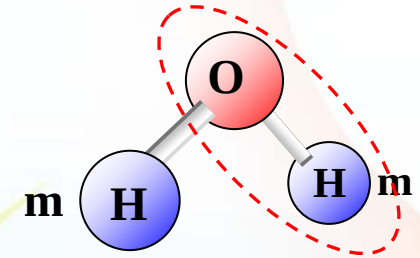


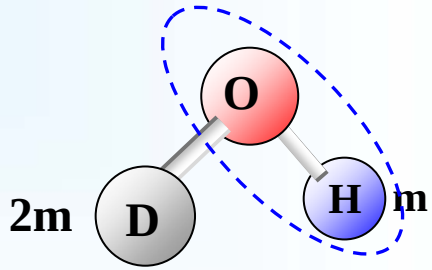
IR exp. Phys. Rev. Lett. **93**, 185703 (2004)

Introduction – model I (ice & water like)

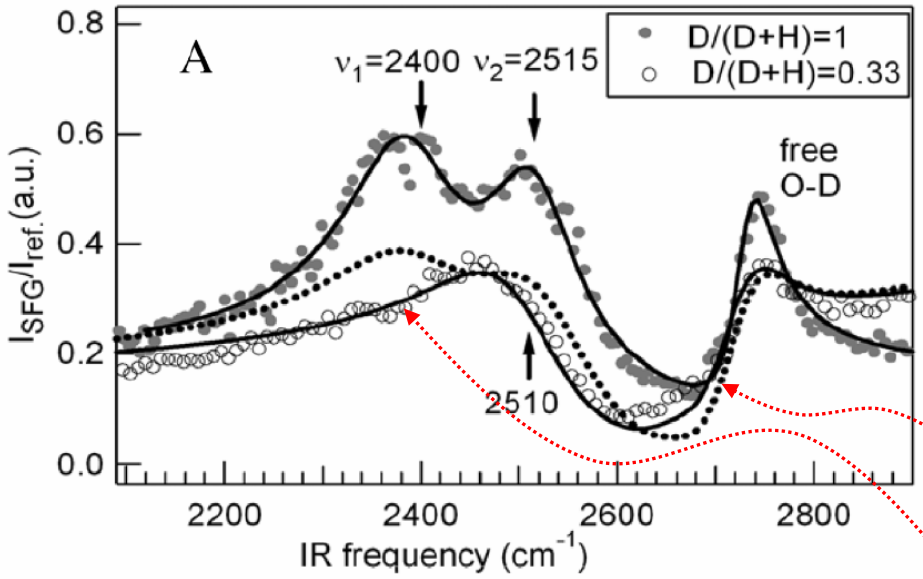
Raymond et al. J. Phys. Chem. B **107**, 546 (2003)







Introduction – model II (overtone of bending mode)



Sovago et al. Phys. Rev. Lett. **100**, 173901 (2008)

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)

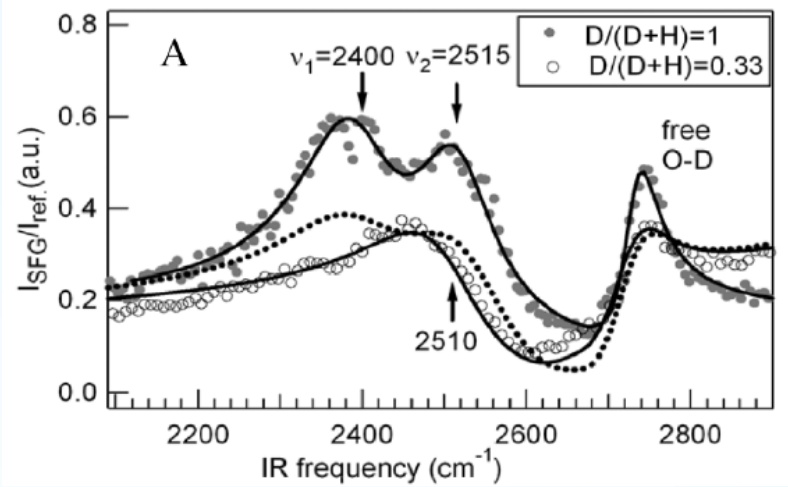
$I_{\nu OD}$ **(HDO)** >> $I_{\nu OD}$ (D_2O)

fitting parameters

	ω_i	Γ_i
ν_1	2400	140
ν_2	2515	120

Introduction – model II (overtone of bending mode)

Sovago et al. Phys. Rev. Lett. **100**, 173901 (2008)

