Hydrogen bonding at the water surface revealed by isotopic dilution spectroscopy

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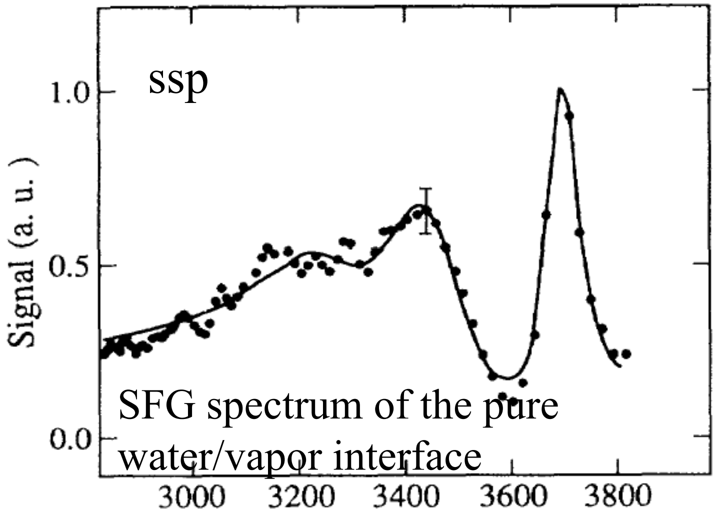
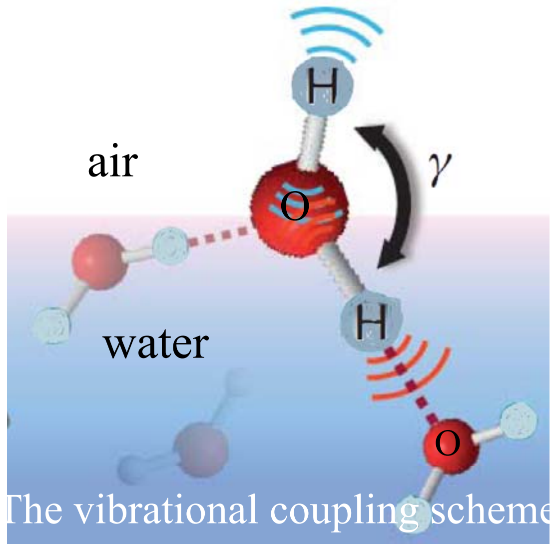
Introduction

The free OH-stretch mode at the air–water interface can be coupled either to OH stretches on other H_2O molecules or to the other OH stretch on the same H_2O molecule

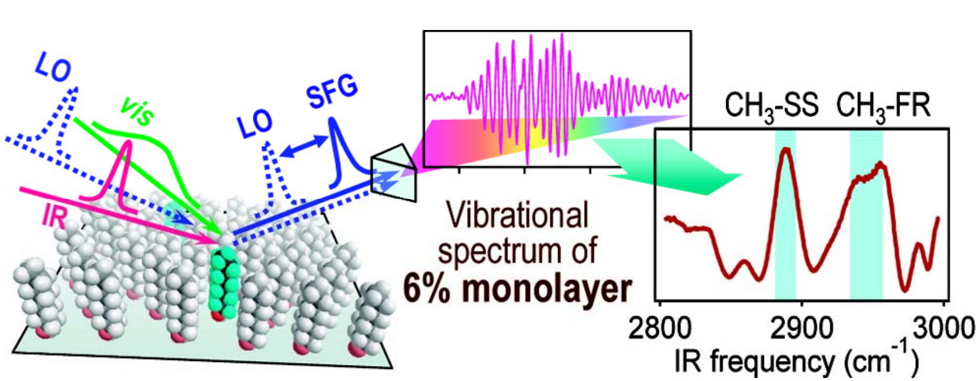


Phys. Rev. Lett. 70, 2313–2316 (1993)

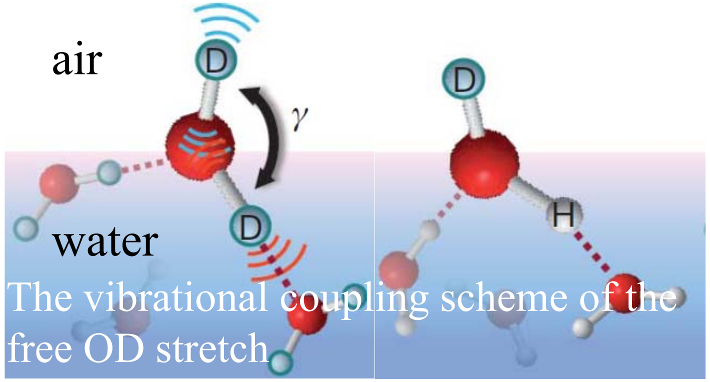


we can't differentiate between the uncoupled free OH-stretch mode and the coupled free OH-stretch mode

