

## One- and two-photon spectra of some selected molecules: a comparative study

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**Abstract.** The complementarity of one- and two-photon spectroscopy has been utilised for throwing light on the following problems of chemical interest: (1) Weak interaction between identical chromophores separated by insulating bridges gives rise to split states of different symmetries. Two-photon spectroscopy (TPA), in conjunction with one-photon absorption (OPA), has been used to identify the states and hence to estimate the magnitude of interaction in bimolecules and trimolecules. From the shifts between the one- and the two-photon spectra, the splittings have been estimated. Calculations confirm that the dominant interaction is the through-bond one. (2) The second type of problem is the identification of *g* and *u* vibrations in molecules. We have initiated studies on three molecules in jet-cooled conditions: 9,10-dihydro-anthracene (DHA), 9,10-dihydro-phenanthrene (DHP) and octa-fluoronaphthalene (OFN). Only the one-photon fluorescence excitation spectra have so far been obtained by us and the TPA spectra are under investigation. (3) The third class of molecules discussed here are the  $\text{Ln}^{3+}$  complexes where  $f^n \Rightarrow f^n$  transitions are intrinsically two-photon allowed. We have studied two  $\text{GD}^{3+}$  single crystals. The CF-splittings, observed clearly in TPA, have been fitted with a parametric model. Some of our observations on the variations of TPA intensity patterns from crystal to crystal, such as circular:linear polarisation ratios, relative intensities of transitions to different *J*-states, do not quite fit in with the Axe–Judd–Downer model. The discrepancies call for a reappraisal of the role of ligand in the TPA process.

**Keywords.** Two-photon spectroscopy; lanthanide spectroscopy; super-sonic-jet-cooled spectroscopy; intramolecular exciton interaction.

The purpose of this overview is to illustrate some complementary features of one- and two-photon spectroscopy with some organic and inorganic molecules of interest to us. In our institute, where the Raman Effect was discovered, we like to view two-photon absorption (TPA) as 'unfolded' Raman Effect. The scheme for Raman transition is shown in figure 1, where the incident photon excites the electronic cloud to a 'non-stationary' or 'virtual' state of average energy indicated by the dotted line, from where it comes *down* to the final state *spontaneously*. If, however, the final state is above the intermediate 'virtual' state, another incident photon is needed to *induce* the transition from the intermediate level to the final state, leading to  $I^2$ -dependent two-photon absorption. The basic expression for the transition probability is the same in two cases, and in as much as Raman tensor has proved to be immensely useful in chemistry for structural studies and for identification of symmetries of states, it is

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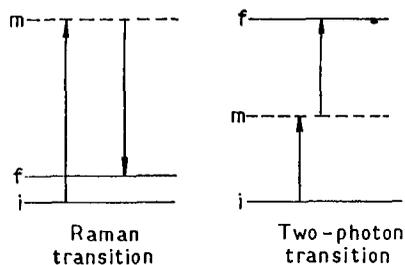


Figure 1. Schematic diagram of Raman and two-photon transition.

pertinent to explore the full potentiality of TPA in providing information on molecular states. Excellent reviews on TPA are given in Swofford and Albrecht (1978), Friedrich and McClain (1980) and Goodman and Rava (1983).

The theory of two-photon absorption was first developed by Goepfert-Mayer (1931), and the cross-section may be expressed as proportional to

$$\left| \sum_m \frac{\langle i | \mathbf{E}_{v_1} \cdot \mathbf{r} | m \rangle \langle m | \mathbf{E}_{v_2} \cdot \mathbf{r} | f \rangle}{\Delta E_{im} - h\nu_1} + \sum_m \frac{\langle i | \mathbf{E}_{v_2} \cdot \mathbf{r} | m \rangle \langle m | \mathbf{E}_{v_1} \cdot \mathbf{r} | f \rangle}{\Delta E_{im} - h\nu_2} \right|^2.$$

