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Aspects of impulsive stimulated scattering in molecular systems

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We introduce a theoretical framework to describe the interaction of an electromagnetic radiation field and a molecular system, such as a single molecule or a molecular crystal. By knowing in advance which electronic transitions are in resonance with the frequencies of the incident radiation, we propose a procedure to reduce the full problem to a description in terms of an effective Hamiltonian that fully takes into account the vibrational (nuclear) degrees of freedom, but that explicitly involves only those electronic states that meet the resonance condition. The influence of the rest of the electronic states appears as the polarizability of the system. We keep only those terms that give rise to Raman scattering but the scheme allows for a systematic inclusion of higher-order multiphoton processes. The resulting effective Hamiltonian is used to study the interaction of ultrashort laser pulses with a single molecule and with a molecular crystal. As applications, we study the interaction of a single ultrashort nonresonant pulse, and a train of such pulses, with a single molecule; we show that via Raman scattering the pulse impulsively transfers momentum to the molecule leaving it in a vibrational coherent state. We also study the interaction of two crossed laser pulses with a molecular crystal and show that a diffraction grating of lattice vibrations is impulsively created.

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I. INTRODUCTION

Since the advent of laser pulses whose duration is shorter than a typical molecular vibrational period [1], the potentiality of preparing specific molecular states and studying their evolution in real time has sparked an enormous amount of experimental [2–6] and theoretical work [7,8,12–17]. A typical experiment in this ultrafast, time-resolved spectroscopy is of the pump-probe type: one or several laser pulses are used to prepare a particular molecular or crystal state, which is afterwards probed either by another laser pulse or by a continuous-wave laser. Here, our main interest is in the *state* prepared by the pump pulses. In this regard interesting physical situations can develop depending on different experimental conditions. For instance, the "carrier" or central frequencies of the pump pulses may or may not be in resonance with electronic transitions [2,3,5]; or the pump pulses may consist of time-delayed sequences of phase-locked pulses [6]; and/or the pulses may be specially shaped so as to produce a specific molecular excitation. The latter technique has become a reality due to the development of very recent techniques on pulse shaping [18]. One important aspect of this type of radiation-matter interaction is the "impulsive" excitation, through Raman scattering, of coherent lattice or molecular vibrations due to the passage of even a single ultrashort light pulse. Yan, Gamble, and Nelson [7] named this process impulsive stimulated scattering (ISS) and gave the first theoretical treatment of it, fully classical and based in the work of Shen and Bloembergen [19]; here, as an application of the theory developed, we show how this process obtains with a nonresonant pulse. Certainly motivated by the different possibilities, further theoretical work has been pursued by several others authors [8–10,13–17]. This article is also an effort to add to the understanding of these optical processes.

Most of the quantum-theoretical treatments of nonlinear optical processes in molecular systems, from the classical works by Hellwarth [20] and Shen [21] to the recent ones by Yan and Mukamel [8], Walsh and Loring [13,14], and Pollard and co-workers [16] among others, have been based in calculating the polarization of the system relying on time-dependent perturbation theory. Typically, the system is assumed to have an *electronic* dipole operator μ that linearly couples to the time-dependent (external) electric field $\mathbf{E}(t)$ of the incident laser radiation. Then, the polarization of the system is calculated as the expectation value of the dipole operator in the molecular state at a given time, via a wave function or density matrix, and the different contributions to the susceptibility are found by expanding such an expectation value in powers of the external field; e.g., to third order in $\mathbf{E}$ one finds $\chi^{(3)}$. This scheme is based on having weak fields. It is of interest to note, however, that the *classical* treatment of Raman scattering introduced by Shen and Bloembergen [19], and used by Nelson and co-workers [2,7,22], is not fully perturbative since in principle one could solve the fully coupled equations of motion for the fields and the Raman mode. Also, there has recently been interest in dealing with strong fields of shaped pulses by Tannor and co-workers [15], who perform exact calculations of the evolution of molecular models of two electronic states.

The purpose of this article is to present a theoretical framework to deal with the interaction of radiation with a molecular system, such that nonlinear effects such as Raman are described in a noncompletely perturbative fashion. Starting with, in principle, a complete formulation of the problem, the result of the appropriate approximation is an *effective* Hamiltonian for the system that explicitly includes *only* those electronic states connected by the resonant frequencies of the incident radiation, as well as the complete manifold of nuclear or vibrational states of the molecular system. The other electronic states *are not* neglected but their effect is taken into account by the *polarizability* of the resonating electronic states. The idea is to use the effective Hamiltonian to solve for the dynamics of the system in an exact manner without further approximations as far as the radiation-matter interaction is concerned. Besides being thus able to tackle nonlinear effects more appropriately, one gains a better understanding of the process. For instance, as a consequence of limiting ourselves to absorption emission and Raman processes *but* including the effect of all the electronic states, one finds that one cannot consider *arbitrarily* strong fields; otherwise, multiphoton processes must be included. This physically expected property has, as a further and important consequence, the fact that effectively reducing the problem to two electronic levels results in a description not correct at *arbitrary* short-time scales. This is a theoretical improvement over, and points to the limitations of models that start from the outset with two electronic levels only [8,12,15]. Moreover, the present theory indicates how higher-order multiphoton processes can systematically be included.

We also point out that since our interest here is the state of the system prepared by the incident radiation, and since the latter is supposed to be laser-type radiation, we shall be dealing with *classical* fields. This is not a limitation of our theory, were we interested in dealing with the *scattered* or "probe" radiation, we should then include the field as a quantal dynamical variable. Walsh and Loring [14] have shown that within the perturbative scheme, differences arise in the scattered signal depending on whether the field is considered classical or quantal. Also, as a consequence of dealing exclusively with classical fields, the Raman scattering is always meant to be stimulated.

The resulting theory shares certain similarities with the treatments proposed by Yan and Mukamel [12] and by Tannor and co-workers [15]. In a sense, the present scheme is also a generalization of the perturbation theory proposed by Langhoff, Epstein, and Karplus [23]. Since we want to deal with the resonating electronic states and, at the same time, not lose the presence of the rest of the electronic manifold, the theory is formulated in terms of projection operators in Hilbert space; it is of interest to mention that Seke [24] has recently proposed a theory based on a similar projection formalism, though dealing with other optical problems, namely the corrections to atomic spectra due to electromagnetic interactions.

The theory is particularly well suited to deal with the interaction of short pulses with molecular systems both in the cases of resonance and off resonance of the central frequency of the pulses with electronic transitions. The treatment also allows for a clear description of one of the main aspects of ISS, that is, that the laser pulses are shorter than the vibrational molecular periods.

In Sec. II we present the formalism and derivation of the effective Hamiltonian, including Raman interactions, of a single molecule interacting with the radiation field. It is assumed that the incident radiation is in resonance with an electronic transition. As we shall see there is no loss of generality in considering a single molecule and a single electronic resonance. As an application of the theory, in Sec. III we deal in more detail with the case of a single molecule in interaction with an ultrashort pulse off resonance with any electronic transition. We show that by virtue of Raman scattering, the pulse indeed "instantaneously" transfers a certain amount of momentum to the molecule, leaving it in a coherent state [22]. We also show how to consider a train of such short pulses. Specializing to a harmonic surface potential, we explicitly show that a nonresonant pulse leaves the molecule in a vibrational quasiclassical state, i.e., a minimum uncertainty wave packet, as opposed to, say, merely a superposition of the $n=0$ and $n=1$ vibrational states. Moreover, the quasiclassical coherent nature of the state generated by nonresonant impulsive excitation makes possible a simple and illuminating analytical derivation of selectivity of vibrational excitation by a train of pulses; this has been rationalized by classical analogy [2] and demonstrated numerically [12].

Section IV is devoted to a molecular crystal in interaction with short off-resonance pulses; adapting the results of Sec. II, we find the corresponding effective Hamiltonian and show that two incident crossed pulses generate, impulsively, a coherent "diffraction grating" of crystal vibrations in a direction transversal to the direction of the incident pulses; we stress that the phonon wave-vector selection (matching condition), as well as the conditions for impulsive excitation, follow as straightforward consequences of the use of the effective Hamiltonian. We conclude the article with comments mainly regarding the incorporation of dephasing and relaxation effects.

II. EFFECTIVE HAMILTONIAN WITH RAMAN TERMS

Although the following derivation can be made very general, we shall specialize to a molecule interacting with a laser pulse in the dipole approximation. Let $H(t)$ be the time-dependent Hamiltonian

$$H(t)=H_M+V(t)\ , \tag{2.1}$$

where H_M is the molecular Hamiltonian. For the type of internal molecular motion in which we are interested here, we shall assume the Born-Oppenheimer approximation to hold for all times. In this approximation the electronic states are given by $|n(\mathbf{R})\rangle$, so that

$$\langle n(\mathbf{R})|H_M|n(\mathbf{R})\rangle \approx T_N+\mathcal{E}_n(\mathbf{R})\equiv H_n\ , \tag{2.2}$$

where T_N is the nuclear kinetic energy and $\mathcal{E}_n(\mathbf{R})$ are the electronic potential-energy surfaces. $\mathbf{R}$ denotes the nuclear coordinates. In writing Eq. (2.2) we have assumed, in particular, that there are no geometrical phase effects [25]. The interaction term $V(t)$ has the form

$$V(t)=-\boldsymbol{\mu}\cdot\mathbf{E}(t)\ , \tag{2.3}$$

with $\boldsymbol{\mu}$ the electronic dipole operator, off diagonal in the representation used, i.e., $\langle n(\mathbf{R})|V(t)|n(\mathbf{R})\rangle=0$. The laser field $\mathbf{E}(t)$ is here treated as classical and it is a given function of time.

We consider the following physical situation. The molecule is initially at $t=t_0$ in its ground electronic state and it may be in an arbitrary nuclear state. A laser pulse hits the molecule at time $t=t_p$; that is, the "center" of the pulse passes through the molecule at t_p. And we want to describe the state of the molecule for times $t>t_p$. Let Ω be the central, or carrier frequency of the pulse, and let τ_L be the time duration of it. We shall consider two cases. First, there is in resonance, when $\Omega\approx\omega_{eg}$ with ω_{eg} being the 0-0 excitation frequency between the ground and, say, the first excited electronic state; in this case, there is an appreciable population transfer from the electronic ground to the first excited state. We will also consider the off-resonance situation, which occurs when the electronic population transfer is negligible. We could be more precise and refer to in resonance when the carrier frequency equals the frequency at the Franck-Condon transition, since this could be much larger than ω_{0-0}. With ω_v being a typical frequency of the active Raman modes, the frequency scales of the problem are as follows:

$$\omega_{eg}\geq\Omega\gg\tau_L^{-1}>\omega_v\ . \tag{2.4}$$

In Fig. 1 these relations are illustrated. Note that in the electronic time scales the pulse is very long.

Although our interest here is in laser pulses, it is important to note that for the development of the theory in this section, it is not necessary that the field be a pulse. Namely, since we want to deal with Raman scattering we would only need to consider two monochromatic fields with frequencies Ω_1 and Ω_2 such that $\Omega_1-\Omega_2\approx\omega_v$, with ω_v the frequency of the Raman active vibrational mode. (And of course, one of the fields in electronic resonance should also be considered.) If the pulse is short enough so that $\tau_L^{-1}>\omega_v$, then there will be stimulated Raman scattering with a single pulse, since many combinations of two components Ω_1 and Ω_2, such that $\Omega_1-\Omega_2\approx\omega_v$, are present within the pulse. This novel aspect due to the shortness of the pulse and some of its consequences will be discussed in the following sections.

