Ultrafast Vibrational Dynamics at Water Interfaces

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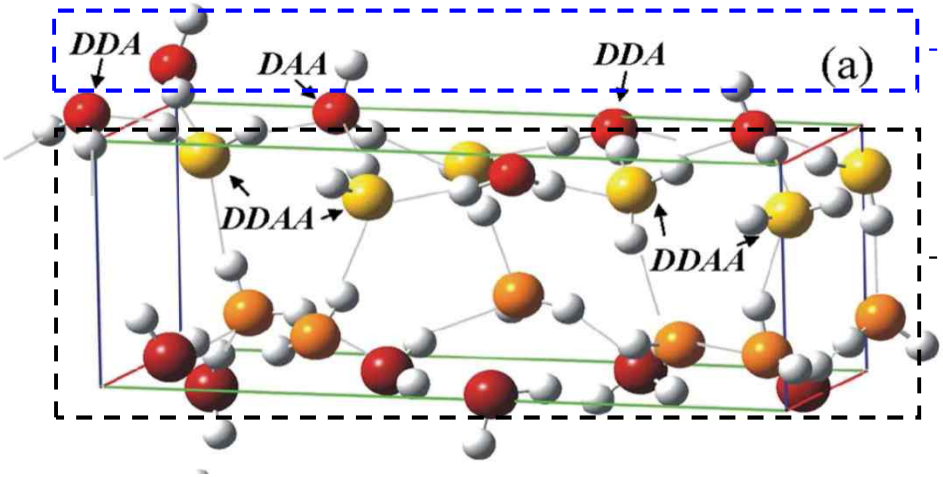
Time-resolved sum-frequency vibrational spectroscopy permits the study of hitherto neglected ultrafast vibrational dynamics of neat water interfaces. Measurements on interfacial bonded OH stretch modes revealed relaxation behavior on sub-picosecond time scales in close resemblance to that of bulk water. Vibrational excitation is followed by spectral diffusion, vibrational relaxation, and thermalization in the hydrogen-bonding network. Dephasing of the excitation occurs in ≤100 femtoseconds. Population relaxation of the dangling OH stretch was found to have a time constant of 1.3 picoseconds, the same as that for excitation transfer between hydrogen-bonded and unbonded OH stretches of water molecules surrounded by acetone.

Science 313, 1945 (2006).

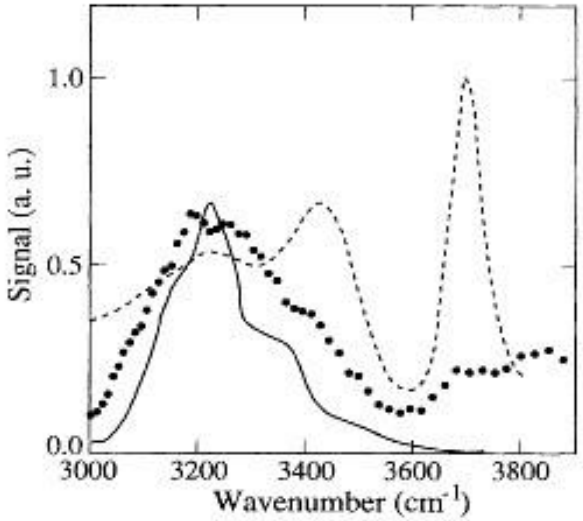
Interfacial Water



Free (dangling) OH bond

Disordered tetrahedral structure
(icelike and liquidlike OH bond)

Phys.Rev.Lett. 100, 096102 (2008).



