

SUPPORTING INFORMATION FOR:

**Exploring hydrogen bond kinetics of methanol-water
solutions by Raman scattering**

Fabing Li^a, Ying Wang^a, Zhiwei Men^a, Chenglin Sun^{a,b*}

*a Coherent Light and Atomic and Molecular Spectroscopy Laboratory, College of Physics, Jilin University,
Changchun 130012, China*

*b Key Laboratory of Physics and Technology for Advanced Batteries, College of Physics, Jilin University,
Changchun 130012, China*

* E-mail: chenglin@jlu.edu.cn

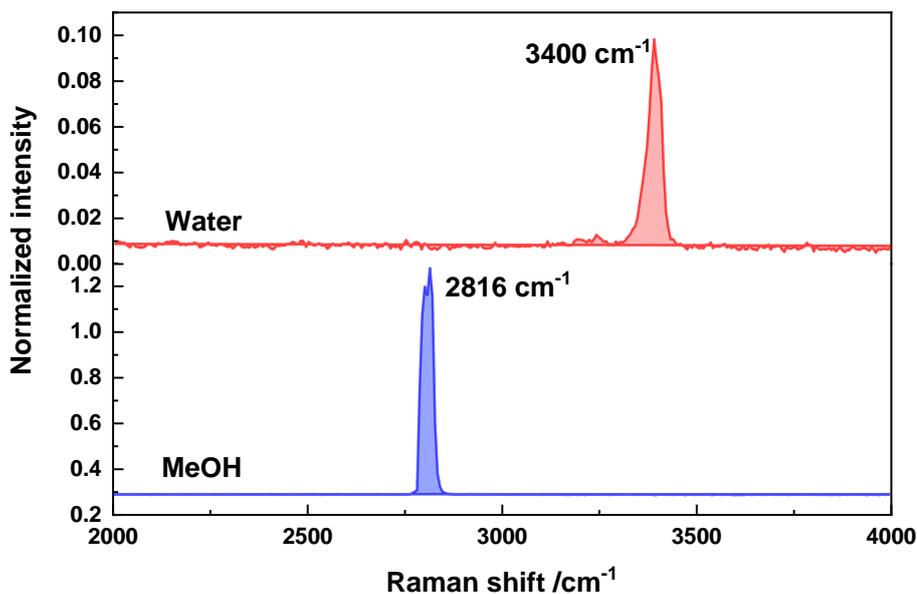


Fig. S1. SRS spectra of pure water and pure MeOH.

Importantly, the peak of SRS results from spontaneous Raman noise amplification. The spectrum of SRS is determined by the maximum Raman gain factor. Therefore, the vibrational peak with the largest scattering cross section is first amplified. Meanwhile, the Stokes field of SRS also consumes the pump power, preventing the amplification of other Raman modes. The SRS peak of liquid water is around 3400 cm^{-1} (the largest scattering cross section), while the peak of MeOH is about 2816 cm^{-1} . So, the peak of SRS can be attributed to the vibration of a single substance in general.

Experiments

Sample

MeOH purchased from Wako Pure Chemical Industries was used as a sample. Deionized water was boiled and passed through a 0.2 Millipore filter. The volume ratios of MeOH (V_E) were 0, 0.05, 0.1, 0.15, 0.2, 0.23, 0.27, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1 (The volume of MeOH divided by the volume of the mixture solutions). Samples were filed in a quartz cell (width, height, and length: $1\times 5\times 10\text{ cm}$). The focal length of the focusing lens was 15 cm.

SRS

The second harmonic of the pulsed Nd-YAG laser (Wavelength: 532 nm; Pulse duration: 12 ns; Repetition rate: 10 Hz; Beam diameter: 4 mm) was used as excitation laser. SRS spectra were obtained by using a long working distance objective lens with 25× magnification and numerical aperture: 4.5. The output scattering light was analyzed by an Ocean Optics HR4000CG-UV-NIR spectrometer with a resolution of 1 cm^{-1} . The experimental setup is shown as Fig. S2.