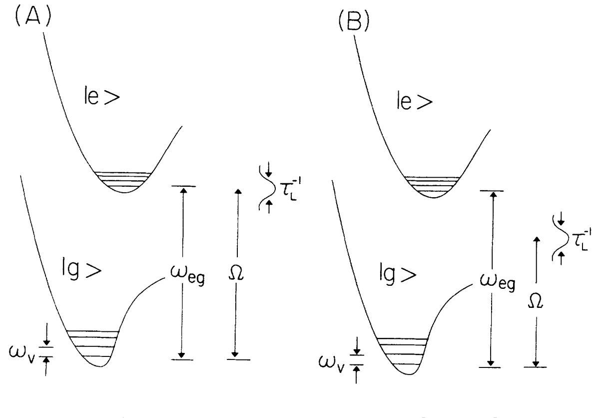

FIG. 1. Schematic potential energy surfaces of the ground and first excited electronic states of a molecule. ω_{eg} is the resonant electronic energy, ω_v is a typical nuclear vibrational frequency, Ω is the central or "carrier" frequency of the laser pulse, and τ_L^{-1} is the spectral width of the pulse. (a) The pulse is in resonance with the electronic transition $\omega_{eg}\approx\Omega\gg\tau_L^{-1}>\omega_v$. (b) The pulse is off resonance with the electronic transition $\omega_{eg}>\Omega\gg\tau_L^{-1}>\omega_v$.

As in any of these problems, we start with the time-dependent Schrödinger equation, in the interaction representation,

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle=V_I(t)|\psi_I(t)\rangle\ , \tag{2.5}$$

where

$$|\psi_I(t)\rangle=e^{(i/\hbar)H_Mt}|\psi(t)\rangle \tag{2.6}$$

and

$$V_I(t)=e^{(i/\hbar)H_Mt}V(t)e^{-(i/\hbar)H_Mt}\ . \tag{2.7}$$

Equation (2.5) must be solved given the initial state $|\psi_I(t_0)\rangle$. Since our interest now is the radiation-matter interaction Hamiltonian, we can deal with a wave-function formalism instead of a density-matrix approach. The latter is certainly necessary in order to correctly account for dephasing and relaxation effects. We defer to Sec. V for further comments on how to include these effects.

The idea now is to obtain an effective Hamiltonian that involves only the electronic ground and first excited states $|g(\mathbf{R})\rangle$ and $|e(\mathbf{R})\rangle$ and that includes the possibilities of absorption emission and Raman interactions. The resonance aspect is a one-photon process while the Raman excitation is a two-photon process. The contribution of the former to the effective Hamiltonian should be proportional to the transition dipole moment $\langle e(\mathbf{R})|\mu|g(\mathbf{R})\rangle$, while the contribution of the latter should be proportional to the *polarizability* of the molecule. But the polarizability operator depends on the rest of the electronic states different from $|g(\mathbf{R})\rangle$ and $|e(\mathbf{R})\rangle$ [20], and therefore, the rest of the excited states should make its presence through the polarizability of the molecule. Thus, instead of simply disregarding those excited electronic states, one can *project them out* in an appropriate manner so as to not lose the effects of their presence. This is done with the following projection operators:

$$\mathcal{P}\equiv|g\rangle\langle g|+|e\rangle\langle e|\ , \tag{2.8}$$

$$\mathcal{Q}\equiv 1-\mathcal{P}=\sum_{n\neq g,e}|n\rangle\langle n|\ , \tag{2.9}$$

where the dependence of the electronic states on the nuclear coordinate $\mathbf{R}$ is implicit. Acting with these operators on Eq. (2.5), one obtains

$$i\hbar\frac{\partial}{\partial t}\mathcal{P}|\psi_I(t)\rangle=\mathcal{P}V_I(t)\mathcal{P}|\psi_I(t)\rangle+\mathcal{P}V_I(t)\mathcal{Q}|\psi_I(t)\rangle \tag{2.10}$$

and

$$i\hbar\frac{\partial}{\partial t}\mathcal{Q}|\psi_I(t)\rangle=\mathcal{Q}V_I(t)\mathcal{P}|\psi_I(t)\rangle+\mathcal{Q}V_I(t)\mathcal{Q}|\psi_I(t)\rangle\ . \tag{2.11}$$

Hence, solving the Schrödinger equation [Eq. (2.5)] is equivalent to solving the coupled equations (2.10) and (2.11) for $\mathcal{P}|\psi_I(t)\rangle$ and $\mathcal{Q}|\psi_I(t)\rangle$, with initial conditions

$$\mathcal{P}|\psi_I(t_0)\rangle=e^{(i/\hbar)H_g t_0}|g\rangle|\phi_g\rangle \tag{2.12}$$

and

$$\mathcal{Q}|\psi_I(t_0)\rangle=0\ , \tag{2.13}$$

where $|\phi_g\rangle$ is the initial nuclear vibrational state.

The formal solution of Eq. (2.11), with initial condition Eq. (2.13), is

$$\mathcal{Q}|\psi_I(t)\rangle=-\frac{i}{\hbar}\int_{t_0}^{t}d\tau\exp_T\left[-\frac{i}{\hbar}\int_{\tau}^{t}d\tau'\mathcal{Q}V_I(\tau')\mathcal{Q}\right]\mathcal{Q}V_I(\tau)\mathcal{P}|\psi_I(\tau)\rangle\ , \tag{2.14}$$

where $\exp_T(\ )$ stands for the time-ordered exponential. Substitution of this solution into Eq. (2.10) yields a closed equation for the projected part

$$i\hbar\frac{\partial}{\partial t}\mathcal{P}|\psi_I(t)\rangle=\mathcal{P}V_I(t)\mathcal{P}|\psi_I(t)\rangle-\frac{i}{\hbar}\mathcal{P}V_I(t)\mathcal{Q}\int_{t_0}^{t}d\tau\exp_T\left[-\frac{i}{\hbar}\int_{\tau}^{t}d\tau'\mathcal{Q}V_I(\tau')\mathcal{Q}\right]\mathcal{Q}V_I(\tau)\mathcal{P}|\psi(\tau)\rangle\ . \tag{2.15}$$

Thus, the solution of the original Schrödinger equation, Eq. (2.5), is equivalent to solving Eq. (2.15) for $\mathcal{P}|\psi_I(t)\rangle$ subject to the initial condition Eq. (2.12). $\mathcal{Q}|\psi_I(t)\rangle$ is found afterwards from Eq. (2.14). So far, everything is exact and we have simply rewritten the Schrödinger equation in a form amenable for our approximations. We note that Eqs. (2.14) and (2.15) are valid for any type of external time-dependent potential $V(t)$ and for projection operators different from those given by Eqs. (2.8) and (2.9), i.e., one can project onto more electronic states depending on the type of external interaction. We also recall that a great deal of the usefulness of this projection-operator scheme [26] rests on the initial condition for $\mathcal{Q}|\psi_I(t_0)\rangle$, Eq. (2.13). This condition allows us to end up with an equation, albeit integrodifferential, for $\mathcal{P}|\psi_I(t)\rangle$ *only*.

Again, we want to describe that a single pulse is capable of producing electronic transitions *and* nuclear excitation through Raman scattering. As other authors have done [12,15], effects of this type can be included by completely *neglecting* the second term in the right-hand side (rhs) of Eq. (2.15) and solving the problem exactly (without relying on a perturbation-theory scheme). Multiphoton transitions, such as Raman, are still present due to the presence of the nuclear vibrational states of the ground and first excited electronic states. However, as already mentioned, this description is incomplete since Raman scattering depends on the molecular polarizability, which in turn is dependent on the whole manifold of electronic states [20]. Thus, although our procedure also consists in reducing the description to a two-electronic-state problem, we will keep, at the same time, the contribution of the other excited electronic states to multiphoton processes. This relies on appropriately neglecting *real*, but no *virtual*, population transfer to the $\mathcal{Q}$ manifold. Our analysis, therefore, focuses on $\mathcal{Q}|\psi_I(t)\rangle$ and in the second term of the rhs of Eq. (2.15). We shall be satisfied with including terms giving rise to the polarizability tensor of the molecule, so as to properly handle Raman scattering.

Thus, we want to obtain from Eq. (2.15) an effective Hamiltonian for the $\mathcal{P}$ manifold, including one- and two-photon processes. First, we note that the second term in the rhs of Eq. (2.15) is an infinite series of time-ordered terms such as

$$\frac{i}{\hbar}\mathcal{P}V_I(t)\mathcal{Q}V_I(\tau_1)\mathcal{Q}\cdots\mathcal{Q}V_I(\tau_{n-2})\mathcal{Q}V_I(\tau)\mathcal{P}\ , \tag{2.16}$$

that is, involving matrix elements of the dipole operator n times, from the $\mathcal{P}$ manifold to the $\mathcal{Q}$ manifold, again to the $\mathcal{Q}$ manifold, and so on, and finally back to the $\mathcal{P}$ manifold. Since each factor of the dipole operator is multiplied by $\mathbf{E}(t)$, each factor represents a one-photon process, the whole term representing a n-photon process. Since, by assumption, the initial population is only in the $\mathcal{P}$ manifold and the resonance condition is only satisfied between states within the $\mathcal{P}$ manifold, we are calling *virtual* the transitions to and within the $\mathcal{Q}$ manifold. The leading-order term is a two-photon process, i.e., quadratic in the field $\mathbf{E}(t)$, and it is responsible for Raman scattering. Therefore, if the external field is not too strong (see below) and one wishes to consider up to Raman scattering only, this can be achieved by approximating the exponentials in Eqs. (2.14) and (2.15) by unity:

$$\exp_T\left[-\frac{i}{\hbar}\int_{\tau}^{t}d\tau'\mathcal{Q}V_I(\tau')\mathcal{Q}\right]\approx 1\ , \tag{2.17}$$

so that the only remaining term is

$$\frac{i}{\hbar}\mathcal{P}V_I(t)\mathcal{Q}V_I(\tau)\mathcal{P}\ . \tag{2.18}$$

This term represents first a (virtual) transition from the $\mathcal{P}$ to the $\mathcal{Q}$ manifold, and then a second (virtual) transition back to the $\mathcal{P}$ manifold. Below we will give the condition for the actual transition rate from the $\mathcal{P}$ to the $\mathcal{Q}$ manifold to be negligible.

Next, we realize that even with the above approximation we still face a nonunitary time evolution with "memory," namely, the $\mathcal{P}$ state in the second term of Eq. (2.15) is evaluated at the integration time variable τ. The validity of both the unitary evolution and the "memoryless," or Markovian, approximations that we need to perform are mathematically based on the same quantity being small; their physical motivation, though, is different and we introduce them separately.

