SUM-FREQUENCY GENERATION: POLARIZATION SURFACE SPECTROSCOPY ANALYSIS OF THE VIBRATIONAL SURFACE MODES ON THE BASAL FACE OF ICE I_h

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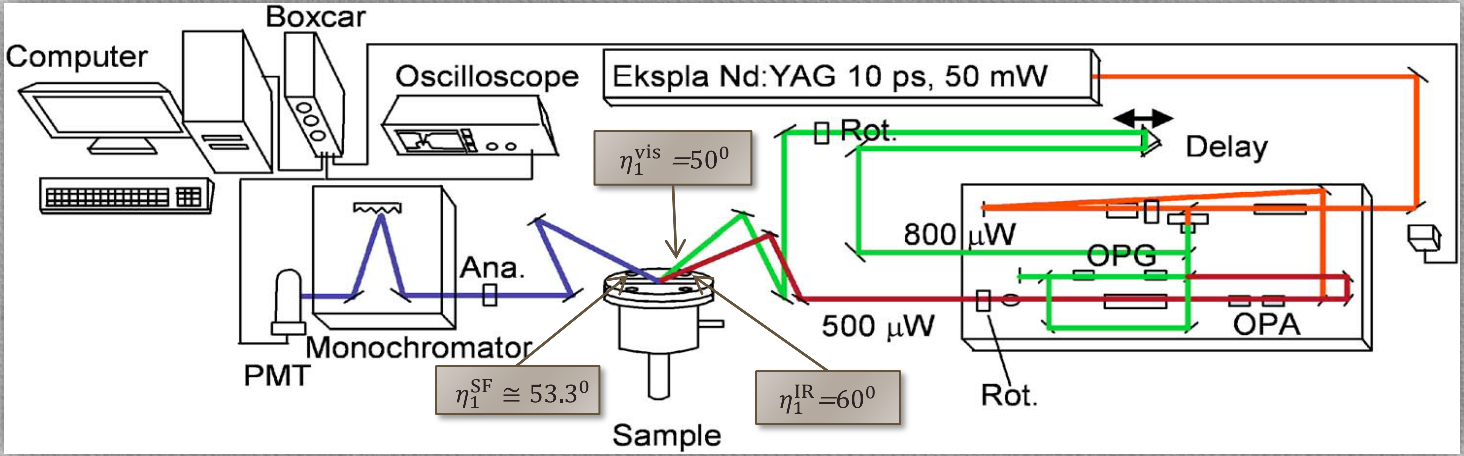
THE JOURNAL OF CHEMICAL PHYSICS 128, 214510 2008

INTRODUCTION

- This paper reports results of a newly developed polarization analysis of the generated sum-frequency signal as a function of wavelength both to deconvolute spectral resonances and to characterize the dynamic polarization associated with the resonances
- The technique is termed polarization-angle null analysis or PAN

EXPERIMENTAL SETUP



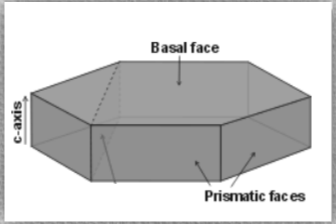
Energies for SFG on ice surfaces:
$I^{vis} = 170\mu J$
$I^{IR} = 40\mu J$

Beam diameters:
for IR $\Longrightarrow$ *1.1 mm*
for vis. $\Longrightarrow$ *1.4 mm*

- The mid-IR beam is directed over gold mirrors onto the top of the sample
- The visible beam consists of the doubled YAG fundamental and is spatially and temporally overlapped with the IR at the sample
- The SF signal is collected by broad band coated (400 nm), front-surface silver mirrors and focused onto the slit of a monochromator

