

Microscopic theory of the transient grating experiment

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We present the first fully microscopic theory of the generation of the transient grating signal from a crystal of interacting molecules. We derive a general expression for the signal, measured at a time immediately after a short probe pulse, in terms of the exciton Green function. This expression agrees with previous calculations of the grating signal, in which the experiment was treated as a diffraction process. It is also shown that the temporal profile of the signal pulse is, in general, different from that of the probe pulse. This result is inconsistent with the usual diffraction picture. Our treatment of this experiment as a transient four-wave mixing process rather than as a diffraction process allows us to derive an expression for the signal in terms of equilibrium correlation functions of the dipole operator. Using this formulation, we discuss the relationship of this experiment to other nonlinear spectroscopic techniques.

I. INTRODUCTION

The motion of electronic excitations (excitons) in condensed phase systems has become an important area of investigation in recent years.¹⁻⁶ In a perfect crystal of identical molecules or atoms at zero temperature, the electronic states are delocalized, and the motion of an electronic excitation through the crystal is coherent or wave-like in character.¹ In the opposite limit of a strongly disordered system, the energy fluctuations arising from causes such as spatial disorder, substitutional disorder, and excitation-lattice interactions overwhelm the intersite interactions, and the electronic excitations are best described as localized molecular or atomic states. In this case, the localized excitations move through the medium with an incoherent or "hopping" motion that can be described by the Pauli Master equation.⁷ An example of such a system is a concentrated dye solution at room temperature.⁸ Since perfectly coherent exciton motion is characteristic of an ideal crystal, it is to be expected that actual crystals of high purity at very low temperatures will exhibit some degree of exciton coherence. The nature of exciton transport in low temperature crystals has been investigated with a variety of experimental methods, including the measurement of exciton trapping by impurities,^{2,4,9} magnetic resonance techniques,^{2,4,10} and the determination of optical line shapes.^{2,4} The experimental observables in these investigations are only indirectly related to exciton motion. For example, in an impurity trapping experiment, quantitative interpretation of the data is complicated by the fact that the dynamics of the trapping process must be understood in addition to the exciton motion. The trapping process is not just a probe but actually affects the exciton dynamics.

The motion of optical excitations can be measured directly in the transient grating (TG) experiment, which has been used to study a wide variety of systems, including molecular crystals,¹¹ ionic crystals,¹²⁻¹⁴ and solutions.^{14,15} This technique has also been used to study the reorientation of molecules in solution¹⁶ and the motion of polymer chains in polymer melts.¹⁷ The TG is a time-resolved experiment in which the sample initially interacts with a pair of simultaneous laser pulses with wave vectors \mathbf{k}_1 and \mathbf{k}_2 . After a delay

period, the sample is probed by a third pulse with wave vector \mathbf{k}_3 , and a coherent signal with wave vector $\mathbf{k}_3 \pm (\mathbf{k}_1 - \mathbf{k}_2)$ is detected. The currently accepted interpretation of this experiment is as follows.^{4,14,18} The pair of excitation pulses creates an optical interference pattern in the sample. In the peaks of this interference pattern, a higher density of excited states will be created in the material than in the nulls. The effect of the simultaneous excitation pulses is thus to create a sinusoidally varying spatial distribution of excited states. Since the complex index of refraction of the material differs in regions of low and high excited state density, the sample has a sinusoidally varying index of refraction, and, therefore, acts as a diffraction grating for the probe pulse. The amplitude of the diffracted signal is proportional to the spatial Fourier transform of the distribution of excited states, evaluated at the grating wave vector $\mathbf{k}_1 - \mathbf{k}_2$. The TG signal, measured as a function of the delay time between excitation and probe, will decay due to the excited state lifetime and to exciton motion that occurs over distances that are large compared to the grating wavelength. The TG experiment provides a direct measure of excited state transport on a distance scale that is determined by $|\mathbf{k}_1 - \mathbf{k}_2|$, and which, therefore, can be adjusted by varying the angle between the excitation beams.

The theoretical description of the TG experiment can be divided into three stages: excitation, time evolution of the excited state during the delay period, and detection with the probe pulse. Previous theoretical treatments of the TG by Kenkre and co-workers^{5,19} and by Garrity and Skinner²⁰ have focused on the first two stages: excitation and evolution. The amplitude of the detected signal is assumed to be proportional to the spatial Fourier transform of the distribution of excited state populations immediately before probing, in accordance with the interpretation of the TG experiment as a diffraction process. In these studies, the time evolution of the spatial distribution of excited states is calculated for a linear chain obeying the stochastic Hamiltonian of Haken and Strobl.^{6,21} The TG signal is shown to be a sensitive measure of exciton coherence. The current interpretation of the third stage of the TG experiment as a diffraction process is phenomenological. It is based on the existence of spatial variations in the index of refraction, a macroscopic

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quantity, and has not been justified from a microscopic perspective.

In this work, we present the first completely microscopic calculation of the generation of the TG signal from a crystal. The calculation is carried out as follows. The density matrix at the time at which the signal is generated is determined from the quantum mechanical Liouville equation. The macroscopic electric polarization that produces the coherent signal is then put as a source into Maxwell's equations, from which the intensity of the coherent signal can be calculated. The TG signal is calculated for a model crystal that is composed of interacting two-level systems. We derive a general expression for the TG signal in terms of the tetradic Green function (superoperator) of the exciton. This expression [Eq. (2.38)] provides a precise definition of the microscopic information content of the TG signal. The amplitude of the signal, measured at a time immediately after the application of a short probe pulse, is shown to be proportional to the spatial Fourier transform of the excited state distribution, evaluated at the grating wave vector, in agreement with the current interpretation of the experiment. We also show that the temporal profile of the signal pulse is not identical to that of the probe. This result is not consistent with the usual diffraction picture.

