Line-shape changes due to optical pumping of Na in buffer gas

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We have observed a collapse of the Na hyperfine doublet into a single peak due to laser-induced optical pumping when the product of laser power and buffer gas pressure exceeds ~0.1 mW Torr. The complex line shapes observed under these conditions have been quantitatively explained by a model which describes the laser-induced change in the population of the ground-state hyperfine levels and also includes pressure broadening and diffusion of atoms out of the laser beam. The line-shape distortion can occur at laser intensities 10^3 below that required for radiative saturation, and must be considered in experiments involving the line shape or the population of the hyperfine levels.

INTRODUCTION

We have observed a striking change in the Doppler-broadened shape of the Na D lines due to optical pumping between hyperfine components of the ground electronic state. This line-shape distortion occurs for a wide range of perturber pressures and laser intensities satisfying the condition that the photon absorption rate is large compared to the rate of diffusion of atoms across the laser beam but small compared to the rate of velocity-changing collisions. These velocity-changing collisions preserve the Maxwell-Boltzmann velocity distribution and lead to a velocity-independent-type of optical pumping, in contrast to other recent observations of optical pumping induced by lasers.[1,2]

We present experimental line-shape measurements and a simple theoretical model which accurately reproduces the observed line shapes. Elbel *et al.*[3] have observed this effect and presented a similar but less complete theoretical description in a paper primarily concerned with the formation of alignment in Na $3p$ + Xe collisions. Our analysis is more general and includes the important processes of collisional line broadening and diffusion of atoms into and out of the laser beam. In addition, we present quantitative comparisons of theory with experiment and a descriptive explanation of the mechanism which leads to the distortion.

EXPERIMENT

Our observations were made with the apparatus shown in Fig. 1 and described more fully by Brunner *et al.*[4] A Coherent Radiation 599 cw dye laser was electronically scanned across one of the Na D lines. The dye laser was power stabilized to 1% and had a linewidth of 2 MHz [full width at half maximum (FWHM)]. Emission perpendicular to the laser propagation direction was collected from a cell containing a mixture of sodium vapor and one of the rare gases. This side emission was imaged onto the photocathode of an RCA 6199 photomultiplier with $f/7$ optics. The line shape was obtained by plotting emission versus laser frequency on an xy recorder. The temperature of the sodium cell was maintained at 82°C. At this temperature the maximum observed absorption was less than 1%, implying insignificant line-shape distortion due to radiation trapping.

The data presented here were taken with 10 Torr of xenon (measured by a capacitance manometer). This relatively high perturber pressure ensures that nearly complete mixing of population between the fine structure levels and among the magnetic sublevels will occur in the excited state.[5] The observed line shapes were found to be independent of the polarization of the incident laser. Changes in laser power were achieved by attenuation with calibrated metal film neutral density filters. The attenuation factors for these filters are known to ±2%. Line shapes for various laser powers are presented in Fig. 2. The striking feature of these line shapes is that, as the laser power increases, the shape changes from a Doppler-broadened hy-

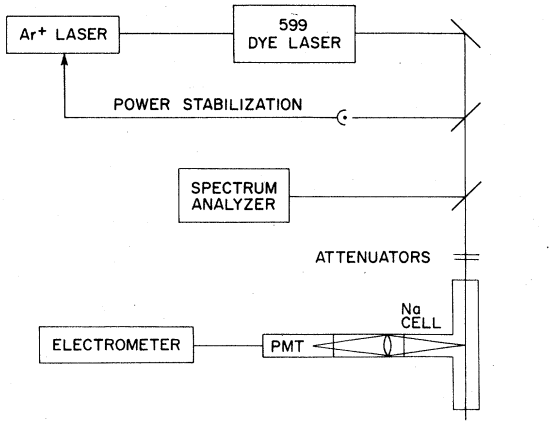

FIG. 1. Diagram of experimental apparatus.