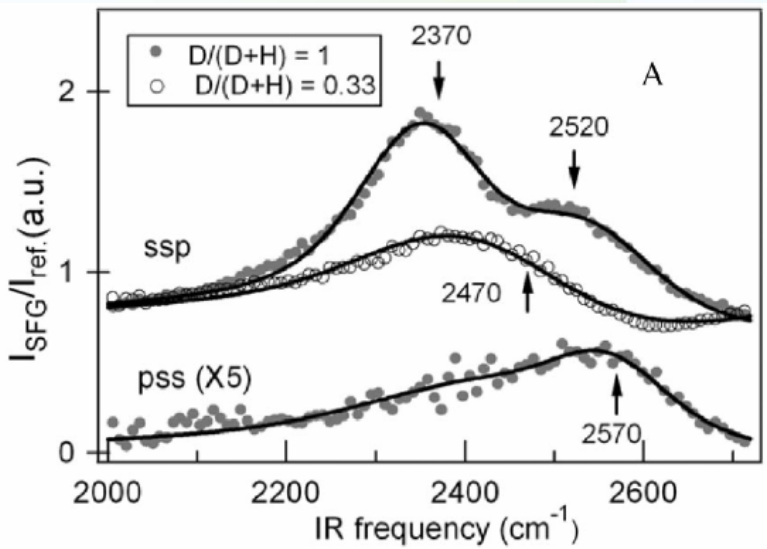


model I ("ss & as stretch OH")

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

$m_D << m_O$

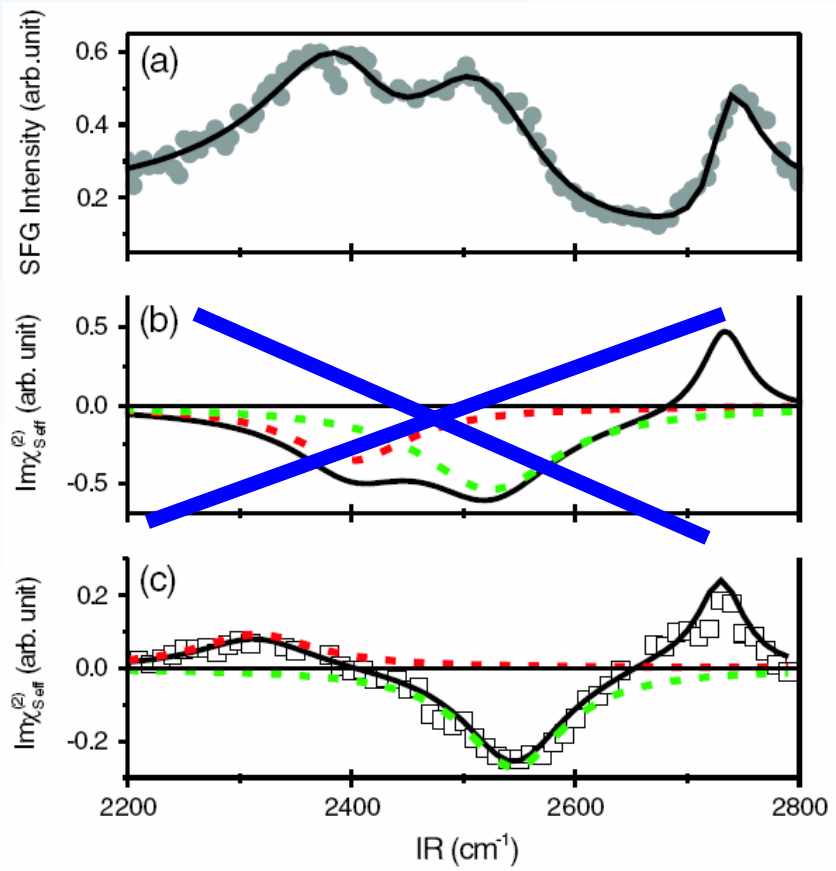
$\nu_{O\text{-}D}(HOD) = (\nu_1 + \nu_2)/2 = 2460\ cm^{-1}$



