Wigner spectrogram representations of heterodyne-detected four-wave-mixing and fluorescence up-conversion

Shaul Mukamel
Department of Chemistry, University of Rochester, Rochester, New York 14619-2321

(Received 7 April 1997; accepted 16 June 1997)

Gated spontaneous emission and four-wave-mixing signals are expressed using a mixed time-frequency representation of the fields (Wigner spectrograms) and of the material response functions. Well-separated and overlapping pulses are described using two-sided (noncausal) and one-sided (causal) spectrograms, respectively. Pump–probe and fluorescence spectra are recast in an anologous form which facilitates the direct comparison of the underlying microscopic dynamics. © *1997 American Institute of Physics.* [S0021-9606(97)01935-1]

I. INTRODUCTION

Nonlinear optical signals are usually calculated either in the time domain or in the frequency domain. A corresponding time or frequency representation of the radiation field is adopted in each case, and the material response is given by either its nonlinear response functions $S^{(n)}$, which depend on n time variables, or susceptibilities $\chi^{(n)}$, which depend on n frequency variables, respectively. These two mathematically equivalent descriptions are related by $n-1$ dimensional Fourier transforms.[1–4] Time-ordered expansions of the optical response functions maintain various degrees of bookkeeping of the time ordering of the interactions with the incoming fields. The density matrix provides a complete time ordering, whereas expansions based on the wave functions only maintain a partial bookkeeping (within the bra or the ket). Such bookkeeping is redundant in the frequency domain, where the order of the various interactions is not controlled and all orderings need to be taken into account. This is why the nth order susceptibilities contain $n!$ times more terms than the response functions, to account for all possible permutations of the incoming fields. The time-domain description is most suitable for impulsive measurements using very short pulses, whereas stationary measurements conducted with monochromatic beams are naturally described in the frequency domain. Experiments involving finite pulses require a hybrid of the two representations. Consider, for example, pump–probe spectroscopy.[5–9] We would like to interpret such measurements in the following intuitive manner: The pump creates a nonequilibrium wave packet which then undergoes some dynamics (vibrational motions, curve-crossing, bond-breaking, etc.), until it is finally detected by the probe. This simple picture, which further allows a classical or a semiclassical interpretation, poses some fundamental questions: How can we relate this evolution to the characteristics of the pump and the probe? How to take into account properly the frequency-time uncertainty in the excitation and detection stages?, and how to interpret these measurements when the pump and the probe overlap in time? The same type of questions apply also to the description of time- and frequency-resolved fluorescence measurements,[10–12] whereby the role of the probe in controlling the temporal and the spectral characteristics of the signal is played by the gating device.[13,14]

In this paper we develop an intermediate mixed time-frequency representation of spontaneous and coherent nonlinear optical signals induced by pulses of arbitrary shape and duration. By representing the various fields using Wigner spectrograms we obtain a clear physical picture that interpolates between the frequency domain and the impulsive limits. Heterodyne-detected four-wave-mixing is discussed in Secs. II and III; the simpler case of well-separated two pulse pairs is analyzed in Sec. II, and extension to the general pulse configuration is given in Sec. III. Formal expressions for time- and frequency-resolved spontaneous emission are derived in Sec. IV. Similar to the heterodyne-detection case, the sequential configuration with a well-separated gate is considered first in Sec. V, and expressions for the general case are given in Sec. VI. Finally, our results are discussed in Sec. VII.

II. HETERODYNE MEASUREMENTS INVOLVING NONOVERLAPPING PAIRS OF PULSES

We consider a material system subjected to the optical electric field

$$E(\mathbf{r},t)=\sum_{j=1}^{4}\left[E_j(t)\exp(-i\omega_j t+i\mathbf{k}_j\cdot\mathbf{r})\right.$$
$$\left.+E_j^*(t)\exp(i\omega_j t-i\mathbf{k}_j\cdot\mathbf{r})\right]. \tag{2.1}$$

Here $E_j(t)$ is the complex amplitude (analytical signal)[15] of the jth field with central frequency ω_j and wave vector $\mathbf{k}_j$. Fields 1, 2, and 3 interact with the system and create the third-order polarization $P^{(3)}$, which generates the signal field. Field 4 does not interact with the system; instead it interferes with the signal field, prior to its detection, to create the heterodyne signal[7,16,17]

$$S_{\rm het}=\mathrm{Im}\int dtE_4(t)P^{(3)}(t). \tag{2.2}$$

Expanding the polarization to third order in the incoming field results in

$$S_{\rm het}=\mathrm{Im}\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}d\tau_3\int_{-\infty}^{\tau_3}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1$$
$$S^{(3)}(t,\tau_3,\tau_2,\tau_1)E_4(t)E(\tau_3)E(\tau_2)E(\tau_1), \qquad (2.3a)$$

with the third-order response function

$$S^{(3)}(t,\tau_3,\tau_2,\tau_1)$$
$$=\left\langle\left(\frac{i}{\hbar}\right)^3[[[V(t),V(\tau_3)],V\tau_2],V(\tau_1)]\right\rangle. \qquad (2.3b)$$