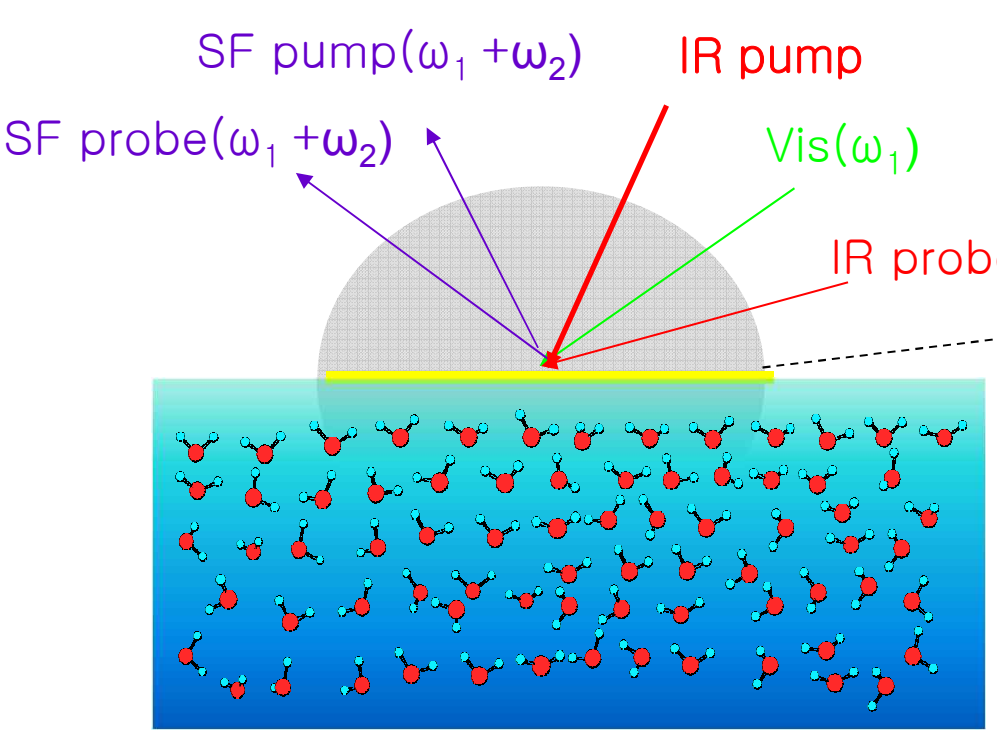
'Dashed line: SFG on air /water interface

'Dotted line: SFG on alcohol /water interface

'Solid line: IR absorption spectra of ice

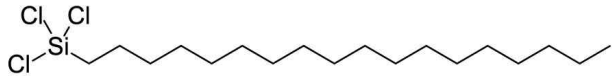
Phys.Rev.Lett. 70, 2313 (1993).

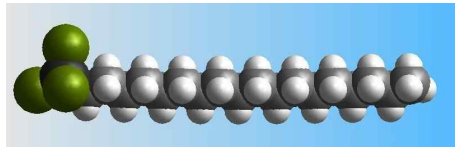
Experimental system



From Ti-Sapphire Laser and its optical parametric amplifier

Fused silica prism (coated or uncoated by OTS)





$$L_{xx}(\Omega)=\frac{2n_1(\Omega)\cos\gamma}{n_1(\Omega)\cos\gamma+n_2(\Omega)\cos\beta},$$

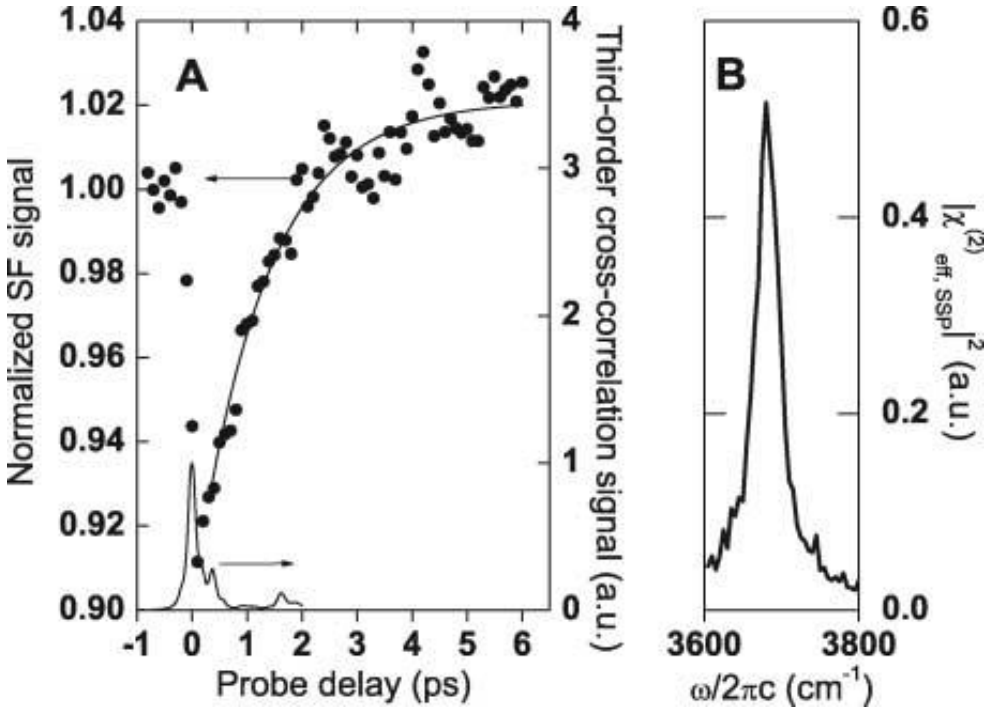
$$L_{yy}(\Omega)=\frac{2n_1(\Omega)\cos\beta}{n_1(\Omega)\cos\beta+n_2(\Omega)\cos\gamma},$$