Several points may be noted about the expression. First, in centro-symmetric systems, the initial and the final states need to be of the same parity, and hence TPA should provide information complementary to one-photon absorption (OPA), the relationship being the same as that between Raman and infrared (IR). How this complementarity can provide information on molecular interaction will be discussed later. Second, the cross-section of the process is several orders of magnitude smaller than the OPA cross-section; however, it is greater than the off-resonance one-photon transition probability and hence is observable at  $\Delta E_{if} = 2h\nu$ . The cross-section can indeed be made appreciable by using intense laser light, specially of pulsed laser. Let us take the case of  $\text{Ln}^{3+}$ -ions. The order of magnitude of electronic Raman cross-sections for  $\text{Ln}^{3+}$ -ions is about  $10^{-30} \text{ cm}^2 \text{ atom}^{-1}$ , whereas TPA cross-sections for the same ions are of the order of  $10^{-53} \text{ cm}^4 \text{ atom}^{-1} \text{ photon}^{-1}$ . For a flux density of  $10^{28} \text{ photons cm}^{-2} \text{ s}^{-1}$ , which is achievable by focussing a pulsed dye laser, the number of photons in TPA fluorescence easily exceeds the number of photons obtained from Raman scattering. Third, the cross-section is dependent on the relative polarisation of the two-photon beams. One can indeed vary the propagation direction and polarisation of the two beams and can obtain full symmetry information of the excited state from such two-colour experiments. In view of the control over the two beams, more symmetry information can be obtained from TPA than from the Raman Effect. However, it is much more convenient to carry out the one-colour experiment and the expression for TPA cross-section then reduces to

$$\left| \sum_m \frac{\langle i | E^\alpha r^\alpha | m \rangle \langle m | E^\alpha r^\alpha | f \rangle}{\Delta E_{im} - h\nu} \right|^2.$$

All the polarisation information, however, is not lost. For example, in a randomly oriented sample, OPA cannot give any symmetry information of the excited state, but the TPA cross-section for circularly polarised photons will be different from that for linearly polarised photons.

Before illustrating the points mentioned above, let us briefly discuss our experimental set-up (details in Nath *et al* 1983). The TPA cross-section being small, it is not advantageous to measure  $I/I_0$  as in OPA. Fluorescence and MPI are two sensitive techniques commonly adopted; our set-up is based on the former. The light from an  $N_2$ -laser-pumped-dye-laser, freed from any accompanying U-V radiation by filters, is appropriately polarised and focussed on the sample by a lens. The fluorescence is collected, passed through a monochromator/filter combination, and detected by an EMI 9813QB photomultiplier. A fraction of the dye laser light also falls on a photo-diode and provides the reference signal  $I_0$ . The signals,  $I$  and  $I_0$  are fed into a box-car which averages them and the  $I_{av}/(I_{av}^0)^2$  is plotted against the wavelength to get the uncorrected fluorescence excitation spectrum. The box-car technique was utilised by us initially. However, it should be noted that a box-car gives  $I_{av}/(I_{av}^0)^2$  whereas what is needed is  $Av(I/I_0^2)$ ; if the signal fluctuates considerably from pulse to pulse, the two quantities may differ appreciably. In order to get rid of the spikes and the flats that occur due to various causes, we now use a computer which puts windows on  $I$  and  $I_0$ , and calculates the required quantity  $Av(I/I_0^2)$  with properly selected slots. Second, it is found that because of other competing processes, the power dependence of the signal  $I$  is frequently less than 2 and even varies over the wavelength regions. In such cases it is advantageous to hold  $I_0$  within a narrow margin by using windows and take the  $Av(I/I_0^n)$  in the computer, where  $n$  is pre-determined from a plot of  $\log I$  vs  $\log I_0$  in the concerned wavelength region. Third, when the lifetime of the emission is long (e.g. milliseconds) we have found it useful to use a gated preamplifier whose impedance switches from 50 ohms to 1 megaohms after a delay. The disturbances due to scattering (this is particularly high in polycrystalline matrix), rf. etc. thus quickly die away while the signal voltage remains appreciable due to the high input impedance. The improvement of the spectra is particularly noteworthy if the signal level is low and there is appreciable scattering from the polycrystalline matrix, as shown in figure 2.