Let us first approximate

$$\mathcal{P}|\psi_I(\tau)\rangle \approx \mathcal{P}|\psi_I(t)\rangle \; , \tag{2.19}$$

and substitute into Eq. (2.15), together with approximation Eq. (2.17):

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\mathcal{P}|\psi_I(t)\rangle &\approx \mathcal{P}V_I(t)\mathcal{P}|\psi_I(t)\rangle \\ &\quad -\frac{i}{\hbar}\int_{t_0}^{t} d\tau\, \mathcal{P}V_I(t)\mathcal{Q}V_I(\tau)\mathcal{P}|\psi(t)\rangle \; . \end{aligned} \tag{2.20}$$

The validity of this approximation is based on *separation of time scales*. Namely, it is necessary that the time scale of the evolution of the state $\mathcal{P}|\psi_I(t)\rangle$ obtained *after* performing the approximation (2.19) be (much) longer than the time scale of the integrand in Eq. (2.20). This approximation is very similar to that one used in derivations of relaxation equations, such as Brownian motion type [27,28], in which the environment evolves in a much shorter scale than that of the system under observation. The penalty that one pays is that the equation thus obtained does not correctly describe the evolution of the state at time scales of the order or shorter than the time scale of the integrand. As we shall see, it is in this short time scale that the "virtual" transitions occur. We can estimate the time scales involved as follows. Let us neglect for the moment the nuclear vibrational degrees of freedom (these evolve in a much longer time scale) and suppose that we have only electronic energy levels E_n. Also, since (by assumption) the pulse is not short in the electronic time scale we can consider a "monochromatic" laser with frequency Ω and amplitude $\mathbf{E}_0$. Then, the first term in the rhs of Eq. (2.20) is approximately given by $\boldsymbol{\mu}_{eg}\cdot\mathbf{E}_0$, where $\boldsymbol{\mu}_{eg}=\langle e|\boldsymbol{\mu}|g\rangle$. Now, the main contribution of the e-e component of the second term in Eq. (2.20) is given by

$$\begin{aligned} \frac{i}{\hbar}\int_{t_0}^{t} d\tau \sum_{n\neq e,g} \boldsymbol{\mu}_{en}\boldsymbol{\mu}_{ne}:\mathbf{E}_0\mathbf{E}_0 e^{i[\Omega-(E_n-E_e)/\hbar]t} \\ \times e^{-i[\Omega-(E_n-E_e)/\hbar]\tau} \; . \end{aligned} \tag{2.21}$$

We note first that there exists a term in the sum, say n^*, which has the *slowest* oscillation frequency of the integrand, namely the smallest resonance off set $\Omega-E_n^*-E_e)/\hbar$; all the other terms in the sum oscillate at higher frequencies. Evidently, the other components g-g and e-g of the second term in Eq. (2.20) also oscillate faster than the n^* term in Eq. (2.21) and we do not have to worry about them now. Performing the integral in Eq. (2.21) for the n^* term yields the largest contribution of Eq. (2.21) (assuming there is not much difference among the different dipole moment matrix elements) to the evolution of the state $\mathcal{P}|\psi_I(t)\rangle$, which is

$$\frac{\boldsymbol{\mu}_{en^*}\boldsymbol{\mu}_{n^*e}:\mathbf{E}_0\mathbf{E}_0}{|(E_{n^*}-E_e)-\hbar\Omega|} \; . \tag{2.22}$$

Therefore, for the separation of time scales approximation to be valid, the smallest frequency of the integrand in Eq. (2.20) must be (much) greater than the (typical) frequency of the time evolution of the state

$$|(E_{n^*}-E_e)/\hbar-\Omega| \gg \frac{\boldsymbol{\mu}_{eg}\cdot\mathbf{E}_0}{\hbar} \; , \tag{2.23}$$

where we have assumed with no loss of generality that either $|\boldsymbol{\mu}_{eg}|>|\boldsymbol{\mu}_{en^*}|$ or that the first term in Eq. (2.20) dominates. The important conclusion from Eq. (2.23) is that the *smallest* resonance off set from the $\mathcal{P}$ to the $\mathcal{Q}$ manifold must be greater than all the electronic "Rabi frequencies" $\boldsymbol{\mu}_{mn}\cdot\mathbf{E}_0/\hbar$ in order for the separation of time scales to be valid. In this sense we are restricted to "weak fields." An obvious but important remark is that if it happens that one of the frequency components of the pulse is such that the above condition, Eq. (2.23), is not well satisfied, then one must reformulate the problem including the electronic state $|n^*(\mathbf{R})\rangle$ in the projected $\mathcal{P}$ manifold. This also tells us that we cannot prescribe a general theory to deal with arbitrarily short pulses since there will always be frequency components of the field in resonance with more and more electronic states. The shortness of the actual pulses is in the nuclear vibrational time scales, as seen in Fig. 1.

We now show that the above condition Eq. (2.23) also renders a Hermitian evolution. This is because, due to the nonresonance condition with the $\mathcal{Q}$ manifold, there is negligible population there. To see that this is the case we calculate the population in the $\mathcal{Q}$ manifold with the two-photon approximation Eq. (2.17) already taken into account,

$$\begin{aligned} \langle\psi_I(t)|\mathcal{Q}\mathcal{Q}|\psi_I(t)\rangle &\approx \frac{1}{\hbar^2}\int_{t_0}^{t} d\tau \int_{t_0}^{t} d\tau' \langle\psi_I(\tau)|\mathcal{P}V_I(\tau)\mathcal{Q}V_I(\tau')\mathcal{P}|\psi_I(\tau')\rangle \\ &= \frac{1}{\hbar^2}\int_{t_0}^{t} d\tau \int_{t_0}^{\tau} d\tau' [\langle\psi_I(\tau)|\mathcal{P}V_I(\tau)\mathcal{Q}V_I(\tau')\mathcal{P}|\psi_I(\tau')\rangle + \langle\psi_I(\tau')|\mathcal{P}V_I(\tau')\mathcal{Q}V_I(\tau)\mathcal{P}|\psi_I(\tau)\rangle] \; , \end{aligned} \tag{2.24}$$

where the second line follows from a rearrangement of the time variables. To be consistent with the separation of time scales approximation we substitute the state at the *earliest* time τ' by the state at the time τ in the second line of Eq. (2.24), thus obtaining

$$\langle \psi_I(t)|\mathcal{Q}|\psi_I(t)\rangle \approx \frac{1}{\hbar^2}\int_{t_0}^{t} d\tau \langle \psi_I(\tau)| \left[\int_{t_0}^{\tau} d\tau' \mathcal{P}V_I(\tau)\mathcal{Q}V_I(\tau')\mathcal{P}+\mathcal{P}V_I(\tau')\mathcal{Q}V_I(\tau)\mathcal{P}\right]|\psi_I(\tau)\rangle$$

$$\approx O\left[\frac{\boldsymbol{\mu}_{en^*}\boldsymbol{\mu}_{n^*e}:\mathbf{E}_0\mathbf{E}_0}{(E_{n^*}-E_e)^2+\hbar^2\Omega^2}\right] \ll 1 \ . \tag{2.25}$$

That is, (at least) to the same order of approximation as the separation of time scales approximation, the population of the $\mathcal{Q}$ manifold is negligible. But, *very importantly*, this does not imply that the second term on the rhs of Eq. (2.20),

$$i/\hbar \int_{t_0}^{t} d\tau' \mathcal{P}V_I(\tau)\mathcal{Q}V_I(\tau')\mathcal{P} \ ,$$

is also negligible altogether, but only its *anti-Hermitian* part. The Hermitian part remains and renders the evolution of $\mathcal{P}|\psi_I(t)\rangle$ unitary. In other words, the statement of unitary evolution in the $\mathcal{P}$ manifold is the same as no population in the $\mathcal{Q}$ manifold; i.e., probability is conserved within the $\mathcal{P}$ manifold.

Therefore, we finally arrive at the effective Schrödinger equation of our problem:

$$i\hbar\frac{\partial}{\partial t}\mathcal{P}|\psi_I(t)\rangle = \mathcal{P}V_I(t)\mathcal{P}|\psi_I(t)\rangle - \frac{i}{2\hbar}\int_{t_0}^{t} d\tau[\mathcal{P}V_I(t)\mathcal{Q}V_I(\tau)\mathcal{P}-\mathcal{P}V_I(\tau)\mathcal{Q}V_I(t)\mathcal{P}]|\psi(t)\rangle \ . \tag{2.26}$$

This equation is to be solved subject to the initial condition given by Eq. (2.12). To summarize, we have reduced our problem to a two-level electronic system, i.e., only involving $|g(\mathbf{R})\rangle$ and $|e(\mathbf{R})\rangle$, and whose evolution is given by an effective, Hermitian, time-dependent Hamiltonian. The first term in the rhs of Eq. (2.26) accounts for absorption emission (one-photon process) between the two electronic states and the second term is the Raman interaction (two-photon process). The latter consists of the polarizability operator as we show below but, of course, the first term contributes to two-photon processes as well.

Although one could have anticipated the form of the effective Hamiltonian, Eq. (2.26), it is important to point out the relevance of its derivation. First, it shows the interplay between the strength of the fields and the optical processes considered, on the one hand, and the time scales within which the description is correct [namely, the description is not correct at time scales of the integrand in the second term of Eq. (2.26)]. And second, it indicates how higher-order multiphoton processes, due to resonances and/or stronger fields, can be systematically included. In these regards, we mention that Yan and Mukamel [12] have arrived to an effective Hamiltonian such as Eq. (2.26) (i.e., quadratic in the external fields) with a density-matrix formalism, but restricting from the outset to a two-level electronic system, Tannor and coworkers [15] also start from a two-level electronic system without polarizability. From the present theory one can see that if the system actually has more than two electronic states, care must be taken regarding the strength of the external fields.

Undoing the interaction representation, the effective Hamiltonian in the manifold $|e(\mathbf{R})\rangle$ and $|g(\mathbf{R})\rangle$ has the following form:

$$H_{\text{eff}}(t) = H_M^{(2)} - \boldsymbol{\mu}^{(2)}\cdot\mathbf{E}(t) - \int_{t_0}^{t} d\tau\, \mathbf{E}(t)\cdot\tilde{\alpha}^{(2)}(t-\tau)\cdot\mathbf{E}(\tau) \ , \tag{2.27}$$

where

$$H_M^{(2)} = |g\rangle H_g\langle g| + |H_e\rangle\langle e| \ , \tag{2.28}$$

$$\boldsymbol{\mu}^{(2)} = |g\rangle\boldsymbol{\mu}_{ge}\langle e| + |e\rangle\boldsymbol{\mu}_{eg}\langle g| \ , \tag{2.29}$$

and the (tensor) polarizability operator $\alpha^{(2)}(\tau)$ is given by

$$\tilde{\alpha}^{(2)}(t-\tau) = \frac{i}{2\hbar}\mathcal{P}\sum_{n\neq g,e}(\boldsymbol{\mu}|n\rangle\langle n|e^{(i/\hbar)H_M(t-\tau)}\boldsymbol{\mu}e^{-(i/\hbar)H_M(t-\tau)} - e^{(i/\hbar)H_M(t-\tau)}\boldsymbol{\mu}e^{-(i/\hbar)H_M(t-\tau)}|n\rangle\langle n|\boldsymbol{\mu})\mathcal{P} \ , \tag{2.30}$$

and, for instance, its matrix element in the ground electronic state $\tilde{\alpha}_{gg}^{(2)} \equiv \langle g|\tilde{\alpha}^{(2)}|g\rangle$ is

$$\tilde{\alpha}_{gg}^{(2)}(t-\tau) = \frac{i}{2\hbar}\sum_{n\neq g,e}[\boldsymbol{\mu}_{gn}\boldsymbol{\mu}_{ng}(t-\tau) - \boldsymbol{\mu}_{gn}(t-\tau)\boldsymbol{\mu}_{ng}] \ , \tag{2.31}$$

where $\mu_{mn}(t) \equiv \langle m|e^{(i/\hbar)H_M t}\boldsymbol{\mu}e^{-(i/\hbar)H_M t}|n\rangle$. It should be clear that $\tilde{\alpha}^{(2)}$ is an operator in both the electronic $\mathcal{P}$ manifold and the nuclear Hilbert spaces.