Experimental method



J. Am. Chem. Soc. **2008,** 130, 2271-2275



The vibrational coupling scheme of the free OD stretch

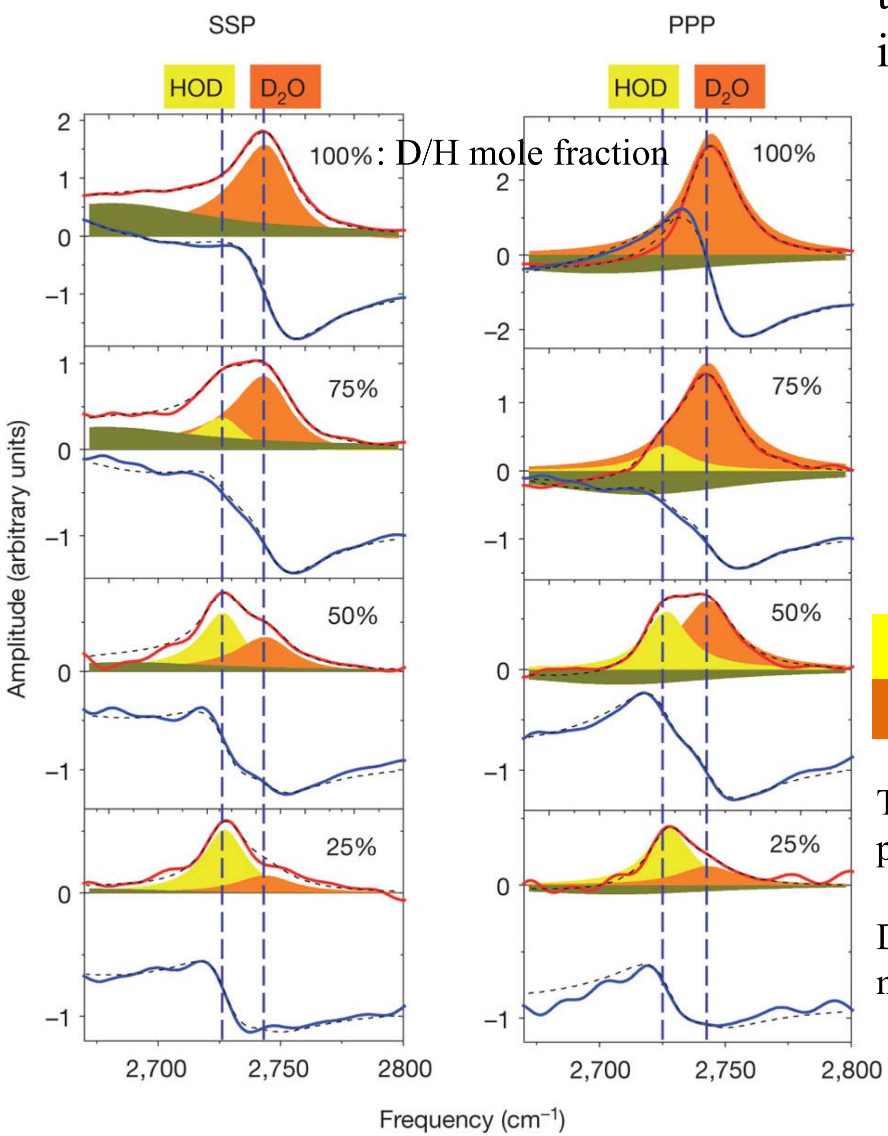
To disentangle vibrational coupling contributions

→use isotopic dilution in D_2O:HOD: H_2O mixtures to gradually turn off the vibrational coupling

→ use the broad-band heterodyne-detected sum frequency generation (HD-SFG)) technique

(The free OD frequency of D_2O can be coupled either to OD stretches on other H_2O molecules or to the other OD stretch on the same D_2O molecule).

The spectra of the free OD stretch at the air–water interface



the relative amplitudes of two peaks change with isotopic dilution

the peak frequencies(OD stretch) in HOD and DOD do not exhibit appreciable shifts on isotopic dilution