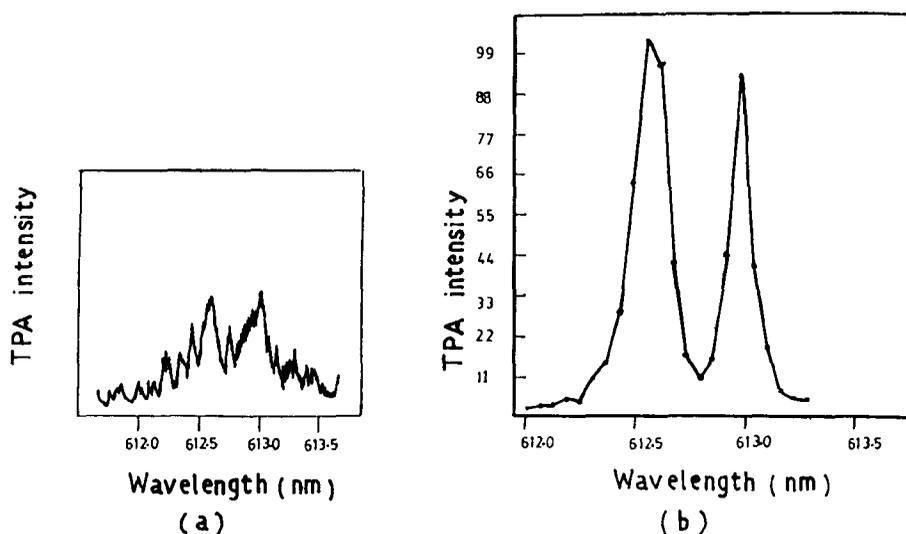


Figure 2. A comparison of two-photon excitation spectrum using (a) boxcar (b) computer controlled system.

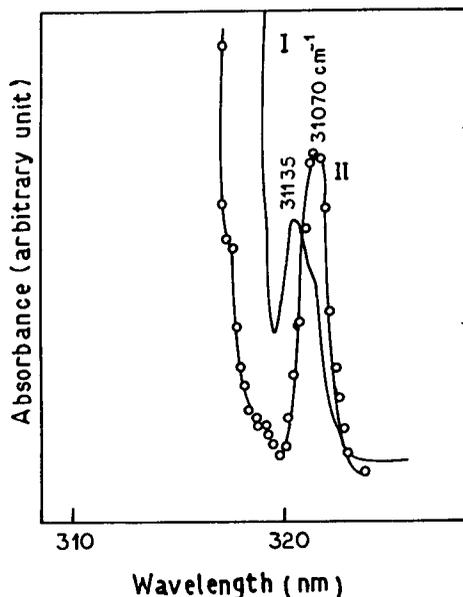


Figure 3. Absorption(I) and normalised two-photon excitation spectra(II) of *trans* dimer of acenaphthylene in methyl-cyclohexane isopentane glass at 77 K.

One of the issues we wanted to settle through a comparison of one- and two-photon spectra is the magnitude of splitting originating from weak interaction between chromophores in poly-chromophoric molecules. For example, in the *trans*-dimer or acenaphthylene there are two naphthalene units joined by a network of saturated carbon atoms. If we neglect the through-bond interaction, such molecules may be considered as finite model systems for the excitonic interaction of the infinite array of molecules in a crystal. The question whether the through-bond interaction is negligible can only be answered by determining the small  $g$ - $u$  splitting and comparing it with calculations. One of the ways to address the problem is to compare the one- with the two-photon spectrum, as shown in figure 3. Though the spectrum is not well-resolved, as is expected for a glassy matrix, it clearly indicates the possibility of such splitting. In fact, when we cool down the matrix to 4 K, we find interesting changes; the first two sharp bands disappear leaving a broad weak 0-0 band on the longer wavelength side of the emission. This confirms the conclusion that a  $g$ -state lies  $\approx 140 \text{ cm}^{-1}$  below the allowed  $u$ -state. Excitonic interaction, calculated on the basis of dipole approximation, gives results in disagreement with experiment. We, therefore, believe that there are through-bond interactions, even though the two  $\Pi$ -chromophores are separated by two saturated carbon atoms (Bhattacharya *et al* 1983; Samanta *et al* 1986).

The capability of polarisation studies may be illustrated with the help of triptycene, an interesting trimer of benzene. Each excited state of benzene is split into one singly and one doubly degenerate states. Thus, the three  ${}^1B_{2U}$  states of  $D_{6h}$  benzene splits into  $A'_1$  and  $E'$  states of  $D_{3h}$  triptycene. Suppose the light propagates along the  $Z$ -axis of the molecule. For  $A'_1 - A'_1$  transition and circularly polarised light, no connecting intermediate state of proper symmetry can be found; the same is true of  $A'_1 - E'_1$  components if linearly polarised light is used. Thus, for oriented samples and light

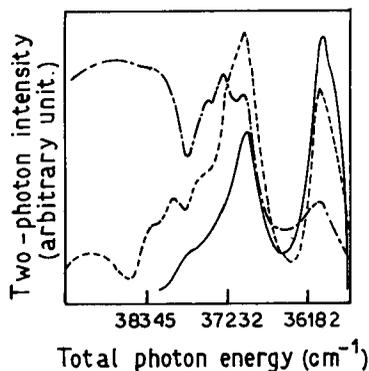


Figure 4. One-photon absorption (—) and two-photon excitation spectra of triptycene with linearly (---) and circularly (-.-.-) polarised light.