We have identified $\tilde{\alpha}^{(2)}$ as the polarizability operator by noting that the Raman term in Eq. (2.27) has the form $-\mathbf{E}(t)\cdot\mathbf{P}_M(t)$ with

$$\mathbf{P}_M(t) = \int_{t_0}^{t} d\tau\, \tilde{\alpha}^{(2)}(t-\tau)\cdot\mathbf{E}(\tau) \ , \tag{2.32}$$

the molecular polarization vector (operator). It is interesting to note that the form obtained for this polarization vector as a causal convolution of the external field with the polarizability is what one would expect from classical electrodynamics [29].

III. OFF-RESONANCE ISS WITH A SINGLE MOLECULE

In this section we analyze the effect of an abrupt pulse whose central frequency is (for simplicity) below the 0-0 ground-first excited electronic transition [see Fig. 1(b)]. Since we are assuming that the duration of the pulse is shorter than the ground vibrational period, this means that within the spectral width of the pulse there are many pairs of frequencies whose differences match the vibrational frequencies. Thus, stimulated Raman scattering occurs within a single pulse. We shall show that the effect of the field is to "impulsively" transfer certain amounts of momentum to the Raman active modes of the molecule (the vibrational degrees of freedom in our example).

We use the general results of Sec. II but consider that none of frequencies of the pulse are in resonance with any of the allowed electronic transitions. Namely, we require that the smallest resonance offset (from the ground electronic state) satisfies

$$|(E_e-E_g)/\hbar-\omega| \gg \frac{\boldsymbol{\mu}_{eg}\cdot\mathbf{E}_0}{\hbar}\ , \tag{3.1}$$

where ω is any frequency within the spectral width of the pulse centered at Ω. If $\Omega \ll (E_e-E_g)/\hbar$ then an adiabatic approximation may be implemented [30] (see Appendix A).

Due to condition (3.1), we, therefore, expect that the population will remain in the ground electronic state and the appropriate projection operator in this case only involves the ground electronic state, i.e., $\mathcal{P}=|g\rangle\langle g|$. The resulting effective Hamiltonian, cf. Eq. (2.26), for the ground electronic becomes

$$H_{\text{eff}}(t)=H_g-\int_{t_0}^{t} d\tau\,\mathbf{E}(t)\cdot\tilde{\alpha}(t-\tau)\cdot\mathbf{E}(\tau)\ , \tag{3.2}$$

where $H_g=T_N+\mathcal{E}_g$ (note that there is no absorption-emission term). The polarizability has the form

$$\tilde{\alpha}(t-\tau)=\frac{i}{2\hbar}\sum_{n\neq g}[\boldsymbol{\mu}_{gn}\boldsymbol{\mu}_{ng}(t-\tau)-\boldsymbol{\mu}_{gn}(t-\tau)\boldsymbol{\mu}_{ng}]\ . \tag{3.3}$$

This expression is essentially α_{gg}, Eq. (2.31), with the difference that the summation now includes all the excited electronic states. The polarizability can also be written in the more compact form

$$\tilde{\alpha}(t-\tau)=\frac{1}{2i\hbar}\langle g|[\boldsymbol{\mu}(t-\tau),\boldsymbol{\mu}]|g\rangle\ . \tag{3.4}$$

In the rest of this section we will restrict ourselves to external fields $\mathbf{E}(t)$ corresponding to a Gaussian transform limited pulse,

$$\mathbf{E}(t)=\mathbf{E}_0 e^{-(t-t_p)^2/2\tau_L^2}\cos\Omega t\ , \tag{3.5}$$

where $\mathbf{E}_0$ is the electric-field amplitude including its polarization, τ_L is the duration of the pulse, Ω is the central frequency of the pulse, and the pulse reaches its maximum amplitude at the time t_p. In frequency space the pulse is a sum of two Gaussians centered at $\pm\Omega$ and width τ_L^{-1}. A short, or abrupt, pulse means that $\tau_L \ll \tau_v$, with τ_v a typical vibration period. We have been also tacitly assuming that $\Omega \gg \tau_v^{-1}$. That is, the central frequency is much larger than the vibrational frequencies, but still smaller than any electronic transition; the relationships among the various frequencies are illustrated in Fig. 1(b).

With the above assumptions, currently experimentally available, the Raman term can be shown to reduce to (see Appendix A)

$$\int_{t_0}^{t} d\tau\,\mathbf{E}(t)\cdot\tilde{\alpha}(t-\tau)\cdot\mathbf{E}(\tau)\approx\mathbf{E}(t)\mathbf{E}(t):\tilde{\alpha}_0\ , \tag{3.6}$$

where $\tilde{\alpha}_0$ is the polarizability at frequency Ω whose (nuclear) matrix elements are given by

$$\langle m_g|\tilde{\alpha}_0|l_g\rangle=\tfrac{1}{2}\sum_{n\neq g}\sum_{k_n}\langle m_g|\boldsymbol{\mu}_{gn}|k_n\rangle\langle k_n|\boldsymbol{\mu}_{ng}|l_g\rangle \times\left[\frac{1}{E_{k_n}-E_{l_g}-\hbar\Omega}+\frac{1}{E_{k_n}-E_{m_g}+\hbar\Omega}\right]\ , \tag{3.7}$$

where $H_n|m_n\rangle=E_{m_n}|m_n\rangle$ are the eigenstates of the nuclear Hamiltonians in the excited electronic states. In deriving Eq. (3.6) it is assumed that t_0 is a time far in the past so that $\mathbf{E}(t_0)\approx 0$. Equations (3.6) and (3.7), with Ω set equal to zero in the denominators of the latter, were obtained by Cina and Romero-Rochin [30] via the adiabatic theorem and time-independent perturbation theory.

In general, $\tilde{\alpha}_0$ is a complicated nonlinear function (operator) of $\mathbf{R}$. In order to keep the treatment as simple as possible, besides not being a bad approximation, we implement the well-known Placzek approximation by expanding the polarizability to first order in $\mathbf{R}$ around the equilibrium configuration $\mathbf{R}^0$ of the nuclei (in the ground electronic state). Taking $\mathbf{R}^0\equiv\mathbf{0}$, one gets

$$\tilde{\alpha}_0\approx\tilde{\alpha}_0^0+\left.\frac{\partial\tilde{\alpha}_0}{\partial R_k}\right|_0 R_k\ , \tag{3.8}$$

where R_k denote the components of the nuclei coordinates (not necessarily in three dimensions). The zeroth-order term $\tilde{\alpha}_0^0$ will give rise to Rayleigh-type scattering and will be dropped in what follows.

For simplicity, we assume a one-dimensional nuclear problem so that

$$\tilde{\alpha}_0\approx\frac{\partial\tilde{\alpha}_0}{\partial R}R\equiv\tilde{\alpha}'R\ , \tag{3.9}$$

thereby defining the differential polarizability $\tilde{\alpha}'$. The Raman term is now written as

$$\tfrac{1}{2}\mathbf{E}(t)\mathbf{E}(t):\tilde{\alpha}'R\equiv\mathcal{V}(t)R\ , \tag{3.10}$$

and the problem for the nuclei thus reduces to solving the following time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\phi_g(t)\rangle=[H_g(\hat{R})-\mathcal{V}(t)\hat{R}]|\phi_g(t)\rangle\ , \tag{3.11}$$

where $|\phi_g(t)\rangle$ is a vibrational wave function of the nuclei in the ground electronic state. We have written $\hat{R}$ to remind ourselves of its operator character.

Formal solution of Eq. (3.11) is

$$|\phi_g(t)\rangle = e^{-(i/\hbar)H_g t} e^{(i/\hbar)\int_{t_0}^{t} d\tau \mathcal{V}(\tau)\hat{R}(\tau)} e^{(i/\hbar)H_g t_0} |\phi_g(t_0)\rangle \ , \tag{3.12}$$

where $\hat{R}(\tau) = e^{(i/\hbar)H_g \tau}\hat{R}e^{-(i/\hbar)H_g \tau}$. We now need to specify the Hamiltonian of the ground electronic state and calculate the propagation of the state. Note that Eq. (3.12) should also be valid for arbitrary shaped light pulses as long as they are sufficiently short.

To illustrate different aspects of Eq. (3.12) we discuss two cases. First, we consider the case of an infinitely short, or abrupt, pulse for an arbitrary ground electronic surface. And second, we specialize to a harmonic surface; several aspects, including the scattering of a second delayed probe pulse shall be analyzed.

a. Infinitely short pulses: arbitrary potential energy surface. Referring to the Gaussian pulse given by Eq. (3.5), one mathematically obtains an infinitely short pulse by taking the limit $\tau_L \to 0$, with $\tau_L |\mathbf{E}_0|^2$ constant. This limit, of course, is meant in the time scale of the nuclear vibrations; it is still long in the time scales of the electronic transitions. Neglecting a term proportional to $\cos(2\Omega t)$, since it does not effectively drive the transition, we obtain a δ-function pulse,

$$\mathcal{V}(t) \approx \tfrac{1}{4}\sqrt{\pi}\tau_L \mathbf{E}_0\mathbf{E}_0 : \tilde{\alpha}' \delta(t - t_p) \ , \tag{3.13}$$

such that

$$\exp\left[\frac{i}{\hbar}\int_{t_0}^{t} d\tau \mathcal{V}(\tau)\hat{R}(\tau)\right] \approx \exp\left[-\frac{i}{\hbar}\left[\frac{\sqrt{\pi}\tau_L}{4}\mathbf{E}_0\mathbf{E}_0\right] : \tilde{\alpha}'\hat{R}(t_p)\right] \ . \tag{3.14}$$

That is, the interaction term becomes a *momentum-transfer operator* (or momentum translation) with magnitude

$$p \equiv \tfrac{1}{4}\sqrt{\pi}\tau_L \mathbf{E}_0\mathbf{E}_0 : \tilde{\alpha}' \ , \tag{3.15}$$

and the time evolution of the state, Eq. (3.12), becomes

$$|\phi_g(t)\rangle = e^{-(i/\hbar)H_g(t - t_p)} e^{(i/\hbar)p\hat{R}} e^{-(i/\hbar)H_g(t_p - t_0)} |\phi_g(t_0)\rangle \ . \tag{3.16}$$