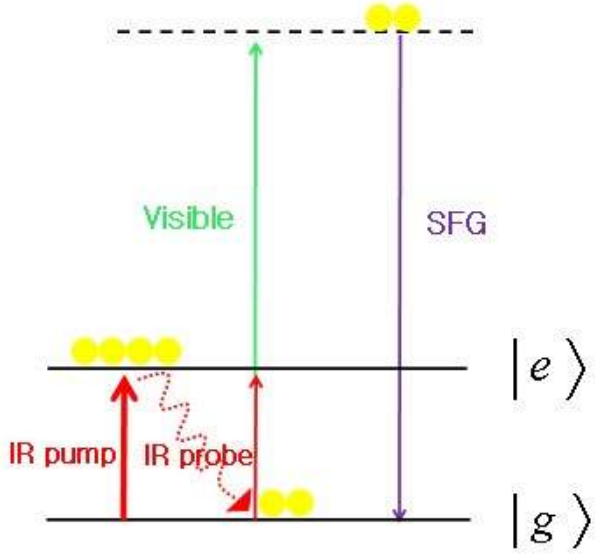
$$L_{zz}(\Omega)=\frac{2n_2(\Omega)\cos\beta}{n_1(\Omega)\cos\gamma+n_2(\Omega)\cos\beta}\left(\frac{n_1(\Omega)}{n'(\Omega)}\right)^2.$$

$$\chi^{(2)}_{\text{eff,SSP}}=L_{yy}(\omega)L_{yy}(\omega_1)L_{zz}(\omega_2)\sin\beta_2\chi_{yyz}$$

