Linewidth-deduction method for nonlinear optical spectroscopy with transform-limited light pulses

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We have developed a Fourier-deconvolution-based linewidth-deduction method for nonlinear optical spectroscopy with transform-limited light pulses. The phase-retrieval problem involved in this method was solved with a phase-retrieval procedure based on the maximum-entropy model. Our proposed method can also help one to surpass the resolution limit set by the uncertainty principle when the amplitude line-shape function of the laser source can be fully predetermined. © 1998 Optical Society of America [S0740-3224(98)00303-8]

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1. INTRODUCTION

Tunable pulsed lasers open the window of nonlinear optical spectroscopy, which has been known for its versatility in probing a variety of materials that are accessible to light. Various nonlinear optical processes offer the possibility of material characterization with extremely high spectral and temporal resolutions that are limited only by the light source used. In the frequency domain an experimental spectrum, $E(\omega)$, can be expressed as a convolution of an intrinsic spectrum, $E'(\omega)$, and a line-shape function, $G(\omega)$, by

$$E(\omega) = G(\omega) * E'(\omega) = \int_{-\infty}^{\infty} G(\omega')E'(\omega - \omega')d\omega', \tag{1}$$

where $*$ denotes the convolution operation. The above expression is valid only when the line-shape function is translation invariant; that is, the line-shape function is independent of the position of the central frequency. By use of the convolution theorem, Eq. (1) becomes

$$F^{-1}\{E(\omega)\} = F^{-1}\{G(\omega)\}F^{-1}\{E'(\omega)\}. \tag{2}$$

If the line-shape function is known, then $E'(\omega)$ can be simply deduced from

$$E'(\omega) = F\left\{\frac{F^{-1}\{E(\omega)\}}{F^{-1}\{G(\omega)\}}\right\}, \tag{3}$$

where F denotes the Fourier transform and F^{-1} denotes the inverse Fourier transform. A procedure based on Eq. (3) to remove the broadening effect of a finite bandwidth of the excitation light from the measured spectrum has been referred to as the Fourier deconvolution process.[1,2] Usually the intensity at different frequency components within the bandwidth of the excitation light is additive, and the deconvolution can be directly applied to the measured power spectrum. However, when a transform-limited light pulse[3] is used, the field amplitudes at different spectral components become additive, and the deconvolution has to be applied to the real and the imaginary parts of the amplitude. To be more precise, here a transform-limited pulse has been referred to as the light pulse with a product of the temporal duration and the spectral bandwidth achieving the minimum allowed by the uncertainty principle.

Without losing the generality, in the following discussion we take infrared–visible sum-frequency generation (IVSFG) spectroscopy[4] as an example. However, it should be noted that the same procedure can be equally applied to any other second- or third-order coherent nonlinear optical spectroscopy.

The sum-frequency signal field is proportional to a surface nonlinear polarization,

$$P_s(\omega_s = \omega_\nu + \omega_{\mathrm{IR}}) = \chi^{(2)}(-\omega_s;\, \omega_\nu,\, \omega_{\mathrm{IR}})E(\omega_\nu)E(\omega_{\mathrm{IR}}), \tag{4}$$

which is induced by two incident beams. One beam has a frequency of ω_ν at the visible spectral region, and the other has an infrared (IR) frequency of ω_{IR}, which is tuned across some vibrational modes of molecules to generate a sum-frequency spectrum. If we consider the situation that the bandwidth of the infrared laser pulses has a finite value, then the measured IVSFG intensity can be expressed as

$$I_s(\omega_s = \omega_\nu + \omega_{\mathrm{IR}}^0) \propto \int |G(\omega_{\mathrm{IR}}) \times \chi^{(2)}(-\omega_s;\, \omega_\nu,\, \omega_{\mathrm{IR}}^0 - \omega_{\mathrm{IR}})|^2 d\omega_{\mathrm{IR}} I(\omega_\nu)I(\omega_{\mathrm{IR}}^0). \tag{5}$$

