ELECTRIC-FIELD-INDUCED TWO-PHOTON PROCESSES

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ABSTRACT

In this paper we outline the novel features associated with two-photon processes in the presence of intense static electric fields. Both electrical polarisation effects and non-linear electro-optical effects are discussed, and their likely orders of magnitude estimated. It is illustrated how the interaction of the electric field with a molecular centre can lead to a relaxation of conventional two-photon selection rules, allowing spectroscopic access to otherwise forbidden excited states. Selection rules for the electro-optical channel are tabulated for some of the more common point groups.

INTRODUCTION

The application of a static electric field can exert an influence on the optical spectroscopy of fluids by two distinct mechanisms. The first is an *electrical polarisation effect*, and relates specifically to fluids containing polar molecules. Here, application of a field can produce macroscopic anisotropy by introducing a degree of molecular alignment. This results in a relaxation of the normal symmetry restrictions on the allowed transitions, leading to distinctive changes of intensity in the various lines of the spectrum. Moreover, suitable choice of beam configuration enables other lines which are usually absent from the spectrum to appear.

The second mechanism, which is of more universal application, is one in which molecular transitions proceed through an *electro-optical interaction* normally absent. Here, the static field perturbs and partially mixes the molecular wavefunctions, thereby allowing some transitions to take place which would otherwise be forbidden. This can give rise to a novel effect wherein application of the field enables certain lines to be switched into the spectrum.

The distinct roles of these mechanisms in conventional (single-photon), absorption spectroscopy have been discussed in two earlier papers (refs.1-2). However, the influence of a static electric field on two-photon interactions, such as two-photon absorption and Raman scattering has, as yet, received only scant attention from spectroscopists (refs. 3-4). Studies of both these

processes in a field-free environment provide key information on molecular structure. It is the purpose of this paper to demonstrate the large amount of additional information which can be obtained by studying the novel electric field-dependence of these interactions, and to consider electric field induced effects in systems where large local fields exist, e.g. within the electrical double layer (ref.5).

SELECTION RULES

The optically (E1×E1)-allowed channel, by means of which two-photon transitions occur in the absence of the static field, and the electro-optic (E1×E1×E1)-allowed channel opened up by application of the field are each associated with a distinct set of selection rules.   In the former case, involving the concerted action of two photons at one molecular centre, the selection rules are governed by how the direct product of the two dipole operators (one for each photon) transforms.   This can be expressed as

$$D^{(1-)} \times D^{(1-)} \rightarrow D^{(0+)} + D^{(1+)} + D^{(2+)} \tag{1}$$

Here the $D^{(0+)}$ is the representation of a scalar, $D^{(1+)}$ that of the rotations $R_{x,y,z}$, and $D^{(2+)}$ that of an index-symmetric traceless rank two tensor. Although electric polarisation causes an associated change of line intensities in the spectra, conventional two-photon selection rules still apply.

For the electro-optical channel a completely different set of selection rules is applicable.   The interaction of the static electric field with the absorbing species may be viewed as a radiation-molecule interaction in the limit of zero frequency.   Consequently the selection rules will be governed by how the direct product of *three* dipole operators transform:-

$$D^{(1-)} \times D^{(1-)} \times D^{(1-)} \rightarrow D^{(0-)} + 3D^{(1-)} + 2D^{(2-)} + D^{(3-)} \tag{2}$$

Since each dipole term is of ungerade symmetry, denoted by the minus sign, the seven resultant irreducible representations must all be of ungerade symmetry. This highlights one of the important differences between two- and three-photon processes, and implies that the electro-optical channel will lead to Laporte- type selection rules, (g ↔ u), whereas the optically allowed channel results in selection rules of the type, (g ↔ g) and (u ↔ u). Thus two-photon absorption transitions induced by the electric field have the characteristics of three-photon absorption (refs.6-8) and field-induced Raman transitions obey selection rules characteristic of hyper-Raman scattering (refs.9-11).

In point groups where the inversion element does not exist, the pluses and minuses can be dropped from eqns. 1 and 2. Under these conditions it is clear that the electro-optical route can still provide access to new excited states, since the allowed transitions can also have the transformation properties of a symmetric traceless, rank three tensor. Table 1 shows the transformation properties of the irreducible representations, given in eqn. 2, for some of the more common point groups. The results are also given for normal one- and two-photon processes to highlight how the electro-optical channel leads to the accessibility of further states.

