# Laser and Two-Photon Processes

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The possibility of observing two-photon processes using the intense beam of the ruby optical maser is considered theoretically for two general types of experiment. The essential approximation in the theory is the hypothesis that excited states exist which connect both the initial and final states by electric dipole transitions having a total oscillator strength $f\sim 1$. Simple formulas are obtained for the two-photon absorption which do not depend on the details of the electronic structure. Recent experiments on the $CaF_2:Eu^{++}$ system are in quantitative agreement with the predictions of the theory.

THIS paper is concerned with the observation of two-photon radiation processes in matter. The intense beams produced by the ruby laser, and the narrow linewidth of these beams, make the observation of these effects possible in principle. It has been reported[1] that the energy emitted through the silvered ends of the ruby rod is about $\sim 10^{-2}$ joule per flash of the pumping lamp. It may be estimated that most of this energy is emitted during a time $\sim 5\times 10^{-4}$ sec and the transmission of the silver coating is about 1%. Therefore it is appropriate to regard the primary laser beam as having an intensity $\sim 2\times 10^{10}$ erg sec$^{-1}$ cm$^{-2}$. This beam is accessible since the reflecting coatings can be replaced by external mirrors. The wave number is 14 400 cm$^{-1}$, so this intensity corresponds to a photon flux

$$F=7\times 10^{21}\ \text{photons/cm}^2\ \text{sec}, \tag{1}$$

and a photon density $2.3\times 10^{11}$ photons/cm$^3$. This flux might be increased by means of lenses or mirrors to concentrate the beam.

Two types of experiments will be considered here to observe two-photon effects.

(a) The laser beam of frequency $\nu_b$ passes through a transparent crystal containing a suitable impurity with a sharp absorption line $\nu_c>\nu_b$. New absorption lines of the crystal should appear at $\nu_c\pm\nu_b$. Therefore a spectrometer or spectrograph is set up with a weak beam passing through the crystal approximately perpendicular to the laser beam. The observation of both extra lines would constitute strong evidence for a two-photon absorption involving one laser photon and one photon from the weak beam. If $\nu_c<\nu_b$ the laser beam should undergo Raman scattering with the scattered beam having frequency $\nu_b-\nu_c$.

(b) The laser beam passes through a transparent crystal containing an absorption band at $\sim 2\nu_b$ and a luminescence level which can be reached from this band but not from any lower bands $\sim\nu_b$. The detection of the luminescence may indicate a two-photon absorption process into the band $\sim 2\nu_b$.

No attempt will be made here to design these experiments or point out the likely sources of error. Consideration will be limited to estimating the magnitudes of the expected two-photon effects. In order to obtain concrete results it is necessary, however, to make certain reasonable assumptions about the crystals to be used in these investigations. The sharp line $\nu_c$ is forbidden and has a very small oscillator strength $f\sim 10^{-6}$ typical of crystal field transitions in the rare earth and transition metal ions in crystals. It will be assumed that the transition occurs through the electric dipole and a hemihedral component of the crystal field rather than through vibrations or the magnetic dipole. Further it will be assumed that "charge transfer" bands[2] exist with large oscillator strength $f\sim 1$ at considerably higher frequency than $\nu_c$ or $\nu_b$.

All two-photon processes require an intermediate state in which one photon is abosrbed or emitted and the atom is in an excited state.[3] It will be assumed that the charge transfer bands act as intermediate atomic states which are coupled through the electric moment $p$ to both the initial and final states of the transition $\nu_c$. If the intermediate state energy is $\hbar\omega_I$, and the oscillator strength is $f\sim 1$, the dipole matrix element is given by

$$p^2\sim e^2\hbar/2m\omega_I. \tag{2}$$

The same matrix element will be assumed to connect the intermediate state to both the initial and final states of $\nu_c$. If $p_c$ is the electric moment matrix element for the sharp line, the absorption coefficient is given by

$$\alpha_c=N(4\pi^2\nu_c p_c^2/c\hbar n_c)g(\nu-\nu_c), \tag{3}$$

where $g(\nu-\nu_c)$ is the line shape function, $N$ is the concentration of impurity ions, and $n_c$ is the index of refraction of the crystal. The line shape function is normalized so that

$$\int_0^\infty g(\nu-\nu_c)d\nu=1. \tag{4}$$

If now $\omega_I\gg 2\pi\nu_c$, $\omega_I\gg 2\pi\nu_b$, second order perturbation theory gives for the absorption coefficient of the extra

[1] R. J. Collins, D. F. Nelson, A. L. Schawlow, W. Bond, C. G. B. Garrett, and W. Kaiser, Phys. Rev. Letters 5, 303 (1960).

[2] See for example the review by D. S. McClure, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1959), Vol. 9, p. 502.

