Pressure-Induced Extra Resonances in Four-Wave Mixing

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The first observation of pressure-induced extra resonant enhancements of a coherent four-wave-mixing signal is reported. When the difference between two input frequencies, ω_1 and ω_2, corresponds to the separation of two unpopulated upper levels, a resonant enhancement of the generated intensity at $2\omega_1 - \omega_2$ is caused by collisions.

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It is well known that four-wave mixing (4WM) and many other nonlinear phenomena can be described by a complex third-order susceptibility $\chi^{(3)}$. Explicit, complete, and general expressions containing 48 terms have recently been given by several authors.[1-3] These terms may be derived from the Liouville equation of motion for the density matrix with damping of atomic states included explicitly. Proper treatment of this damping may also be described by separate Feynman diagrams for bra and ket vectors.[2,4] The terms may be rearranged and combined, so that half of them are small corrections which vanish in the limit of zero damping, or in many cases of lifetime broadening by spontaneous emission. This was first pointed out for $\chi^{(2)}$ processes many years ago.[5]

For the purpose of further discussion $\chi^{(3)}$ describing the parametric generation of a combination frequency $\omega_p = \omega_a + \omega_b - \omega_c$ by a system in the ground state $|g\rangle$ with $\rho_{gg} = 1$, with all polarization directions parallel, is reproduced in the form

$$\chi^{(3)}(-\omega_p, \omega_a, \omega_b, -\omega_c) = \frac{NL\hbar^{-3}}{6} \sum_{k,t,j} \mu_{gk}\mu_{kt}\mu_{tj}\mu_{jg}\left[\frac{1}{(\omega_{tg}+\omega_a-\omega_c+i\Gamma_{tg})(\omega_{jg}-\omega_c+i\Gamma_{tg})}\left(\frac{1}{\omega_{kg}+\omega_p+i\Gamma_{kg}}+\frac{1+K_2(\omega_a-\omega_c,\omega_b-\omega_c)}{\omega_{kg}-\omega_b-i\Gamma_{kg}}\right)\right] + 11 \text{ similar expressions}. \quad (1)$$

The labels k, t, and j denote the intermediate states; μ_{kt} is the electric-dipole matrix element connecting states $|k\rangle$ and $|t\rangle$, with energy separation $\hbar\omega_{kt}$, and linewidth Γ_{kt}, etc. The damping correction term K_2 is given by

$$K_2(\omega_a-\omega_c, \omega_b-\omega_c) = \frac{i(\Gamma_{tj}-\Gamma_{tg}-\Gamma_{gj})+i(\Gamma_{kj}-\Gamma_{kg}-\Gamma_{gj})(\omega_{tg}+\omega_a-\omega_c+i\Gamma_{tg})/(\omega_{kj}-\omega_b+\omega_c-i\Gamma_{kj})}{\omega_{tk}+\omega_p+i\Gamma_{tk}}. \quad (2)$$

This term predicts that pressure-induced extra resonances in 4WM (PIER4) signals should be observed when $\omega_{kj} = \omega_b - \omega_c$, that is, when the difference in input frequencies equals the separation between two unpopulated excited material states $|k\rangle$ and $|j\rangle$ of the same parity. This resonance does not require the simultaneous occurrence of one-photon resonances at ω_{kg} or ω_{jg}, but one should not detune too far away from these, so that the impact approximation yielding the Lorentzian line shapes may be used, and the magnitude of the correction terms remains appreciable.

