Direct Comparison between Ultrafast Optical Kerr Effect and High-Resolution Light Scattering Spectroscopy

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The dynamical response of matter measured by femtosecond optical Kerr effect spectroscopy is directly compared with the high-resolution light scattering spectrum obtained by a tandem Fabry-Pérot interferometer. Using simple liquids as samples, we have for the first time confirmed experimentally that the material responses obtained by these time- and frequency-domain measurements completely agree with each other in a frequency region extending over 3 orders of magnitudes.

The recent development of ultrafast laser techniques has opened a new research field for numerous kinds of conventional linear and nonlinear optical spectroscopy, and various transient phenomena have been directly observed by these spectroscopic techniques. Optical Kerr effect (OKE) spectroscopy is one such measurement, in which an ultrashort pump pulse creates time-dependent optical anisotropy which is monitored by a probe pulse through two crossed polarizers. In the past ten years, various OKE measurements using femtosecond light pulses have been performed for a variety of materials in order to investigate the ultrafast relaxational phenomena in these materials [1–8].

Although the OKE response is described in terms of the third-order dielectric susceptibility tensor of matter, it is well known that the nuclear contribution to the OKE process reduces to the product of the first-order dielectric tensors, and hence the Fourier transform of its transient response is essentially equivalent to the ordinary light scattering measurement under stationary excitation. However, to our knowledge, no direct comparison between these two experiments has been reported yet. This may be partly because a high-resolution study is needed for both the time- and frequency-domain measurements, in addition to the necessity of highly reliable data for further analysis.

The significance of verifying their equivalence experimentally has been expanding, because the time-domain measurement often offers important information in place of the ordinary light scattering experiment. One such example is the characterization of disordered materials where continuously or hierarchically distributed fluctuations play an essential role in their dynamics [9]. Since the time-domain method is essentially free from the limit of resolution in the frequency range, material fluctuation which has a very narrow frequency spectrum can be easily measured. Consistent results obtained by both the time- and frequency-domain measurements can offer reliable information on the fluctuations in these materials in an extremely wide frequency

range. Another example is to discriminate between the relaxational and overdamped oscillation modes in phase transition studies [10], where line-shape analysis of the light scattering spectrum often encounters difficulties.

To shed light on such problems, we have performed a detailed investigation using both the ultrafast OKE and high-resolution light scattering spectroscopy, and have compared the data by using the time-domain Fourier transform. Complete agreement has been obtained for various samples in the frequency range from 3 GHz to 6 THz with no adjustable parameter. In the present paper, we will describe the details of our experiment and the data analysis.

The principle of the experiments is as follows. The impulsive response of matter and its frequency spectrum are generally connected through the fluctuation-dissipation theorem. In optical spectroscopy, the nonlinear dielectric response due to the OKE obtained under impulsive excitation and the light scattering spectrum are connected through this theorem. The third-order nonlinear polarization of matter under the Born-Oppenheimer approximation was given by Hellwarth [11] and is decribed as

$$P_i(t) = \sigma_{ijkl} E_j(t) E_k(t) E_l(t) + \Phi_{ij}(t) E_j(t)$$
$$\equiv Q_{ij}(t) E_j(t),$$

with

$$\Phi_{ij}(t) \equiv \int_{-\infty}^{t} dt' R_{ijkl}(t - t') E_k(t') E_l(t'),$$

where the first and second terms on the right side express the electronic and nuclear contributions to the nonlinear polarization. $R_{ijkl}(t)$ is the nuclear contribution of the material response function with

$$R_{ijkl}(t) = \frac{1}{2} i\hbar^{-1} V \langle [\chi_{ij}(t), \chi_{kl}(0)] \rangle \theta(t).$$

Here, $\chi_{ij}(t)$ is the ij component of the time-dependent linear dielectric susceptibility tensor, $\theta(t)$ a step function, and V the volume. $[A, B] = AB - BA$ for operators A and B, and $\langle \cdots \rangle$ means the average over the thermal

equilibrium states. A simple calculation shows that the light scattering spectrum $S_{\mathrm{LS}}(\Delta\omega)$ corresponding to this material response in the photon-counting detection mode is

$$S_{\mathrm{LS}}(\Delta\omega) = \omega_2^3 C_{ijkl} \int_{-\infty}^{\infty} dt \, e^{i\Delta\omega t} \langle \chi_{ij}(t) \, \chi_{kl}(0) \rangle$$

