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

Maria Sovago,[1] R. Kramer Campen,[1] George W. H. Wurpel,[2] Michiel Müller,[3] Huib J. Bakker,[1] and Mischa Bonn[1,*]

[1]*FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ, Amsterdam, The Netherlands*

[2]*Molecular Biophysics, Debye Institute, Utrecht University, P.O. Box 80000, 3508 TA Utrecht, The Netherlands*

[3]*Swammerdam Institute for Life Sciences, University of Amsterdam, P.O. Box 94062, 1090 GB Amsterdam, The Netherlands*

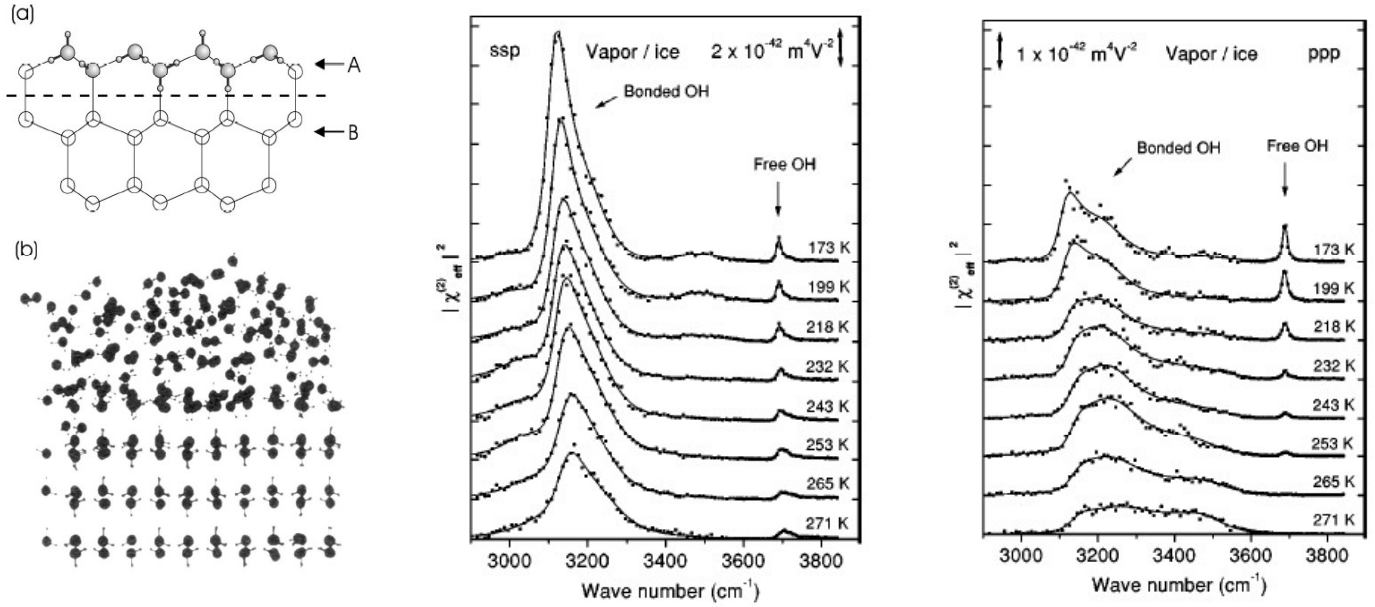
(Received 22 December 2007; published 28 April 2008)

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.