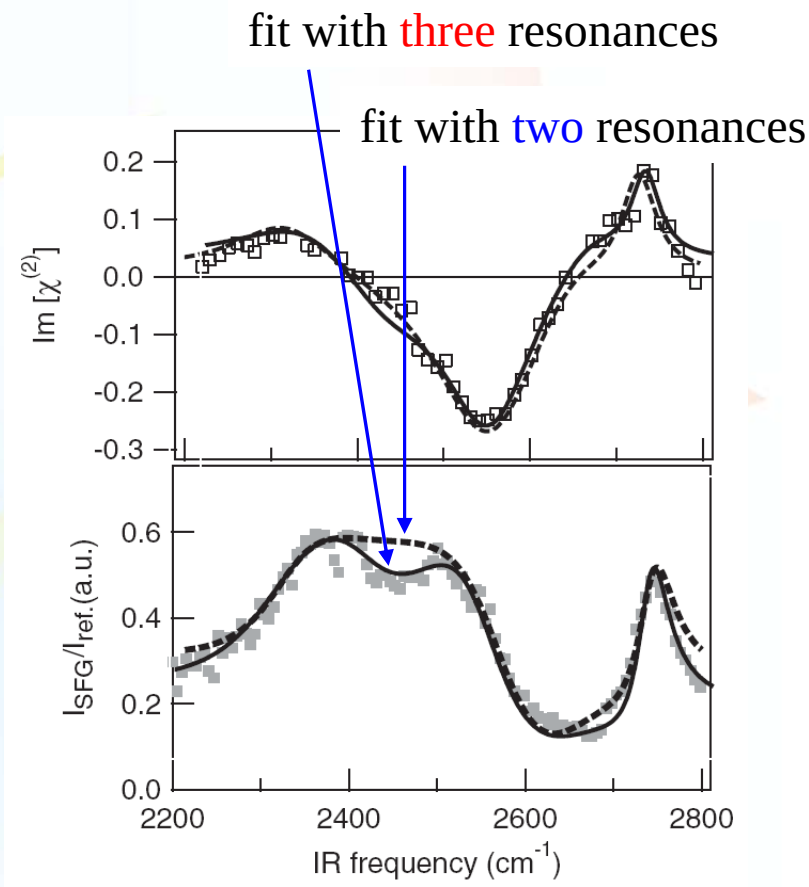
if ν_2 = 2460 cm^{-1} peak originates from the **as** mode

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

Comment & Replay



Tian and Shen. Phys. Rev. Lett. **101**, 139401 (2008)



Sovago et al. Phys. Rev. Lett. **101**, 139402 (2008)

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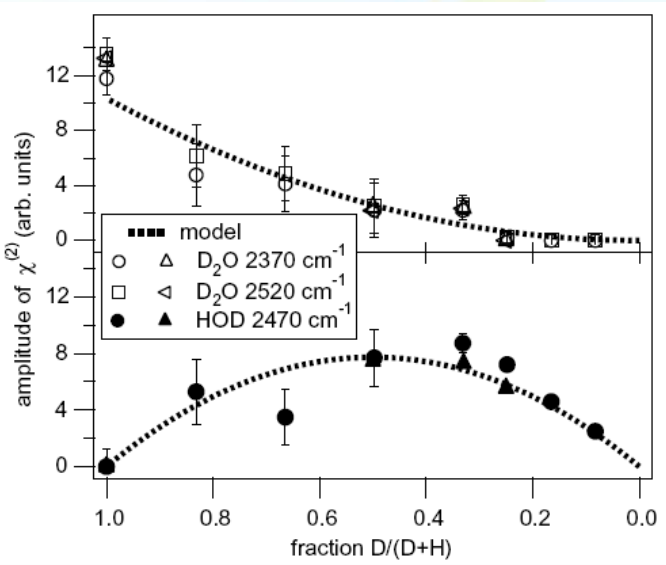
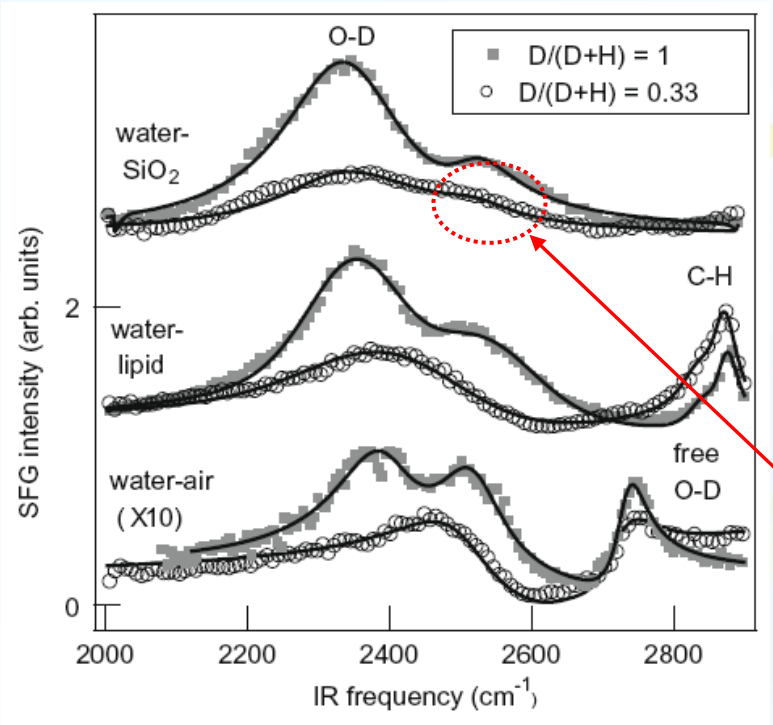
FRONTIERS ARTICLE