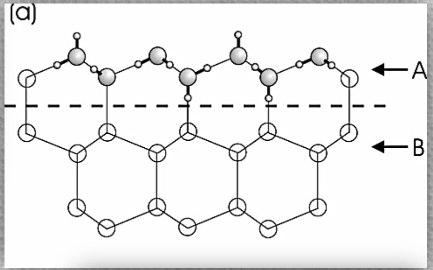
Sample preparing

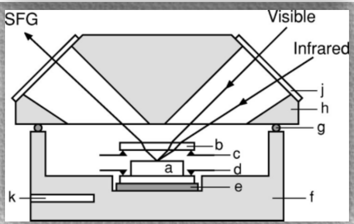
- Single-crystal ice samples
  - 1 $in.$ diameter, 4 $in.$ long
  - a dislocation density ~$10^2/cm^2$ on the basal surface
  - the growth process, quality control, and evaluation of the crystal $\Longrightarrow$ J. Chem. Phys. 127, 214502 (2007)



http://www.lsbu.ac.uk/water/ice1h.html

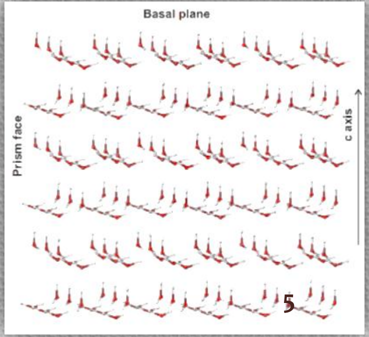
Side view of an ideal basal surface of ice I_h





Physical Review B 66, 085401(2002)

- An ~ 4 mm thick slice of the crystal is mounted on an indium coated copper platform inside a sealed stainless steel sample cell and conduction cooled by a liquid nitrogen bath.
- The cell is sealed with a 5–8 mm thick IR-quartz window to allow beam access.
- The thermocouple is welded to the sample surface prior to cooling by placing a drop of nanopure water onto the sample and pressing the thermocouple into the drop until it freezes.



Polarization angle null analysis

- The intensity of the SF beam detected at a certain polarization

$$I(\omega^s) = A\left|E^s(\omega^s)\cdot\chi : E^{vis}(\omega^{vis})E^{IR}(\omega^{IR})\right|^2$$

- For sixfold symmetry, the hyperpolarizability tensor contains only seven nonzero elements χ_{xxz}, χ_{yyz}, χ_{xzx}, χ_{yzy}, χ_{xxz}, χ_{zyy}, and χ_{zzz}
- For the PAN analysis the polarization of the IR beam is fixed at *p* polarization $\Longrightarrow$ the SFG intensity is given by

$$\begin{aligned}
I^s(\theta_1^s,\theta_1^{vis}) = (&-L_{xx}^s\cos\eta_1^s\cos\theta_1^s\chi_{xxz}L_{zz}^{IR}L_{xx}^{vis}\sin\eta_1^{IR}\cos\eta_1^{vis}\cos\theta_1^{vis}\\
&-L_{xx}^s\cos\eta_1^s\cos\theta_1^s\chi_{xzx}L_{xx}^{IR}L_{zz}^{vis}\cos\eta_1^{IR}\sin\eta_1^{vis}\cos\theta_1^{vis}+L_{yy}^s\sin\theta_1^s\cos\theta_1^s\chi_{yyz}L_{zz}^{IR}L_{yy}^{vis}\sin\eta_1^{IR}\sin\theta_1^{vis}\\
&+L_{zz}^s\sin\eta_1^s\cos\theta_1^s\chi_{zxx}L_{xx}^{IR}L_{xx}^{vis}\cos\eta_1^{IR}\cos\eta_1^{vis}\cos\theta_1^{vis}+L_{zz}^s\sin\eta_1^s\cos\theta_1^s\chi_{zzz}L_{zz}^{IR}L_{zz}^{vis}\sin\eta_1^{IR}\sin\eta_1^{vis}\cos\theta_1^{vis})^2 I^{vis}I^{IR}
\end{aligned}$$