$$= \frac{4\hbar}{V} \, \omega_2^3 [n_T(\Delta\omega) + 1] \, C_{ijkl} \, \mathrm{Im}\tilde{R}_{ijkl}(\Delta\omega),$$

where the angular frequency difference between the incident light (ω_1) and the emitted photon (ω_2) is denoted by $\Delta\omega$, and C_{ijkl} is a constant related to the polarization directions of the incident light and emitted photon, the scattering geometry, the detection efficiency, and the power of the incident light. The factor $n_T(\Delta\omega) + 1$ is the so-called Bose factor with the phonon occupation number $n_T(\Delta\omega)$ for the angular frequency of the phonon $\Delta\omega$ at temperature T. Here, a tilde over a function means it is to be Fourier transformed. Thus the nuclear contribution to the third-order nonlinear dielectric response function obtained under impulsive excitation and the light scattering spectrum are connected with each other through the Fourier-transform relation.

Optical heterodyne detection (OHD) of the OKE signal is particularly suitable to confirm the above relation experimentally, since the signal obtained is linear in the third-order dielectric susceptibility. The analysis of OHD-OKE has been already reported in detail [6,7]; namely, the signal intensity of the OHD-OKE measurement is expressed as

$$S_{\mathrm{OKE}}(\tau) = C_{\mathrm{OKE}} \int_{-\infty}^{\infty} dt \, E_{\mathrm{LO},i}^*(t - \tau) E_{p,j}(t - \tau) Q_{ij}(t)$$

$$= C_{\mathrm{OKE}} \int_{-\infty}^{\infty} dt \{ \sigma_{ijkl} \delta(t)$$

$$+ R_{ijkl}(t) \} G_{ijkl}^{(2)}(t - \tau),$$

where $G_{ijkl}^{(2)}(t)$ is the intensity autocorrelation function of the input laser pulses, C_{OKE} is a constant, and $E_{p,j}(t)$ and $E_{\mathrm{LO},i}(t)$ denote the jth and ith components of the electric fields of the probe beam and the background electric field introduced for OHD, respectively. Since the OHD-OKE signal is expressed by the convolution of the intensity autocorrelation function of the input laser with the material response function, the Fourier transform of this relation immediately gives the frequency response function. Since the electronic OKE contributes only to the real part, the imaginary part of the Fourier transform solely gives the nuclear response function according to the relation

$$\mathrm{Im}\tilde{S}_{\mathrm{OKE}}(\Delta\omega) = C_{\mathrm{OKE}} \, \mathrm{Im}\tilde{R}_{ijkl}(\Delta\omega) \, \mathrm{Re}\tilde{G}_{ijkl}^{(2)}(\Delta\omega).$$

In an ordinary OKE measurement in liquids, the components of the third-order dielectric tensor which contribute to the measurement are only $\chi_{1212} + \chi_{1221}$ and hence are connected with the depolarized light scattering which is related to χ_{12}. Therefore, under the appropriate selection of the polarization conditions, the imaginary part of the Fourier transform of the OHD-OKE signal divided by the Fourier transform of the intensity autocorrelation function is directly comparable to the frequency-domain light scattering spectrum divided by the Bose factor $n_T(\Delta\omega) + 1$ in addition to the frequency factor ω_2^3.

The OKE measurement was performed using a mode-locked Ti:sapphire laser as an excitation source. The typical power and the duration of the mode-locked pulse with a repetition rate of 80 MHz were 500 mW and 80 fs, respectively. A part of the incident light beam from the Ti:sapphire laser was split by a thin glass plate and used as a probe beam, while the remaining light was used as a pump beam. Both the pump and probe beams were led into the optical delays and then focused into a sample cell. The probe beam was passed through a prism polarizer (extinction ratio of 10^{-6}), the polarization direction of which was directed at $45°$ to that of the input laser beam. A polarization analyzer was placed behind the sample at the crossed polarization direction to the input polarizer. A $\lambda/4$ plate was inserted between the input polarizer and the focusing lens, and was rotated so that its optic axis deviates slightly ($\sim 1°$) from the polarization direction of the input polarizer. This ensures the optical heterodyne detection in the OKE measurement; i.e., a part of the probe beam is passed through the polarization analyzer (out-of-phase local oscillator) and is superimposed on the birefringent signal which is induced by the pump pulse.

