Some new aspects of lanthanide optical spectroscopy: circular dichroism and two-photon absorption

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Abstract. It has been shown that circular dichroism (CD) and two-photon absorption (TPA) spectroscopies are capable of throwing new light on $f^n \Rightarrow f^n$ optical transitions. High-resolution circular dichroism of single crystals can provide information on the chiral environment as well as on the magnetic and electric quadrupolar transition moments of lanthanide ions, and thus can be exploited for the purpose of assignment of bands. TPA, on the other hand, although capable of resolving crystal-field components better than one-photon absorption, exhibits puzzling intensity features, which need to be sorted out before it can be generally used as a diagnostic tool.

Keywords. Lanthanide optical spectroscopy; circular dichroism; two-photon absorption; chiral environment.

1. Introduction

The importance of rare earth (RE) compounds in various fields is well-recognised, recent discovery of high temperature ceramic superconductors adding a new dimension to it. Quite apart from applied interest such as laser technology etc., spectroscopic study of RE ions is interesting for its own sake. If the "atom in molecule" concept has any validity at all, then it is for the RE compounds where the concept of angular momentum still retains its sense. The wavefunctions and charge distribution of Ln^{3+} ions are only slightly perturbed by ligand or crystal fields, and in that sense, it is a good testing ground for perturbational approaches. Spectral analysis yields average values of various powers of the distance of the electron from the nucleus and average values of electron-repulsion integrals which can be compared with theory. Since the RE series consists of closely related atoms, study of systematic variation within the group offers interesting possibilities. Second, transition moments higher than electric dipoles acquire appreciable magnitude in heavy elements and the sharp line-spectra of RE ions provide spectroscopists a rare opportunity for investigating these usually neglected moments. Third, the RE ions are good probes for phase transitions (including magnetic ones), for biological systems, for multiplicity of sites and for interactions between ions. NMR shift reagents are widely used by organic chemists for eliciting structural information. Lastly, the luminiscent well-defined excited states of this well-knit group of ions in various hosts offer a variety of energy gaps, electronic

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symmetries, site symmetries and lattice frequencies for testing the predictions of theories of non-radiative processes.

Investigations on $f^n \Rightarrow f^n$ transitions in lanthanide and actinide ions have so far been confined primarily to one-photon absorptions and emissions. Such one-photon transitions, being mostly forced electric dipolar in nature, yield valuable information on the odd and even parameters of the crystal field and on the magnitude of the most important photon-electron interaction term, namely the interaction of the electric field of light with the electric dipole moment of the molecule. Nevertheless, it is imperative to find out what additional information can be obtained from other now-established forms of optical spectroscopy, namely circular dichroism (CD) and two-photon absorption (TPA), which focus attention on 'negligibly' small but interesting terms of the photon–electron interaction Hamiltonian. In this work we shall try to illustrate the potential of CD and TPA spectroscopy of lanthanide ions with examples chosen from our own work.

2. Circular dichroism

The photon–electron interaction term can be written as,

$$H' = -(\dot{e}/mc)\bar{A}\cdot\bar{P} + (e^2/2mc^2)\bar{A}\cdot\bar{A}, \tag{1}$$

where $\bar{A}$ is the vector potential of electromagnetic radiation, $\bar{P}$ is the momentum of the electron and the other terms have their usual significance. For ordinary light intensities if we neglect the last term, write $A = A_0 e^{i\bar{k}\cdot\bar{r}}$ (where $\bar{k}$ is the propagation vector equal to $2\pi/\lambda$), and expand the exponential as a series function of r/λ, a parameter for electronic extension, we get the following expression for H',

$$H' = \bar{E}\cdot\bar{D} + \bar{H}\cdot\bar{M} + \bar{E}\cdot\bar{\bar{Q}}\cdot\bar{Z} + \text{higher order terms.} \tag{2}$$

Here the first term stands for the interaction between the electric field of light and the electric dipole moment of the molecule, the second term for that between the magnetic field of light and the magnetic dipole moment of the molecule, and the third term represents the interaction between the quadrupole moment of the molecule and the electric field of light. The first term, being several orders of magnitude larger than the other terms, dominates in absorption spectroscopy, swamping the effects of the other terms. However, if we consider circular dichroism (CD), that is, the difference between absorption probabilities of the left (LC) and the right circularly (RC) polarised light, it can be shown that the large term arising from $\bar{E}\cdot\bar{D}$ alone cancels itself off, thus providing an unique opportunity to investigate relatively small terms of H'. When the magnetic field is absent and consequently, the wavefunction can be chosen to be real, the difference of the two matrix elements $|\langle f|H'^{LC}|i\rangle|^2$ and $|\langle f|H'^{RC}|i\rangle|^2$ can be calculated in a straightforward way (Karmakar 1988), apart from some factors, as,

$$\text{Im}\{D_x^{fi}\cdot M_x^{if} + D_y^{fi}\cdot M_y^{if}\} + \pi v^{fi}/c\,\text{Re}\{D_x^{fi}\cdot Q_{yz}^{if} - D_y^{fi}\cdot Q_{xz}^{if}\} +$$

$$+ \text{higher order terms.} \tag{3}$$

In deriving this expression the propagation direction of light is chosen as z. Thus, only the cross terms between D and M, D and Q, and D and higher order terms

