Fundamental and applied studies of hyper-Raman scattering

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Introduction

The hyper-Raman (HR) effect, controlled by the transition hyperpolarizability $[\beta_{\rho\sigma\pi}]_{fi}$, arises when intense laser radiation is incident upon a sample, giving rise to scattering at frequencies $2\nu_0 \pm \nu_{fi}$, where ν_{fi} are usually frequencies associated with vibrational transitions. By analogy with normal Raman scattering spectra may be excited under either resonant or non-resonant conditions and in the former case a significant enhancement of the signal may be observed. HR scattering exhibits different selection rules and relative band intensities from the traditional vibrational spectroscopic techniques of IR absorption and normal Raman scattering. The motivation for studying HR scattering is thus due to the novel spectroscopic information which may be obtained. Nevertheless, the HR effect is very weak; it can only be observed when the incident laser irradiance is very high, and is therefore experimentally difficult.

The properties of resonance HR scattering (RHR) were described by Long and Stanton[1] and the first measurement was reported for diphenylbutadiene by Horwitz *et al.*[2] Subsequently, a number of observations have been reported, mostly from extensively π-conjugated organic molecules, which all display large static hyperpolarizabilities. There are three possible resonance conditions: at ν_0, $2\nu_0$ or both ν_0 and $2\nu_0$. To date, only resonance at $2\nu_0$ has been observed.

We carried out HR and RHR experiments on a number of organic compounds and found that good quality RHR spectra could be obtained from π-conjugated species. However, the experimental arrangement in the Ultrafast Laboratory did not yield good signal-to-noise ratio for non-resonant excitation. We obtained results for fluorescein, all-*trans*-retinal, methyl orange and β-carotene, and the RHR spectra of fluorescein and all-*trans*-retinal (figure 1) were examined in detail, supported by DFT calculations, using the *Gaussian03* package[3].

Experimental section

RHR scattering of 10^{-3} mol dm^{-3} solutions of fluorescein in methanol and all-*trans*-retinal in cyclohexane were excited by a Ti-sapphire laser at 800 nm, and recorded on a Spex Triplemate spectrometer with CCD detection. Spectra were acquired over 5 s and averaged over 20 acquisitions. The sample solution was flowed through a jet in order to avoid heating of the sample and the laser power was maintained at a level just below that at which the onset of continuum generation and surface SHG occurred.

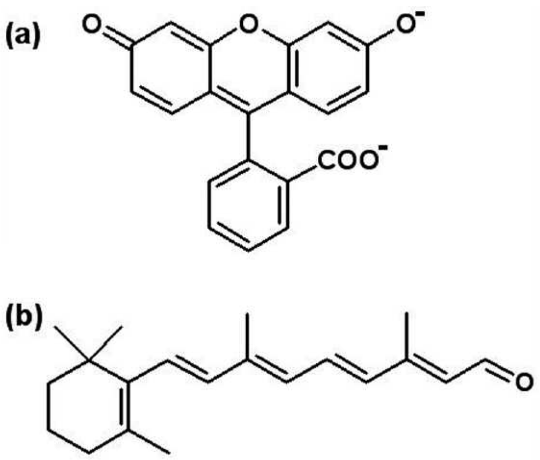

Figure 1. Structures of (a) fluorescein and (b) all-trans retinal.

RHR spectrum of fluorescein

One of the advantages of studying RHR, as opposed to RR scattering, is that for resonance with an electronic transition close to $2\nu_0$ the sample may be transparent to radiation at ν_0 such that laser heating of the sample is avoided, and if fluorescence occurs it will usually be a frequency well below $2\nu_0$. Thus RHR is particularly suitable for the investigations of strongly fluorescent species such as fluorescein. The fluorescein dianion exhibits a very intense π-π* absorption band at ca. 500 nm and excitation in this region yields very strong fluorescence. Previously fluorescein has been studied by Raman spectroscopy using longer wavelength excitation[4], and also by SERRS[5], which is another excellent method for overcoming problems due to fluorescence.

The RHR spectrum of fluorescein is shown in figure 2. All bands correspond to those which have previously been observed in the normal Raman spectrum, which suggests that the RHR spectrum is controlled by an A-term scattering mechanism, which would also be predominant in the Raman spectrum under preresonance conditions. Detailed band assignments were facilitated by SCF-DFT calculations at the B3-LYP/cc-pVDZ level. Modelling of the RHR relative band intensities was done using CIS/cc-pVDZ calculations of the geometry in the resonant excited state. The computed spectrum was in good agreement with the experimental data.

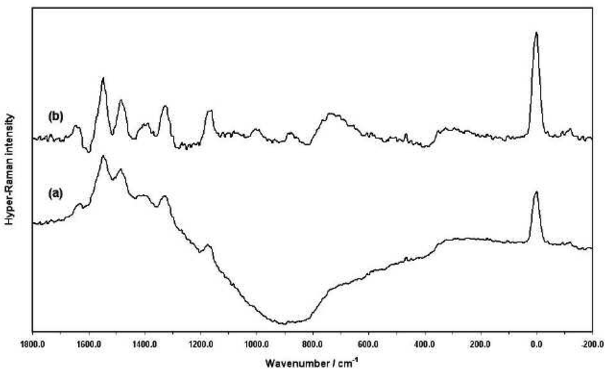

Figure 2. RHR spectrum of fluorescein excited at 800 nm, (a) raw data, and (b) after baseline subtraction.

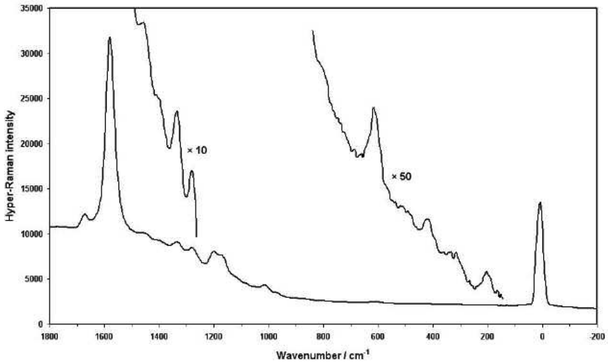

Figure 3. RHR spectrum of all-trans-retinal excited at 800 nm.

RHR spectrum of all-*trans*-retinal

The RHR spectrum of all-*trans*-retinal, shown in figure 3, corresponds with that previously reported by Mizono *et al*.[6] The spectrum is dominated by a very strong band at 1579 cm^{-1} attributed to the n(C=C) stretch of the conjugated C=C bonds. This is also the strongest band in the normal resonance Raman (RR) spectrum[7], indicating that an A-term mechanism is responsible for both RR and RHR scattering in all-*trans*-retinal.

Several other weaker bands are observed in the 600-1500 cm^{-1} region, attributed to in-plane modes of the polyene chain, and the v(C=O) mode appears as a weak band at 1670 cm^{-1}. The previously reported band assignments[7] have been re-examined using B3-LYP/cc-pVDZ calculations. Measurements of band depolarization ratios reveal that the RHR scattering results from an A-term scattering mechanism involving resonance with only a single resonant state. This is supported by modelling of the RHR relative band intensities using CIS/cc-pVDZ calculations but is in contradiction with the previous assertion that two excited states are involved[6].

References

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