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Interference between nonresonant three-photon absorption and third-harmonic generation and the cancellation of four-photon resonances

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We investigate the theory of cancellation by interference between the absorption of three fundamental laser photons and one third-harmonic photon. The theory is formulated in terms of the density matrix so as to take detunings, dephasing, and laser bandwidth into account. The result is a theory of cancellation for finite detuning that explains how four-photon resonances can be canceled by a three-photon mechanism, if there is an atomic level at near three-photon resonance. We obtain explicit conditions for this to happen, and perform calculations pertaining to a recent experiment [D. Charalambidis *et al.*, Phys. Rev. A (to be published)] where cancellation of 4+1 resonantly enhanced multiphoton ionization has been observed.

It is by now well established [1–4] that the enhancement of three-photon-resonant five-photon ionization through the $6s(J=1)$ state of Xe will diminish and eventually disappear into the nonresonant background, if the gas pressure is raised to a certain value. The accepted explanation relies on the interference between the reabsorption of the resonantly generated third harmonic (TH) and the absorption of three pump-laser photons (Fig. 1). If the magnitude and phase of the TH are appropriate, the interference can be destructive, hence the term "cancellation." It can be properly thought of as cancellation of the excitation of the resonant ($6s$) state. The effect has been observed in a number of other cases. The papers of Glownia and Sander [1], Miller *et al.* [2], Jackson and Wynne [3,4], Normand, Morellec, and Reif [5], Payne and Garret [6], and of Agarwal and Tewari [7] have provided much insight into the physics of cancellation on resonance.

Recent experiments [8] have posed a broader question:

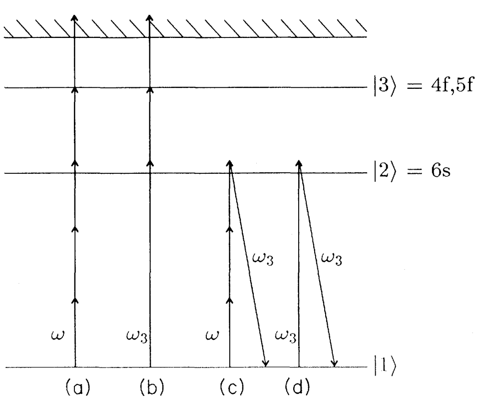

FIG. 1. The involved processes. Ionization through absorption of either (a) three-laser photons or (b) one-harmonic photon and subsequent ionization. Absorption of either (c) three-laser photons or (d) one-harmonic photon and subsequent coherent reemission at ω_3. (c) Yields TH generation and (d) causes a refractive index at ω_3.

Can this type of cancellation be responsible for the deenhancement (partial cancellation) of certain four-photon resonances? The context of the question is depicted in Fig. 1 where the frequency of the laser necessary for four-photon resonance with some state (say $4f$) in Xe is such that three photons are also at near resonance but not on resonance with the $6s$ state. Can the deenhancement of the four-photon resonance then be attributed to cancellation of the three-photon (absorption) process, even though no three-photon state exists at $3\hbar\omega$? If yes, how does the phenomenon depend on the detuning from three-photon resonance, and what determines the maximum range of detunings allowing this deenhancement?

It is the purpose of this paper to answer these questions, which have led us to a reexamination and generalization of the theory of these (interference) phenomena. This generalization is more than formal because, as we show below, without a quantitative calculation of all atomic parameters one cannot even assert if the effect will exist at any pressure. For cancellation *on* three-photon resonance, on the other hand, once the qualitative physics has been established, one knows that cancellation will occur at some pressure. This important difference between cancellation on resonance and off resonance explains why it has been possible until now to sidestep the details of atomic structure in reported theoretical discussions. It goes without saying, of course, that, even on resonance, knowledge of the atomic parameters becomes necessary if the theory is to predict the pressure at which cancellation will occur.

We have performed the analysis in the density-matrix formalism for the atomic response, coupled to a plane wave with a slowly varying amplitude governed by the Maxwell equations. The density matrix is chosen since it offers a natural way to handle detunings, the laser bandwidth as well as the decay of the coherence and of the population. At the same time it carries no intrinsic assumptions; whether or not the problem can be analyzed by means of a simple susceptibility approach will depend on the various parameters involved in the problem.

The approach taken was to eliminate the density matrix from the wave equation, solve it, and substitute it back into the density matrix to see if the obtained third-harmonic field actually caused cancellation. This elimination will not always be valid, but for parameters from the experiment at hand [8], it turns out that the decay of coherence, Γ, is roughly 2 orders of magnitude larger than the three-photon Rabi frequency, Ω_3, from the ground state to 6*s*. Under this condition, the elimination (via the rate equation approximation) is valid. When in addition the single-rate approximation is valid, one regains a picture in which the field equations can be handled by means of susceptibilities. The decay rate γ of the 6*s* state due to two-photon ionization is 1 order of magnitude smaller than Ω_3, and the very large Γ is entirely due to the laser bandwidth ($\simeq 2$ cm^{-1}). Thus for a much smaller laser bandwidth, the approximation would break down.

