Two-Photon Near-Resonance Light Scattering from an Atomic Level

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We have studied the time-resolved spectra, the energy-resolved spectra, and the total intensity of light emission induced by near-resonance two-photon excitation to the $4^2D_{3/2}$ and $4^2D_{5/2}$ levels of Na over the detuning range $-7\ \mathrm{cm}^{-1} \leq \Delta \leq 7\ \mathrm{cm}^{-1}$. The time-resolved spectra of Na perturbed by Ar exhibit a fast adiabatic component and a slow resonance-fluorescence component. The cross section for phase-shifting, T_2-type collisions in this atomic system is $\sigma = 110 \pm 20\ \text{Å}^2$.

There has been recently a revival of interest in near-resonant light scattering from atoms, molecules, and solids.[1-8] All this work has been concerned with the scattering of one photon, i.e., second-order, optical processes. In this Letter we report the first experimental study of near-resonance two-photon scattering from a collisionally perturbed atom. This process involves direct and resonant scattering of two photons impinging on an atomic gaseous sample into a one-photon continuum. This effect can be described in terms of a third-order optical process which is more general than the conventional two-photon–induced fluorescence[9] and should also not be confused with third-harmonic generation.[10] The present work provides new information on near-resonance third-order optical processes and yields new results on collisional effects in two-photon spectroscopy. From the practical point of view our studies of two-photon scattering from an atomic system do not suffer from difficulties[3] associated with radiation-trapping effects.

We have measured the time-resolved spectrum, the energy-resolved spectrum, and the total intensity of light emission induced by near-resonance two-photon excitation to the $4^2D_{3/2}$ and $4^2D_{5/2}$ levels of Na perturbed by Ar. The reemission was measured in the transitions $4^2D_{3/2}$, $4^2D_{5/2} \rightarrow 3^2P_{3/2}$ and $4^2D_{3/2} \rightarrow 3^2P_{1/2}$ which could be well resolved in energy. The laser frequency ω_L was tuned so that $2\omega_L$ was in near-resonance with the states $4^2D_{3/2}$ and $4^2D_{5/2}$, while ω_L was far off resonance ($\sim 300\ \mathrm{cm}^{-1}$) with the intermediate states $3^2P_{3/2}$ and $3^2P_{1/2}$. In our experiments the bandwidth of the dye laser was $\Delta\nu = 0.05\ \mathrm{cm}^{-1}$, about equal to the hyperfine splitting $0.06\ \mathrm{cm}^{-1}$ of the $3^2S_{1/2}$ level[11] and exceeding the fine splitting of $0.03\ \mathrm{cm}^{-1}$ between the $4^2D_{3/2}$ and $4^2D_{5/2}$ states.[11] These splittings are smaller than the Doppler broadening $\delta = 0.06\ \mathrm{cm}^{-1}$ (at 360°C), and therefore the three-level approximation for this photon-scattering process is adequate.

The available theory[4-8] of second-order optical processes, recently extended for a three-level system,[8] together with the theory of two-photon time-resolved spectroscopy,[12] can be readily extended for the third-order process at hand. For a stationary, collisionally perturbed assembly of atoms excited from the ground state by two monochromatic light beams, the energy-resolved intensity distribution is

$$I(\omega_1, \omega_2; \omega) = \frac{N|\beta_{ab}|^2\gamma_b}{(\omega_1+\omega_2-\omega_{ba})^2+(\gamma_b+\hat{\Gamma})^2}\left[\delta(\omega_{ca}-\omega_1-\omega_2+\omega)+\frac{\hat{\Gamma}}{\pi\gamma_b}\frac{(\gamma_b+\hat{\Gamma})}{(\omega_{bc}-\omega)^2+(\gamma_b+\hat{\Gamma})^2}\right], \quad (1)$$