propagation along Z, TPA of  $A'_1 - A'_1$  is observable with linearly polarised light and  $A'_1 - E'$  with circularly polarised light. The conclusion obviously needs modification when randomly oriented molecules are used. It can be shown that for the  $A'_1 - A'_1$  transition, the circ/linear ratio lies between 0 and 0.25 while for the  $A'_1 - E'$  transition it should be 1.5. Our spectrum is shown in figure 4. The longest wavelength band is observed in the one-photon spectrum and relatively strongly in circularly polarised spectrum and hence assigned to the  $A'_1 \rightarrow E'$  transition. In the region around  $38,650 \text{ cm}^{-1}$ , no band appears in one-photon spectrum and in circularly polarised two-photon spectrum, but a distinct broad band appears in linearly polarised two-photon spectrum. The broad band has been ascribed by us to the  $A'_1 \rightarrow A'_1$  transition (Kundu *et al* 1987). However, the 0-0 origin of the band is debatable. Our MNDO calculation shows that the separation between  $A'_1 - E'$  should be about  $1000 \text{ cm}^{-1}$ . Indeed there is a small peak in linearly polarised TPA at about  $37,000 \text{ cm}^{-1}$  to the blue of the  $A'_1 \rightarrow E'$  origin, which may be taken as the origin of the  $A'_1 \rightarrow A'_1$  transition.

The case of a similar dimer of benzene, dihydroanthracene, is more complicated, for the bent molecule does not have a centre of symmetry; secondly, there is clearly the possibility of double minima in potential energy curves for both ground and excited states. A comparison of one- and two-photon excitation spectra suggests the presence of principally TPA-allowed  $g$ -state lower than principally OPA-allowed  $u$ -state (Samanta *et al* 1987). A small but definite gap between absorption and emission lends further support to this idea. However, the condensed phase spectrum suffers from a lack of resolution. We have therefore obtained the OPA-spectrum of jet-cooled molecules (Chakraborty and Chowdhury 1990). An irregular series of low-frequency bands appear; presumably, these arise from the vibration corresponding to the butterfly motion around the line joining the two  $-\text{CH}_2-$  units. It is to be noted that the vibrational spacings are non-uniform, which can either be explained by assuming (a) two electronic states or (b) tunnel splitting in the excited state double well. We could explain our data well with the help of the latter assumption (figure 5). We tentatively believe that the diffuseness of the spectrum beyond  $150 \text{ cm}^{-1}$  from the origin is due to the presence of another electronic state; this can be confirmed or refuted by obtaining the two-photon-resonant jet MPI spectrum.

Another molecule where the TPA could be of help to settle between different alternatives is dihydrophenanthrene. In this case the one-photon-jet-excitation spectrum

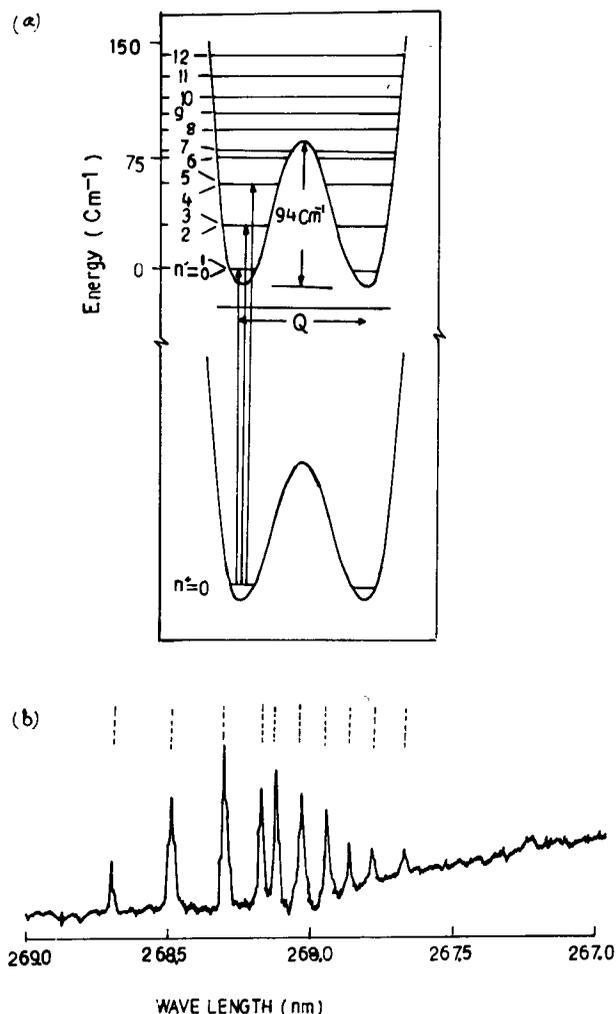


Figure 5. Fluorescence excitation jet spectrum of dihydroanthracene (b) and the proposed potential energy curve (a) for the excited state.