PRL **100, 173901 (2008)**

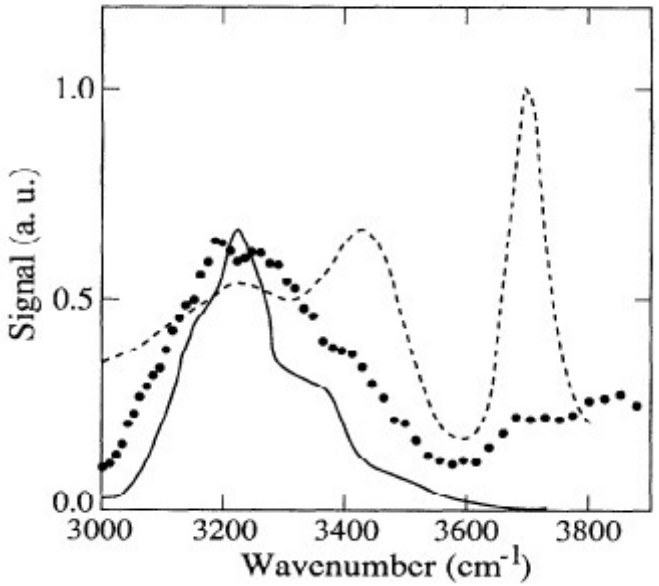
Previous assignment of OH vibrational modes in water SFG spectra was..

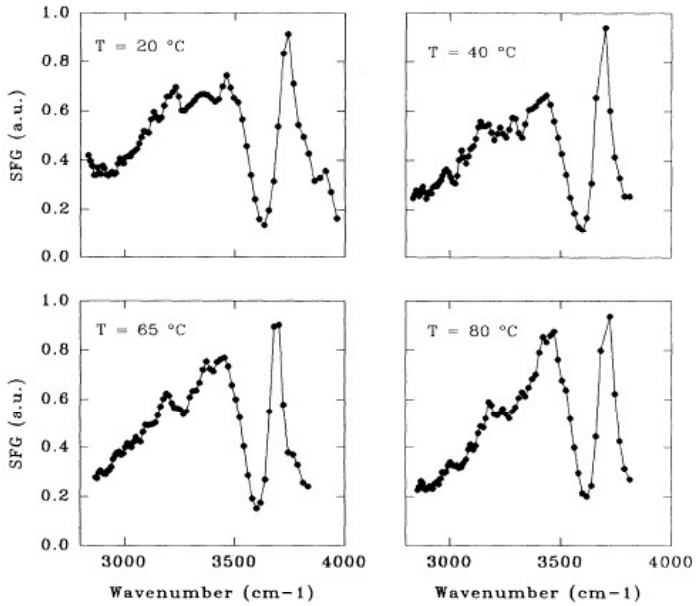
⟶ Icelike around 3200cm^{-1} and Liquidlike around 3450cm^{-1}



Ex) surface melting of ice interface, peak around 3450cm^{-1} as increasing of temperature.

PHYSICAL REVIEW B **66, 085401 (2002)**





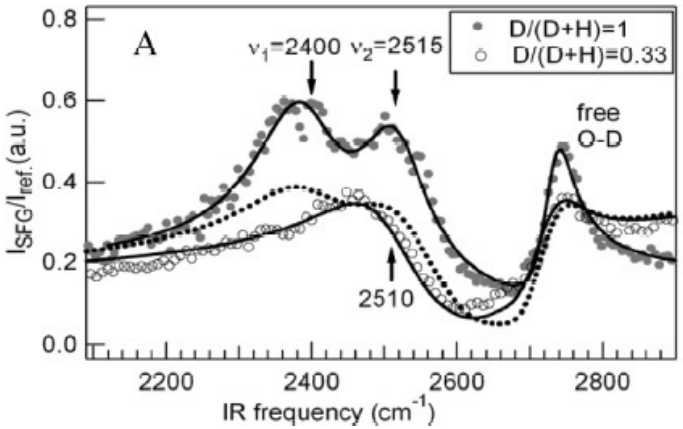
Phys. Rev. Lett. **70, 2313 (1993).**

Ex) Inducing icelike structure by coverting of alcohol at water interface and band structure changes with temperature in air water interface

OR

⟶ Symmetric and antisymmetric vibrational modes assigned.