appear in the expression of CD. The terms which survive depend on the symmetry of the medium. If the products of two wavefunctions and one operator of the matrix element do not belong to the totally symmetric A_i representation of the symmetry group of the medium, that matrix element will become zero. Thus, in presence of an inversion symmetry or a reflection plane, the contributions from both cross terms, $D \cdot M$ and $D \cdot Q$ vanish. *In spherically symmetric 3-dimensional rotation, group R_3 (note that inversion symmetry is absent), which may be exemplified by a solution of optically active molecules or a collection of disoriented screws or powders of an optically active substance, the vectors D and M belong to the the same representation and hence their scalar product survives, while the vector D and any tensor of rank 2 (such as $\bar{\bar{Q}}$) or higher, belongs to different representations, thus leading to zero overall contribution of the second and other terms in the expression* (3) *above.* It follows that the ideal medium for the study of the first term in the above expression is a solution. Unfortunately, the metal–ligand bond in rare earths is labile which leads to immediate racemisation. Of course, one can study a rare earth complex with an optically active ligand (Brittain 1983). Such studies throw light on the mixing of ligand and metal orbitals; however, the chiral centre being elsewhere, it is not possible to relate the observed circular dichroism with the chirality of the environment of the lanthanide ion. It is therefore necessary to study the Ln^{3+} ion in optically active crystals where the CD values of the Ln^{3+} ion transitions originate from the asymmetric environment of the Ln^{3+} ion. Following the first report of such studies by Sen *et al* (1977), extensive investigations have been carried out by our group and others (Richardson 1980; Schwartz *et al* 1980, 1982; Chatterjee and Chowdhury 1981, 1982; Sen and Chowdhury 1981; Richardson and Faulkner 1982; Chatterjee *et al* 1984; Karmakar *et al* 1984, 1986, 1987; Chowdhury and Karmakar 1985; Nath *et al* 1985; Banerjee *et al* 1987; May *et al* 1987; Vala *et al* 1987) on high-resolution CD spectra of crystal-field-component-to-crystal-field-component transitions of trivalent Ln^{3+} ions in various axial and cubic chiral crystals. The site and crystal symmetries of four crystal systems studied extensively (Richardson 1980; Schwartz *et al* 1980, 1982; Chatterjee and Chowdhury 1981, 1982; Sen and Chowdhury 1981; Richardson and Faulkner 1982; Chatterjee *et al* 1984; Karmakar *et al* 1984, 1986, 1987; Chowdhury and Karmakar 1985; Nath *et al* 1985; Banerjee *et al* 1987; May *et al* 1987; Vala *et al* 1987) are shown in figures 1–4. It is to be noted that, in contrast to spherically symmetric solutions or powder media, all the terms of (3) survive in such media. Since powders of chiral crystals may be considered as media with R_3 symmetry where only the electric dipole–magnetic dipole interference term survives, they should be ideal for investigating the $D \cdot M$ term; however, scattering and consequent depolarisation introduce considerable uncertainty. We have therefore chosen oriented single crystals. We shall return to the subject of higher order contribution later, but let us neglect them for the present and discuss the salient features of the CD spectra of single crystals on the basis of electric dipole–magnetic dipole interference only.

The first thing to note is that the sign of the $\bar{D} \cdot \bar{M}$ term, and consequently of the CD, depends on the relative orientation of the two transition moments and may be positive as well as negative. This sometimes allows higher resolution in CD spectroscopy. In lanthanides the crystal field splitting is small and transitions to two crystal field states frequently overlap. If the signs of two adjacent CD bands are opposite, the CD spectroscopy shows better resolution as compared to simple absorption spectroscopy. An illustration is given in figure 5, where we have improved
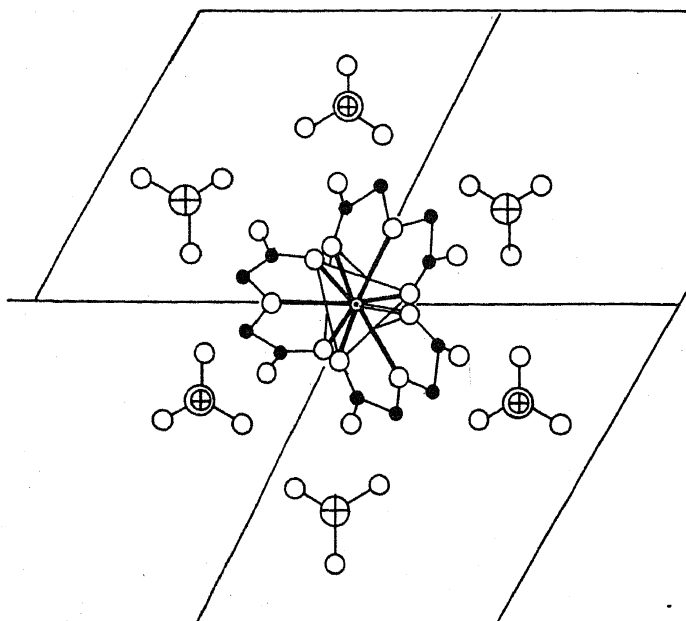
Figure 1. A view down the trigonal axis of the Ln (oxydiacetate) complex as it exists in crystalline $Na_3Ln(oxydiacetate)_3 \cdot 2NaClO_4 \cdot 6H_2O$. The six nearest neighbour ClO_4^- ions are also shown. The chiral site symmetry is D_3.