If we define the fields of the pump laser and the harmonic as E_1 and E_3, respectively, we have

$$E_1 = \mathcal{E} \exp[i(\omega t - kz)] + \text{c.c.} \tag{1}$$

and

$$E_3 = \mathcal{E}_3 \exp[i(\omega_3 t - k_3 z)] + \text{c.c.}, \tag{2}$$

while the total field is

$$E = E_1 + E_3 . \tag{3}$$

For the amplitude of the harmonic, the result is

$$\mathcal{E}_3 \simeq -\frac{\chi^{(3)}}{\chi^{(1)}} \mathcal{E}^3 e^{i\Delta k^{\text{NR}} z} \simeq -\frac{\mu_{12}^{(3)}}{\mu_{12}} \mathcal{E}^3 e^{i\Delta k^{\text{NR}} z} . \tag{4}$$

Here $\chi^{(3)}$ and $\chi^{(1)}$ are third- and first-order susceptibilities at ω_3; $\mu_{12}^{(3)}$, μ_{12} are three- and one-photon matrix elements between the ground state and the 6*s*, and Δk^{NR} is the nonresonant phasemismatch at ω_3. The last $\simeq$ comes from the assumption that only the resonant χ's contribute. The approximations in obtaining this result will be discussed shortly.

The above field can easily be fed back into the density-matrix equations, where it is seen that the coupling between the ground state and 6*s* vanishes, i.e.,

$$\mathcal{E}_3 \mu_{12} e^{-ik_3 z} + \mathcal{E}^3 e^{-i3kz} \mu_{12}^{(3)} = 0 . \tag{5}$$

This is cancellation—the coupling to 6*s* is gone; the path via the 6*s* near resonant to the four-photon states gives no ionization.

To investigate exactly where the detuning (or nonresonance) of the 6*s* state becomes important, one must look at the approximations made in obtaining Eq. (5) for the third-harmonic field, $\mathcal{E}_3$. First, one has to justify ignoring some of the solution for $\mathcal{E}_3$ containing a decaying exponential in *z* (where the laser beam propagates in the *z* direction). The decay is caused by an imaginary part in the refractive index at ω_3, and the condition for this decay to have the exponential removed is (with *N* denoting the number of atoms per volume, i.e., pressure, and Δ the detuning from three-photon resonance)

$$z \gg \frac{n_3 c}{2\pi\omega_3} \frac{\Delta^2 + \Gamma^2/4}{|\mu_{12}|^2 N\Gamma/2} . \tag{6}$$

This will be called the *pressure condition*, since it naturally shows that cancellation will take place at high pressure, not low. At the same time, the way Δ enters the equation shows that the pressure must be increased quadratically in the detuning for off-resonance cancellation. However, this condition, seemingly, has no limit to how far off-resonance cancellation works relative to the 6*s*.

This is not the case for the conditions connected to the neglect of the nonresonant part of the χ's, mentioned above. These conditions, which we shall call *single-state conditions*, require the following. (1) $\chi^{(1)} \simeq \chi^{\text{R}(1)}$, i.e., $\chi^{\text{R}(1)} \gg \chi^{\text{NR}(1)}$. (2) $\chi^{(3)} \simeq \chi^{\text{R}(3)}$, i.e., $\chi^{\text{R}(3)} \gg \chi^{\text{NR}(3)}$. (3) Nonresonant ionization has to be negligible; recall that the ionization process considered is only the doubly resonant path using the 6*s* to reach the four-photon states. If the background (all paths to the four-photon state not using the 6*s*) is dominant, the cancellation might take place, but it will cancel a pathway that is below the background anyway. The condition can be stated ($|3\rangle$ denoting a four-photon state and $\mu_{13}^{(4)}$ the four-photon matrix element to $|3\rangle$) as

$$\mu_{13}^{(4)} \simeq \frac{\mu_{12}^{(3)} \mu_{23}}{\Delta + i\Gamma/2} . \tag{7}$$

It is important to note how the previous three *single-state* conditions clearly show that cancellation of a four-photon resonance by means of a three-photon mechanism is only conceivable if three photons are so close to resonance with a three-photon state that it is the only relevant state at that level. In the end of the paper, we present calculations investigating these conditions. Here we must emphasize that nonresonant cancellation (in contrast to resonant cancellation) demands a quantitative calculation to assess whether it can occur at any pressure. The reason is clear from the above conditions which, when exactly on resonance, are automatically satisfied.