The microscopic theory of the transient grating is presented in Sec. II. We also present an expression for the TG signal in terms of an equilibrium correlation function of four dipole operators. The correlation function formalism allows us to relate the TG observable to other nonlinear experiments, such as the photon echo²² and steady-state four-wave mixing.²³

In Sec. III we discuss the validity of the interpretation of the TG as a diffraction process and consider the temporal profile of the signal pulse. We show that in the limit that the duration of the probe pulse is small compared to the inverse rates of all relaxation processes, the temporal profile of the signal pulse is determined by excited state relaxation processes. In this limit, the diffraction interpretation does not provide a complete description of the experiment.

II. THE TRANSIENT GRATING SIGNAL

In the transient grating (TG) experiment, the sample first interacts with an electric field of the form

$$E(\mathbf{r}, t) = E_1(\mathbf{r}, t) \cos(\omega_1 t - \mathbf{k}_1 \cdot \mathbf{r}) + E_2(\mathbf{r}, t) \cos(\omega_2 t - \mathbf{k}_2 \cdot \mathbf{r}), \quad (2.1)$$

where $\omega_2 = \omega_1$.

After a delay period, a probe pulse of the form

$$E(\mathbf{r}, t) = E_3(\mathbf{r}, t) \cos(\omega_3 t - \mathbf{k}_3 \cdot \mathbf{r}) \quad (2.2)$$

is applied. The macroscopic electric polarization of the crystal P is related to the density matrix ρ by

$$P = \text{Tr}[\hat{\mu}\rho], \quad (2.3)$$

where $\hat{\mu}$ is the transition dipole operator for the crystal. Each of the N sites in the crystal is taken to be a two-level system, in which case $\hat{\mu}$ is given by

$$\hat{\mu} = \sum_{j=1}^N \hat{\mu}_j, \quad (2.4)$$

$$\hat{\mu}_j = \mu(a_j^\dagger + a_j). \quad (2.5)$$

μ is the magnitude of the site transition dipole, and a_j (a_j^\dagger) is the annihilation (creation) operator for an excitation at the site labeled j . These operators obey the relations

$$[a_j, a_n] = [a_j, a_n^\dagger] = 0, \quad j \neq n, \quad (2.6a)$$

$$a_j^\dagger a_j + a_j a_j^\dagger = 1. \quad (2.6b)$$

The time evolution of the density matrix is governed by the Liouville equation:

$$\frac{d\rho}{dt} = \frac{-i}{\hbar} [H, \rho], \quad (2.7)$$

$$H = H_0 + V, \quad (2.8)$$

$$V = -\hat{\mu} \cdot \mathbf{E}. \quad (2.9)$$

H_0 is the Hamiltonian of the crystal in the absence of radiation. Equation (2.7) can be written in terms of the tetradic Liouville operator:

$$\frac{d\rho}{dt} = \frac{-i}{\hbar} L\rho, \quad (2.10)$$

$$(L\rho)_{ab} = \sum_{cd} L_{ab,cd} \rho_{cd}, \quad (2.11)$$

$$L_{ab,cd} = H_{ac} \delta_{bd} - H_{db} \delta_{ac}. \quad (2.12)$$

From Eqs. (2.8) and (2.12), L can be written as

$$L = L_0 + \mathcal{V}, \quad (2.13)$$

where

$$L_0 = [H_0,], \quad (2.14)$$

$$\mathcal{V} = [V,]. \quad (2.15)$$

The solution of Eq. (2.10) in the absence of radiation is given by

$$\rho(t + \tau) = \mathcal{G}(\tau)\rho(t), \quad (2.16)$$

where $\mathcal{G}(t)$ is the tetradic time evolution operator that obeys the equation

$$\frac{d\mathcal{G}(t)}{dt} = \frac{-i}{\hbar} L_0 \mathcal{G}(t), \quad (2.17)$$

with the initial condition that $\mathcal{G}(0)$ is the unit tetradic. We define \mathcal{G}_e (\mathcal{G}_p) to be the tetradic time evolution operator in the presence of the excitation (probe) field. These operators satisfy the equations

$$\frac{d\mathcal{G}_e}{dt} = \frac{-i}{\hbar} (L_0 + \mathcal{V}_1 + \mathcal{V}_2) \mathcal{G}_e, \quad (2.18)$$

$$\frac{d\mathcal{G}_p}{dt} = \frac{-i}{\hbar} (L_0 + \mathcal{V}_3) \mathcal{G}_p, \quad (2.19)$$

$$\mathcal{V}_\alpha = [V_\alpha,], \quad (2.20)$$

$$V_\alpha = - \sum_{j=1}^N \hat{\mu}_j \cdot \mathbf{E}_\alpha(\mathbf{r}_j, t) \cos(\omega_\alpha t - \mathbf{k}_\alpha \cdot \mathbf{r}_j), \quad \alpha = 1, 2, 3. \quad (2.21)$$

The polarization at a site labeled 1 at the end of the TG pulse sequence is given by

$$P(\mathbf{r}_1, t) = \bar{P}(\mathbf{r}_1, t) + \text{c.c.}, \quad (2.22)$$

$$\bar{P} = \text{Tr}[\bar{\mu}_1 \rho(t)], \quad (2.23)$$

$$\bar{\mu}_1 = \mu a_1, \quad (2.24)$$

$$\rho(t) = \mathcal{G}_p(\tau_p) \mathcal{G}(t) \mathcal{G}_e(\tau_e) \rho(0). \quad (2.25)$$

