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Electronic and thermal contributions to the polarisation spectrum of DQCI

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Abstract. Polarisation spectroscopy (PS) experiments were performed on 1,3′-diethyl 1-2,2-quinolythiacarbocyanine iodide (DQCI) to study the contribution of the thermal grating effect to the PS signal. It is shown that this contribution can be significantly reduced.

1. Introduction

The polarisation spectroscopy (PS) technique is being widely used for determining ultra-fast relaxation times in the condensed phase (Song *et al* 1978, Lee *et al* 1980, Taira and Yajima 1981). This frequency domain technique provides a very good signal-to-noise ratio with a relatively simple experimental arrangement. Unfortunately, when PS is applied to certain materials (such as organic dye solutions), a 'thermal grating' effect frequently masks the coherent signal arising from the resonant interaction of the medium with the two light waves (pump and probe) of frequencies ω_1 and ω_2 at $\Delta\omega = \omega_1 - \omega_2 = 0$ (Andrews and Hochstrasser 1980). The lifetime of the induced thermal grating is of the order of hundreds of nanoseconds, in contrast with the electronic grating with lifetimes in the picosecond to subpicosecond range. The thermal grating effect appears as a narrow peak centred at $\Delta\omega = 0$ with a spectral linewidth usually limited by the resolution of the particular set-up. To do an accurate analysis of the PS lineshape, it may be important to reduce the thermal contribution as much as possible and to be able to correct the spectrum for the remaining thermal signal. The relationship between the electronic and thermal contributions and their dependence on experimental parameters must be known before a correction can be made.

One way of reducing the thermal contribution is to use a solvent with thermal properties that hinder the formation of a thermal grating (for example, water). However, the choice of a solvent is often limited by the solubility of the substance under study.

We show in this paper that it is possible to significantly minimise the thermal grating effect (while maintaining a good signal-to-noise ratio) by choosing a particular pump beam intensity for a given sample concentration. We also show that it is possible to determine the magnitude of the thermal contribution by comparing polarisation spectra taken separately for linear and circular polarisations of the pump beam, and that the electronic contribution is obtained by subtracting the two spectra. We apply this technique to the organic dye DQCI, and obtain a value for the effective population relaxation time T_1.

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2. Methods

The PS technique measures the polarisation change induced by a circularly or linearly polarised pump beam (ω_1) on a linearly polarised probe beam (ω_2). The experimental arrangement for the observation of the polarisation signal is shown in figure 1. Two dye lasers (Molectron DL200) are pumped by a nitrogen laser (Molectron UV1000) at a repetition rate of 30 pulses/s. The dye laser pulses are about 6 ns long, and have a spectral linewidth of $0.4\,\text{cm}^{-1}$. The pump beam power normally used is around 10 kW, and the probe beam is about ten times weaker. The two beams overlap inside a glass sample cell (0.25 mm internal width) focused by a system of mirrors and 22 cm focal length lenses. The time coincidence of the two light pulses in the sample area is adjusted by retarding the pump beam. The intensity of the pump beam is accurately set by a calibrated variable attenuator. The polarisation (circular or linear) of the pump beam at the sample cell is chosen with a Babinet compensator.

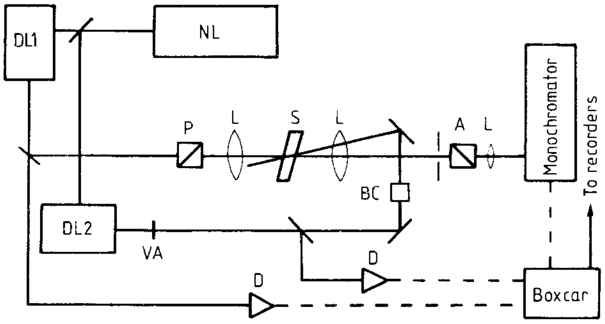

Figure 1. Schematic of the polarisation spectroscopy system, consisting of: a sample cell, S; a nitrogen laser, NL; two dye lasers, DL1, DL2; a polariser, P; an analyser, A; lenses, L; a Babinet compensator, BC; a variable attenuator, VA; detectors, D; and the detection electronics.

The samples were one millimolar solutions of 1,3′-diethyl 1-2,2-quinolythiacarbocyanine iodide (DQCI) in water and ethanol. The probe beam wavelength was fixed at the maximum of the absorption band (580 nm), and the PS spectra were obtained by scanning the pump beam around this value. The scans were between 0.3 and $1\,\text{nm min}^{-1}$, and the boxcar was set to average 30 pulses/s. The overall resolution of the experimental set-up was about $0.8\,\text{cm}^{-1}$.