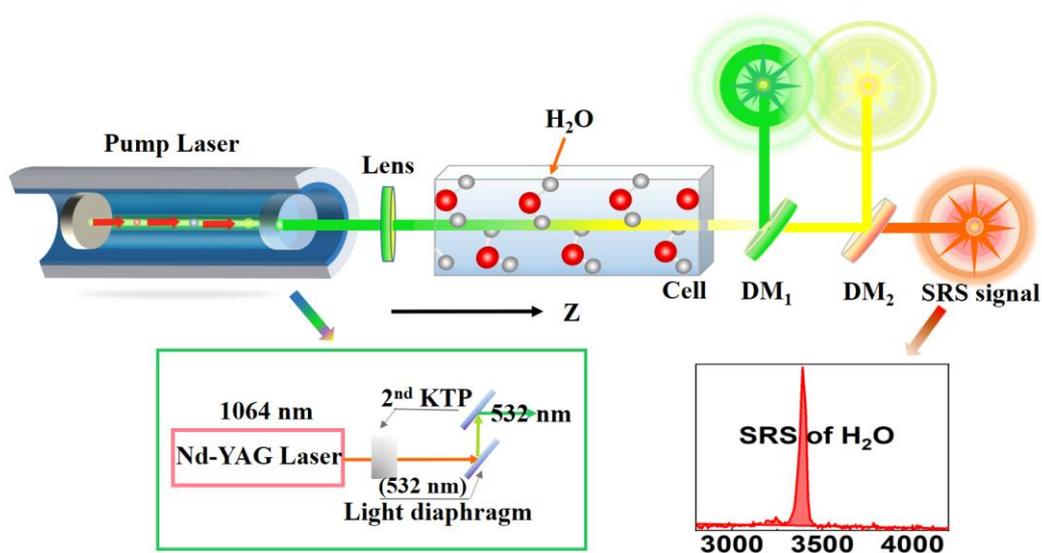


Fig. S2. Schematic diagram of the experimental setup to measure SRS spectra; DM: dichroic mirror.

Spontaneous Raman scattering:

The scanning speed of Spontaneous Raman spectra was $10\text{ cm}^{-1}/\text{s}$ and the spectral resolution was 1 cm^{-1} . The spectra were measured by Renishaw InVia Raman micro spectrometer. Samples were excited by an Argon laser at 514.5 nm and an output power of 5 mW. Raman spectra were gained by using a long working distance objective lens with 50× magnification located in different samples and detected with a CCD detector.

Spontaneous Raman spectra of MeOH-water solutions

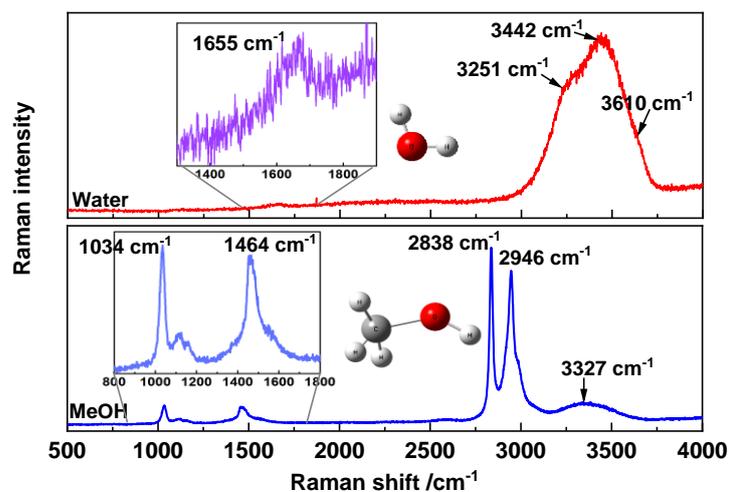


Fig. S3. Raman spectra of liquid water and MeOH.

Table. S1. Attribution of Raman peaks of liquid water and MeOH.