Group	Single-photon process	Two-photon process	Electro-optically allowed two-photon process
C	A_u, B_u	A_g, B_g	A_u, B_u
C_{2v}	A_1, B_1, B_2	A_1, A_2, B_1, B_2	A_1, A_2, B_1, B_2
C_{3v}	A_1, E	A_1, A_2, E	A_1, A_2, E
C_{4v}	A_1, E	A_1, A_2, B_1, B_2, E	A_1, A_2, B_1, B_2, E
D_{2h}	B_{1u}, B_{2u}, B_{3u}	A_g, B_{1g}, B_{2g}, B_{3g}	$\underline{A_u}$, B_{1u}, B_{2u}, B_{3u}
D_{3h}	A_2'', E'	A_1', A_2', E', E''	A_1', $\underline{A_1''}$, A_2', A_2'', E', E''
D_{4h}	A_{2u}, E_u	A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_g	A_{1u}, A_{2u}, $\underline{B_{1u}}$, $\underline{B_{2u}}$, E_u
D_{6h}	A_{2u}, E_u	A_{1g}, A_{2g}, E_{1g}, E_{2g}	$\underline{A_{1u}}$, A_{2u}, $\underline{B_{1u}}$, $\underline{B_{2u}}$, E_{1u}, $\underline{E_{2u}}$
T_d	T_2	A_1, E, T_1, T_2	A_1, $\underline{A_2}$, E, T_1, T_2
O_h	T_{1u}	A_{1g}, E_g, T_{1g}, T_{2g}	A_{1u}^*, E_u, T_{1u}, $\underline{T_{2u}}$
$D_{\infty h}$	Σ_u^+, Π_u	Σ_g^+, Σ_g^-, Π_g, Δ_g	Σ_u^+, $\underline{\Sigma_u^-}$, Π_u, $\underline{\Delta_u}$, Φ_u

Table 1: Representations of the transition operators for single-photon, two-photon, and electro-optically allowed two-photon processes. The underlining in the fourth column denotes representations which are uniquely allowed through the electro-optical two-photon interaction, and the asterisk denotes a representation which is only allowed in double-beam EFITPA and electric field induced resonance-Raman scattering.

ELECTRIC-FIELD-INDUCED TWO-PHOTON ABSORPTION (EFITPA)

In EFITPA, electrical polarisation effects do not only give rise to intensity enhancement, but with careful choice of beam configuration they can allow observation of transitions forbidden in the absence of the field. Fig.1
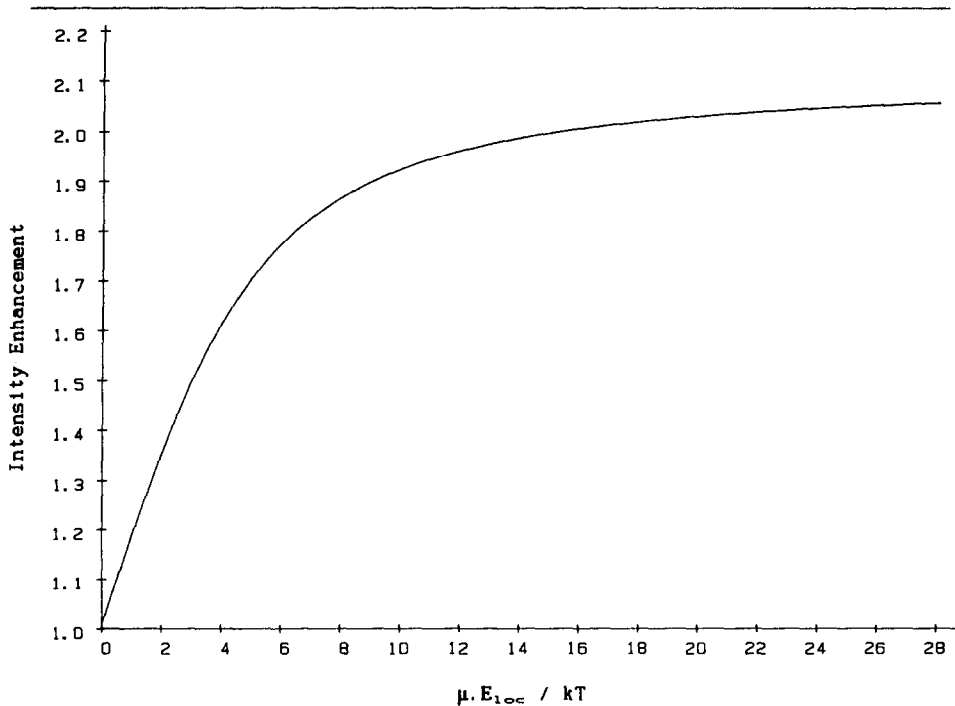
Fig. 1: Intensity enhancement for a component $D^{(0-)}$ transition as a function of $\mu.E_{loc}/kT$

