

Theory of second-harmonic generation from atom pairs in solids

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We present a theoretical study of the second-harmonic generation from pairs of two-level atoms in solids. The density-matrix formalism is used to obtain the nonlinear polarization governing the process. The second-harmonic polarization depends on the laser frequency, the interaction potential between the atoms, and the laser intensity. The signal line shape may exhibit power broadening and shift of resonances.

I. INTRODUCTION

Studies of cooperative optical transitions involving pairs and triads of atoms in solids have been of large interest in recent years.¹⁻¹⁰ Phenomena such as cooperative absorption,¹ frequency upconversion in crystals,²⁻⁴ and glasses,⁵ stimulated emission by atom pairs,⁶ and dispersion interactions between excited atoms⁷ are examples of effects which may occur when the active atoms interact among themselves.

From a practical point of view the studies in this area are of interest, for example, to determine the interaction potential among ions,² to develop very sensitive site-selective spectroscopy,^{3,8,9} and to develop upconversion lasers which operate in the blue-green region with large efficiency.⁶

The basic element in all the effects referred above is a pair (or a triad) of atoms and the experimental investigations with weakly doped samples have provided basic information related to their intrinsic behavior. Experimentally, cooperative single-photon absorption by atom pairs in doped solids was first demonstrated by Varsanyi and Dieke¹ who observed that weak absorption occurs at the sum of transition frequencies of the coupled atoms. This effect was qualitatively understood considering that it is the interaction potential between the atoms that allows the pair excitation to occur. Since then, many other experiments have been carried out where one photon interacts resonantly with a two-neighbor atom system.

The excitation of an atom pair in a two-photon absorption process was first studied in Ref. 10. In this process two photons with energy $\hbar\omega$ each interact resonantly with a pair of atoms having transition frequencies ω_a and ω_b , respectively. The resonance in this case is given by $2\omega = \omega_a + \omega_b$. The same process is also allowed for pairs of identical atoms and experimental evidence of this effect was reported for rare-earth doped solids³ and atomic vapors.¹¹ More recently the same process was further investigated by other authors.¹²

Although our interest here is focused in solid-state systems, we note that there is a close relationship between condensed-matter studies and experiments on laser-induced collisions where various linear and nonlinear optical processes were observed.^{11,13-15} In particular,

several authors¹³⁻¹⁵ report evidences of collision-assisted second-harmonic generation (SHG) in atomic vapors.

In principle, SHG by atom pairs can also be observed in solids doped with appropriate atoms or ions and we present here a theoretical approach to describe this effect. Basically, we propose that atom pairs may allow coupling between the laser field with its second harmonic, even in a centrosymmetric environment, via a nonlinear polarization which is a function of the laser intensity, the laser frequency detuning with respect to the atom-pair energy levels and the atom-atom interaction potential.

After a discussion, in Sec. II, on the physical characteristics of the atomic states involved in the SHG process we derive, in Sec. III, the stationary second-harmonic polarization induced in the ensemble of atom pairs and the signal line shape. Possible experiments to observe the effects studied here, are briefly discussed at the end of Sec. III.

II. BASIC ASSUMPTIONS

The active atoms are impurities such as trivalent rare-earth (RE) ions introduced in a large bandgap solid and we consider atom pairs formed by identical two-level RE atoms in the presence of a linearly polarized single-mode monochromatic radiation field.

To simplify the problem, we assume that the SHG process will be more effective when the distance between the atoms is smaller than the light wavelength. For such atom pairs the crystalline field has the same strength in both atom-pair sites. Atoms separated by large distances behave as isolated atoms and may not contribute to the SHG process.

Figure 1 indicates the energy levels for the isolated atoms and the manifold of energy levels for the two-atom complex. The noninteracting states $|\bar{\mu}\rangle$, $\mu=0,1,2,3$, of the atom pair corresponding to the atomic ground and excited states are defined as

$$|\bar{0}\rangle = |0\rangle_1 \otimes |0\rangle_2, \quad (1a)$$

$$|\bar{1}\rangle = \frac{1}{\sqrt{2}} [|0\rangle_1 \otimes |1\rangle_2 + |1\rangle_1 \otimes |0\rangle_2], \quad (1b)$$

$$|\bar{2}\rangle = \frac{1}{\sqrt{2}} [|0\rangle_1 \otimes |1\rangle_2 - |1\rangle_1 \otimes |0\rangle_2], \quad (1c)$$

$$|\bar{3}\rangle = |1\rangle_1 \otimes |1\rangle_2, \quad (1d)$$

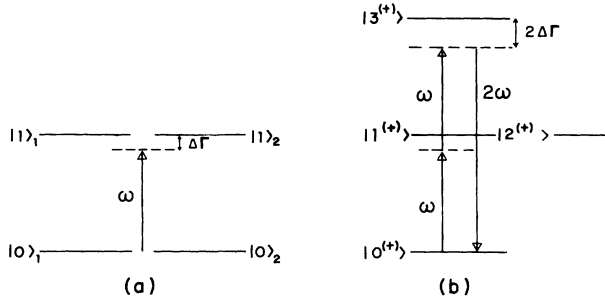


FIG. 1. (a) Energy levels for two identical isolated two-level atoms; (b) the manifold of energy levels for the two-atom pair.

