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Development of single-channel heterodyne-detected sum frequency generation spectroscopy and its application to the water/vapor interface

Shoichi Yamaguchi[a)]
Department of Applied Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura, Saitama 338-8570, Japan

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Single-channel heterodyne-detected sum frequency generation (HD-SFG) spectroscopy for selectively measuring vibrational spectra of liquid interfaces is presented. This new methodology is based on optical interference between sum frequency signal light from a sample interface and phase-controlled local oscillator light. In single-channel HD-SFG, interferometric and spectrometric measurements are simultaneously carried out with an input IR laser scanned in a certain wavenumber range, which results in a less task than existing phase-sensitive sum frequency spectroscopy. The real and imaginary parts of second-order nonlinear optical susceptibility ($\chi^{(2)}$) of interfaces are separately obtained with spectral resolution as high as 4 cm^{-1} that is approximately six times better than existing multiplex HD-SFG. In this paper, the experimental procedure and theoretical background of single-channel HD-SFG are explicated, and its application to the water/vapor interface is demonstrated, putting emphasis on the importance of a standard for the complex phase of $\chi^{(2)}$. [http://dx.doi.org/10.1063/1.4927067]

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CrossMark

Development of single-channel heterodyne-detected sum frequency generation spectroscopy and its application to the water/vapor interface

- Single-channel HD-SFG
  - Experimental section (Schematic setup)
  - Theoretical section (principle)

- The spectral resolution is as high as 4 cm^{-1} (~ 6 times better than HD-SFG)

- Application to the water/vapor interfaces
  - Data and $\chi^{(2)}$ spectra
  - Complex-phase correction for the $\chi^{(2)}$ spectrum