In this paper, we report the first observation of collisional enhancement of a four-wave-mixing signal. The wave mixing was done in sodium vapor and the relevant energy levels and frequencies are depicted in Fig. 1. Only two incident

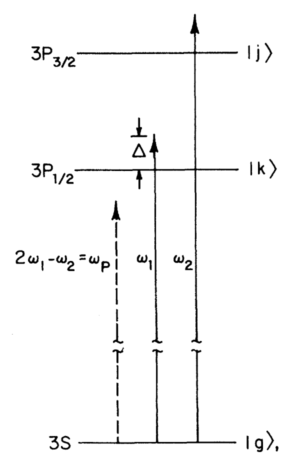

FIG. 1. Choice of frequencies for the PIER4 experiment and the relevant energy levels of the free Na atom.

frequencies are used: $\omega_a = \omega_b = \omega_1$ and $\omega_c = \omega_2$. Both are chosen close to the $3s$-$3p$ transition frequencies. This choice of frequencies requires the selection of the $3s$ state as the $|t\rangle$ state, as the higher s and d states allowed by selection rules are much further away from resonance. For the levels as drawn in Fig. 1, no combination of frequencies is exactly resonant. However, since all frequencies are near one-photon transitions, competing effects of $\chi^{(5)}$ or sequential processes of populating an excited state followed by 4WM must be carefully ruled out by experimental checks.

For natural line broadening by spontaneous emission in the absence of collisions, $\Gamma_{kj}{}^N = \Gamma_{kg}{}^N + \Gamma_{gj}{}^N$ and $K_2 = 0$. In the presence of collisions, this equality no longer holds and $\Gamma_{kj} = \Gamma_{kj}{}^N + \gamma_{kj}p$. Recent measurements of these quantities in Na with use of photon-echo techniques have been performed by Mossberg *et al.*[6] They show that $\gamma_{kj} \approx \gamma_{kg} \approx \gamma_{gj}$. This leaves $\Gamma_{kj} - \Gamma_{kg} - \Gamma_{gj} \propto p$ and $K_2 \neq 0$, giving rise to a resonant enhancement of the 4WM signal at $\omega_1 - \omega_2 = \omega_{kj}$, which increases with increasing pressure.

The experimental setup consists of two home-built Hänsch-type dye lasers pumped by a Molectron nitrogen laser. Both lasers operate without any intracavity etalons and have spectral widths of 0.3–0.5 cm^{-1}. The sodium is in a heat-pipe oven (not operated in the heat-pipe mode) and maintained at a vapor pressure of ~5 mTorr (~10^{14} cm^{-3}). Helium is introduced into the cell at a pressure range of 1–1000 Torr. A novel three-dimensional phase-matching geometry[7] has been used in these experiments. The three input beams, at ω_1 from the same laser and one at ω_2, are not coplanar. The ω_2 beam propagates on one side of the plane defined by the ω_1 beams, and the generated frequency propagates on the other. The generated 4WM signal is spatially filtered, sent through a spectrometer with 8 cm^{-1} resolution to a photomultiplier followed by a Molectron boxcar integrator, and plotted on a chart recorder. We found the beam geometry to be crucial in working with very small frequency differences, $\omega_1 - \omega_2$. Spatial discrimination against scattered light was possible even for degenerate ($\omega_1 = \omega_2$) 4WM where the use of a spectrometer for frequency discrimination offers no help.

In Fig. 2(a) a PIER4 signal at $\omega_2 - \omega_1 = 17$ cm^{-1} is shown for $\Delta = 5$ cm^{-1} and a He pressure of 800 Torr. The resonance linewidth corresponds to a convolution of laser linewidths and is larger than the collisional broadening. The signal to noise ratio was about 50:1. A similar resonance was observed for $\omega_2 - \omega_1 = -17$ cm^{-1}.