shows a long progression on the origin as well as on each of the vibronic bands. This molecule is non-planar with a dihedral angle of  $20^\circ$  in the ground state, and the intensity pattern can be explained well by assuming a  $20^\circ$  change in the dihedral angle in the excited state. The long-progression of  $\approx 100 \text{ cm}^{-1}$  in the observed spectrum indicates that the excited potential is harmonic with planar equilibrium conformation although the ground state has double minima. One of the interesting observations is that the spacing between lines in the progression alternates (Chakraborty and Chowdhury 1991). One of the possibilities, but not clearly the only one and certainly not without ambiguity, is that the ground state has a small tunnel splitting of  $5 \text{ cm}^{-1}$ . If this occurs, then two-photon spectroscopy should be able to settle the point.

The above examples illustrate how TPA could be of use in assignment of states and in determination of magnitudes of weak interactions. Much less attention has been paid

so far to the problem of determination of TPA cross-sections and relating them to the electronic structures of the molecules. Determination of the absolute cross-section being difficult, we have focussed our attention on the comparison of cross-sections between states of similar nature of a series of related molecules and between different transitions within the same molecule. The trivalent lanthanide ions with a host of  $f^n$ -states of different symmetries offer themselves as good testing grounds for the theories of TPA intensities. The crystal field effect being small for  $f^n$ -states, simple rules are expected from nearly preserved spherical symmetries. Perhaps, it may be recalled that the first two-photon experiment was carried out on an  $f \rightarrow d$  transition of divalent  $\text{Eu}^{2+}$  ion (Kaiser and Garrett 1961), but the field remained neglected till recently when Bloembergen and his collaborators obtained relative TPA cross-sections of several  $\text{Ln}^{3+}$  ions and reported some puzzling features (Downer *et al* 1982; Downer and Biswas 1983). We intend to further elaborate these discrepancies between theory and experiment. Only fluoride crystals have been studied so far. In view of the possibility that ligands might play a dominating role even in the intrinsically two-photon allowed  $f^n \rightarrow f^n$  transitions, we have studied two non-fluoride single crystals – gadolinium elpasolite (Gd–El) where the  $\text{Gd}^{3+}$  ion sits in the centrosymmetric octahedral environment of  $\text{Cl}^-$  ions and gadolinium diglycolate (Gd–DG) where O-ligands provide a nonsymmetric  $D_3$  environment.

Before discussing the intensity problem we would like to point out several advantages of TPA as a spectroscopic tool for lanthanides. First, in centrosymmetric systems the O–O bands are not allowed in one-photon  $f^n \rightarrow f^n$  transition unless, of course, the magnetic dipole or electric quadrupole intensities are high. The predominance of phonon bands and their overlapping in one-photon spectrum make the detection of CF splittings difficult. Background absorption by the medium also interferes with the detection of one-photon  $f^n \rightarrow f^n$  transitions. On the other hand, the two-photon spectrum stands out clearly over the background and shows the splittings, as shown in figure 6(a) for the Gd–El crystal. Even for non-centrosymmetric systems, the one-photon band widths are larger than the two-photon widths, as is the case with Gd–DG single crystal (Kundu *et al* 1990). Second, since one-photon transitions are induced by mixing of  $f^n$  and  $f^{n-1}d$  (or  $f^{n-1}g$ ) states through spherical harmonics  $Y_l^m$  ( $l \leq 6$ ), the non-restrictive selection rule  $\Delta J \leq 6$  is not of any use in sorting out overlapping  $J$  states. On the other hand, TPA selection rules should, in principle, be able to pick out  $\Delta J \leq 2$  transitions, if, of course, no extensive  $J$ -mixing occurs. The same comment is applicable to the resonance second harmonic generation process, as has been demonstrated by us sometime back with a  $\text{Gd}^{3+}$  single crystal (Karmakar *et al* 1983).