During the experiments we found, as anticipated (Wieman and Hansch 1976, Stert and Fischer 1978), that the PS signal dependence on the pump beam intensity is between linear and quadratic depending on the angle between the polariser and the analyser (we notice that even with crossed polarisers, the intensity of the signal itself affects this dependence). The underlying concept is the coherent superposition of the probe leakage and the nonlinear response of the system, which results in a mixture of $|\chi^{(3)}|$ and $\mathrm{Im}\,\chi^{(3)}$, where $\chi^{(3)}$ is the third-order susceptibility. Depending on the absolute value of $\chi^{(3)}$ and on the probe leakage, we observe spectra with dependences which are between linear and quadratic (both included). The angle between the polarisers can be chosen to make the quadratic contribution negligible. Since 'real' polarisers have a finite extinction ratio ($1:10^6$ in our case), part of the probe beam leaks through the crossed polarisers giving rise to a situation analogous to uncrossing ‘perfect’ polarisers.

If the pump beam is polarised linearly at a 45° angle with the probe polarisation plane, and if the polarisers are crossed and have a finite extinction ratio, the pump intensity dependence of the PS signal can be calculated in a manner analogous to that explained by Stert and Fischer (1978). At the centre of the absorption line, and for a small saturation, we obtain

$$I_E = I_0(\varepsilon + 2\sqrt{\varepsilon} A_E I_p + A_E^2 I_p^2) \tag{1}$$

where I_0 and I_p are the probe and pump intensities and ε is the extinction ratio of the polarisers. A_E is given by

$$A_E = \frac{1}{8} \frac{\alpha_0(1-d)}{I_s} \tag{2}$$

where α_0 is the nonsaturated absorption coefficient, $d = \alpha_\parallel/\alpha_\perp$, $\alpha_\parallel$ and $\alpha_\perp$ are the absorption coefficients in the directions parallel and perpendicular to the pump polarisation plane and I_s is the saturation intensity. An analogous intensity dependence is obtained for the case where the polarisers are uncrossed by a small angle (Stert and Fischer 1978).

Similarly, the thermal grating signal mixes with the probe leakage signal. However, any mixing of the two signals cannot be measured by our system, whose bandwidth is much greater than the bandwidth of the thermal grating signal. For this reason, the intensity dependence of the thermal part must be at least quadratic. This dependence has been studied by Eichler *et al* (1972); the intensity of the thermal signal I_T, for low light beam powers (of the order of 10^4 W cm^{-2}), can be expressed as:

$$I_T = I_0 \frac{T(1-T)^2(\mathrm{d}n/\mathrm{d}\theta) 2\pi t_p^2}{\rho^2 c^2 \lambda^2} I_p^2 \tag{3}$$

where T is the transmission of the sample, $\mathrm{d}n/\mathrm{d}\theta$ is the thermal gradient of the refractive index, λ is the wavelength of the absorbing light, ρ is the density, c is the specific heat of the solvent and t_p is the length of the incident laser pulse (considered rectangular in shape) which is much shorter than the relaxation time of the thermal grating. Since our pump powers are of the order of 10^7 W cm^{-2}, much higher than those assumed for equation (3), we can expect a power dependence on I_p which is greater than quadratic (see Eichler *et al* 1971).

3. Discussion

Figure 2 shows a PS spectrum of DQCI in ethanol with a large thermal grating contribution. The figure shows two traces: the upper trace corresponds to a spectrum taken with a linearly polarised pump field at a 45° angle with the direction of the linear probe field polarisation, while the lower trace (in the same scale) was taken with a circularly polarised pump field. The circular polarisation spectrum shows a single peak with a width of 0.7 ± 0.2 cm^{-1} over a flat, negligible background. The size and width of this peak resemble those of the central peak (on top of a broader 3 cm^{-1} structure of electronic origin) in the upper trace. When the experimental conditions are varied increasing the pump beam intensity, the two peaks increase in the same proportion.