Here $G(\omega)$ is the amplitude line-shape function of the IR pulses. However, when a transform-limited coherent IR pulse is used, the resulting IVSFG signal intensity should be rewritten as[5]

$$I_s(\omega_s = \omega_\nu + \omega_{\mathrm{IR}}^0) \propto \left| \int G(\omega_{\mathrm{IR}}) \times \chi^{(2)}(-\omega_s;\, \omega_\nu,\, \omega_{\mathrm{IR}}^0 - \omega_{\mathrm{IR}}) \times d\omega_{\mathrm{IR}} \right|^2 I(\omega_\nu) I(\omega_{\mathrm{IR}}^0). \quad (6)$$

This is because, for a transform-limited light pulse, two spectral components in the electric field, which have a frequency separation smaller than the spectral width of the light source, can still interfere with each other during the pulse duration. The difference between Eqs. (5) and (6) also suggests that one can distinguish a transform-limited light source from a non-transform-limited one by examining the spectral broadening caused by the finite bandwidth of the light.

For the IVSFG spectroscopy with transform-limited pulses, Eq. (6) should be used, where the convolution integral is applied to the real and the imaginary parts of the nonlinear susceptibility. Therefore the crucial step in the Fourier-deconvolution-based linewidth-deduction procedure for coherent nonlinear optical spectroscopy with transform-limited pulses is to retrieve the phase information from the measured power spectra and then to restore the real and the imaginary parts of the nonlinear optical susceptibility.

It is, however, disappointing that we cannot use the important analyzing technique of Kramers–Kronig dispersion relations[6,7] to solve the phase-retrieval problem in the deconvolution procedure for a coherent spectrum measured with transform-limited pulses. This is because the real and the imaginary parts of the susceptibility after convolution with the laser amplitude line-shape function no longer satisfy Kramers–Kronig dispersion relations. In this paper we show that the maximum-entropy phase-retrieval procedure[8–11] (MEPRP) can be used for solving this important problem.

2. MAXIMUM-ENTROPY PHASE-RETRIEVAL PROCEDURE

Before demonstrating the applicability of MEPRP for solving the phase-retrieval problem in the linewidth-deduction procedure, we should first briefly describe MEPRP. The entropy for a measured spectrum $S(f)$ in the frequency interval $[f_1, f_2]$ is defined as

$$h \propto \int_{f_1}^{f_2} \log S(f)\, \mathrm{d}f. \quad (7)$$

In the MEPRP a normalized frequency $\nu \equiv (f - f_1)/(f_2 - f_1)$ is normally introduced to simplify the calculation. By using variational calculus with the Lagrange multiplier method, one can find a solution that maximizes the spectral entropy under the constraint of satisfying some data points that have been obtained from some spectral measurements. The solution for $2M + 1$ spectral points has been found to be

$$\hat{S}(\nu) = \frac{|\beta|^2}{\left| 1 + \sum_{k=1}^{M} a_k \exp(i 2\pi k \nu) \right|^2}. \quad (8)$$

The unknown coefficients a_k and $|\beta|^2$ in the above equation can be deduced from the following matrix equation:

$$\begin{bmatrix} R(0) & R(-1) & \dots & R(-M) \\ R(1) & R(0) & \dots & R(1-M) \\ \vdots & \vdots & \ddots & \vdots \\ R(M) & R(M-1) & \dots & R(0) \end{bmatrix} \begin{bmatrix} 1 \\ a_1 \\ \vdots \\ a_M \end{bmatrix} = \begin{bmatrix} |\beta|^2 \\ 0 \\ \vdots \\ 0 \end{bmatrix}, \quad (9)$$

where $R(m)$ is the autocorrelation function that can be obtained from the Fourier transform of a power spectrum $S(\nu)$ by

$$R(m) = \int_0^1 S(\nu) \exp(-i 2\pi m \nu)\, d\nu. \quad (10)$$

We prepare a continuous power spectrum, $S(\nu)$, with a cubic spline interpolation from the discrete spectral points. The continuous Fourier transform shown in Eq. (10) is then applied to get the autocorrelation function.