Solution	Raman shift	Assignment
Water	3610 cm^{-1}	Free OH
	3442 cm^{-1}	The skin mode (Weak H-bonds)
	3251 cm^{-1}	The bulk mode (Strong H-bonds)
	1655 cm^{-1}	Bending vibrational mode
MeOH	3327 cm^{-1}	OH stretching vibrational mode
	2946 cm^{-1}	Bending overtones
	2838 cm^{-1}	CH_2 stretching mode
	1464 cm^{-1}	C-H asymmetric deformation mode
	1034 cm^{-1}	C-O stretching mode

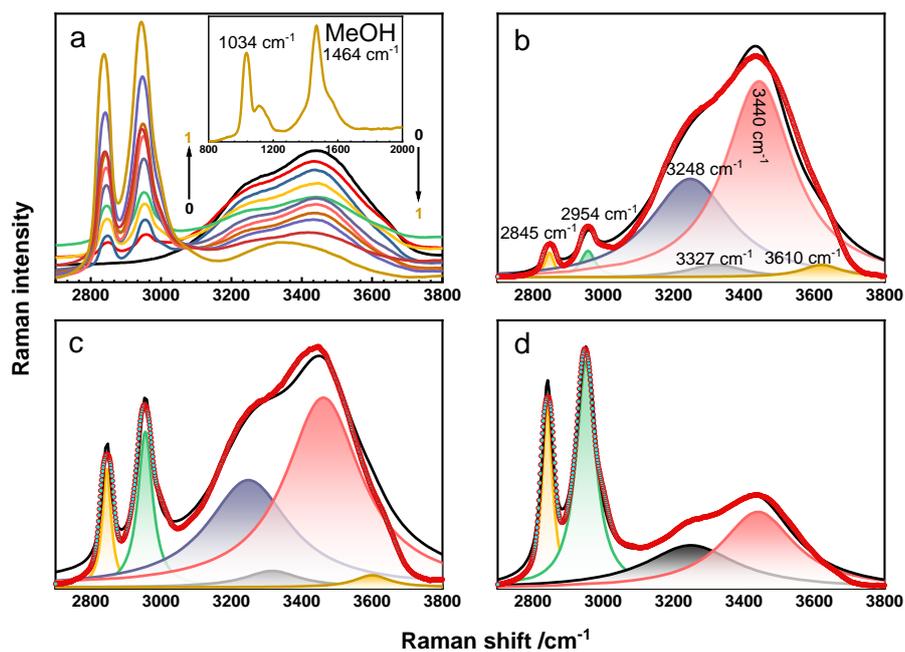


Fig. S4. (a) Spontaneous Raman spectra of MeOH-water solutions with different V_E . Fitting Peaks of mixture solutions by Lorentz line type at (b) $V_E = 0.1$, (c) $V_E = 0.3$ and (d) $V_E = 0.8$. Attribution of Raman peaks: 3610 cm^{-1} (Free OH); 3440 cm^{-1} (Weak HB); 3248 cm^{-1} (Strong HB); 3327 cm^{-1} (OH stretching of MeOH); 2954 cm^{-1} (Bending overtones); 2845 cm^{-1} (CH_2 stretching).

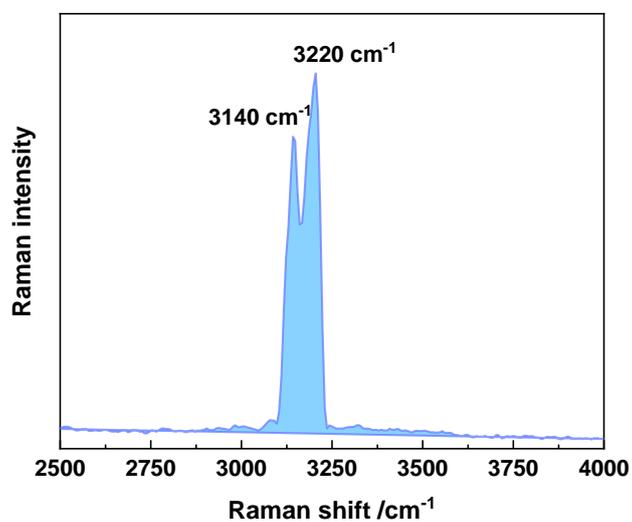


Fig. S5. SRS spectra of ice *Ih*.