Hydrogen bonding strength of interfacial water determined with surface sum-frequency generation

Maria Sovago, R. Kramer Campen, Huib J. Bakker, Mischa Bonn *



Experimental results



two peaks collapse onto one

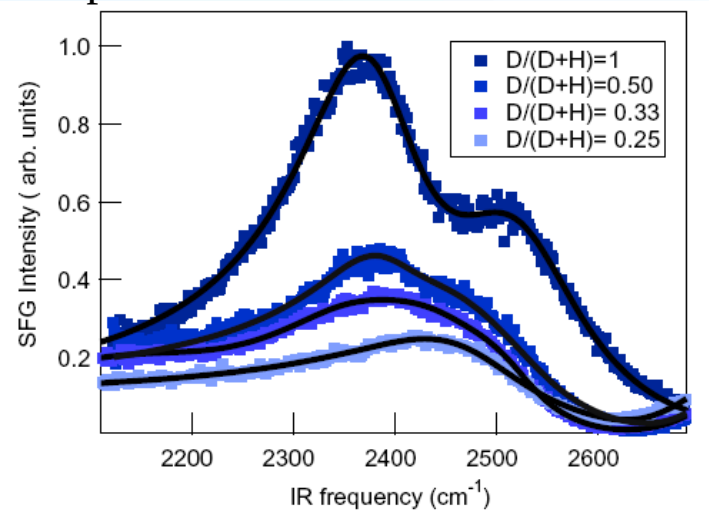
D/(D+H)=0.33

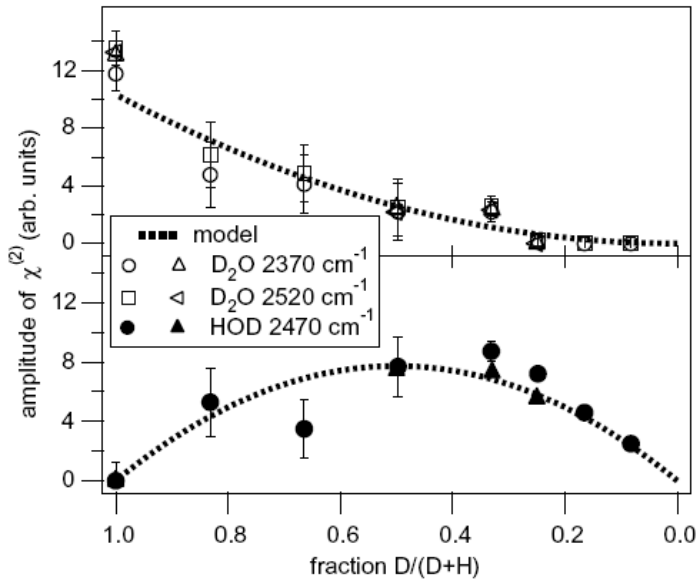
n (HDO) ~ 4 * n (D_2O)

