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Visible–infrared two-dimensional Fourier-transform spectroscopy

Nadia Belabas and Manuel Joffre

Laboratoire d’Optique et Biosciences, Institut National de la Santé et de la Recherche Médicale U451—Centre National de la Recherche Scientifique Unité Mixte de Recherche 7645—École Polytechnique—École Nationale Supérieure des Techniques Avancées, 91128 Palaiseau Cedex, France

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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, \( \chi^{(p)} \), which are \( n + 1 \)-rank tensors. Conversely, the position, magnitude, and shape of the features of a complex map of \( \chi^{(p)} \) hold all the information about existing couplings and inhomogeneities within the sample. They can in turn be related to the structural properties of crystals and to couplings between bond stretches. The latter can provide information about the three-dimensional structure of molecules and small peptides. The dynamics of molecular environments can also be retrieved. 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 \( E_{\text{emission}} \) 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 \( E_{\text{emission}} \) and not the ensemble-averaged electrical polarization, \( P^{(n)} \), here we define the effective \( n \)-th-order response \( \Xi^{(n)} \) as

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

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 \( \chi^{(j)} \chi^{(n-j)} \), 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, but most experimental demonstrations are done through manipulation in the time domain with multiple-pulse Fourier-transform nonlinear spectroscopy (nDFTSY), i.e., the optical analog of multiple quantum nuclear magnetic resonance. In nDFTSY, the parameters are time delays \( \tau_i, 2 \leq i \leq p + 1, \) 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

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

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

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 only with two pulses, in contrast with centrosymmetric and in particular liquid samples, \( n = 3, 5 \), which are active only at the \( \chi^{(3)} \) level. Electronic couplings are addressed in the visible, vibrational couplings, in the infrared or in the visible via Raman scattering. 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 interferometry (multichannel detection) or time-domain interferometry with a local oscillator or reference field \( E_2(t - \tau_1) \) (single-channel detector). In both cases one
must be aware that Fourier transforms of unequally spaced data (because of either unjustified interpolation or uneven time steps) result in distorted, aliased, and blurred maps. The stabilization and control of the time delays may be more demanding than the requirements for processing data from Fourier-transform spectral interferometry, but a time-domain interferometry setup is more versatile, as only one detector has to be replaced if one wishes to measure a new part of \( \mathcal{X}(n) \), i.e., a new spectral domain. Furthermore, time-domain interferometry is a widely used technique in the mid-infrared, where multichannel detectors are not easily available.

In this Letter we present a two-dimensional \((p = 1)\) Fourier-transform visible excitation–infrared emitted field measurement. In our experiment a visible pulse sequence excites through second-order nonlinear processes \((n = 2)\) a low-frequency polarization that in turn radiates a mid-infrared field according to Eq. (1). The emitted field is measured with a broadband mid-infrared (center at 10 \( \mu \)m) reference field generated by optical rectification. In contrast with previously reported all-infrared or all-visible experiments, electronic and vibrational couplings can be simultaneously addressed in our visible–infrared configuration.

In practice (see the experimental layout in Fig. 1), the infrared emitter is excited by a sequence of 16-fs 0.2-nJ 800-nm pulses delivered by a Ti:sapphire oscillator. The time delay \( \tau_2 \) between the two visible (800-nm) pulses is the Fourier conjugate of a visible spectral axis \((\omega_2 \text{ or } \omega_3)\). The emitted field is measured in amplitude and phase by time-domain interferometry, i.e., through a linear correlation measurement with a reference infrared field, \( E_1 \). Note the rather unconventional geometry used in the experiment, the measured field being transmitted through the GaAs sample used for generation of the reference field through optical rectification. This approach, already discussed in detail previously, allows dispersion compensation between the signal and the reference fields, since both undergo the same dispersion through propagation in the GaAs sample after the reference field has been generated in the first micrometer of the sample (one absorption length). We also checked that the free-carrier absorption in GaAs was kept at a negligible level so as not to change the spectrum of the signal field.

The time delay, \( \tau_1 \), between the signal field and \( E_1 \) transforms into mid-infrared spectral variable \( \omega_1 \). A two-dimensional Fourier transform of the cross term in the experimental data, with respect to both \( \tau_1 \) and \( \tau_2 \), thus yields \( E_1^*(\omega_1)E(2)(\omega_2, \omega_3 + \omega_1)E_2^*(\omega_2)E_3(\omega_2 + \omega_1) \), from which the desired two-dimensional map of \( \mathcal{X}(2) \) can be deduced. It is noteworthy that the spectral phase of the reference and exciting fields is of no concern in this work, since we report only on the magnitude of the two-dimensional response \( |\mathcal{X}(2)| \), which can be directly deduced from the magnitude of the two-dimensional Fourier transform. For the same reason, the zero time delay between the reference and the signal field can be set arbitrarily.

