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The time development of adiabatic two-photon absorption: II. Rate equation regime

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Abstract. The time dependence of the two-photon absorption process is experimentally investigated in the intermediate intensity rate equation regime, where incoherent relaxation plays an important role, as a function of laser linewidth and Doppler width. The saturation effects observed are in excellent agreement with the predictions of Allen and Stroud.

1. Introduction

Allen and Stroud (1982) have recently developed a general theory of n-photon excitation from n independent lasers which includes effects of saturation, Stark shift, laser bandwidth and spontaneous emission. It was assumed that no intermediate states were resonantly excited. In the most general case, the formalism reduced to a set of equations analogous to the Bloch equations. For the case of negligible saturation, the low-intensity limit, these equations simplified to a double-integral expression for the population of the excited level as a function of time. The time dependence of the two-photon absorption process in this regime has been thoroughly investigated experimentally in I (Allen *et al* 1982) and demonstrated excellent agreement with theory.

In a higher-intensity regime, where saturation plays a significant role but the incoherent processes destroy the Rabi oscillations, the Bloch equations reduce to a set of rate equations with a time-dependent rate. This is when $\gamma_b+\gamma_L \gg \Omega^{(n)}(t)$, $1/\tau_p$, where γ_b and γ_L are the widths of the resonant atomic state and the laser radiation respectively, $\Omega^{(n)}(t)$ is the composite Rabi frequency arising from the n-photon field and τ_p is the pulse duration. If the phase diffusion model (Eberly 1976, Georges and Lambropoulos 1978) relating to a Gaussian laser output is invoked, and I demonstrated that this is appropriate for our Hansch-type dye laser, the Bloch formalism reduces to

$$\langle \dot{x}_{bb}(t)\rangle_L = -2\gamma_b\langle x_{bb}(t)\rangle_L - \langle \dot{x}_{aa}(t)\rangle_L \tag{1a}$$

$$\langle \dot{x}_{aa}(t)\rangle_L = \frac{2\mathcal{M}^2_{NPA}}{\hbar^{2n}} \mathrm{Re}\Big(\varepsilon^{(n)}(t)\int_0^t dt'\varepsilon^{(n)}(t')$$
$$\times \exp[-(\gamma_b - i\delta)(t-t') + i\Delta(t) - \tfrac{1}{2}\gamma_L^2(t-t')^2](\langle x_{bb}(t)\rangle_L - \langle x_{aa}(t)\rangle_L)\Big) \tag{1b}$$

where $\langle\ \rangle_L$ represents the ensemble average over the randomly fluctuating laser phase,

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x_{bb} and x_{aa} are the populations of the excited state and lower state respectively,

$$\varepsilon^{(n)}(t) = |\varepsilon_1(t)||\varepsilon_2(t)| \ldots |\varepsilon_n(t)|,$$

δ is the detuning from resonance, $\Delta(t)$ the Stark shift and $\mathcal{M}_{NPA}$ the generalised n-photon electric dipole moment matrix element. The effect of Doppler broadening may also be included by averaging over the Maxwell–Boltzmann distribution of atomic velocities. In order to do this we need to replace the atomic detunings from resonance in equation (1b) by their velocity-dependent generalisations

$$\delta(\boldsymbol{v}) = \bar{\delta} + \boldsymbol{k} \cdot \boldsymbol{v}$$

where $\bar{\delta}$ is the rest frame detuning and $\boldsymbol{k} = \boldsymbol{k}_1 + \boldsymbol{k}_2 + \ldots + \boldsymbol{k}_n$ the sum of the n-photon wavevectors. The velocity-averaged expression is

$$\langle \dot{x}_{bb}(t) \rangle_{L,v} = -2\gamma_b \langle x_{bb}(t) \rangle_{L,v} - R(t)(\langle x_{bb}(t) \rangle_{L,v} - \langle x_{aa}(t) \rangle_{L,v}) \tag{2a}$$

$$\langle \dot{x}_{aa}(t) \rangle_{L,v} = R(t)(\langle x_{bb}(t) \rangle_{L,v} - \langle x_{aa}(t) \rangle_{L,v}) \tag{2b}$$

where the time-dependent rate is

$$R(t) = \frac{\mathcal{M}_{NPA}^2}{\hbar^{2n}} (\varepsilon^{(n)}(t))^2 \left(\frac{2\pi}{\gamma_L^2 + \gamma_D^2} \right)^{1/2} \exp\left(-\frac{(\Delta(t) + \bar{\delta})^2}{2(\gamma_L^2 + \gamma_D^2)} \right). \tag{2c}$$

In these expressions $\langle \; \rangle_v$ represents the velocity average and γ_D is the Doppler width.

