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Water Liquid Structure as Studied by Raman and Hyper-Raman Spectroscopy

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Abstract

Despite extensive studies over the years, anomalous behavior of water as a liquid still remains a mystery. We challenge this mystery by state-of-the-art Raman and hyper-Raman spectroscopy.

Raman spectroscopy: We have observed 140 Raman spectra of water in the temperature range -23°C ~ 45°C [1]. We analyze this set of Raman spectra by multivariate curve resolution with alternate least-squares (MCR-ALS) [2] and hypothetical addition multivariate analysis with numerical differentiation (HAMAND) [3] to identify three distinct liquid structures of water, Forms A, B and C (Figure 1). From the temperature dependent fractions of Forms A, B and C (Fig. 1(b)), we are able to simulate the temperature dependence of water density. Assuming that the density of Form C is the same as that of ice Ih, the simulation successfully reproduces the temperature dependence with a maximum at the right temperature (Fig. 1(c)). The mystery of density maximum of water has thus been given an unequivocal solution. Form C identified as nanometer-size ice crystallite might well be called “nano-ice” (Fig. (d)).

Hyper-Raman (HR) spectroscopy: HR scattering provides unique vibrational information distinct either from infrared absorption (IR) or Raman scattering. We have applied HR spectroscopy to water to find that HR indeed gives water vibrational spectra quite different from those of IR and Raman [4]. Contrary to IR and Raman, HR scattering exhibits strong intermolecular librational bands in the low wavenumber region with much higher intensities than those of the intra-molecular ones. The analysis of temperature dependent HR spectra of liquid water is ongoing to obtain three HR spectra corresponding to Forms A, B and C.

Keywords: Water, Nano-ice, hyper-Raman

References:

- [1] Okajima, Ando, Hamaguchi, Bull. Chem. Soc. Jpn, 91, 991-997 (2018).
- [2] Ando, Hamaguchi, J. Biomed. Opt.19: 011016(2013).
- [3] Ando, Hamaguchi, J. Spectrosc. Soc. Jpn.64: 280(2015).
- [4] Korepanov, Yu, Hamaguchi, J. Raman. Spectroscopy, 49, 1742-1746 (2018).

Fig. 1: (a) Raman spectra of the three forms of water, Forms A (red line), B (blue line), C (at -23°C , green line), and that of ice at -13°C (black line). (b) Temperature dependent fractions of Forms A (red dot), B (blue dot) and C (green dot). TH indicates the homogeneous nucleation temperature of water. (c) Temperature dependence of estimated water density (open circles) with the observed (black solid line) and the extrapolated density of higher temperature water, Form (A+B). (d) Conceptual illustration of the three forms of water assumed in the present study; Form A, destructured hydrogen-bonded water, Form B, structured hydrogen-bonded water and Form C, nanometer-size ice crystallite “nano-ice”.