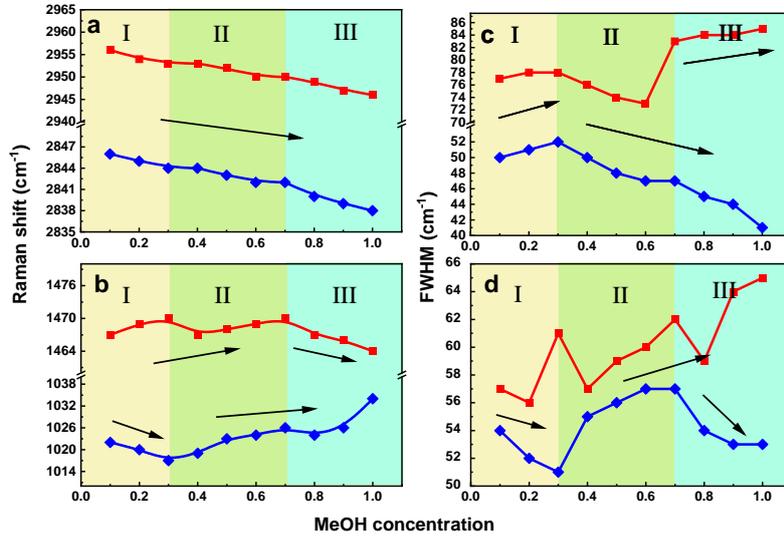


Fig. S6. (a) Raman shifts and (c) FWHM of CH₂ stretching mode (blue) and bending overtones (red) vs V_E in spontaneous Raman spectra; (b) Raman shifts and (d) FWHM of C-O stretching (blue) and C-H asymmetric deformation (red) mode depend on V_E in spontaneous Raman spectra.

We obtained the Raman shifts and FWHM of MeOH as a function of V_E in spontaneous Raman spectra at water-MeOH solutions (Fig. S6). We find that Raman shifts of MeOH have a small transition around 0.3 and 0.7. It is well known that spontaneous Raman shifts can sensitively reflect changes in the association structure of substances [1-4]. Therefore, Fig. S6 indicates that the MeOH-water association structure exhibits a transition at 0.3 and 0.7. Importantly, the change of the association structure leads to a shift in the spontaneous Raman scattering cross section in the solution.

In addition, the intensity of the SRS peak is dependent on its Raman gain coefficient. As is known to all, the Raman gain coefficient is inversely proportional to FWHM of corresponding spontaneous Raman peak. As clearly is shown in Fig. S6(c), the FWHM of the two peaks of CH stretching vibration from spontaneous Raman spectra is

inversely proportional to the SRS peak intensity in the range of 0.3 to 1. This inverse relationship proves the correctness in Fig. 3(d).

References

- [1] Sun, C. Q.; Zhang, X.; Zhou, J.; Huang, Y. L.; Zhou, Y. C.; Zheng, W. T. Density, Elasticity, and Stability Anomalies of Water Molecules with Fewer than Four Neighbors, *J. Phys. Chem. Lett.* **2013**, *4*, 2565-2570.
- [2] Li, F.; Men, Z.; Li, S.; Wang, S.; Li, Z.; Sun, C. Study of Hydrogen Bonding in Ethanol-Water Binary Solutions by Raman Spectroscopy, *Spectrochim. Acta, Part A.* **2018**, *189*, 621.
- [3] Dixit, S.; Poon, W. C. K.; Crain, J. Hydration of Methanol in Aqueous Solutions: a Raman Spectroscopic Study, J. Crain, *J. Phys.: Condens. Matter.* **2000**, *12*, L323.
- [4] Medders, G. R.; Paesani, F. Infrared and Raman Spectroscopy of Liquid Water Through “First-Principles” Many-Body Molecular Dynamics. *J. Chem. Theory Comput.* **2015**, *11*, 1145-1154.