Here the time dependence of $V(\tau)$ is determined by the purely molecular Hamiltonian (H) with no fields

$$V(t)=\exp\left(\frac{i}{\hbar}Ht\right)V\exp\left(-\frac{i}{\hbar}Ht\right). \qquad (2.3c)$$

The various third-order techniques differ by the choice of the signal wave vector $\mathbf{k}_s=\pm\mathbf{k}_1\pm\mathbf{k}_2\pm\mathbf{k}_3$. For brevity we did not expand the field E into its modes in Eq. (2.3a). This must be done in specific applications which require the selection of a particular wave vector $\mathbf{k}_s$ for the signal.

Many techniques employ partially time-ordered pulse sequences. A common case involves the application of a pair of pulses (E_1 and E_2), and the signal generated by the third pulse (E_3) is finally detected using the heterodyne (E_4) pulse. The pulses in each pair (E_1, E_2) and (E_3, E_4) may overlap temporally, however the two pairs are well separated. Typical examples of techniques carried out in this mode include transient gratings, CARS, and pump–probe.[3] The calculation and interpretation of the signal in this case is simpler than the most general case, whereby all pulses may overlap. We shall therefore consider it first and defer the treatment of the general pulse configuration to the next section. The temporal overlap of the pulse pairs results in additional contributions to the signal known as coherent artifacts, which do not have a simple classical interpretation.

The analysis of nonlinear measurements may be facilitated by adopting a joint time-frequency (spectrogram) representation for the fields. The concept of a spectrogram can be traced back to Wigner, who recognized its utility since the early days of quantum mechanics.[18,19] The amplitude of a wave function $\psi(x)$ represents the probability of finding a particle at a given point, whereas its phase is related to the momentum. Wigner proposed to represent the state of the system by the phase-space quasiprobability distribution

$$\rho(q,p)=\frac{1}{2\pi\hbar}\int dx\,\psi^*(q-x/2)\psi(q+x/2)\exp\left(\frac{i}{\hbar}px\right). \qquad (2.4)$$

The information contained in the phase of the wave function is now introduced through the momentum p variable. This remarkable distribution allows us to treat quantum dynamics in phase-space while retaining the complete quantum characteristics of the system. In the classical limit it reduces to the classical phase-space distribution. The same idea can be translated to the time-frequency domain. The time-dependent phase of an electric field $E(t)$ can be expressed using a frequency variable. Given two fields, we define the spectrogram, which represents their joint spectral and temporal profile.

$$W_{\overline{jk}}(t,\omega)\equiv\int_{-\infty}^{\infty}E_j^*(t-\tau/2)E_k(t+\tau/2)\exp(i\omega\tau)d\tau. \qquad (2.5)$$

(Throughout this article, an index with an overbar, e.g., $\overline{j}$, represents the complex conjugated field E_j^*.) Such spectrograms are commonly used in the visualization of acoustic signals[20–22] and have more recently been adopted to optical fields as well.[14,23–30] Unlike the field itself, the spectrogram can be measured by nonlinear correlation techniques. Progress in pulse shaping, with control over both envelope and phase of optical fields,[24,31,32] makes such a representation very attractive for the description of coherent radiative processes.[33,34] The temporal (spectral) integrals over the diagonal spectrograms (with $j=k$) give the spectral (temporal) power spectra of the field:

$$\int\frac{d\omega}{2\pi}W_{j\overline{j}}(t,\omega)=|E_j(t)|^2;$$

$$\int dt\;W_{j\overline{j}}(t,\omega)=|E_j(\omega)|^2. \qquad (2.6)$$

For well-separated pulses, the upper limit of the τ_2 integration in Eq. (2.3a) may be changed from τ_3 to ∞; this allows us to separate the integration variables into two independent pairs (τ_1,τ_2) and (τ_3,t). Making use of Eq. (2.5), Eq. (2.3) can then be recast in the form[14,35]

