A New Type of Two-photon Forward Radiation in Pure Liquids

Hong-tao Bian, Yi Rao, Yan-yan Xu, An-an Liu, Yuan Guo, and Hong-fei Wang

State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, the Chinese Academy of Sciences, Beijing, China, 100080
(Dated: February 1, 2008)

Unexpected spectral features are observed in the two photon spectrum of the pure water in the forward direction when an 80 femtosecond laser pulse is focused at $10^{10}\text{W cm}^{-2}$ or less. Such intensity is much lower than the breakdown or stimulated threshold of the liquid water. The two broad features are about $2700\text{cm}^{-1}$ and $5000\text{cm}^{-1}$ red shifted from the hyper-Rayleigh wavelength, respectively, and they are quadratic with the laser intensity. They do not match the known Raman or hyper-Raman frequencies of water, and they are both centered at a narrow angle in the forward direction. Several other liquids also exhibited similar but molecular specific spectral features.

PACS numbers: 42.62.Fi, 42.65.-k, 61.25.Em, 78.47.+p

Different optical processes can be observed when intense laser pulses with different intensities are propagated in the condensed or gaseous media. Incoherent processes such as Rayleigh and Raman scattering can be observed in all directions, while most of the coherent or stimulated processes, such as stimulated Raman, dielectric breakdown, self focusing and continuum generation, are generally centered in the forward direction.[1, 2]

Here we report the observation of the unexpected spectral features in the two photon spectrum of the pure water in the forward direction when an 80 femtosecond laser pulse is focused into liquid water at the intensity of $10^{10}\text{W cm}^{-2}$ or less. The two observed broad features are about $2700\text{cm}^{-1}$ and $5000\text{cm}^{-1}$ red shifted from the hyper-Rayleigh wavelength, respectively, and they are quadratically dependent on the input laser intensity. To our surprise, they do not match the known Raman or hyper-Raman frequencies of water, and they are both centered at a narrow angle in the forward direction. Several other liquids also exhibited similar but molecular specific spectral features. The difference of the spectral shift between the water and the heavy water might be attributed to the isotope effect. Since the laser intensity here is much lower than the breakdown or stimulated threshold of the liquid water,[3, 4, 5] the mechanism of this new type of two photon forward radiation is yet to be determined.

The schematic of the angular and spectral resolved two-photon scattering measurement in Fig. 1(a) was similar to the setup reported previously.[6] A broadband tunable mode-locked Ti:Sapphire laser (Tsunami 3960C) is pumped by a 10W CW laser (Millennia Xs), producing 80fs pulses at 82 MHz repetition rate. The typical laser power is 500mW at 800nm with a 9nm bandwidth. A 50mm focal lens focuses the laser beam into a D-shaped quartz cell with the diameter of 15mm filled with the sample liquid. The sample cell is fixed at the center position of a rotating goniometer mounted with the detection optics, enables detection of the scattered light in different angular directions. The signal is collected by a condenser lens with $f=50\text{mm}$, then focused into the monochrometer (0.1m, Beijing Optical Instrument Factory WDG10) with a 2nm resolution, and detected with a single photon counting system (PMT: Hamamatsu PMT R585, Preamplifier: Stanford Research System SR240, and photon counter: SRS SR400). With a laser power of 500mW, the power intensity at the beam waist is $1.0 \times 10^{10}\text{W cm}^{-2}$.

For the pure water excited at 800nm, the spectral features in the forward and 90° direction are significantly different as in Fig. 1(b). The signal from the empty cell is essentially zero. This eliminates the possibility that the observed signal is generated from any other optical components in the entire optical path. The hyper-Rayleigh and hyper-Raman peaks in the 90° direction are the same as that in the backward direction reported by Webb et al. and in the 90° direction by Terhue et al.[7, 8] The hyper-Raman peak at 463nm corresponds to a Raman shift of 3400 cm$^{-1}$, which is vibrational band of the hydrogen bond of the bulk water. The weak 660 cm$^{-1}$ and 1600 cm$^{-1}$ hyper-Raman peaks of the bulk water reported by Webb et al. are also weak but discernable in our 90° direction spectra.

