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Rapid Communications

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Nonimpact degenerate four-wave mixing in Na perturbed by He

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Collisionally induced four-wave mixing (FWM) signals have been observed in Na vapor broadened by He buffer gas at large detunings from resonance. Analytical expressions are developed which do not use the collisional impact approximation and which accurately describe the dependence of the FWM intensity on laser detuning and incident laser intensity. The measurements and the theory are used to calculate the nonimpact collisional line shape for the Na-He system for detunings of 40 to 200 cm^{-1} from the D line resonances.

Coherent phenomena which owe their origin to dephasing collisions were first predicted[1] and observed[2] in $\chi^{(3)}$ processes, in particular in four-wave mixing (FWM). With a few exceptions,[3–5] most of the theoretical treatments[6] of these nonlinear optical effects consider the collision process within the impact approximation. This approximation is appropriate for small detunings of the incident lasers from resonance, but it is known[3,7] to break down when the product of the detuning and the collisional duration is large, $\Delta\tau_c \gg 1$. For most of the reported experiments[6] on FWM, the impact approximation is valid. The one notable exception[8] is the Ba-Ar system, where a FWM signal was observed for detunings up to 10 cm^{-1} from resonance, and a breakdown of this approximation was indicated.

In this Rapid Communication, we report on degenerate FWM experiments in the Na-He system, with laser detunings in the range of 50–200 cm^{-1} from resonance. Since the collision time, τ_c, is of the order of 10^{-12} sec, these experiments clearly fall outside the domain of the impact approximation. We derive an expression for degenerate FWM in a two-level system which does not assume the impact approximation and allows arbitrarily strong incident fields propagating with different **k** vectors. The theory successfully predicts the experimentally observed FWM intensity as a function of laser detuning, incident laser intensity, He gas pressure, and Na density.

The experimentally measured parameters and the expression we derive for the FWM intensity can be used to obtain the nonimpact collisional absorption line shapes of the D lines of the Na-He system. Such line shapes can also be obtained from sensitive emission spectral measurements[9] as well as from nonlinear laser methods which probe the excited-state population.[10] Our technique improves on these methods in that it yields the absolute line-shape function, whereas from the other methods only relative values for the line shape as a function of detuning from resonance were obtained.

The relationship between collisional physics and FWM can be illustrated using the quasistatic picture[11] for the collision process. In Fig. 1 we show the potentials[12] of the Na-He ground state $X\,^2\Sigma$ and the $A\,^2\Pi$ and $B\,^2\Sigma$ excited states, as a function of the distance between the colliding Na atom and a single He atom in its ground state. An en-

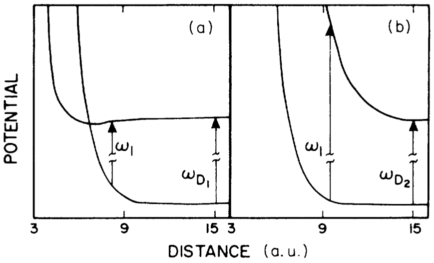

FIG. 1. Molecular-state potentials for the Na-He system (from Ref. 12) as a function of interatomic distance. In (a) we show the potential of the ground state $X\,^2\Sigma$ and the lower excited state $A\,^2\Pi$ and in (b) the ground state with the upper excited state, $B\,^2\Sigma$. An energy close to $\hbar\omega_0$ has been subtracted from the excited-state energies in order to display them on the same scale. At large distances, ω_0 is just the Na atomic resonance frequency, while at small interatomic distances the resonance frequency decreases (red detuning) for the $A\,^2\Pi$ state and increases (blue detuning) for the $B\,^2\Sigma$ state, as indicated by ω_1.

