INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION (IVR) IN SELECTED S\textsubscript{1} LEVELS ABOVE 1000 cm\textsuperscript{-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 (pFT). 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\textsuperscript{a, b} at higher energies have focussed on the two close lying vibrational levels at 1200 cm\textsuperscript{-1} in the S\textsubscript{1} electronic state of pFT which were assigned to two zero-order bright states (ZOBSs), whose characters predominantly involve C-CH\textsubscript{3} 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\textsubscript{3} mode, despite these levels being separated by only 35 cm\textsuperscript{-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\textsubscript{1} levels above 1000 cm\textsuperscript{-1} in pFT. Such ZEKE spectra have been recorded via a number of S\textsubscript{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.