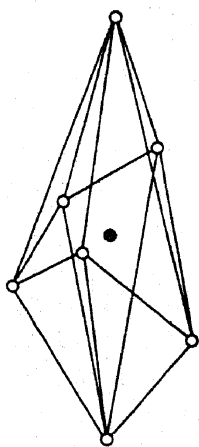**Figure 2.** The coordination polyhedra of Er^{3+} in Er-pyrogermanate $(Er_2Ge_2O_7)$ (only the first coordination sphere is shown). The site symmetry is distorted 7-coordinated pentagonal bipyramid.

the resolution further by pressing a laser into service as the light source (Vala *et al* 1987). Secondly, intensities in the CD spectrum and the absorption spectrum do not run parallel to one another. Mixed dipolar transitions with high magnetic dipole transition moments are expected to be intense in the CD spectra. Since the the selection rule for a magnetic dipolar transition is $\Delta J = 0, \mp 1$, CD may be used for identifying such transitions. It may be pointed out that the forced electric dipolar selection rule $\Delta J \leqslant 6$ for one-photon transition is of little value as a diagnostic tool in RE spectroscopy. There are wavelength regions where J-states crowd together, and crystal field (CF) splitting of states leads to interpenetration of each other's components. If one of the overlapping transitions is weak, because of spin or any other selection
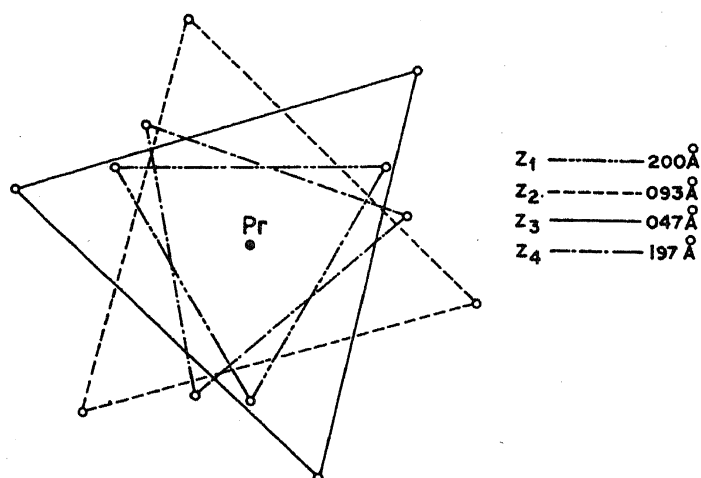
Figure 3. The coordination polyhedron of Pr^{3+} in Pr double-nitrate $[K_3Pr_2(NO_3)_9]$. O indicates oxygen ligands. The unit cell symmetry is O and the site symmetry is dodecahedral.

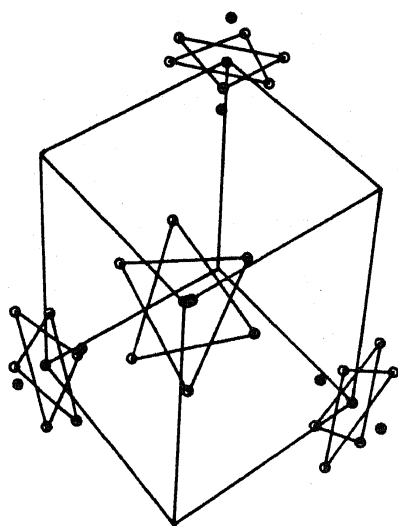**Figure 4.** Arrangement of four chiral $UO_2(CH_3COO)_3^-$ ions in the cubic unit cell. Uranium and oxygen atoms only are shown. Uranium atoms are at the corners of the cube, oxygens of the uranyl moiety are along the three-fold axes of the cube and the acetate oxygens are displayed as a joined triangle. One of the oxygen atoms is slightly above the plane of the other and rotated counter-clockwise by an angle of 52°. The unit cell symmetry is T.

rule, and the other strong, it becomes hard to identify the CF components through simple polarised absorption spectroscopy. In such situations, CD spectroscopy can be utilised for identifying the components of $\Delta J = 0$, ± 1 transitions. We have used high-resolution single crystal CD spectroscopy (Karmakar *et al* 1984, 1986, 1987), we believe for the first time, to unmask the components of the following weak forbidden transitions: $^4I_{15/2} \Rightarrow {}^2K_{15/2}$ transition of Er^{3+}, $^3H_6 \Rightarrow {}^1I_6$ transition of Tm^{3+} and $^7F_6 \Rightarrow {}^5G_{5,6}$, $^5L_{7,6}$ transitions of Tb^{3+}. Figure 6 shows one such spectrum. It should, however, be pointed out that complications may arise due to spin-orbit and J-mixing in some cases.