$$S_{\rm het}=\int\int\int\int\frac{d\omega_1 d\omega_2}{2\pi 2\pi}dt_1\;dt_2 W_{4l}(\omega_2,t_2)$$
$$S^0_{\rm het}(\omega_2,t_2;\omega_1,t_1)W_{kj}(\omega_1,t_1), \qquad (2.7a)$$

with

$$S^0_{\rm het}(\omega_2,t_2;\omega_1,t_1)=\mathrm{Im}\int_0^{\infty}d\tau_1\int_0^{\infty}d\tau_2\;\exp(i\omega_1\tau_1+i\omega_2\tau_2)$$
$$\times\left\langle\left(\frac{i}{\hbar}\right)^3[[[V(t_2+\tau_2/2),V(t_2-\tau_2/2)],V(t_1+\tau_1/2)],V(t_1-\tau_1/2)]\right\rangle. \qquad (2.7b)$$

Here, j,k,l assume the values 1, $\overline{1}$, 2, $\overline{2}$, and 3, $\overline{3}$. $S^0_{\rm het}$ is an ideal *snapshot spectrum* corresponding to pulses with sharply defined frequency and time. It contains all the molecular information necessary for the analysis of measurements conducted with realistic pulses; the actual signal is obtained by convoluting the snapshot spectrum with the field spectrograms [Eq. (2.5)]. In this form the distinct roles of the spectral and temporal profiles of the pulses and of the molecular response are clearly separated. It should be noted that despite the integrations over time and frequency variables, the heterodyne signal $S_{\rm het}$ still depends on frequency and time parameters (not specified here) which characterize the pulse spectrograms.[21,23,36]

III. THE GENERAL HETERODYNE SIGNAL

The main technical difficulty in evaluating Eq. (2.3) is disentangling the multiple time integrations and breaking them into simpler factors involving fewer integrations. To that end we perform the following change of time variables: We shall retain the τ_2 and τ_3 variables and replace t by $s_3=t-\tau_2$ and τ_1 by $s_2=\tau_2-\tau_1$. The integration limits of the new variables s_2 and s_3 are from 0 and ∞, independent of the other variables; this makes it possible to factorize the time integrals. We thus have

$$S_{\rm het}=\int_{-\infty}^{\infty}d\tau_3\int_0^{\infty}ds_3\int_{-\infty}^{\tau_3}d\tau_2\int_0^{\infty}ds_2 \times S^{(3)}(\tau_3+s_3,\tau_3,\tau_2,\tau_2-s_2)E_4^*(\tau_3+s_3) \times E_l(\tau_3)E_k(\tau_2)E_j(\tau_2-s_2). \tag{3.1}$$

Here j,k,l run over all indices of 1, $\overline{1}$, 2, $\overline{2}$, and 3, $\overline{3}$.

The finite (τ_3) limit of the τ_2 integration makes it impossible to factorize the integrations using the Wigner spectrograms defined earlier. This is, however, feasible if we introduce different, one-sided, spectrograms[21,23,36]

$$W^{\pm}_{jk}(\tau,\omega)=\int_0^{\infty}ds\ E_j(\tau\pm s)E_k(\tau)\exp(-i\omega s), \tag{3.2a}$$

with the inverse transform

$$\theta(s)E_j(\tau+s)E_k(\tau)=\int W^{\pm}_{jk}(\tau,\omega)\exp(i\omega s)d\omega. \tag{3.2b}$$

The ordinary Wigner spectrogram is not causal; its value at times t depends on the field at all earlier and later times. In contrast, W^+ and W^- are causal and depend on the fields only at later or earlier times, respectively.

Upon the substitution of these definitions in Eq. (3.1), it assumes the form

$$S_{\rm het}=\mathrm{Im}\int_{-\infty}^{\infty}d\tau_3\int_{-\infty}^{\tau_3}d\tau_2\int d\omega_2\int d\omega_3\ S^0_{\rm het}(\tau_3\omega_3;\tau_2\omega_2)W^+_{4l}(\tau_3,\omega_3)W^-_{kj}(\tau_2,\omega_2), \tag{3.3a}$$

with

$$S^0_{\rm het}(\tau_3\omega_3;\tau_2\omega_2)=\int_0^{\infty}ds_3\int_0^{\infty}ds_2\ \exp(i\omega_3s_3+i\omega_2s_2) \times\left\langle\left(\frac{i}{\hbar}\right)^3[[[V(\tau_3+s_3),V(\tau_3)],V(\tau_2)]V(\tau_2-s_2)]\right\rangle. \tag{3.3b}$$

This form is formally very similar to Eqs. (2.6), which only hold for well-separated pulses. It is possible to introduce a unified definition of causal and noncausal Wigner transforms[21]

$$W_{jk}(\tau,\omega;\sigma)=\int ds E_j(\tau+\sigma s)E_k[\tau-(1-\sigma)s]\exp(-i\omega s), \tag{3.4}$$

$\sigma=1/2$, 1, 0, then give the ordinary (noncausal) W, W^+, and W^-, respectively.