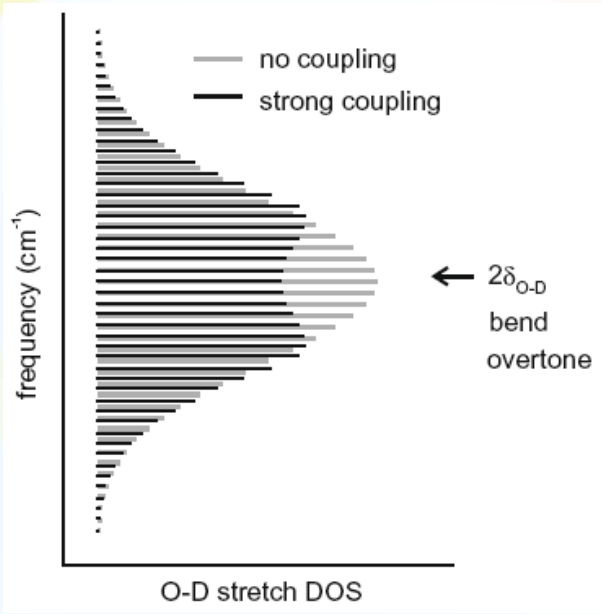
D_2O contribution

Experimental results

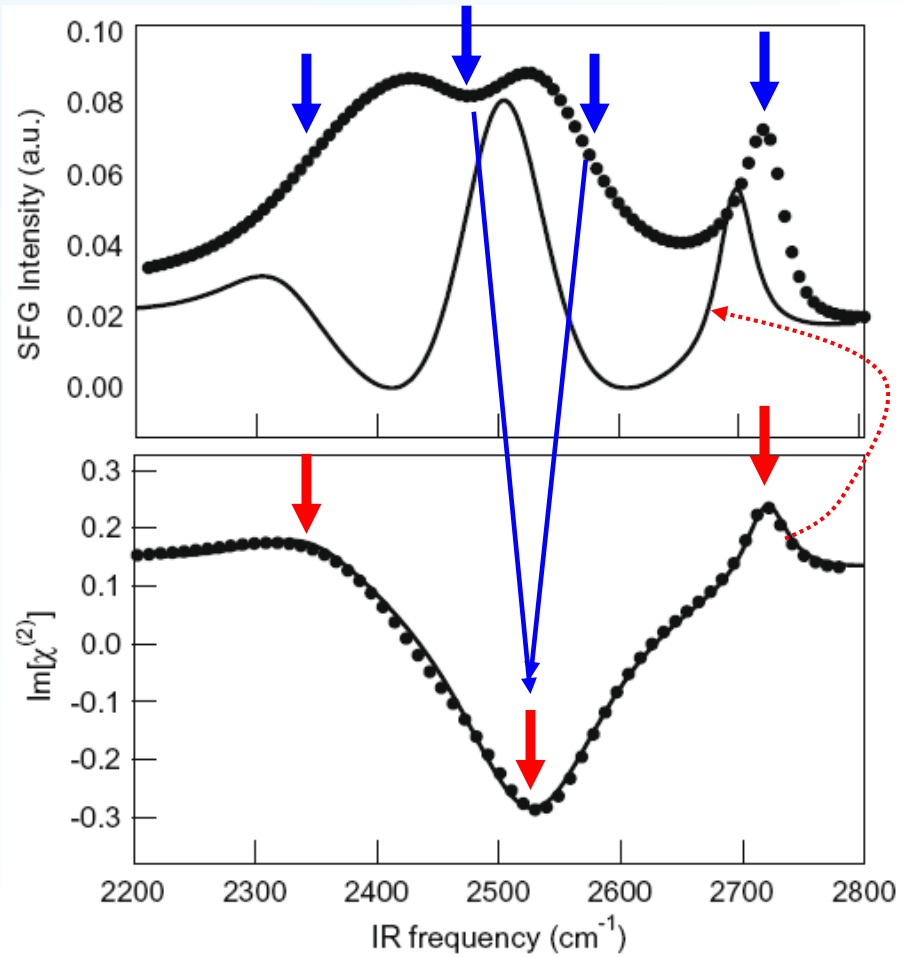
water/lipid interface







Simulated SFG spectrum



same sign of the two peaks

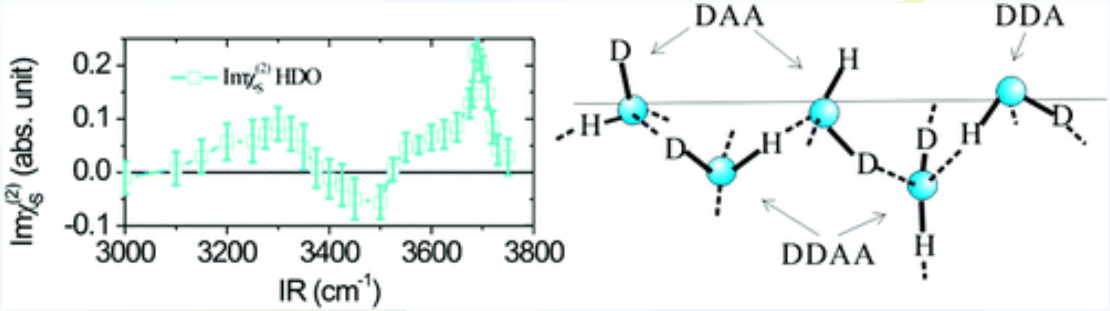
J|A|C|S COMMUNICATIONS

Published on Web 02/11/2009

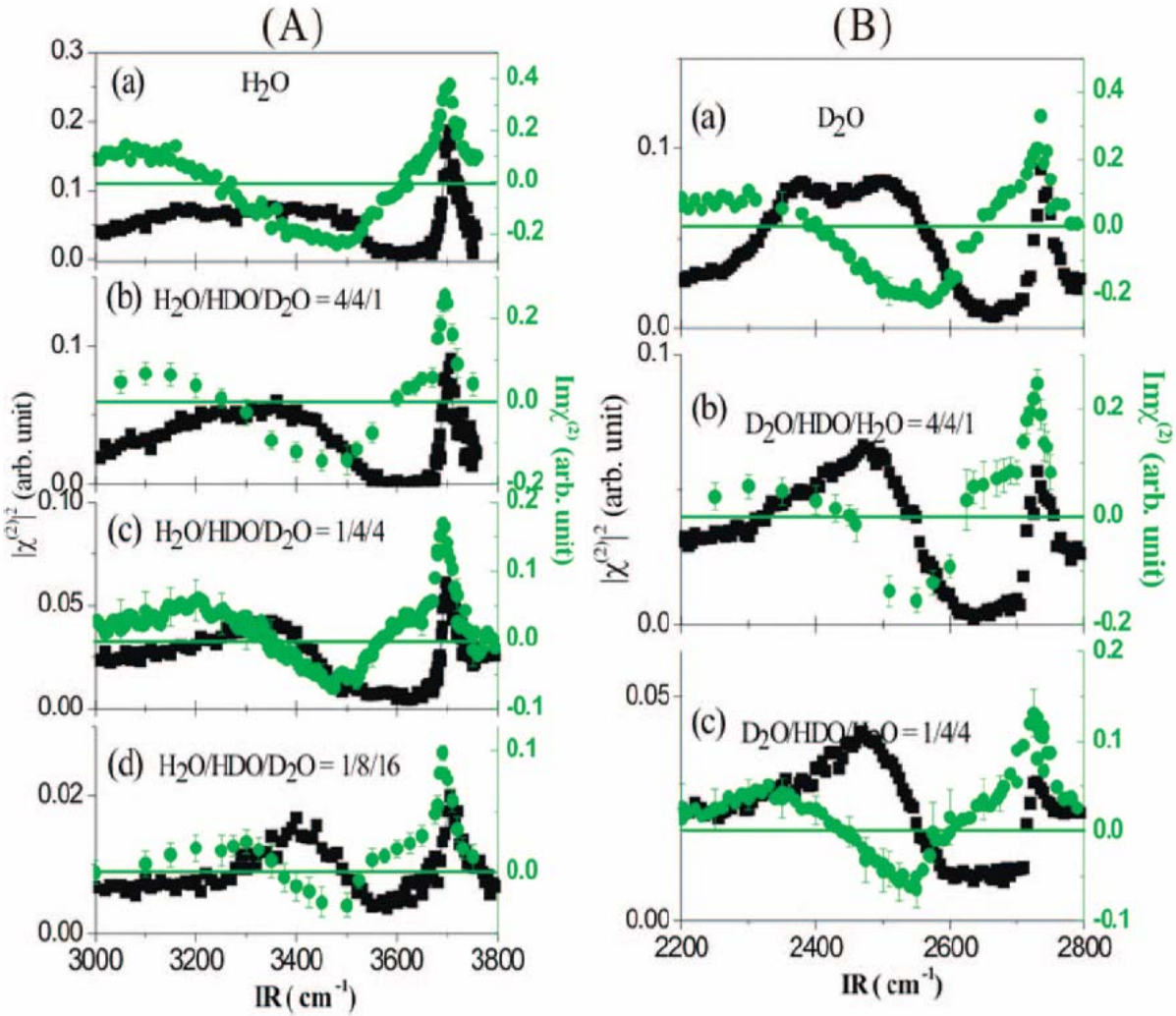
Isotopic Dilution Study of the Water/Vapor Interface by Phase-Sensitive Sum-Frequency Vibrational Spectroscopy

Chuan-Shan Tian and Y. Ron Shen*

