

Supporting Information for

Hydrogen-bonding structure in self-formed
nanodroplets of water adsorbed on amorphous
silica revealed by surface-selective vibrational
spectroscopy

Shu-hei Urashima,^{†a,b} Taku Uchida,^{†a} and Hiroharu Yui^{*a,b}

^a *Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162–8601, Japan.*

^b *Water Frontier Science & Technology Research Center, Research Institute for Science & Technology, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162–8601, Japan.*

[†]Note: SU and TU are of equal contribution.

1. Phase-rotated $\text{Im}\chi^{(2)}$ spectra.

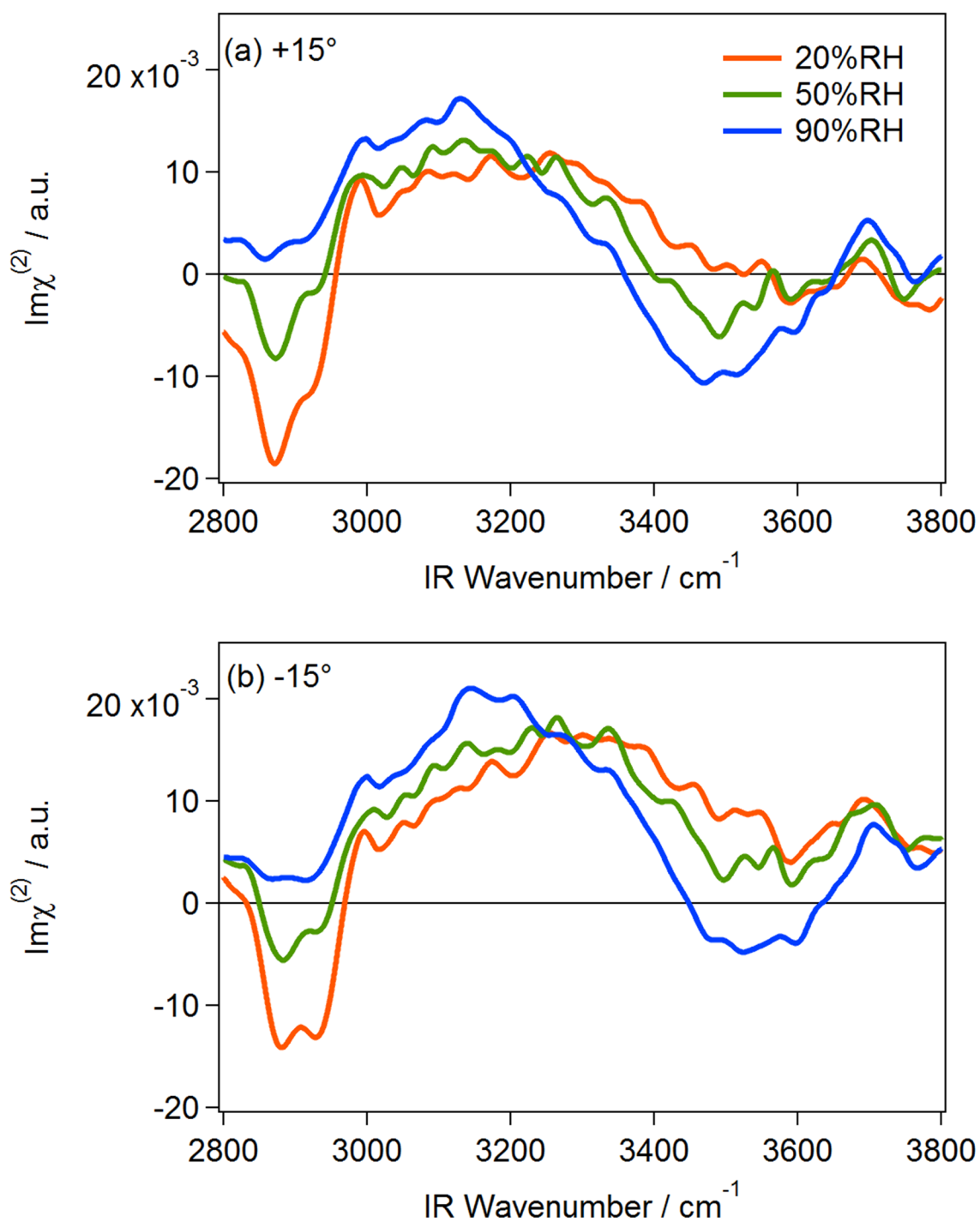


Figure S1. $\text{Im}\chi^{(2)}$ spectra of the vapor/silica after phase rotation of (a) $+15^\circ$ and (b) -15° . The rotation angle of $\pm 15^\circ$ is potential phase error. Note that essential feature of the spectra is unchanged even after the rotation.

2. $|\chi^{(2)}|^2$ spectra reconstructed from complex $\chi^{(2)}$.

