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Published in:
Journal of Chemical Physics

Document Version:
Publisher's PDF, also known as Version of record

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Cite as: J. Chem. Phys. 149, 167101 (2018); https://doi.org/10.1063/1.5023579
Submitted: 25 January 2018 . Accepted: 13 June 2018 . Published Online: 29 October 2018


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Comment on “Water-water correlations in electrolyte solutions probed by hyper-Rayleigh scattering” [J. Chem. Phys. 147, 214505 (2017)]

Y. Chen,1 H. I. Okur,1 N. Dupretuis,1 J. Dedic,1 D. M. Wilkins,2 M. Ceriotti,2 and S. Roke1,a)

1Laboratory for Fundamental BioPhotonics (LBP), Institutes of Bio-Engineering (IBI) and Materials Science (IMX) and Lausanne Center for Ultrafast Science (LACUS), Lausanne, Switzerland
2Laboratory of Computational Science and Modeling (COSMO), Institute of Materials (IMX), School of Engineering (STI), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland

(Received 25 January 2018; accepted 13 June 2018; published online 29 October 2018)

https://doi.org/10.1063/1.5023579

In Ref. 1, nanosecond second harmonic scattering (SHS) experiments were performed on KCl solutions of light (H2O) and heavy water (D2O) that do not display a difference between the H2O and D2O solutions. The results were compared to a recent femtosecond Elastic Second Harmonic Scattering (fs-ESHS) study of electrolyte solutions. The fs-ESHS study showed that 21 different electrolytes cause the same trend in the SH response of water: an increase from the level of the SH response from pure water, occurring at μM concentrations, and leveling off at ~1 mM.2 Experiments performed in H2O and D2O resulted in curves that were qualitatively the same, but quantitatively different: the half-saturation concentration is shifted from 55 μM for H2O to 310 μM for D2O. The intensity increase is less pronounced for D2O than for H2O: The saturation intensity for D2O is 1.09 times the intensity of pure D2O, while the saturation intensity for H2O is 1.33 times the intensity of pure H2O. The nanosecond SHS experiments of Refs. 1 and 3 do not display a significant difference between H2O and D2O for KCl solutions and show a half saturation concentration of 45 μM for both solutions. At the same time, the magnitude of the saturation SH intensity was 1.667 for D2O/KCl solutions, which was adjusted to 2.23 in Ref. 3. In Ref. 1, the difference in half saturation concentration between Refs. 1 and 2 was explained by a contamination argument: it was suggested that electrolyte solutions of D2O in the fs-ESHS study2 would have some kind of contamination that would amount to several hundreds of μM in ionic strength. However, electrolyte purity is unlikely to be the source of the difference between Refs. 1 and 2. We used 21 different electrolytes with the highest available purity. In order for the contamination claims to be valid, all of these salts would have to have the same amount of impurity that would have to be different when dissolved in D2O or H2O. Alternatively, the possible impurity arising from the water used is also excluded. The water, both H2O and D2O, which was used as a reference and from which the salt solutions were prepared in Ref. 2, has <1.7 × 10−6 M ionic strength measured before and after the 50 s duration experiments, concentrations that are two orders of magnitude away from the claimed hundreds of μM contamination. The conductivity of the prepared salt solutions matches with the one expected from the amount of weighed-in salt. In addition, the suspected exceeding impurity in D2O than in H2O would shift the curves in a different manner than observed.

The change in saturation intensity and difference between H2O and D2O are explained in Ref. 1 to arise from hyper-Raman peaks that are also recorded in the spectral window of integration (50 nm, ~5 times the bandwidth of our laser pulse). The fact that hyper-Raman scattering occurs in liquid water is true. Figure 1(a) displays a spectrum recorded in the same spectral window as we used for detecting the SH intensity. The reported saturation intensity2 would have been <9(3)% different for H2O (D2O) if a narrower bandpass filter was used, but no changes to the key observations of Ref. 2 derive from it. It will not raise the measured saturation values to those recorded in the commented work and it cannot explain the difference between the saturation intensities for H2O and D2O in our study. For the 100 ns pulse experiments in Refs. 1 and 3, the recorded spectral response also comprises hyper-Raman peaks even for a detection window of 2 nm, which seems narrow, but is in fact >50 times the 1 cm−1 (~0.03 nm) bandwidth of what would be the elastically emitted SH response from the used nanosecond laser pulses. In addition, the results of Table 3 in Ref. 1 suggest a larger difference when comparing different bandwidths for the nanosecond experiments than in our femtosecond experiments. Another difference with our experiments suggested by Table 3 is that when plotting intensity ratios of different polarization combinations, each having a different hyper-Raman response, an error will be made in the intensity ratios if one assumes that the ratio comprises only SH light.