These are in sharp contrast to the two broad and strong spectral features at 448nm ($2700\text{cm}^{-1}$ red shifted from the sharp 400nm hyper-Rayleigh band) and 500nm ($5000\text{cm}^{-1}$ red shift) in the forward spectrum. These two peaks correspond to no known Raman or Hyper-Raman band of the liquid water. Very differently, in other forward scattering processes, such as stimulated Raman, dielectric breakdown, laser-induced plasma generation and superbroadening processes,[3, 5, 9] the Stokes Raman band dominated the forward spectra. On the other hand, the laser intensity in our work is only $10^{10}\text{W cm}^{-2}$ or less, much less than the thresholds of these other forward scattering processes.
FIG. 1: (a) Schematic illustration of the forward direction and 90 degree direction hyper-rayleigh scattering. (b) Spectra of the pure water in the forward direction (Top) and in the 90° direction (Bottom) with the fundamental wavelength at 800nm. The laser power is 500mW. The solid line and dot line denote the monochromator with 1mm and 2mm slit. Both the input and output polarization are p polarized (vertical).

Denisov et al. discussed the transverse(TO) and longitudinal(LO) modes of hyper-Raman scattering from the liquid.[10, 11] Basically, both the TO and the LO modes can be observed in the 90° direction, while in the forward direction only the LO modes appear. Therefore, the 448nm and 500nm bands in the forward direction observed here can not be attributed to the process similar to the ordinary Raman or hyper-Raman processes. In addition, they do not fit with the known Raman and hyper-Raman frequencies. Therefore, we surmise that these two new bands have to be a new type of forward radiation from the two-photon excitation.

The polarization of the 400nm, 448nm and 500nm peaks are all parallel to the input polarization of the fundamental. Using the 1mm slit instead of the 2mm slit for both the entrance and the exit of the monochromator, the width of the 400nm hyper-Rayleigh narrows from 16nm to 9nm, which is the band width of the 800nm femtosecond pulse. However, the widths of the 448nm and 500nm bands are broad and remain unchanged. This indicates that the broadening mechanism for these two new and broad spectral features is quite different from that of the hyper-rayleigh processes,[16] even though they follow the same polarization dependence. If the widths of these two peaks are due to any fast molecular dynamic interactions, the time scale of these interactions must be in the range of 30 to 15 femtosecond, respectively.

The angle resolved measurements of the 400nm, 448nm and 500nm peaks in Fig. 1 are shown in Fig. 2. The angular dependence of the 400nm peak is again distinctively different from the 448nm and 500nm peaks. As expected for the hyper-Rayleigh process, the angular dependence here for the 400nm peaks follows the \( \cos^2\theta \) function centering at the forward direction. Therefore, no additional information can be gained by looking in directions other than the classic 90° angle for the hyper-rayleigh process.[12, 13]

On the other hand, the angular dependence of the 448nm and 500nm peaks is distinctively very narrow and centered at the forward direction. The two curves may have small difference, but they certainly imply a very different mechanism from that of the hyper-Rayleigh or hyper-Raman processes, where no such strong angular anisotropy has ever been observed, except for processes such as the stimulated Raman or superbroadening.

However, the power dependence measurements eliminated the possibility of any above threshold processes, such as the stimulated or superbroadening processes. The power dependence of the forward 400nm, 448nm
The incident laser power was varied from 50mW to 500mW, i.e. from about $10^9 W cm^{-2}$ to $10^{10} W cm^{-2}$. The spectral features in Fig. 1 and the angular dependence in Fig. 2 remain unchanged with the laser intensity. The power index for the three peaks are essentially the same as $1.9 \pm 0.1$, indicating a clear two-photon process instead of any above-threshold behavior. Furthermore, no laser-induced breakdown or plasma generation process was observed.