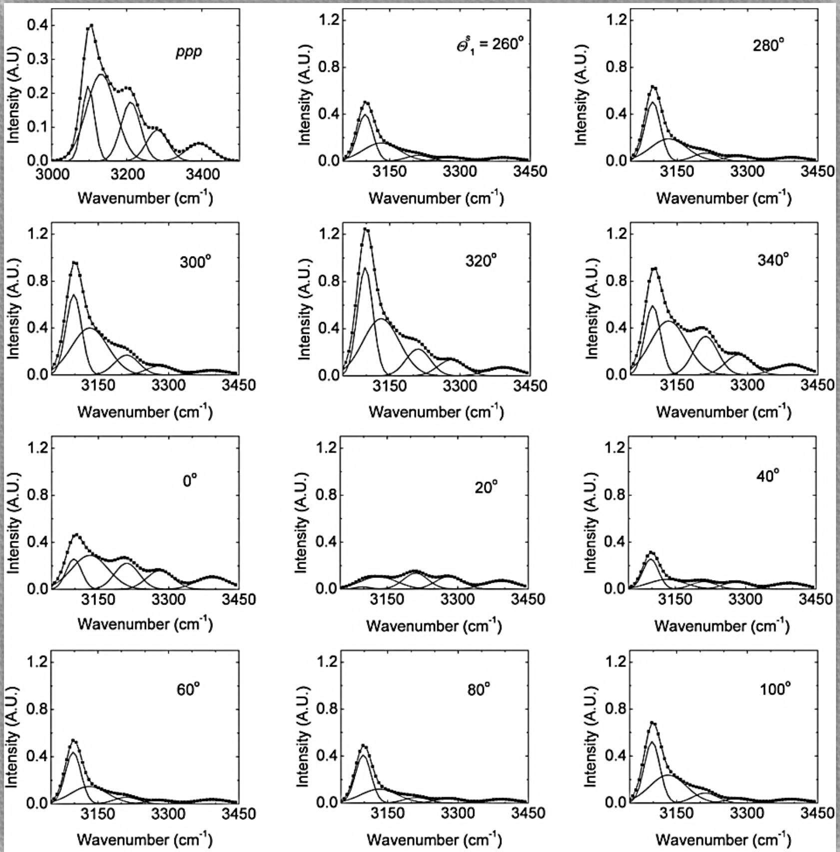
- The χ_{xxz}/χ_{zzz} ratio can be obtained from PAN analysis by setting equal to zero

$$\frac{\chi_{xxz}}{\chi_{zzz}} = \left(\frac{B}{D}-\frac{C}{D}\tan\theta_0^s\right)^{-1}$$

$$B=\cos\eta_1^s\cos\eta_1^{vis}L_{xx}^sL_{xx}^{vis}\cos\theta_1^{vis},\ C=L_{yy}^sL_{yy}^{vis}\sin\theta_1^{vis},\ D=\sin\eta_1^s\sin\eta_1^{vis}L_{zz}^sL_{zz}^{vis}\cos\theta_1^{vis}$$ $\Longrightarrow$ The Fresnel factors

RESULTS

- SFG spectroscopy is used to determine the orientation of molecules on a surface $\Longrightarrow$ can be deduced from the ratio of $\chi_{xxz}/\chi_{zzz} \Longrightarrow$ is calculated from the measured ssp and ppp intensities
- Both calculations result from the experimental setup: all beams travel through the cell window, which is at an angle to the beams.
- Since the infrared beam is p polarized, it remains p polarized upon transmission through the window, hence is p polarized at the sample.
- The visible beam is incident on the sample window at a 45° polarization.
- This method is chosen because the Fresnel and optical factors change with the visible polarization angle.
- The ppp spectrum was chosen for the initial identification of the surface oscillators.