The rather unmanageable expression for the two-photon cross-section.

$$\left| \sum_m \frac{\langle i | \mathbf{E} \cdot \mathbf{r} | m \rangle \langle m | \mathbf{E} \cdot \mathbf{r} | f \rangle}{\Delta E_{im} - h\nu} \right|^2$$

was simplified by Axe (1964) by replacing  $\Delta E_{im}$  by average constant value  $E$ , independent of  $m$  – a trick first suggested by Judd and by Ofelt for systematising the term-to-term one-photon intensities of trivalent lanthanides. This suggestion has enjoyed, in view of lack of any workable alternative approach, reasonable degree of success and has been widely accepted by lanthanide spectroscopists. Application of

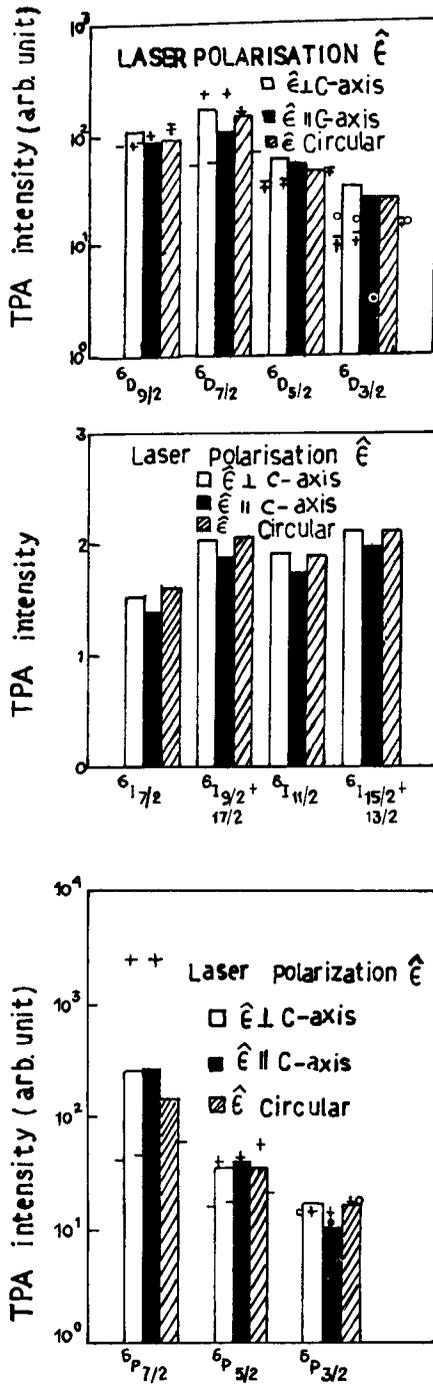


Figure 6. (a) Two-photon excitation spectra of  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$  and  $Gd^{3+}$  in gadolinium elpasolite crystal system. (b) Relative two-photon excitation line strength of  ${}^6P_j$  in the same system. Note that filled circles and plus signs denote the calculated values obtained from second and third (LS) order calculations respectively.

closure property reduces the expression to

$$(\mathbf{E}\mathbf{E})^2 [1/(\Delta E_{im} - hv)]^2 |\langle i|\mathbf{r}\mathbf{r}|f\rangle|^2,$$

from which three conclusions follow (Downer 1983).

- (1) The TPA cross-section should be independent of the nature of the crystal and of polarisation direction of the linearly polarised light. However, figures 6 and 7 show that the prediction is not valid.
- (2) It follows from the  $(\mathbf{E}\mathbf{E})^2$  term that circularly polarised light will have TPA absorption strength 1.5 times that of linearly polarised light; this conclusion is independent of the nature of the excited state. Again figures 6 and 7 show that circular to linear ratio does indeed depend on the transition.
- (3) The product of two vector operators,  $\mathbf{r}\mathbf{r}$ , can be broken down into sum of three tensor operators  $U^{(2)}, U^{(1)}, U^{(0)}$ . The  $U^{(1)}$  term will be absent in one-colour experiment. Since the number operator  $U^{(0)0}$  will not connect orthogonal ground and excited states, the TPA cross-section will be proportional to  $U^{(2)}$  matrix elements between ground and excited states, which of course can be easily calculated from the standard tables of Nielson and Koster (1964). For  $Gd^{3+}$ , the term-to-term TPA intensities of the transitions  $^8S_{7/2} \rightarrow ^6P_{7/2}, ^6P_{5/2}, ^6P_{3/2}$  should be in the ratio 1:0.7:0.1. Once again figures 6 and 7 show that this is not what is observed. It also follows from the  $\Delta J \leq 2$