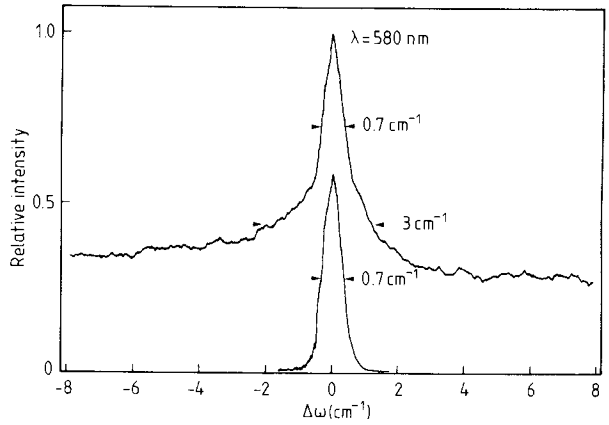

Figure 2. PS spectrum of DQCI (upper trace) with a large thermal contribution (lower trace).

This indicates that the central peak in the upper trace is mostly due to the thermal grating (Andrews and Hochstrasser 1980), which is not expected to vary with the polarisation of the pump field since its projection on the polarisation of the probe field is invariant. These observations are consistent with the following hypotheses.

(i) In the water solution of DQCI, $\chi^{(3)}_{1122} = \chi^{(3)}_{1212}$ for the electronic response (Song *et al* 1978), even when the spectra are taken in a high absorption region. The same occurs in the ethanol solution. A similar phenomenon applies to small molecules for $\Delta J = 0$ transitions (Q lines), where J is the rotational moment (Marcano and Platonenko 1979, Teets 1978). The dye molecules, being larger and structurally more complex, must have an even greater moment of inertia. It can be assumed that the electronic dye-molecule transitions are predominantly excited without a detectable change in their rotational moment.

(ii) The PS spectrum is separable into an electronic and a thermal part ($\chi^{(3)}_{\text{total}} = \chi^{(3)}_{\text{electronic}} + \chi^{(3)}_{\text{thermal}}$), and the temperature dependence of the electronic part is negligible considering the temperature variations caused by the thermal grating (Souma *et al* 1980). The fact that the resolution of our system is much less than the bandwidth of the thermal signal implies, in view of this second hypothesis, that the coherent superposition of the electronic and thermal signals is not detectable. In other words, what we detect is the sum of the intensities of the two signals. The topic of whether or not the electronic and thermal signals can be separated is mentioned by Andrews and Hochstrasser (1980).

When a circular pump polarisation spectrum is subtracted from its corresponding linear polarisation spectrum, the remaining trace shows a central peak in a ratio with respect to the background that varies between 1.5 : 1 and 2 : 1 for the different traces. The corresponding pump intensity variation of the circular polarisation peak with respect to its background is much greater than this.

The water-solution spectra do not show the thermal grating structure (the circularly polarised pump signal is negligible). This is due to the particular properties of water as a solvent. It is known that the thermal grating effect depends strongly on the thermal refractive index gradient, the specific heat and the thermal conductivity of the solvent (Eichler *et al* 1972, 1973). For this reason, the thermal effect is reduced by at least a factor of ten. However, DQCI does not dissolve well in water, and the concentration required for a good signal is difficult to obtain.

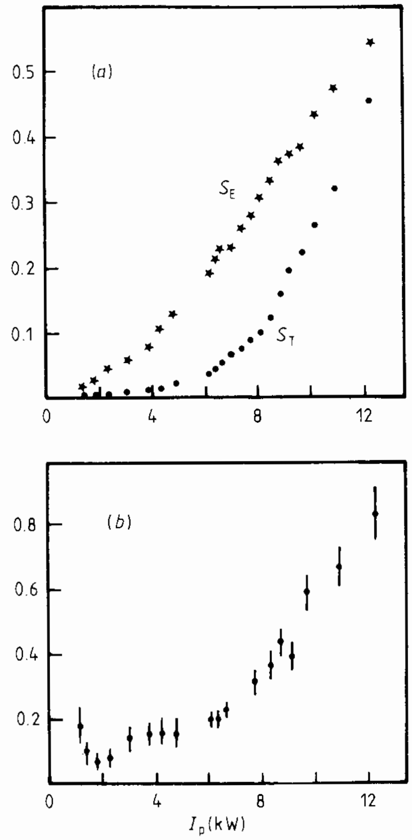

Figure 3. Intensity dependence of the PS signal in the centre of the spectrum for a 0.8 millimolar solution and an effective transmission of 0.4%. (*a*) Pump intensity dependence of the electronic (S_E) and thermal (S_T) contributions. (*b*) Pump intensity dependence of the ratio (S_T/S_E) of the electronic and thermal components.