τ_e and τ_p are the durations of the excitation and probe pulses, and t is the delay time between pulses. $\rho(0)$ is the initial density matrix, which will be taken to be $|0\rangle\langle 0|$, where $|0\rangle$ is the crystal ground state. Substitution of Eq. (2.25) into Eq. (2.23) yields

$$\bar{P}(\mathbf{r}_1, t) = \text{Tr}[R \mathcal{G}(t) \rho(\tau_e)], \quad (2.26)$$

$$\rho(\tau_e) \equiv \mathcal{G}_e(\tau_e) \rho(0), \quad (2.27)$$

$$R \equiv \mathcal{G}_p^\dagger(\tau_p) \bar{\mu}_1. \quad (2.28)$$

Equation (2.28) is derived in Appendix A. The matrix elements of the Hermitian conjugate of a tetradic operator are given by

$$\mathcal{G}_{ab,cd}^\dagger = [\mathcal{G}_{cd,ab}]^*. \quad (2.29)$$

Equation (2.26) shows that the calculation of the polarization can be divided into three steps. First, $\rho(\tau_e)$, the density matrix at the end of the excitation period is calculated. Next, the evolution of the density matrix during the delay time is determined. The polarization is given by the expectation value at the time of probing of the transient grating detection operator R of Eq. (2.28). [Note that R in Eq. (2.28) is an ordinary (dyadic) operator.]

We will make the following assumptions in the calculation of R and $\rho(\tau_e)$. The excitation and probe pulses are taken to have rectangular temporal profiles and to be sufficiently short that the intersite interactions may be neglected in calculating the time evolution of the system during the pulse. The rotating wave approximation is applied. The excitation fields are taken to be weak, and $\rho(\tau_e)$ is calculated to first order in the amplitude of each field. If the excitation fields are sufficiently weak, the TG experiment can be used to measure the dynamics of singly excited states of the crystal. If the excitation fields are intense, the signal will have a contribution from multiply excited states.

The detection operator R of Eq. (2.28) is evaluated in Appendix A. R is shown to have matrix elements with wave vectors 0 , \mathbf{k}_3 , and $2\mathbf{k}_3$. Only $R(\mathbf{k}_3)$, the contribution with wave vector \mathbf{k}_3 , will contribute to the TG signal,

$$R(\mathbf{k}_3) = -i\mu \exp[i(\mathbf{k}_3 \cdot \mathbf{r}_1 - \omega_3 \tau_p)] \times \sin(\theta_3/2) \cos(\theta_3/2) [2a_1^\dagger a_1 - I], \quad (2.30)$$

$$\theta_3 = \mu E_3 \tau_p / \hbar. \quad (2.31)$$

In Eq. (2.30), I is the unit operator. We next turn to the calculation of $\rho(\tau_e)$, the density matrix after excitation. In the previous theoretical treatments of the TG by Kenkre and co-workers^{5,19} and by Garrity and Skinner,²⁰ two types of excitation have been considered. In the first type, which we will denote *coherent preparation*, the excitation pulses prepare an exciton eigenstate. In the second sort, denoted *incoherent preparation*, $\rho(\tau_e)$ is assumed to be diagonal in the site representation. This condition is believed to describe an experiment in which the system is initially excited into a higher vibronic state that rapidly relaxes to the state of interest. The phase relationship between two sites is thus rapidly destroyed.¹³ In Appendix B, we calculate $\rho(\tau_e)$ in second order in the amplitudes of the excitation fields. The result is

$$\rho_{mn}(\tau_e) = C_{mn} \{ (\theta_1 \theta_2 / 4) \{ \exp[i(\mathbf{k}_1 \cdot \mathbf{r}_m - \mathbf{k}_2 \cdot \mathbf{r}_n)] + \exp[i(\mathbf{k}_2 \cdot \mathbf{r}_m - \mathbf{k}_1 \cdot \mathbf{r}_n)] \} + (\theta_1^2 / 4) \exp[i\mathbf{k}_1 \cdot (\mathbf{r}_m - \mathbf{r}_n)] + (\theta_2^2 / 4) \exp[i\mathbf{k}_2 \cdot (\mathbf{r}_m - \mathbf{r}_n)] \}, \quad (2.32)$$

$$\rho_0(\tau_e) = -\sum_m \rho_{mm}(\tau_e), \quad (2.33)$$

$$\theta_j = \mu E_j \tau_e / \hbar. \quad (2.34)$$

In Eq. (2.32), $\rho_{mn} = \langle 0 | a_m \rho a_n^\dagger | 0 \rangle$, and in Eq. (2.33), $\rho_0 = \langle 0 | \rho | 0 \rangle$. The TG signal is generated by the terms in Eq. (2.32) that are linear in the amplitudes of each of the excitation fields. The coefficient C_{mn} is determined by the excitation process. In the case of coherent preparation, $C_{mn} = 1$, and for incoherent preparation, $C_{mn} = \delta_{mn}$.

The density matrix after excitation in the TG experiment has been calculated previously in the incoherent preparation case by Kenkre and co-workers^{5,19} and in the coherent preparation case by Garrity and Skinner.²⁰ Their results can be combined into the expression

$$\rho_{mn}(\tau_e) \propto C_{mn} \cos(\boldsymbol{\kappa} \cdot \mathbf{r}_n) \cos(\boldsymbol{\kappa} \cdot \mathbf{r}_m), \quad (2.35)$$

$$\boldsymbol{\kappa} = (1/2)(\mathbf{k}_1 - \mathbf{k}_2), \quad (2.36)$$

where C_{mn} is defined as in Eq. (2.32). Equation (2.35) was obtained for a linear chain with lattice vector \mathbf{a} , under the condition that the excitation beams are oriented symmetrically with respect to the lattice $[(\mathbf{k}_1 + \mathbf{k}_2) \cdot \mathbf{a} = 0]$. Equation (2.32) gives $\rho(\tau_e)$ for any lattice type and beam geometry. If $(\mathbf{k}_1 + \mathbf{k}_2) \cdot \mathbf{a}$ is assumed to vanish and the amplitudes of the excitation fields are taken to be equal ($\theta_1 = \theta_2$), Eq. (2.32) reduces to Eq. (2.35).