OHD is superior for the present study because a high signal-to-noise ratio is obtainable and also because the signal intensity is linear in the material response function as described above. The signal was detected by an avalanche photodiode and was amplified by a lock-in amplifier. To evaluate the finite width of the input laser pulse, the intensity autocorrelation function was measured by placing a nonlinear crystal (KH_2PO_4) at the sample position. In order to obtain highly reliable data, a chopper is inserted in both the pump and probe beams with different chopping frequencies, and the lock-in amplifier is operated at their sum frequency. This technique greatly improves the signal-to-noise ratio by reducing the effect of unwanted scattering of the pump or probe beam in the sample. A typical signal-to-noise ratio for OKE measurements in CS_2 is 10^4.

The frequency-domain measurement was performed by means of a double monochromator for a wide frequency range and a Sandercock-type tandem Fabry-Pérot interferometer for a high-resolution study [12]. The typical free spectral range employed for the interferometer was 100 GHz with a scanning range of ± 300 GHz, and its finesse was more than 100. The light scattering was measured under the depolarized condition, i.e., the polarization of the detected light scattering was perpendicular to that of

the exciting laser. This enabled us not only to compare directly the spectrum with the OKE data, but also to remove the unwanted stray light due to the exciting laser. Samples chosen in the present study were simple liquids such as CS_2, benzene, toluene, and nitrobenzene. These liquid samples were filtered or centrifuged to remove dust in the sample, and were then placed into a 1-mm-thick sample cell for the OKE and 1-cm cuvette for the light scattering measurement. The light scattering was measured in 90° scattering configuration.

First, we show typical examples of the time- and frequency-domain measurements on nitrobenzene in Figs. 1(a) and 1(b). This sample is particularly interesting for our purpose because its transient response extends over a wide time range [Fig. 1(a)]. The inset shows the fast transient response. The dashed line is the intensity autocorrelation function of the laser pulse, and the solid line indicates the OKE response which consists of an electronic Kerr component showing a peak at the time origin, a fast decaying component with a time constant

around ~300 fs, and a much more slowly decaying component with that of ~30 ps [5].

The frequency-domain measurements obtained with the double monochromator and the Sandercock-type tandem Fabry-Pérot interferometer (inset) are shown in Fig. 1(b). The light scattering spectrum consists of a very strong peak around the center and a weak shoulder at both sides. The former is called a central mode or mountain mode and comes from the orientational fluctuation due to the cooperative motion of liquid molecules, while the shoulders are called low-frequency phonon modes and come from the librational motion of the individual molecules around their mean configuration. Roughly speaking, the very slowly decaying component in the time response corresponds to the central peak, while the fast decaying component corresponds to the low-frequency phonon modes.

In order to compare these data, we first carried out the Fourier transformation of the OKE data which were measured up to 300 ps after excitation. Then, its imaginary part was divided by the Fourier transform of the intensity autocorrelation function of the incident laser pulse. The calculated data are shown as closed circles in Fig. 2. The very sharp peak around the origin is due to the central mode, while the tail extending to 200 cm^{-1} is due to the low-frequency phonon modes. The small hump around 180 cm^{-1} is due to the intramolecular vibrational mode [13].

The light scattering spectrum divided by the frequency and Bose factors is also shown in Fig. 2. The dashed line is obtained with the double monochromator. It agrees with the time-domain data over the whole region of the measurement except for the region of very small wave number. On the other hand, the solid line is obtained with the high-resolution Sandercock-type interferometer
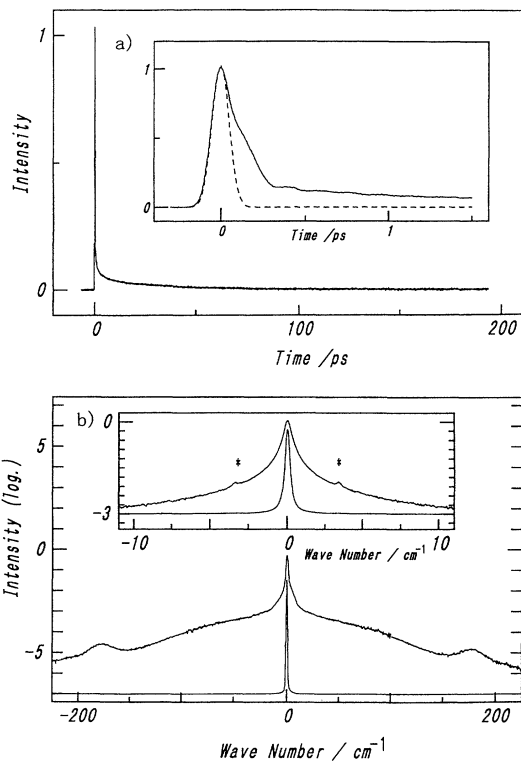