where $|a\rangle \equiv 3^2S_{1/2}$, $|b\rangle \equiv 4^2D_{3/2}$ or $4^2D_{5/2}$, and $|c\rangle = 3^2P_{3/2}$ or $3^2P_{1/2}$ correspond to the ground state, the near-resonant state, and the final state, respectively, which are characterized by the energies $\epsilon_i (i = a, b, \text{or } c)$. $\omega_{ba} = (\epsilon_b - \epsilon_a)\hbar$, $\omega_{bc} = (\epsilon_b - \epsilon_c)/\hbar$, and $\omega_{ca} = (\epsilon_c - \epsilon_a)/\hbar$ represent the atomic level spacings. ω_1 and ω_2 are the frequencies of the exciting photons, while ω is the frequency of the emitted photon. γ_b is the rate of the $|b\rangle \rightarrow |c\rangle$ radiative decay process and β_{ab} corresponds to the two-photon radiative

coupling term,

$$\beta_{ab}=\sum_r\left[\frac{\langle a|\hat{\mu}\cdot\vec{\epsilon}_1E_1|r\rangle\langle r|\hat{\mu}\cdot\vec{\epsilon}_2E_2|b\rangle}{\epsilon_a-\epsilon_r+\hbar\omega_1}+\frac{\langle a|\hat{\mu}\cdot\vec{\epsilon}_2E_2|r\rangle\langle r|\hat{\mu}\cdot\vec{\epsilon}_1E_1|b\rangle}{\epsilon_a-\epsilon_r+\hbar\omega_2}\right], \quad (2)$$

associated with two optical fields $\vec{E}_i(t)=\hat{\epsilon}_iE_i\times\cos\omega_it$ (where $i=1$, 2) and their respective polarization vectors $\vec{\epsilon}_i$; $\hat{\mu}$ is the electric dipole operator. $|r\rangle$ labels all intermediate off-resonant states, including the state $|c\rangle$. $\hat{\Gamma}$ is the rate associated with phase-shifting collisions (proper T_2 processes).[6] Finally, N is the number density of the active atoms. Equation (1) is expected to be valid below saturation within the framework of the stochastic model[5,8] in the central, impact region of the two-photon spectrum.

The total energy-integrated emission intensity F for the special case of excitation with a single laser with peak frequency ω_L is

$$F=N|\beta_{ab}|^2(\gamma_b+\hat{\Gamma})\int dx\frac{\bar{S}(x-2\omega_L)}{(x-\omega_{ba})^2+(\gamma_b+\hat{\Gamma})^2}, \quad (3)$$

where $\bar{S}(x-2\omega_L)=\int dy\,S(x-y-\omega_L)S(y-\omega_L)$, with $x=\omega_1+\omega_2$ and $y=\omega_1$, corresponds to the self-convolution of the normalized spectral distributions $S(\omega_i-\omega_L)$ of the laser (where $i=1$, 2). Two limiting situations are of interest: (I) On resonance when $|\Delta|=|\omega_{ba}-2\omega_L|\ll(\gamma_b+\hat{\Gamma})$ and if $\Delta\nu\gg(\gamma_b+\hat{\Gamma})$, we get

$$F=\pi N|\beta_{ab}|^2\bar{S}(\omega_{ba}-2\omega_L). \quad (4a)$$

(II) Far off resonance when $|\Delta|\gg\delta\gg(\gamma_b+\hat{\Gamma})$ and if $\bar{S}(x-2\omega_L)$ decays faster than a Lorentzian, we get

$$F=N|\beta_{ab}|^2(\gamma_b+\hat{\Gamma})/\Delta^2, \quad (4b)$$

where $\Delta=2\omega_L-\omega_{ba}$. Equation (4b) provides a convenient method for the experimental determination of $\hat{\Gamma}$. The pressure dependence of $\hat{\Gamma}$ is

$$\hat{\Gamma}=\alpha\langle v_F\rangle\sigma_Fp_F+\alpha\langle v\rangle\sigma p, \quad (5)$$

where σ_F and σ are the cross sections for phase-shifting collisions induced, respectively, by the foreign gas at pressure p_F and by the target gas at pressure p, $\langle v_F\rangle$ and $\langle v\rangle$ are the relative velocities of a foreign gas atom and of the target atom, respectively, both with respect to the target atom, and $\alpha=1.34\times10^{16}$ cm^{-3} Torr^{-1}.

