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Visible–infrared two-dimensional Fourier-transform spectroscopy

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We report on a new class of optical multidimensional Fourier-transform spectroscopy associated with a visible excitation–infrared emission configuration, in which the emitted field results from second-order optical nonlinearities. This configuration is demonstrated on a phase-matched sample of known nonlinear response by coherent measurement of the mid-infrared field emitted after a femtosecond visible double-pulse excitation. © 2002 Optical Society of America

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Optical spectroscopy techniques serve to provide knowledge of matter through the detection of radiated electric fields stemming from the oscillating electric dipole density, P , induced in a sample by the total incident field, E . In the perturbative regime, the response function of the material under study is entirely described by the set of its successive electrical susceptibilities, $\chi^{(n)}$, which are $n + 1$ -rank tensors. Conversely, the position, magnitude, and shape of the features of a complex map of $\chi^{(n)}$ hold all the information about existing couplings and inhomogeneities within the sample. They can in turn be related to the structural properties of crystals¹ and to couplings between bond stretches.^{2–4} The latter can provide information about the three-dimensional structure of molecules and small peptides.^{5,6} The dynamics of molecular environments can also be retrieved.⁷ Outcomes of any optical measurement in the perturbative regime can of course be derived from these complex tensors. Complete measurement of the centerpiece $\chi^{(n)}$ is achieved only with multidimensional spectroscopy (nDSY). In practice, nDSY consists of measuring the field $E_{\text{emission}}^{(n)}$ radiated by the n th-order nonlinearity of a material as a function of p ($1 \leq p \leq n - 1$) independent parameters to retrieve the n th-order nonlinear response $\Xi^{(n)}$ of the sample ($p = n - 1$) or one of its projections ($p < n - 1$). As the measured observable is the field $E_{\text{emission}}^{(n)}$ and not the ensemble-averaged electrical polarization, $P^{(n)}$, here we define the effective n th-order response $\Xi^{(n)}$ as

$$E_{\text{emission}}^{(n)}(\omega_1) = \int \Xi^{(n)}(\omega_2, \dots, \omega_{n+1}) E(\omega_2) \dots E(\omega_{n+1}) \delta\left(\omega_1 - \sum_{i>1} \omega_i\right) d\omega_2 \dots d\omega_n, \quad (1)$$

where $\Xi^{(n)}$ incorporates not only macroscopic $\chi^{(n)}$ but also a propagation term [see Eq. (3), below] and, in the case $n > 2$, terms including $\chi^{(j)}$, where $j < n$ is associated with cascading effects. In summary, an nDSY measurement removes the integral in Eq. (1) by spreading the intricate and integrated emission $E_{\text{emission}}^{(n)}$ along p additional axes; for known E and

$p = n - 1$ this spreading allows retrieval of the map of $\Xi^{(n)}$ in n frequency dimensions.

The p parameters can be the wavelength of tunable continuous lasers,⁴ but most experimental demonstrations are done through manipulation in the time domain with multiple-pulse Fourier-transform nonlinear spectroscopy^{1–3,5,7} (nDFTSY), i.e., the optical analog of multiple quantum nuclear magnetic resonance.⁸ In nDFTSY, the parameters are time delays τ_i , $2 \leq i \leq p + 1$, in a sequence of femtosecond pulses E_i [$E = \sum_{i=2}^{p+2} E_i(t - \tau_i)$, $\tau_{p+2} = 0$]. In the case of $p = n - 1$ studied experimentally below, the cross term of interest in Eq. (1) is

$$E_{\text{crossterm}}^{(n)}(\omega_1) = \int \Xi^{(n)}(\omega_2, \dots, \omega_{n+1}) E_2(\omega_2) \exp(i\omega_2\tau_2) \times E_3(\omega_3) \exp(i\omega_3\tau_3) \dots \delta\left(\omega_1 - \sum_{i>1} \omega_i\right) d\omega_2 \dots d\omega_n. \quad (2)$$

In nDFTSY, the spectral map of $\Xi^{(n)}$ is retrieved with Fourier transforms of Eq. (2) relative to the τ_i Fourier conjugate of the ω_i .

The number of pulses, their wavelengths, their relative phases, and the beam geometry of the pulses within the exciting sequence are chosen according to the physics under study in the sample [i.e., according to the process involved in $\Xi^{(n)}$]: The second-order nonlinearity of noncentrosymmetric samples is probed with only two pulses,¹ in contrast with centrosymmetric and in particular liquid samples^{2,3,5,7} ($n = 3, 5$), which are active only at the $\chi^{(3)}$ level. Electronic couplings are addressed in the visible^{1,7}; vibrational couplings, in the infrared^{3,5} or in the visible via Raman scattering.² Noncollinear geometry or a suitable set of phases of the exciting pulses can be used to isolate cross term (2). In all cases the phase between the exciting pulses must be stabilized as explained below.

