Abstract

Recent development of frequency-domain four-wave-mixing (FD-4WM) spectroscopy has opened a new research field in material science, with its capability for the direct measurement of material response function. Further, this method has been demonstrated for the diagnostic use of a femtosecond pump pulse. Thus the FD-4WM technique has enormous potential capabilities as a spectroscopic tool. In the present thesis, we have further improved the FD-4WM method and have extended it to the following two different aims by utilizing specialized pump pulses.

With the usual FD-4WM method, the excitable frequency range is restricted within a range determined by the spectral width of the pump pulses, e.g. $\sim$ 150 cm^{-1} for $\sim$ 100 fs pump pulse. First, in order to overcome this difficulty, we have applied a white light pulse for one of the pump pulses, and have made it possible to obtain a wide spectral range simultaneously without scanning the wavelength of the pump pulse. In the present study, the white pulse is generated by supercontinuum generation technique, and the Raman spectra in a wide frequency range, as wide as $\sim$ 1000 cm^{-1}, can be measured in a short time. Further, we successfully demonstrate the usefulness of this method for suppressing disturbing fluorescence background in Raman spectra. In fact, because of the directivity of the signal beam, we confirm that the fluorescence background is sufficiently suppressed simply by placing a spatial filter on its way. In addition, since the wavelengths of the pump and probe beams can be chosen to be essentially arbitrary, it is possible to choose the wavelengths of the pump beams to be far from the resonant wavelength of fluorescent material, while the probe wavelength at a sensitive region of the detector. Actually, under our experimental condition, we have proved that a wide-range Raman spectrum of the solvent is clearly observed within a short time under the presence of the high concentration of rhodamine dye up to 10^{-5} mol/l.

Secondly, we have applied linearly-chirped two pump pulses as a novel method for the selective excitation of phonons. We set the amounts of the dispersions of both pulses to be the same with each other. The center frequency of the pump pulse changes linearly with time. Therefore, the difference of the center frequency between the two pulses depends basically on the separation between these pulses. Furthermore, since the frequency width of a linearly-chirped pulse at a certain moment is determined by the amount of the dispersion, the spectral broadening is limited by the frequency width at a moment. When the linearly-chirped pump pulses are employed as selective phonon excitation, the center frequency and spectral width of the excited phonon can be selected arbitrarily only by changing the delay time and dispersion of the pump pulses. In the present work, we have confirmed, using the FD-4WM technique with a grating pair for generating the dispersion, that the narrow-band excitation of phonon is actually accomplished for the low-frequency Raman region of liquid CS_2. We have found that the phonons with a width as narrow as 3 cm^{-1} are excited using an originally broad pulse of 100 cm^{-1}, which clearly demonstrates the capability of this method.