Since experiments are usually done in a focused laser beam rather than a plane wave, we have also solved the problem in a Gaussian beam. It turns out that all the above conditions stay unchanged, except that the *pressure condition* will have the confocal parameter *b* taking the role of *z*. It is interesting to compare the *pressure condition* with the phase-matching condition for a tightly focused beam. The latter reads [9]

$$\Delta k b \simeq -2 , \tag{8}$$

and the *pressure condition* can be written

$$|\text{Im}(\Delta k)| b \gg 1 . \tag{9}$$

Since Δk is proportional to the pressure, and since $|\text{Im}(\Delta k)| \ll |\Delta k|$ for any detuning out of the 6*s* line shape, the pressure needed for cancellation is much higher than the pressure giving phase matching at any given detuning from the 6*s*. Formulated more sharply, for cancellation to work, one has to have a pressure where TH generation is almost gone due to very bad phase matching. Thus the role of pressure is not to generate enough harmonic. At the same time, the *pressure condition* for a focused beam is symmetric in $\pm\Delta$, so that cancellation is equally possible for a detuning below the 6*s* as for a detuning above. Phase-matching considerations require a detuning to the blue of the resonance for macroscopic

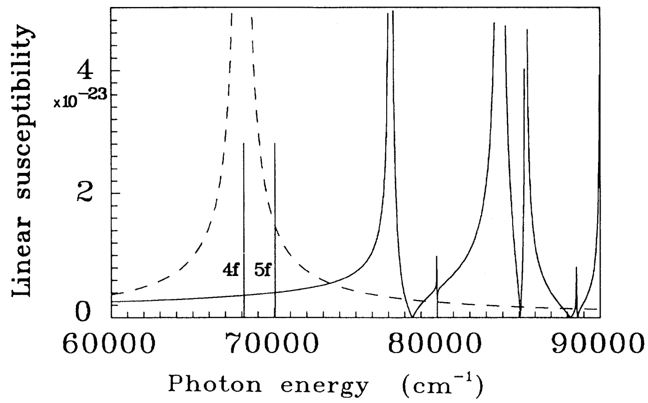

FIG. 2. $\chi^{(1)}/N$. Dashed line is resonant 6*s* diagram, solid line is all nonresonant diagrams. Marked positions show the three-photon energies corresponding to four-photon resonance with the 4*f* and 5*f* states.

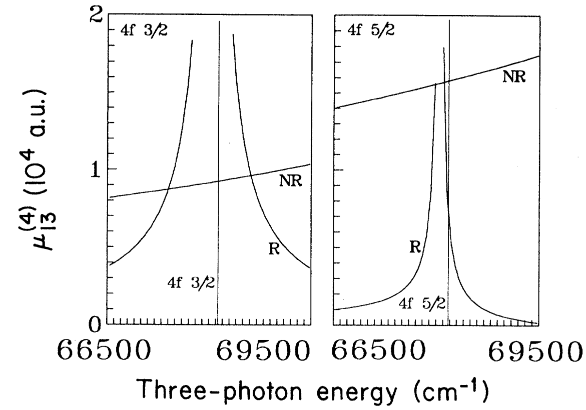

FIG. 4. Four-photon matrix elements to the $4f[\frac{3}{2}]$ and $4f[\frac{5}{2}]$ states, divided into the resonant (R) and nonresonant (NR) parts with respect to the 6*s* state. Marked positions show the three-photon energies corresponding to four-photon resonance with the two 4*f* states.

third harmonic to be generated. As is clear from the above considerations, cancellation does not rely on a large macroscopic third harmonic and it should be seen with detunings to the red of the 6*s*, as long as the pressure and single-state conditions are satisfied.

In the calculations, the main question has been the following: For the relevant four-photon states ($4f[j=\frac{3}{2}]_{J=2}$, $4f[\frac{5}{2}]_2$, $5f[\frac{3}{2}]_2$, and $5f[\frac{5}{2}]_2$ in Xe), the 4*f* states require a detuning from the 6*s* of $\simeq 100$ cm^{-1} and the 5*f* state $\simeq 2000$ cm^{-1}. Will the 6*s* state still be dominating enough to cause the cancellation?

We have used the multichannel quantum defect (MQDT) approach of L'Huillier, Tang, and Lambropoulos [10] to obtain matrix elements. Conditions (1) and (2) of the single-state conditions are seen from Figs. 2 and 3 to be well satisfied—the dominance of the 6*s* resonance parts of the linear and third-order susceptibilities stretches out well beyond 2000 cm^{-1}.