Physics Department, University of California at Berkeley, Berkeley, California 94720



Experimental results



$|\chi^{(2)}|^2$:

changes into a single broad band

$Im\,\chi^{(2)}$:

one positive
+ one negative
resonance band

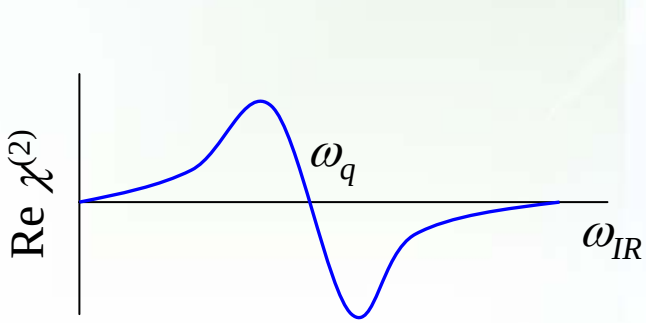
Phase sensitive SFVG

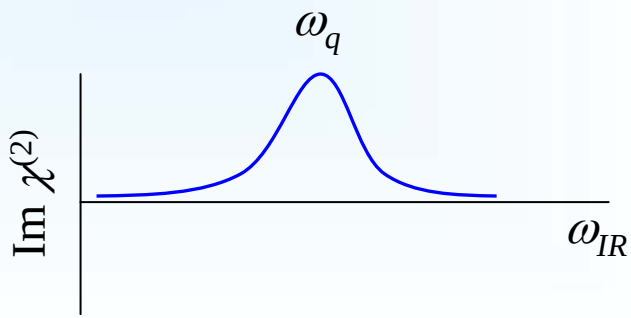
$$I_{SFG} \propto \left|\chi^{(2)}\right|^2 = \left|\chi^{(2)}_{NR} + \int \frac{\vec{\vec{A}}_q \rho(\omega_q)}{\omega_{IR} - \omega_q + i\Gamma_q} d\omega_q\right|^2$$