The third point of interest in lanthanide crystal CD spectroscopy lies in the challenging problem of spectra–structure correlation. The CD in the crystals studied
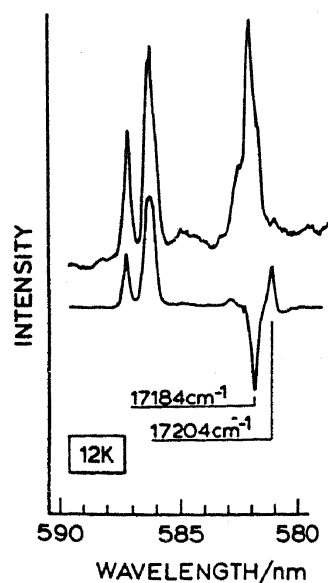
Figure 5. A comparison of resolution capability: dye laser axial absorption (upper trace) and circular dichroism (lower trace) of the Nd^{3+}-diglycolate crystal at 12K. The splitting of the lowest energy band in the CD spectrum is due to a ground state splitting of $20\,cm^{-1}$ (adapted from Vala *et al* 1987).
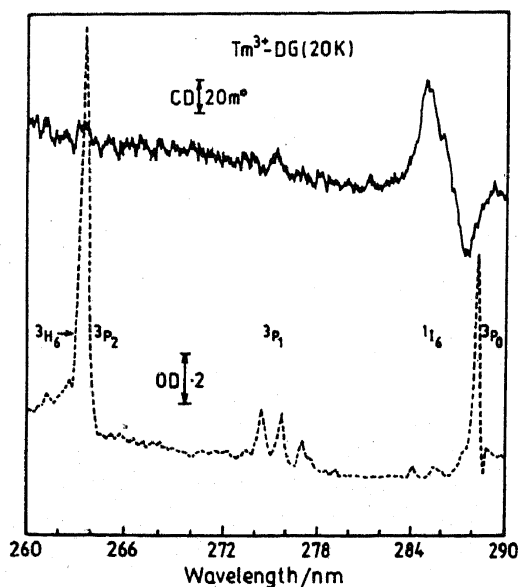

Figure 6. CD and absorption (axial) spectra of Tm-diglycolate crystal at 20K. The components of the $^3H_6 \Rightarrow {}^1I_6$ transition become prominent in the CD spectrum (adapted from Karmakar *et al* 1987).

by us originates from the chiral environment of the Ln^{3+} ion and should provide a good test of the CF-parameters, odd and even. The three-parametric Judd-Ofelt theory provides a framework for discussion of integrated absorption intensities at room temperature of different term-to-term transitions of Ln^{3+} ions. However, interpretation of the intensities of each CF-component-to-CF-component transition is still an elaborate and difficult exercise. Unlike the oscillator strength calculation, the signs of the moments are important in CD calculation. Therefore, a still more rigorous test
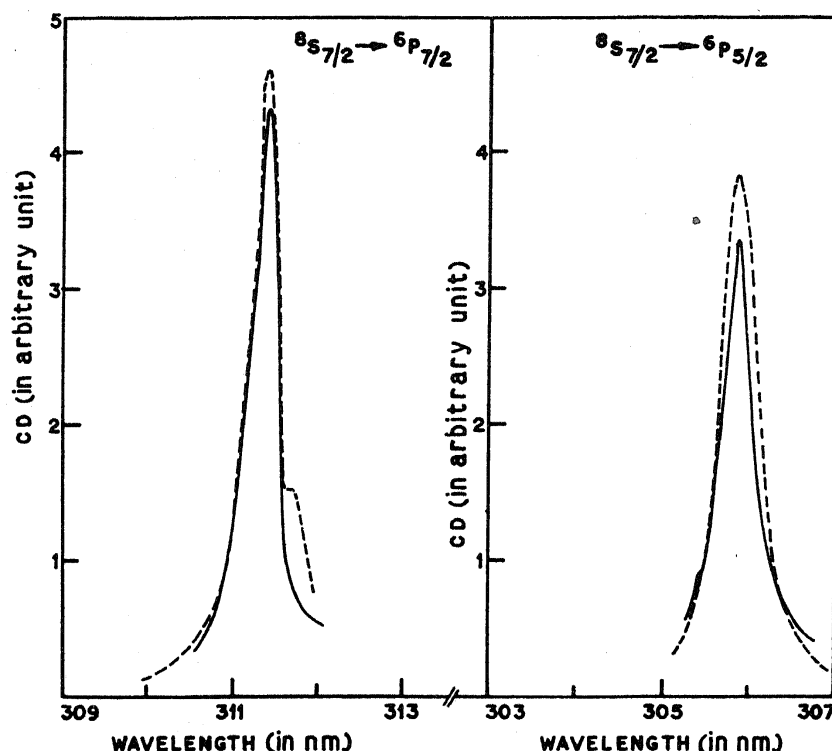
Figure 7. Comparison of a CD simulated spectrum (-----) with the experimental CD spectrum (———) for $^8S_{7/2}$ to $^6P_{7/2}$ and $^6P_{5/2}$ transitions of Gd-diglycolate single crystal at room temperature. The stark components are not resolved in the observed spectrum (T Kundu, A K Banerjee and M Chowdhury, unpublished). Only relative magnitudes for CD should be compared.

of the wavefunction and CF-parameters is provided by comparison of the simulated CD-spectrum with the experimental one. This spectra–structure correlation was first attempted by S C Bera, D Mukherjee and M Chowdhury with limited success (Sen and Chowdhury 1981a; Nath *et al* 1985). Richardson has subsequently achieved a good correlation in the case of Sm^{3+} in the DG crystal (Richardson and Faulkner 1982; May *et al* 1987). We have recently carried out an elaborate semi-empirical parametric calculation of energy level positions, dipole strengths and rotational strengths of Gd^{3+} transitions in the DG crystals (T Kundu, A K Banerjee and M Choudhury, unpublished results). Figure 7 compares the simulated spectrum with the experimental one for the group of $^8S \rightarrow ^6P$ transitions in the above crystal. It may be pointed out that although the agreement is good for $^8S \rightarrow ^6P$ or ^6D transitions, the fitting of the group of $^8S \rightarrow ^6I$ transitions is still a frustrating experience.

