

## INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION (IVR) IN SELECTED $S_1$ LEVELS ABOVE 1000 $\text{cm}^{-1}$ IN PARA-FLUOROTOLUENE.

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With increasing vibrational wavenumber, the density of states of a molecule is expected to rise dramatically, especially so when low wavenumber torsions (internal rotations) are present, as in the case of *para*-fluorotoluene (*p*FT). This in turn is expected to lead to more opportunities for coupling between vibrational modes, which is the driving force for intramolecular vibrational energy redistribution (IVR). Previous studies<sup>a,b</sup> at higher energies have focussed on the two close lying vibrational levels at  $1200 \text{ cm}^{-1}$  in the  $S_1$  electronic state of *p*FT which were assigned to two zero-order bright states (ZOBSS), whose characters predominantly involve C-CH<sub>3</sub> and C-F stretching modes. A surprising result of these studies was that the photoelectron spectra showed evidence that IVR is more extensive following excitation of the C-F mode than it is following excitation of the C-CH<sub>3</sub> mode, despite these levels being separated by only  $35 \text{ cm}^{-1}$ . This observation provides evidence that the IVR dynamics are mode-specific, which in turn may be a consequence of the IVR route being dependent on couplings to nearby states that are only available to the C-F mode.

In this work, in order to further investigate this behaviour, we have employed resonance-enhanced multiphoton ionisation (REMPI) spectroscopy and zero-kinetic-energy (ZEKE) spectroscopy to probe  $S_1$  levels above  $1000 \text{ cm}^{-1}$  in *p*FT. Such ZEKE spectra have been recorded via a number of  $S_1$  intermediate levels allowing the character and coupling between vibrations to be unravelled; the consequence of this coupling will be discussed with a view to understanding any IVR dynamics seen.

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<sup>a</sup>C. J. Hammond, V. L. Ayles, D. E. Bergeron, K. L. Reid and T. G. Wright, *J. Chem. Phys.*, **125**, 124308 (2006)

<sup>b</sup>J. A. Davies, A. M. Green, A. M. Gardner, C. D. Withers, T. G. Wright and K. L. Reid, *Phys. Chem. Chem. Phys.*, **16**, 430 (2014)