whose energies $E_\mu = \hbar\omega_\mu$ are 0, E_1 , $E_2 = E_1$, and $E_3 = 2E_1$, respectively. The states $|0\rangle_{1,2}$ and $|1\rangle_{1,2}$ refer to the isolated atoms. The antisymmetric state $|\tilde{2}\rangle$ is decoupled from the other symmetric states and the atom pair behaves as a three-level system.¹⁶

The effect of the potential \hat{V} which governs the interactions between the atoms, is taken into account through the atom-pair states $|\mu^{(+)}\rangle$ which are obtained from the states $|\tilde{\mu}\rangle$. In the framework of first-order perturbation theory, the atom-pair states are related to the corresponding noninteracting ones by

$$|\mu^{(+)}\rangle = |\tilde{\mu}\rangle + \sum_{\nu \neq \mu} \frac{|\tilde{\nu}\rangle \langle \tilde{\nu} | \hat{V} | \tilde{\mu}\rangle}{E_\mu - E_\nu}. \quad (2)$$

Notice that in this approximation the wave functions are modified while the energy levels remain unshifted. This approach is valid only for weak interactions between the active atoms.

For pairs of RE ions the interaction potential may contain all order multipoles and the variation of $|\langle \tilde{\nu} | \hat{V} | \tilde{\mu}\rangle|$ with the ions separation is given by A/r^s , where $s = 6, 8$, and 10 for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interaction, respectively.¹⁷ The strong distance dependence of $|\langle \tilde{\nu} | \hat{V} | \tilde{\mu}\rangle|$ can lead to higher-order processes dominating at small distances^{17,18} especially as they can be allowed in first order, while the dipole moments of $4f-4f$ transitions vanish under the Laporte rule and require the crystal-field interaction to mix the higher-lying $5d$ orbitals. For example, numerical calculations reported in Ref. 18 show that dipole-quadrupole interaction may be larger than dipole-dipole interaction for ions separated by less than 10 \AA .

Therefore, in the following development only dipole-quadrupole interaction is considered, being represented in the basis of the noninteracting states by

$$\hat{V} = \begin{pmatrix} 0 & \sqrt{2}V_{00;10} & 0 & 0 \\ \sqrt{2}V_{01;00} & 0 & 0 & \sqrt{2}V_{10;11} \\ 0 & 0 & 0 & 0 \\ 0 & \sqrt{2}V_{11;01} & 0 & 0 \end{pmatrix}, \quad (3)$$

where the matrix elements are $\hat{V}_{\mu\nu} = \langle \tilde{\mu} | \hat{V} | \tilde{\nu}\rangle$ in the noninteracting basis and $V_{ij;kl} = {}_1\langle i | {}_2\langle j | \hat{V} | k \rangle_2 | l \rangle_1$ in the bare atomic basis of the two-atom Hilbert space. Equation (3) corresponds to a particular choice of symmetry

for the noninteracting states which participate in the process. For instance, if $|0\rangle_{1,2}$ correspond to s states, then the excited states $|1\rangle_{1,2}$ should have a p symmetry. Of course, other multipole potentials would require excited states of different symmetries and Eq. (3) should be modified.¹⁷

Hence from Eqs. (2) and (3) we obtain that the interaction potential mixes up the noninteracting states $|\tilde{\mu}\rangle$ in such a way that the atom-pair states assume the form

$$|0^{(+)}\rangle = |\tilde{0}\rangle - \sqrt{2} \left[\frac{V_{01;00}}{E_1} \right] |\tilde{1}\rangle, \quad (4a)$$

$$|1^{(+)}\rangle = |\tilde{1}\rangle + \sqrt{2} \left[\frac{V_{00;10}}{E_1} \right] |\tilde{0}\rangle - \sqrt{2} \left[\frac{V_{11;01}}{E_1} \right] |\tilde{3}\rangle, \quad (4b)$$

$$|2^{(+)}\rangle = |\tilde{2}\rangle, \quad (4c)$$

$$|3^{(+)}\rangle = |\tilde{3}\rangle + \sqrt{2} \left[\frac{V_{10;11}}{E_1} \right] |\tilde{1}\rangle. \quad (4d)$$