In this report, Mischa's group performed SFG spectroscopy on $D_2O/HDO/H_2O$ mixture to remove



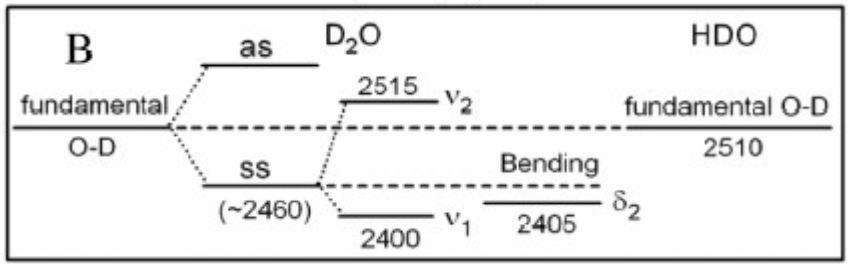
In pure case there's two peaks. But after isotopic dilution, two peaks are merged into one peaks.

Because isotopic dilution do not affect to water structure, there should be two peaks if icelike and liquidlike assignment is correct.

Claimed that previous assignment about bound OH has some problem.

Also, they claimed that two peaks are not orignated from ss and as vibrational modes of water.

Because if ss = 2400cm^{-1} and as = 2515cm^{-1} than fundamental single OD vibrational mode will be 2460cm^{-1}.



They suggested that these two peaks came from intra molecular coupling of bending mode overtone (1210cm^{-1}) and ss mode (2460cm^{-1}) of D_2O. (Fermi resonance)

For HDO, they said that bending overtone is 2900cm^{-1} . So, Fermi resonance can not occur.

Immediately, C.S Tian and Y.R.Shen gave some comments to Maria Sovago and Mischa Bonn.

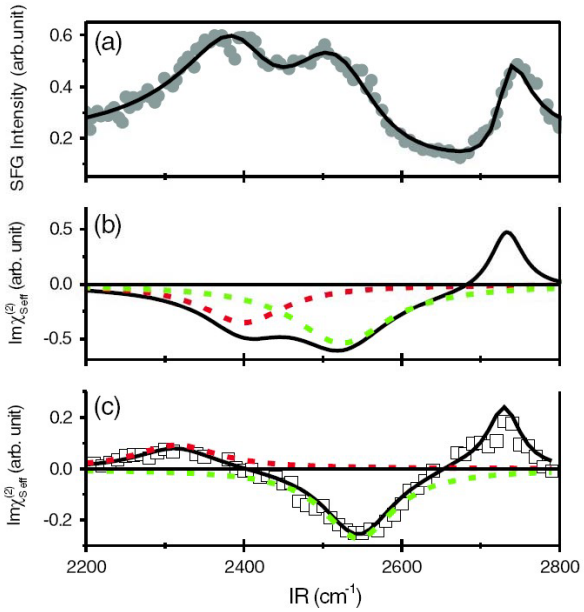
http://prl.aps.org/abstract/PRL/v101/i13/e139401

Critical points are….

→ In this experiment OD spectrum was not only affected by HDO but also D_2O.

→ From phase sensitive SFG experiment, these two peaks have opposite sign in complex part of spectrum.

→ Also, peak assignment about 2510cm^{-1} is unnatural.



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

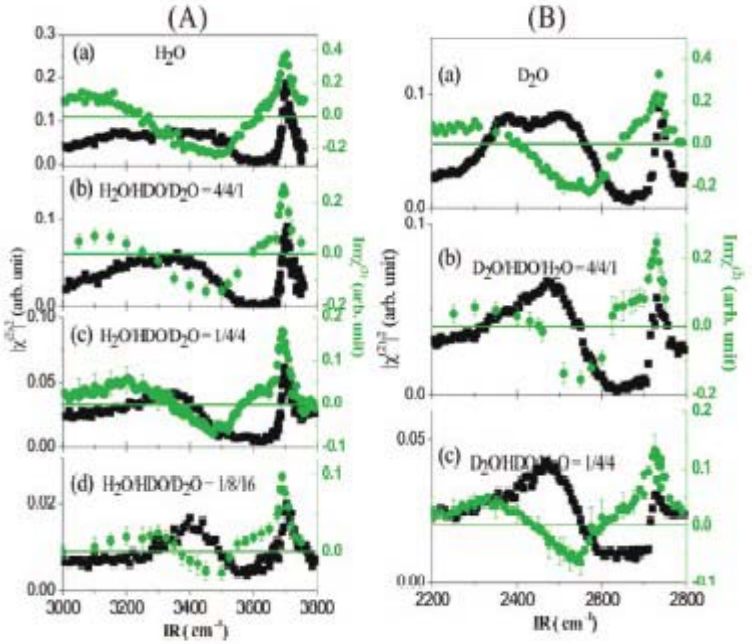
Received December 5, 2008; E-mail: yrshen@berkeley.edu