IV. TIME- AND FREQUENCY-GATED SPONTANEOUS EMISSION

We consider a molecular system driven by external fields and characterized by the time-dependent polarization operator $\widetilde{P}(t)$. The system emits a radiation field $\sim\widetilde{P}(t)$ which is detected using a temporal followed by and a spectral gate.[13,37] The time-gating process involves mixing the emitted field with a second field, E_t, creating the frequency-sum signal field (fluorescence-up-conversion).[13,14,38] E_t transmits the field only for a short time interval centered around t_0, resulting in the gated field

$$E'(t)=E_t(t;t_0)\widetilde{P}(t), \tag{4.1}$$

where $E_t(t;t_0)$ is the temporal transmission function. Following the up-conversion process, the field is passed through a spectral gating device (a spectrometer), which transmits energy in a specific frequency interval centered at some selected frequency ω_0, as given by its spectral transmission function $F_s(\omega;\omega_0)$. The gated field now becomes

$$E(\omega)=F_s(\omega;\omega_0)E'(\omega). \tag{4.2}$$

Here $E'(\omega)$ and $E(\omega)$ are the fields before and after passing through the gate. We shall denote them the bare and the gated signal, respectively. Equation (4.2) can be recast in time domain using the convolution,

$$E(t)=\int_{-\infty}^{\infty}F_s(t-t_1;\omega_0)E'(t_1)dt_1. \tag{4.3}$$

For reasons of causality, $F_s(\tau;\omega_0)$ must vanish identically for $\tau<0$. Combining Eq. (4.1) and Eq. (4.3), we obtain for the gated field,[39]

$$E_{st}(t)=\int_{-\infty}^{\infty}d\tau F_s(t-\tau;\omega_0)E_t(\tau;t_0)\widetilde{P}(\tau). \tag{4.4}$$

The detected signal, which depends parametrically on ω_0 and t_0, is given by the integrated intensity of the gated field,

$$S_{st}(t_0,\omega_0)=\int dt|E_{st}(t)|^2. \tag{4.5}$$

Putting all of these together yields

$$S_{st}(t_0,\omega_0)=\int dt\int dt_1\int dt_2 \; F_s(t-t_1;\omega_0)F_s^*(t-t_2;\omega_0) \times E_t(t_1;t_0)E_t^*(t_2;\omega_0)\langle\tilde{P}(t_1)\tilde{P}(t_2)\rangle. \tag{4.6}$$

To highlight the joint role of the temporal and spectral profiles of the fields we shall recast this result in a different form. Making the change of variables: $\overline{t}=(t_1+t_2)/2$; $s=t_1-t_2$, and introducing the Wigner function for the time gate,

$$W_{tt}(\overline{t},\omega;t_0)=\int ds\; E_t^*(\overline{t}-s/2;t_0)E_t(\overline{t}+s/2;t_0), \tag{4.7}$$

Eq. (4.5) assumes the form

$$S_{st}(t_0,\omega_0)=\int dt\int d\overline{t}\int ds\int d\omega\;\exp(i\omega s) \times F_s^*(t-\overline{t}-s/2;\omega_0)F_s(t-\overline{t}+s/2;\omega_0) \times W_{tt}(\overline{t},\omega;t_0). \tag{4.8}$$

We next introduce the Fourier transform of the spectral gate amplitude

$$F_s^*(t-\overline{t}-s/2;\omega_0)F_s(t-\overline{t}+s/2;\omega_0) =\int\int d\omega_1\; d\omega_2\; F_s(\omega_1;\omega_0)F_s^*(\omega_2;\omega_0) \times\exp[i(\omega_1-\omega_2)(t-\overline{t})+i(\omega_1-\omega_2)s]. \tag{4.9}$$

The t integration can now be performed, resulting in $\delta(\omega_1-\omega_2)$. We finally obtain

$$S_{st}(t_0,\omega_0)=\int d\overline{t}\int d\omega_1\Phi_{st}(\overline{t},\omega;t_0,\omega_0)S_0(\overline{t},\omega_1). \tag{4.10}$$