Coherent detection of $E_{\text{emission}}^{(n)}(\omega_1)$ is necessary as both the amplitude and the phase of this field are required for computing the Fourier transforms. One can then use either Fourier-transform spectral interferometry⁹ (multichannel detection) or time-domain interferometry with a local oscillator or reference field $E_1(t - \tau_1)$ (single-channel detector). In both cases one

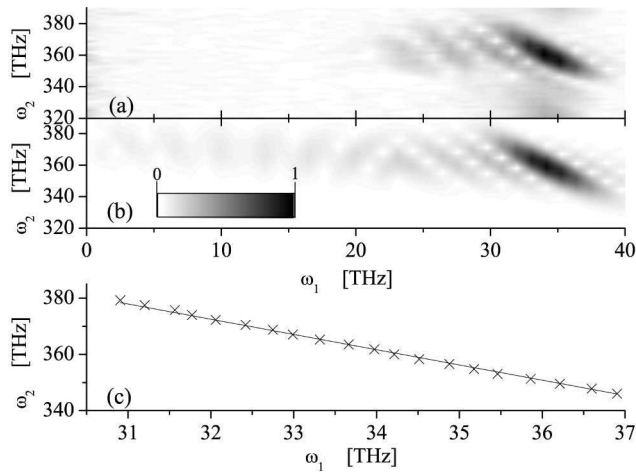


Fig. 2. (a) $|\Xi^{(2)}(\omega_2, \omega_1)E_1(\omega_1)E_2(\omega_2)E_3(\omega_2 + \omega_1)|$ frequency dependency as determined by a two-dimensional Fourier transform of the experimental data (τ_1 from -426.9 to 426.9 fs in $\delta\tau_1 = 6.67$ fs increments; τ_2 from -285.4 to 285.4 in $\delta\tau_2 = 4\lambda_{\text{diode}}/c \approx 8.9$ fs increments). (b) Theoretical results for $|\Xi^{(2)}(\omega_2, \omega_1)E_1(\omega_1)E_2(\omega_2)E_3(\omega_2 + \omega_1)|$, assuming that E_2 and E_3 are 35-THz Gaussian centered around 375 THz. (c) Comparison between (solid line) the phase-matching slope calculated from the refractive indices of AgGaS₂ and (crosses) the experimental maxima of map (a). These maxima are determined through a parabolic fit of cuts of the two-dimensional map for each value of ω_2 , which results in a resolution far better than $\delta\omega_1$.

axis and $\Delta k = k_e(\omega_3) - k_o(\omega_2) - k_o(\omega_1)$. For this proof-of-principle experiment, as the crystal has no resonance in the spectral domain under study, $\Xi^{(2)}$ is dominated by the bracketed term of phase matching, which serves as a model two-dimensional nonlinear response.

The two visible exciting pulses are polarized each along one of the crystal axis (see the inset of Fig. 1) so that the mid-infrared emission results from only the cross term we are seeking and not from each individual pulse. Note that the use of different polarizations on the two beams breaks the symmetry between ω_2 and ω_3 : Phase matching can be achieved here only when $\omega_3 > \omega_2$. The magnitude of $\Xi^{(2)}(\omega_2, \omega_3)$ is plotted in Fig. 2(a) as a function of $\omega_1 = \omega_3 - \omega_2$ and of ω_2 . As expected, the obtained result is dominated by phase matching and exhibits several oscillations of the sinc function.

The $|\Xi^{(2)}(\omega_2, \omega_3)|$ map can be simulated with no adjustable parameter by use of Eq. (3) [see Fig. 2(b)]. The good agreement between theory and experiment [Fig. 2(c)] demonstrates the validity of the technique.

Although the precision of the 10- μm τ_1 interferometer should be more than ten times less critical than the precision of the 800-nm τ_2 interferometer, inaccuracies in τ_1 have measurable effects and result in the aliased ghosts along ω_2 that can be seen in Fig. 2(a). Passive stabilization and control of τ_1 is thus the next step toward analysis of more-complicated samples for retrieval of full real and imaginary information of $\Xi^{(n)}$.

To summarize, multiple-pulse nonlinear spectroscopy disentangles overlapping contributions to

a complex emission by spreading them along one or more additional axes, thus characterizing the emitting sample. The retrieved multidimensional map (or its projection) of the nonlinear response gives precious insight into couplings between energy levels. In our demonstration of two-dimensional Fourier-transform visible-infrared measurement of a phase-matched AgGaS₂ sample, we took special care to ensure accurate and optimal sampling of our temporal data. This technique could be useful for understanding a molecular system such as a protein complex in which electronic (visible) excitation of an optically active cofactor sets vibrational dipoles in a coherent oscillation.¹⁵ It might also prove especially enlightening in the study of quantum wells in which the one dimension of visible frequencies is related to the interband transitions (hence to the wave vector), whereas emission that is due to intersubband transitions is along the other axis in the infrared spectral domain.

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