Following the same procedure, we can also derive the solution for the nth order nonlinear susceptibility

$$\hat{\chi}^{(n)}(\nu) = \frac{|\beta| \exp[i\phi(\nu)]}{1 + \sum_{k=1}^{M} a_k \exp(i 2\pi k \nu)}. \quad (11)$$

Note that the coefficients $|\beta|$ and a_k in the above equation can be obtained from Eq. (9); the only quantity that cannot be determined from the power spectrum $S(\nu)$ is the error-phase function $\phi(\nu)$. Therefore the crucial step in MEPRP is to estimate the error phase $\phi(\nu)$ reliably. Fortunately, unlike the real phase (i.e., the phase of $\chi^{(n)}$), which usually contains steplike changes as the frequency is scanned across resonances, it has been found that the error phase $\phi(\nu)$ exhibits a fairly smooth behavior.[10] Usually a linear interpolation of two known error-phase values $\phi(\nu_1)$ and $\phi(\nu_2)$, which can be deduced from the measured real-phase values at the same frequencies, will yield a good estimate for the entire error-phase function. In the analysis of coherent anti-Stokes Raman scattering spectra, the error phase can even be approximated by a constant that can be obtained simply from some *a priori* knowledge of the imaginary part of the nonlinear susceptibility.[8] When more phase values are known, a better estimate for the error-phase function can be obtained by a polynomial interpolation.

In Fig. 1 we first show how a finite laser bandwidth affects the error-phase behavior of an isolated spectral peak. Here we assume the amplitude line shape to be a Gaussian distribution function,

$$G(\nu) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{1}{2} \frac{\nu^2}{\sigma^2} \right), \quad (12)$$

and the resonant nonlinear susceptibility to be Lorentzian,

$$\chi^{(2)}(\nu) = \frac{A}{(\nu_0 - \nu) - i\gamma}. \quad (13)$$

The values of σ/γ used in Figs. 1(a), 1(b), and 1(c) have been chosen to be 0.1, 1, and 2, respectively. In the left column of Fig. 1 the dot points indicate the input spectra

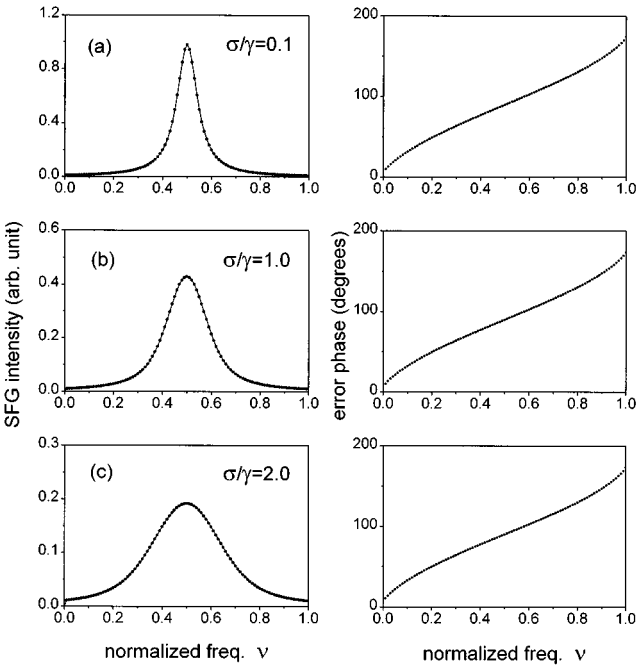

Fig. 1. Effects of a finite laser bandwidth on an error-phase function with a varying broadening ratio of (a) $\sigma/\gamma = 0.1$, (b) $\sigma/\gamma = 1.0$, and (c) $\sigma/\gamma = 2.0$. The dot points in the left column denote the simulated spectra, and their predicted results from the maximum-entropy model are represented by the solid curves. The dotted curves in the right column show the error-phase functions for the corresponding simulated spectra on the left side. The parameter M used in the calculations with the maximum-entropy model was chosen to be 50.

and the solid curves represent the results predicted from Eq. (8) by use of the maximum-entropy method. For different values of σ/γ used in the calculations, the error-phase functions remain almost the same. This is true even in the case shown in Fig. 1(c), where the spectrum has been considerably broadened. This result suggests that the MEPRP should be applicable to a broaden spectra and can be used to solve the phase-retrieval problem in the linewidth-deduction procedure for coherent spectra measured with transform-limited light pulses.