Here

$$S_0(\overline{t},\omega_1)=\int ds\langle\tilde{P}(t-s/2)\tilde{P}(t+s/2)\rangle\exp(i\omega_1 s), \tag{4.11}$$

and

$$\Phi_{st}(\overline{t},\omega;t_0,\omega_0)=\int d\omega_1|F_s(\omega_1;\omega_0)|^2W_{tt}(\overline{t},\omega_1-\omega';t_0). \tag{4.12}$$

$S_0(\overline{t},\omega_1)$ is the *bare autocorrelation signal* corresponding to an ideal infinitely resolved gating both in time and frequency, and $\Phi(t',\omega';t_0,\omega_0)$ is the joint gate function that depends on the transmission functions of both the spectral and time gates, as well as the order in which they are applied. Common models for the gate functions were introduced and displayed in Ref. 14. The bare signal is not positive definite and it may even assume negative values. The gated signal, in contrast, is written as a squared amplitude (of the gated field) and is therefore always positive. The gate function $\Phi(t',\omega';t_0,\omega_0)$ is usually localized in both time and frequency. An ideal time gate, $\Phi(t',\omega';t_0,\omega_0)=\delta(t_0-t')$, yields the time-resolved signal,

$$I_{\text{auto}}(t_0)\equiv\int S_0(t_0,\omega)d\omega=|\tilde{P}(t_0)|^2, \tag{4.13a}$$

whereas an ideal spectral gate, $\Phi(t',\omega';t_0,\omega_0)=\delta(\omega_0-\omega')$, gives the frequency-resolved signal,

$$I_{\text{auto}}(\omega_0)\equiv\int S_0(t_0,\omega_0)dt_0=|\tilde{P}(\omega_0)|^2. \tag{4.13b}$$

Note, however, that it is not possible to construct an ideal temporal and spectral gate, $\Phi(t',\omega';t_0,\omega_0)=\delta(t_0-t')\delta(\omega_0-\omega')$, since it violates the fundamental uncertainty of Fourier transforms $\Delta\omega\Delta t\geqslant 1$.

The gated signal can be alternatively recast in the form:

$$S_{st}(t_0,\omega_0)=\int d\omega_1|F_s(\omega_1;\omega_0)|^2S_{st}^0(t_0,\omega_1), \tag{4.14a}$$

with

$$S_{st}^0(t_0,\omega_1)=\int d\overline{t}\int d\omega W_{tt}(\overline{t},\omega_1-\omega,t_0)S_0(\overline{t},\omega), \tag{4.14b}$$

S_{st}^0 being the up-conversion signal obtained with an ideal spectral gate. Note that the time and frequency arguments of W_{tt} satisfy the uncertainty relation $\Delta\omega\Delta t\simeq 1$. Φ_{st} also takes into account the finite spectrometer bandwidth and the uncertainty is no longer transform-limited ($\Delta\omega\Delta t>1$).

These results form the basis for the analysis presented in the following section, where we expand the polarization perturbatively in the pump field and derive a mixed time-frequency expression for the signal. As in the case of heterodyne detection, we shall first consider the simpler situation whereby the gate is temporarily well separated from the pump. Proceeding along the same lines of Sec. II we obtain a compact closed expression for the signal. The more general case of arbitrary timing of the gate will be considered in Sec. VI.

V. FLUORESCENCE UP-CONVERSION WITH A WELL-SEPARATED TIME GATE

Spontaneous light emission (SLE) at short times contains a direct scattering (Raman) contribution, and a long-time fluorescence component. When the gate does not overlap temporally with the pump, the Raman contribution is negligible and the calculation is greatly simplified.[40] Expanding the polarization $\tilde{P}$ to first order in the pump we obtain

$$\langle\tilde{P}(t_1)\tilde{P}(t_2)\rangle=\int_{-\infty}^{t_1}d\tau_1\int_{-\infty}^{t_2}d\tau_2 \; \langle V(\tau_1)V(t_1)V(t_2)V(\tau_2)\rangle E(\tau_1)E(\tau_2). \tag{5.1}$$

For a well-separated gate, we can change both upper integration limits to ∞. Making the rotating wave approximation, Eq. (4.10) can then be recast in the form

$$S_{\mathrm{SLE}}(t_0,\omega_0)=\int\int\int\int dt\ d\omega\ dt'\ d\omega' \times\Phi_{st}(t,\omega';t_0,\omega_0)\overline{S(t,\omega;t',\omega')} \times W_{11}^{-}(t,'\omega'), \tag{5.2}$$

with the bare (snapshot) spectrum

$$\overline{S_{\mathrm{SLE}}}(t\omega;t'\omega')=\int_0^\infty ds\int_0^\infty ds'\ \exp(is'\omega'+is\omega) \langle V(t'+s')V(t+s)V(t-s)V(t'-s')\rangle \tag{5.3}$$