Sodium vapor in argon buffer gas was excited by a N_2-laser–pumped tunable dye laser. The dye-laser pulse had an energy of 25 μJ, a pulse duration of 10 nsec, and a spectral width of $\Delta\nu=0.05$ cm^{-1}, and was operated at a rate of 20 pulses/sec. The laser was tuned near 5787.3 Å, which corresponds to half the energy for the Na $3^2S_{1/2}\rightarrow4^2D_{3/2}$ or $4^2D_{5/2}$ transition. The laser beam was focused into the sodium cell; the peak intensity at the focus was 8 MW cm^{-2}. The Na density was varied in the range 10^{14}–10^{16} cm^{-3} by changing the cell temperature over the range 350–450°C. The optical cell with specially designed windows was flushed with Ar gas whose pressure could be varied in the range above 0.08 Torr. The re-emitted light was monitored at a right angle to the exciting beam. It was focused into the entrance slit of a $\frac{3}{4}$-m monochromator and detected by a photomultiplier with a gated (0.5 μsec) photon-counting system. Time-resolved spectra were measured by a delayed coincidence technique. The laser peak power was sufficient to saturate the two-photon $3^2S_{1/2}\rightarrow4^2D_{3/2,5/2}$ transition at resonance. The laser beam was attenuated by neutral density filters and all the measurements reported herein were conducted below saturation.

The time-resolved near-resonance third-order photon scattering spectrum (Fig. 1) from Na perturbed by Ar over the detuning range -7 cm$^{-1}\leq\Delta\leq+7$ cm^{-1} reveals the following features: (1) Two components are exhibited in the time-resolved spectrum for all values of Δ. They correspond to an adiabatic fast component $J_F(t)$, having the temporal characteristics of the pulse, and a slow atomic decay component $J_s(t)$. (2) The slow "resonance-fluorescence" (RF) component $J_s(t)\alpha\exp(-t/\tau)$ for $t>T=30$ nsec is characterized by the decay time $\tau=52\pm3$ nsec, which corresponds to the radiative decay time of the Na $4D$ state.[13] τ is independent of Na pressure in the range 0.1–1 Torr and of the Ar pressure over the range 0.08–20 Torr. (3) The ratio R of the time-integrated intensity of the resonance fluorescence to that of the direct scattering was evaluated disregarding interference effects so that

$$R\simeq[\int_0^TJ_s^s(t)dt+\int_T^\infty J_s(t)\,dt]/\int_0^T[J(t)-J_s^s(t)]\,dt,$$

where $J(t)$ is the total intensity, while $J_s^s(t)$ was obtained from an extrapolation of $J_s(t)$ to $0<t<T$, using the experimental pulse shape. R increases with increasing pressure at constant Δ [Figs. 1(b) and 1(c)]. This observation is consistent with theoretical predictions[5,6] concerning the enhanced contribution of the RF component at higher