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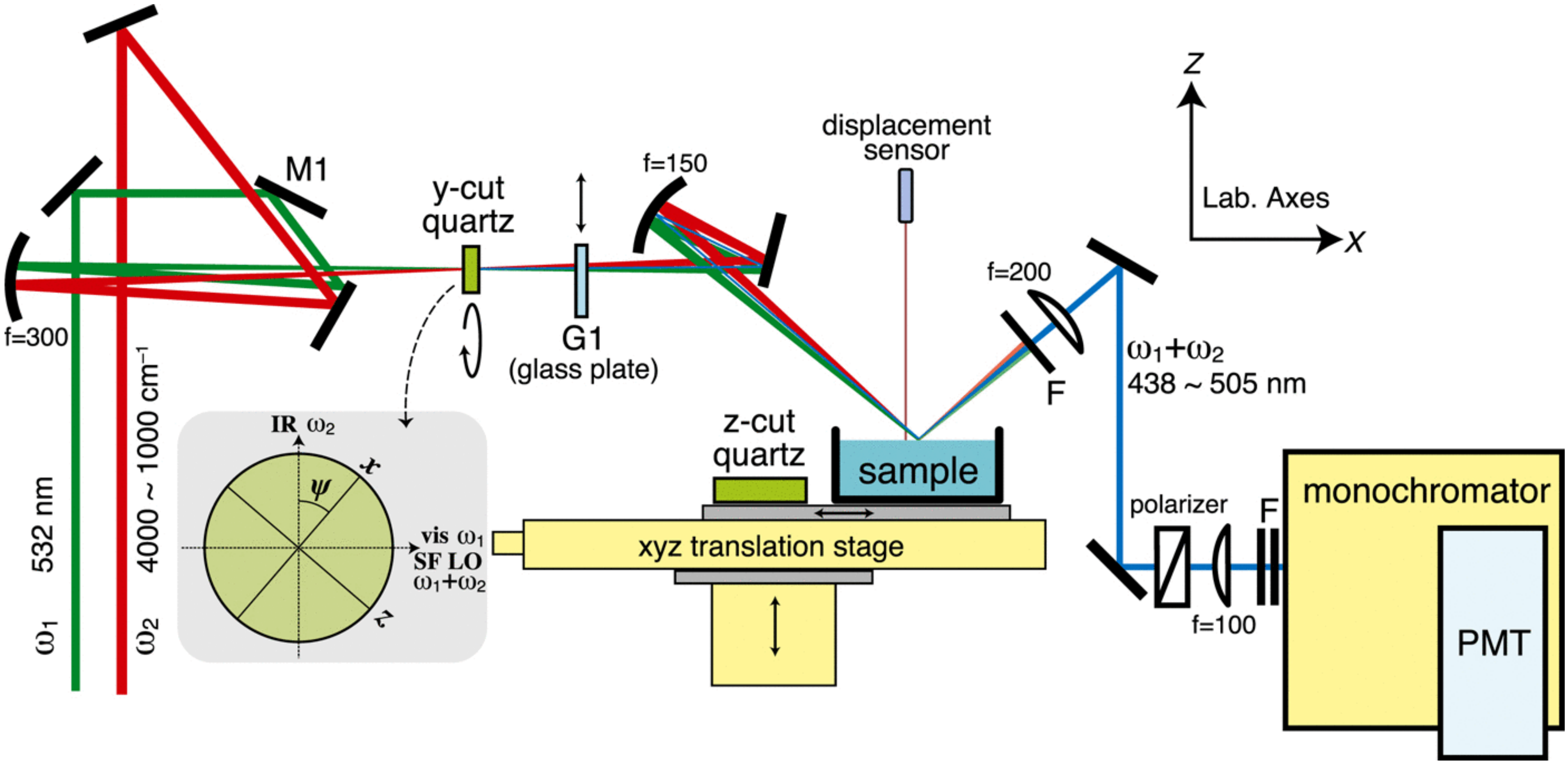
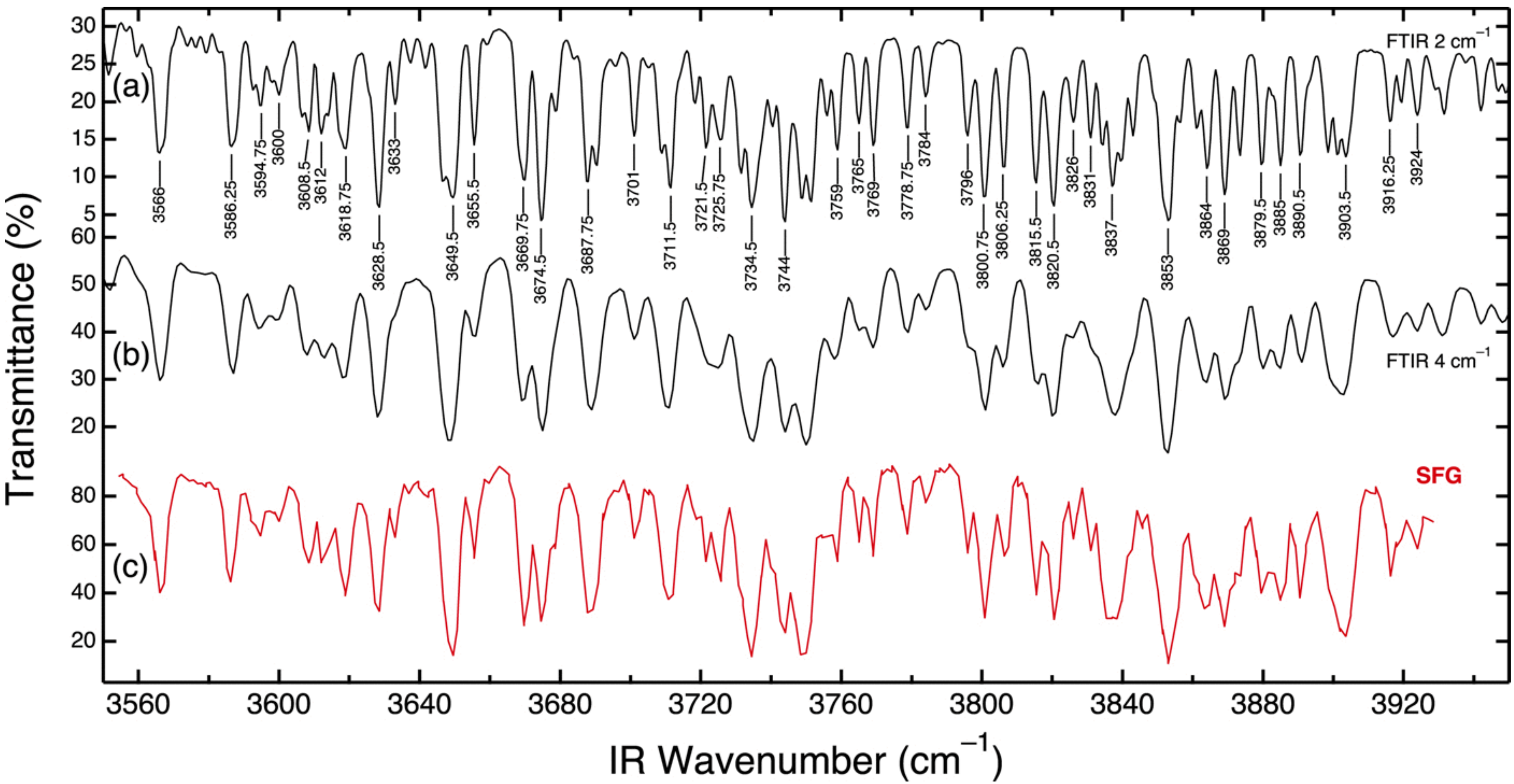
Schematic of the optical setup of single-channel HD-SFG