ergy of approximately $\hbar\omega_0$ was subtracted from the excited-state potentials, where $\omega_0 = \omega_{P_{1/2}}$ or $\omega_{P_{3/2}}$, is the unperturbed Na resonance frequency, so that details of the potential functions should be visible. At large distances, where the impact approximation is valid, the difference in potential is just the $\hbar\omega_0$. During the collision, however, the "collisional resonance frequency" will be a function of the distance between the Na and the He atom, and can increase or decrease from ω_0, as indicated by ω_1. For three input laser beams at a detuned frequency ω_1, the intensity of the FWM signal can thus be "resonantly enhanced" for those colliding atomic pairs having the right interatomic distance. The variation of the FWM intensity with a detuning therefore provides a direct mapping of the interatomic potentials, since each laser detuning corresponds to a particular separation of the colliding atoms. The results presented here establish the relationship between the line shape and the FWM intensity and are used to determine the absolute absorption line shape of the Na-He D lines for a range of detunings from 40 to 200 cm^{-1}. The collisional potentials[12,13] can be derived from the absorption line shapes using various well-established procedures.[11,14]

A perturbation theory of FWM, outside the impact limit, was developed previously,[4] and can be used for sufficiently weak fields. This theory, though general in the sense that it also applies to nondegenerate FWM, calculates processes that require a nonlinear susceptibility up to orders of $\chi^{(3)}$, and therefore does not account for strong (saturating) fields. Other treatments,[6] which account for saturating fields, are not appropriate in the nonimpact regime.

The validity of the two-level approximation, used in our calculation,[15] is a fortunate consequence of the shape of the Na-He potential functions shown in Fig. 1. For laser detunings to the red side of D_1 only the $A\,^2\Pi$ potential contributes "resonantly," and to the blue side of the D_2 transition only the $B\,^2\Sigma$ potential is of significance. Therefore, for laser detunings far below the D_1 or above the D_2 resonance lines, where our experiments were performed, the approximation of a two-level system is very good.

The derivation[15] of the expected FWM intensity involves the insertion of the appropriate propagation factor, $e^{i(\mathbf{k}\cdot\mathbf{r})}$, for each of the three incident beams into the optical Bloch equations, with a laser detuning dependent collisional damping rate.[16] Using the rotating-wave approximation, and with the selection of only those polarization terms which have the fourth-wave propagation factor, $\exp[i(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3)\cdot\mathbf{r}] = \exp[i(\mathbf{k}_s\cdot\mathbf{r})]$, the desired polarization can be written as

$$P_{\text{FWM}} = \frac{N\,|eX_{12}|^2}{V\pi\hbar\Delta} E_1E_2E_3\cos(\mathbf{k}_s\cdot\mathbf{r} - \omega t) \sum_{n=1}^{\infty} (-1)^{n+1} \left[\frac{\pi L_{12}\,|eX_{12}|^2}{2\gamma\hbar^2}\right]^n f_n E^{2(n-1)}\,, \tag{1}$$

where X_{12} is the dipole matrix element, Δ is the detuning, L_{12} is the normalized absorption line shape, 2γ is the spontaneous decay rate, $E^2 = E_1^2 + E_2^2 + E_3^2$, and f_n is a numerical factor depending on the relative amplitudes of the three input fields E_1, E_2, and E_3.

The summation in Eq. (1) corresponds to the various orders of the susceptibility, so that $n=1$ corresponds to $\chi^{(3)}$, $n=2$ to $\chi^{(5)}$, etc. The nonimpact line shape L_{12} appears explicitly in the expression for the polarization and can be evaluated from the interaction potential using the unified Franck-Condon approach.[14] Far from resonance, where the experiments were performed, there is no significant residual Doppler broadening and the line shape can be approximated as

$$L_{12} = PC_{12}/\Delta^x\,, \tag{2}$$

where P is the buffer gas pressure and C_{12} and x are parameters of the line shape which depend on the interaction potential. (For a Lorentzian line shape $x=2$ and $C_{12} = \gamma'/\pi P$.) Evaluating f_n in Eq. (1) explicitly for values up to $n=4$ we obtain

$$P_{\text{FWM}} \propto E^3\Delta^{-(x+1)}(1 - 2.3B + 5.6B^2 - 13.4B^3)\,, \tag{3}$$

and therefore the FWM intensity is given by

$$I_{\text{FWM}} = AI^3\Delta^{-(2x+2)}(1 - 4.7B + 16.7B^2 - 53B^3)\,, \tag{4}$$

where

$$B = \frac{\pi L_{12}\,|eX_{12}|^2}{2\gamma\hbar^2}E^2 \propto PC_{12}I\Delta^{-x}\,.$$