Another point of interest in CD spectroscopy lies in the possibility of identifying transitions which have contributions from quadrupolar or still higher order transition moments. The electric dipole moment squares are normally 10^7 times larger than the squares of electric quadrupole moments and hence simple absorption experiments are not particularly suitable for detection of electric quadrupolar contributions. On the other hand, since the electric quadrupolar moment is only one order of magnitude less than magnetic dipole moments, its percentage contribution to optical activity may not be negligible. As pointed out earlier, comparison of a powder spectrum with a single crystal spectrum is one way of recognising quadrupolar and higher order

contributions (Chowdhury and Karmakar 1985). Another strategy might be to look for the direction dependence of CD in cubic crystals. In cubic crystals the interference between electric dipole and magnetic dipole moments causes *isotropic* CD, whereas the higher order contribution to CD should, in principle, depend on the direction of propagation of light. The first optically active cubic crystal studied from this view point was anhydrous lanthanum double nitrate, $K_3Ln_2(NO_3)_9$ (Chowdhury and Karmakar 1985). It was observed that for some transitions there was a small but definite change in CD, when the light was propagated in two different directions. Since this crystal belongs to the O-group and since M and Q, span different representations in the O-group, it can be shown that CD due to quadrupole–dipole interference is zero for the O-group. The observed result, therefore, means that even higher order terms contribute to the CD of the above system. In order to recognise the quadrupolar contribution, it is necessary to work with a cubic crystal whose point symmetry is T instead of O. The single crystal of sodium uranyl acetate, Na $UO_2(CH_3COO)_3$, offers itself as an excellent candidate to test this point, for its space group is $P\,2_13$ ($Z=4$). Uranyl transitions have been studied thoroughly by Denning and coworkers and the quadrupolar nature of the transition established unequivocally (Denning *et al* 1979). We have demonstrated, to our knowledge for the first time, how
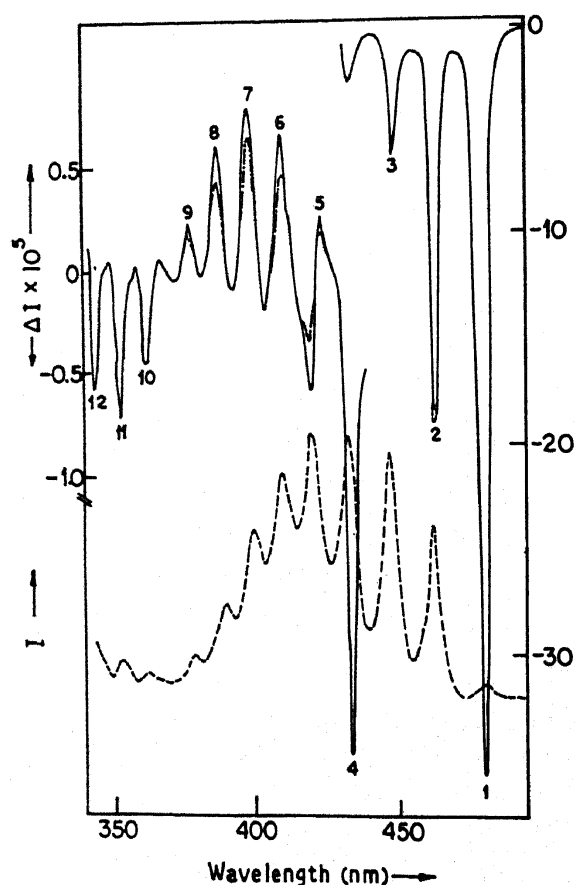
Figure 8. Room temperature CD spectra for the uranyl ion in a sodium uranyl acetate single crystal. The spectra for $k \parallel (110)$ and $k \parallel (111)$ are shown as solid and dotted lines. The absorption spectrum is also shown (dashed lines). *I*, the absorption in an arbitrary scale and ΔI, the difference in absorption of the left and right circularly polarised light is in optical density units (adapted from Banerjee *et al* 1987).

the electric quadrupolar contribution to the optical activity of the molecule can be established by measurement of the CD spectra of two faces (Banerjee *et al* 1987). Figure 8 shows the CD spectra of the (100) and (111) planes of a single crystal of uranyl acetate. A small but reproducible variation of CD has been observed for bands 2 to 9, while bands 1, 10–12 show very little variation. Bands 2 to 9 are called M and D series and have been previously assigned to the $\Sigma_g^+ \Rightarrow \Delta_g(\sigma\delta)$ transition, the band 1 (F series) to the $\Sigma_g^+ \Rightarrow \Pi_g(\sigma\delta)$ transition and bands 10–12 (UV-series) to the $\Sigma_g^+ \Rightarrow \Phi_g(\sigma\phi)$ transition, the symbols referring to representations of the idealised $D_{\alpha h}$ point group of the UO_2^{++} ion, and the symbol within brackets denotes the configuration of the orbitals occupied by two electrons. The quadrupolar contribution for the UV series is expected to be zero and indeed CD intensities for the (111) and (100) are found to be the same for bands 10–12. The band belonging to the F-series is expected to mix considerably with $\Pi_g(\sigma\pi)$ and thus borrows magnetic dipole intensity. A large CD intensity is therefore expected. However, the quadrupolar contribution has been shown to be small for the F-series, and indeed the CD intensities of the two faces are nearly the same. The quadrupolar contributions for the M- and D-series have previously been demonstrated to be large and this is in conformity with the observed difference in the (100) and (111) spectra of bands 2–9.

