

Femtosecond time-resolved dispersion relations studied with a frequency-domain interferometer

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Difference phase and transmission spectra (DPS and DTS) due to induced phase modulation of probe pulses in CS₂ were measured with a femtosecond frequency-domain interferometer. Signals that satisfy the Kramers-Kronig (KK) relations with opposite signs were observed. At zero time delay, DTS and DPS were both even functions with respect to the probe center frequency due to the fifth- and third-order nonlinearities, respectively. The conditions for applying the KK relations to time-resolved data were obtained theoretically and verified experimentally.

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The Kramers-Kronig (KK) relations [1] connect the real and imaginary parts of the linear susceptibility $\chi(\omega)$. It has also been proven that the KK relations can be extended to nonlinear optics as long as the causality condition is satisfied for a response function [2]. For example, in pump-probe spectroscopy in the steady-state regime, they are reduced to the standard KK relations, which hold to all orders in the pump field if the pump frequency is fixed at a single mode and the probe frequency is tuned over the whole frequency. In this case, a nonlinear change must not be caused by the probe but only by the pump. If the probe causes, for example, self-induced absorption saturation, the KK relations do not apply, as shown by Yariv [1]. On the other hand, the KK relations are usually unapplicable in time-resolved spectroscopy, because there is a pump pulse, which causes the time-dependent change in the state of a material before the probe field is applied to break the causality condition.

It is important to know how dispersion relations are described in time-resolved spectroscopy, but the study of time-resolved dispersion relations has been difficult so far because of experimental difficulties in measuring time-resolved difference phase spectra (DPS) compared with difference transmission spectra (DTS). A frequency-domain interferometer (FDI) that we have developed recently, however, enables us to study them because both DTS and DPS can be simultaneously obtained with femtosecond time resolution. In this Rapid Communication, with the FDI we observed dispersion relations inherent in time-resolved spectroscopy, which are substantially different from the standard KK relations. They are caused by the pump-induced modulation of the probe amplitude or phase in pump-probe measurements. We also show both theoretically and experimentally that even in time-resolved spectroscopy the standard KK relations are applicable under the special conditions.

The experimental procedure is described in a previous Letter [3]. Laser pulses of 620-nm wavelength, 60-fs duration, 2- μ J energy, and 10-kHz repetition rate were used and divided into pump, probe, and reference pulses.

For frequency-domain interferometry, the reference and probe were displaced temporally by 370 fs, which was fixed throughout the measurements, and DPS were measured as a function of the time delay τ of the probe from the pump. By blocking the reference beam, the ordinary pump-probe measurements were performed to obtain DTS. The polarizations of all the pulses were parallel and all the measurements were performed at room temperature.

In order to study the time-resolved dispersion relations, we measured transparent liquid CS₂, the dynamics of which is well known [4–7]. Figure 1 shows signals for CS₂ in a 1-mm cell at a -40-fs time delay to demonstrate how DPS are obtained by the FDI. Open circles show DPS, which are derived from the fringe shifts between a'

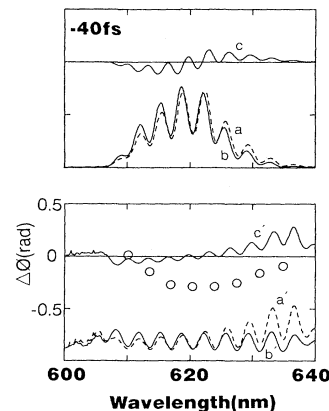


FIG. 1. Upper: interference spectra directly observed for CS₂ at $\tau = -40$ fs with excitation (a), without excitation (b), and their difference (c). The time displacement between the reference and probe is 370 fs. Lower: a , b , and c are normalized by the transmitted probe spectrum to obtain a' , b' , and c' , respectively. Open circles (DPS) are calculated from the fringe-valley shifts between a' and b' as $2\pi(\lambda_i - \lambda_i^{\text{ex}})/(\lambda_{i+1} - \lambda_i)$, where λ_i^{ex} and λ_i are the i th fringe-valley wavelengths with and without excitation, respectively.

and b' . The systematic errors due to the amplitude change [3] are estimated to be less than 0.01 rad, so that they can be neglected.