Schematic of the optical setup of single-channel HD-SFG. The ω_1 and ω_2 lights propagate nearly collinearly with a small vertical shift after the mirror M1. A light-blue thin line drawn between the glass plate G1 and the sample interface represents the LO light. The sample can be replaced with the *z*-cut quartz by the xyz automatic translation stages. F stands for optical filters. The positive direction of the P polarization of the ω_2 pulse at the incidence of the sample interface is defined to be along the positive directions of the laboratory *X* and *Z* axes. The inset shows relation between the polarizations of the ω_1, ω_2, and LO pulses and the crystal axes of the *y*-cut quartz.

Calibration for the ω_2 pulse



IR transmittance spectra of water vapor measured using the FTIR spectrometer with the resolution set at (a) 2 cm^{-1} and (b) 4 cm^{-1}, and (c) using the single-channel HD-SFG setup. The wavenumber calibration for the ω_2 pulse in this spectral region was performed using all the bands to which the peak positions are appended in (a).

Theory

Pick up optical interference between the SF signal and LO lights (*y*-quartz: LO, ω_1 - ‖, ω_2 -⊥)

$$\chi_{y-cut} \propto \sin^2 \psi \cos \psi$$

$$E_{LO} = \chi_{y-cut} E_1 E_2$$

The SF signal light is generated either at the sample interface and at the reference *z*-cut quartz surface

$$E_S = i\chi_S E_1 E_2 \exp\{i(\phi_1 + \phi_2)\}$$

$$E_R = i\chi_R E_1 E_2 \exp\{i(\phi_1 + \phi_2)\}$$

Theory

$$E_{L+S} = R_S E_{LO} exp(i\phi_{LO}) + ES = [RS\chi_{y-cut} Rexp\ (i\phi_{LO}) + i\chi_S exp\{i(\phi_1 + \phi_2)\}]E_1 E_2$$

$$\Delta I_S = |E_{L+S}(\psi = 90° - \delta)|2 - |E_{L+S}(\psi = 90° + \delta)|2$$
$$= |R_S E_{LO} exp(i\phi_{LO}) + ES|2 - | - R_S E_{LO} exp(i\phi_{LO}) + ES|2$$
$$= 2i[\chi^*_{y-cut}\chi_S exp\{i(\phi_1 + \phi_2 - \phi_{LO})\} - \chi_{y-cut}\chi^*_S exp\{i(-\phi_1 - \phi_2 + \phi_{LO})\}]RS|E_1 E_2|^2$$

$$E_{L+R} = [RR_{\chi_{y-cut}} exp(i\phi_{LO}) + \chi_R exp\{i(\phi_1 + \phi_2)\}]E_1 E_2$$

$$\Delta I_R = |E_{L+R}(\psi = 90° - \delta)|2 - |E_{L+S}(\psi = 90° + \delta)|2$$
$$= 2[\chi^*_{y-cut} exp\{i(\phi_1 + \phi_2 - \phi_{LO})\} + {\chi_{y-cut}} exp\{i(-\phi_1 - \phi_2 + \phi_{LO})\}]\chi_R R_R |E_1 E_2|^2$$

$$D \equiv -4\chi^*_{y-cut} exp\{i(\phi_1 + \phi_2 - \phi_{LO})\} R_S |E_1 E_2|^2$$
$$\Delta I_S = Im[D\chi_S] = Im\, D\, Re\, \chi_S + Re\, D\, Im\, \chi_S$$

