Interferometric observation of femtosecond free induction decay

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Femtosecond free induction decay of cobalt–phthalocyanine in pyridine and of octaethyl porphine in pyridine was observed by use of a white-light interferometer with a resolution time of 6 fs. Also, frequency-domain complex optical constants of the samples were obtained by Fourier-transform analysis of the phase-sensitive interferograms.

It has been generally believed that ultrashort optical pulses are necessary for the observation of optical coherent transient phenomena with high time resolution. Much effort has been devoted to the generation of ultrashort laser pulses, and light pulses as short as 6 fs are now available.[1] The generation of such ultrashort pulses at arbitrary wavelength regions, however, is still not an easy task. To avoid the difficulty, an alternative method that uses incoherent light was developed for nonlinear coherent spectroscopy, in which the time resolution is determined by the correlation time of the incoherent light. For example, the accumulated photon-echo measurements were carried out with incoherent light from laser sources[2-4] or from a nonlaser source.[5]

On the other hand, to our knowledge, no study has been reported on the observation of linear coherent transient phenomena by use of incoherent light, although it was used for other applications such as the measurement of dispersion of optical elements for femtosecond pulses.[6,7] In this Letter we report the observation of femtosecond optical free induction decay[8,9] (FID), using a Michelson interferometer a white-light source. As in nonlinear spectroscopy, the time resolution is determined by the correlation time of the incoherent light, which is equal to the inverse of the spectral width of the incoherent light. In this experiment we can easily obtain high time resolution simply by using broad spectral white light, that is, temporally incoherent light. Moreover, the interferometric technique yields not only the amplitude but also the phase of the FID signal. Therefore by Fourier transforming the FID signal we can obtain the complex optical constants of the samples without relying on the Kramers–Kronig analysis.

The experimental system[10] based on a Michelson interferometer is shown in Fig. 1. The white-light source was a halogen lamp whose spectrum extends from 450 to 800 nm. The path length of one arm of the interferometer was modulated at 20 kHz by a piezoelectric actuator. The amplitude of the path-length modulation was ~250 nm. The path length of the other arm could be scanned by a translational stage. The signal at the frequency of the path-length modulation was obtained by a lock-in amplifier through a change in the path length of one

arm. An interferogram produced by a beam of light at 632.8 nm from a He–Ne laser was simultaneously monitored for calibration of the path length.

We measured two kinds of interferogram with this system. One was the autocorrelation $C_A(\tau)$ of the white light, and the other was the cross correlation $C_C(\tau)$ between the light transmitted through the sample solution and the light transmitted through only the solvent. In the measurement of the autocorrelation the same types of glass cell containing only the solvent were inserted into both arms of the interferometer. The samples that we measured were pyridine solutions of cobalt–phthalocyanine (Co-Pc) and octaethyl porphine (OEP). The solvent is transparent in the visible region. We obtained the cross correlation by inserting a cell containing a sample solution into one arm and one containing only the solvent into the other. Thus the change in the optical path length that was due to the glass cell and the solvent was compensated for.

Because we measured the signal by using path-length modulation our interferograms are not the autocorrelation or the cross correlation in a strict sense. Both the autocorrelation and cross-correlation functions obtained by path-length modulation measurements are modified from the true correlation functions in the same way as described by the following relation:

$$C'(\omega) = 2iJ_1\left(\frac{A\omega}{c}\right)C(\omega). \qquad (1)$$

Here $C(\omega)$ and $C'(\omega)$ are the Fourier transform of the true interferogram and that of the modulated interferogram, respectively, for either the autocorrelation or the cross correlation. $J_1(A\omega/c)$ is the first-order Bessel function, in which A is the path-length modulation amplitude and c is the velocity of light in vacuum. Since $J_1(z)$ is proportional to z in the lowest order of z, it can easily be seen that the obtained signals correspond to the time derivative of the true correlation when the modulation amplitude is small compared with the wavelength of the light. However, even in the case of large path-length modulation, the complex transmission coefficients obtained by Fourier-transform analysis of the interferograms are not
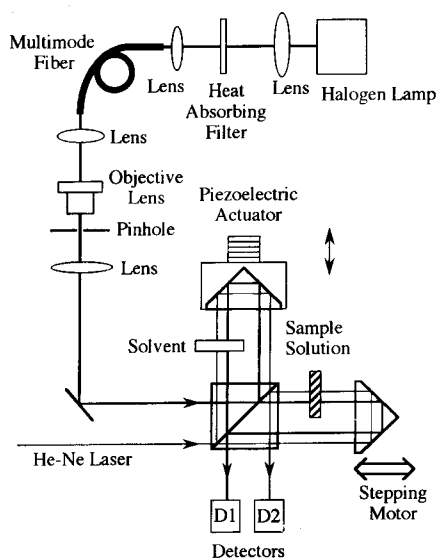
Fig. 1. Schematic of the experiment for the interferometric measurement of the FID of the sample solution.
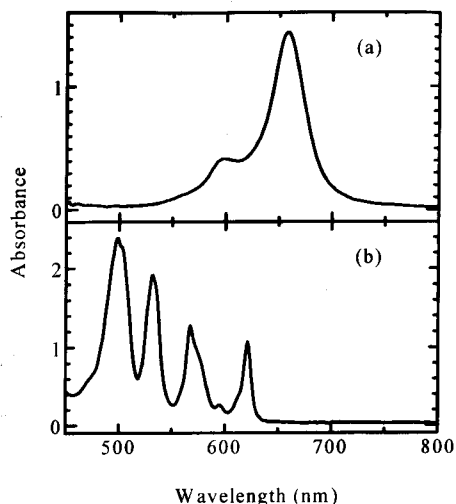

Wavelength (nm)

Fig. 2. Absorption spectra of (a) Co-Pc and (b) OEP in pyridine obtained by use of a monochromator. The concentrations of the solution were 1.0×10^{-4} and 9.4×10^{-4} mol/L for (a) and (b), respectively.

affected by this fact. In this sense we can regard them as the autocorrelation and the cross correlation.

The absorption spectra of Co-Pc and OEP in pyridine at room temperature are shown in Fig. 2. In the visible region the absorption spectrum of Co-Pc is rather simple and consists of a single peak with a shoulder; on the other hand, that of OEP has several separated peaks.

The obtained interferograms are shown in Fig. 3. All the correlation curves are plotted so that the zero crossings between the maximum peak and the minimum peak of the interferograms are aligned up at the delay-time origin. Figure 3(a) is the autocorrelation of the white light, and Figs. 3(b) and 3(c) are the cross correlations for Co-Pc and OEP, respectively. The width of the envelope of the autocorrelation was ~6 fs, which is the time resolution of the present measurements of FID. The cross-correlation curve can be regarded as the waveform of the optical pulse

after it passes through the sample that originally had a waveform of the autocorrelation; that is, the relation between the autocorrelation and the cross-correlation functions is exactly the same as that between the incident and the transmitted light fields:

$$E_o(\tau) = \int_{-\infty}^{\infty} dt\, h(t) E_i(\tau - t),$$

$$C_C(\tau) = \int_{-\infty}^{\infty} dt\, h(t) C_A(\tau - t). \qquad (2)$$

Here $E_o(\tau)$ and $E_i(\tau)$ are the incident and the transmitted light fields, respectively, and $h(t)$ is the impulse response function of the sample. This relation is satisfied even for the modified correlation functions $C_A{'}(\tau)$ and $C_C{'}(\tau)$.

If a sample is irradiated by resonant ultrashort pulses, a coherent oscillating dipole is induced therein, and the induced dipole decays while emitting light in the same direction as that of the incident light. Since the phase of the emitted light from the induced dipole is shifted by π with respect to that of the incident light, destructive interference between the incident light and the FID signal results in a waist in the waveform of the transmitted light through the sample at the trailing edge of the incident pulse.[11,12] This waist and the π phase shift between the incident light and the FID signal are clearly seen in the curve for Co-Pc shown in Fig. 3(b). This situation becomes rather complicated in the case of OEP because of the existence of several separated peaks in the absorption curve.

The complex transmission coefficient $T(\omega)$ of the sample solution, which is the Fourier transform of $h(t)$, can be calculated from the interferograms by the following equation:

$$T(\omega) = \frac{\mathcal{F}\{C_C(\tau)\}}{\mathcal{F}\{C_A(\tau)\}} = |T(\omega)| \exp[i\phi(\omega)]. \qquad (3)$$