In the rotating wave approximation, the Hamiltonian describing the atom pair in the presence of the light field can be represented by

$$\hat{H} = \sum_{\mu=0,1,3} \hbar\omega_\mu |\mu^{(+)}\rangle \langle \mu^{(+)}| - [\hbar(g_{10}^{(+)} |1^{(+)}\rangle \langle 0^{(+)}| + g_{31}^{(+)} |3^{(+)}\rangle \langle 1^{(+)}|) A e^{-i\omega t} + \text{H.c.}], \quad (5)$$

where $\hbar g_{\mu\mu}^{(+)}$ represents the matrix elements of the atomic electric-dipole moment; the electric field of the incident light beam is represented by $\text{Re } A e^{-i\omega t}$ and $\hbar\omega_\mu$ is the energy of state $|\mu^{(+)}\rangle$. For the results reported here, we have considered laser frequencies close to resonance with $\omega_1 = E_1/\hbar$. Note, however, that the dipole moments are different from the free-atom values and their corrected expressions (up to first order in the interaction potential) are

$$g_{10}^{(+)} = \tilde{g}_{10} + \frac{\sqrt{2}}{\hbar A} V_{00;10}^* \quad (6a)$$

and

$$g_{31}^{(+)} = \tilde{g}_{31} + \frac{\sqrt{2}}{\hbar A} V_{10;11}^*. \quad (6b)$$

Physically the effect of the atom interactions is to favor the creation of a nonzero-dipole matrix element $D_{03} = \langle 0^{(+)} | \hat{d}_1 + \hat{d}_2 | 3^{(+)} \rangle$, where \hat{d}_i is the atomic dipole transition operator for atom i ($i = 1, 2$). The electric dipole of the atom pair can be calculated using Eqs. (4a) and (4d) to obtain

$$D_{03} = \frac{2}{E_1} g_{10}^* (V_{10;11} - V_{00;01}). \quad (7)$$

Note that the occurrence of atom-atom interactions is essential for the existence of D_{03} and thus a second-harmonic polarization may be induced. In other words, the interaction between the two atoms breaks the symme-

try allowing a dipole oscillating at 2ω to be created by the electromagnetic field in each atom pair. Therefore, the presence of these dipoles originates a polarization, $P_{\text{SH}}(2\omega)$, which will be the source for the SHG.

III. SECOND-HARMONIC POLARIZATION AND SIGNAL LINE SHAPE

In the previous section we have shown that the electric dipole responsible for the second-harmonic generation, D_{03} , depends linearly on the atom-atom interaction potential. We also recall that as the state $|2^{(+)}\rangle$ is decoupled from the others, the atom pair behaves as a three-level system with states $|0^{(+)}\rangle$, $|1^{(+)}\rangle$, and $|3^{(+)}\rangle$. Hence, the ensemble of pairs is described by the density operator $\hat{\rho}$, with matrix elements $\rho_{ij} = \langle i^{(+)} | \hat{\rho} | j^{(+)} \rangle$, which satisfies the Liouville equation given by

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] + \left. \frac{d\hat{\rho}}{dt} \right|_{\text{rel}}, \quad (8)$$

where the relaxation terms are described by

$$\left. \frac{d\rho_{ij}}{dt} \right|_{\text{rel}} = -\Gamma_{ij}\rho_{ij} \quad (i \neq j), \quad (9a)$$

$$\left. \frac{d\rho_{00}}{dt} \right|_{\text{rel}} = -\gamma_{10}\rho_{11}, \quad (9b)$$

$$\left. \frac{d\rho_{33}}{dt} \right|_{\text{rel}} = -\gamma_{13}\rho_{33}, \quad (9c)$$

with the relaxation rates denoted by Γ_{ij} and γ_{ij} ($i, j = 0, 1, 3$).