Equations (3.16) shows that from t_0 to the arrival of the pulse t_p the system evolves under its Hamiltonian H_g. At $t = t_p$ the field transfers a momentum p with magnitude given by Eq. (3.15) and for $t > t_p$ the system again evolves under its own dynamics. Since we have assumed a weak field one does not expect to obtain a large amplitude motion, due to the momentum transferred [22,31]. In principle, however, one can obtain larger amplitudes by simply hitting the molecule with a train of pulses [18], i.e., ultrashort pulses separated by time intervals longer than the duration of each pulse. The result follows straightforwardly and is given by

$$\begin{aligned} |\phi_g(t)\rangle = {} & e^{-(i/\hbar)H_g(t - t_N)} e^{(i/\hbar)p_N \hat{R}} \\ & \times e^{-(i/\hbar)H_g(t_N - t_{N-1})} \cdots e^{-(i/\hbar)H_g(t_2 - t_1)} e^{(i/\hbar)p_1 \hat{R}} \\ & \times e^{-(i/\hbar)H_g(t_1 - t_0)} |\phi_g(t_0)\rangle \ , \end{aligned} \tag{3.17}$$

where the pulses arrive at $t_1, t_2, \ldots, t_N$, and we have allowed for different momentum transfer for each pulse. Of course, one can amplify or diminish the amplitude motion of the nuclear vibrations depending on the ratio between the delay time of successive pulses and the molecular vibrational period. A train of pulses appropriately timed may also be used to selectively amplify or filter among several Raman active modes, since those not in phase will not be amplified, besides being naturally relaxing [12]. Such effects can be seen more easily in a harmonic surface, as we now discuss.

b. Harmonic potential-energy surface. The above results are valid for any one-dimensional energy surface potential. We can gain further understanding by considering a harmonic potential, i.e., we assume

$$H_g = \hbar\omega_0(a^\dagger a + \tfrac{1}{2}) \ . \tag{3.18}$$

In order to apply Eq. (3.12) we need the position operator $\hat{R}(t)$, which is simply given by

$$\hat{R}(t) = \left[\frac{\hbar}{2M\omega_0}\right]^{1/2} (a e^{-i\omega_0 t} + a^\dagger e^{i\omega_0 t}) \ , \tag{3.19}$$

and substitution of this equation into Eq. (3.12) can be straightforwardly shown to yield [32]

$$e^{-(i/\hbar)H_g t} \exp\left[\frac{1}{\hbar}\int_{t_0}^{t} d\tau \mathcal{V}(\tau)\hat{R}(\tau)\right] e^{(i/\hbar)H_g t_0} = e^{-(1/2)|\beta(t)|^2} e^{i\beta^*(t)a^\dagger} e^{i\beta(t)a} e^{-(i/\hbar)H_g(t - t_0)} \ , \tag{3.20}$$

where

$$\beta(t) = \left[\frac{1}{2\hbar M\omega_0}\right]^{1/2} \int_{t_0}^{t} d\tau \mathcal{V}(\tau) e^{i\omega_0(t - \tau)} \ . \tag{3.21}$$

With this result several aspects of ISS can be easily seen. First, we show that after the passage of a short pulse (or pulses) the system is left in a coherent state. For a harmonic potential this is best exemplified, since for an initial state with population only in its ground vibrational state the coherent state for later times corresponds to the so-called quasiclassical state. That is, let $|\phi_g(t_0)\rangle \equiv |0_g\rangle$, with $|0_g\rangle$ the ground vibrational state. Then, with Eq. (3.20) we obtain

$$|\phi_g(t)\rangle = e^{-(i/2)\omega_0(t - t_0)} e^{-(1/2)|\beta(t)|^2} (e^{i\beta^*(t)a^\dagger}|0_g\rangle) \ . \tag{3.22}$$

That the above is a minimum uncertainty wave packet can be seen by writing it in its position representation, $\phi_g(R,t) = \langle R|\phi_g(t)\rangle$,

$$\phi_g(R,t)=\left[\frac{M\omega_0}{\pi\hbar}\right]^{1/4} e^{-(i/2)\omega_0(t-t_0)}e^{-(1/2\Delta^2)[R-R_0(t)]^2+(i/\hbar)P_0(t)[R-R_0(t)]+(i/\hbar)S_0(t)} , \tag{3.23}$$

where $\Delta=(\hbar/M\omega_0)^{1/2}$ is the width of the wave packet. $R_0(t)$ and $P_0(t)$ are the position and momentum expectation values, i.e., the values at the center of the wave packet:

$$R_0(t)=\langle\phi_g(t)|\hat{R}|\phi_g(t)\rangle$$

$$=\frac{1}{M\omega_0}\int_{t_0}^{t} d\tau\, \mathcal{V}(\tau)\sin\omega_0(t-\tau) , \tag{3.24}$$

and

$$P_0(t)=\langle\phi_g(t)|\hat{P}|\phi_g(t)\rangle=\int_{t_0}^{t} d\tau\, \mathcal{V}(\tau)\cos\omega_0(t-\tau) . \tag{3.25}$$

The phase $S_0(t)$ in Eq. (3.23) is the classical action of the parameters $R_0(t)$ and $P_0(t)=M\dot{R}_0(t)$, i.e.,

$$S_0(t)=\int_{t_0}^{t} d\tau(\tfrac{1}{2}M\dot{R}_0^2-\tfrac{1}{2}M\omega_0^2R_0^2) . \tag{3.26}$$

Equations (3.23)–(3.26) are valid for any short pulse. Suppose now that the pulse has the Gaussian form as in Eq. (3.5) and suppose that its passage occurs at $t_p=-t_D$ with $t_D \ll -t_0$ and $t_D \gg \tau_L$. Hence, we have

$$\mathcal{V}(\tau)\approx\tfrac{1}{2}\mathbf{E}_0\mathbf{E}_0{:}\tilde{\alpha}'e^{-(\tau+t_D)^2/\tau_L^2} , \tag{3.27}$$

and, therefore, from Eq. (3.24) we find that for $t<-t_D$, the vibration amplitude $R_0=0$, and for $t+t_D>\tau_L$ its value is given by

$$R_0(t)=\frac{\sqrt{\pi}}{4M\omega_0}\tau_L\mathbf{E}_0\mathbf{E}_0{:}\tilde{\alpha}'e^{-\omega_0^2\tau_L^2/4}\sin\omega_0(t+t_D) . \tag{3.28}$$

From this equation we find that the condition for the pulse to be impulsive is

$$\frac{\omega_0^2\tau_L^2}{4}\leq 1 , \tag{3.29}$$

that is, the vibrational period must be shorter than the duration of the pulse or, equivalently, the spectral band of the pulse must be broader than the vibrational frequency. This is the expected condition to have stimulated Raman scattering within a single pulse [7].

Now consider that a second pulse impinges on the molecule at time $t=0$. Let the amplitude of this pulse be $\mathbf{E}_p$. Since the delay time t_D is much greater than the duration of the pulses, the first and second pulses do not overlap and we find from Eq. (3.24) that for $t>0$ the amplitude of the vibrations is simply the sum of the two amplitudes produced by the pulses,

$$R_0(t)=R_p\sin\omega_0t+R_e\sin\omega_0(t+t_D) , \tag{3.30}$$

where the amplitude R_e can be read off Eq. (3.28) and R_p is given by an analogous expression by changing $\mathbf{E}_0$ by $\mathbf{E}_p$. Equation (3.30) can be written in the more convenient form

$$R_0(t)=R_\Sigma\sin(\omega_0t+\phi) , \tag{3.31}$$

where the total amplitude R_Σ is given by

$$R_\Sigma^2=R_p^2+R_e^2+2R_eR_p\cos\omega_0t_D , \tag{3.32}$$

and the phase ϕ is

$$\tan\phi=\frac{R_e\sin\omega_0t_D}{R_p+R_e\cos\omega_0t_D} . \tag{3.33}$$

Equations (3.32) and (3.33) show that depending on the ratio of the vibrational period to the delay time the amplitude of the vibrations can be amplified or diminished, e.g., for in phase, $\omega_0t_D=2n\pi$, maximum amplification is achieved. Clearly, if there are several Raman active modes present, the above discussion shows how selectivity of a particular mode can be achieved; this is due to the quasiclassical coherent nature of the state generated by the nonresonant excitation.

Thus, the impulsive aspect of the interaction and the coherence of the resulting state is fully demonstrated and, indeed, the analogy of a "child in a swing" is quite appropriate [22]; however, it is worth pointing out a shortcoming of this analogy. When pushing a swing, the momentum transfer is at the turning point (where potential energy is maximum), while the momentum transfer by successive ultrashort light pulses occurs at the point of maximum kinetic energy, where it is most effective in further increasing the energy. We recall once more that although the minimum uncertainty wave packet, Eq. (3.23), is a coherent state with occupancy probability different from zero in all vibrational states, in an actual realization the occupancy will be mainly in the first few states (consistent with a weak-field approximation). But as we have shown, a train of pulses timed in phase with the oscillation can, in principle, increase the vibration amplitude. Although this has been known for a while [2], technical problems have prevented the realization of trains of pulses that could transfer enough momentum to the molecule so as to produce a large vibration amplitude. Various schemes have been proposed to rectify this situation, based mainly on *resonant* pulse shaping [33] and on the use of sequences of appropriately phase-locked pulses [31]. The present theory can handle both cases.

The results given by Eqs. (3.28)–(3.33) have been obtained by Yan, Gamble, and Nelson [7] in their treatment using classical mechanics. Their spectroscopic results, such as the spectral changes of the scattered pulse (e.g., being blueshifted if in phase with the vibration and redshifted if out of phase) also follow from the present analysis. For this, we assume the probe pulse is "weak" and, therefore, one can use it as the "source" field in the wave equation for the scattered field $\mathbf{E}_s$, the polarization $\mathbf{P}$ of the medium; i.e., we should solve

$$\nabla\times[\nabla\times\mathbf{E}_s(\mathbf{r},t)]-\frac{n^2}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E}_s(\mathbf{r},t)=\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{P}(\mathbf{r},t)\ , \tag{3.34}$$

with **P** the polarization of the medium

$$\begin{aligned}\mathbf{P}(t)&=N\int_{t_0}^{t}d\tau\langle\phi_g(t)|\tilde{\alpha}(t-\tau)|\phi_g(t)\rangle\cdot\mathbf{E}_p(\tau)\\&\approx N\tilde{\alpha}'\cdot\mathbf{E}_p(t)R_0(t)\ .\end{aligned} \tag{3.35}$$

In the above equations, N is the number of molecules per unit of volume in the sample, n the index of refraction of the medium, and c the velocity of light. In order to account for the special dependence of the fields, one makes the transformation $t\rightarrow[t-(n/c)z]$ in the time dependence of the incident fields, cf. Eq. (3.5), assuming z is the direction of propagation of the fields. For the details of the consequences of Eqs. (3.34) and (3.35), see Ref. [7]. The last point we want to emphasize here is that by virtue of Eq. (3.24) for $R_0(t)$, where we find its dependence quadratic on the field $\mathbf{E}_0$, and Eq. (3.35) for $\mathbf{P}(t)$, we can see that the optical process is of the type $\chi^{(3)}$ and the corresponding susceptibility can be read off Eq. (3.35).

IV. OFF-RESONANCE ISS IN A MOLECULAR CRYSTAL

In this section we formulate the theory for a molecular crystal interacting with short laser pulses off resonance with the electronic transitions. As an example of this treatment, we shall show that the simultaneous passage of two crossed short laser pulses creates in the system, via stimulated Raman scattering, a coherent standing wave of lattice vibrations (optical phonons), i.e., the so-called phonon diffraction grating [2]. The model for the molecular crystal is a linearly coupled exciton-phonon system [34]. This system represents a crystal of molecules with two electronic states (excitons) in linear coupling with the lattice phonon modes. This model has been extensively used to study transport properties in molecular crystals and in the present context has also been studied by Walsh and Loring [14] using perturbation theory.