In the simple case of two-photon absorption the Stark shift $\Delta(t)$ is given by $\Delta(t) = \alpha \Omega(t)$ where α is a function of the dipole moments and detunings from real intermediate states (Allen and Stroud 1982)

$$\alpha = \frac{\mathcal{M}_S}{2\mathcal{M}_{TPA}} = \left(\sum_i \frac{|\boldsymbol{d}_{ia} \cdot \boldsymbol{\varepsilon}_1|^2}{\delta_{ia}} - \sum_i \frac{|\boldsymbol{d}_{bi} \cdot \boldsymbol{\varepsilon}_2|^2}{\delta_{bi}} \right) \times \left(8 \left| \sum_i \frac{(\boldsymbol{d}_{bi} \cdot \boldsymbol{\varepsilon}_2)(\boldsymbol{d}_{ia} \cdot \boldsymbol{\varepsilon}_1)}{\delta_{ia}} + \frac{(\boldsymbol{d}_{bi} \cdot \boldsymbol{\varepsilon}_1)(\boldsymbol{d}_{ia} \cdot \boldsymbol{\varepsilon}_2)}{\delta_{ia}} \right| \right)^{-1}$$

where Σ_i represents the summation over all real intermediate states and $\boldsymbol{\varepsilon}_i = \boldsymbol{\varepsilon}_i(t)/|\varepsilon_i(t)|$. The expression for the time-dependent rate thus becomes

$$R(t) = \frac{\Omega^{(2)^2}(t)}{4} \left(\frac{2\pi}{\gamma_L^2 + \gamma_D^2} \right)^{1/2} \exp\left(-\frac{(\alpha \Omega^{(2)}(t) + \bar{\delta})^2}{2(\gamma_L^2 + \gamma_D^2)} \right) \tag{3}$$

where the two-photon Rabi frequency is

$$\Omega^{(2)}(t) = 2\mathcal{M}_{TPA} |\varepsilon_1(t)||\varepsilon_2(t)| / \hbar^2.$$

2. Experiment

This study investigates the theoretical predictions for the time evolution of the upper-state population excited via a two-photon absorption as a function of laser and Doppler linewidth. As in I we used a dual-wavelength nitrogen-pumped Hansch-type dye laser (Marx *et al* 1976) which produced pulses of 5 ns FWHM at powers of up to 600 W. The dye used was 8×10^{-3} M Rh6G in MeOH and was tuned to give two-photon absorption from the 3s ^{2}S ground state to the 4d ^{2}D state in atomic sodium. The sodium was contained in a quartz cell in a small oven maintained at 200 °C. Excitation to the upper level was monitored by observing the decay from 4d ^{2}D to

3p ^{2}P at 5688 Å. A narrow band pass filter was employed to isolate the fluorescent signal from the excitation wavelengths. The advantage of observing the 4d ^{2}D–3p ^{2}P decay compared with observing the cascade transition 4p ^{2}P–3s ^{2}S at 3302 Å was that the time dependence of the upper-level population could be monitored directly and was not convoluted with any subsequent decay.

The fluorescent signal was processed by a PAR boxcar integrator incorporating 163 and 164 plug-ins, the output from which could be plotted in analogue form or digitised and stored on magnetic cassette tape. Sensible pulse averaging was insured by using a discriminator which only allowed the boxcar to trigger when the input laser pulse intensity peaked within a preset range.

Experiments were carried out using two values of Doppler width. Initially, excitation to the upper level was achieved by the absorption of two photons from the same beam tuned to 5787 Å. This gave a Doppler width of 3.38 GHz. Secondly, by using the standard technique of counterpropagating beams (Cagnac *et al* 1973) at wavelengths of 5784 and 5790 Å, the Doppler width was reduced to zero. The laser linewidth could be adjusted by the insertion of etalons into the Hansch-type cavities to yield 0.34 or 3.60 GHz. Linearly polarised light was used throughout. For the study involving counterpropagating beams, the axes of polarisation of the beams were parallel. The available combinations of laser and Doppler widths allowed a thorough investigation of the dynamics in the saturated regime where incoherent processes dominate and the rate equation expression for the population of the upper level was expected to hold.