Condition (3) is more problematic. For the $4f[\frac{3}{2}]_2$ and $4f[\frac{5}{2}]_2$ the results are shown in Fig. 4. It seems that the former has a strong resonant path through 6*s*, while the latter does not. This implies that $4f[\frac{3}{2}]_2$ will show cancellation and $4f[\frac{5}{2}]_2$ will not. The 6*s* state in the calculation had almost 100% *s*-wave character, in spite of evidence [11] that it should have almost 30% *d* wave in it. We could remedy this by readjusting the *d* character of the 6*s* state. There are two *d* channels to add from, and one could take 15% of each with either the same or opposite sign. The two choices will give either $4f[\frac{3}{2}]_2$ or $4f[\frac{5}{2}]_2$ a strong resonant path and the other a vanishing resonant path. We chose to give the $4f[\frac{5}{2}]_2$ the strong resonant path. This gives very good agreement with experiment, where, indeed, the $4f[\frac{3}{2}]_2$ shows cancellation and the $4f[\frac{5}{2}]_2$ does not.

For the 5*f* states, as can be seen from Fig. 5, the picture is that the resonant path is too weak, whatever we do to the 6*s* state. However, both 5*f* states have exhibited some degree of cancellation in the experiment. This again sug-

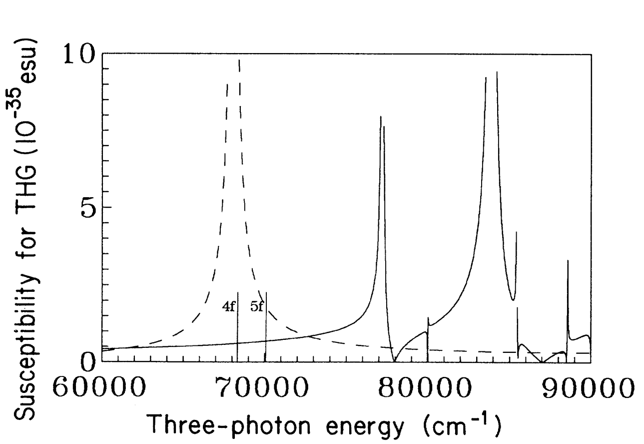

FIG. 3. $\chi^{(3)}/N$. Dashed line is resonant 6*s* diagram, solid line is all nonresonant diagrams. Marked positions show the three-photon energies corresponding to four-photon resonance with the 4*f* and 5*f* states.

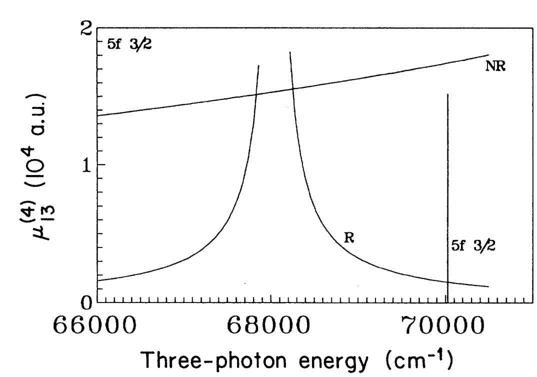

FIG. 5. Four-photon matrix elements to the $5f[\frac{3}{2}]$ state, divided into the resonant (R) and nonresonant (NR) parts with respect to the 6*s* state. Marked positions show the three-photon energies corresponding to four-photon resonance with the $5f[\frac{3}{2}]$ state. The picture for the $5f[\frac{5}{2}]$ is similar with respect to the small dominance of the resonance.

gests that we do not have as good matrix elements as would be desired. Since the comparison is between four-photon resonant and nonresonant matrix elements, an error of a factor of 2 in some crucial matrix element could give an error of an order of magnitude in the four-photon matrix elements. This would be adequate to make the resonant path dominant.

The last two paragraphs above encapsulate a remarkable and unexpected interplay between cancellation of four-photon resonances and atomic structure. The application of our theory to the interpretation of the experimental data has revealed delicate inadequacies in some of our MQDT parameters. These are effects that one normally expects to detect through energy and angular distributions of photoelectrons and not in harmonic generation.

In summary, we have developed a generalized theory of cancellation between nonresonant harmonic generation and three-photon absorption. We have derived quantitative conditions for the existence of the effect and have demonstrated its applicability to the interpretation of recent observations and its strong and demanding connection with the underlying atomic structure. With respect to the experiment of Charalambidis *et al.* [8], we have shown that even for fairly large detunings, three-photon cancellation (in the sense that all cancellation can be discussed at the three-photon absorption) is responsible for the observed cancellation of 4+1 resonantly enhanced multiphonon ionization peaks. At the same time, the results for focused beams will lead to a much more detailed understanding of the interplay between phase-matching, enhancement and cancellation in experiments where TH generation plays a role. We will elaborate on all of these points and derivations in a longer paper.

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