OH signal was enhanced by total internal reflection

1) Free OH bonding

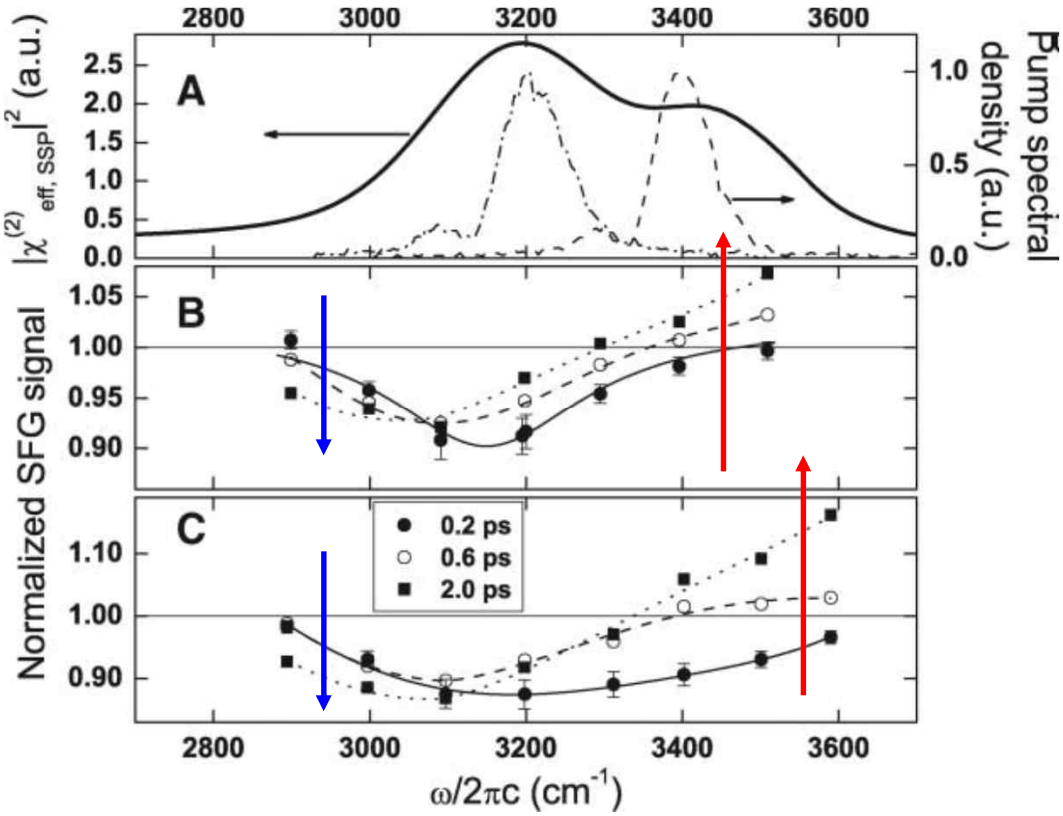


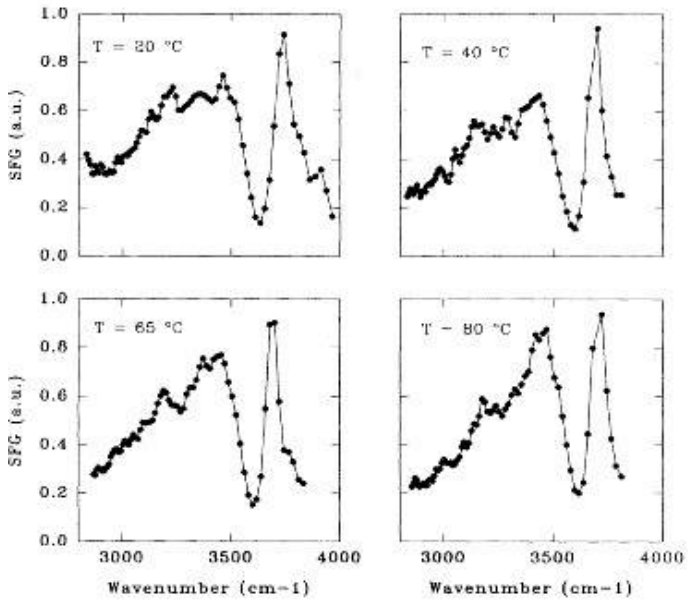


Recovery time of free OH vibrational mode
(Population relaxation) ~ 1.3ps

Dephasing time of free OH vibrational mode ~ 300fs

2) Bound OH bonding





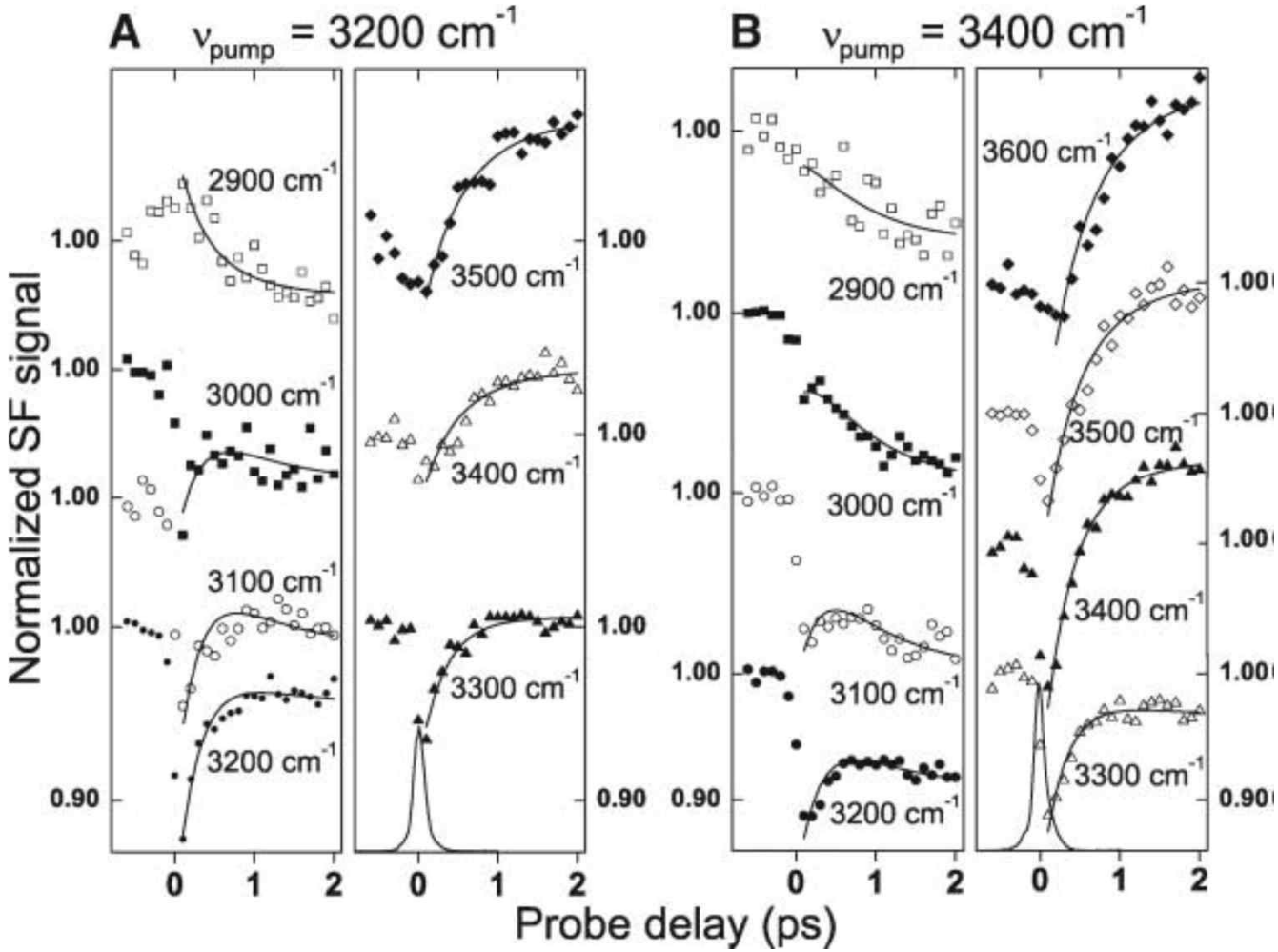
Phys.Rev.Lett. 70, 2313 (1993).

➡ Spectral hole burning (depletion of SF probe signal) showed up

Over shot in high frequency and under shot in low frequency region

➡ Due to thermalization of interfacial water (exhale heat) – lasted over 50ps

3) Detailed experiment



$$S(t) = 1 - (1 - S_0)e^{-(t-100)T_v} + \Delta S[1 - e^{-(t-100)/T_t}] \quad (1)$$

Tv: vibrational relaxation time constant

Tt: thermalization time constant

4) Analysis

$$S(t) = 1 - (1 - S_0)e^{-(t-100)/T_v} + \Delta S(1 - e^{-(t-100)/T_t})$$

Tv: vibrational relaxation time constant / Tt: thermalization time constant

S_0: SF probe signal at t=100fs / ΔS: SF probe signal difference by thermalization (~2ps)

From model fitting –Tv ~ 300fs / Tt ~700fs

➡ Near 3300cm^{-1}, 1- S_0 is much greater than ΔS means that vibrational relaxation is dominant process

➡ On left (low frequency), right (high frequency) side of spectrum , ΔS is much greater than 1- S_0 means that thermalization is dominant

Summary & next step

1) Dynamics of interfacial water is investigated by time-resolved SFVS.

2) Vibrational relaxation time of Free OH is ~1.3ps and is longer than bounded OH.

3) Thermalization and vibraitonal relaxation time were measured.