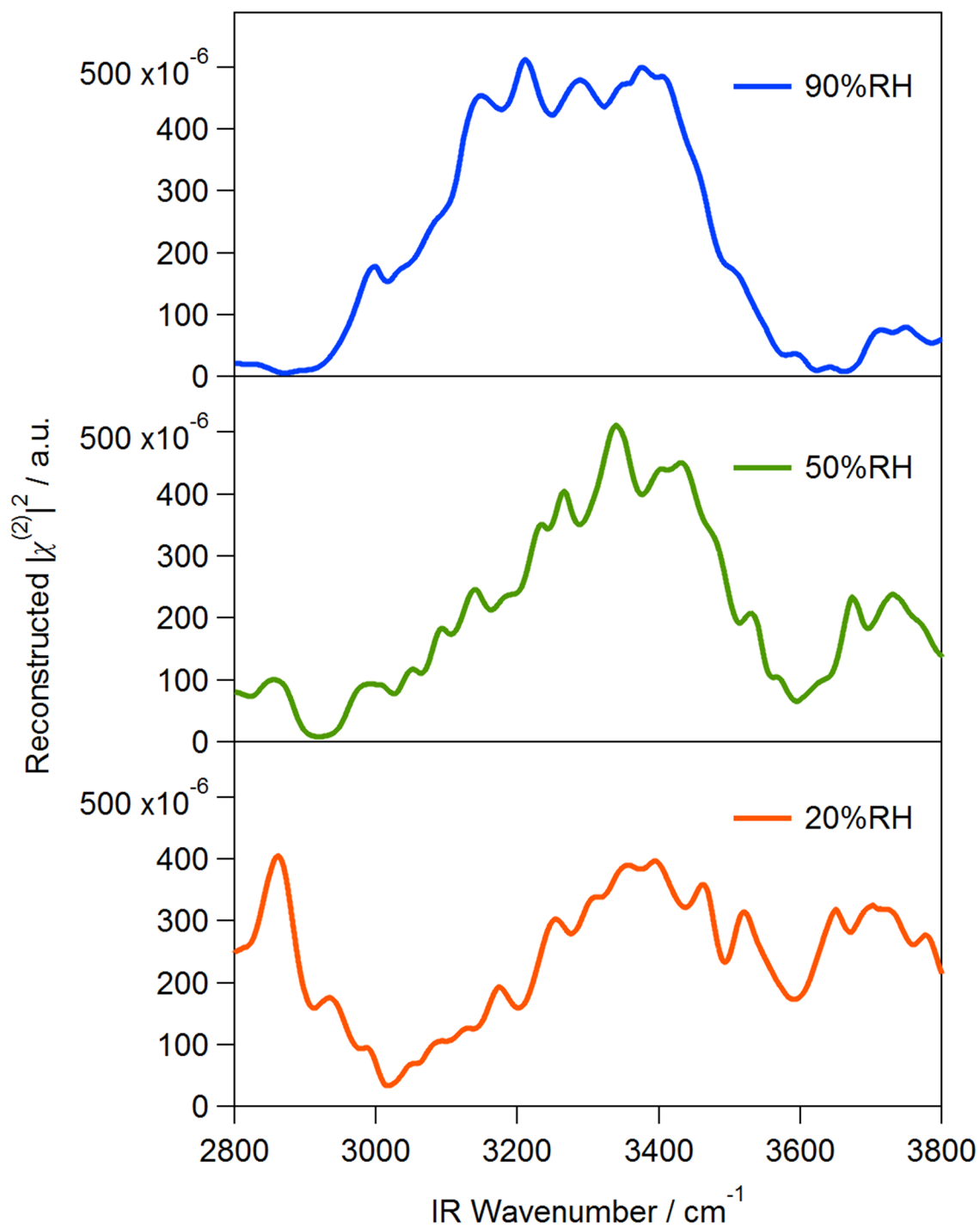


Figure S2. $|\chi^{(2)}|^2$ spectra of the vapor/silica interface (reconstructed from complex $\chi^{(2)}$ spectra).

3. Contact angle measurements

To confirm the cleanliness of the silica surface, we measured contact angle of silica several hours after the cleaning. It was measured with 2 μl of water with drop shape analyzer (KRÜSS, DSA-25). We checked the contact angle 0-4 hours after the cleaning, and the silica substrate was cleaned by UV/ozone cleaner for 30 minutes each time after the contact angle measurements: for example, after the measurement of “1 hour after cleaning”, we again cleaned the sample and waited for 2 hours for “2 hour after cleaning”. This is because the silica got highly hydrophobic once the substrate gets wet and dried in the lab air. The measurements were repeated four times to obtain average and standard deviation.

As shown in Figure S3, the contact angle was about 13° even four hours after the cleaning, suggesting the silica kept hydrophilic in our measurement duration.