RESULTS

Peak	1	2	3	4	5
Center (cm^{-1})	3098	3132	3211	3281	3393
Width (cm^{-1})	16.6	38.7	25.9	28.4	35.1

- Surface sum-frequency spectra are commonly fit with a Lorentzian line shape.
- The natural line shape for ice is obscured because the SFG spectrum of the ice surface originates from a hydrogen-bonded network, oscillating in a collective motion.
- Gaussian lines are used to fit the ice spectra.
- Attempts to fit the spectra using phase-corrected Lorentzians could not reproduce the steep rise on the red side of 3100 cm^{-1}
- Fits with five oscillators showed good fit stability and fit the experimental data reasonably well.
- Using fewer than five oscillators does not reproduce the polarization angle dependence of the spectra.
- The determined centers and widths of the five Gaussians are tabulated in Table I.

- The SFG intensity equation with the simplification due to χ_{xxz} /χ_{zzz}

$$I^s = \tilde{A}\left[\left(ED\chi_{zzz} - EB\chi_{xxz}\right)\cos\theta_1^s + EC\chi_{xxz}\sin\theta_1^s\right]^2$$

- $\tilde{A}$ and E scale χ_{xxz} and χ_{zzz} but do not affect the ratio, so χ_{xxz} and χ_{zzz} are used as fitting parameters P_1 and P_2,

$$I^s = \tilde{A}\left[\left(DP_1 - BP_2\right)\cos\theta_1^s + CP_2\sin\theta_1^s\right]^2$$

- The effect of unequal attenuation on the visible beam is calculated from the Fresnel factors and the input angle

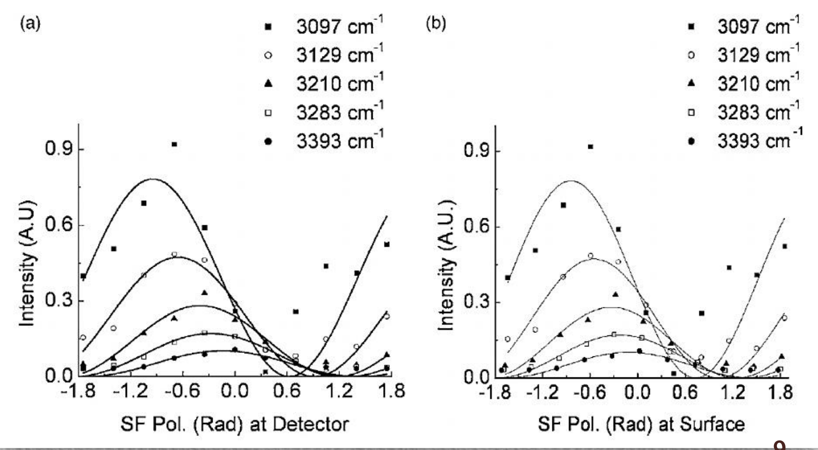
$$\tan\theta_1^{vis}(after\ window) = \frac{L_{ss}^{lin}}{L_{pp}^{lin}}\tan\theta_1^{vis}(before\ window)$$

- For an input polarization at 45° the actual polarization at the sample is 39° resulting in the following values for the geometric parameters B, C, and D: B = 0.3031; C = 0.3542; D = 0.2821.
- The surface polarization at the sample, $\theta_1^{s,surf}$, can be calculated by

$$\tan\theta_1^{s,surf}(at\ the\ sample) = \frac{L_{pp}^{lin}}{L_{ss}^{lin}}\tan\theta_1^{s}(at\ the\ detector)$$

- The PAN angles (θ_0^S) obtained from the fit are listed in Table II.