Figure 2 shows both DTS (c) and DPS (open circles) for CS_2 at -50 -, 0 -, 50 -, and 190 -fs delays, together with probe spectra with (a) and without (b) excitation. The excitation density is ca. $1.9 \times 10^{-3} \text{ J/cm}^2$. Figure 3 shows average phase shifts in the probed region as a function of time delay, which was calculated from the Fourier transform (FT) of the interference signals in the upper part of Fig. 1 in order to use the information on all of the fringes [8]. The results are fit to a phenomenological expression of the femtosecond optical Kerr dynamics in CS_2 [4–7] as follows:

$$\Delta\Phi(t) = \alpha I(t) + \beta \Theta(t) \exp(-t/T_1) [1 - \exp(-t/T_2)].$$

Here the first term represents the electronic response, where the normalized pump pulse intensity $I(t)$ is assumed to have a squared hyperbolic-secant envelope of 60-fs full width at half maximum. The second term represents the nuclear response due to the orientational relaxation, where $\Theta(t)$ is the normalized step function, $T_1 = 1.6 \text{ ps}$, and $T_2 = 75 \text{ fs}$ [5,7]. α and β are appropriate constants with $\alpha/\beta = 2$. Although the nuclear response consists of several origins with different kinetics, the fit to the behavior until 200 fs time delay is not much different even if other terms are also included. The experimental results (dots) are very well fit to the fitting function (solid line), so that the signal shows typical dynamics in CS_2 .

Since the excitation is nonresonant, there should be no change in the absorption and no appreciable dispersion of the refractive-index change within the observed spectral range. In fact, the spectrally integrated probe intensity is unchanged on excitation for any time delay within experimental errors. It is therefore reasonably considered that the observed dispersion relations are caused by induced phase modulation [9,10] of the probe pulse. At $\pm 50 \text{ fs}$,

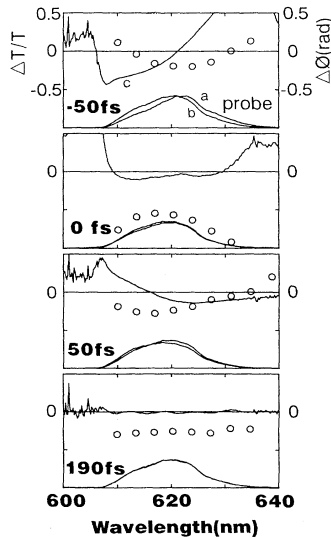


FIG. 2. Transmitted probe spectra with excitation (a) and without excitation (b), DTS (c), and DPS (open circles) for CS_2 at -50 -, 0 -, 50 -, and 190 -fs time delays.

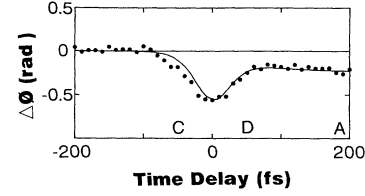


FIG. 3. Average phase shifts (dots) in the probed spectral region as a function of time delay and the fitting function (solid curve). The conditions (C), (D), and (A) are satisfied at -50 -, 50 -, and 190 -fs time delays, respectively (see text).

the probe pulse shows frequency shifts, which are proportional to the time derivative of the phase change that is shown in Fig. 3. At zero delay, since the probe pulse overlaps with the electronic Kerr response, the probe phase decreases at the leading edge and increases at the trailing edge to cause both red and blue shifts in the probe spectrum, resulting in spectral broadening (self-phase-modulation [9]). In contrast, at 190 fs the DPS is constant and the DTS is zero, because the probe phase is modulated little at this delay due to almost steady phase change, as shown in Fig. 3.

Since DPS and DTS are proportional to the change in the real and imaginary parts of the susceptibility $\chi(\omega)$, respectively, their mutual relations can be directly compared with the standard KK relations. The DTS and DPS at -50 and 190 fs satisfy the KK relations qualitatively. However, the spectra at 0 fs clearly violate the KK relations, because both DTS and DPS are even functions with respect to the center frequency of the probe, whereas the KK relations connect an even function with an odd function. Further, the sign of the DTS at 50 fs is opposite that at -50 fs , which is unusual, because through the KK relations the refractive index should increase on the longer-wavelength side of the absorption increase. These results can be explained in the following way.