Theory

Quantities measured with the glass plate

$$\Delta I'_S = 2i[\chi^*_{y-cut}\chi_S exp\{i(\phi'1 + \phi'2 - \phi'_{LO})\} - \chi_{y-cut}\chi^*_S exp\{i(-\phi'1 - \phi'2 + \phi'_{LO})\}]R_S|E_1E_2|^2$$

$$\Delta I'_R = 2[\chi^*_{y-cut} exp\{i(\phi'1 + \phi'2 - \phi'_{LO})\} + \chi_{y-cut} exp\{i(-\phi'1 - \phi'2 + \phi'_{LO})\}]\chi_R R_R|E_1E_2|^2$$

$$D' \equiv -4\chi^*_{y-cut} exp\{i(\phi'1 + \phi'2 - \phi'_{LO})\}RS|E_1E_2|^2$$

$$\Delta I'_S = Im\, D' Re\chi_S + Re\, D' Im\chi_S$$

Theory

$$D \equiv -4\chi^{*}_{y-cut} exp\{i(\phi_1 + \phi_2 - \phi_{LO})\}R_S|E_1E_2|^2$$

$$\Delta I_S = Im[D\chi_S] = Im\, D\, Re\, \chi_S + Re\, D\, Im\, \chi_S$$

$$D' \equiv -4\chi^{*}_{y-cut} exp\{i(\phi'1 + \phi'2 - \phi'_{LO})\}RS|E_1E_2|^2$$

$$\Delta I'_S = Im\, D' Re\chi_S + Re\, D' Im\chi_S$$

$$\begin{pmatrix} Re\,\chi_S \\ Im\,\chi_S \end{pmatrix} = \begin{pmatrix} Im\,D & ReD \\ Im\,D' & Re\,D' \end{pmatrix}^{-1} \begin{pmatrix} \Delta I_S \\ \Delta I'_S \end{pmatrix} = \frac{1}{Im\,DRe\,D' - Re\,DIm\,D'} \begin{pmatrix} Re\,D' & -ReD \\ -Im\,D' & Im\,D \end{pmatrix} \begin{pmatrix} \Delta I_S \\ \Delta I'_S \end{pmatrix}$$