I is the total power density of the incident laser beams and A is a factor which depends on the Na density, He pressure, FWM interaction length, and phase-matching factor. The measurements of the FWM intensity as a function of detuning, reported here, allow us to experimentally determine the values of x and C_{12} in Eq. (2), for each of the two excited states of Na-He.

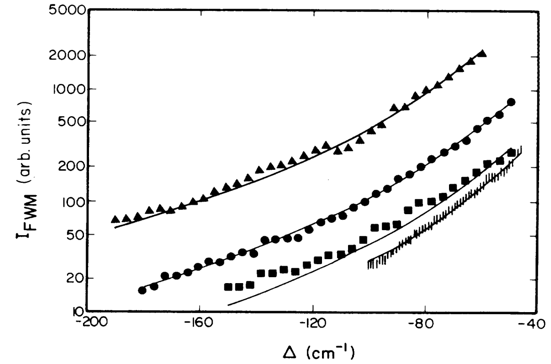

FIG. 2. FWM signal as a function of detuning from the D_1 resonance. The data indicated by ▲, |, ●, and ■ are for Na densities of 2.2, 0.4, 1.7, and 1.3×10^{13} cm^{-3}, incident laser intensities of 3.7, 2.2, 2.8, and 1.2 MW/cm^2, and He pressures of 169, 347, 347, and 722 Torr, respectively. The solid lines are calculated from Eq. (4) using the measured laser intensities and He pressures and a value of $x=0.8$ and $C_{12}=3.7\times10^{-19}$ $\text{sec}\,(\text{cm}^{-1})^{0.8}/\text{Torr}$.

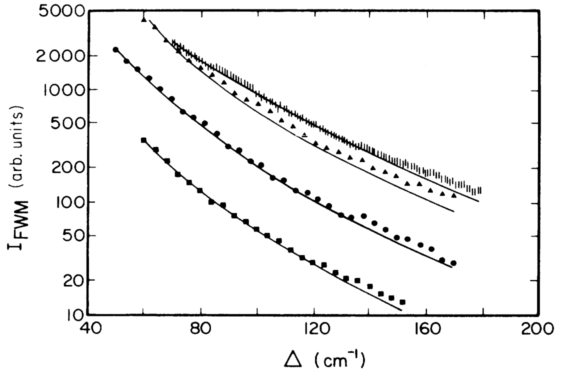

FIG. 3. FWM signal as a function of detuning from the D_2 resonance. The data indicated by ▲, |, ●, and ■ are for Na densities of 1.7, 1.5, 2.2, and 1.3×10^{13} cm^{-3}, incident laser intensities of 2.9, 2.4, 1.6, and 0.75 MW/cm^2, and He pressures of 169, 347, 347, and 722 Torr, respectively. The solid lines are calculated from Eq. (4) using the measured laser intensities and He pressures and a value of $x=1.1$ and $C_{12}=4.6\times10^{-18}$ sec(cm^{-1})$^{1.1}$/Torr.