The Hamiltonian of the crystal is

$$\begin{aligned}H_s&=H_e+H_{\mathrm{ph}}+H_{e-\mathrm{ph}}\\&=\hbar\sum_n\omega_e a_n^\dagger a_n+\hbar\sum_q\omega_{\mathbf{q}}b_{\mathbf{q}}^\dagger b_{\mathbf{q}}\\&\quad+\frac{1}{\sqrt{N}}\sum_{n,\mathbf{q}}\omega_{\mathbf{q}}\chi_{\mathbf{q}}^n(b_{-\mathbf{q}}+b_{\mathbf{q}}^\dagger)a_n^\dagger a_n\ ,\end{aligned} \tag{4.1}$$

where the operators $a_n^\dagger$ create an excitation of the molecule at site n, while $b_{\mathbf{q}}^\dagger$ create a phonon of wave vector $\mathbf{q}$. $\hbar\omega_e$ is the electronic excitation energy of a single molecule and $\omega_{\mathbf{q}}$ is the frequency of the normal mode of wave vector $\mathbf{q}$. The electron-phonon coupling coefficient is given by $\chi_{\mathbf{q}}^n$, and due to translational symmetry it obeys

$$\chi_{\mathbf{q}}^n=\chi_{-\mathbf{q}}^{n*}=\chi_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{R}_n}\ , \tag{4.2}$$

where $\mathbf{R}_n$ is the vector position of site n in the crystal. In writing Eq. (4.1) we have not considered the possibility of excitonic hopping among different sites, necessary for a correct description of transport properties but not so for the present purposes. Moreover, the limitation to a molecular crystal with two-level molecules only does not prevent us from capturing the essential aspects of the polarizability, especially for the off-resonance condition here discussed; this is because the system actually has many (infinite in principle) electronic states, two in each site. This will become clearer below.

The radiation-matter interaction potential, in the electronic-dipole and quasiclassical approximations, is given by

$$V(t)=-\sum_n\boldsymbol{\mu}_n\cdot\mathbf{E}(\mathbf{R}_n,t)\ , \tag{4.3}$$

where $\boldsymbol{\mu}_n$ is the electronic-dipole operator of the molecule at site n,

$$\boldsymbol{\mu}_n=\boldsymbol{\mu}(a_n^\dagger+a_n)\ , \tag{4.4}$$

with $\boldsymbol{\mu}$ the transition dipole moment of each molecule. Note that the (classical) electric field $\mathbf{E}(R_n,t)$ in Eq. (4.3) not only depends on time but is also evaluated at each molecular site n.

The crystal states, which we shall denote as $|\Psi\rangle$, are sums of products of the type

$$\prod_n|s_n\rangle\otimes\prod_{\mathbf{q}}|m_{\mathbf{q}}\rangle\ , \tag{4.5}$$

where $|s_n\rangle$ are electronic states with $s_n=0$ and $s_n=1$ for the exciton at site n in its ground and excited states, respectively. $|m_{\mathbf{q}}\rangle$are the occupation number states for phonons of wave vector $\mathbf{q}$, with $m_{\mathbf{q}}=0,1,2,\ldots$.

With the use of the following unitary operator,

$$U=\exp\left[-\frac{1}{\sqrt{N}}\sum_{n,\mathbf{q}}\chi_{\mathbf{q}}^n(b_{-\mathbf{q}}-b_{\mathbf{q}}^\dagger)a_n^\dagger a_n\right]\ , \tag{4.6}$$

it is well known [34] that the system Hamiltonian H_s is diagonalized as

$$\begin{aligned}\tilde{H}_s&=UH_sU^\dagger\\&=\hbar\sum_n\tilde{\omega}_e a_n^\dagger a_n+\hbar\sum_{\mathbf{q}}\omega_{\mathbf{q}}b_{\mathbf{q}}^\dagger b_{\mathbf{q}}\\&\quad-\frac{\hbar}{N}\sum_{n,n',\mathbf{q}}\omega_{\mathbf{q}}\chi_{\mathbf{q}}^n\chi_{\mathbf{q}}^{n'*}a_n^\dagger a_{n'}^\dagger a_n a_{n'}\ ,\end{aligned} \tag{4.7}$$

where

$$\tilde{\omega}_e=\omega-\frac{\hbar}{N}\sum_{\mathbf{q}}\omega_{\mathbf{q}}|\chi_{\mathbf{q}}^n|^2\ . \tag{4.8}$$

The operator U, Eq. (4.6), also transforms the dipole operator, which is then expressed in terms of "dressed" excitons,

$$\begin{aligned}\tilde{\boldsymbol{\mu}}_n&=U\boldsymbol{\mu}_nU^\dagger\\&=\boldsymbol{\mu}\left\{a_n^\dagger\exp\left[-\frac{1}{\sqrt{N}}\sum_{n,\mathbf{q}}\chi_{\mathbf{q}}^n(b_{-\mathbf{q}}-b_{\mathbf{q}}^\dagger)\right]\right.\\&\quad\left.+a_n\exp\left[\frac{1}{\sqrt{N}}\sum_{n,\mathbf{q}}\chi_{\mathbf{q}}^n(b_{-\mathbf{q}}-b_{\mathbf{q}}^\dagger)\right]\right\}\ .\end{aligned} \tag{4.9}$$

The crystal state is accordingly transformed as $|\tilde{\Psi}\rangle = U|\Psi\rangle$.

The physical problem is that initially at t_0, the crystal is in a state with all of the molecules in their electronic ground states and, in general, the phonons are in an arbitrary state, i.e.,

$$|\Psi(t_0)\rangle = |0\rangle \otimes |\Psi_{\text{ph}}(t_0)\rangle \ , \tag{4.10}$$

where $|0\rangle = \prod_n |s_n = 0\rangle$. At a later time a laser pulse, or several laser pulses, hit the crystal. The pulses are such that none of their frequency components are in resonance with the electronic transitions $\tilde{\omega}_e$. Therefore, after the passage of the pulses the crystal remains with the excitons unexcited, but the phonon modes will be coherently excited due to stimulated Raman scattering; our purpose is to describe this state.

Therefore, the appropriate projection operators for this case are

$$\mathcal{P} = |0\rangle\langle 0| \ , \tag{4.11}$$

and $\mathcal{Q} = 1 - \mathcal{P}$ projects onto all crystal states such that there is at least one excited molecule. It is straightforward to verify that, cf. Eq. (4.6),

$$U\mathcal{P}U^{\dagger} = \mathcal{P} \ . \tag{4.12}$$

We now follow the procedure and approximations presented in Sec. II and arrive at the corresponding effective Schrödinger equation, in the interaction picture,

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\mathcal{P}|\tilde{\Psi}_I(t)\rangle &= -\frac{i}{2\hbar}\int_{t_0}^{t} d\tau [\mathcal{P}\tilde{V}_I(t)\mathcal{Q}\tilde{V}_I(\tau)\mathcal{P} \\ &\qquad -\mathcal{P}\tilde{V}_I(\tau)\mathcal{Q}\tilde{V}_I(t)\mathcal{P}]\mathcal{P}|\tilde{\Psi}_I(t)\rangle \ , \end{aligned} \tag{4.13}$$

where

$$\tilde{V}_I(t) = e^{(i/\hbar)\tilde{H}_s t}\tilde{V}(t)e^{(-i/\hbar)\tilde{H}_s t} \ , \tag{4.14}$$

and the tildes refer to the operators unitarily transformed by U.

Since all the molecules remain in their ground states [not that there is no absorption-emission term $\mathcal{P}\tilde{V}_I(t)\mathcal{P}$ in Eq. (4.13)] the problem reduces to an interaction between the lattice phonons and the radiation field. This can be made explicit by multiplying on the left of Eq. (4.13) by $\langle 0|$; by undoing the interaction representation at the same time, we obtain

$$i\hbar\frac{\partial}{\partial t}|\Psi_{\text{ph}}(t)\rangle = H_{\text{eff}}(t)|\Psi_{\text{ph}}(t)\rangle \ , \tag{4.15}$$

where, very importantly, the state $|\Psi_{\text{ph}}(t)\rangle$ is the actual phonon state without the transformation U. This is because the molecules remain in their ground electronic states; namely, the crystal state at all times t is

$$|\Psi(t)\rangle = |0\rangle \otimes |\Psi_{\text{ph}}(t)\rangle \ , \tag{4.16}$$

and, therefore,

$$|\tilde{\Psi}(t)\rangle = U|\Psi(t)\rangle = |\Psi(t)\rangle \ . \tag{4.17}$$

The effective Hamiltonian in Eq. (4.15) is given by

$$\begin{aligned} H_{\text{eff}}(t) = H_{\text{ph}} - \frac{i}{2\hbar}\int_{t_0}^{t} d\tau \sum_n \sum_{n'} \sum_{N\neq 0} [&\mathbf{E}(\mathbf{R}_n,t)\mathbf{E}(\mathbf{R}'_n,\tau):\langle 0|\tilde{\boldsymbol{\mu}}_n|N\rangle\langle N|\tilde{\boldsymbol{\mu}}_{n'}(t-\tau)|0\rangle \\ &-\mathbf{E}(\mathbf{R}_n,\tau)\mathbf{E}(\mathbf{R}'_n,t):\langle 0|\tilde{\boldsymbol{\mu}}_n(t-\tau)|N\rangle\langle N|\tilde{\boldsymbol{\mu}}_{n'}|0\rangle] \ , \end{aligned} \tag{4.18}$$

where $|N\rangle$ denote all excitonic states with *at least* one excited electronic state; and

$$\tilde{\boldsymbol{\mu}}_n(t) = e^{-(i/\hbar)\tilde{H}_s t}\tilde{\boldsymbol{\mu}}_n e^{(i/\hbar)\tilde{H}_s t} \ . \tag{4.19}$$

We now evaluate the second term in Eq. (4.18) to explicitly find the polarizability of the crystal. First, it is straightforward to find that

$$\begin{aligned} \langle 0|\tilde{\boldsymbol{\mu}}_n|N\rangle &= \boldsymbol{\mu}\langle 0|a_n|1_n\rangle \exp\left[\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\chi_{\mathbf{q}}^{n}(b_{-\mathbf{q}} - b_{\mathbf{q}}^{\dagger})\right] \\ &= \boldsymbol{\mu}\delta_{1_n,N}\exp\left[\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\chi_{\mathbf{q}}^{n}(b_{-\mathbf{q}} - b_{\mathbf{q}}^{\dagger})\right] \ , \end{aligned} \tag{4.20}$$

where $|1_n\rangle = |s_1 = 0\rangle|s_2 = 0\rangle \cdots |s_n = 1\rangle \cdots$ is the state with only the molecule at site n being excited; the second line follows from the orthonormality of the states. Moreover, it can also be easily verified that

$$e^{(i/\hbar)\tilde{H}_s t}|1_n\rangle = |1_n\rangle e^{i\tilde{\omega}_e t}e^{(i/\hbar)H_{\text{ph}} t} \tag{4.21}$$

and

$$e^{(i/\hbar)\tilde{H}_s t}|0\rangle = |0\rangle e^{(i/\hbar)H_{\text{ph}} t} \ . \tag{4.22}$$

Use of Eqs. (4.20)–(4.22) in Eq. (4.18) yields the effective Hamiltonian for the phonon part of the crystal in interaction with the radiation field:

$$H_{\text{eff}}(t)=H_{\text{ph}}-\frac{i}{2\hbar}\int_{t_0}^{t}\sum_{n}\mathbf{E}(\mathbf{R}_n,t)\mathbf{E}(\mathbf{R}_n,\tau)\left\{e^{-i\tilde{\omega}_e(t-\tau)}\exp\left[\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\chi_{\mathbf{q}}^{n}(b_{-\mathbf{q}}-b_{\mathbf{q}}^{\dagger})\right]e^{-(i/\hbar)H_{\text{ph}}(t-\tau)}\right.$$
$$\left.\times\exp\left[-\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\chi_{\mathbf{q}}^{n}(b_{-\mathbf{q}}-b_{\mathbf{q}}^{\dagger})\right]e^{(i/\hbar)H_{\text{ph}}(t-\tau)}-\text{H.c.}\right\} . \tag{4.23}$$

Within the approximations of weak fields, separation of time scales and unitary evolution in the $\mathcal{P}$ manifold discussed in Sec. II, the above Hamiltonian is quite general for the crystal model that we are using and correctly takes into account the two-photon type of interactions. The precise form of the field is also arbitrary.

