

## Hydrogen-bonding and Vibrational Coupling of Water in a Hydrophobic Hydration Shell as Observed by Raman-MCR and Isotopic Dilution Spectroscopy

*Mohammed Ahmed, Ajay K. Singh and Jahur A. Mondal\**

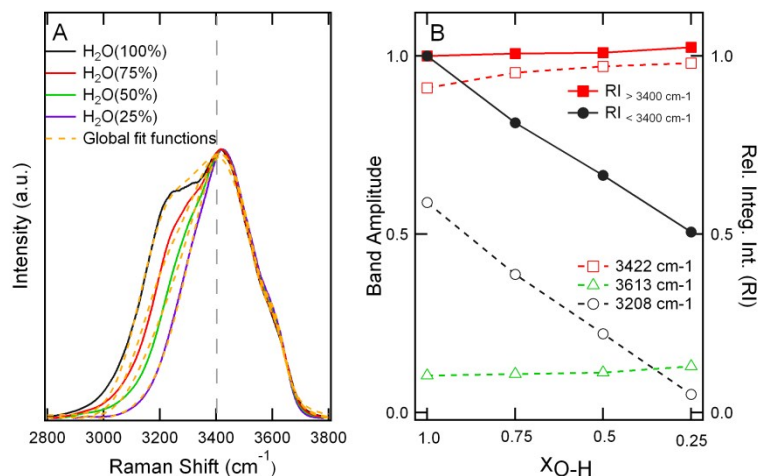
Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India.

Email: [mondal@barc.gov.in](mailto:mondal@barc.gov.in)

### Supplementary Material.

#### Global analysis of the OH stretch band of bulk water with isotopic dilution

Raman spectra of different isotopically diluted water ( $\text{H}_2\text{O}(100\%)$  i.e. neat water;  $\text{H}_2\text{O}(75\%)$  i.e. ( $\text{H}_2\text{O}/\text{D}_2\text{O} = 75/25$ , v/v);  $\text{H}_2\text{O}(50\%)$ , and  $\text{H}_2\text{O}(25\%)$ ) are shown in Figure S1A. It is well known that isotopic dilution reduces the intra- and intermolecular coupling but does not affect the H-bond strength of water.<sup>1,2</sup> Therefore, the intensity normalization of the spectra at the peak ( $3400\text{ cm}^{-1}$ ) provides a clear indication of the effect of intra- and intermolecular coupling on the OH stretch band. As can be seen from Figure S1A, on increasing isotopic dilution, the intensity below the centre frequency ( $3400\text{ cm}^{-1}$ ) decreases whereas, there is no significant change in the region above the centre frequency. Qualitatively, the spectrum of neat water (black curve) shows at least three component bands that are centered around  $\sim 3200$ ,  $3400$  and  $3600\text{ cm}^{-1}$ , respectively. Therefore, a global analysis of the OH stretch bands corresponding to different isotopic dilutions with a three component Gaussian function provides information about the variation of the amplitudes of these component bands with isotopic dilution. The dashed lines in Figure S1A are the global fit-functions (fitting parameters are summarized in Table S1).



**FigureS1.** (A) Global fitting of the normalized Raman spectra of isotopically diluted water with three component Gaussian fitting functions. Dashed lines represent the fitting functions. (B) Plot of the amplitude of the component bands (dashed lines: black (3208  $\text{cm}^{-1}$ ), red (3422  $\text{cm}^{-1}$ ), and green (3613  $\text{cm}^{-1}$ )) vs. the mole fraction of O-H oscillators ( $X_{\text{O-H}}$ ) in water. Variations of relative integrated intensity above 3400  $\text{cm}^{-1}$  (red solid line) and below 3400  $\text{cm}^{-1}$  (black solid line) vs.  $X_{\text{O-H}}$  are shown in the right axis of the same panel.

**Table S1.** Global fitting parameters of the normalized Raman spectra of neat and isotopically diluted water

Water with different isotopic dilution	Amplitudes of component bands		
	Band-1 ( $\nu_c = 3208 \text{ cm}^{-1}$ , $\Gamma = 217.2 \text{ cm}^{-1}$ )	Band-2 ( $\nu_c = 3422 \text{ cm}^{-1}$ , $\Gamma = 271.35 \text{ cm}^{-1}$ )	Band-3 $\nu_c = 3613 \text{ cm}^{-1}$ , $\Gamma = 78.6 \text{ cm}^{-1}$
H <sub>2</sub> O(100%)	0.586	0.91	0.1
H <sub>2</sub> O(75%)	0.387	0.953	0.11
H <sub>2</sub> O(50%)	0.221	0.97	0.11
H <sub>2</sub> O(25%)	0.051	0.98	0.13

Variation of the amplitude of the component bands (centre frequencies in  $\text{cm}^{-1}$ : 3208 (band-1), 3422 (band-2), 3613 (band-3)) with isotopic dilution (represented as the mole fraction of OH oscillator ( $X_{\text{OH}}$ )) is shown in Figure S1B. On decreasing  $X_{\text{OH}}$ , the amplitude of band-1 (3208  $\text{cm}^{-1}$ )

<sup>1</sup>) decreases significantly, whereas those of band-2 (3422 cm<sup>-1</sup>) and band-3 (3613 cm<sup>-1</sup>) do not change appreciably (dashed lines in Figure S1B). The decrease of the amplitude of band-1 results from the intra- and intermolecular vibrational decoupling due to isotopic dilution. Thus, the response of intra- and intermolecularly coupled water is largely confined in the low frequency region of the OH stretch (3200 cm<sup>-1</sup>). The invariance of the amplitudes of band-2 and band-3 is a manifestation that the H-bond strength of water does not change on isotopic dilution. Accordingly, on increasing isotopic dilution, the relative integrated intensity in the red region of

the OH stretch band  $(RI_{<3400} = [\int_{2800}^{3400} I_v dv]_{HOD} / [\int_{2800}^{3400} I_v dv]_{H2O})$  decreases and that in the blue region

$(RI_{>3400} = [\int_{3400}^{3800} I_v dv]_{HOD} / [\int_{3400}^{3800} I_v dv]_{H2O})$  does not change. It is observed that, on isotopic dilution,

$RI_{<3400}$  goes parallel to the amplitude of band-1; and  $RI_{>3400}$  goes parallel to the amplitude of band-2 and band-3 (Figure S1B). Thus, the relative integrated intensity above and below the centre frequency ( $RI_{>3400}$  and  $RI_{<3400}$ ) of the OH stretch band, which can be easily obtained, provides insight into the modification of H-bonding and intra-/intermolecular coupling of water. We have applied this methodology to the spectra of hydration shell water, which has been discussed in the main text.

## References.

1. D. E. Hare and C. M. Sorensen, *J. Chem. Phys.*, 1992, **96**, 13-22.
2. J. Wiafe-Akenten and R. Bansil, *J. Chem. Phys.*, 1983, **78**, 7132-7137.