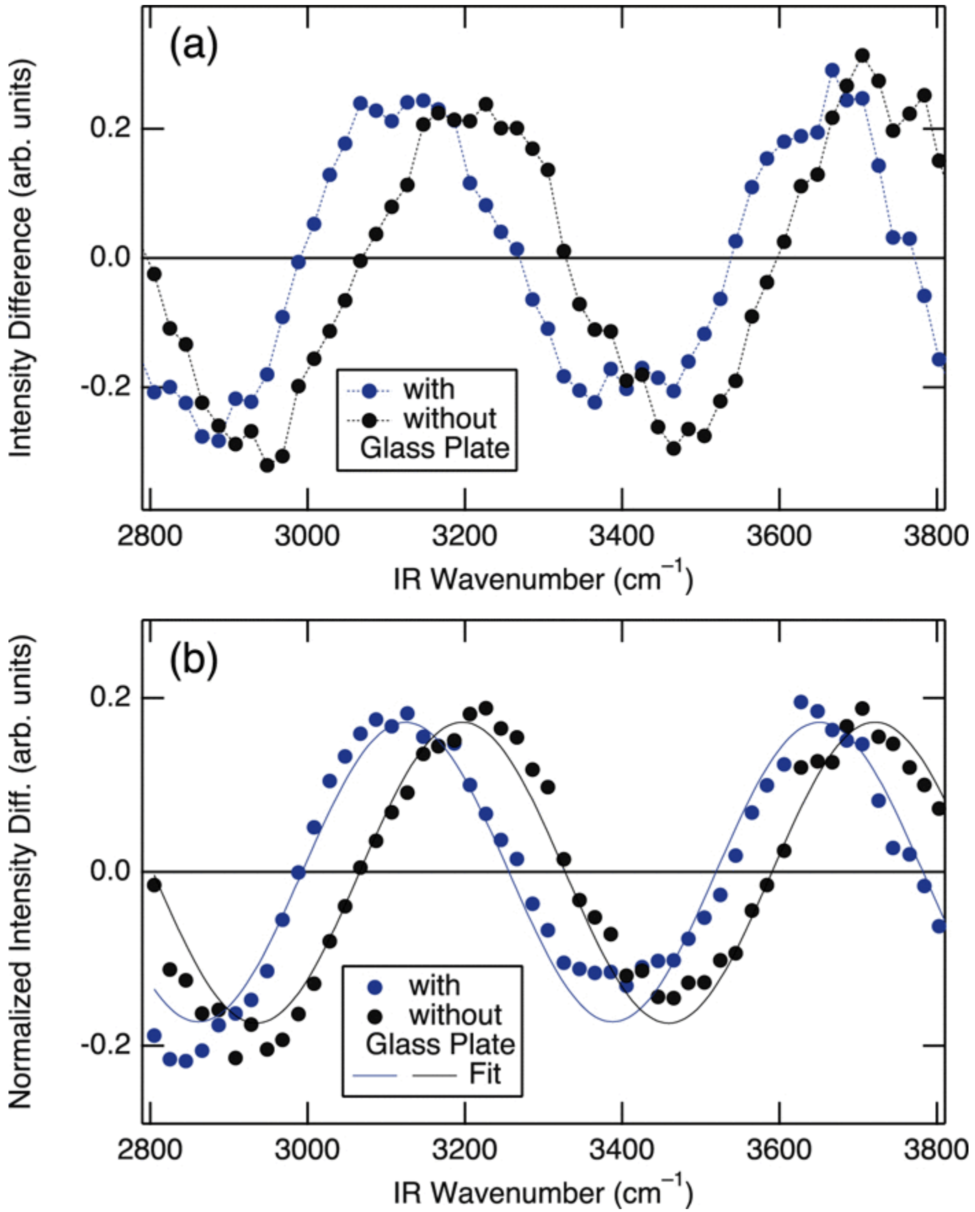
Reχ_S and Imχ_S are obtained by measuring ΔI_R, $\Delta I'_R$, ΔI_S, and $\Delta I'_S$.

Reference z-cut quartz surface

(a) Intensity differences (ΔI_R and $\Delta I'_R$) between the total electric fields with ψ = 90° ± 0.5°. Black and blue circles stand for the experimental data of ΔI_R and $\Delta I'_R$, respectively. Dotted lines just connect the data points.

(b) ΔI_R and $\Delta I'_R$ normalized by $\chi_R^2|E_1E_2|^2$. Black and blue circles stand for the experimental data of normalized ΔI_R and $\Delta I'_R$, respectively. Solid lines represent fits based on a sine function.