[3] The general theory for these processes was first given by M. Göppert-Mayer, Ann. Physik 9, 273 (1931) without simplifying assumptions which make possible a comparison with experiment.

lines at $\nu_c \pm \nu_b$

$$\alpha = \frac{16\pi^2 \omega_I^2 p^4}{\hbar^2 c^2 n_c^2 \omega \omega_b} NFg(\nu - \nu_c \pm \nu_b), \tag{5}$$

where $\omega = 2\pi\nu$. When $p^2$ is estimated according to (2), this can be written

$$\alpha = \left(\frac{e^2}{mc^2}\right)^2 \frac{c^2}{n_c^2 \nu \nu_b} NFg(\nu - \nu_c \pm \nu_b). \tag{6}$$

It is of course assumed here that $\nu_c > \nu_b$ as in experiment (*a*). If $\nu_c < \nu_b$ and (2) is valid, the cross section for Raman scattering per impurity ion is

$$\sigma_R = \frac{4\pi}{n_c^3} \frac{\nu}{\nu_b} \left(\frac{e^2}{mc^2}\right)^2. \tag{7}$$

Similarly the cross section for absorbing two laser photons as in experiment (b) is

$$\sigma_A = \left(\frac{e^2}{mc^2}\right)^2 \frac{c^2}{n_c^2 \nu_b^2} Fg(2\nu_b - \nu_c), \tag{8}$$

where now $g(\nu - \nu_c)$ describes the absorption band of the crystal. The quantity

$$(e^2/mc^2) = 2.82 \times 10^{-13} \text{ cm} \tag{9}$$

is the classical radius of the electron.

Experiment (*a*) is most conveniently discussed by comparing the absorption coefficient for the extra lines with that of the natural line. From (3) and (6),

$$\frac{\alpha}{\alpha_c} = \frac{1}{2\pi^2 f n_c} \left(\frac{e^2}{mc^2}\right) \frac{c\omega_I F}{\nu_c \nu_b \nu}. \tag{10}$$

For the typical values (with $\tilde{\nu}$ the wave number $= \nu/c$)

$$\begin{aligned} \tilde{\nu}_b &= 14\,400 \text{ cm}^{-1}, \\ \tilde{\nu}_c &= 30\,000 \text{ cm}^{-1}, \\ (\tilde{\omega}_I/2\pi) &= 60\,000 \text{ cm}^{-1}, \\ \tilde{\nu} &= 15\,600 \text{ cm}^{-1}, \\ f &= 10^{-6}, \\ n_c &= 1.5, \end{aligned} \tag{11}$$

this gives

$$\alpha/\alpha_c \sim 1 \times 10^{-4}. \tag{12}$$

This shows that the extra two-photon lines might be difficult to observe unless the laser intensity could be increased by a factor of $10^3$ over the normal beam (1). Such a concentration is not out of the question in view of the very small divergence of the beam.

Experiment (b) is conveniently discussed by comparing the two-photon absorption cross section $\sigma_A$ with the Raman scattering cross section $\sigma_R$. From (7) and (8) with $\nu = \nu_b$

$$\frac{\sigma_A}{\sigma_R} = \frac{c^2 n_c}{4\pi \nu_b^2} Fg(2\nu_b - \nu_c). \tag{13}$$

The Raman cross section (7) is evidently of the order

$$\sigma_R \sim 3 \times 10^{-25} \text{ cm}^2, \tag{14}$$

and does not depend on the beam strength. For this reason the Raman effect is not being considered here as a two-photon effect, but only as a convenient measure for $\sigma_A$. If $\tilde{\nu}_b = 14\,400$ cm$^{-1}$, $n_c = 1.5$, and the absorption band has a width $\Delta\tilde{\nu} \sim 10^3$ cm$^{-1}$, the two-photon absorption is given by

$$\sigma_A \sim (1/7)\sigma_R. \tag{15}$$

Thus if the concentration of ions is $N \sim 10^{19}$ cm$^{-3}$, the number of fluorescent photons per unit volume of the crystal would be

$$\sigma_A NF \sim 3 \times 10^{15} \text{ photons/cm}^3 \text{ sec}. \tag{16}$$

All of the estimates have been based upon the assumption of intermediate states with large oscillator strength. There may of course be a large number of excited states which can act as intermediate states, and in this case $\hbar\omega_I$ is a suitable average energy of these states and $p^2$ is the sum of the contributions of all these states. Therefore it is probable that $p^2$ corresponds to an oscillator strength of at least $\sim 0.1$. The use of (2) may overestimate two-photon effects by a factor of $10^2$, since these effects go as $p^4$. This suggests that experiment (a) may be quite difficult, while experiment (b) should be relatively convenient. Both experiments would seem to be possible. In the recent experiments of Kaiser and Garrett[4] on $CaF_2$:$Eu^{++}$, fluorescent emission has been observed and attributed to two-photon absorption as in experiment (b). The absorption cross section is reported to be in satisfactory agreement with (8) in regard to magnitude and dependence on *F*. The significance of this agreement is that two-photon absorption in a given absorption band specified only by its spectral shape $g(\nu - \nu_c)$ can be calculated without any further knowledge of the electronic structure.

[4] W. Kaiser and C. G. B. Garrett, Phys. Rev. Letters **7**, 229 (1961).