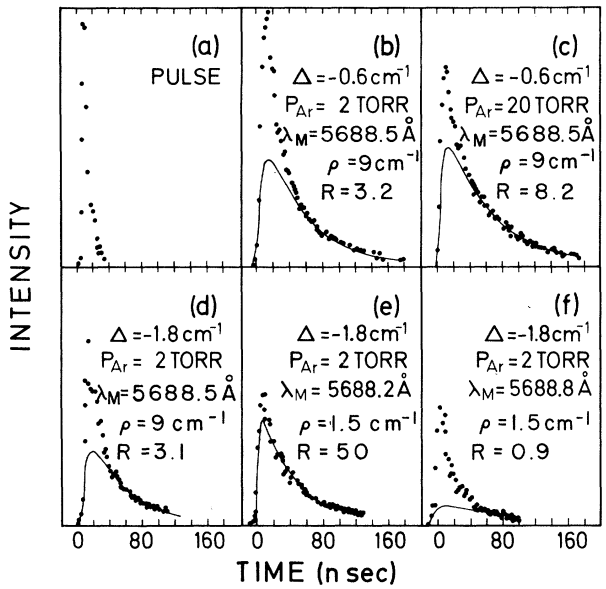

FIG. 1. Time-resolved spectra of the $4^2D_{3/2,5/2} \rightarrow 3^2P_{3/2}$ transition in Na. λ_M is the monochromator wavelength, ρ is the spectral resolution (full width at half-maximum), Δ is the detuning energy, and R is the ratio of the slow to the fast components. In (b)–(d) $\rho \gg \Delta$, so that both the resonance fluorescence (RF) and the Raman scattering (RS) components were monitored. In (e) and (f), $\rho \lesssim \Delta$ and the monochromator was set at the central wavelength of the RF component (e) and of the RS component (f). The residual slow component in (f) and the fast component in (e) result from insufficient spectral resolution. The dots represent experimental data, while the solid lines represent the fit for the slow component.

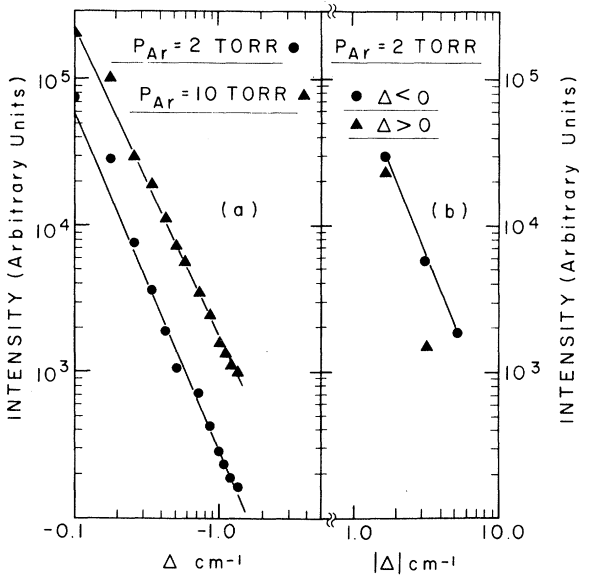

FIG. 2. The dependence of the total re-emitted light intensity, F, on the detuning energy Δ. $\lambda_M = 5688.5$ Å, $\rho = 9$ cm^{-1}, $p_{Na} = 10^{-1}$ Torr, and $p_{Ar} = 2$–10 Torr. (a) For small values of $|\Delta|$, F obeys the relation $F \propto |\Delta|^{-2.0 \pm 0.2}$. (b) For larger values of $|\Delta|$, this relation holds only for $\Delta < 0$ while significant deviations from this relation are exhibited for $\Delta > 0$.

pressures. (4) The relative contribution of RF for large values of Δ (between 2δ and 100δ) at constant pressure is practically independent of Δ. We have found that at $p_{Na} = 10^{-1}$ Torr and $p_{Ar} = 2$ Torr, $R = 2.9 \pm 0.3$ for values of $|\Delta|$ in the range 0.11 to 3.43 cm^{-1}, while $R = 3.1 \pm 0.3$ at $\Delta = -6.86$ cm^{-1}, and $R = 2.4 \pm 0.2$ at $\Delta = +6.86$ cm^{-1}. These results concur with recent theoretical predictions[6] that the time correlation function for phase shifts is exponential and R far off resonance is independent of Δ. We also note that for $|\Delta| = 6.86$ cm^{-1} there is a slight asymmetry in R for negative and positive values of Δ. (5) We were able [see Figs. 1(d)–1(f)] to separate spectrally the two time-resolved components. Tuning the laser to $\Delta = -1.8$ cm^{-1}, we observed $R = 50$ for the time-resolved emission at 5688.2 Å, which corresponds to ω_{bc}, and $R \sim 0.9$ for the emission at 5688.8 Å, which corresponds to $2\omega_L - \omega_{ca}$. This simultaneous determination of time- and energy-resolved spectra constitutes a convincing argument for the assignment of the two time-resolved components. (6) Finally, we observed that for $\Delta = 0$ there are still two components in the time-resolved spectrum. This result is expected as in the present case $\Delta\nu \cong \delta$.