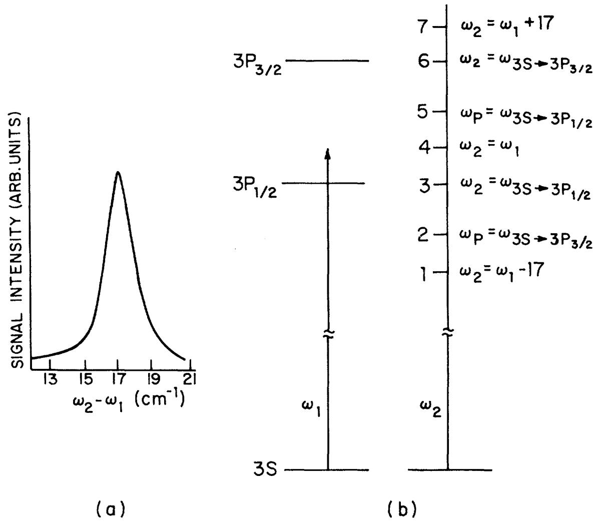

FIG. 2. (a) A typical PIER4 signal for a He pressure of 800 Torr and a detuning of $\Delta = 5$ cm^{-1}. The width corresponds to a convolution of the laser linewidths, and is larger than the collisional broadening. (b) All possible resonances of $\chi^{(3)}(-2\omega_1 + \omega_2, \omega_1, \omega_1, -\omega_2)$ as a function of ω_2, for fixed ω_1 in the vicinity of the yellow Na doublet.

Figure 2(b) depicts all possible resonances in ω_2 for a given ω_1. Resonances 3 and 6 occur when the input frequency ω_2 equals a material resonance; resonances 2 and 5, when the generated frequency ω_p equals a material frequency. These resonances occur also in the absence of a buffer gas. Resonances 1 and 7 are the PIER4 signals, as described above. They are given by the correction K terms and are absent in the absence of collisions. Resonance 4 is collisionally induced degenerate 4WM, and has contributions both from the K terms and the regular terms in $\chi^{(3)}$, as discussed below.

All these resonances have been observed, but a single scan of ω_2 over the entire range is not readily interpretable, because of the changing phase-matching conditions at different ω_2 frequencies. Also, resonances 1, 4, and 7 are as much as three orders of magnitude weaker than the other ones.

Since both ω_1 and ω_2 are near the $3s$-$3p$ transition, one has to consider the possibility of atoms excited to the $3p$ state, and a 4WM signal generated from the populated $3p$ state. This excited-state (ES) signal is expected to have a resonance enhancement at $\omega_1 - \omega_2 = \pm 17$ cm^{-1}, where the $3p_{1/2}$

state is the ground state, the $3p_{3/2}$ state is the "Raman" level, and the $4d$ (or the $3s$) state is the intermediate level. In order to check whether the signal observed in our experiment and referred to as a PIER4 signal could possibly be generated from real populations in the excited state, we introduced an additional pump beam resonant at the $3s$-$3p_{1/2}$ transition to intentionally generate the ES signal. In order to observe the pressure and pump detuning dependence free from complications due to PIER4 signals, we studied the ES signal at frequencies close to the $3p$-$4d$ transition and at large detuning of ω_1 ($\Delta = 57\ \text{cm}^{-1}$), where the PIER4 signal was not observed. In both of these cases we obtained strong ES signals with a signal-to-noise ratio of at least 1000:1. In Fig. 3 the ES signal intensity is plotted as a function of pressure for different values of pump detuning $\delta = \omega_{\text{pump}} - \omega_{3s\to 3p_{1/2}}$. The curves are normalized to the ES as measured at low helium