However, as stated above, the validity of the retrieved \( \mathcal{X}(2) \) map yielded by a double Fourier transform of interferometric signal \( S(\tau_1, \tau_2) \) depends strongly on the accuracy of the temporal axes \( \tau_1 \) and \( \tau_2 \). \( \tau_1 \) is swept with a 0.1-\( \mu \)m step motor with no additional stabilization, as stability was \textit{a priori} not an issue in the mid-infrared wavelength domain. \( \tau_2 \) is actively stabilized by means of a 3-\( \mu \)m (10-fs) stroke piezoelectric transducer. The time–domain interferences \( Q_1 \) of a \( \lambda_{\text{diode}} = 670 \) nm laser diode propagating along the interferometer are used as a feedback signal, allowing precision of \( \pm 30 \) nm or 0.1 fs on \( \tau_2 \). For resolution of \( \delta \omega_{2} = 1.75 \) THz (58.3 cm\(^{-1}\)) on \( \omega_2, \tau_2 \) is scanned along 570.8 fs by means of a 0.1-\( \mu \)m step motor. To scan \( \tau_2 \) while keeping track of the interference order (fringe number) of \( Q_1 \), we use a second time-domain interference signal, \( Q_2 \), with a phase differing from \( Q_1 \) by \( \pi/2 \). \( Q_2 \) is obtained by placement of a quarter-wave plate in one arm of the interferometer and detection of both polarizations at the output of a Glan polarizer. Permanent tracking of \( Q_1 \) and \( Q_2 \) with a microcontroller makes possible accurate knowledge of \( \tau_2 \) at any time. Even though the smallest time step along this visible \( \tau_2 \) interferometer is \( \lambda_{\text{diode}}/c \), since the central wavelength and the bandwidth of the Ti:sapphire are well known, this system allows an optimal rate of sampling.

As a test of the technique and of the experimental setup, we measured the nonlinear response \( \mathcal{X}(2)(\omega_2, \omega_3) \) of AgGaS\(_2\), a birefringent crystal that can be phase matched for mid-infrared generation through difference-frequency mixing. The crystal is cut at \( \phi = 45^\circ \) and \( \theta = 47^\circ \) for type II phase matching. In this case the nonlinear response is

\[
\mathcal{X}(2)(\omega_2, \omega_3) = \exp[ik_0(\omega_1)L] \frac{\omega_2^2}{4c^2k_0(\omega_1)} \times \chi^{(2)}(-\omega_1; \omega_3, -\omega_2) \left[ \exp(\Delta k L) - 1 \right],
\]

where \( k_0(\omega_j) \) is the amplitude of the wave vector at the frequency \( \omega_j \) along the extraordinary (ordinary)
better than

dv

step toward analysis of more-complicated samples for
axis and $D$

diffractive indices of AgGaS$_2$

line) the phase-matching slope calculated from the re-
tered around 375 THz. (c) Comparison between (solid
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-dimen-
sional Fourier transform of the experimental data ($\tau_1$ from
$-426.9$ to $426.9$ fs in $\delta \tau_1 = 6.67$ fs increments; $\tau_2$ from
$-285.4$ to $285.4$ in $\delta \tau_2 = 4\lambda_{\text{diode}}/c = 8.9$ 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 cen-
tered around $375$ THz. (c) Comparison between (solid line) the phase-matching slope calculated from the re-
fractive indices of AgGaS$_2$ 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 $\omega_2$, which results in a resolution far
better than $\delta \omega_1$.

axis and $\Delta k = k_c(\omega_3) - k_c(\omega_2) - k_c(\omega_1)$. 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 $\omega_2$ and
$\omega_3$. 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 $\omega_2$. 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 ad-
justable 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 $\tau_1$ interfero-
meter should be more than ten times less critical than
the precision of the $800$-nm $\tau_2$ interferometer, inaccura-
cies in $\tau_1$ have measurable effects and result in the
aliased ghosts along $\omega_2$ that can be seen in Fig. 2(a).
Passive stabilization and control of $\tau_1$ 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 spec-
troscopy 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
AgGaS$_2$ sample, we took special care to ensure ac-
curate 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 oscilla-
tion. 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 tran-
sitions (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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address is nadia.belabas@polytechnique.org.

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