3. Two-photon absorption

In the previous section, we have expanded the interaction Hamiltonian in powers of r/λ and found that higher order terms express themselves in circular dichroism. If, however, instead of expanding the Hamiltonian, we extend the perturbation theory to higher orders, all the phenomena nonlinear in light intensity can be arrived at. The second-order perturbation theory leads to the possibility of one molecule absorbing simultaneously two photons of light of frequency $v = \Delta E_{if}/2h$, the cross section of the process being proportional to

$$\left| \sum_m \langle i|\bar{E}\cdot\bar{D}|m\rangle \langle m|\bar{E}\cdot\bar{D}|f\rangle/(\Delta E_{im} - \hbar\omega) \right|^2. \tag{4}$$

When $\omega = \Delta E_{if}/2\hbar$, the first-order process does not occur due to mismatch of energy allowing the two-photon absorption process to be studied if, of course, the light intensity is high enough. Fluorescence following the absorption of the two photons (TPF) is one of the convenient ways of monitoring the phenomenon.

In a centrosymmetric system, a matrix element $\langle i|\bar{E}\cdot\bar{D}|m\rangle$ will be zero unless the states i and m are of opposite parity. This means that the initial state i and the final state f have to be of the same parity. Thus, in contrast to one-photon transition, two-photon absorption is an intrinsically allowed process for $f^n \Rightarrow f^n$ transition. If the Ln^{3+} is embedded in a centrosymmetric system, the 0–0 bands of $f^n \Rightarrow f^n$ transitions are forbidden unless, of course, the magnetic dipole or the electric quadrupole transition moment is exceptionally large. In such cases the one-photon spectrum consists of vibronic bands, mostly lattice modes, and the determination of the precise location of electronic states becomes problematic. For centrosymmetric systems, therefore, TPF may be utilised for determining the crystal field splitting pattern of states. Figure 9 shows the splitting of ^6D states of GD^{3+} in the elpasolite single crystal determined by us through TPF spectroscopy (L Kundu and M Chowdhury,
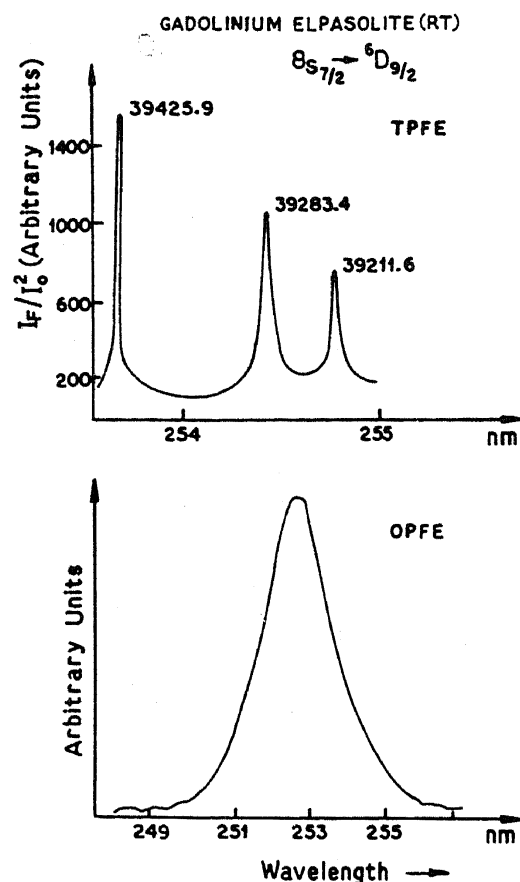
Figure 9. Comparison of the two-photon fluorescence excitation spectrum (TPFE) with the one-photon fluorescence excitation spectrum (OPFE) for $^8S_{7/2} \Rightarrow {}^6D_{9/2}$ transition in a centrosymmetric gadolinium elpasolite single crystal at room temperature. Note the lack of resolution of OPFE (Denning *et al* 1979).

unpublished results). It may be noted that the corresponding one-photon spectrum shows only a broad unresolved absorption profile. Similarly, TPF of Ln^{3+} ions in solution can resolve the CF-component-to-CF-component transition while the one-photon transition spectrum is broad and featureless. Principally for the same reason, TPF is a useful tool for identifying a multiplicity of sites such as are present when a trivalent Ln^{3+} ion replaces a divalent ion e.g. Gd^{3+} in CaF_2 (Cordero-Montalvo 1985). Another use of TPA is to unmask an $f^n \Rightarrow f^n$ transition when the crystal has considerable background absorption. Thus the ^1S state of Pr^{3+} cannot be located in most crystal systems by one-photon absorption, but it has been located by TPF in crystals by Bloembergen and others (Cordero-Montalvo and Bloembergen 1984).