$\overline{S}$ represents an emission spectrum at t, ω induced by an ideal pump (E_1), which is infinitely sharply defined both in frequency and in time $W_1(t',\omega')=\delta(t'-t_0)\delta(\omega'-\omega_0)$. Even though such a pulse is unrealistic, the bare spectrum is extremely useful since the actual spectrum is simply obtained by convoluting it with the actual Wigner spectrogram of the pump. As in Sec. II, we have expressed the signal using ordinary (two-sided) rather than one-sided spectrograms. This representation is closely connected with the classically intuitive doorway/window picture of sequential pump–probe or spontaneous emission spectroscopy.[3,35]

VI. FLUORESCENCE UP-CONVERSION WITH AN ARBITRARY GATE

When the gate is not well separated from the pump we may proceed in an analogous manner to our analysis of heterodyne detection in Sec. III and derive general expression for the signal in terms of a one-sided joint Wigner spectrogram representing the gate and the pump fields. This form is obtained in the Appendix. In this section we adopt a different route. We first separate the signal into three components representing specific time orderings of the fields. This will result in a less compact expression than that of the Appendix. However, this expression now depends on the pure Wigner spectrograms of the pump and the gate, which makes its physical origin more transparent.

We start with the following form [see Eq. (4.14a)]

$$S_{\mathrm{SLE}}(t_0,\omega_0)=\int d\omega_1|F_s(\omega_1;\omega_0)|^2S^0_{\mathrm{SLE}}(t_0,\omega_1). \tag{6.1}$$

S^0_{SLE} represents the spectrum for an ideal spectral gate

$$S_{\mathrm{SLE}}(t_0,\omega_1)=\int dt_1\int dt_2\langle\tilde{P}(t_1)\tilde{P}(t_2)\rangle \times E_t(t_1;t_0)E_t^*(t_2;t_0) \times\delta[t-(\tau_1+\tau_2)/2]\exp[i\omega_1(t_1-t_2)]. \tag{6.2}$$

This expression can be recast in the form[40]

$$S_{\mathrm{SLE}}=S^{\mathrm{I}}_{\mathrm{SLE}}+S^{\mathrm{II}}_{\mathrm{SLE}}+S^{\mathrm{III}}_{\mathrm{SLE}}+\mathrm{c.c.}, \tag{6.3a}$$

where

$$S^{\mathrm{I}}_{\mathrm{SLE}}(t_0,\omega_1)=\int dt\int_{-\infty}^{t}d\tau_3\int_{-\infty}^{\tau_3}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1 \times E_1(\tau_1)E_1^*(\tau_2)\exp[i\omega_1(t-\tau_3)] \times\langle V(\tau_2)V(\tau_3)V(t)V(\tau_1)\rangle E_t(t;t_0) \times E_t(\tau_3;t_0), \tag{6.3b}$$

$$S^{\mathrm{II}}_{\mathrm{SLE}}(t_0,\omega_1)=\int dt\int_{-\infty}^{t}d\tau_3\int_{-\infty}^{\tau_3}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1E_1^*(\tau_1) \times E_1(\tau_2)\exp[i\omega_1(t-\tau_3)] \langle V(\tau_1)V(\tau_3)V(t)V(\tau_2)\rangle E_t(t;t_0)E_t(\tau_3;t_0), \tag{6.3c}$$

$$S^{\mathrm{III}}_{\mathrm{SLE}}(t_0,\omega_1)=\int dt\int_{-\infty}^{t}d\tau_3\int_{-\infty}^{\tau_3}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1E_1^*(\tau_1)E_1(\tau_3) \times\exp[i\omega_1(t-\tau_2)]\langle V(\tau_1)V(\tau_2)V(t)V(\tau_3)\rangle \times E_t(t;t_0)E_t(\tau_2;t_0). \tag{6.3d}$$