In order to solve for the density matrix elements, we make a double expansion where we consider a Fourier series in the frequency ω and a power series in the interaction potential $\lambda \hat{V}$,

$$\rho_{ij} = \sum_{m,n} \rho_{ij}^{(m,n)} e^{-im\omega t} \lambda^n. \quad (10)$$

However, only the resonant terms which correspond to $m = \pm 1, 0, \pm 2$ are considered. Substituting Eqs. (5), (9), and (10) into Eq. (8) and making the rotating wave approximation we obtain a set of coupled differential equations involving the several elements of $\hat{\rho}$. For zero order in the atom-atom interaction potential ($n = 0$) we obtain

$$i\dot{\rho}_{00}^{(0,0)} = \bar{g}_{10} A \rho_{01}^{(-1,0)} - \bar{g}_{10}^* A^* \rho_{10}^{(1,0)} + i\gamma_{10} \rho_{11}^{(0,0)}, \quad (11a)$$

$$i\dot{\rho}_{33}^{(0,0)} = \bar{g}_{31} A^* \rho_{31}^{(1,0)} - \bar{g}_{31} A \rho_{13}^{(-1,0)} - i\gamma_{31} \rho_{33}^{(0,0)}, \quad (11b)$$

$$i\dot{\rho}_{10}^{(1,0)} = \bar{g}_{10} A (\rho_{11}^{(0,0)} - \rho_{00}^{(0,0)}) - \bar{g}_{31}^* A^* \rho_{30}^{(2,0)} + (\omega_1 - \omega - i\Gamma_{10}) \rho_{10}^{(1,0)}, \quad (11c)$$

$$i\dot{\rho}_{31}^{(1,0)} = \bar{g}_{31} A (\rho_{33}^{(0,0)} - \rho_{11}^{(0,0)}) + \bar{g}_{10}^* A^* \rho_{30}^{(2,0)} + (\omega_3 - \omega_1 - \omega - i\Gamma_{31}) \rho_{31}^{(1,0)}, \quad (11d)$$

$$i\dot{\rho}_{30}^{(2,0)} = \bar{g}_{10} A \rho_{31}^{(1,0)} - \bar{g}_{31} A \rho_{10}^{(1,0)} + (\omega_3 - 2\omega - i\Gamma_{30}) \rho_{30}^{(2,0)}. \quad (11e)$$

Another set of coupled differential equations for first order in \hat{V} ($n = 1$) is given by

$$i\dot{\rho}_{00}^{(0,1)} = \bar{g}_{10} A \rho_{01}^{(-1,1)} - \bar{g}_{10}^* A^* \rho_{10}^{(1,1)} + i\gamma_{10} \rho_{11}^{(0,1)} + B_1, \quad (12a)$$

$$i\dot{\rho}_{33}^{(0,1)} = \bar{g}_{31} A^* \rho_{31}^{(1,1)} - \bar{g}_{31} A \rho_{13}^{(-1,1)} - i\gamma_{31} \rho_{33}^{(0,1)} + B_2, \quad (12b)$$

$$i\dot{\rho}_{10}^{(1,1)} = \bar{g}_{10} A (\rho_{11}^{(0,1)} - \rho_{00}^{(0,1)}) - \bar{g}_{31}^* A^* \rho_{30}^{(2,1)} + (\omega_1 - \omega - i\Gamma_{10}) \rho_{10}^{(1,1)} + B_3, \quad (12c)$$

$$i\dot{\rho}_{31}^{(1,1)} = \bar{g}_{31} A (\rho_{33}^{(0,1)} - \rho_{11}^{(0,1)}) + \bar{g}_{10}^* A^* \rho_{30}^{(2,1)} + (\omega_3 - \omega_1 - \omega - i\Gamma_{31}) \rho_{31}^{(1,1)} + B_4, \quad (12d)$$

$$i\dot{\rho}_{30}^{(2,1)} = \bar{g}_{10} A \rho_{31}^{(1,1)} - \bar{g}_{31} A \rho_{10}^{(1,1)} + (\omega_3 - 2\omega - i\Gamma_{30}) \rho_{30}^{(2,1)} + B_5, \quad (12e)$$

where the source terms are linear in the interaction potential and the terms B_i ($i = 1-5$) are given by

$$B_1 = \frac{\sqrt{2}}{\hbar} (V_{30;10}^* \rho_{01}^{(-1,0)} - V_{00;10} \rho_{10}^{(1,0)}), \quad (13a)$$

$$B_2 = \frac{\sqrt{2}}{\hbar} (V_{10;11} \rho_{31}^{(1,0)} - V_{10;11}^* \rho_{13}^{(-1,0)}), \quad (13b)$$

$$B_3 = \frac{\sqrt{2}}{\hbar} [(\rho_{11}^{(0,0)} - \rho_{00}^{(0,0)}) V_{00;10}^* - V_{10;11} \rho_{30}^{(2,0)}], \quad (13c)$$

$$B_4 = \frac{\sqrt{2}}{\hbar} [(\rho_{33}^{(0,0)} - \rho_{11}^{(0,0)}) V_{10;11}^* + V_{00;10} \rho_{30}^{(2,0)}], \quad (13d)$$

$$B_5 = \frac{\sqrt{2}}{\hbar} (V_{00;10}^* \rho_{31}^{(1,0)} - V_{10;11}^* \rho_{10}^{(1,0)}). \quad (13e)$$

Equations (11)–(13) allow the calculation of $P_{\text{SH}}(2\omega)$ including the effects of the atom-atom interaction up to second order.