3. LINEWIDTH DEDUCTION WITH THE DECONVOLUTION TECHNIQUE

In Fig. 2 we illustrate the detailed procedure of the Fourier deconvolution process. The dot points in Fig. 2(a) represent a broadened two-peak spectrum with $\sigma/\gamma = 1$. The dotted curves in Figs. 2(b) and 2(c) denote the real and the imaginary parts of the susceptibility deduced from MEPRP. Here we estimate the error phase by using a linear interpolation. The dotted curves on the right-hand side of the figure represent the corresponding inverse Fourier transform results. In Figs. 2(d) and 2(e) the dashed curves denote the inverse Fourier transform of the amplitude line-shape function of the light source. The solid curves in Figs. 2(d) and 2(e) show the inverse Fourier transforms of the real and the imaginary parts that are free from the broadening effect. These curves were obtained from the dividing of the inverse Fourier transforms with that of the line-shape function. Note that from the dashed curves in Figs. 2(d) and 2(e), the inverse Fourier transform of the line-shape function vanishes at a sufficiently long time. Therefore the value in the braces of $F\{\}$ on the right-hand side of Eq. (3) can increase to infinity. This explains why in Figs. 2(d) and 2(e) there are large amplitudes of oscillation in the long local time regime. In order to avoid this problem, we chose a cutoff value on the time coordinate when the Fourier transform in Eq. (3) was performed. The cutoff values on the time coordinate for the real and the imaginary parts of the susceptibility can be different, and they were chosen to be 120 and 150 in this example. The deconvoluted real and imaginary parts are described with the solid curves in Figs. 2(b) and 2(c). Combining the deconvoluted real and imaginary parts, we can generate a deconvoluted spectrum, which is indicated by the solid curve in Fig. 2(a). Although this deconvoluted spectrum shows significant differences from the broaden one that is also shown in Fig. 2(a), we cannot determine how similar the deconvoluted spectrum is to the intrinsic spectrum.

In Fig. 3 we show the comparison between the deconvoluted spectra (solid curves) and the intrinsic spectra (open circles) with various values of σ/γ. We found that the results from the Fourier deconvolution are still reliable in the case when σ is comparable to γ. In Fig. 3(d) the distortion occurring in the deconvoluted spectrum can be as-

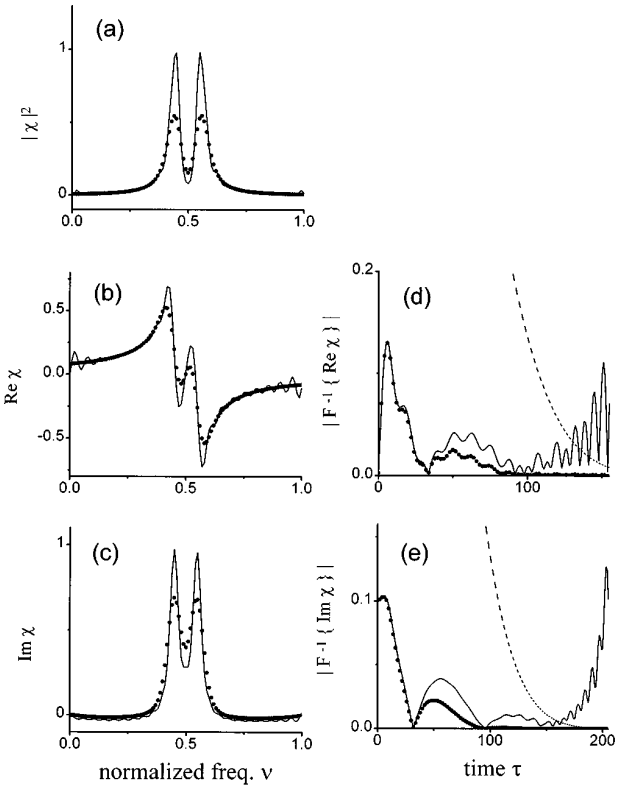

Fig. 2. (a) Broadened spectrum with $\sigma/\gamma = 1.0$ (dot points) and the spectra after deconvolution (solid curve). (b) Real parts and (c) imaginary parts of the nonlinear susceptibility before (dotted curve) and after (solid curve) deconvolution. The corresponding inverse Fourier transforms are shown in (d) and (e) with the same types of curves. The dashed curves in (c) and (d) represent the inverse Fourier transform of the amplitude line-shape function of the light source. The parameter M used in the calculations with the maximum-entropy model has a value of 50.