This result can also be obtained by combining Eqs. (9.10b) with (5.28) of Ref. 3 and adding the time gate to each term. [The spectral gate can be simply added at the end using Eq. (6.1) and we will not consider it any longer.] Proceeding along the lines of Sec. III, we change variables $t=\tau_3+s$; $\tau_1=\tau_2-s_1$ and obtain

$$S^{\mathrm{I}}_{\mathrm{SLE}}(t_0,\omega_1)+S^{\mathrm{II}}_{\mathrm{SLE}}(t_0,\omega_1) =\int_{-\infty}^{\infty}d\tau_3\int_0^\infty ds\int_{-\infty}^{\tau_3}d\tau_2\int_0^\infty ds_1E_1(\tau_2-s_1)E_1^*(\tau_2) \times E_t(\tau_3+s;t_0)E_t(\tau_3;t_0)\exp(i\omega_1s), [\langle V(\tau_2)V(\tau_3)V(\tau_3+s)V(\tau_2-s_1)\rangle +\langle V(\tau_2-s_1)V(\tau_3)V(\tau_3+s)V(\tau_2)\rangle], \tag{6.4a}$$

$$S^{\mathrm{III}}_{\mathrm{SLE}}(t_0,\omega_1)=\int_{-\infty}^{\infty}d\tau_3\int_0^\infty ds\int_{-\infty}^{\tau_3}d\tau_2\int_0^\infty ds_1 \times E_1^*(\tau_2-s_1)E_1(\tau_3)E_t(\tau_3+s;t_0) \times E_t(\tau_2;t_0)\exp[i\omega_1(\tau_3-\tau_2+s)] \times\langle V(\tau_2-s_1)V(\tau_2)V(\tau_3+s)V(\tau_3)\rangle. \tag{6.4b}$$

These results can be recast using one-sided Wigner functions

$$S^{\mathrm{I}}_{\mathrm{SLE}}(t_0,\omega_1)+S^{\mathrm{II}}_{\mathrm{SLE}}(t_0,\omega_1) =\int_{-\infty}^{\infty}d\tau_3\int_{-\infty}^{\tau_3}d\tau_2\int d\omega_3\int d\omega_2W_{11}^{-}(\tau_2,\omega_2) \times W_{tt}^{+}(\tau_3,\omega_1-\omega_3;t_0)F(\tau_3,\omega_3;\tau_2,\omega_2) \tag{6.5a}$$

$$S^{\mathrm{III}}_{\mathrm{SLE}}(t_0,\omega_1)$$
$$=\int_{-\infty}^{\infty}d\tau_3\int_{-\infty}^{\tau_3}d\tau_2\int d\omega_3\int d\omega_2 W_{11}(\tau_2,\omega_2)$$
$$\times W^{+}_{1t}(\tau_3,\omega_1-\omega_3;t_0)F'(\tau_3,\omega_3;\tau_2,\omega_2). \quad (6.5b)$$

Here

$$F(\tau_3,\omega_3;\tau_2,\omega_2)=\int_0^{\infty}ds\int_0^{\infty}ds_1\ \exp(i\omega_3 s-i\omega_2 s_1)$$
$$\times[\langle V(\tau_2)V(\tau_3)V(\tau_3+s)V(\tau_2-s_1)\rangle$$
$$+\langle V(\tau_2-s_1)V(\tau_3)V(\tau_3+s)V(\tau_2)\rangle], \quad (6.6a)$$

and

$$F'(\tau_3,\omega_3;\tau_2,\omega_2)=\int_0^{\infty}ds\int_0^{\infty}ds_1\ \exp(i\omega_3 s-i\omega_2 s_1)$$
$$\times\langle V(\tau_2-s_1)V(\tau_2)V(\tau_3+s)V(\tau_3)\rangle. \quad (6.6b)$$

$S^{\mathrm{I}}+S^{\mathrm{II}}$ represent a sequential process (pump-first, gate-later). Consequently, they depend separately on the pump-spectrogram which describes the preparation of an excited-state wave packet, and on the gate spectrogram which represents the ''window'' through which the system is probed. Only the coherent S^{III} (Raman-type) contribution depends on the joint field-gate spectrogram. This is to be contrasted with the equivalent expression given in the Appendix, which does not keep track of the time ordering and depends solely on the joint pump-gate spectrogram.

VII. DISCUSSION

In this article we showed how both heterodyne-detected four-wave mixing and gated spontaneous emission may be expressed in terms of Wigner spectrograms of the incoming fields and the gate. Sequential optical processes that can be represented by two pairs of well-separated pulses are given by noncausal (two-sided) spectrograms. More generally, however, the signals depend on one-sided (positive or negative) causal spectrograms that maintain the necessary bookkeeping of time ordering.