We use the definitions of the thermal and electronic signals given above to study their pump intensity dependence. By varying the pump beam intensity with a calibrated variable attenuator we obtained the intensity dependence of the electronic (S_E) and thermal (S_T) contributions shown in figure 3(*a*), measured at the centre of the PS spectrum. As expected, the dependences are different. S_E represents a linear combination of linear and quadratic functions of the pump intensity, while S_T has a higher-order intensity dependence (cubic in our case). Figure 3(*b*) shows the intensity dependence of the ratio of the thermal and electronic components (S_T/S_E). For high pump intensities, the thermal grating dominates the electronic signal. For low pump intensities, the thermal grating contribution decreases more rapidly than the electronic one (the thermal contribution is less for lower values of S_T/S_E). There is a region around 5 kW in which S_T/S_E does not increase significantly, and the signal-to-noise ratio is still acceptable: this is the best pump beam intensity for taking the spectrum with minimum thermal grating contribution. The use of lower pump intensities not only results in a lower signal-to-noise ratio, but also has the disadvantage that the probe leakage becomes significant with respect to the PS signal.

Figure 4 shows a PS spectrum of DQCI in ethanol solution with a small thermal contribution, obtained with a pump beam intensity about 30% lower than in the spectrum shown in figure 2. The central peak in the upper trace of figure 4 is considerably broader than the central peak in figure 2 (the small difference in the widths of the peaks in the circular pump polarisation spectra of figures 2 and 4 is probably due to slightly different system resolutions, since the thermal structure is much smaller than our resolution). This confirms that they are due to the two different processes discussed here. After subtracting the small thermal peak shown in the lower trace from the PS spectrum, we are left with a 3 cm^{-1} wide peak corresponding to a population relaxation time $T_1 = 3.5$ ps.

By slightly changing the angle of the analyser (labelled A in figure 1), we obtained the PS trace in figure 5, which shows a two-peak spectrum with asymmetry in the broader structure. This electronic structure can be explained as the simple addition of a Lorentzian curve with a dispersive lineshape due to a small birefringence in the cell windows (Teets 1978).

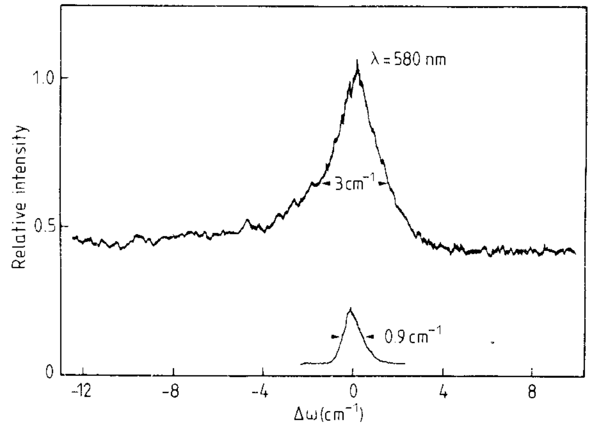

Figure 4. PS spectrum of DQCI showing a single electronic structure (upper trace) with a small thermal effect (lower trace).

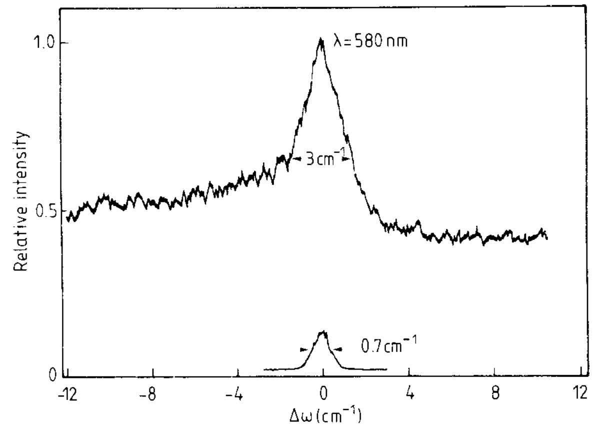

Figure 5. PS spectrum of DQCI showing Lorentzian and dispersive contributions.

It can be seen that the reduction of the thermal contribution makes possible the study of the electronic third-order polarisation in the $\Delta\omega \simeq 0$ region of the PS spectrum of a medium such as DQCI. A method for reducing the thermal grating contribution is proposed. We conclude that the electronic part can be obtained by subtracting the circularly polarised pump signal from the linearly polarised pump spectrum.

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