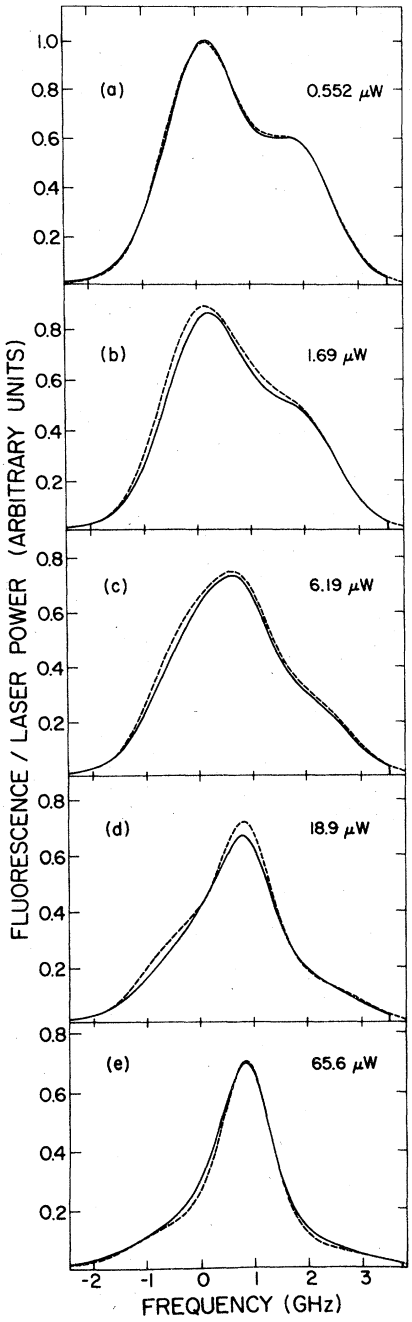

FIG. 2. Fluorescence divided by laser power vs frequency for the $3S_{1/2} \rightarrow 3P_{3/2}$ transition in Na with 10-Torr Xe buffer gas. Experimental line shapes are shown as solid curves; theoretical line shapes are shown as dashed curves.

perfine doublet to a single, structureless line. It should be emphasized that this severe distortion occurs at laser powers so small that radiative saturation effects are unimportant.

THEORY

For sodium, the ground-state hyperfine splitting (1.772 GHz) is comparable to the Doppler width (1.5 GHz FWHM). The excited-state hyperfine splitting is small compared to the Doppler width and will be ignored. Thus the absorption line shape for a gas of sodium atoms in the weak-field limit is a superposition of two Voigt profiles separated by the ground-state hyperfine splitting and weighted by level degeneracy factors (5 for $3sF=2$ to 3 for $3sF=1$) [see Fig. 2(a)]. Optical pumping distorts the line shape by altering the distribution of population between the ground-state hyperfine levels. The key idea in our model is that this type of optical pumping persists at ratios of perturber pressure to laser intensity which are high enough that velocity-changing collisions thermalize the velocity distribution rapidly compared to an absorption-emission cycle. This prevents hole burning, hence the velocity distributions are always Maxwell-Boltzmann.

To understand how this leads to the kind of line-shape distortion observed, consider what happens as the laser is tuned near the Doppler center of the transition from one of the ground-state hyperfine levels. If atoms diffuse out of the beam slowly, the laser interacts for a long time with the same atoms, eventually pumping most of them to the other ground-state hyperfine level. Since the laser is far from the Doppler center of this other hyperfine line, the steady-state absorption is small. The absorption is limited by the rate of excitation of the weaker hyperfine component. Now consider the laser being tuned midway between the two hyperfine lines. Atoms in the Doppler wings of both lines are excited and those which are optically pumped from one hyperfine level to the other can be reexcited since their velocities will be rapidly thermalized. In this manner an atom with velocity $+v_0$ can be excited from the $F=1$ state, decay to the $F=2$ state, have its velocity changed to $-v_0$ and hence be reexcited from the $F=2$ state. This leads to a large steady-state absorption rate when the laser is tuned between the two hyperfine lines. The progressive decline of absorption at the centers of the hyperfine lines and the relative growth between the lines as laser power is increased can be clearly seen in Fig. 2.

We can account for these shapes quantitatively by solving a set of rate equations which allow for absorption from the two ground-state hyperfine levels (R_i), spontaneous decay from the excited state (γ_s), and diffusion (D). The efficiency of the optical pumping process depends on recycling fractions—i.e., the fraction of atoms excited

from a given ground-state hyperfine level which decay back down to the same level. In our model, the excited-state population is broken into two groups: atoms excited from $3sF=1$ and atoms excited from $3sF=2$; the recycling fractions appear as parameters.