Pump–probe spectroscopy is a special case of heterodyne-detected four-wave mixing. The technique involves only two pulses: the pump (1) and the probe (2). In this case the probe serves also as the heterodyne field. The probe differential absorption is then given by Eqs. (2.7) and (3.3) provided we substitute 1 for the indices j and k, and 2 for the indices j and 4. Comparing these with Eqs. (5.2) or (6.5) illustrates the close formal connection between the description of pump–probe and spontaneous light emission spectroscopies.[39] Both techniques are expressed using (different) combinations of four-point correlation functions of the material system: Both depend on a pump field. The gating field in SLE plays a very similar role to the probe in pump–pulse spectroscopy. Sequential measurements conducted with nonoverlapping pulse pairs have an obvious classical interpretation in terms of preparation, evolution, and detection stages. For overlapping pulses the signals are more complicated. However, in either case they may be expressed using Wigner spectrograms of the fields. Various methods are now available to measure optical electric fields (both amplitudes and phases).[24,16,17] The spectrograms provide a convenient way for visualizing these fields and incorporating explicitly the roles of their spectral and temporal profiles in the resulting signals. Recent applications demonstrated how Wigner spectrograms can be used in the study of the role of electronic correlations in semiconductors[16] and conjugated polyenes,[30] and the nature of exciton dynamics in biological complexes.[30] Mixed time-frequency representations should also be helpful in the analysis of higher order measurements[41–43] involving multiple sequences of pulses.

ACKNOWLEDGMENTS

The support of the National Science Foundation and the U.S. Air Force Office of Scientific Research is gratefully acknowledged.

APPENDIX: NON-TIME-ORDERED EXPRESSION FOR GATED SPONTANEOUS EMISSION

Expanding Eq. (4.11) to second order in the pump, and substituting in Eq. (4.14b), gives

$$S^{0}_{\mathrm{SLE}}(t,\omega)=\int dt_1\int dt_2\int_{-\infty}^{t_1}d\tau_1\int_{-\infty}^{t_2}d\tau_2$$
$$\langle V(\tau_1)V(t_1)V(t_2)V(\tau_2)\rangle$$
$$\times E_1(t_1)E_t^{*}(t_2)E_1(\tau_1)E_1(\tau_2)$$
$$\times\delta[t-(t_1+t_2)/2]\exp[i\omega(\tau_1-\tau_2)]. \quad (A1)$$

Introducing the time variables $\tau_1=t_1-s_1$; $\tau_2=t_2-s_2$, we obtain

$$S^{0}_{\mathrm{SLE}}(t,\omega)=\int dt_1\int dt_2\int_0^{\infty}ds_1\int_0^{\infty}ds_2$$
$$\langle V(t_1-s_1)V(t_1)V(t_2)V(t_2-s_2)\rangle$$
$$\times E_t(t_1)E_t^{*}(t_2)E_1(t_1-s_1)E_1(t_2-s_2)$$
$$\times\delta[t-(t_1+t_2)/2]\exp[i\omega(t_1-t_2-s_1+s_2)]. \quad (A2)$$

Defining

$$F(t_1\omega_1;t_2\omega_2)=\int_0^{\infty}ds_1\int_0^{\infty}ds_2\ \exp(i\omega_1 s_1+i\omega_2 s_2)$$
$$\times\langle V(t_1-s_1)V(t_1)V(t_2)V(t_2-s_2)\rangle, \quad (A3)$$

we have

$$\overline{S(t_1\omega)}=\int dt_1\int dt_2\int d\omega_1\int d\omega_2\delta[t-(t_1+t_2)/2]$$
$$\times\exp[i\omega(t_1-t_2)]F(t_1\omega_1;t_2\omega_2)$$
$$\times W^{-}_{1t}(t_1,\omega_1)W^{-}_{1t}(t_2,\omega_2). \quad (A4)$$

This form only depends on the joint Wigner spectrogram of the pump and the gate.

$$W^{-}_{1t}(t,\omega)\equiv\int_0^\infty ds\ E_t(t)E_1^*(t-s)\exp(i\omega s). \tag{A5}$$

This spectrogram attains a simple form when the pump and the gate are temporally well separated. To see that we first write $\exp(i\omega s)=\exp[i\omega t-i\omega(t-s)]$. For well-separated pulses we can change the lower integration limit to $-\infty$ and obtain

$$W^{-}_{1t}(t,\omega)\cong E_t(t)E_1(\omega)\exp(i\omega t). \tag{A6}$$

Using this form, the present expression reproduces the results of Sec. V, which were given in terms of the separate pump and the gate spectrograms.

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