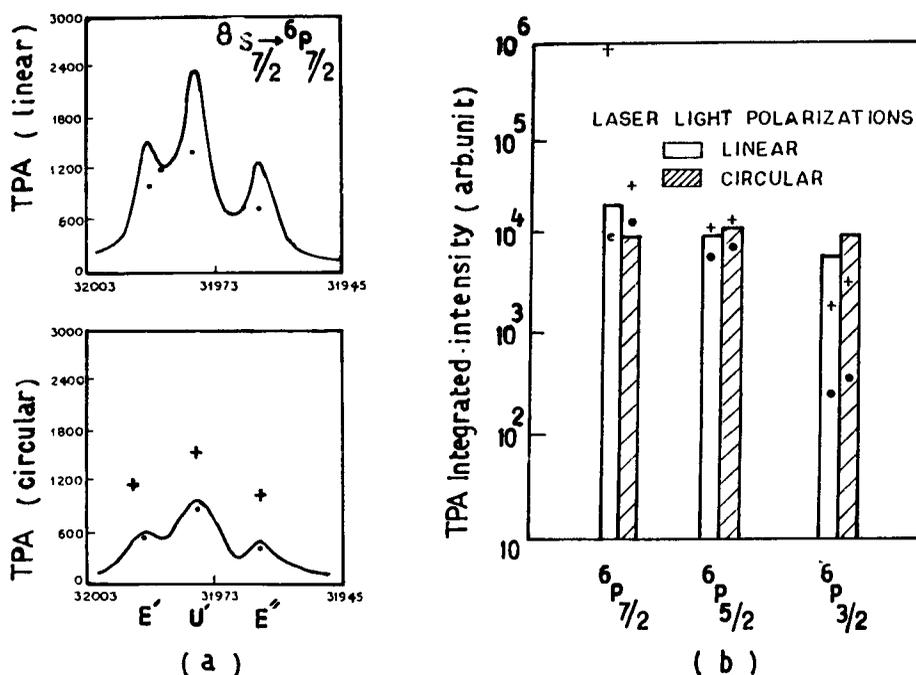


Figure 7. Relative two-photon line strengths of  $^6P$ ,  $^6D$ , and  $^6I$ , in gadolinium diglycolate single crystal for three polarisations of the excitation beam. Note that horizontal lines and plus marks denote the predictions of second and third (LS) order theory. If the predicted relative intensities change appreciably when  $J$  mixing is taken into account, it is shown by open circles.

selection rule that  ${}^8S_{7/2} \rightarrow {}^6I_{13/2,15/2}$  transitions should be forbidden. This expectation is not borne out by experiment (figure 7c).

Judd has pointed out that Axe's (1964) approach needs to be slightly modified in view of the spin-forbidden nature of the transitions (Judd and Pooler 1982). It is to be remembered that the intermediate coupled (IC) free ion wavefunctions for initial and final states are diagonalised within  $f^n$ -states only; spin-orbit coupling between *intermediate* states may be additional sources of TPA intensity. This means that the perturbation theory has to be extended to third order, the additional third-order contribution being proportional to

$$\left| \sum_{m,n} \frac{\langle i|\mathbf{r}|m\rangle \langle m|L \cdot S|n\rangle \langle n|\mathbf{r}|f\rangle}{(\Delta E_{im} - h\nu)(\Delta E_{in} - h\nu)} \right|^2,$$

where  $m, n$  refers to intermediate  $f^{n-1}d$  (or  $f^{n-1}g$ ) states of octet and sextet multiplicity respectively. If now the same controversial assumption is made that  $\Delta E_{im}$  and  $\Delta E_{in}$  are replaceable by average value  $\bar{E}$ , the third-order TPA cross-section becomes proportional to  $(1/\bar{E}^4) |\langle i|\mathbf{r}(L \cdot S)\mathbf{r}|f\rangle|^2$ . The net consequence of this is that the  $U^{(11)0}$  part of the operator can no longer be neglected and this will produce additional intensities to linear polarisation for  $\Delta J = 0$  transitions; this will upset the calculations discussed above. Our third-order calculations from the two crystals show that Judd's suggestion does indeed explain, to a limited extent, the higher intensity of the  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$  transition relative to the  ${}^8S_{7/2} \rightarrow {}^6P_{5/2,3/2}$  transitions, and the higher linear:circular polarisation ratio for the  ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$  transition. However, quantitative agreement is still lacking. Qualitatively also, the variation of the circular:linear ratio for various  $\Delta J \neq 0$  transitions, and variation of relative intensities between crystals remain unexplained by Judd's brilliant third-order extension. We have diagonalised the crystal field matrix and used crystal field wavefunctions for the initial and final states in our calculation. This, however, takes into account the crystal field effect only partially, since our calculation does not take into account the crystal field mixing of intermediate  $f^{n-1}d$  states. Our results are shown in figures 6 and 7. Our calculated results are not sensitive to crystal field parameters while the experimental results are. Discrepancies with respect to  ${}^8S \rightarrow {}^6D$  or  ${}^6I$  groups of transitions are even larger (Kundu *et al* 1990; Kundu and Chowdhury, unpublished results).