$2,728 \pm 2\ cm^{-1}$: free OD stretch of the HOD

$2,745 \pm 2\ cm^{-1}$: free OD stretch of the pure D_2O

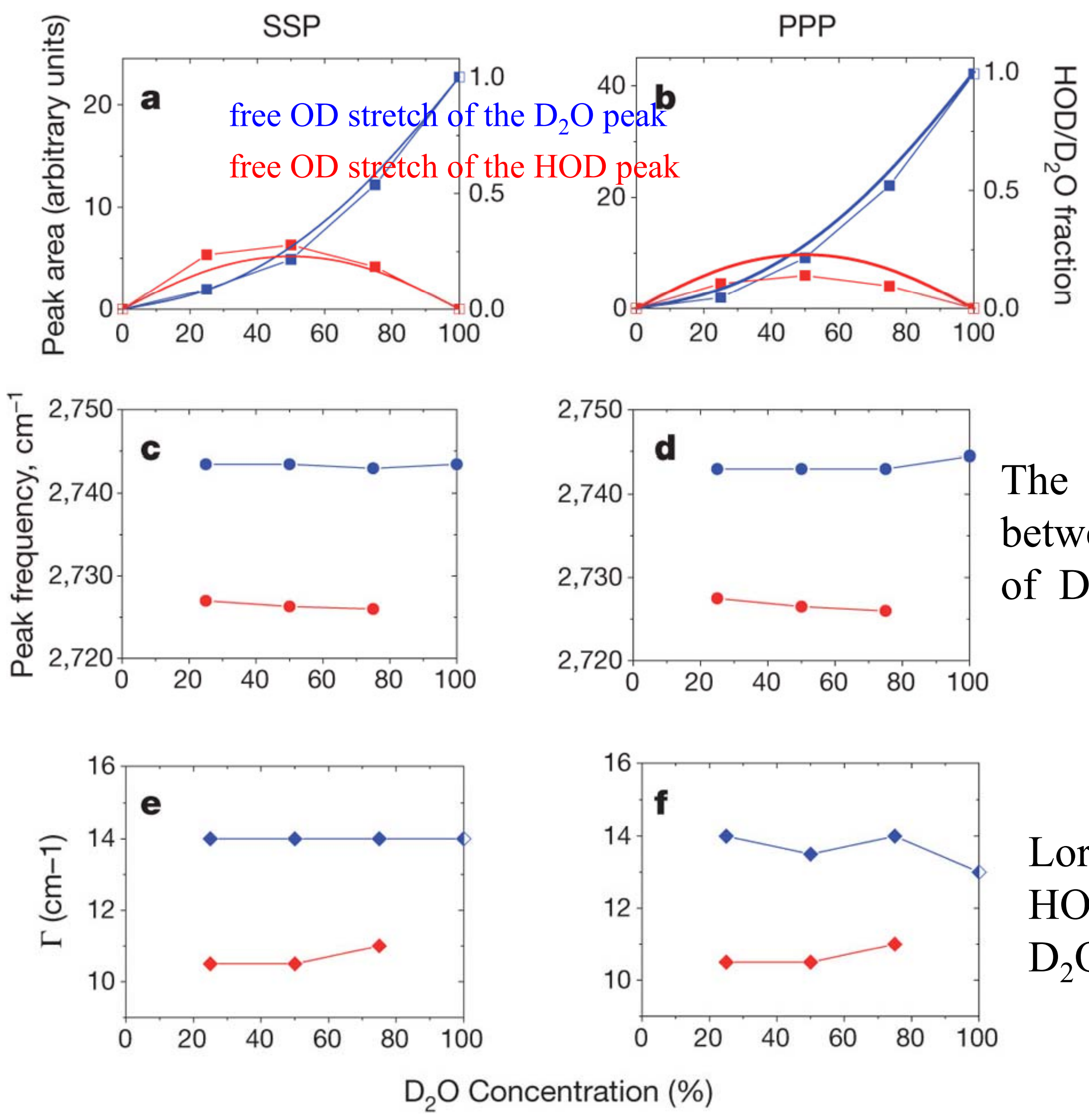
The solid blue and red lines are the measured real and imaginary parts of the SFG signal.

Dashed lines represent the fits to a sum of Lorentzian terms and a nonresonant background:

$$\chi^{(2)}(\omega_{\text{infrared}}) \propto A_{\text{nonresonant}} e^{i\phi_{\text{nonresonant}}} + \sum_j \frac{B_j \Gamma_j}{(\omega_{\text{infrared}} - \Omega_j) + i\Gamma_j}$$

Changes in vibrational spectra with isotopic dilution

The fitting results are summarized below Figure



The amplitude of the HOD peak first increases and then decreases with dilution

The difference *is* Δ =17±1.5 cm^{-1} between the free OD stretch of HOD and of D_2O

Lorentzian linewidth of the free OD of HOD is Γ_{HOD}=11±1.5cm^{-1}, whereas for D_2O it is Γ_{DOD}=14±1 cm^{-1}

Result & discussion

The free OD frequency of HOD molecules (2,728 cm^{-1}) at the air–water interface

The OD-stretch local mode of HOD molecules (2,727 cm^{-1}) in the gas phase

↓

the free OD mode of HOD at the air–water interface is decoupled from all other vibrational modes in the system.

↕

The free OD frequency of D_2O molecules is blueshifted from free OD frequency of HOD

↓

The sign of the shift can be understood in terms of a simple model of two coupled oscillators

conclusion

- For the stretching mode of free OH around 3,700 cm^{-1}, the OH vibrational coupling model presented here would predict a smaller shift between OH mode in HOD and in H_2O.

- It is more difficult to observe two distinct peaks for the free OH of HOD and H_2O.