Laser Chem., 1999, Vol. 19, pp. 79–82
Reprints available directly from the publisher
Photocopying permitted by license only

PICOSECOND RAMAN EXCITATION PROFILE AND TRANSIENT ABSORPTION SPECTRUM OF S_1 QUATERPHENYL IN SOLUTION

W. T. TONER[a,*], P. MATOUSEK[b], A. W. PARKER[b] and M. TOWRIE[b]

[a] *Clarendon Laboratory, Parks Road, Oxford, OX1 3PU UK;*
[b] *Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX UK*

(Received 28 April 1997)

Intensity changes in Stokes resonance Raman spectra of photoexcited quaterphenyl are found to result from 17 ps timescale changes in resonance frequency and width and also in Franck–Condon displacements. The 766 cm^{-1} anti-Stokes band shows a significant hot population which decays on a similar timescale. The results show that population relaxation, vibronic coupling and solvent reorganisation are all significant on this timescale.

Keywords: Raman spectrum; transient absorption; quaterphenyl

Resonance Raman and absorption spectra were measured with ~ 1 ps resolution using a 40 kHz laser-OPA system [1] in order to study the time-dependence of Stokes band intensities of photoexcited S_1 quaterphenyl in solution [2]. White light continuum was used for the absorption measurements and the spectrally filtered output of the OPA provided a transform-limited Raman probe. The pump wavelength was 277 nm.

All prominent bands in the transient absorbance shown in Figure 1 shift to the blue between 2 and 50 ps by $\sim 0.4\%$ of the resonance

*Corresponding author.

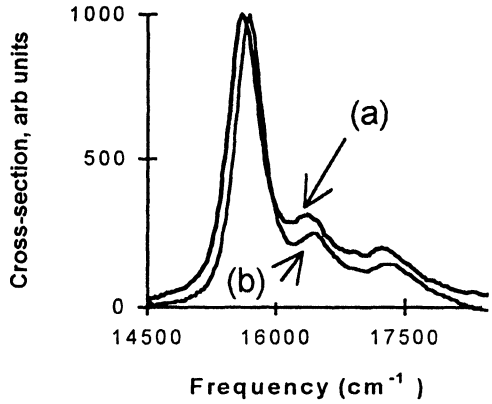

FIGURE 1 Transient absorbance of S_1 quaterphenyl in THF at (a) 2 ps and (b) 50 ps after photoexcitation.

energy and reduce in width. The evolution is smooth, with a 17 ps time constant. Cooling the bath at fixed pump probe time delay results in a small red-shift, and a 37 +/− 5°C temperature drop produces the same reduction in 0−0 bandwidth as does relaxation. The 766 cm^{-1} Raman band exhibits the same differences between relaxation and cooling.

Ratios of Raman excitation profiles (REPs) computed from the data in Figure 1 are compared with measured intensity ratios in Figure 2, and Figure 3 is a comparison of the 766 cm^{-1} intensity with the

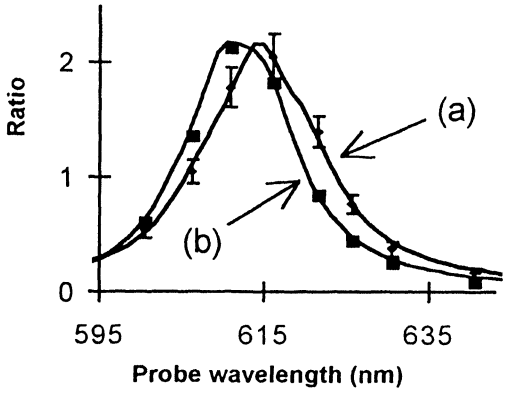

FIGURE 2 Raman intensity ratios compared with REP ratios computed from data in Figure 1 at (a) 2 ps and (b) 50 ps. Representative error shown.

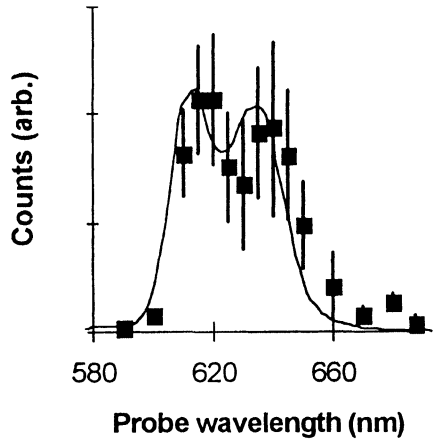

FIGURE 3 Excitation profile of 766 cm^{-1} Stokes Raman band.

computed REP. Bands at 1624 and 766 cm^{-1} are indentified as fundamentals and the 1532 cm^{-1} band as the first overtone of 766. Franck–Condon displacement ratios deduced from this data show significant changes with time and temperature. The observed changes in resonance parameters and in displacements fully account for the Stokes intensity changes.

The time-dependence of the 766 cm^{-1} anti-Stokes intensity is shown in Figure 4. The initial transient is attributed to ultrafast energy transfer from $v > 1$ levels to other modes. Since REPs and Stokes data indicate that resonance and displacement changes should have < 10% effect on the anti-Stokes intensity at the 676.6 nm probe wavelength used, the subsequent slow decrease is due to the decay of a residual hot population in $v = 1$. At 2 ps, the population excess in this mode corresponds to a temperature 175 +/− 100°C above the bath, which is much larger than the 37°C deduced from the bandwidth change. This mode has little anharmonicity and appears isolated; both factors may contribute to its slow decay. As few modes are likely to share these properties it is estimated that the total population energy is no more than a few times the $\sim 60\,cm^{-1}$ per molecule observed.

The similarity of the electronic and Raman band changes indicates vibronic coupling and the resonance energy change of $\sim 70\,cm^{-1}$ implies a change in $S_0 - S_1$ potential suggesting a solvent reorganisa-

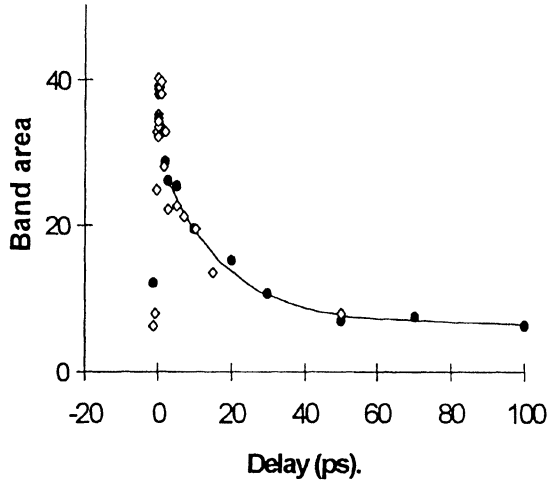

FIGURE 4 Time dependence of 766 cm^{-1} anti-Stokes intensity.

tion effect. It is an open question whether the population and potential changes are causally related.

References

[1] Matousek, P., Parker, A. W., Taday, P. F., Toner, W. T. and Towrie, M. (1996). *Opt. Comm.*, **127**, 307.
[2] Towrie, M., Matousek, P., Parker, A. W., Toner, W. T. and Hester, R. E. (1995). *Spectrochim. Acta*, **A51**, 2491 and references therein.