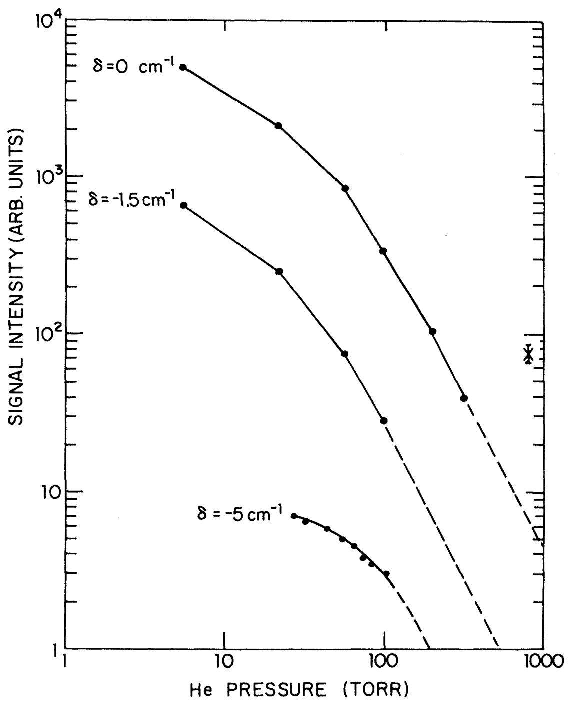

FIG. 3. ES signal compared to PIER4 signal. Cross is the amplitude of a typical PIER4 signal shown in Fig. 2(a). The solid lines are drawn for different pump detunings, $\delta = 0$, $-1.5\ \text{cm}^{-1}$, and $-5.0\ \text{cm}^{-1}$; and the dashed curves are an extrapolation ($\sim p^{-2}$) to higher pressures. The pressure dependence was measured under conditions such that the PIER4 signal was absent. The PIER4 signal observed at $\Delta = 5\ \text{cm}^{-1}$ is several orders of magnitude larger than the ES signal expected for $\delta = -5\ \text{cm}^{-1}$, and it has the opposite trend as a function of pressure.

pressure, zero pump detuning, and conditions otherwise identical to those under which the PIER4 signal was observed. The sharp decrease in ES signal with increasing pressure is due to the fast equalization of populations in the $3p$ doublet. The cross sections for transfer of population by inelastic collisions are known,[8] and a simple set of rate equations using these cross sections can, in general, account for the observed strong dependence on pressure. Figure 3 proves beyond doubt that the PIER4 signal is not generated from atoms in the excited state, but as an extra measure of safety we observed that if under conditions of a PIER4 signal a pump, resonant with a $3s$-$3p$ transition is turned on, the PIER4 signal goes down. The opposite is expected and observed for ES signals.

In conclusion, several additional comments should be made: (a) The PIER4 signal has a close theoretical relationship to the collisional redistribution discussed by Berman[9] and the observation of collisionally induced two-photon absorption resonance observed by Liao, Bjorkholm, and Berman,[10] as well as Raman and resonance fluorescence observed by Raymer and Carlsten.[11] In fact, for a choice of frequencies and resonant conditions appropriate for two-photon absorption, the general expression for $\chi^{(3)}$ in Eq. (1) reproduces the results in Refs. 8 and 9. In spite of this close theoretical connection, it should be emphasized that the PIER4 signals here are coherent. To our knowledge this is the first observation of a coherent signal generated by the introduction of an incoherent perturbation of a random nature (collisions). The explanation is that the destructive interference between two possible coherent pathways (diagrams) is eliminated by the collisions.[12]

(b) The resonance at $\omega_1 = \omega_2$ has been observed and it has contributions from the regular terms in $\chi^{(3)}$, as well as from the K terms. This resonance signal only exists in the presence of collisions and increases in proportion to the square of the helium pressure.[13]

(c) At Na-vapor pressures of above 100 mTorr, we could detect contributions of Na_2 dimers to the 4WM signals. The data reported here were all taken at a vapor pressure of 5 mTorr, where the molecular contribution is negligible.

(d) The expression (1) for $\chi^{(3)}$ is based on the assumption of a Markovian damping process leading to a Lorentzian line shape for each of the resonance lines. This is valid only in the impact approximation, $\Delta \ll \tau_c^{-1}$, where τ_c is the He-Na collision duration. For damping effects with larger detunings, the appropriate expression for $\chi^{(3)}$ should be rederived. Experimentally, no PIER4 signals are observable for large detunings, although ES signals with $\Delta \gg \tau_c^{-1}$ have been seen in the absence of a pump laser (if the Na density is high enough).

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