In order to illustrate predictions of the theory and to make comparisons with other works, we now implement the one-phonon, or Placzek, approximation and specialize to laser pulses. Note that in the polarizability, the second term of Eq. (4.23), there appear all types of possible phonon excitations; namely, given appropriate fields, it is possible to generate 1, 2, 3, or any number of phonon excitations. For simplicity, we shall limit ourselves to Raman processes in which only one phonon is created or annihilated. This corresponds to the picture in which a photon of frequency Ω_1 interacts with the Raman active mode of frequency $\omega_{\mathbf{q}}$, and as a result a phonon of frequency $\omega_{\mathbf{q}}$ is created (annihilated) accompanied by a scattered photon of frequency $\Omega_1 \pm \omega_{\mathbf{q}}$. We will see below that this situation corresponds precisely to the Placzek approximation. Thus, we approximate

$$\exp\left[\pm\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\chi_{\mathbf{q}}^{n}(b_{-\mathbf{q}}-b_{\mathbf{q}}^{\dagger})\right]\approx 1\pm\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\chi_{\mathbf{q}}^{n}(b_{-\mathbf{q}}-b_{\mathbf{q}}^{\dagger}) . \tag{4.24}$$

We consider Gaussian laser pulses of the type

$$\mathbf{E}_l(\mathbf{r},t)=\mathbf{E}_l^0\exp\left[-\left[t-\frac{\hat{k}_l\cdot\mathbf{r}}{c'}\right]^2\Big/2\tau_L^2\right]\times\cos\Omega_l\left[t-\frac{\hat{k}_l\cdot\mathbf{r}}{c'}+\phi_l\right] , \tag{4.25}$$

where the subindex l differentiates among the different pulses present in a given situation. $\mathbf{E}_l^0$ includes the magnitude and polarization of the field, the vector $\hat{k}_l$ denotes the *direction* of propagation of the pulse, c' is the speed of light in the medium, Ω_l the central or carrier frequency, and ϕ_l is an arbitrary phase.

With the one-phonon approximation, Eq. (4.24), and for pulses all with their carrier frequencies equal to Ω, in Appendix B we show that the effective Hamiltonian reduces to

$$H_{\text{eff}}(t)\approx H_{\text{ph}}+H_R(t) , \tag{4.26}$$

where the Raman Hamiltonian $H_R(t)$ is given by

$$H_R=\frac{1}{2\hbar\sqrt{N}}\sum_{n}\sum_{\mathbf{q}}\omega_{\mathbf{q}}\chi_{\mathbf{q}}^{n}\tilde{\alpha}_e:\mathbf{E}(\mathbf{R}_n,t)\mathbf{E}(\mathbf{R}_n,t)(b_{-\mathbf{q}}+b_{\mathbf{q}}^{\dagger}) , \tag{4.27}$$

where $\tilde{\alpha}_e$ is an electronic polarizability tensor given by

$$\tilde{\alpha}_e=\boldsymbol{\mu}\boldsymbol{\mu}\left[\frac{1}{(\tilde{\omega}_e-\Omega)^2}+\frac{1}{(\tilde{\omega}_e+\Omega)^2}\right] . \tag{4.28}$$

In obtaining this expression we have assumed that (a) the off-resonance condition is obeyed by all the frequency components of the laser pulses, (b) t_0 is a time far in the past such that $\mathbf{E}(t_0)\approx 0$, (c) the (optical) phonon frequencies $\omega_{\mathbf{q}} \ll |\Omega-\tilde{\omega}_e|$, and (d) we have dropped terms giving rise to Reyleigh-type scattering (see Appendix B). From Eq. (4.27) we see that indeed the one-phonon approximation is equivalent to the Placzek approximation: the polarizability is linear in the normal-mode coordinate $Q \sim b_{-\mathbf{q}}+b_{\mathbf{q}}^{\dagger}$.

Having found the effective Hamiltonian, the time evolution of the state of the crystal is given by

$$|\Psi_{\text{ph}}(t)\rangle=e^{-(i/\hbar)H_{\text{ph}}t}\exp_T\left[-\frac{i}{\hbar}\int_{t_0}^{t}d\tau\, e^{(i/\hbar)H_{\text{ph}}\tau}H_R(\tau)e^{-(i/\hbar)H_{\text{ph}}\tau}\right]e^{(i/\hbar)H_{\text{ph}}t_0}|\Psi_{\text{ph}}(t_0)\rangle . \tag{4.29}$$

To illustrate predictions of this theory, we now show how two noncollinear short laser pulses impulsively create a coherent diffraction grating in the crystal [2]. For this, let the external field be given by

$$\mathbf{E}(\mathbf{r},t)=\mathbf{E}_l(\mathbf{r},t)+\mathbf{E}_2(\mathbf{r},t) , \tag{4.30}$$

where $\mathbf{E}_1$ and $\mathbf{E}_2$ propagate along different directions $\hat{k}_1$ and $\hat{k}_2$. Considering only the cross term $\mathbf{E}_1(\mathbf{R}_n,t)\mathbf{E}_2(\mathbf{R}_n,t)$ and assuming that both fields have the same polarization and amplitude $\mathbf{E}_0$, the integrated term in Eq. (4.29) becomes

$$\mathcal{J}\equiv-\frac{i}{\hbar}\int_{t_0}^{t}d\tau\, e^{(i/\hbar)H_{\mathrm{ph}}\tau}H_R(\tau)e^{-(i/\hbar)H_{\mathrm{ph}}\tau}$$
$$=\frac{i}{\hbar^2}\tilde{\alpha}_e{:}\mathbf{E}_0\mathbf{E}_0\frac{\tau_L^2}{2\pi\sqrt{N}}\int_{t_0}^{t}d\tau\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\sum_{n}\sum_{\mathbf{q}}\omega_{\mathbf{q}}\chi_{\mathbf{q}}\varepsilon(\omega)\varepsilon(\omega')e^{i(\omega-\omega')\tau}\exp\left[i\left[\hat{k}_1\frac{\omega'}{c'}-\hat{k}_2\frac{\omega}{c'}+\mathbf{q}\right]\cdot\mathbf{R}_n\right]$$
$$\times(b_{-\mathbf{q}}e^{-i\omega_{\mathbf{q}}\tau}+b_{\mathbf{q}}^{\dagger}e^{i\omega_{\mathbf{q}}\tau})\,, \tag{4.31}$$

where

$$\varepsilon(\omega)=\tfrac{1}{2}(e^{-(\omega-\Omega)^2\tau_L^2/2}+e^{-(\omega+\Omega)^2\tau_L^2/2})\,. \tag{4.32}$$

First, we note that by performing the sum over n we get

$$\frac{1}{\sqrt{N}}\sum_{n}\exp\left[i\left[\hat{k}_1\frac{\omega'}{c'}-\hat{k}_2\frac{\omega}{c'}+\mathbf{q}\right]\cdot\mathbf{R}_n\right]$$
$$=\sqrt{N}\,\delta\left[\hat{k}_1\frac{\omega'}{c'}-\hat{k}_2\frac{\omega}{c'}+\mathbf{q}\right]\,, \tag{4.33}$$

that is, phonons will be excited if their wave vector $\mathbf{q}$ obeys the matching condition,

$$\mathbf{q}=\pm\left[\hat{k}_1\frac{\omega'}{c'}-\hat{k}_2\frac{\omega}{c'}\right]\,. \tag{4.34}$$

Since the values of ω and ω' are within the spectral width of the pulses, it is clear that many phonons will be excited within a certain band around the "central" wave vector given by

$$\pm\mathbf{q}_0=\pm(\hat{k}_1-\hat{k}_2)\frac{\Omega}{c'}\equiv\mathbf{k}_1-\mathbf{k}_2\,, \tag{4.35}$$

which will have the strongest intensity. Now, since both wave vectors (±, for each selected pair) will be equally excited, it is then clear that a *standing* wave will ensue in the crystal that, in turn, will create a (temporary) diffraction grating from which a delayed pulse can be scattered.

Note also that for short pulses and thin samples, we can extend the limits of the time integration to $\pm\infty$. Hence, integration over τ yields factors $\delta(\omega-\omega'\pm\omega_{\mathbf{q}})$ that indicate that, in addition to phonon wave-vector matching, frequency matching must also be satisfied. For optical phonons this does not present a problem since the corresponding dispersion relations are usually very flat.

For definiteness and simplicity in the calculation, let us assume a single optical-phonon branch with frequency $\omega_{\mathbf{q}}\approx\omega_E$ for all values of $\mathbf{q}$, and keep only the wave vector $\mathbf{q}_0$ in Eq. (4.31). All the integrals can now be performed and we obtain

$$\mathcal{J}\approx\frac{-i}{\hbar}\tilde{\alpha}_e{:}\mathbf{E}_0\mathbf{E}_0\frac{\sqrt{\pi}\sqrt{N}}{4}\omega_E\tau_L e^{-\omega_E^2\tau_L^2/4}$$
$$\times[(\chi_{\mathbf{q}_0}b_{-\mathbf{q}_0}+\chi_{\mathbf{q}_0}^{*}b_{-\mathbf{q}_0}^{\dagger})+(\chi_{-\mathbf{q}_0}b_{\mathbf{q}_0}+\chi_{-\mathbf{q}_0}^{*}b_{\mathbf{q}_0}^{\dagger})]\,. \tag{4.36}$$

We note from this equation, again as in Sec. III, that the condition for impulsive Raman excitation is that the duration of the pulses be smaller than the vibrational period, i.e., $\omega_E\tau_L<1$. The expression (4.36) enters into the evolution of the crystal state, cf. Eqs. (4.29) and (4.31), in the same way as in the case of a single molecule with a harmonic ground electronic potential-energy surface [see Eqs. (3.18) *et seq.*]. Therefore, without repeating the mathematical details here, we can see that by virtue of Eq. (4.36) all the phonon states with wave vector different from $\pm\mathbf{q}_0$ will be left unaffected while those satisfying the wave-vector matching condition will receive an instantaneous momentum transfer and a coherent standing wave with wave vector $\mathbf{q}_0$ will be produced. In particular, if initially those phonon states are not excited, after the passage of the pulses they will be left in a *bona fide* coherent or quasiclassical state. Since, in fact, a whole band of phonons is excited, however narrow, in the course of time there will be an effect of loss of coherence in the diffraction grating thus produced, in addition to loss of coherence due to anharmonic couplings and relaxation effects.