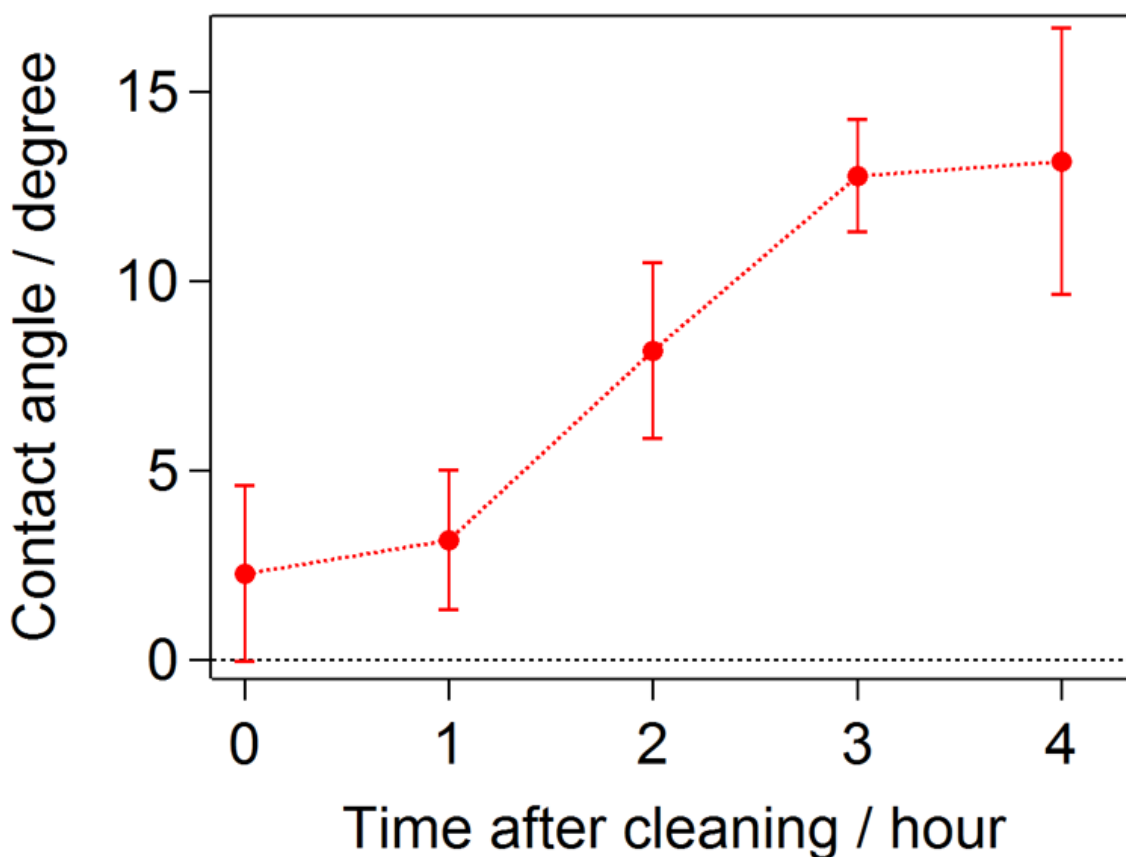


Figure S3. Time dependence of contact angle of the silica substrate. The contact angle was sometimes below detection-limit at 0 hour (just after the cleaning) and it was regarded as 0 degree for convenience. Error bars correspond standard deviation.

4. Fresnel analysis

In the main text, we compared our $\text{Im}\chi^{(2)}$ spectra with those evaluated in literature¹ (Ref. 11 in the main text). Because we found significant difference between them, it is necessary to check whether the difference is due to spectral distortion or not. Here we demonstrate that the spectral distortion is not crucial for the comparison.

In ssp- (our experimental configuration) and ppp-polarization (configuration in Ref. 11), what is observed, *i.e.* effective nonlinear susceptibility $\chi_{\text{eff,ssp}}^{(2)}$ or $\chi_{\text{eff,ppp}}^{(2)}$, is described as:

$$\chi_{\text{eff,ssp}}^{(2)} = L_{3Y}L_{1Y}L_{2Z} \sin \theta_{2r} \chi_{YYZ}^{(2)} ,$$

or

$$\begin{aligned} \chi_{\text{eff,ppp}}^{(2)} = & -L_{3X} \cos \theta_{3r} \left(L_{1X}L_{2Z} \cos \theta_{1i} \sin \theta_{2i} \chi_{XXZ}^{(2)} + L_{1Z}L_{2X} \sin \theta_{1i} \cos \theta_{2i} \chi_{XZX}^{(2)} \right) \\ & + L_{3Z} \sin \theta_{3r} \left(L_{1X}L_{2X} \cos \theta_{1i} \cos \theta_{2i} \chi_{ZXX}^{(2)} + L_{1Z}L_{2Z} \sin \theta_{1i} \sin \theta_{2i} \chi_{ZZZ}^{(2)} \right) , \end{aligned}$$

where L_{1J} , L_{2J} , and L_{3J} are Fresnel factors of incident visible, incident infrared, and generated sum-frequency (SF) lights, respectively (for $J = X, Y, Z$). θ_{1i} , θ_{2i} , and θ_{3r} are incident (or reflection) angle of the visible, infrared, and SF lights. $\chi_{IJK}^{(2)}$ is nonlinear susceptibility of the interface (for $I, J, K = X, Y, Z$). Of these parameters, only L_{2X} and L_{2Z} can affect the spectral shape because the Fresnel factors are dependent on refractive index, which drastically varies at resonance. L_{2X} and L_{2Z} can be described as:

$$L_{2X} = \frac{2n_a \cos \theta_t}{n_a \cos \theta_t + n_b \cos \theta_i}$$

$$L_{2Z} = \frac{2n_b \cos \theta_r}{n_a \cos \theta_t + n_b \cos \theta_r} \left(\frac{n_a}{n'} \right)^2 ,$$

with

$$n' = \sqrt{\frac{n_a^2 + n_b^2 + 4}{2(n_a^{-2} + n_b^{-2} + 1)}} ,$$

where θ_i , θ_r , and θ_t are incident, reflected, and transmitted angle of infrared light. n_a

and n_b are the refractive index of the incident phase and transmitted phase, respectively. Because air and silica are both non-resonant at the frequency range of 2800-3800 cm^{-1} , Fresnel factors for air/silica system is to be constant. However, in fact, the refractive index of silica surface should be varied because of resonance of the adsorbed water. Because it is too complicate to estimate the refractive index of the interface with presence of the adsorbed water, here we calculated the Fresnel factors for silica/liquid water system as an ultimate model for the spectral distortion. As shown in Figure S4, Fresnel factor L_{2Z} in our experimental configuration (incident from air with angle of 50 degree with ssp polarization) is almost constant (Figure S4a). In the configuration of Ref. 11 (incident through silica with angle of 75 degree with ppp polarization), although neither L_{2Z} (Figure S4b) nor L_{2X} (Figure S4c) was constant, the curves are almost linear in the region of 3000-3700 cm^{-1} . Because no peak-like feature was found unlike some of the previous studies^{2,3}, we concluded that VSG spectra obtained by us and in Ref. 11 were nearly distortion free.

