Response to "Comment on 'Water-water correlations in electrolyte solutions probed by hyper-Rayleigh scattering'" [J. Chem. Phys. 149, 167101 (2018)]

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The preceding Comment[1] addresses the difference between hyper-Rayleigh scattering (HRS) or second harmonic scattering (SHS) observations reported for H_2O and D_2O electrolyte solutions in two recent experiments.[2,3] The Comment[1] proposes that the different experimental results are due to the use of nanosecond laser pulses in Ref. 2 as compared to femtosecond laser pulses in Ref. 3 and that water is modified by higher-order inelastic effects for ns pulses, but not for fs pulses. Deviation from quadratic laser power dependence for the HRS intensity, $I \propto P^2$, is given as evidence for this conclusion.

The laser power dependence data shown in Fig. 1 of Ref. 1 has been re-plotted in Fig. 1. To facilitate comparison, the I/P^2 values for the 190 fs and 5 ps pulses are scaled to match I/P^2 for the 100 ns pulses at $P = 0$. One sees that all of the curves in this graph depart from a horizontal line that represents quadratic power dependence for the HRS signal. This is because propagation of the focused laser beam in the sample is altered by thermal defocusing[4,5] and Kerr lens self-focusing[4,6] effects, which change the diameter of the beam waist and the intensity at the focus. The molecular response producing HRS is still quadratic in light intensity, even though it is not quadratic in beam power due to nonlinear propagation effects for the laser beam.

Thermal defocusing is due to the absorption of laser light by the water sample, heating the sample along the laser beam path and producing a radial density and refractive index gradient that defocuses the laser beam. The strength of thermal defocusing is proportional to the average laser beam power and the exponential optical absorption coefficient of the sample.[5] Self-focusing is due to the cubic nonlinear susceptibility which mediates the fast optical Kerr response and the nonlinear refractive index and is a function of the peak pulse power P_m.[4,6] The minimum beam diameter decreases as peak power increases, with catastrophic self-focusing and generation of an ultrafast white light continuum at a critical threshold peak power P_{cr}.[6] Note that power, not intensity, determines whether self-focusing will occur.[4]

The widely used z-scan method uses far-field observations of nonlinear beam propagation to sensitively measure thermal, orientational, and electronic nonlinear refraction and absorption.[7,8] Z-scans for H_2O and D_2O at 1064 nm show

that thermal lensing is the dominant nonlinearity for low peak power pulses.[9] The effect of thermal lensing on the HRS signal has been determined by numerical beam propagation calculations including the self-consistent solution of the diffusion equation with periodic pulse heat input from the Gaussian beam (but neglecting convection), and the calculated results agree with experimental measurements.[9] Such calculations using the slowly varying envelope approximation are adequate for thermal defocusing, but not for strong self-focusing.[4] The variation of I/P^2 seen in Fig. 1 for HRS with ns pulses is entirely consistent with thermal lensing calculations.

Laser beam parameters for typical HRS measurements in Fig. 1 are summarized in Table I. The pulse peak power increases from 5 kW for 100 ns pulses to 1.6 MW for 190 fs pulses. The critical self-focusing power P_{cr} for water is 7 MW, obtained from measurements at 796 nm in Ref. 6, made using 140 fs pulses focused to 27 μm waist diameter at low power, with P_{cr} scaled to 1028 nm using $P_{cr} \propto \lambda^2$.[4] The measured decrease in beam waist diameter with increasing pulse peak power for $P_m < P_{cr}$ will produce an HRS signal with power dependence $I/P^2 \propto 1/(1 - P_m/P_{cr})^4$ as P_m approaches P_{cr}. The Kerr self-focusing effect is negligible for the 100 ns pulses, small for the 5 ps pulses, and large for the 190 fs pulses. Thermal defocusing in D_2O is weak since the optical absorption in D_2O is small, and it is nearly the same for ns pulses at 1064 nm and ps and fs pulses at 1028 nm since the absorption is about the same at 1064 nm and 1028 nm (Table I).[10] The effect of thermal defocusing can be expressed as a Taylor series $I/P^2 \propto (1 - a_1 P + a_2 P^2 + \cdots)$, so for small enough P one expects a small linear decrease in I/P^2 as P increases. Kerr self-focusing for the ps pulses is stronger than the thermal defocusing in D_2O, so the combined effects give a net slow increase in I/P^2 versus P. Kerr self-focusing is much larger for the fs pulses and overwhelms thermal defocusing in D_2O. Due to the larger absorption coefficient for H_2O as compared to D_2O,[10] thermal defocusing in H_2O is 11 times stronger for the ns pulses at 1064 nm, and 18 times stronger for the ps and fs pulses at 1028 nm. Thermal defocusing is much larger than Kerr self-focusing for the ns and ps pulses in H_2O, and I/P^2 rapidly decreases as P increases. For the fs pulses in H_2O, the Kerr self-focusing still overwhelms the strong thermal defocusing and I/P^2 rapidly increases as P increases, although more slowly than for the fs pulses in D_2O.