To calculate the theoretical fluorescent response, it was necessary to measure the input laser intensity as a function of time and to fit it by a least-squares routine to an analytic curve. As in I it was found that a function of the form $At^n \exp(-kt)$ gave a good description, and having determined the parameters, A, n and k, the expression was used to yield the time-dependent two-photon Rabi frequency in equation (3). For the transition investigated, $\alpha = -0.262$.

The dye laser was tuned so that the fluorescent signal was a maximum at the peak of the input intensity. Consequently, the term $(\alpha\Omega^{(2)}(t)+\bar{\delta}(t))$ in the exponent of equation (3) is equal to zero only at peak pulse intensity, and is equivalent to a finite detuning at zero intensity. The characteristic curve of the atomic saturation was found by inserting neutral-density filters into the exciting beam and measuring the resulting integrated fluorescent response using the boxcar 164 plug-in set with an aperture of 50 ns duration.

In figures 1 and 2 we see that the integrated fluorescent intensity I_F plotted against the square of the laser intensity (or product of intensities for counterpropagating beams) exhibits a linear region for intensities less than 1·5 MWcm^{-2} (0·3 MWcm^{-2} for counterpropagating) for the chosen laser linewidths. This linearity is the essential feature of a two-photon absorption in an unsaturated or low-intensity domain (Marx *et al* 1978). At higher intensities, the deviation from I^2 becomes readily apparent. Two manifestations of the effect of saturation are observed. The most obvious is that the integrated fluorescent response and therefore the fluorescent peak height approaches an asymptotic value. The full curves represent the theoretical peak height of the fluorescent response not, we should note, the integrated fluorescence. In figure 1, it may be seen that for intensities greater than 4.5 MWcm^{-2} the theoretical peak response no longer describes accurately the measured integrated fluorescent signal. This is due to the second observable saturation effect, that of a change in time evolution. Such intensities result in a distinct shift of the peak of the fluorescent

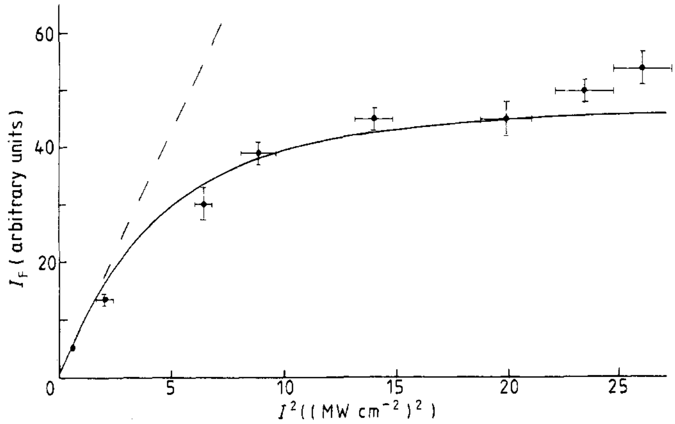

Figure 1. The atomic saturation characteristic for copropagating two-photon absorption where $\gamma_D = 3.38$ GHz and $\gamma_L = 3.60$ GHz. The integrated fluorescent intensity (I_F) is plotted against the square of the laser peak pulse focused intensity (I^2).

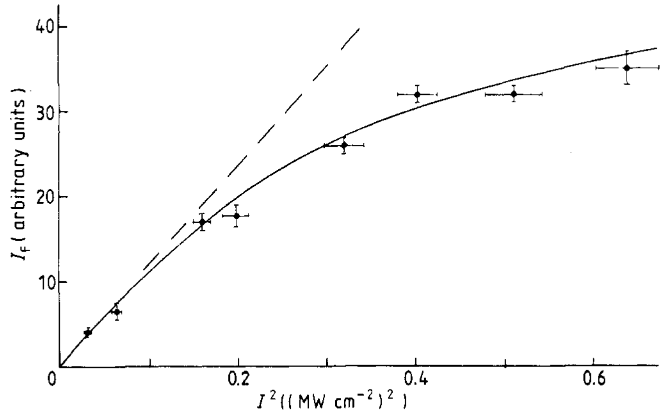

Figure 2. The atomic saturation characteristic for counterpropagating two-photon absorption where $\gamma_D = 0$ and $\gamma_L = 0.34$ GHz. The integrated fluorescent intensity (I_F) is plotted against the square of the laser peak pulse focused intensity (I^2).

response to earlier times. However, the peak height and position in time of the spontaneous decay remain essentially constant. Consequently, an increased integrated fluorescence is measured. Figures 3 and 4 show time evolutions measured with the boxcar 163 plug-in incorporating an S-1 type sampling head. These correspond to different values of the product I_1I_2 on the saturation curves of figures 1 and 2. The full curves represent the theoretical curves computed from equation (2*a*).