We must, however, point out that while integrated term-to-term intensities are in disagreement with theoretical expectations, the *relative* intensities of crystal-field-component-to-crystal-field-component transitions within a term generally agree with calculated values. One of the observed spectra along with theoretically calculated values is shown in figure 6a.

The gross discrepancies mentioned above cannot be due to inaccurate parametrisation of the crystal field. They might disappear if crystal field mixing between intermediate  $f^{n-1}d$  states are taken into account by developing the theory to fourth order. We, however, feel that this kind of perturbation approach is not the best way to consider ligand field effects on intrinsically allowed TPA transitions. Indeed, an alternative approach for non-centrosymmetric systems has been outlined by Reid and Richardson (1984) and by Sztuckei and Strek (1986). Within the framework of the independent particle model, one may write the wavefunctions as a product of wavefunctions of metal states and ligand states and include the ligand excited states and metal excited states amongst intermediate states. If we leave aside charge-transfer

(CT) states, the following two additional types of terms result from ligand excited states:

$$\text{Type-1 } \sum_{j,\beta} \frac{\langle \Phi_M^i \Phi_L^\alpha | \mathbf{r} | \Phi_M^i \Phi_L^\beta \rangle \langle \Phi_M^i \Phi_L^\beta | H_{\text{INT}} | \Phi_M^j \Phi_L^\alpha \rangle \langle \Phi_M^j \Phi_L^\alpha | \mathbf{r} | \Phi_M^f \Phi_L^\alpha \rangle}{(E_{M'L'} - \hbar\omega)(E_{M'L''} - \hbar\omega)}$$

$$\text{Type-2 } \sum_{\beta,\gamma} \frac{\langle \Phi_M^i \Phi_L^\alpha | \mathbf{r} | \Phi_M^i \Phi_L^\beta \rangle \langle \Phi_M^i \Phi_L^\beta | H_{\text{INT}} | \Phi_M^f \Phi_L^\gamma \rangle \langle \Phi_M^f \Phi_L^\gamma | \mathbf{r} | \Phi_M^f \Phi_L^\alpha \rangle}{(E_{M'L'} - \hbar\omega)(E_{M'L''} - \hbar\omega)}$$

Both terms contribute to non-centrosymmetric systems, but in centrosymmetric systems, like our Gd-elpasolite, only the last one contributes, if dipole-interaction is the only term considered under  $H_{\text{INT}}$ . The contribution of type-2 terms has not been considered so far; it is necessary to see whether its contribution can explain some of the anomalies observed with Gd-El crystal (L Kundu and M Chowdhury, unpublished results). Some physical insight may be obtained for a subgroup of terms for which  $\beta = \gamma$ . The contribution from the group of terms may roughly be interpreted as borrowing from two-photon transition probability of ligands. Typically, the TPA cross-section of  $\Pi$ -ligands is  $10^3$  times higher than that of  $\text{Ln}^{3+}$  ions. For example, for  $\text{Ln}^{3+}$  TPA cross-section has been measured to be  $10^{-53/54} \text{ cm}^4 \text{ s atom}^{-1} \text{ photon}^{-1}$ , while for an organic  $\pi$ -system the same is typically of the order of  $10^{-50/51} \text{ cm}^4 \text{ s atom}^{-1} \text{ photon}^{-1}$ . Therefore, a 10% admixture of ligand states with metal states is sufficient to explain some of the anomalies observed. However, a quantitative development of the idea should wait till we have more information on ligand states. It is also necessary to point out that type-1 terms can also contribute to centrosymmetric systems through expansion of  $H_{\text{INT}}$  such that dipole-quadrupole or quadrupole-quadrupole interactions between metal and ligand charge clouds are taken into account. Lastly, it is quite possible that CT states, serving as intermediate states, have large contributions. More extensive investigations on suitable complexes are needed to correlate the anomalies with the presence of low-lying CT states.

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