In order to solve the above set of equations for an arbitrary laser intensity, in the steady-state regime, we look for the density-matrix element $\rho_{30}^{(2,1)}$ which can be obtained by dropping the time derivatives and performing several algebraic manipulations with Eqs. (11) and (12). Hence, assuming that $\rho_{00}^{(0,0)} + \rho_{11}^{(0,0)} + \rho_{33}^{(0,0)} = 1$, $\bar{g}_{31} = \bar{g}_{10} = g$, $\Gamma_{30} = 2\Gamma_{10}$, and that the atoms are initially in the ground state, we obtain the zero-order solution using Eq. (11).

The first-order solution in \hat{V} is obtained after substitution of the zero-order solution into Eqs. (12) and (13) which gives $\rho_{30}^{(2,1)}$. The expressions obtained are written in several levels of new quantities, so that we give them in the Appendix.

Finally, the induced second-harmonic polarization is given by

$$P_{\text{SH}}(2\omega) = N \rho_{30}^{(2,1)} D_{03}, \quad (14)$$

where N is the number of pairs per unit volume.

In principle, Eq. (14) includes the effects of the electromagnetic field in all orders and describe saturation effects such as light shifting and power broadening of the energy levels.¹⁹ A numerical analysis was done to display

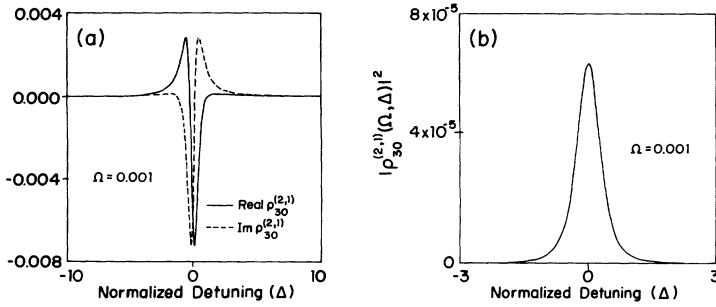


FIG. 2. Dependence of the SH line shape as a function of the normalized frequency detuning, $\Delta = (\omega_1 - \omega) / \Gamma_{01}$, for $\Omega = 0.001$. (a) Real (solid line) and imaginary (dashed line) parts of $\rho_{30}^{(2,1)}$; (b) $|\rho_{30}^{(2,1)}|^2$ vs Δ .

the SH line-shape behavior as a function of the laser input intensity and we have considered $\gamma_{10} = \gamma_{31} = \gamma = 1$, $\Gamma_{10} = \Gamma_{31} = \Gamma = 0.5\gamma$, and $V_{11;01} = V_{01;00} = 1 + i$. The results obtained are illustrated in Figs. 2–4 as a function of the normalized frequency detuning, $\Delta = (\omega_1 - \omega) / \Gamma_{10}$, and the input laser intensity.

For low intensities corresponding to a Rabi frequency $\Omega = g|A| < 1$, the SH line-shape behavior is quite simple as shown in Figs. 2(a) and 2(b). For the choice of parameters used, we show in Fig. 2(a) that the real part of $\rho_{30}^{(2,1)}$ changes sign at $\Delta = \pm 1$ going from a negative value at the line center to a positive value out of resonance (for negative values of Δ), being zero for ω far from resonance. On the other hand, the imaginary part of $\rho_{30}^{(2,1)}$ also presents a dispersive behavior and $|\rho_{30}^{(2,1)}|^2$ corresponds to a squared Lorentzian curve whose amplitude is proportional to $(\Delta^2 + 1)^{-2}$. For large input intensities, the SH line shape becomes more complex. In the region of intermediate Rabi frequencies ($1 \leq \Omega \leq 10$) the curves in Figs. 3(a) and 3(c) show that $\text{Re}\rho_{30}^{(2,1)}$ and $\text{Im}\rho_{30}^{(2,1)}$, close to the zero detuning region, split into two dips which become more distinguished for increasing values of Ω . The corresponding line shapes are shown in the Figs. 3(b) and 3(d). The different structures of $\text{Re}\rho_{30}^{(2,1)}$ and $\text{Im}\rho_{30}^{(2,1)}$ are due to

Rabi splitting of the energy levels and the spectrum becomes asymmetric with respect to the sign of Δ . For large intensities, $\Omega > 10$, the contribution of the real part of $\rho_{30}^{(2,1)}$ in the vicinity of resonance ($\Delta \approx 0$) is negligible as shown in Fig. 4(a) for $\Omega = 100$. Notice also the behavior of the two positive peaks of $\text{Re}\rho_{30}^{(2,1)}$. For low intensities these two peaks occur near $\Delta = \pm 1$ but for increasing values of Ω they move in the direction of larger detunings. The amplitude of $\text{Re}\rho_{30}^{(2,1)}$ at these points are already saturated for $\Omega \geq 10$.