J. AM. CHEM. SOC. 2009, *131*, *2790–2791*

Shen's group claimed that……

→ Only by fitting about intensity spectrum, it is hard to determine the imaginary part of spectrum because, fitting doesn't converse to unique one.

They took PS-SFG experiment on OH ,OD range.

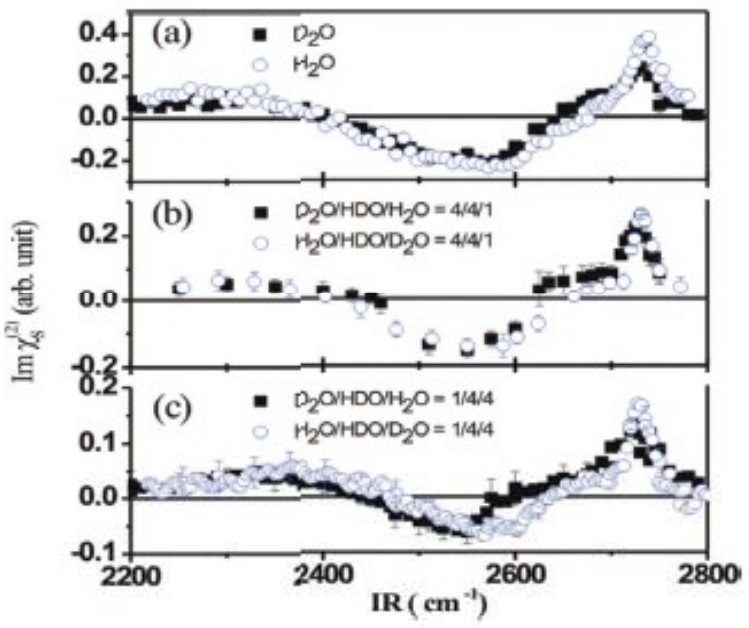


Also, they saw two peaks merged into one peak as HDO contribution increase.

There exist positive and negative OH,OD band before and after isotopic dilution….

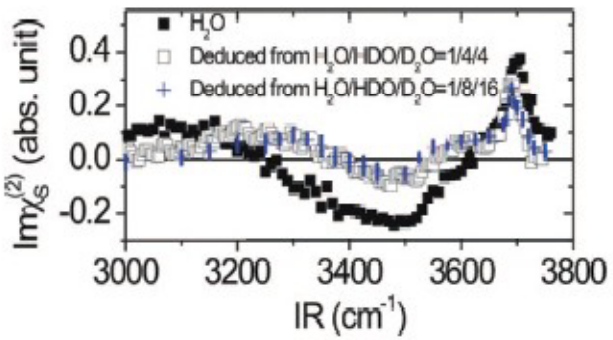
So, there're still two components

Because, OD ,OH spectral shape were same, D_2O,HDO,H_2O have same interfacial structure.