It should be noted that only one curve has been normalised to the experimental peak height, the others have their relative positions defined by the theory and, as in I, show excellent agreement between theory and experiment. The variation of time dependence with intensity is most evident in figure 3, where it was observed that for a peak laser intensity of the order of 5 MW cm^{-2}, the corresponding fluorescent signal reached a maximum in a time 2.5 ns earlier than for that of an unsaturated response.

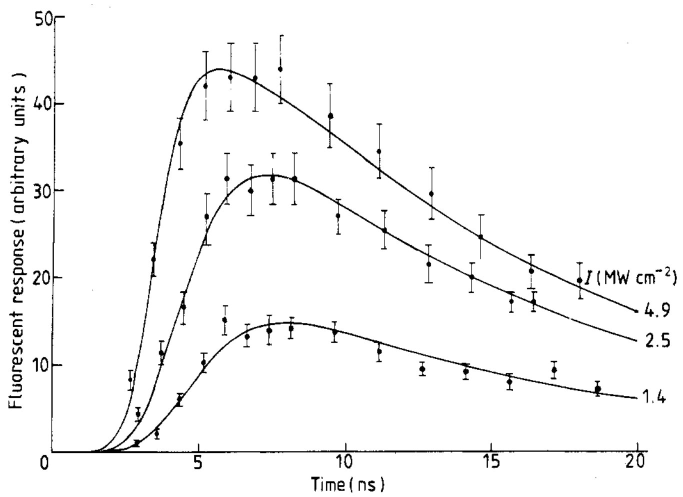

Figure 3. The theoretical and experimental time development of two-photon absorption for $\gamma_D = 3.38$ GHz and $\gamma_L = 3.60$ GHz.

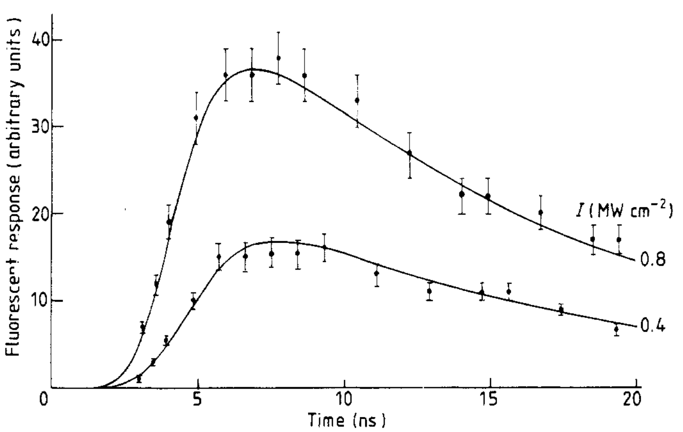

Figure 4. The theoretical and experimental time development for two-photon absorption for $\gamma_D = 0$ and $\gamma_L = 0.34$ GHz. The intensity indicated against the curve is equal to $\sqrt{I_1 I_2}$.

Although the shift of the fluorescent peak to an earlier time is not as apparent in figure 4, the experiment does demonstrate that a high degree of saturation may be achieved at lower laser intensities when Doppler width and laser linewidth are reduced. This is consistent with setting $\gamma_D = 0$, $\gamma_L \rightarrow 0$ in equation (3).

3. Conclusions

We have demonstrated that in the rate equation regime, where effects such as the Stark shift make non-negligible contributions, excellent agreement has been found between experiment and the theoretical predictions of Allen and Stroud. This lends further support to the validity of their theoretical model of n-photon absorption. It might be noted too that the rate equations examined here and the low-intensity double-integral formulation discussed in I predict the same numerical results to better than 1% for those intensities (~ 0.2 MW cm^{-2}) where either theory might be thought to be appropriate.

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