$$= \left|\mathrm{Re}\,\chi^{(2)} + \mathrm{Im}\,\chi^{(2)}\right|^2$$

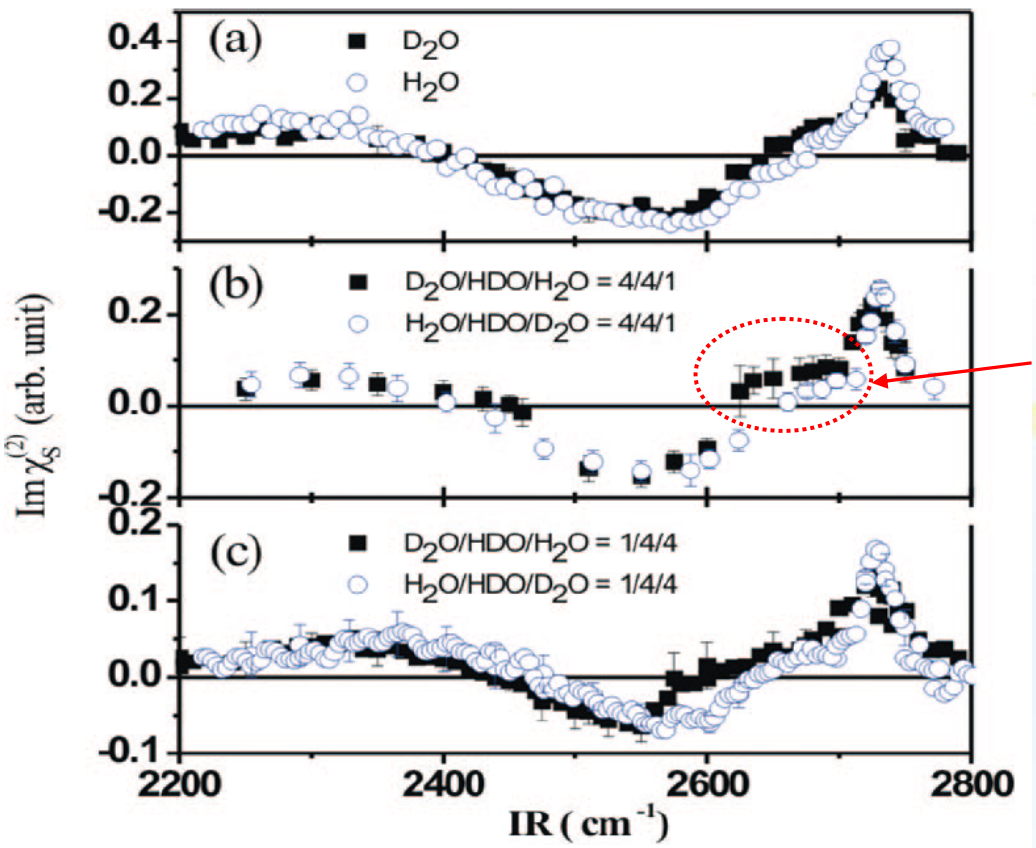
$$\mathrm{Re}\,\chi^{(2)} = \chi^{(2)}_{NR} + \int \frac{\vec{\vec{A}}_q \rho(\omega_q)(\omega_{IR} - \omega_q)}{(\omega_{IR} - \omega_q)^2 + \Gamma_q^{\,2}} d\omega_q$$

$$\mathrm{Im}\,\chi^{(2)} = \int \frac{\vec{\vec{A}}_q \rho(\omega_q)\Gamma_q}{(\omega_{IR} - \omega_q)^2 + \Gamma_q^{\,2}} d\omega_q$$