These two new peaks in the forward direction are not from some unexpected two-photon fluorescence process of the liquid or any possible impurity, either. To demonstrate this, the excitation fundamental wavelength was changed every 20nm from 740nm to 880nm, and the positions of these two new peaks shift with the excitation wavelength just like the ordinary hyper-Rayleigh and hyper-Raman processes. Data for 800nm and 840nm are shown in the top and middle panels in Fig. 4. However, the relative intensity of the new peaks to that of the hyper-Rayleigh peak in the forward direction does change with the excitation wavelength, as observed for all the liquids measured below.

Other common liquids also have the similar results as those of the pure water. The forward spectra of the pure methanol (Sigma-Aldrich, HPLC grade, 99.9%), heavy water (Acros, NMR grade, 99.95%) and acetonitrile (Scharlau, HPLC grade, 99.99%) are shown in the bottom panel of Fig. 4. Here the spectral purity of these liquids are thoroughly examined against samples from other sources. Similar to water, all the peaks here, except for the hyper-Rayleigh peak at 400nm, do not match any known Raman or hyper-Raman frequencies of each molecule. In all these cases, the intensities of these new spectral features are in the same order of the forward hyper-Rayleigh scattering intensity.

It is intriguing that these frequencies are molecular or molecular group specific. The second peak of liquid methanol is at the same position of the pure water (2700 cm$^{-1}$), while the second peak of the heavy water has a smaller shift (2100 cm$^{-1}$) from its hyper-Rayleigh peak. The ratio between these two frequency shifts is 1.3, in the ballpark of the isotope effect factor for the O-H vibrational frequencies. However, because both 2700 cm$^{-1}$ and 2100 cm$^{-1}$ correspond to no known vibrational frequencies of water and heavy water, such value only implies isotope effect, but may well be just accidental. To test this idea, experiments on pure ethanol and ethylene glycol were performed. The methanol, ethanol and ethylene glycol all have the same two peak positions red shifted from the hyper-Rayleigh peak at 400nm, even though their relative intensities vary. This seems to indicate that the molecules with O-H groups have similar peak positions. On the other hand, spectral features for different molecular groups must be different. To further support this idea, the new spectral feature found for the liquid acetonitrile in the same figure is different from all the above, indicating molecular or molecular group specificity of these spectral features. Other common liquids,
such as $CS_2$ and $CCl_4$, were also tested and similar behaviors were observed. However, the optical purities of the purest samples from the suppliers have not been as satisfactory as the ones reported here, and further studies are warranted.

Since there is no such forward spectral features observed in the one photon Raman studies,[5, 9], what we observed is likely a unique process involves at least two photons. Since the frequencies observed do not match known Raman or hyper-Raman frequencies, it may come from some collective or correlated properties of the liquid. Recently, based on some abnormal depolarization ratios in the hyper-Rayleigh measurement of the pure liquids in the 90° direction, Shelton et al. discussed the possibility of the long range orientational correlation in pure liquids.[17, 18, 19, 20] There is no evidence so far to make the connection between the abnormal hyper-Rayleigh measurement and the new spectral features observed here. But certainly they all point to some new understandings of the molecular and optical physics of the molecular liquids.

In conclusion, new spectral features from two-photon excitation were observed in the forward direction from liquid water and other pure liquids. The intensities of these new spectral features are in the same order of the forward hyper-Rayleigh scattering intensity. The laser intensity used in these studies is $10^{10}$ W cm$^{-2}$ or less, i.e. well below the threshold for laser-induced breakdown and stimulated processes in these pure liquids. The strong forward angular dependence indicates that these features are not from the simple incoherent linear or non-linear scattering processes. Experimental results showed that these new spectral features are two-photon radiations, but clearly not from the hyper Raman process, nor the two-photon fluorescence process, and nor the above threshold processes such as the stimulated processes and the superbroadening generation. These new spectral features are also unique for molecules with different molecular structures, and they do not match any known Raman and hyper-Raman frequencies. To our knowledge, there is no known mechanism in this range of laser intensity can explain these experimental observations. Therefore, the origin and the mechanism of such process warrant further experimental and theoretical investigations.

HFW is thankful for the support from the National Natural Science Foundation of China (NSFC No.20425309, No.20533070). YG is thankful for the support from the National Natural Science Foundation of China (NSFC No.20425309).