The KK relations are derived from the complex integration of $\chi(\omega)/(\omega - \omega_0)$ in the lower half of the complex ω plane [1]. $\chi(\omega)$ is obtained from the Fourier transform of $P(t)$ in the following way:

$$\begin{aligned} P(t) &= \chi(t) \circ E(t) = \int_0^\infty dt' \chi(t') E(t-t'), \\ P(\omega) &= F(P(t)) = \chi(\omega) E(\omega), \\ \chi(\omega) &= \int_0^\infty dt \exp(-i\omega t) \chi(t). \end{aligned} \quad (1)$$

Here \circ denotes the convolution operation, $E(t)$ is a probe field, $P(t)$ is the polarization induced in a material by $E(t)$, and $\chi(t) = 0$ when $t < 0$ because of causality. Since $t > 0$ in $\exp(-i\omega t)$ in Eq. (1), $\chi(\omega)$ has no poles in the lower half ω plane to satisfy the KK relations. In time-resolved spectroscopy, however, the causality condition is not satisfied, because there is a pump pulse, which excites the material to cause the polarization change

$$\begin{aligned} \Delta P(t) &= \chi(t) \circ [E(t) \Delta N(t)] \\ &= \int_0^\infty dt' \chi(t') E(t-t') \Delta N(t-t'), \end{aligned} \quad (2)$$

where $\Delta N(t)$ represents the change in the state of the ma-

terial due to the pump, and depends on τ such that $\Delta N(t) = \Delta N'(t + \tau)$. Equation (2) describes the level population term [11] in the perturbation expression, whereas the following discussion can also be made for the coherent coupling term. The susceptibility change is then expressed by

$$\Delta\chi(\omega) = F(\Delta P(t))E(\omega) \\ = \frac{\chi(\omega)}{E(\omega)} \int_{-\infty}^{\infty} dt \exp(-i\omega t) E(t) \Delta N(t). \quad (3)$$

In general, $\Delta\chi(\omega)$ has poles in both half planes because the Fourier integration is over all t . Therefore the KK relations are not satisfied. However, the KK relations are strictly satisfied in the following special cases:

(A) When $\Delta N(t)$ is constant (ΔN_0),

$$\Delta\chi(\omega) = \frac{\chi(\omega)}{E(\omega)} \int_{-\infty}^{\infty} dt \exp(-i\omega t) E(t) \Delta N_0 \\ = \Delta N_0 \chi(\omega).$$

(B) When $E(t)$ is a δ function [$E_0\delta(t)$],

$$\Delta\chi(\omega) = \frac{\chi(\omega)}{E_0} \int_{-\infty}^{\infty} dt \exp(-i\omega t) E_0 \delta(t) \Delta N(t) \\ = \Delta N(0) \chi(\omega) = \Delta N'(\tau) \chi(\omega).$$

(C) When $\Delta N(t) = 0$ over $t < 0$ (negative delays),

$$\Delta\chi(\omega) = \frac{\chi(\omega)}{E(\omega)} \int_0^{\infty} dt \exp(-i\omega t) E(t) \Delta N(t).$$

(D) When $\Delta N(t) = 0$ over $t > 0$ (positive delays) and $\chi(\omega)$ is constant (χ_0),

$$\Delta\chi(\omega) = \frac{\chi_0}{E(\omega)} \int_{-\infty}^0 dt \exp(-i\omega t) E(t) \Delta N(t).$$

Since this function has no poles in the upper half ω plane,

$$\Delta\chi(\omega) = \chi(\omega) \int d\omega' E_{\text{ex}}(\omega') \Delta N_c(\omega - \omega') / E(\omega) \\ = \chi(\omega) \int d\omega' E_{\text{ex}}(\omega') \eta(\omega - \omega') \int d\omega'' E_{\text{ex}}^*(\omega'') \chi(\omega - \omega' - \omega'') E(\omega - \omega' - \omega'') / E(\omega),$$

which requires the same additional conditions for $E(\omega)$. Therefore the conditions (C) and (D) also hold. Even for the higher order in the pump field, one can readily see that a similar discussion can be made as long as the probe field is weak enough to be limited to first order. In summary, the conditions (A) to (D) are criteria for applying the KK relations to time-resolved data in the weak-probe-field limit.

As shown in Fig. 3, the conditions (C), (D), and (A) are approximately satisfied at -50 -, 50 -, and 190 -fs time delays, respectively, since $\Delta\Phi(\tau)$ is expected to be proportional to $\Delta N(t)$. The conditions (A) and (B) are physically equivalent: the probe pulse must not experience a time-dependent change in amplitude or phase which causes an induced modulation effect. These conditions are obtained as a natural extension of the condition in the steady-state nonlinearity, where the spectral width of the pump must be much narrower than that of the probe for the KK relations to be satisfied. On the other hand, the

it obeys the KK relations with opposite signs. For (C) and (D), additional conditions are required because $1/E(\omega)$ may generally cause singularity. First, $1/E(\omega)$ must not have poles over $|\omega| < \infty$ in the lower and upper half planes for (C) and (D), respectively. Second, $\Delta\chi(\omega)/(\omega - \omega_0)$ must fall off more rapidly than $1/\omega$. Since $\Delta\chi(\omega)$ can be rewritten in the form