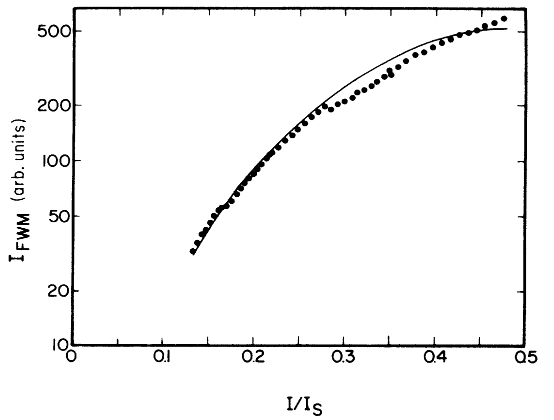

FIG. 4. FWM signal as a function of normalized laser intensity, I/I_s. The laser was detuned 90 cm^{-1} to the red of D_1 resonance, and the other parameters are a Na density of 2.2×10^{13} cm^{-3}, and a He pressure of 722 Torr. The solid line is calculated from Eq. (4) using the values of x and C_{12} determined in Fig. 2.

The experiments were performed using a Nd:YAG laser pumped dye laser split into three incident beams in the folded boxcars[17] geometry. The 40-mm-long Na cell had hot sapphire windows and could be filled with variable pressures of He buffer gas. The energy of each individual laser pulse was measured[18] and the fourth-wave intensity was recorded separately for each incident energy within a range of ±5%. The spectral width of the 4-nsec long laser pulse was 0.25 cm^{-1} for most of the experiments, and we found that the insertion of an etalon to reduce the linewidth to ~0.05 cm^{-1} had no significant effects on the results. Depending on the variable buffer gas pressure, Na density, and laser intensity, FWM signals were easily observed up to detunings of 200 cm^{-1} from resonance.

The FWM intensity as a function of detuning is shown in Figs. 2 and 3 for detunings to the red of the D_1 and to the blue of the D_2 lines, respectively. Four different representative sets of data are shown in each figure, corresponding to different conditions of gas pressure, Na density, and laser intensity as indicated in the Figure captions. The solid line in each case is the theoretical fit to the data, from Eq. (4), in which C_{12} and x were used as free parameters. All the data were very well fitted with a single set of parameters for each of the two figures. The best set of parameters yields $x=0.8$ and $C_{12}=3.7\times10^{-19}$ for the $A^2\pi$ line shape and $x=1.1$ and $C_{12}=4.6\times10^{-18}$ for the $B^2\Sigma$ line shape. [The units for C_{12} are sec (cm^{-1})^x/Torr.] The fit is very sensitive to the value of x, and an $x=2$ (Lorentzian) assumption would result in a deviation from the data by more than an order of magnitude. The success of Eq. (4) in predicting the behavior of degenerate nonimpact FWM is demonstrated by the fact that the experimental data is well described by the same set of x and C_{12} values for a large range of laser intensities, Na densities, and He pressures. The x parameter of the $B^2\Sigma$ line shape can also be compared to a previous measurement,[10] and the two results are found to agree within 10% of each other.

The laser intensity dependence of the FWM signal shows clear saturation behavior as shown in Fig. 4, where we plot the intensity of the fourth wave as a function of I/I_s, where I_s is the saturation intensity defined as

$$\frac{I}{I_s}=\frac{f_2}{f_1}\frac{\pi L_{12}|eX_{12}|^2}{2\gamma\hbar^2}E^2=2.3B\,.$$

These data were obtained for a −90-cm^{-1} detuning from the D_1 line with a buffer gas pressure of 722 Torr and a Na density of 2.2×10^{13} cm^{-3}. The solid line is the result obtained from Eq. (4), using the previously determined values for x and C_{12}. As in Figs. 2 and 3, the contributions of terms up to $n=4$, corresponding to I^6, were significant for our experimental conditions, and were included in the calculation of the solid curve. The $n=5$ term was determined to contribute less than 5% to the result and justifies the termination of the sum at $n=4$.

In summary, we have measured the degenerate FWM intensity near the Na D lines in the presence of He buffer gas with a pressure varying from ~170 Torr to 1 atm. The measurements were performed for laser detunings up to 200 cm^{-1} from the D lines, well outside the range of validity of the impact approximation. Theoretical expressions for the degenerate FWM intensity were derived under conditions of nonimpact and arbitrarily strong laser intensity. The measured FWM intensity as a function of laser detuning was used to determine the collisional absorption line shape for the Na-He system.

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