shows the field-dependence of a component weight-0 transition. The increase in the intensity corresponds to the degree of molecular alignment within the fluid. Calculations show that molecules with large electric-susceptibilities experience local fields 10-100 times greater than the external field. Thus nitrobenzene would typically show an intensity enhancement of about 2 at applied field strengths of 10^8 Vm^{-1}. This property could be exploited in amplifying transition rates by choosing solvents with large electric-susceptibilities.

The electro-optical mechanism permits access to vibronically excited states inaccessible through normal two-photon absorption. As discussed in the previous section, these new states can be accessed because of the ungerade nature of the dipole moment operator and the incorporation of a weight-3 component. In fact, electro-optical EFITPA intensities should be of comparable size to those of three-photon absorption. As with the electrically polarised channel, local fields can be exploited, especially since the rate has an E^2-

dependence. A local field of ten times the external field would thus lead to a one hundred-fold intensity enhancement. Thus, it is feasible that EFITPA transitions could be comparable in strength to pure two-photon transitions under favourable conditions.

In studying the effects of an applied external electric field on the infrared multiphoton dissociation of CF_2HCl, Gozel and van den Bergh (ref.12) recorded an apparent linear relationship between the reaction yield and the square of the field. The quantum electrodynamical rate for an electro-optical electric-field-induced multiphoton absorption process is proportional to the square of the field (refs.13-14). The observations are therefore consistent with an electro-optical effect of the kind discussed above.

Several methods are available for the collection of EFITPA spectra. In some cases the process will lead to fluorescence from the excited state(s) so formed. The detection of the fluorescent photons can be conducted with a high degree of sensitivity as there is likely to be a large frequency shift between the incident and emitted photons. This method is of particular use when the molecules involved have a high quantum yield of fluorescence. Alternatively, it may prove useful to consider one of the many available resonance-enhanced multiphoton ionisation techniques (ref. 15).

ELECTRIC-FIELD-INDUCED RAMAN SPECTROSCOPY (EFIRS)

In the presence of a static electric field the intensities of allowed Raman transitions change. Calculations show, and experimental evidence confirms (refs.16-19), that electric fields of 10^7-10^9 Vm^{-1} can lead to intensity enhancement ratios of 2-3 (see Fig. 1). Furthermore, transitions forbidden in isotropic media may be observed when an electric field is applied. Because the standard depolarisation ratio analysis used in characterising vibrational transition symmetry is only valid for isotropic fluids (ref.20), the analysis of molecules close to electrode surfaces, for example, is less straightforward and requires five intensity measurements at specific scattering angles for a complete symmetry analysis (ref.13).

In addition, fields of such a high magnitude should give rise to observable electro-optical phenomena. It can be shown that the electro-optical route should give comparable intensities to hyper-Raman scattering, and in certain media with high dielectric constants, e.g. aqueous media, transition intensities may be over 100 times more intense. Square-wave modulation of the electric field coupled with phase-sensitive detection could help to distinguish the electric- field-induced processes from conventional Raman

scattering.

Analysis of the electro-optical Raman scattering tensor shows that the specific selection rule $\Delta v = \pm 1$ still dominates, and consequently the symmetry selection rules for this interaction are quite different to those obtained for normal Raman spectroscopy. In this case, Table 1 illustrates the symmetry of vibrations which are allowed in infra-red absorption (single-photon process), normal Raman scattering (two-photon process), and electro-optically allowed Raman scattering. To perform a complete symmetry analysis of the electro-optical Raman transitions it is necessary to take *five* intensity measurements. These intensities can be used to specify two intensity ratios whose determination is sufficient to characterise the symmetry class of each transition (ref. 21).

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