$$\Delta\chi(\omega) = \chi(\omega) \int d\omega' \Delta N(\omega') E(\omega - \omega') / E(\omega),$$

it is necessary that $E(\omega - \omega')/E(\omega) \rightarrow O(\omega^\delta)$, with $\delta \leq 0$ as $\omega \rightarrow \infty$. Both first and second conditions are satisfied for, e.g., a hyperbolic secant or Lorentzian envelope $E(\omega)$, but not for a Gaussian envelope $E(\omega)$. The pulse shape of a mode-locked laser is well approximated by a hyperbolic-secant function [12], so that the additional conditions are usually satisfied.

The coherent coupling term to second order in the pump field and to first order in the probe field is, for example, expressed by

$$\Delta P(t) = \chi(t) \circ [E_{\text{ex}}(t) \Delta N_c(t)], \\ \Delta N_c(t) = \eta(t) \circ [E_{\text{ex}}^*(t) P(t)] \\ = \int_{-\infty}^t dt' \eta(t - t') [E_{\text{ex}}^*(t') P(t')],$$

where $E_{\text{ex}}(t)$ is a pump pulse field, $*$ denotes complex conjugate, and $\eta(t)$ is a response function that represents energy relaxation dynamics and is zero over $t < 0$. This term is called the perturbed free-induction-decay term [11].

Obviously the conditions (A) and (B) hold also for this term, but a brief discussion is needed for (C) and (D) as follows. If $E_{\text{ex}}(t) = 0$ over $t < 0$ or $t > 0$, the Fourier integration can be over $t > 0$ or $t < 0$, respectively. Further, the susceptibility change is expressed by

conditions (C) and (D) are inherent in time-resolved spectroscopy. In particular, although it has been pointed out that the KK relations with opposite signs are mathematically derived from the integration over the upper half ω plane [1], such relations are not realistic because it means that the causality condition is violated. The condition (D), however, tells us that one can really observe such relations in time-resolved spectroscopy, as shown in Fig. 2.

At zero delay, none of the above conditions is satisfied, so that the KK relations do not apply. Here, both real and imaginary parts are even functions with respect to the probe center frequency. This shows the nonlinear dispersion relations inherent in time-resolved spectroscopy, because they are caused by the instantaneous electronic response [$\Delta\Phi(t) = \alpha I(t) \propto E^2(t)$] as follows:

$$E(t) \exp[i\Delta\Phi(t)] = E(t) [1 + i\Delta\Phi(t) - \frac{1}{2}\Delta\Phi^2(t) \\ - (i/6)\Delta\Phi^3(t) + \dots]. \quad (4)$$

Since $\Delta\Phi(t)$ is an even function with respect to time zero, the FT of Eq. (4) is also an even function with respect to zero frequency. In the lowest order, the spectral broadening observed in the DTS is caused by the third term $-\frac{1}{2}\Delta\Phi(t)^2$ (fifth-order nonlinearity), while the broadening in the DPS is caused by the second term, $i\Delta\Phi(t)$ (third-order nonlinearity).

We only investigate the dispersion relations that are due to $F(E(t)\Delta N(t))/E(\omega)$ in Eq. (3), i.e., the induced modulation effect, which differs substantially from the standard KK relations. For absorptive materials, on the other hand, time-resolved dispersion relations depend on both $\chi(\omega)$ and $F(E(t)\Delta N(t))/E(\omega)$, as shown in Eq. (3). Due to the factor of $\chi(\omega)$, they are usually not much different from the standard KK relations. This is the reason why DTS and DPS in $\text{CdS}_x\text{Se}_{1-x}$ doped glass seem to satisfy the KK relations qualitatively [3].

In conclusion, we observed generalized dispersion relations in time-resolved pump-probe spectroscopy such as the KK relations with opposite signs at positive delays

and the even functions for both real and imaginary parts at zero delay, which are both due to the induced modulation effect of the probe pulse. The standard KK relations are obtained as a special case of the generalized relations. That is, the standard KK relations hold approximately, if short enough probe pulses are used such that the modulation effect is negligible or if the probe arrives earlier at the sample than the pump, i.e., at negative delays. These conditions are experimentally important. For example, since an optical Stark effect in time-resolved spectroscopy appears dominantly for negative delays [11,13], the KK relations can be applied to the transmission change due to the Stark shift to obtain the net change in the refractive index at the shifted absorption peak.

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