

Subharmonic Raman effect in nonlinear mixing

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Following the recent experiments of Trebino and Rahn [Opt. Lett. 12, 912 (1987)], I show on general grounds the existence of the fractional Raman resonances in a variety of nonlinear mixing processes in atomic vapors, molecules, and solids. I present theoretical models, both classical and quantum, for such resonances.

In this Letter I report, on general grounds, the existence of the fractional Raman resonances in nonlinear spectroscopy. I define the fractional Raman resonances by the condition

$$\omega_l - \omega_s = \omega_R/n, \quad (1)$$

where ω_l and ω_s are the frequencies of the pump and probe fields, respectively, ω_R is the frequency of the Raman mode, and n is an integer. I also show that such fractional resonances have widths Γ_R/n , where Γ_R is the usual Raman linewidth. I demonstrate the almost universal existence of such a fractional Raman effect in nonlinear mixing experiments in any type of medium.

In the usual coherent anti-Stokes Raman spectroscopy experiment, the scan of the four-wave mixing signal as a function of the probe frequency ω_s yields the Raman resonance $\omega_l - \omega_s = \omega_R$. The usual coherent anti-Stokes Raman spectroscopy experiments are characterized in terms of the third-order nonlinearities of the medium. The situation could be different, however, if the intensities of the pump and probe started to become large. In such a case higher-order nonlinearities, $\chi^{(5)}$, $\chi^{(7)}$, etc. would begin to be important; for example, one would have to include contributions from fifth-order nonlinearities. Such considerations can lead to the existence of fractional Raman resonances. To demonstrate this I consider several models that are typically used to describe the vibrational Raman effect,¹⁻³ the electronic Raman effect,^{4,5} etc.

Perhaps the simplest treatment of the vibrational Raman effect is based on the two-oscillator model in which different charged oscillators with charges e and z and with amplitudes \mathbf{x} and \mathbf{Q} describe, respectively, the electronic and ionic motion. Such oscillator models are extensively used for the interpretation of the experimental data.^{1,2} I show how the oscillator model leads to the existence of the fractional Raman effect. I represent the coupling between the electronic and ionic oscillator by the potential term

$$V = \sum C_{ijk} x_i x_j Q_k, \quad (2)$$

where x_i 's and Q_j 's represent components of the ampli-

tudes \mathbf{x} and \mathbf{Q} . For simplicity I use the following approximation: electron mass $m \ll$ ionic mass M . Thus, to zeroth order in V , the electronic and ionic motions are given by

$$\mathbf{x}(\omega) = \frac{1}{e} \alpha_e(\omega) \cdot \epsilon(\omega), \quad \mathbf{Q}(\omega) \approx \frac{1}{z} \alpha_{\text{ion}}(\omega) \cdot \epsilon(\omega). \quad (3)$$

Here $\alpha_e(\omega)$ [$\alpha_{\text{ion}}(\omega)$] is the electronic (ionic) polarizability of the molecule. Remember that $\alpha_e(\omega)$ [$\alpha_{\text{ion}}(\omega)$] shows resonance at the frequency ω_e (ω_R) of the electronic (ionic) oscillator. Note that $Q(\omega) \approx 0$ since the applied field is at optical frequency. A calculation using Eq. (2) shows that the induced polarization at the four-wave mixing frequency $2\omega_l - \omega_s$ can be written as

$$\mathbf{p}^{(3)}(2\omega_l - \omega_s) = -\frac{2}{e^2} \alpha_e(2\omega_l - \omega_s) \cdot \mathbf{C} \cdot \alpha_e(\omega_l) \cdot \epsilon^*(\omega_l) \mathbf{Q}(\omega_l - \omega_s), \quad (4)$$

where

$$\mathbf{Q}(\omega_l - \omega_s) = -\frac{1}{z^2 e^2} \alpha_{\text{ion}}(\omega_l - \omega_s) \cdot \mathbf{C} \cdot \alpha_e(\omega_l) \times \alpha_e^*(\omega_s) \cdot \epsilon^*(\omega_l) \epsilon(\omega_s) \quad (5)$$

and where \mathbf{C} denotes a third-rank tensor with components C_{ijk} . Equation (4) defines the third-order nonlinear susceptibility responsible for four-wave mixing in the present system. The usual Raman resonance arises from the term $\alpha_{\text{ion}}(\omega_l - \omega_s)$.