The behavior of $\text{Im}\rho_{30}^{(2,1)}$ is similar. The amplitudes at $\Delta \approx \pm 1$ decrease for increasing values of Ω and the peaks corresponding to maximum and minimum amplitudes shift to larger values of Δ at the same time as they broaden. However, for very large intensities, the saturated value of $\text{Im}\rho_{30}^{(2,1)}$ becomes zero irrespective of the laser frequency detuning. It is interesting to note that the sidebands have well-defined dispersionlike structures and the line shape becomes symmetric.

The SH line-shape behavior illustrated in Figs. 2–4 is quite rich in comparison with the results obtained for isolated atoms but unfortunately there are no previously reported experiments to compare with our results. As suggested before possible systems to investigate are the large

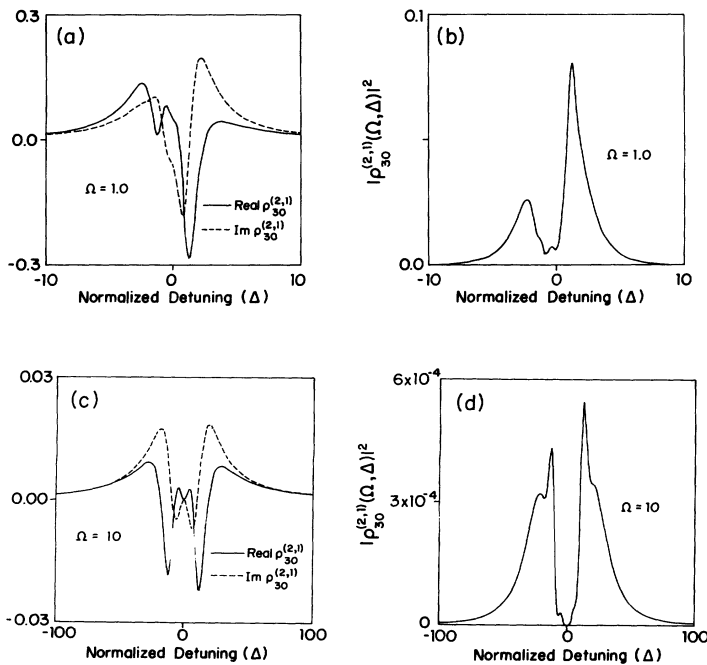


FIG. 3. Dependence of the SH line shape as a function of Δ . The real and imaginary parts of $\rho_{30}^{(2,1)}$ and of $|\rho_{30}^{(2,1)}|^2$ are shown for (a) and (b) $\Omega = 1$ and (c) and (d) $\Omega = 10$.

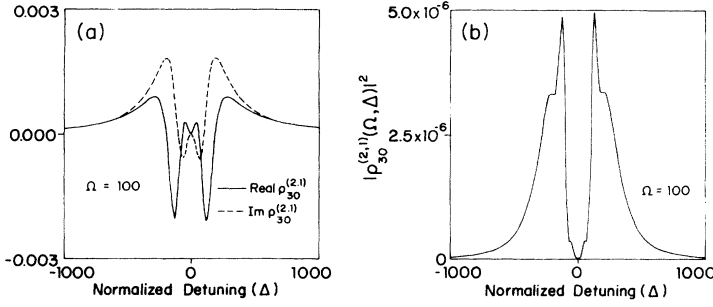


FIG. 4. Behavior of the SH line shape as a function of Δ for a large Rabi frequency ($\Omega = 100$).

bandgap insulators doped with trivalent rare-earth ions (RE^{3+}). The large amount of previous studies in these materials indicates that some crystalline hosts favor clustering of ions. Crystalline CdCsBr_3 doped with RE^{3+} , for example, seems to be a possible candidate for observing SHG assisted by pairs because the majority of trivalent ions introduced in this host usually form symmetric dimers along parallel crystalline chains.⁹ Of course, a comparison with experimental results may require samples of good quality to reduce effects due to crystalline-field inhomogeneities.