TPF intensities have a number of puzzling features. Axe simplified the expression for TPA cross-section by assuming ΔE_m as constant for all m (Axe 1964). This kind of approximation, it may be recalled, was originally made by Judd and Ofelt in order to arrive at a tangible expression for intensities of one-photon bands of Ln^{3+} ions, and the three-parametric semi-empirical equation is popularly used for systematisation of the term intensities. If ΔE is taken out of the summation sign of (4), then closure approximation leads to $P_{if}^{TPA} \propto |\langle i|\bar{r}\bar{r}|f\rangle|^2$. In other words the two-photon intensities should be proportional to the $U^{(2)}$ matrix element of the states and independent of
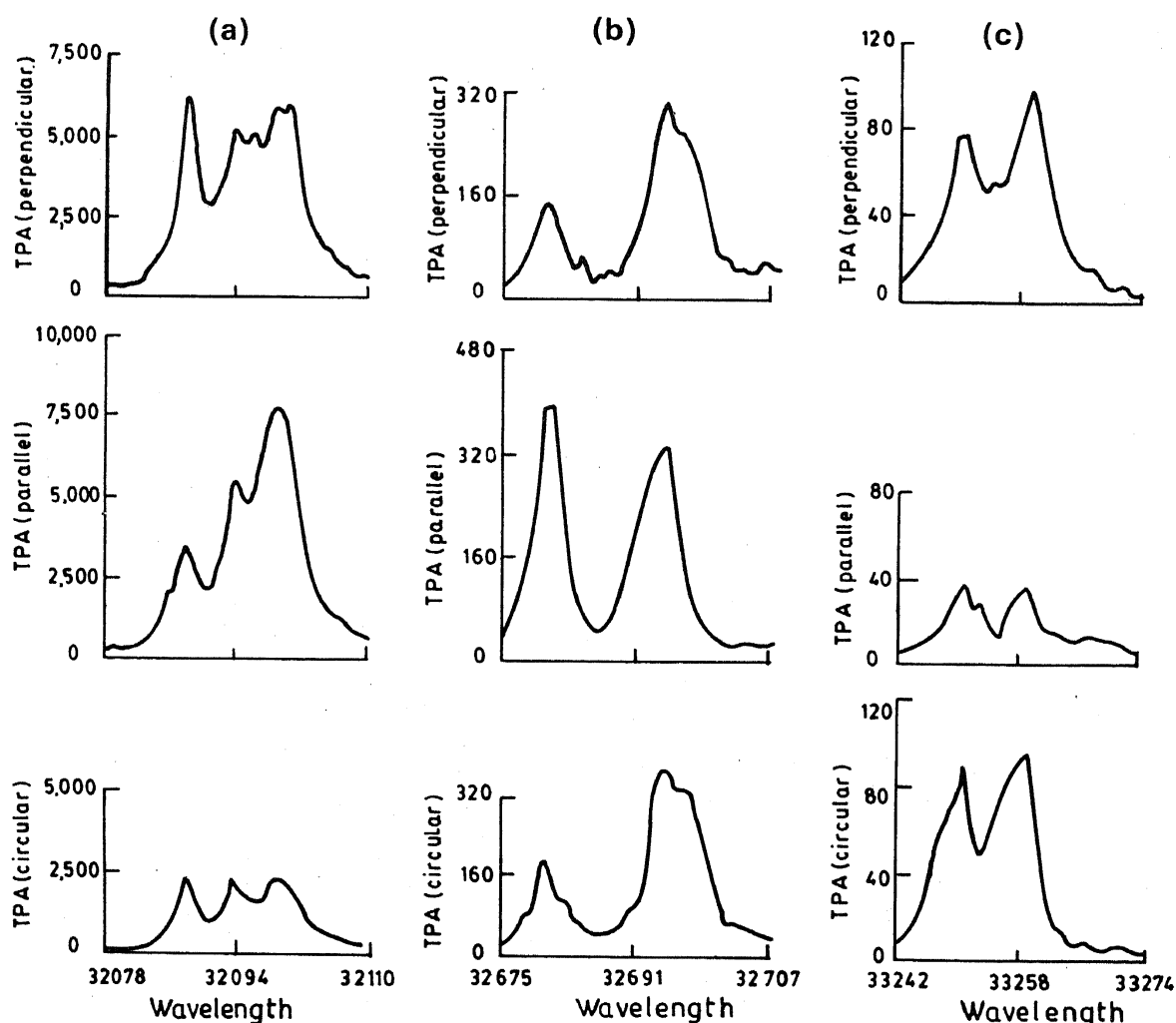
Figure 10. Experimental polarised two-photon fluorescence excitation spectrum of $^6P_{7/2}$(a), $^6P_{5/2}$(b), and $^6P_{3/2}$(c) in gadolinium diglycolate single crystal at room temperature. The vertical scales are only relative (T Kundu, A K Banerjee and M Chowdhury, unpublished).