Direct quantitative information concerning the cross sections for optical T_2 processes in this atomic system was obtained from a study of the total energy-integrated emission intensity. In Fig. 2(a) we portray F vs Δ, which for -2 cm$^{-1} \lesssim \Delta \lesssim 2$ cm^{-1} exhibits the relation $F \propto \Delta^{-2}$ expected from Eq. (4b). These results provide the first determination of a two-photon absorption line shape of a collisionally perturbed atomic level.[12] From the data at $p_{Ar} = 2$ Torr and $p_{Ar} = 10$ Torr, we deduce $\hat{\Gamma}/p_{Ar}\gamma_b = 0.5 \pm 0.1$ Torr^{-1}. Complementary results were obtained from the study of the dependence of F on the pressure p_{Ar} of the perturbing Ar gas (Fig. 3). On resonance, F is practically independent of p_{Ar} in accordance with Eq. (4a). For $\Delta \gg \delta$, F exhibits a linear dependence on p_{Ar} at constant Na pressure, as expected from Eqs. (4b) and (5). From the linear dependence of the intercept of the plots of F vs p_{Ar} on p_{Na} in the range $p_{Na} = 0.0$–0.1 Torr, we assert that, in this range of p_{Na}, self-induced phase shifts by Na are negligible. We have thus taken $\hat{\Gamma} = \alpha \langle v_{Ar} \rangle \sigma_{Ar} p_{Ar}$ and calculated $\hat{\Gamma}/\gamma_b$ from Eq.

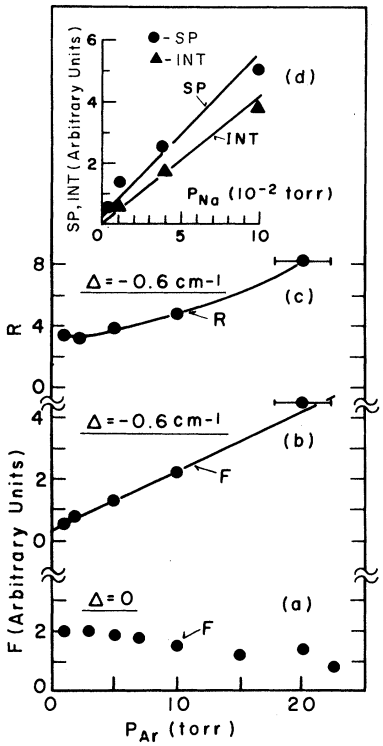

FIG. 3. (a),(b) Dependence of total re-emitted intensity (F) on Ar pressure for $p_{Na}=0.1$ Torr and (a) $\Delta=0$ and (b) $\Delta=-0.6$ cm^{-1}. (c) Dependence of R on p_{Ar} for $p_{Na}=0.1$ Torr and $\Delta=-0.6$ cm^{-1}. (d) Dependence on sodium pressure of the intercept (INT) and of the slope (SP) of F vs p_{Ar} plots.

(4b), utilizing our data at $\Delta=\pm 0.15$, ± 0.5, ± 1.0, and ± 1.5 cm^{-1}, which result in $\alpha\sigma_{Ar}\langle v_{Ar}\rangle/\gamma_b=0.7\pm 0.2$ Torr^{-1}. This result agrees with the value obtained from Fig. 2. We thus obtain $\sigma_{Ar}=110\pm 20$ Å^2 for the cross section for phase-shifting collisions. This value, which is consistent with some line-broadening data,[14] is larger than a gas kinetic cross section and may involve a contribution from cross relaxation between the $4^2D_{3/2}$ and $4^2D_{5/2}$ levels.

The impact approximation is adequate to provide a quantitative interpretation of time- and energy-resolved two-photon scattering in the range $|\Delta|<100\delta$. For larger values of $|\Delta|$, R exhibits some indication of asymmetry and F vs Δ^{-2} (Fig. 2) exhibits a definite asymmetry with respect to the sign of Δ. Such deviations from the impact approximation for very large Δ (>10 cm^{-1}) values have recently been reported[3] for energy-resolved one-photon scattering spectra.

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