If the laser and Stokes fields become strong, then the higher-order terms must be accounted for in computing the induced polarization. I examine the consequence of the probe field's becoming strong,⁶ i.e., I look for a six-wave mixing contribution to four-wave mixing geometry:

$$p(2\omega_l - \omega_s) = \chi^{(5)}(\omega_l, \omega_l, -\omega_s, \omega_s - \omega_s) \epsilon^2(\omega_l) \times \epsilon^{*2}(\omega_s) \epsilon(\omega_s), \quad (6)$$

where for brevity I have ignored all the tensorial indices. For the two-oscillator model the induced polarization at $2\omega_l - \omega_s$ can also arise from the following terms:

$$e\mathbf{x}(2\omega_l - \omega_s) = -\frac{2}{e} \alpha_e(2\omega_l - \omega_s) \cdot \mathbf{C} \cdot \mathbf{x}(\omega_s) \mathbf{Q}(2\omega_l - 2\omega_s), \quad (7a)$$

$$\mathbf{Q}(2\omega_l - 2\omega_s) = -\frac{1}{z^2} \alpha_{\text{ion}}(2\omega_l - 2\omega_s) \cdot \mathbf{C} \cdot \mathbf{x}(2\omega_l - \omega_s) \mathbf{x}^*(\omega_s), \quad (7b)$$

and thus the fifth-order contribution to the induced polarization is

$$\mathbf{p}(2\omega_l - \omega_s) = \frac{2}{e^2 z^2} \alpha_e(2\omega_l - \omega_s) \cdot \mathbf{C} \cdot \mathbf{x}(\omega_s) [\alpha_{\text{ion}}(2\omega_l - 2\omega_s) \cdot \mathbf{C} \cdot \mathbf{x}^*(\omega_s) \mathbf{p}^{(3)}(2\omega_l - \omega_s)], \quad (7c)$$

where $p^{(3)}$ is the usual third-order contribution to the nonlinear polarization and is given by Eq. (4). Note that since $\alpha_{\text{ion}}(\omega)$ has a resonance at $\omega = \omega_R$ with a width Γ_R , and since the nonlinear polarization [Eq. (7c)] has a term $\alpha_{\text{ion}}(2\omega_l - 2\omega_s)$, Eq. (7c) leads to the presence of the fractional Raman resonance, i.e., resonances at

$$\omega_l - \omega_s = \omega_R/2 \quad (8)$$

with a width $\Gamma_R/2$. The fractional Raman resonance can be seen if the Stokes field (probe field in the usual terminology of the pump-probe experiments) becomes strong since the extra contribution [Eqs. (7)] is proportional to the third power of the amplitude of the Stokes field. It is clear from the above analysis that still higher-order nonlinearities would lead to other fractional Raman resonances.

A way to study the subharmonic Raman resonances would be to isolate such contributions as Eqs. (7). This can be done in a six-wave mixing experiment⁶ involving the study of the coherently generated radiation at $3\omega_l - 2\omega_s$ characterized by the nonlinear susceptibility $\chi^{(5)}(\omega_l, \omega_l, \omega_l, -\omega_s, -\omega_s)$. It is clear that the coherent radiation at $3\omega_l - 2\omega_s$ is generated by the term

$$e\mathbf{x}(3\omega_l - 2\omega_s) = -\frac{2}{e} \alpha_e(3\omega_l - 2\omega_s) \cdot \mathbf{C} \cdot \mathbf{x}(\omega_l) \mathbf{Q}(2\omega_l - 2\omega_s), \quad (9)$$

where \mathbf{Q} is still given by Eq. (7b). Thus the six-wave mixing would exhibit the fractional Raman resonance [Eq. (8)]. Finally, note that in the six-wave mixing geometry the signal can also arise from the mixing of eight waves⁶ [characterized by the nonlinearity $\chi^{(7)}(\omega_l, \omega_l, \omega_l, -\omega_s, -\omega_s, \omega_s, -\omega_s)$], but all these eight waves result in the signal at the frequency $3\omega_l - 2\omega_s$ and in the direction $3\mathbf{k}_l - 2\mathbf{k}_s$. In the context of the two-oscillator model,

$$e\mathbf{x}(3\omega_l - \omega_s) = -\frac{2}{e} \alpha_e(3\omega_l - 2\omega_s) \cdot \mathbf{C} \cdot \mathbf{x}(\omega_s) \mathbf{Q}(3\omega_l - 3\omega_s), \quad (10)$$

where

$$\mathbf{Q}(3\omega_l - 3\omega_s) = -\frac{1}{z} \alpha_{\text{ion}}(3\omega_l - 3\omega_s) \cdot \mathbf{C} \cdot \mathbf{x}^*(\omega_s) \mathbf{x}(3\omega_l - 2\omega_s) \quad (11)$$

and where Eq. (9) is to be used for $\mathbf{x}(3\omega_l - 2\omega_s)$ on the right-hand side of Eq. (11). The contribution [Eq. (10)] to the signal in the six-wave mixing geometry will show the fractional Raman resonance ($\omega_R/3$) with $\Gamma_R/3$.