FIG. 1. (a) Femtosecond OKE spectroscopy on liquid nitrobenzene. The inset gives the fast transient response (solid line) with the intensity autocorrelation function of the laser pulse (dashed line). (b) Linear and logarithmic plots of high-resolution light scattering spectrum measured by a double monochromator. The inset gives those obtained by a Sandercock-type tandem Fabry-Pérot interferometer. * indicates the ghost of the interferometer.
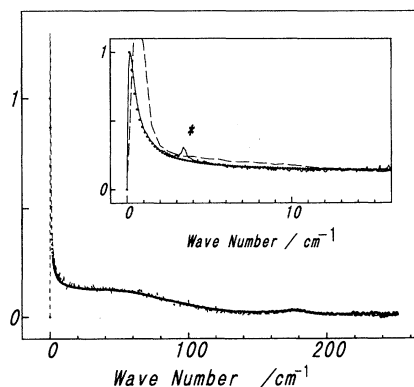

FIG. 2. Frequency response function of liquid nitrobenzene obtained by ultrafast OKE (closed circles) and high-resolution light scattering spectrum obtained by a double monochromator (dashed line) and a Sandercock-type tandem Fabry-Pérot interferometer (solid line). * indicates the ghost of the interferometer.
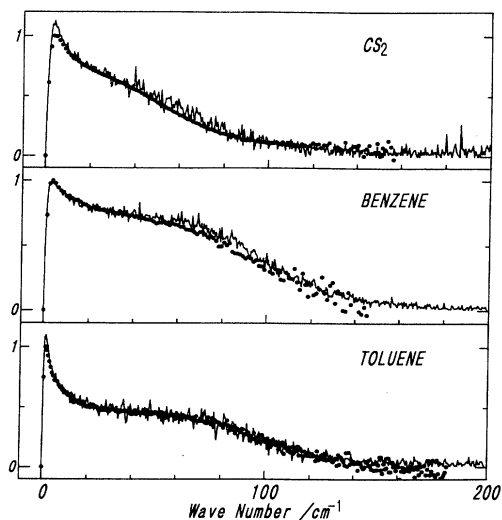
FIG. 3.   Frequency response function of (a) CS_2, (b) benzene, and (c) toluene in liquid phase obtained by ultrafast OKE (closed circles) and light scattering spectrum measured by a double monochromator (solid lines).

and it agrees even near the origin. Using these two monochromators, we can verify the time- and frequency-domain measurements are in very good agreement with each other over 3 orders of magnitude in the frequency or time range. In Fig. 3, we show the results on three different liquids. The closed circles and solid lines are the data obtained by the time- and frequency-domain measurements, respectively. Good agreement is also obtained for these samples, which further confirms the validity of our measurement.

Although the accuracy of the present measurements seems almost self-evident from these figures, it is found that the agreement is excellent (within the error of $\sim2\%$) below 100 cm^{-1}, while it is fair (within that of $\sim30\%$) above 150 cm^{-1}. In the high-frequency region, the finite duration of the laser pulse causes a statistical error in the time-domain measurement. However, much more important is that the measurements of the autocorrelation and OKE should be performed under conditions as identical as possible; namely, even a small difference between the time origins for the two measurements and/ or between the time profiles of the laser pulse is vital when comparing directly the Fourier-transformed data with the light scattering spectrum. It has been found that such differences are often related to the mechanical stability of the optical system including the laser. In the low frequency region, on the other hand, the deviation comes mainly from the misalignment of the Fabry-

Pérot interferometer and the optical delay. Therefore, we repeated the measurements many times and paid special attention to the alignment and stability of the optical system even during the measurements.

In conclusion, the ultrafast transient response to a femtosecond light pulse and the high-resolution light scattering spectrum have been shown for the first time to be equivalent from the experimental standpoint. This means that the time- and frequency-domain measurements become complementary and offer *consistent* information on the material fluctuations. This fact greatly extends the frequency or time range measurable by the optical method. Particularly, the application of the time-domain method greatly extends the time range toward the slow region and can actually offer very important information on the slow dynamics in disordered materials. Furthermore, owing to the lack of a Bose factor, the femtosecond OKE is also suited for the accurate measurement of the low-frequency phonon modes [7]. These characteristics are ideal for the investigation of the frequency distribution of the fluctuation or phonon structure in a wide variety of materials. Studies along these lines by means of both time- and frequency-domain measurements are now in progress.

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