The trace in Eq. (2.26) can now be carried out, using Eqs. (2.30)–(2.34). The unit operator in Eq. (2.30) does not contribute to \bar{P} , because $\rho(\tau_e)$ in Eqs. (2.32) and (2.33) has zero trace. The ground state population $\rho_0(\tau_e)$ in Eq. (2.33) does not contribute to the trace. The final result is

$$\bar{P}(\mathbf{r}_1, t) = -i\mu \sin(\theta_3/2) \cos(\theta_3/2) [\theta_1 \theta_2 / 4] \times \exp(-i\omega_3 \tau_p) \{ A(\mathbf{k}_4, t) \exp(i\mathbf{k}_4 \cdot \mathbf{r}_1) + A(\mathbf{k}'_4, t) \exp(i\mathbf{k}'_4 \cdot \mathbf{r}_1) \}, \quad (2.37)$$

$$A(\mathbf{k}_4, t) = \sum_{j,l} C_{jl} \mathcal{G}_{11,jl}(t) \exp[i(\mathbf{k}_1 \cdot \mathbf{r}_{j1} - \mathbf{k}_2 \cdot \mathbf{r}_{l1})], \quad (2.38)$$

$$A(\mathbf{k}'_4, t) = \sum_{j,l} C_{jl} \mathcal{G}_{11,jl}(t) \exp[i(\mathbf{k}_2 \cdot \mathbf{r}_{j1} - \mathbf{k}_1 \cdot \mathbf{r}_{l1})], \quad (2.39)$$

$$\mathbf{k}_4 = \mathbf{k}_3 + \mathbf{k}_1 - \mathbf{k}_2, \quad (2.40)$$

$$\mathbf{k}'_4 = \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1, \quad (2.41)$$

$$\mathbf{r}_{j1} = \mathbf{r}_j - \mathbf{r}_1. \quad (2.42)$$

$\bar{P}(\mathbf{r}_1, t)$ has two spatial Fourier components with wave vectors \mathbf{k}_4 and \mathbf{k}'_4 corresponding to the two “diffracted” beams in the TG experiment. The two signals have identical time dependence, so for simplicity we will consider the TG signal with wave vector \mathbf{k}_4 . In the slowly varying amplitude approximation²⁴ the intensity of the signal with a given frequency and wave vector is proportional to the absolute square of the contribution to \bar{P} with that frequency and wave vector:

$$S(\mathbf{k}_4, t) \propto |A(\mathbf{k}_4, t)|^2. \quad (2.43)$$

Equations (2.38) and (2.43) constitute the primary result of this work. The time dependence of the TG signal for a particular model of exciton dynamics is obtained by substituting the appropriate $\mathcal{G}(t)$ into Eq. (2.38) and taking the absolute square.

Equations (2.38) and (2.43) provide a general expression for the TG signal in terms of $\mathcal{G}(t)$, the tetradic time evolution operator of the crystal in the absence of radiation. It is more common to express spectroscopic observables in terms of equilibrium correlation functions of the transition dipole operator or other relevant operators. For example, $I(\omega)$, the low power absorption line shape of a system with a dipole allowed transition, is given by²⁵

$$I(\omega) \propto \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle \hat{\mu}(t) \hat{\mu}(0) \rangle. \quad (2.44)$$

Skinner, Andersen, and Fayer²² have shown that the photon echo signal from a collection of two-level systems is proportional to the square of

$$\langle \hat{\mu}(-t) \hat{\mu}(0) \hat{\mu}(t) \hat{\mu}(0) \rangle, \quad (2.45)$$

where t is the delay time between pulses. In Appendix C, we show that Eq. (2.38), which relates the TG amplitude to \mathcal{G} , can be written in the form

$$A(\mathbf{k}_4, t) = \mu^{-4} \sum_{j,l} C_{jl} \langle \hat{\mu}_l(0) \hat{\mu}_1(t) \hat{\mu}_1(t) \hat{\mu}_j(0) \rangle \times \exp[i(\mathbf{k}_1 \cdot \mathbf{r}_{j1} - \mathbf{k}_1 \cdot \mathbf{r}_{l2})]. \quad (2.46)$$

μ is the magnitude of the site transition dipole. $\hat{\mu}_j(t)$ is the transition dipole operator for site j in the Heisenberg picture. $\hat{\mu}_1$ is the partial transition dipole operator that is defined in Eq. (2.24). As in Eqs. (2.44) and (2.45), the angular brackets in Eq. (2.46) represent a trace over the equilibrium density matrix. The TG signal is proportional to the absolute square of Eq. (2.46). Comparison of Eqs. (2.45) and (2.46) shows that both the photon echo and the TG experiment probe equilibrium correlation functions of products of four dipole operators. The third order susceptibility $\chi^{(3)}$, which is measured in a steady-state four-wave mixing experiment, can also be expressed in terms of four-point correlation functions of the dipole operator.²³

III. DISCUSSION

In the previous theoretical treatments of the transient grating experiment, the signal was taken to be proportional to the square of the difference of the excited state density at the peak and null of the grating:^{5,19,20}

$$S(t) \propto [\rho_{mm}(t)|_{\mathbf{r}_m=0} - \rho_{mm}(t)|_{(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r}_m = \pi}]^2. \quad (3.1)$$

