Non-Markovian Behavior of Material Response in Liquids observed by Linear and Nonlinear Optical Spectroscopy

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Recently we have reported the detailed investigations on the material response for pure liquids using low-frequency light scattering (LS) and femtosecond optically heterodyne-detected optical Kerr effect (OHD-OKE) spectroscopy [1-3]. It is found that the LS spectrum of liquid generally shows a strong quasi-elastic component due to the cooperative orientational fluctuation of liquid molecules, called relaxational mode or central mode, the width of which changes drastically with temperature. Its temperature dependence is usually expressed by an Arrhenius type, or in glass-forming liquid, it is known to follow Vogel-Fulcher-Tammann law.

The relaxational mode in liquid is believed to show a Lorentzian shape, which seemingly contradicts the relation known for the Stokes (S) and anti-Stokes (AS) LS intensity ratio derived from the time-reversal symmetry:

$$I_S / I_{AS} = \exp[-\Delta\omega / kT], \qquad (1)$$

where $\Delta\omega$, k and T are the material excitation energy, Boltzmann constant, and absolute temperature, respectively. We have measured the LS spectrum of liquid carbon disulfide in the vicinity of the relaxational mode and have found that the spectrum is really symmetric with respect to the incident photon energy and the relation (1) actually breaks down up to the half width of the peak. This result is quite significant, because the fluctuation-dissipation theorem in quantum version does not hold in this system.

In OHD-OKE experiment, the material response is usually expressed in terms of a fast inertia response, which then tends to show a slow exponential response at a later time. Considering that a Lorentzian spectral shape just corresponds to an exponential response, we focus ourselves on the onset of the exponential response, which just corresponds to the symmetric spectral range in the LS experiment.

It is well known that the exponential response is resulted from the Markovian approximation of the system and its onset is explained in terms that the time scale of the material response is comparable with that of the heat bath. In this sense, from the LS and OHD-OKE experiments, it is concluded that the fluctuation related to the relaxational mode bears non Markovian nature in liquid carbon sulfide, which tends to be Markovian with decreasing temperature, implying the increase of the system size with attaining macroscopic character.

In the present study, we will further advance our study to search for the similar Markovian-non Markovian crossover in liquids. Particularly, we will focus ourselves on the α-β bifurcation known in glass forming liquid under low temperatures.

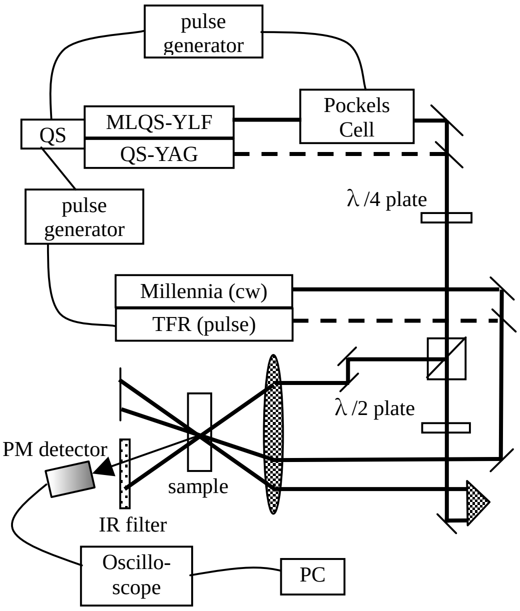

Fig.1 Experimental setup for four-wave mixing spectroscopy to measure extremely slow dynamics in liquids for the time range from μs to s

For this purpose, we have constructed four-wave mixing spectroscopy using a picosecond CW mode-locked, Q-switched YLF laser with a pulse picker (Pockels cell) for the measurement from sub μs to ms, while a pulsed Q-switched YAG laser for the measurement from ms to s as an excitation source. Detailed experimental setup is shown in Fig. 1. A CW probe beam is normally employed to monitor the material response, while the slow dynamics is measured by means of an electronically synchronized Q-switched YLF laser (TFR) as a probe. The performance and experimental data for the precise determination of the material response function under low temperatures will be presented.

References

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