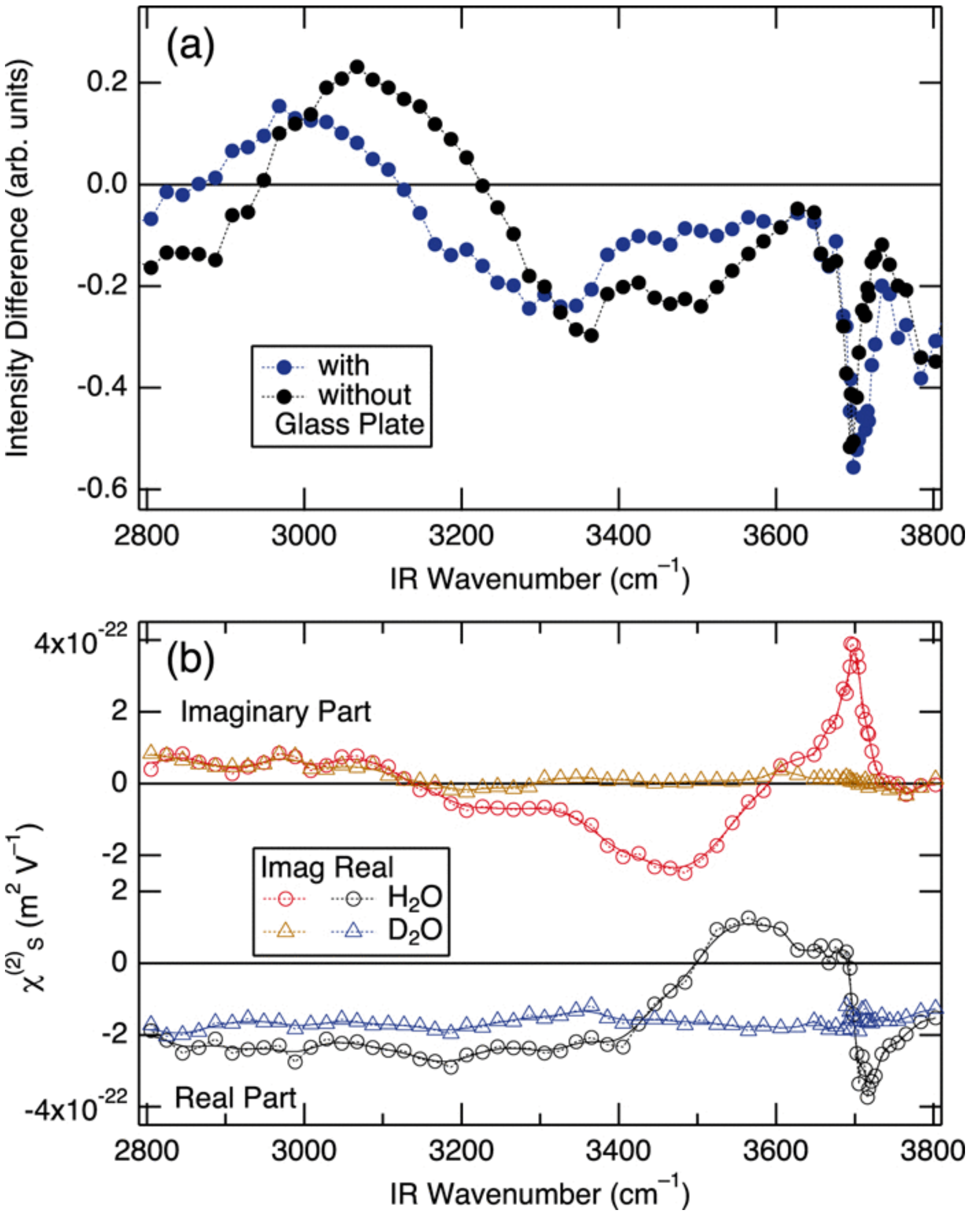
$$\frac{\Delta I_R}{\chi_R^2|E_1E_2|^2} = 2\left[\chi^*_{y-cut}exp\{i(\phi_1+\phi_2-\phi_{LO})\} + \chi_{y-cut}exp\{i(-\phi_1-\phi_2 + \phi_{LO})\}\right]\chi_R^{-1}R_R$$



Sample interface

(a) Intensity differences (ΔI_S and $\Delta I'_S$) between the total electric fields with ψ = 90° ± 0.5° for the H_2O/vapor interface. Black and blue circles stand for the experimental data of ΔI_S and $\Delta I'_S$, respectively. Dotted lines just connect the data points.

(b) χ_S spectra of the H_2O/vapor interface (red: imaginary, black: real) and the D_2O/vapor interface (orange: imaginary, blue: real). Open circles represent the experimental data, and dotted lines just connect the data points. Solid lines are eye guide.