In Eq. (3.1), t is the time delay between excitation and probing. This result was derived by assuming that the TG signal is generated by diffraction of the probe pulse from a grating of excited states.^{4,11} In Sec. II we presented a microscopic calculation of the TG signal at a time immediately after a short probe pulse. In this section, we show that the calculation of Sec. II is consistent with Eq. (3.1) and hence with the interpretation of the TG experiment as a diffraction process. We also consider the temporal profile of the signal pulse, an issue that is not treated in Sec. II, and establish some limita-

tions of the diffraction picture. In Eq. (2.26) we express the complex polarization \bar{P} [see Eq. (2.23)] that generates the TG signal as the expectation value at the time of probing of the detection operator R . This operator is defined in Eq. (2.28);

$$\bar{P}(\mathbf{r}_1, t) = \text{Tr}[R\rho(t + \tau_e)]. \quad (3.2)$$

Substitution of Eq. (2.30), which gives the component of R with the appropriate wave vector, into Eq. (3.2) yields

$$\bar{P}(\mathbf{r}_1, t) \propto \exp(i\mathbf{k}_3 \cdot \mathbf{r}_1) \rho_{11}(t + \tau_e). \quad (3.3)$$

The polarization that generates the signal with wave vector $\mathbf{k}_3 \pm (\mathbf{k}_1 - \mathbf{k}_2)$ is obtained by substituting the contribution to $\rho_{11}(t + \tau_e)$ with wave vector $\pm (\mathbf{k}_1 - \mathbf{k}_2)$ into Eq. (3.3). In the slowly varying amplitude approximation,²⁴ the TG signal is proportional to the absolute square of the spatial Fourier transform of \bar{P} , evaluated at the wave vector $\mathbf{k}_3 \pm (\mathbf{k}_1 - \mathbf{k}_2)$. The signal is, therefore, proportional to the square of the Fourier transform of the density of excited states [$\rho_{11}(t + \tau_e)$], evaluated at the wave vector $\pm (\mathbf{k}_1 - \mathbf{k}_2)$, in agreement with Eq. (3.1). Thus, Eqs. (2.26) and (2.30), together with the slowly varying amplitude approximation, are equivalent to Eq. (3.1).

In Sec. II we calculated the TG signal, measured at a time immediately after the application of a short probe pulse, as a function of the delay time between probe and excitation pulses. We did not consider the temporal profile of the TG signal pulse. To investigate the shape of the TG signal pulse, we must consider the time evolution of the system *after* the probe pulse has interacted with the sample. Consider the complex polarization \bar{P} [see Eq. (2.23)] at a time τ after the application of the probe pulse:

$$\bar{P}(\mathbf{r}_1, t + \tau) = \text{Tr}[\bar{\mu}_1 \mathcal{G}(\tau) \mathcal{G}_p(\tau_p) \mathcal{G}(t) \mathcal{G}_e(\tau_e) \rho(0)]. \quad (3.4)$$

In Sec. II we calculated \bar{P} at $\tau = 0$. Equation (3.4) is valid under the conditions of Sec. II, namely that the applied pulses are short compared to all excited state relaxation processes. Under these conditions, the temporal profile of the signal pulse is determined by the matrix elements of $\mathcal{G}(\tau)$ that contribute to the trace in Eq. (3.4). This result is at variance with the interpretation of the experiment as a diffraction process, according to which the temporal profile of the signal pulse is determined by the temporal profile of the probe pulse. Calculation of the polarization in Eq. (3.4) for nonzero τ for a crystal of interacting absorbers is not straightforward. In its most general form, this calculation involves the dynamics of two or more interacting excited states. The shape of the TG signal pulse can be calculated in a straightforward way in two limits: (i) the absorbers do not interact, (ii) the dephasing rate of the transition of each two-level system ($1/T_2$) is large compared to the interactions between the absorbers. In either of these cases, the many-body Green functions $\mathcal{G}(\tau)$ in Eq. (3.4) can be replaced with the Green function $\mathcal{G}^{(1)}(\tau)$, which is a one-body tetradic operator in the space of the absorber labeled 1. Equation (3.4) then takes the form

$$\bar{P}(\mathbf{r}_1, t + \tau) = \text{Tr}[\bar{\mu}_1 \mathcal{G}^{(1)}(\tau) \rho(\tau_e + t + \tau_p)], \quad (3.5)$$

where $\rho(\tau_e + t + \tau_p)$ is the density matrix at the end of the probe pulse. The trace in Eq. (3.5) can be partially performed to yield

$$\bar{P}(\mathbf{r}_1, t + \tau) = \mathcal{G}_{\beta\alpha, \beta\alpha}^{(1)}(\tau) \bar{P}(\mathbf{r}_1, t). \quad (3.6)$$

The labels α and β refer, respectively, to the ground and excited states of site 1. For a two-level system with transition frequency Ω and dephasing time T_2 ,

$$\mathcal{G}_{\beta\alpha, \beta\alpha}^{(1)}(\tau) = \exp[-i\Omega\tau - \tau/T_2]. \quad (3.7)$$

Substituting Eq. (3.7) into Eq. (3.6), gives

$$\begin{aligned} \bar{P}(\mathbf{r}_1, t + \tau) = & \exp[-i(\Omega - \omega_3)\tau - \tau/T_2] \\ & \times \exp(-i\omega_3\tau) \bar{P}(\mathbf{r}_1, t). \end{aligned} \quad (3.8)$$