Excitation of pairs having different distances among the atoms can be done with conventional tunable lasers and the pair assignment is possible using site-selective spectroscopy.^{2-4,8,9} The real and the imaginary parts of the density matrix components can be investigated using homodyne or heterodyne detection schemes to access the in-phase and in-quadrature components of the SH field.

In conclusion, we mention that the present approach of modeling the interaction among atom pairs and the electromagnetic field may be extended to investigate the third-order nonlinear response which will give rise to new effects not observed in isolated atoms.

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APPENDIX

In this appendix we give the expressions of the density-matrix elements for zero and first order in the atom-atom interaction potential (\hat{V}) that contribute to the second-harmonic signal. For zero order in \hat{V} , the steady-state solution, is obtained from Eqs. (11) by putting the time derivatives equal to zero. The set of equations for any arbitrary laser intensity is given by

$$i\gamma_{10}\rho_{11}^{(0,0)} = \bar{g}_{10}^* A^* \rho_{10}^{(1,0)} - \bar{g}_{10} A \rho_{01}^{(-1,0)}, \quad (\text{A1a})$$

$$i\gamma_{31}\rho_{33}^{(0,0)} = \bar{g}_{31}^* A^* \rho_{31}^{(1,0)} - \bar{g}_{31} A \rho_{13}^{(-1,0)}, \quad (\text{A1b})$$

$$D\rho_{10}^{(1,0)} = \bar{g}_{31}^* A^* \rho_{30}^{(2,0)} - \bar{g}_{10} A (\rho_{11}^{(0,0)} - \rho_{00}^{(0,0)}), \quad (\text{A1c})$$

$$D\rho_{31}^{(1,0)} = \bar{g}_{31} A (\rho_{11}^{(0,0)} - \rho_{33}^{(0,0)}) - \bar{g}_{10}^* A^* \rho_{30}^{(2,0)}, \quad (\text{A1d})$$

$$2D\rho_{30}^{(2,0)} = \bar{g}_{31} A \rho_{10}^{(1,0)} - \bar{g}_{10} A \rho_{31}^{(1,0)}, \quad (\text{A1e})$$

where $D = (\omega_1 - \omega - i\Gamma)$ and we have considered $\Gamma_{10} = \Gamma_{31} = \Gamma$.

Solving the above system of equations, for the case where $\bar{g}_{10} = \bar{g}_{31} = g$, $\gamma_{10} = \gamma_{31} = \gamma$, and $\rho_{00}^{(0,0)} + \rho_{11}^{(0,0)} + \rho_{33}^{(0,0)} = 1$, we obtain for zero order in \hat{V}

$$\rho_{11}^{(0,0)} = \frac{-i\Omega^2}{\gamma|F|^2} [S_1(\rho_{00}^{(0,0)} - \rho_{11}^{(0,0)}) + S_2(\rho_{11}^{(0,0)} - \rho_{33}^{(0,0)})], \quad (\text{A2a})$$

$$\rho_{33}^{(0,0)} = \frac{-i\Omega^2}{\gamma|F|^2} [S_1(\rho_{11}^{(0,0)} - \rho_{33}^{(0,0)}) + S_2(\rho_{00}^{(0,0)} - \rho_{11}^{(0,0)})], \quad (\text{A2b})$$

$$\rho_{10}^{(1,0)} = \frac{\Omega}{F} [(2D^2 - \Omega^2)(\rho_{00}^{(0,0)} - \rho_{11}^{(0,0)}) - \Omega^2(\rho_{11}^{(0,0)} - \rho_{33}^{(0,0)})], \quad (\text{A2c})$$

$$\rho_{31}^{(1,0)} = \frac{\Omega}{F} [(2D^2 - \Omega^2)(\rho_{11}^{(0,0)} - \rho_{33}^{(0,0)}) - \Omega^2(\rho_{00}^{(0,0)} - \rho_{33}^{(0,0)})], \quad (\text{A2d})$$

$$\rho_{30}^{(2,0)} = \frac{\Omega^2 D}{FS_3}, \quad (\text{A2e})$$

where $\Omega = g|A|$, $F = D(D^2 - 2\Omega^2)$, and

$$S_1 = 2F^* D^2 - 2F(D^*)^2 - S_2, \quad (\text{A3a})$$

$$S_2 = 2i\Omega^2 \text{Im}F, \quad (\text{A3b})$$

$$S_3 = 1 - \frac{3i\Omega^2}{\gamma|F|^2} \left[S_1 - \frac{i\Omega^2}{\gamma|F|^2} (S_1^2 - S_2^2) \right]. \quad (\text{A3c})$$