H_2O/vapor interface

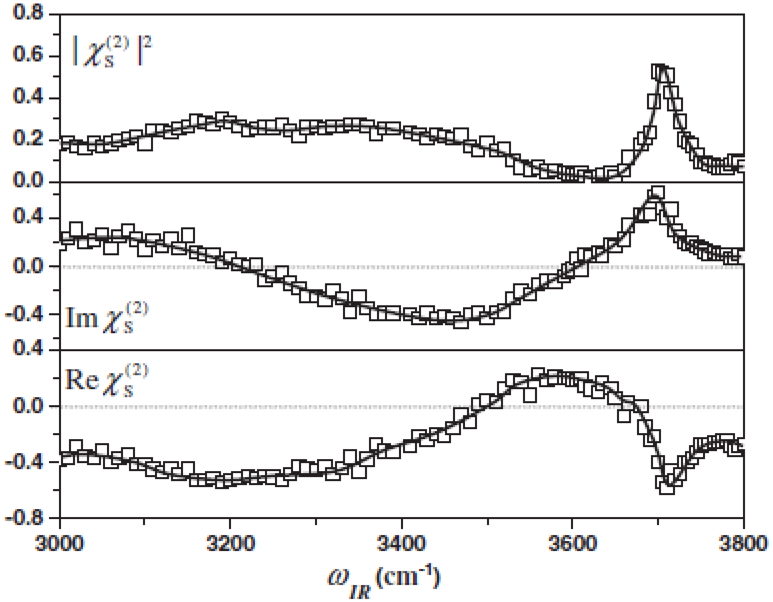
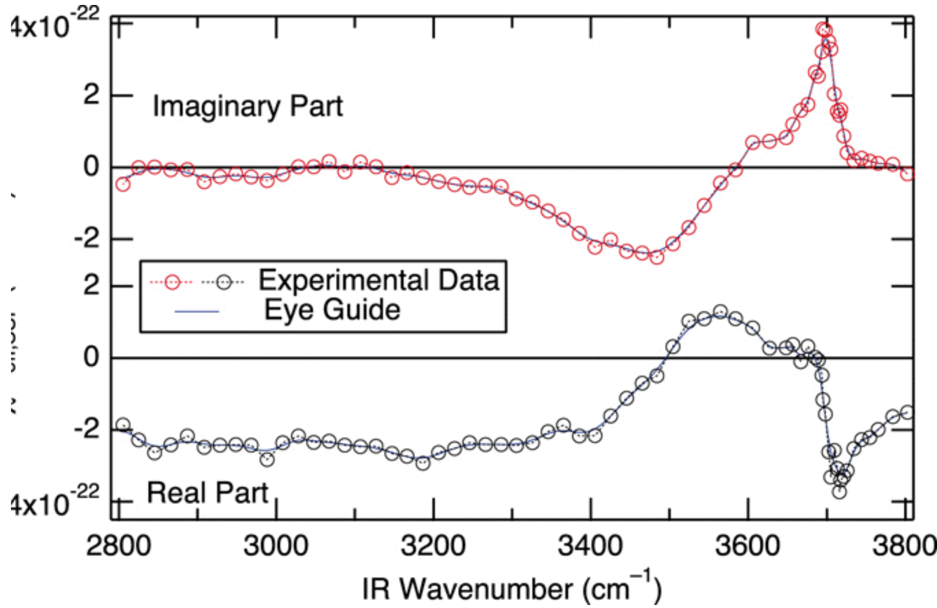


FIG. 1. Spectra of $|\chi_S^{(2)}|^2$, Im$\chi_S^{(2)}$, and Re$\chi_S^{(2)}$ for neat water-vapor interface in the OH stretch range obtained with the phase-sensitive sum-frequency vibrational spectroscopy (PS-SFVS). The curves are for eye guiding.

Shen, Phys. Rev. Lett. **2008**



$^{(2)}{}_{eff,SSP}$ spectrum of the H_2O/vapor interface (red: naginary, black: real) after the complex-phase correction. pen circles represent the experimental data, and dotted nes just connect the data points. Solid lines are eye guide.

Conclusion

- Single-channel HD-SFG from the water/vapor interface
  - at the same time to separately obtain the real and imaginary parts of $\chi^{(2)}$
- The Im $\chi^{(2)}_{eff,SSP}$ spectrum of the H_2O/vapor interface has the “positive band” in 3000–3200 cm^{-1} and the small band at 3640 cm^{-1}, <u>the former of which is negated in the present study</u>
- <u>The complex-phase correction using nonresonant D_2O as a standard guarantees the reliability of the present experimental data.</u>
- Molecular dynamics simulation studies of the water/vapor interface that reproduced the positive band in 3000–3200 cm^{-1} should be reconsidered.