In the following expressions, n_1^0 and n_2^0 are the equilibrium populations of the ground-state $F=1$ and $F=2$ levels in the absence of an applied laser field, and α_{ij} is the fraction of atoms excited from state i which decay back down to state j. It is assumed that the stimulated absorption rate is small compared to the spontaneous decay rate ($I \ll 12$ mW/cm^2). The rate equations are

$$\dot{n}_1 = -D(n_1 - n_1^0) - R_1 n_1 + \alpha_{11}\gamma_s n_3 + \alpha_{21}\gamma_s n_4 ,$$
$$\dot{n}_2 = -D(n_2 - n_2^0) - R_2 n_2 + \alpha_{12}\gamma_s n_3 + \alpha_{22}\gamma_s n_4 ,$$
$$\dot{n}_3 = -\gamma_s n_3 + R_1 n_1 ,$$
$$\dot{n}_4 = -\gamma_s n_4 + R_2 n_2 .$$

The steady-state solution of these equations for the absorption rate per unit volume $A(=n_1R_1 + n_2R_2)$ is

$$A = \frac{n_1^0 R_1[D + (\alpha_{12} + \alpha_{21})R_2] + n_2^0 R_2[D + (\alpha_{12} + \alpha_{21})R_1]}{D + \alpha_{12}R_1 + \alpha_{21}R_2} . \quad (1)$$

The frequency-dependent stimulated absorption rates R_i are Voigt profiles,

$$R_i = \gamma_s (I/I_s) V_i(\omega) , \quad (2)$$

where

$$V_i(\omega) = \frac{\gamma_s}{2} \int_{-\infty}^{\infty} dv \frac{e^{-v^2/v_{th}^2}}{\sqrt{\pi} v_{th}} \frac{\Gamma}{\Gamma^2 + (\omega - kv - \omega_i)^2} . \quad (3)$$

In these expressions, $\gamma_s = 6.3 \times 10^7$ sec^{-1} is the spontaneous decay rate; $I_s = 12$ mW/cm^2, the saturation intensity; $\Gamma = \frac{1}{2}(\gamma_s + wp)$, the Lorentzian half width at half maximum; w is the pressure-broadening coefficient, and $v_{th} = (2kT/m)^{1/2}$.

The absorption profile above [Eq. (1)] reduces to a more familiar result in two limiting cases. If the stimulated absorption rates R_i are small compared to the diffusion rate D, then the absorption profile [Eq. (1)] will be a superposition of two Voigt profiles as expected for a gas at equilibrium in the weak-field limit:

$$A^0 = n_1^0 R_1 + n_2^0 R_2 .$$

This simple result is also recovered in the case where atoms excited out of one ground-state hyperfine level cannot decay to the other ground-state hyperfine level ($\alpha_{12} = \alpha_{21} = 0$).

The theoretical absorption profile Eq. (1) is compared with experiment in Fig. 2. The branching ratios were chosen to be statistical ($\alpha_{12} = \frac{5}{8}$, $\alpha_{21} = \frac{3}{8}$). An approximate form of the Voigt profile was used.[6] The pressure-broadening coefficient for Na-Xe was taken from the work of McCartan and Farr,[7] and the diffusion coefficient D was estimated from data in the review article by Happer.[8] The absolute scale for the set of theoretical curves was adjusted by matching the amplitude of the experimental profile at the lowest power [Fig. 2(a)]. No further adjustment in the vertical scale for the theoretical plots with other laser powers was made. The model predicts the correct relative scaling with power to within a few percent. The frequency scale was determined with a calibrated spectrum analyzer. An auxiliary sodium cell was used to observe Lamb dips in absorption which serve as an absolute frequency reference. The frequency labeled "0 GHz" in Fig. 2 was shifted from the Lamb-dip reference by the known pressure shift[7] and corresponds to the resonance frequency for atoms in the ground-state $F=2$ level with $v=0$. We have also made comparisons of the model with experimental line shapes using lower buffer-gas pressures and other rare-gas perturbers. The model agrees with experiment to within a few percent, with slightly better agreement for the lighter perturbers.

DISCUSSION

Several approximations are inherent in our model. We have assumed a Maxwell-Boltzmann velocity distribution for the active atoms in spite of the velocity selective excitation by the laser. This assumption is justified if velocity-changing collisions thermalize the ground-state velocity distributions rapidly compared to an absorption-emission cycle. Assuming a cross section of 30 Å^2 (this corresponds to large-angle scattering—total elastic scattering cross sections are ~500 Å^2 [9]), the rate of ground-state velocity-changing collisions is 5×10^6 sec$^{-1} \times p$ (Torr). This is to be compared to the absorption rate $\simeq 5 \times 10^6$ sec$^{-1} \times I$ (mW/cm^2) for atoms in the laser selected velocity class, and the spontaneous emission rate $\simeq 6 \times 10^7$ sec^{-1}. For large pressure to laser intensity ratios [$p/I \geq 1$ Torr (mW/cm^2)$^{-1}$] the ground-state velocity distribution will be unaffected by the laser.