Results & Discussion



nearly identical
(after frequency rescaling 1.35)

slightly different

but, **OH and OD on HDO are decoupled**

would like to use the spectrum of the **HDO/vapor** interface

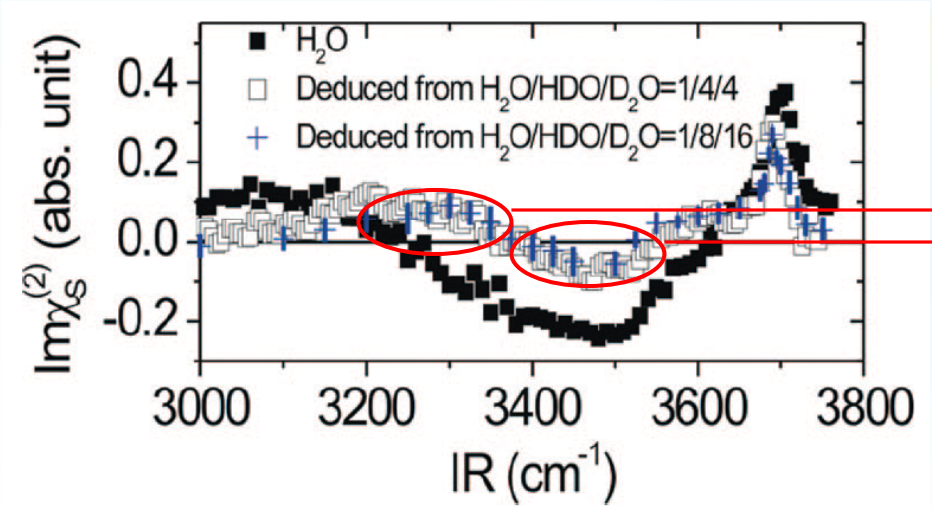
Results & Discussion

limited amount of dilution :

- contamination by interfering contributions from $\chi^{(2)}_{NR}$
- remnant H_2O in the diluted mixture

$$I_{SFG} \propto \left| \chi^{(2)}_{NR} + \int \frac{\vec{A}_q \rho(\omega_q)}{\omega_{IR} - \omega_q + i\Gamma_q} d\omega_q \right|^2$$

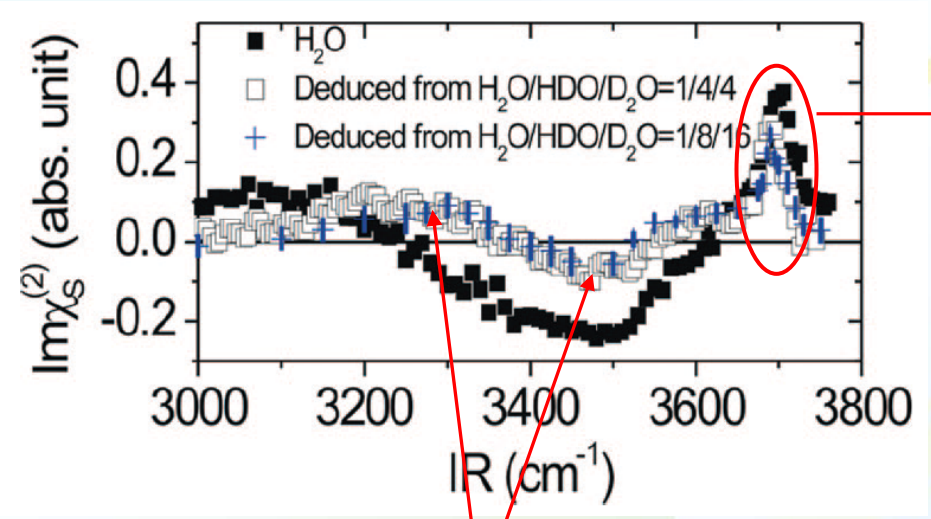
$H_2O/HDO/D_2O$ = 1/8/16 : <u>subtracting out the small contribution</u> of H_2O



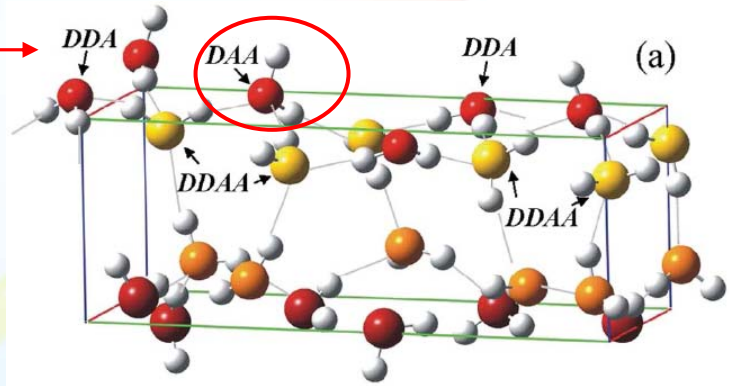
must come from the **OH of HDO**

Results & Discussion

10 cm^{-1} red shifted



coupling between the dangling OH : not negligible



Ji et al. Phys. Rev. Lett. **100**, 096102 (2008)

same position with IR absorption bands of HDO **in bulk ice and liquid**