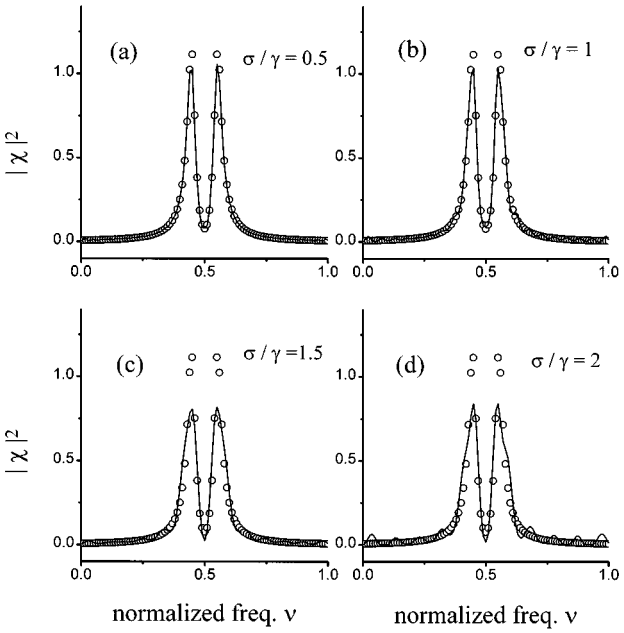

Fig. 3. Comparison of the intrinsic (open circles) and the deconvoluted (solid curves) spectra with different degrees of broadening (a) $\sigma/\gamma = 0.5$; (b) $\sigma/\gamma = 1.0$; (c) $\sigma/\gamma = 1.5$; (d) $\sigma/\gamma = 2.0$.

cribed to a smaller cutoff value on the time coordinate that has to be chosen to avoid the growing oscillation in the long local time region.

4. DISCUSSION

For a practical application of our linewidth-deduction scheme we have to know the amplitude line-shape function of the excitation pulse. For a transform-limited light source the amplitude line-shape function is just the Fourier transform of the temporal envelope of the optical field. It is feasible to deduce the temporal profile of an optical field directly from an experimental measurement with a technique such as the frequency-resolved optical gating method.[12] The Fourier transform of a symmetric temporal envelope is a real and even function. This implies that if the measured power spectrum of the light source turns out to have a Gaussian distribution, which is usually a good approximation in many real sources,[13] we can then simply take its square root as the amplitude line-shape function of the light source.

The uncertainty principle prohibits the result of a measurement from simultaneously achieving unlimited high spectral and temporal resolutions. If a spectroscopic measurement has to possess a time-resolved capability,[14] the best temporal resolution that one can achieve is to perform the measurement with a transform-limited light source. Otherwise, any further improvement in the temporal resolution can only be obtained at the expense of the spectral resolution. The linewidth-deduction method proposed here can free one from this dilemma to some extent. One can achieve this first by sacrificing some spectral resolution to obtain a better temporal resolution in the time-resolved measurement and then by improving the spectral resolution of the degraded spectrum using our proposed procedure. In this way, better temporal and spectral resolutions than those allowed by the uncertainty principle can be obtained. According to our previous analysis, when $\sigma \leqslant \gamma$, we can tolerate the sacrifice to deduce reliably the intrinsic spectra. This result does not violate the uncertainty principle since the raw data from the experimental measurement still obey the uncertainty principle, and the improvement in spectral resolution needs the extra information about the amplitude line-shape function of the light source.

In summary, we have solved the phase-retrieval problem in the linewidth-deduction procedure for nonlinear optical coherent spectra measured with transform-limited light pulses. The obtained intrinsic spectra with our proposed procedure are more suitable than the raw spectra to be fitted by a theoretical curve, which typically has been derived from the assumption of an infinitesimal light bandwidth. Our proposed method is also useful for improving the spectral resolution over the limit of the uncertainty principle as long as the amplitude line-shape function of the light source be fully characterized.

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