Here $\mathcal{F}\{\}$ denotes the Fourier transform of the function inside the braces. The transmittance of the
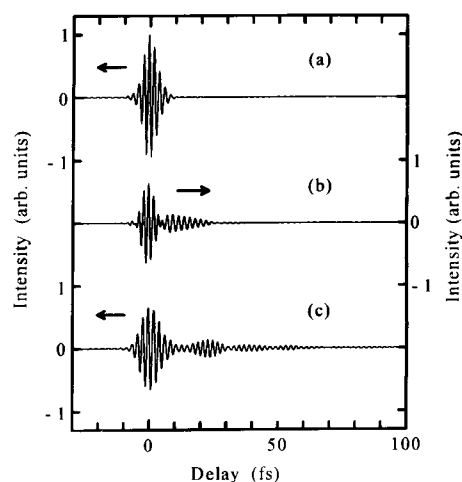

Delay (fs)

Fig. 3. Interferograms obtained with the white-light interferometer: (a) autocorrelation of the white light; (b), (c) cross correlations between the white light and the light transmitted through the Co-Pc solution and the OEP solution, respectively.
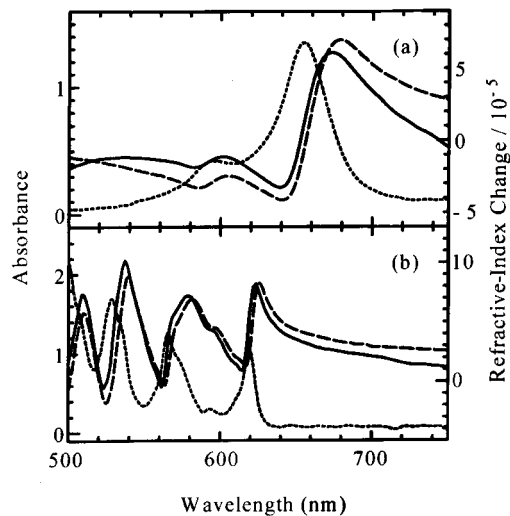
Fig. 4. (a) Absorption spectrum of a Co-Pc solution obtained by Fourier transformation of the interferograms measured by a Michelson interferometer (short-dashed curve), the change of the refractive index from neat pyridine to the Co-Pc solution obtained by Fourier transformation of the interferograms measured with a Michelson interferometer (solid curve), and the re-fractive-index change obtained by Kramers–Kronig analysis of the absorption spectrum measured with a monochromator (long-dashed curve). (b) Corresponding curves for OEP.

light through the sample solution is the squared mag-nitude, $|T(\omega)|^2$, and the phase spectrum of the light is given by $\phi(\omega)$. The absorbance $A(\omega)$ is calculated from the transmittance $|T(\omega)|^2$, and the change of re-fractive index from neat pyridine, $\Delta n(\omega)$, is calculated from the phase $\phi(\omega)$ by the following equations:

$$A(\omega) = -\log|T(\omega)|^2, \qquad \Delta n(\omega) = \frac{c}{\omega d}\,\phi(\omega), \qquad (4)$$

where $d = 1.5$ mm is the thickness of the sample solution.

The absorption spectra of Co-Pc and OEP obtained by the Fourier-transform analysis are shown as the short-dashed curves in Figs. 4(a) and 4(b), respec-tively. Their remarkable agreement with the ab-sorption spectra obtained by a conventional method that uses a monochromator, as shown in Figs. 2(a) and 2(b), demonstrates the accuracy of our Fourier-transform technique. The solid curves in Figs. 4(a) and 4(b) for Co-Pc and OEP, respectively, show the change of refractive index compared with that of neat pyridine obtained by the Fourier transforma-tion. The long-dashed curves in Figs. 4(a) and 4(b) show the refractive-index change calculated with the

Kramers–Kronig analysis by use of the absorption spectra obtained with a monochromator, as shown in Figs. 2(a) and 2(b), respectively. The region of the absorption spectrum from 450 to 800 nm for Co-Pc and that from 450 to 710 nm for OEP were used for the calculation, and it was assumed that there is no absorption outside these regions. The agreement between these spectra is fairly good, although the dis-crepancy is larger near both edges of the observed spectral region. The refractive index obtained with the Fourier-transform analysis is more reliable than that obtained with the Kramers–Kronig analysis be-cause no assumption was made for the calculation of the refractive index from the experimentally ob-tained interferograms. The discrepancies near the edges are probably due to the presence of absorption bands outside the observed spectral region.

In summary, femtosecond FID signals from solu-tions of organic dye molecules were observed with a resolution time of 6 fs by use of a white-light interfer-ometer. In addition, the complex optical constants, i.e., the absorbance and the refractive-index change, were obtained by a Fourier-transform analysis of the interferograms.

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