ω_3 is the frequency of the probe pulse. If $|\Omega - \omega_3| \ll \omega_3$, the polarization of Eq. (3.8) will produce a signal with frequency ω_3 . In the slowly varying amplitude approximation²⁴ the signal intensity is proportional to the absolute square of the component of \bar{P} with appropriate frequency and wave vector. [See Eq. (2.43).] Therefore, $S(t + \tau)$, the signal at a time τ after the application of the probe pulse, is related to the signal at $\tau = 0$ by

$$S(t + \tau) \propto \exp(-2\tau/T_2) S(t). \quad (3.9)$$

For a delta function probe pulse, the temporal profile of the TG signal in the limits (i) and (ii) described above is an exponential decay with time constant $T_2/2$. This is the decay that would be measured in an optical free induction decay experiment for the same model.²⁶ Equation (3.9) shows that the diffraction interpretation of the TG is not a complete description of the experiment under the condition that the applied pulses are short compared to all relaxation times. This result should be relevant to the interpretation of TG experiments with picosecond pulses on molecular crystals at very low temperatures. If T_2 is much smaller than the probe pulse duration, which is the case for typical experiments on molecular materials at room temperature, the treatment here does not apply. In this limit, the temporal profile of the signal pulse will be determined by the temporal profile of the probe pulse, in accordance with the interpretation of the experiment as a diffraction process.

The field of nonlinear spectroscopy of condensed phase systems has grown rapidly in the last two decades. One consequence of this rapid growth is that the theory associated with a given experiment may have been developed just for that experiment, and may not make clear the connection to other techniques. The method of Sec. II is applicable to any nonlinear spectroscopic experiment on an optically thin sample. (If the sample is optically dense, propagation effects which are neglected in Sec. II must be included.) By applying the method of Sec. II to a variety of nonlinear spectroscopic techniques, one can unambiguously establish the information content of a given experimental observable and also clarify the relationships among different experiments.

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APPENDIX A

In this Appendix, we derive the expressions for the transient grating detection operator R that are given in Eqs.

(2.28) and (2.30). From Eqs. (2.23), (2.25), and (2.27) we have

$$\bar{P}(\mathbf{r}_1, t) = \text{Tr}[\tilde{\mu}_1 \mathcal{G}_p(\tau_p) \mathcal{G}(t) \rho(\tau_e)]. \quad (A1)$$

$\mathcal{G}_p(\tau_p)$, the tetradic time evolution operator during the probe pulse, is related to $G_p(\tau_p)$, the dyadic (ordinary) time evolution operator by

$$\rho(\tau_p + t) = \mathcal{G}_p(\tau_p) \rho(t) = G_p(\tau_p) \rho(t) G_p^\dagger(\tau_p), \quad (A2)$$

$$\frac{dG_p}{d\tau} = \frac{-i}{\hbar} (H_0 + V_3) G_p. \quad (A2a)$$

Substituting Eq. (A2) into Eq. (A1) and using the invariance of the trace of a product under cyclic permutations, gives

$$\bar{P} = \text{Tr}[R \mathcal{G}(t) \rho(\tau_e)], \quad (A3)$$

$$R = G_p^\dagger(\tau_p) \tilde{\mu}_1 G_p(\tau_p). \quad (A4)$$

Equation (A4) is identical to Eq. (2.28).

We next derive an expression for the matrix elements of R in Eq. (A4). As discussed in Sec. II, we assume that the probe pulse is sufficiently short that intersite interactions can be neglected while the pulse is on. Under this assumption, the density matrix evolves according to

$$\frac{d\rho}{dt} = \frac{-i}{\hbar} [H, \rho], \quad (A5)$$

$$H = \sum_{j=1}^N \{ \hbar\Omega_j a_j^\dagger a_j - \hat{\mu}_j E_3 \cos(\mathbf{k}_3 \cdot \mathbf{r}_j - \omega_3 t) \}. \quad (A6)$$

$\hbar\Omega_j$ is the transition energy of each site, and $\hat{\mu}_j$ is the transition dipole operator of Eq. (2.5). We assume that $\tau_p^{-1} \gg |\omega_3 - \Omega|$. In this case, the excitation pulses are sufficiently short that the detuning of the radiation frequency from the material frequency does not affect the time evolution. Equation (A5) is most conveniently solved in a coordinate frame that rotates at ω_3 :

$$\tilde{\rho}(t) = W_3^\dagger(t) \rho(t) W_3(t), \quad (A7)$$

$$W_3(t) = \exp\left[-i\omega_3 t \sum_j a_j^\dagger a_j\right]. \quad (A8)$$

In the rotating wave approximation,²⁶ $\tilde{\rho}$ obeys

$$\frac{d\tilde{\rho}}{dt} = -i[\tilde{H}, \tilde{\rho}], \quad (A9)$$

$$\begin{aligned} \tilde{H} = & -(\mu E_3 / 2\hbar) \sum_j [a_j^\dagger \exp(i\mathbf{k}_3 \cdot \mathbf{r}_j) + a_j \\ & \times \exp(-i\mathbf{k}_3 \cdot \mathbf{r}_j)]. \end{aligned} \quad (A10)$$

The solution of Eq. (A9) is

$$\tilde{\rho}(t + \tau) = \tilde{G}_p(\tau) \tilde{\rho}(t) \tilde{G}_p^\dagger(\tau), \quad (A11)$$

$$\tilde{G}_p(\tau) = \exp[-i\tilde{H}\tau]. \quad (A12)$$

Since \tilde{H} in Eq. (A10) is a sum of one-body operators, \tilde{G}_p factors into a product of one-body operators:

$$\tilde{G}_p = \prod_j \tilde{G}_p^{(j)}. \quad (A13)$$

The matrix elements of $\tilde{G}_p^{(j)}$ can be calculated from Eqs. (A10) and (A12),

$$[\tilde{G}_p^{(j)}(\tau)]_{\alpha\alpha} = [\tilde{G}_p^{(j)}(\tau)]_{\beta\beta} = \cos(\theta_3/2), \quad (A14)$$