It has been assumed that some mechanism (such as a magnetic field) is responsible for mixing the m states of the $3s$ hyperfine levels. The rate equations contain only the total populations of the ground-state hyperfine levels. A ground-state polarization would certainly alter the absorption profile. Ground-state polarization is avoided if the excitation rates R_i are smaller than the ground-state m_F-mixing rate. m_F-mixing by the earth's magnetic field will prevent polarization of

the ground state for laser intensities well below the saturation intensity unless the field happens to coincide with the laser polarization axis.

The absorption line shape also depends on the branching ratios (α_{ij}) for decay from the excited state. For pressures greater than about 10 Torr, the excited-state population is almost completely collisionally mixed by fine structure-changing collisions and m-mixing collisions. In this case the branching ratios for decay back down to the ground state will be statistical ($\alpha_{12}=\frac{5}{8}$, $\alpha_{21}=\frac{3}{8}$), and the line shape will be polarization independent. However, for smaller pressures, the branching ratios may depend on pressure and polarization.

In summary, our model should be valid when the following two experimental conditions are met:

$$I \ll 12 \text{ mW/cm}^2,$$

$$p/I > 1 \text{ Torr } (\text{mW/cm}^{-2})^{-1}.$$

The first condition justifies the neglect of stimulated emission and (for our apparatus) ground-state polarization. The second condition ensures that velocity-changing collisions will keep the ground-state velocity distributions Maxwell-Boltzmann.

Having shown that our model applies over a wide range of intensities and pressures we now discuss the conditions under which significant line-shape distortion—or equivalently distortion of the ground-state hyperfine ratios—will occur. The shape of the absorption profile [Eq. (1)] depends on the ratio of the excitation rates R_i to the diffusion rate D. This ratio is basically the number of optical pumping cycles possible while an atom is in the laser beam. The line shape will be distorted unless this ratio is small ($R_i/D \ll 1$). The excitation rate is proportional to the laser power divided by the beam area: $R_i \propto P/d^2$, where d is the beam diameter. For perturber pressures low enough that the pressure-broadened width is small compared to the Doppler width ($p < 20$ Torr) the excitation rate R_i depends only weakly on pressure (for laser frequencies within a few Doppler widths from resonance). The diffusion rate is inversely proportional to the pressure times beam diameter squared: $D \propto 1/pd^2$. The ratio of excitation rate to diffusion rate thus depends on the laser power times the pressure and is independent of the beam size. Hence the degree of distortion of the line shape is a function of laser power times pressure. This scaling is illustrated in Fig. 3 which shows line shapes at 5 and 1 Torr of Xe keeping the product of laser power times pressure fixed at $\simeq 100$ μW Torr. On resonance ($\omega = \omega_i$) we have $R_i/D \simeq 100P$ (mW) p (Torr). Optical pumping will produce a line shape with more than 1% distortion unless the product of laser power times pressure is smaller than 10 μW Torr. Thus this form of optical pumping can place severe constraints on experiments involving the line shape or the ground-state hyperfine populations.

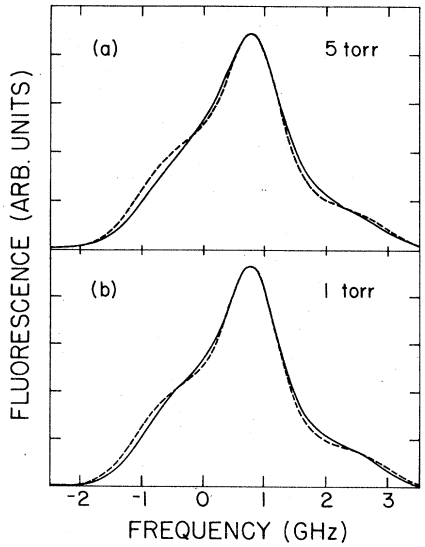

FIG. 3. Fluorescence vs laser frequency for the Na $D2$ line with (a) 5-Torr Xe and 20 mμW of laser power, (b) 1-Torr Xe and 100 mμW of laser power. Experimental line shapes are shown as solid curves; theoretical line shapes are shown as dashed curves.

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