There are numerous other differences in the way the experiments are performed: the use of a home-built vs a well-characterized commercially available laser, the use of multiple post-processing and corrective steps vs the reporting of raw data. In addition, related to Ref. 1 there is insufficient published experimental ns data comparing H2O and D2O. Finally, we believe that the major difference between both experiments is in the laser parameters, most notably the pulse duration. The fact that the femtosecond experiments are elastic second-order scattering experiments while the nanosecond experiments are inelastic higher-order scattering experiments supports this hypothesis.

a)sylvie.roke@epfl.ch
One of the most important metrics of the interaction of a laser pulse and a medium is given by recording the emitted intensity as a function of the incident power. For a second-order process, a plot of SH intensity (I) over the square of the incident laser power (P) should result in a straight horizontal line. Figure 1(b) shows such data for our experiments employing 190 fs pulses in H$_2$O and D$_2$O. The graph has a horizontal section, indicating that the interactions are purely of second-order when one uses a laser power below 85 mW (200 kHz pulses) for H$_2$O or 100 mW for D$_2$O. If energy is indeed transferred from the pulse to the liquid, these inelastic effects will change the spectral shape of the emitted SH light. The inset of Fig. 1(a) shows that indeed above 85 mW, the peak shape becomes distorted. These spectral changes appear on top of the ESHS response, which appears together with weak second-order hyper-Raman bands that are also observed. Thus, both higher-order interactions and inelastic effects are visible from a certain threshold for femtosecond experiments, and one should remain below this threshold in order to measure purely second-order effects. Had we measured at 150 mW, not knowing about the data below 100 mW for D$_2$O and below 150 mW for H$_2$O, the results of our measurements would have been very different.

In the nanosecond study of Ref. 1, 100 ns pulses were used. The I/P$^2$ data are reproduced from Fig. 2 of Ref. 1 in Fig. 1(c). These data do not lie on a horizontal line but decrease with increasing power, indicating a significant contribution of non-second-order processes. Since the measured scattered spectra around the SH frequency for D$_2$O are broadened for 100 ns pulses$^5$ and the peak width changes for added ions,$^4$ it is clear that inelastic scattering processes contribute to the signal. This difference suggests that while the femtosecond experiments can provide snapshots of the instantaneous structure of a liquid, nanosecond experiments probe a more indirect metric that comprises a time averaged response from a liquid interacting with an electromagnetic field with possible structural distortions coming from the higher order and inelastic effects. It could be argued that the frequency of the light is too high for the molecules to follow the changes of the electromagnetic field and therefore the field does not impact the liquid structure. However, the electromagnetic wave is polarized linearly and the field oscillates in the same plane for 100 ns, long enough for the liquid to react to it. Thus, the measured effects of Fig. 1(c) will likely be related to the response time of the liquid. The orientational relaxation time of the hydrogen-bond network of H$_2$O and D$_2$O is different, but on the order of 1-10 ps.$^6$ Figure 1(c) shows I/P$^2$ curves using 5 ps pulses obtained by stretching the 190 fs pulses with all other parameters remaining the same as in Fig. 1(b). The obtained I/P$^2$ curves are no longer straight lines, suggesting that as soon as the pulse duration becomes longer than the orientational relaxation time of the liquid, higher-order processes start to play a role in the detected response.

Thus, the principal difference between our measurements and those in the commented work is the fact that we probe elastic snapshots of the instantaneous liquid, while in the commented work, a more complicated set of processes are involved that need to be disentangled. Given the trend of the data in Fig. 1, it is unlikely that extrapolating the curves in Fig. 1(c) to the limit P $\rightarrow$ 0 correctly addresses this difference.

This work was supported by the Julia Jacobi Foundation and the European Research Council (Grant No. 616305).

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