$$\begin{aligned} [\tilde{G}_p^{(j)}(\tau)]_{\alpha\beta} = & -[\tilde{G}_p^{(j)}(\tau)]_{\beta\alpha}^* \\ = & i \exp(-i\mathbf{k}_3 \cdot \mathbf{r}_j) \sin(\theta_3/2), \end{aligned} \quad (A15)$$

$$\theta_3 = \mu E_3 \tau / \hbar. \quad (\text{A16})$$

$|\alpha\rangle$ is the ground state and $|\beta\rangle$ is the excited state of the two-level system labeled j . From Eqs. (A2), (A7), and (A11), we can relate the rotating frame propagator \tilde{G}_p to the propagator G_p :

$$G_p(\tau) = W_3(\tau) \tilde{G}_p(\tau). \quad (\text{A17})$$

Substitution of Eq. (A17) into Eq. (A4) relates the detection operator R to \tilde{G}_p :

$$R = \tilde{G}_p^\dagger(\tau_p) W_3^\dagger(\tau_p) \tilde{\mu}_1 W_3(\tau_p) \tilde{G}_p(\tau_p), \quad (\text{A18})$$

$$R = \exp[-i\omega_3 \tau_p] \tilde{R}, \quad (\text{A19})$$

$$\tilde{R} = \tilde{G}_p^\dagger(\tau_p) \tilde{\mu}_1 \tilde{G}_p(\tau_p). \quad (\text{A20})$$

Since $\tilde{\mu}_1$ is a one-body operator in the space of site 1, Eq. (A20) can be written as

$$\tilde{R} = \tilde{G}_p^{(1)\dagger}(\tau_p) \tilde{\mu}_1 \tilde{G}_p^{(1)}(\tau_p). \quad (\text{A21})$$

The matrix elements of \tilde{R} can now be calculated from Eqs. (A14) and (A15):

$$\begin{aligned} \tilde{R} = & -i\mu \cos(\theta_3/2) \sin(\theta_3/2) \exp(i\mathbf{k}_3 \cdot \mathbf{r}_1) [a_1^\dagger a_1 - a_1 a_1^\dagger] \\ & + a_1 \cos^2(\theta_3/2) + a_1^\dagger \sin^2(\theta_3/2) \exp(2i\mathbf{k}_3 \cdot \mathbf{r}_1). \end{aligned} \quad (\text{A22})$$

Only the first term in Eq. (A22) has the correct wave vector to contribute to the TG signal. From Eqs. (A19) and (A22) we have Eq. (2.30).

APPENDIX B

In this Appendix we evaluate $\rho(\tau_e)$, the density matrix after excitation in the transient grating experiment. As in Appendix A, we assume that the excitation pulses are sufficiently short that intersite interactions can be neglected during excitation. Under this assumption ρ evolves according to

$$\frac{d\rho}{dt} = \frac{-i}{\hbar} [H, \rho], \quad (\text{B1})$$

$$\begin{aligned} H = & \sum_j \{ \hbar \Omega a_j^\dagger a_j - \hat{\mu}_j [E_1 \cos(\mathbf{k}_1 \cdot \mathbf{r}_j - \omega_1 t) \\ & + E_2 \cos(\mathbf{k}_2 \cdot \mathbf{r}_j - \omega_2 t)] \}, \end{aligned} \quad (\text{B2})$$

where $\omega_1 = \omega_2$.

Equation (B1) is conveniently solved in a coordinate frame that rotates at ω_1 . In analogy to Eq. (A7), we define

$$\tilde{\rho}(t) = W_1^\dagger(t) \rho(t) W_1(t), \quad (\text{B3})$$

$$W_1 = \exp\left[-i\omega_1 t \sum_j a_j^\dagger a_j\right]. \quad (\text{B4})$$

In the rotating wave approximation,²⁶ $\tilde{\rho}$ obeys

$$\frac{d\tilde{\rho}}{dt} = -i[\tilde{H}, \tilde{\rho}], \quad (\text{B5})$$

$$\tilde{H} = -\sum_j (X_j^* a_j^\dagger + X_j a_j), \quad (\text{B6})$$

$$X_j = (\mu/2\hbar) [E_1 \exp(-i\mathbf{k}_1 \cdot \mathbf{r}_j) + E_2 \exp(-i\mathbf{k}_2 \cdot \mathbf{r}_j)]. \quad (\text{B7})$$

Equation (B5) has the solution

$$\tilde{\rho}(t + \tau) = \tilde{G}_e(\tau) \tilde{\rho}(t) \tilde{G}_e^\dagger(\tau), \quad (\text{B8})$$

$$\tilde{G}_e(\tau) = \exp[-i\tilde{H}\tau]. \quad (\text{B9})$$

Since \tilde{H} [in Eq. (B6)] is a sum of one-body operators, the

many-body operator \tilde{G}_e [in Eq. (B9)] factors into a product of one-body operators:

$$\tilde{G}_e = \prod_j \tilde{G}_e^{(j)}. \quad (\text{B10})$$

$\tilde{G}_e^{(j)}$ is the time evolution operator of a two-level system during a square pulse, and its matrix elements can be evaluated in a straightforward fashion from Eqs. (B6), (B7), and (B9):

$$[\tilde{G}_e^{(j)}(\tau)]_{\alpha\alpha} = [\tilde{G}_e^{(j)}(\tau)]_{\beta\beta} = \cos(|X_j|\tau), \quad (\text{B11})$$

$$[\tilde{G}_e^{(j)}(\tau)]_{\alpha\beta} = -[\tilde{G}_e^{(j)}(\tau)]_{\beta\alpha}^* = i(X_j/|X_j|) \sin(|X_j|\tau). \quad (\text{B12})$$