Multiplying 1.35 factor on frequency range, OD, OH spectrum have similar spectral shape

So, in the spectrum of D_2O/HDO/H_2O mixture, imaginary part can be separate by each component

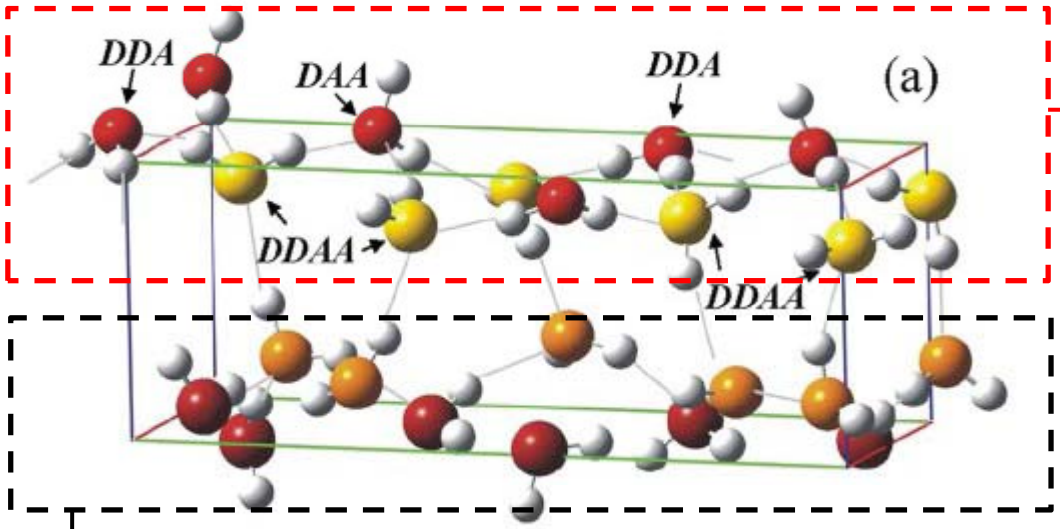


Deduced Imaginary part into HDO contribution.

Confirmed that still two components exist

DDAA,DAA,DDA OH contribute icelike structure at first two layers .

Shen's group claimed that ''still we are correct".