Oscillator(cm^{-1})	θ_0^S	$\theta_0^{S,surf}$	$P_2 = \chi_{xxz}$	$P_1 = \chi_{zzz}$	χ_{xxz}/χ_{xxz}
3098	36	42	1.86	-0.09	-20.07
3132	52.5	58.5	1.02	-0.98	-1.04
3211	67	71	0.48	-1.26	-0.38
3281	74	77	0.26	-1.15	-0.23
3393	82	84	0.10	-1.01	-0.1



DISCUSSION

- ✓ The polarization direction depends on the relative values of the surface hyperpolarizabilities χ_{xxz} and χ_{zzz}.
- ✓ Figure 4 shows the dynamic polarizability: The surface response is a hyperpolarizability, a product of the dynamic polarizability ellipsoid and the transition dipole
- ✓ The product, the hyperpolarizability, is illustrated in Fig. 5
- ✓ A -ve ratio means that during the vibration the polarizability in one direction increases while the polarizability in the other direction diminishes: the polarizations are out of phase.
- ✓ A +ve sign indicates that the transverse and longitudinal components of the polarizability change in concert.
- ✓ The SF polarization angle null PAN is determined by the relative magnitude and sign of the χ_{xxz} and χ_{zzz} components, resulting in a rotation of the lobes of the SFG intensity.

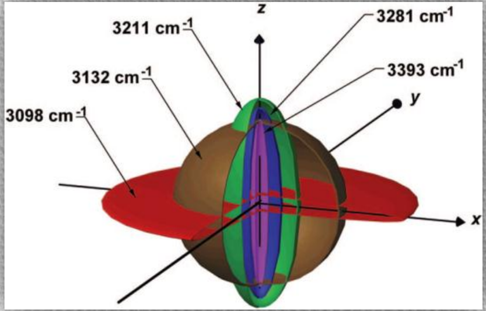


FIG. 4. Color Polarizability ellipsoids for the five oscillators on the basal face of ice Ih.

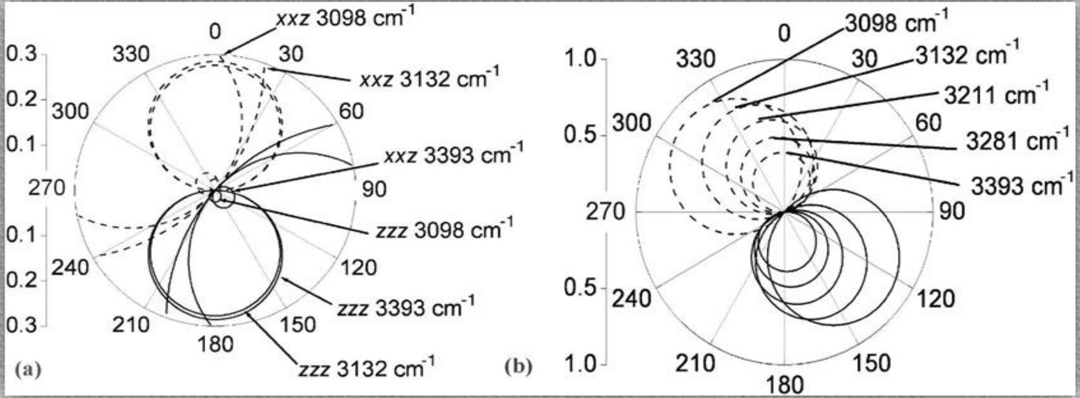


FIG. 5. a) The xxz and zzz contributions to the SFG intensity as a function of the analyzer polarization angle for three representative modes. The dashed lobes all have the same phase. b) The relative SFG amplitude as a function of the analyzer polarization angle, again the dashed lines indicate the same phase.

SUMMARY

- There are at least five identifiable oscillators within the hydrogen-bonded region in PAN.
- The longest wavelength resonance has a dynamic polarizability that is parallel to the surface normal.
- With increasing frequency, the modes are increasingly longitudinal.
- The shortest wavelength hydrogen-bonded peak is predominately longitudinal.

- Previous experiments have shown that the shortest wavelength resonances are the most fragile, the most sensitive to disturbances of the surface.
- The coupling in the longitudinal modes is easily disrupted, but the transverse modes are robust.

- Within the dipole approximation, the sum-frequency intensity shows a $\sin(\theta - \theta_0)$ dependence on rotation of a polarizer in the sum-frequency beam, where θ_0 is the null angle.
  - The longest wavelength resonance shows a deviation from this dipolar dependence.