Recall that in the foregoing we have chosen a simple oscillator model to demonstrate our basic result, which could also be obtained from the general form of the higher-order nonlinear susceptibilities. The general form will also yield the selection rules, which I shall consider in a later publication.

Next I present a model calculation that demonstrates the existence of the fractional Raman effect in atomic systems. Consider a three-level model⁴ in which the state $|1\rangle$ is connected to the states $|2\rangle$ and $|3\rangle$ by a dipole transition. The transition $|2\rangle \leftrightarrow |3\rangle$ is the two-photon Raman transition. The state $|1\rangle$ decays to the states $|3\rangle$ and $|2\rangle$ by spontaneous emission. Let Γ_{ij} be the decay rate associated with the off-diagonal element Γ_{ij} of the density matrix. The nonlinear response of this model system can be calculated exactly by using numerical methods. Such numerical studies show the existence of a variety of new resonances including fractional Raman resonances in signals obtained by nonlinear mixing of the pump and probe fields. The fractional Raman resonance can, however, be understood in terms of a higher-order perturbation theory that is valid if the input fields are detuned far from the intermediate resonance. My calculations are based on the following interaction Hamiltonian (H.c. denotes the Hermitian conjugate):

$$H = [\epsilon_l \exp(-i\omega_l t) + \epsilon_s \exp(-i\omega_s t)] \cdot (\mathbf{d}_{13}|1\rangle\langle 3| + \mathbf{d}_{12}|1\rangle\langle 2|) + \text{H.c.}, \quad (12)$$

and the phenomenological relaxation terms in the density matrix equations show that the nonlinearly induced polarization at $2\omega_l - \omega_s$ is

$$p(2\omega_l - \omega_s) = p^{(3)}(2\omega_l - \omega_s) \times \left\{ 1 + \frac{i|\mathbf{d}_{12} \cdot \epsilon_s|^2}{\hbar^2[\Gamma_{23} + i(\omega_{23} - 2\omega_l + 2\omega_s)](\omega_{13} - \omega_l)} + \dots \right\}. \quad (13)$$

Here $p^{(3)}$ is the usual four-wave mixing contribution, which is nonzero if ϵ_l and ϵ_s are polarized such that $\mathbf{d}_{12} \cdot \epsilon_l \neq 0$ and $\mathbf{d}_{12} \cdot \epsilon_s \neq 0$. If such matrix elements are zero, then one has to consider a multilevel model. The second term inside the braces shows how the fractional Raman resonance will arise owing to the increase in the Stokes field or the probe field. In writing Eq. (13) we ignored terms involving higher powers of ϵ_s and ϵ_p , i.e., we retained terms inside the braces that are of zeroth order in ϵ_p and of second order in ϵ_s . In atomic systems the levels $|2\rangle$ and $|3\rangle$ can be degenerate levels split by a magnetic field. These may also correspond to the hyperfine levels. The above model calculation is capable of handling all these situations. When both ϵ_l and ϵ_s are intense and tuned close to the electronic resonance ω_{13} or ω_{12} , then the nonlinear mixing signal would exhibit considerable structure as a result of a variety of submultiple Rabi resonances.^{7,8}