the nature of the crystal field. It follows immediately that TPA should obey the selection rule $\Delta J \leqslant 2$, and that it should not matter whether the electric vector of light is parallel or perpendicular to the c axis of an axial crystal. Axe's theory also leads to the conclusion that in one-colour experiments, circularly polarised light will always lead to higher absorptions compared to linearly polarised light. Unfortunately, experiments do not bear out these simple, diagnostically useful predictions, as was first demonstrated (Downer and Bevas 1983; Downer *et al* 1983). Our TPF spectra of Gd-diglycolate, shown in figure 10, also corroborates these findings of Downer and co-workers for Gd^{3+}: LaF_3. The initial suspicion for the discrepancy naturally falls on the Judd–Ofelt type approximation made by Axe (1964). Judd and Pooler (1982), however, pointed out that Gd^{3+} transitions are spin-forbidden and hence the theory needs to be developed upto third order taking into account spin-orbit interactions between intermediate configurations. They used an expression of the type:

$$\left| \sum_m \sum_n \frac{\langle i|E{\cdot}D|m\rangle \langle m|\,L{\cdot}S|n\rangle \langle n|E{\cdot}D|f\rangle}{\Delta E_{im}\,\Delta E_{in}} \right|^2 ,$$

$$(fd)(fd)$$

(5)

which reduces to the following simplified form on assuming ΔE_{im} and ΔE_{in} as constants and on applying closure,

$$|\langle i|(E \cdot D)(L \cdot S)(E \cdot D)|f\rangle|^2. \tag{6}$$

This means that the transition tensor will have a $U^{(0)}$ component (active in the linear polarisation) in addition to a $U^{(2)}$ component. Their expression can explain why the $(\text{TPA})_{^8S_{7/2}\Rightarrow^6P_{7/2}}$: $(\text{TPA})_{^8S_{7/2}\Rightarrow^6P_{5/2}}$ intensity ratio is much higher than that given by Axe's second-order theory, and why $(\text{TPA})_{\text{linear}} \gg (\text{TPA})_{\text{circular}}$ for the $^8S_{7/2} \Rightarrow ^6P_{7/2}$ transition. The third-order theory of Judd and Pooler (1982) although qualitatively successful, fails to explain our data quantitatively, even if we take crystal field induced J-mixing into account. This is shown in table 1 (T Kundu, A K Banerjee and M Choudhury, unpublished results). These discrepancies are inherent in the model assumed and cannot be corrected by adjustment of crystal-field parameters. We therefore conclude that there are other sources of TPA intensities of Ln^{3+} complexes and that the ligands play a more significant role than supposed by Judd and Pooler (1982) and Downer and co-workers (Downer and Bevas 1983; Downer *et al* 1983). In fact suggestions have been put forward that the intermediate states m and n may involve ligand excited states (Reid and Richardson 1984; Sztucki and Strek 1986). We believe that metal orbitals do get mixed with ligand orbitals and the two-photon $f^N \Rightarrow f^N$ transitions

Table 1. Relative intensities of $^8S \Rightarrow ^6P$ and $^8S \Rightarrow ^6D$ two-photon transitions for Gd-diglycolate.

Intensity. ratio	Observed	(Second order)	(Third order[a] using IC wavefunction)	(Third order[a] using CF wavefunction)
$P_{7/2}/P_{5/2}$				
$E \perp c$	30·0	2·3	106·0	102·0
$E \parallel c$	24·0	2·4	98·0	91·0
E circular	10·0	2·4	1·6	1·6
$P_{5/2}/P_{3/2}$				
$E \perp c$	3·1	26·4	3·9	4·0
$E \parallel c$	9·4	29·2	4·1	5·0
E_{circular}	3·3	21·0	3·6	3·5
$P_{7/2}^{\text{lin}}/P_{7/2}^{\text{cir}}$	2·9	0·76	52·0	52·0
$P_{7/2}/P_{3/2}$				
$E \perp c$	96·0	61·0	416·0	415·0
$E \parallel c$	229·0	70·0	407·0	461·0
E_{circular}	36·0	50·0	5·6	5·6
$D_{7/2}^{\text{lin}}/D_{7/2}^{\text{cir}}$	1·3	0·76	2·1	4·3
$D_{3/2}^{\text{lin}}/D_{3/2}^{\text{cir}}$	1·3	0·7	0·7	1·2

[a]Third-order correction includes spin-orbit interaction in the intermediate (f^6d) configuration.

borrow intensity from two-photon cross-sections of ligand transitions. However, this tentative suggestion needs tc be confirmed by actual numerical calculation.

4. Concluding remarks

We have tried to explore the implication of 'negligible' terms in the complete expression for transition probability in the specific area of rare earth optical spectroscopy. Apart from providing information on magnetic dipolar and electric quadrupolar moments, circular dichroism is an useful diagnostiᴄ tool for identifying $\Delta J = 0$, ± 1 transitions in a chiral environment. Similarly, TPA could be expected to be equally useful for identifying $\Delta J \leqslant 2$ transitions but this expectation is not fulfilled. In this respect, resonant second harmonic generation has been more successful (Karmakar *et al* 1983). The potential of other forms of nonlinear spectroscopy in characterising Ln^{3+} optical transitions is therefore worth exploring. Incidentally, it may be mentioned that Mukherjee and Chowdhury (1972) theoretically predicted two-photon CD or intensity-dependent CD; however, no experimental work has been done so far. We intend to explore this aspect further.

Acknowledgements

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