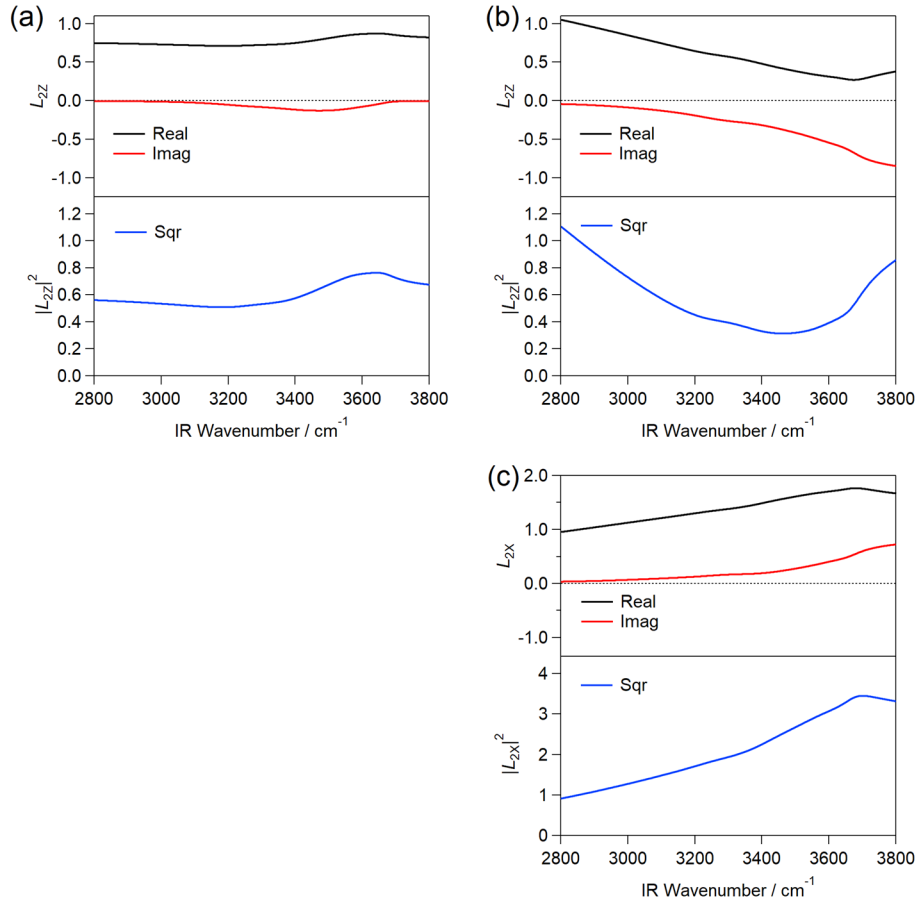


Figure S4. Calculated Fresnel factors of silica/liquid water interface. (a) L_{2Z} in our experimental configuration (laser is incident from air with angle of 50°). (b, c) L_{2Z} and L_{2X} in configuration of Ref. 11 in the main text (laser is incident from silica with angle of 75°).

References

1. O. Isaienko and E. Borguet, *Langmuir*, 2013, **29**, 7885-7895.
2. E. H. G. Backus, N. Garcia-Araez, M. Bonn and H. J. Bakker, *J. Phys. Chem. C*, 2012, **116**, 23351-23361.
3. L. Wang, S. Nihonyanagi, K.-i. Inoue, K. Nishikawa, A. Morita, S. Ye and T. Tahara, *J. Phys. Chem. C*, 2019, **123**, 15665-15673.