Icelike contribution

PRL **100, 096102 (2008)**

Liquidlike contribution

J|A|C|S
COMMUNICATIONS

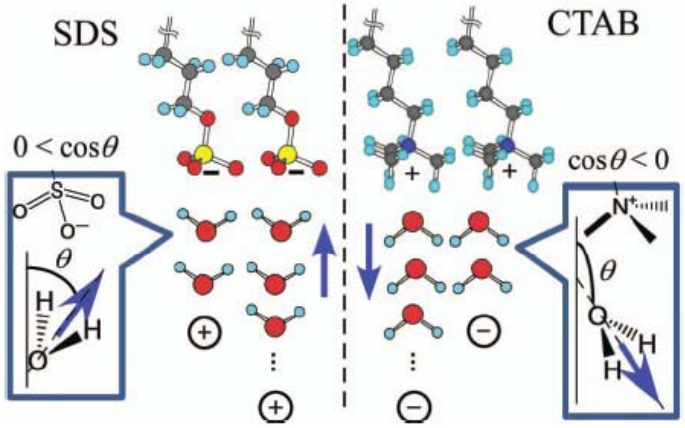
Published on Web 04/29/2010

Water Hydrogen Bond Structure near Highly Charged Interfaces Is Not Like Ice

Satoshi Nihonyanagi, Shoichi Yamaguchi, and Tahei Tahara*

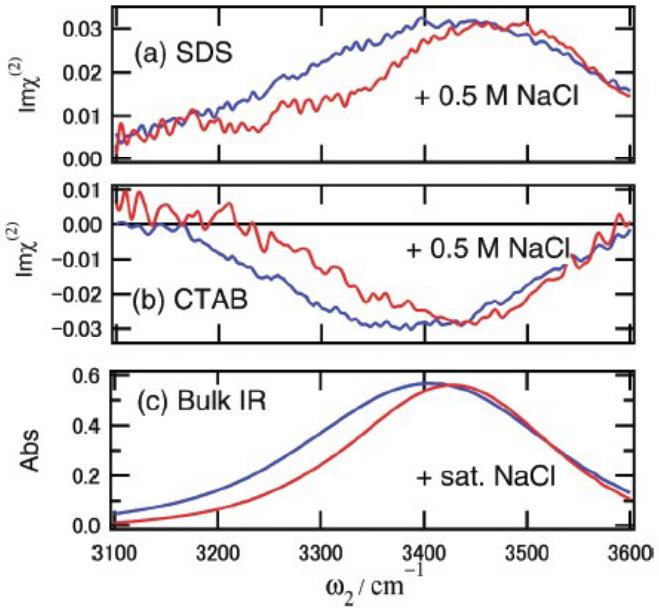
Molecular Spectroscopy Laboratory, Advanced Science Institute (ASI), RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Received January 6, 2010; E-mail: tahei@riken.jp



J. Chem. Phys. **130, 204704 2009**

They saw water flip-flop directly by PS-SFG setup In charged interface..



Water spectrum under charged interface has broadband and has single sign.

Unlike usually water/vapor interface icelike contribution didn't appear.....

So, there is no icelike structure on charged interface....

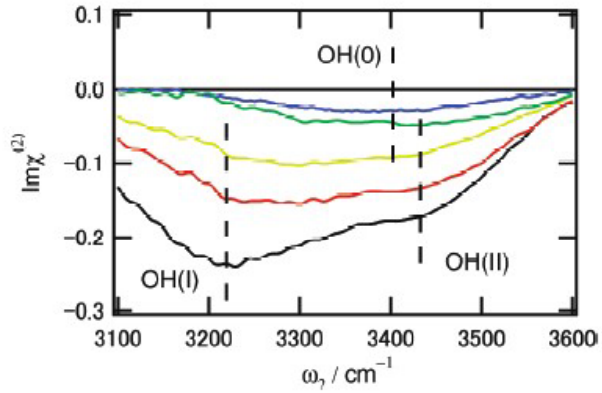


Figure 3. The complex $\chi^{(2)}$ spectra of airy interfaces of aqueous 0.1 mM CTAB solutions at variuos isotopic concentrations (black, H_2O; red, H_2O/HOD/D_2O = 9:6:1; yellow, 1:2:1; green, 1:6:9; blue, 1:12:33). The SF, ω_1, and ω_2 beams were *s*-, *s*-, and *p*- polarized, respectively.

Also in isotopic dilution experiment, Band converged to single component.

They claim that this single band came from ss and fr between ss and bending overtone rely on Mischa's conclusion.

Also they agree with the Shen group's result (they said icelike as OH(X) band). But they claim that this kind of OH(X) band didn't appear at charged interface / water.

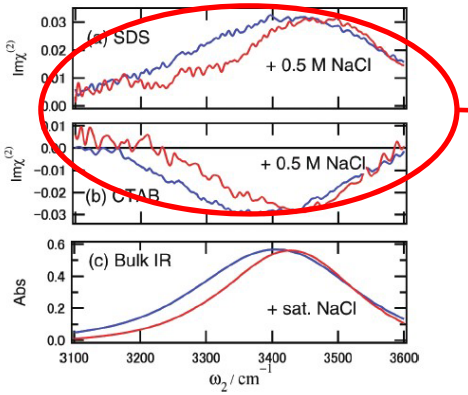


Figure 1. Complex $\chi^{(2)}$ spectra of airy interfaces of aqueous (a) 0.5 mM SDS and (b) 0.1 mM CTAB solutions of HOD (H_2O/HOD/D_2O = 1:12:33) in the absence (blue lines) and presence (red lines) of 0.5 M NaCl. The red curves were magnified by 2 for (a) and 3 for (b). The SF, ω_1, and ω_2 beams were *s*-, *s*-, and *p*- polarized, respectively. (c) Bulk absorption spectra of HOD (H_2O/HOD/D_2O = 1:12:33) (blue) and that of saturated NaCl HOD solution (red).