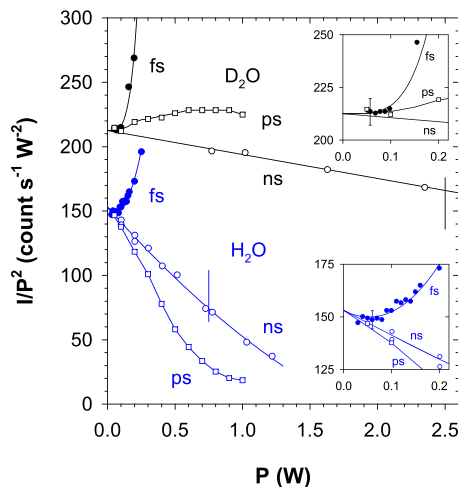a)shelton@physics.unlv.edu

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FIG. 1. The power dependence for the HRS signal intensity measured with 190 fs (filled circles), 5 ps (open squares), and 100 ns (open circles) laser pulses, in H_2O (bottom, blue) and D_2O (top, black), from Ref. 1. The insets show the results for H_2O (bottom) and D_2O (top) on an expanded scale. HRS measurements in Ref. 3 with fs pulses were made at 60 mW (inset point with error bar), and ns pulse measurements in Ref. 2 were made at 0.75 W for H_2O and 2.5 W for D_2O (vertical bars).

The deviations from constant I/P^2 are accounted for by well-understood beam propagation effects that change the laser beam focal diameter and intensity in the sample. Although higher-order effects that can directly contribute to the observed HRS signal begin to appear at the high peak power of the fs pulses, there is no evidence for such higher-order effects at the low peak power of the ns pulses. This interpretation of the data in Fig. 1 is supported by the agreement between the results for $I_{VV}(H_2O)/I_{VV}(D_2O)$ obtained from fs measurements near $P = 0$ (0.8 in Fig. S4 of Ref. 3) and ns measurements extrapolated to $P = 0$ (0.82 ± 0.02 in Table III of Ref. 2). The only discrepancy between the experiments in Refs. 2 and 3 is in measurements for the ion concentration dependent increase in the HRS intensity I_{VH} (or I_{HH}) as compared to I_{HV} (which does not increase). The ion induced signal increase is determined in Ref. 2 (with ns pulses) from the ratio of HRS intensities I_{VH} and I_{HV} measured at the same time, in the same sample, with the same focused laser beam.[11] The ratio I_{HV}/I_{VH} so obtained is immune to the effects of thermal defocusing and uncertain laser beam parameters, since these effects are the same for both signals and cancel out in the ratio. Non-quadratic power dependence for ns pulses due to thermal lensing does not account for the difference between HRS observations reported for H_2O and D_2O electrolyte solutions in Refs. 2 and 3.

TABLE I. Typical laser beam parameters for Fig. 1.

Parameter			
Pulse duration	100 ns	5 ps	190 fs
Average power = P	2 W	1 W	0.06 W
Pulse repetition rate = R	4 kHz	200 kHz	200 kHz
Pulse energy = P/R	0.5 mJ	5 μJ	0.3 μJ
Pulse peak power = P_m	5 kW	1 MW	1.6 MW
P_{cr}[6]	7 MW	7 MW	7 MW
Wavelength	1064 nm	1028 nm	1028 nm
H_2O abs. coefficient[10]	0.13 cm^{-1}	0.25 cm^{-1}	0.25 cm^{-1}
D_2O abs. coefficient[10]	0.012 cm^{-1}	0.014 cm^{-1}	0.014 cm^{-1}

The saturation intensity and half saturation ion concentration measured for H_2O electrolyte solutions in Refs. 2 and 3 are in agreement when the effect of the filter bandwidth is included. The ns HRS measurements for H_2O in Ref. 2 with the filter bandwidth increased from 2 to 46 nm give a lower saturation intensity agreeing with the value measured in Ref. 3 using fs pulses and 50 nm filter. The complementary experiment where the fs HRS filter bandwidth is decreased from 50 nm does not produce a corresponding increase in the saturation intensity because the spectral width of the fs laser pulses limits the resolution of fs HRS measurements to about 6 nm, which is much larger than the 2 nm filter bandwidth used for the ns HRS measurements.

For D_2O electrolyte solutions, the filter bandwidth effect does not account for the large difference between the results in Refs. 2 and 3. The discrepancy for D_2O remains unresolved.

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