$|\alpha\rangle$ is the ground state and $|\beta\rangle$ is the excited state of the two-level system labeled j . Under the assumption that the crystal is in its ground state prior to the application of the pulses, $\rho_{mn}(\tau_e)$ is given by

$$\rho_{mn}(\tau_e) = [\tilde{G}_e(\tau_e)]_{m0} [\tilde{G}_e^\dagger(\tau_e)]_{0n}, \quad (\text{B13})$$

$$[\tilde{G}_e]_{m0} = [\tilde{G}_e^{(m)}]_{\beta\alpha} \prod_{j \neq m} [\tilde{G}_e^{(j)}]_{\alpha\alpha}. \quad (\text{B14})$$

In Eqs. (B13) and (B14), $|m\rangle = a_m^\dagger |0\rangle$, where $|0\rangle$ is the crystal ground state. Substituting Eqs. (B11) and (B12) into Eqs. (B13) and (B14), and keeping terms that are second order in the field amplitudes, gives

$$\begin{aligned} \tilde{\rho}_{mn}(\tau_e) = & (\theta_1 \theta_2 / 4) \{ \exp[i(\mathbf{k}_1 \cdot \mathbf{r}_m - \mathbf{k}_2 \cdot \mathbf{r}_n)] \\ & + \exp[i(\mathbf{k}_2 \cdot \mathbf{r}_m - \mathbf{k}_1 \cdot \mathbf{r}_n)] \} \\ & + (\theta_1^2 / 4) \exp[i\mathbf{k}_1 \cdot (\mathbf{r}_m - \mathbf{r}_n)] \\ & + (\theta_2^2 / 4) \exp[i\mathbf{k}_2 \cdot (\mathbf{r}_m - \mathbf{r}_n)], \end{aligned} \quad (\text{B15})$$

$$\theta_j = \mu E_j \tau_e / \hbar. \quad (\text{B16})$$

The first term in Eq. (B15) is linear in the amplitude of both fields and will contribute to the TG signal. The second and third terms in Eq. (B15) are quadratic in the amplitude of one of the fields and will not contribute to a signal with wave vector $\mathbf{k}_3 \pm (\mathbf{k}_1 - \mathbf{k}_2)$. The ground state population $\tilde{\rho}_{00}(\tau_e)$ also has a contribution that is linear in each field:

$$\tilde{\rho}_0 = -(\theta_1 \theta_2 / 2) \sum_j \cos[(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r}_j]. \quad (\text{B17})$$

Equation (B17) is presented for the sake of completeness, although, as discussed in Sec. II, this term does not contribute to the TG signal. The derivation of Eq. (B15) corresponds to the case of coherent preparation, discussed in Sec. II. In this situation, the excitation pulses prepare an exciton eigenstate. A second type of excitation, incoherent preparation, is discussed in Sec. II. In this case, the off-diagonal elements of $\tilde{\rho}(\tau_e)$ are assumed to vanish. We can modify Eq. (B15) to include both types of preparation by multiplying it by a coefficient C_{mn} . For incoherent preparation, $C_{mn} = \delta_{mn}$, and for coherent preparation, $C_{mn} = 1$. The rotating frame transformation of Eq. (B3) can now be inverted. This transformation does not affect populations or intersite coherences. Therefore, $\tilde{\rho}_{mn} = \rho_{mn}$ and $\tilde{\rho}_0 = \rho_0$. The contribution of $\rho(\tau_e)$ that is linear in the amplitude of each field is given by Eqs. (2.32) and (2.33).

APPENDIX C

In this Appendix we derive Eq. (2.46), which relates the TG signal to an equilibrium correlation function of site tran-

sition dipole operators. The first step is to express the tetradic matrix element $\mathcal{S}_{11,jl}(t)$ in Eqs. (2.38) and (2.39) in terms of the dyadic (ordinary) time evolution operator G . [See Eq. (A2).]

$$\mathcal{S}_{11,jl}(t) = G_{1,j}(t)G_{l,1}^\dagger(t). \quad (\text{C1})$$

The right-hand side of Eq. (C1) can be written as $\mu^{-4} C(t)$, where

$$C(t) = \text{Tr}[\tilde{\mu}_1 G(t) \hat{\mu}_j \rho(0) \hat{\mu}_l G^\dagger(t) \tilde{\mu}_1]. \quad (\text{C2})$$

$\hat{\mu}_j$ is the site transition dipole operator, defined by

$$\hat{\mu}_j = \mu(a_j^\dagger + a_j), \quad (\text{C3})$$

where μ is the magnitude of the dipole. $\tilde{\mu}_1$ is the operator μa_1 . $\rho(0) = |0\rangle\langle 0|$, where $|0\rangle$ is the crystal ground state. Performing a cyclic permutation of the operators in Eq. (C2) yields

$$C(t) = \text{Tr}[\hat{\mu}_l G^\dagger(t) \tilde{\mu}_1 \hat{\mu}_1 G(t) \hat{\mu}_j \rho(0)]. \quad (\text{C4})$$

Inserting the unit operator GG^\dagger between $\hat{\mu}_1$ and $\tilde{\mu}_1$ in Eq. (C4), gives

$$\begin{aligned} C(t) &= \text{Tr}[\hat{\mu}_l(0) \hat{\mu}_1(t) \tilde{\mu}_1(t) \hat{\mu}_j(0) \rho(0)] \\ &= \langle \hat{\mu}_l(0) \hat{\mu}_1(t) \tilde{\mu}_1(t) \hat{\mu}_j(0) \rangle. \end{aligned} \quad (\text{C5})$$

$\hat{\mu}_j(t)$ is the transition dipole operator in the Heisenberg picture:

$$\hat{\mu}_j(t) = G^\dagger(t) \hat{\mu}_j G(t). \quad (\text{C6})$$

When Eq. (C5) is substituted into Eq. (2.38), the result is Eq. (2.46).

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