The steady-state solution for first order in \hat{V} , is obtained, in the same way, from Eqs. (12). The set of equations is given by

$$i\gamma\rho_{11}^{(0,1)} = \Omega(\rho_{10}^{(1,1)} - \rho_{01}^{(-1,1)}) - B_1, \quad (\text{A4a})$$

$$i\gamma\rho_{33}^{(0,1)} = \Omega(\rho_{31}^{(1,1)} - \rho_{13}^{(-1,1)}) + B_2, \quad (\text{A4b})$$

$$D\rho_{10}^{(1,1)} = \Omega[\rho_{30}^{(2,1)} - (\rho_{11}^{(0,1)} - \rho_{00}^{(0,1)})] - B_3, \quad (\text{A4c})$$

$$D\rho_{31}^{(1,1)} = -\Omega[\rho_{30}^{(2,1)} + (\rho_{33}^{(0,1)} - \rho_{11}^{(0,1)})] - B_4, \quad (\text{A4d})$$

$$2D\rho_{30}^{(2,1)} = \Omega(\rho_{10}^{(1,1)} - \rho_{31}^{(1,1)}) - B_5, \quad (\text{A4e})$$

where the terms B_i ($i = 1-5$) are given by Eqs. (13).

Assuming that $\rho_{00}^{(0,1)} + \rho_{11}^{(0,1)} + \rho_{33}^{(0,1)} = 0$, we may solve the above set of coupled equations and find, for the

density-matrix elements, in first order in \hat{V}

$$\rho_{11}^{(0,1)} = \frac{-2\Omega}{\gamma} [(\text{Im}R_2)(\rho_{11}^{(0,1)} - \rho_{00}^{(0,1)}) - (\text{Im}R_1)(\rho_{33}^{(0,1)} - \rho_{11}^{(0,1)}) + \text{Im}R_3] + \frac{iB_1}{\gamma}, \quad (\text{A5a})$$

$$\rho_{33}^{(0,1)} = \frac{-2\Omega}{\gamma} [(\text{Im}R_2)(\rho_{11}^{(0,1)} - \rho_{33}^{(0,1)}) - (\text{Im}R_1)(\rho_{11}^{(0,1)} - \rho_{00}^{(0,1)}) - \text{Im}R_4] - \frac{iB_2}{\gamma}, \quad (\text{A5b})$$

$$\rho_{1,0}^{(1,1)} = R_1(\rho_{33}^{(0,1)} - \rho_{11}^{(0,1)}) - R_2(\rho_{11}^{(0,1)} - \rho_{00}^{(0,1)}) - R_3, \quad (\text{A5c})$$

$$\rho_{3,1}^{(1,1)} = R_1(\rho_{11}^{(0,1)} - \rho_{00}^{(0,1)}) - R_2(\rho_{33}^{(0,1)} - \rho_{11}^{(0,1)}) + R_4, \quad (\text{A5d})$$

$$\rho_{30}^{(1,1)} = \frac{\Omega}{2D} \left\{ \frac{2\Omega D^2}{R_5} [\beta_5(\beta_1 - 1) - \beta_3(1 - \beta_4) + \beta_2\beta_5 - \beta_3\beta_4] - R_3 - R_4 \right\} - \frac{B_5}{2D}, \quad (\text{A5e})$$

where

$$R_1 = \frac{\Omega^3}{2D(D^2 - \Omega^2)}, \quad R_2 = \frac{\Omega(2D^2 - \Omega^2)}{2D(D^2 - \Omega^2)},$$

$$R_3 = \frac{L_1\Omega^2 + L_2(2D^2 - \Omega^2)}{4D^2(D^2 - \Omega^2)},$$

$$R_4 = \frac{L_2\Omega^2 + L_1(2D^2 - \Omega^2)}{4D^2(D^2 - \Omega^2)},$$

$$R_5 = (1 - \beta_1)(1 - \beta_4) + \beta_2\beta_4,$$

and

$$L_1 = 2DB_3 + \Omega B_5, \quad L_2 = \Omega B_5 - 2DB_4,$$

$$\beta_1 = \frac{-2\Omega}{\gamma} \text{Im}(2R_2 - R_1),$$

$$\beta_2 = \frac{-2\Omega}{\gamma} \text{Im}(R_2 - 2R_1),$$

$$\beta_3 = \frac{-2\Omega}{\gamma} \text{Im}(2R_3 - R_4) + \frac{i}{\gamma}(2B_1 - B_2),$$

$$\beta_4 = \frac{-2\Omega}{\gamma} \text{Im}(R_1 + R_2),$$

$$\beta_5 = \frac{-2\Omega}{\gamma} \text{Im}(R_3 + R_4) + \frac{i}{\gamma}(B_1 + B_2).$$

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