The two models described above, which can de-

scribe the Raman effect in a wide class of system, convincingly demonstrate the occurrence of the fractional Raman resonances⁹ in nonlinear mixing experiments with strong pump and probe fields. Clearly one can develop a general quantum theory along the lines of the existing quantum theories for the conventional Raman effect. In what follows I present another general argument based on the nonlinear susceptibilities $R^{(n)}$ of a system *dressed* by a strong field. The general form¹⁰ of the second-order (with respect to the pump field) nonlinearity for a dressed system shows the existence of fractional Raman resonances in nonlinear spectroscopy. Let us consider a multilevel system interacting with a strong probe field ϵ_s . The field ϵ_s dresses the energy levels of the atom, so the energy spacings, dipole matrix elements, etc. depend on the strength of the field ϵ_s . Since ϵ_s mixes levels of different parities, the dressed states do not have well-defined parities, and thus the dipole matrix element d_{ij} is nonzero in the dressed-state basis. The relaxation parameters Γ_{ij} also depend on ϵ_s . Let us denote the complex frequencies of the dressed states by $\Lambda_{ij} = \omega_{ij} - i\Gamma_{ij}$. The steady-state density matrix $\rho^{(0)}$ depends on the applied field ϵ_s . Various examples of the systems dressed by the field are found in the literature.^{5,11} Let us now examine four-wave mixing from such a system. I evaluate the induced polarization $p(2\omega_l - \omega_s)$ to second order in the field ϵ_l but to all orders in ϵ_s . [Conventionally one evaluates $p(2\omega_l - \omega_s)$ to second order in ϵ_l but to first order in ϵ_s .] The signal in four-wave mixing geometry will be obtained from

$$p_\mu(2\omega_l - \omega_s) = \sum_{\alpha\beta} R_{\mu\alpha\beta}^{(2)}(\delta, \delta)\epsilon_\alpha(\omega_l)\epsilon_\beta(\omega_l),$$

$$R_{\mu\alpha\beta}^{(2)}(\delta, \delta) = \frac{N}{2} \sum_{ijk} \rho_{ii}^{(0)} \left(d_{ik}d_{kj}d_{ji} \left\{ \left[\frac{\mu\alpha\beta}{(\Lambda_{ji} - \delta)(\Lambda_{ki} - 2\delta)} + \frac{\beta\alpha\mu}{(\Lambda_{ij} - 2\delta)(\Lambda_{ik} - \delta)} \right. \right. \right.$$

$$\left. \left. - \frac{\alpha\mu\beta}{(\Lambda_{jk} - 2\delta)(\Lambda_{ji} - \delta)} - \frac{\beta\mu\alpha}{(\Lambda_{jk} - 2\delta)(\Lambda_{ik} - \delta)} \right] + d_{ik}^\alpha d_{ki}^\beta d_{jj}^\mu \left(\frac{1}{\Lambda_{ik} - \delta} + \frac{1}{\Lambda_{ki} - \delta} \right) \right.$$

$$\left. \times [C_{kj}(2\delta) - C_{ij}(2\delta)] \right\} + (\alpha \rightarrow \beta), \quad \delta = \omega_l - \omega_s. \quad (14)$$

Here $\mu\alpha\beta$ stands for the product of the dipole matrix elements $(d_{ik}^+)_\mu(d_{kj}^-)_\alpha(d_{ji}^-)_\beta$, with d^\pm being the positive- and negative-frequency components of the dipole moment operator. The coefficients C depend on the field-dependent inelastic rates.¹⁰ The $R^{(2)}$ as defined by Eqs. (14) depends on all powers of ϵ_s through the dependence of the d 's, Λ 's, and ρ_{ij} 's on ϵ_s , and its expansion in powers of ϵ_s yields the usual susceptibilities $\chi^{(n)}$, e.g., $\chi^{(3)}$ and $\chi^{(5)}$ above. The fractional Raman effect in four-wave mixing can be shown to arise from, for example, the nonvanishing of the coefficient of the term $\rho_{ii}(d_{ik}^+)_\mu(d_{kj}^-)_\alpha(d_{ji}^-)_\beta$ for i and k such that $\Lambda_{ki} \approx \omega_R$. Note that the selection rules also follow from Eqs. (14) when we consider the nonvanishing of the matrix elements such as d_{ik} in the dressed-state

basis. Thus the fractional Raman resonances in nonlinear mixing can also be understood in terms of the dressed or renormalized $R^{(2)}$ process in the medium. A similar analysis can be given for other nonlinear mixing experiments. For example, the radiation at $3\omega_l - 2\omega_s$ can be generated by the renormalized $R^{(3)}(\delta, \delta, \delta)$ or by the third-order nonlinearity of a dressed system.¹² Such a nonlinearity, following the above analysis, would lead to the fractional Raman resonance $\omega_R/3$ in a six-wave mixing experiment.

In conclusion, I have shown, using both perturbative and nonperturbative models, how the fractional Raman resonances can arise in more-or-less all nonlinear mixing experiments in strong fields. Such fractional Raman resonances have reduced linewidths.

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