V. COMMENTS

In this article we have presented a simple theoretical framework to study impulsive stimulated scattering from molecular systems. These results should have immediate application in molecular systems in gas, liquid, and solid phases. The main result is the derivation of an effective, Hermitian Hamiltonian for the radiation-matter interaction that accounts for absorption-emission interaction among the possible electronic resonances, as well as Raman interactions with the vibrational or nuclear degrees of freedom. It is important to stress several aspects: (a) One must know in advance whether there are electronic resonances or not in order to define the manifold of electronic states in which the effective Hamiltonian acts; (b) the theory gives a systematic procedure for an effective inclusion of multiphonon processes; (c) since the time evolution is approximated as unitary within the manifold of the electronic states involved in the resonance, the ensuing dynamics are only correct in time scales longer than the inverse of the smallest electronic resonance offset, cf. Eqs. (2.22) and (2.23); this in turn shows that one cannot consider arbitrarily strong electric fields. It is within this short time scale that the population is not conserved within the resonance manifold, and when the virtual transitions take place.

The theory is well suited to deal with ultrashort light pulses which, depending on the dynamics to probe, may be in the picosecond or femtosecond time scale. We have analyzed in more detail the case in which the light pulse is off resonance with any electronic transition. With the physical assumption that the molecule remains during the whole interaction process in its ground electronic state, we have demonstrated the impulsive aspect of the radiation as well as the coherent excitation of the molecule; the previous results of Nelson and co-workers [2,7] using classical mechanics are, therefore, completely recovered. We emphasize that because we use the effective Hamiltonian we are able to follow the dynamics without resorting to perturbation theory; of course, the simplicity of the systems chosen allows for an analytical calculation. But besides giving a more fundamental foundation to the classical theory, our treatment offers a greater potentiality. For instance, we can deal with more realistic potential-energy surfaces and with electronic transitions; the time evolution would have to be performed numerically, but there are already well developed techniques to propagate these types of states. Note that the problem becomes relatively simple the moment that one linearizes the polarizability operator, i.e., the Placzek approximation Eq. (3.8); but one could just as well keep the full expression for the polarizability. As seen in Sec. IV, the theory can be easily adapted to describe molecular crystals with Raman active modes in interaction with short pulses; the frequencies and wave-vector matching conditions again are consequences of the use of the effective Hamiltonian in an otherwise exact calculation. As an application, we have analyzed the typical geometry of two crossed pulses that generate a diffraction grating [2].

We have kept the treatment as simple as possible and have not tried to include very important effects such as loss of coherence and relaxation. These effects can be implemented by switching to a density-matrix formalism once the effective Hamiltonian has been obtained. Relaxation terms can be added in the manner of Redfield [35] or with any other of its variants [36]. That is, the equation for the density matrix $\rho(t)$ is

$$\dot{\rho}(t)=\frac{1}{1\hbar}[H_{\text{eff}}(t),\rho(t)]+\mathcal{R}\rho(t) \;,$$

where $\mathcal{R}$ is a relaxation operator. Of course, one can also include relaxation in a more phenomenological fashion; for instance, in our example of a harmonic surface, this effect can be easily included by multiplying $R_0(t)$, Eq. (3.28), by $e^{-\gamma t}$, with γ a damping coefficient. Other effects, such as inhomogeneous broadening and thermal effects, can be achieved by considering an assembly of molecules with a given distribution of frequencies and by assuming the system to be initially in thermal equilibrium. All these effects, although essential for the explanation of observable phenomena, are not needed to elucidate the main aspects of the radiation-matter interaction with which we are dealing.

Finally, a more complete theory along the lines here introduced that would fully describe the whole spectroscopic process should take into account, on the one hand, the depletion and/or gain of the incident pulses resulting from the creation and/or annihilation of vibrations in the medium. In other words, one should take into account the dynamics of the field and solve the coupled evolutions. On the other hand, the theory should also take into account that the fields are also quantal; for the incident pulses this does not present a problem since lasers are, in fact, "quasiclassical" radiation states, but for the scattered pulses this aspect is of particular importance. Walsh and Loring [14] have shown, at least within perturbation theory, that differences may arise depending on whether the scattered fields are considered quantum or classical.

It is our hope that this treatment will serve as a complement of the already used theories and that it will add to the understanding of the spectroscopic phenomena that can now be achieved, in a more or less routine fashion, due to the remarkable experimental advances.

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APPENDIX A: DERIVATION OF EQ. (3.6)

We want to evaluate the integral

$$I(t)\equiv\int_{t_0}^{t} d\tau\,\mathbf{E}(t)\cdot\tilde{\alpha}(t-\tau)\cdot\mathbf{E}(\tau) \;, \tag{A1}$$

with $\mathbf{E}(t)$ given by Eq. (3.5) and $\tilde{\alpha}(t-\tau)$ by

$$\tilde{\alpha}(t-\tau)=\frac{i}{2\hbar}\sum_{n\neq g}(\boldsymbol{\mu}|n\rangle\langle n|e^{(i/\hbar)H_M(t-\tau)}\boldsymbol{\mu}e^{-(i/\hbar)H_M(t-\tau)}-e^{(i/\hbar)H_M(t-\tau)}\boldsymbol{\mu}e^{(i/\hbar)H_M(t-\tau)}|n\rangle\langle n|\boldsymbol{\mu}) \;. \tag{A2}$$

Using the Fourier decomposition of $\mathbf{E}(t)$,

$$\mathbf{E}(t)=\frac{1}{2\sqrt{2\pi}}\mathbf{E}_0\tau_L\int_{-\infty}^{\infty}d\omega\,e^{i\omega t}(e^{-(\omega-\Omega)^2/2\tau_L^2}+e^{-(\omega+\Omega)^2/2\tau_L^2}) \;. \tag{A3}$$

Then, taking matrix elements of $I(t)$ between two vibrational states $\langle m_g|$ and $|l_g\rangle$ and performing the integral over τ in Eq. (A1), we get

$$\langle m_g|I(t)|l_g\rangle=\frac{\tau_L}{4\hbar\sqrt{2\pi}}\mathbf{E}(t)\mathbf{E}_0:\sum_{n\neq g}\sum_{k_n}\boldsymbol{\mu}_{m_g k_n}\boldsymbol{\mu}_{k_n l_g}\int_{-\infty}^{\infty}d\omega\left(e^{-(1/2)(\omega-\Omega)^2\tau_L^2}+e^{-(1/2)(\omega+\Omega)^2\tau_L^2}\right)$$
$$\times\left[e^{-i\omega_{k_n l_g}t}\frac{e^{i(\omega_{k_n l_g}-\omega)t}-e^{i(\omega_{k_n l_g}-\omega)t_0}}{\omega_{k_n l_g}-\omega}\right.$$
$$\left.+e^{i\omega_{k_n m_g}t}\frac{e^{-i(\omega_{k_n m_g}-\omega)t}-e^{-i(\omega_{k_n m_g}-\omega)t_0}}{\omega_{k_n m_g}+\omega}\right], \tag{A4}$$

where $\omega_{k_n m_g}=(E_{k_n}-E_{m_g})/\hbar$.

Now, due to the Gaussian amplitudes in the integrals, ω is restricted to values $|\omega|\leq\Omega\pm\tau_L^{-1}$, and since all the incident-field frequency components are off resonance with all the electronic transitions, we can safely evaluate the denominators at $\omega\approx\Omega$. (In the extreme adiabatic case we can approximate $\omega\approx 0$.)

With this approximation the integrals over ω can be performed. The term proportional to $e^{-i\omega t}$ yields back $\mathbf{E}(t)$, while the term proportional to $e^{-i\omega t_0}$ gives $\mathbf{E}(t_0)$; the latter is further approximated as $\mathbf{E}(t_0)\approx 0$, since t_0 is a time far in the past.

The final result is

$$\langle m_g|I(t)|l_g\rangle\approx\mathbf{E}(t)\mathbf{E}(t):\langle m_g|\tilde{\alpha}_0|l_g\rangle\ , \tag{A5}$$

which is Eq. (3.6) with $\tilde{\alpha}_0$ given as in Eq. (3.7).

APPENDIX B: DERIVATION OF EQ. (4.27)

We start from the Raman part of the effective Hamiltonian, Eq. (4.23),

$$H_R(t)=-\frac{i}{2\hbar}\int_{t_0}^{t}\sum_n\mathbf{E}(\mathbf{R}_n,t)\mathbf{E}(\mathbf{R}_n,\tau)\left[e^{-i\tilde{\omega}_e(t-\tau)}\exp\left[\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\chi_{\mathbf{q}}^n(b_{-\mathbf{q}}-b_{\mathbf{q}}^\dagger)\right]e^{-(i/\hbar)H_{\text{ph}}(t-\tau)}\right.$$
$$\left.\times\exp\left[-\frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\chi_{\mathbf{q}}^n(b_{-\mathbf{q}}-b_{\mathbf{q}}^\dagger)\right]e^{(i/\hbar)H_{\text{ph}}(t-\tau)}-\text{H.c.}\right]\ . \tag{B1}$$

Introducing the one-phonon approximation, Eq. (4.24), we get

$$H_R(t)\approx-\frac{i}{2\hbar}\int_{t_0}^{t}\sum_n\mathbf{E}(\mathbf{R}_n,t)\mathbf{E}(\mathbf{R}_n,\tau):\boldsymbol{\mu}\boldsymbol{\mu}$$
$$\times\left\{(e^{-i\tilde{\omega}_e(t-\tau)}-e^{i\tilde{\omega}_e(t-\tau)})+e^{-i\tilde{\omega}_e(t-\tau)}\sum_{\mathbf{q}}\chi_{\mathbf{q}}^n[b_{-\mathbf{q}}(1-e^{i\omega_{\mathbf{q}}(t-\tau)})-b_{-\mathbf{q}}^\dagger(1-e^{-i\omega_{\mathbf{q}}(t-\tau)})]-\text{H.c.}\right\}\ . \tag{B2}$$

The first term gives rise to Rayleigh (elastic) scattering and will be dropped in what follows. Introducing the Fourier transform of the field into Eq. (B2),

$$\mathbf{E}(\mathbf{R}_n,\tau)=\frac{\tau_L}{\sqrt{2\pi}}\int_{-\infty}^{\infty}d\omega\, e^{-i\omega(\tau-\hat{k}\cdot\mathbf{R}_n/c')}\boldsymbol{\varepsilon}(\omega)\ , \tag{B3}$$

where

$$\boldsymbol{\varepsilon}(\omega)=\tfrac{1}{2}\mathbf{E}_0(e^{-(\omega-\Omega)^2\tau_L^2/2}+e^{-(\omega+\Omega)^2\tau_L^2/2})\ , \tag{B4}$$

and performing the integral over τ yield terms with denominators $(\omega\pm\tilde{\omega}_e)$ and $(\omega\pm\tilde{\omega}_e\pm\omega_{\mathbf{q}})$, similarly to the case in Appendix A. Assuming for definitude a far from resonance field $\tilde{\omega}_e\gg\omega\gg\omega_{\mathbf{q}}$ for all frequencies ω within the pulse, we can approximate *in the denominators* $\omega\approx\Omega$. With this approximation one can perform back the integral over ω of the Fourier decomposition (see Appendix A) and obtain terms proportional to $\mathbf{E}(\mathbf{R}_n,t)$ and $\mathbf{E}(\mathbf{R}_n,t_0)$; the latter is negligible if t_0 is a time far in the past. This yields Eq. (4.27).

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