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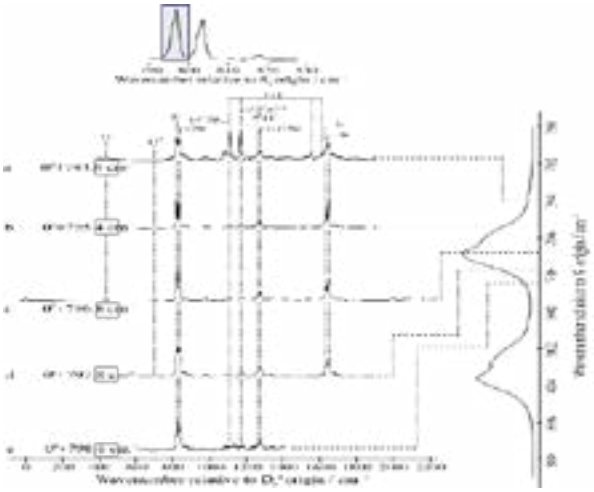
Unpicking vibrational and vibrational torsional couplings in substituted benzenes

Timothy G Wright, William D Tuttle, Adrian M Gardner and **Laura E Whalley**
University of Nottingham, UK

We initially present vibrationally-resolved electronic spectra obtained using resonance-enhanced multi-photon ionization (REMPI) spectroscopy. The spectra are obtained from jet-cooled seeded expansion using lasers. The spectra exhibit many bands, identifying the energetic positions of vibrational levels in the S_1 electronic state; a number of these are found to arise from overlapped and/or interacting vibrational levels. By fixing one laser at the energy of one of those levels, we then ionize the electronically-excited molecule and record zero-kinetic-energy (ZEKE) spectra, whose assignment allows the deduction of the make-up of the intermediate S_1 vibrational levels. In many cases, we can identify the so-called zero-order states (ZOSs) which have coupled to give the resultant eigenstate; this coupling occurs as a result of Fermi resonance. As well as pure vibrations, we find that these ZOSs may be torsional levels or vibration-torsion (vibtor) levels. The coupling of the ZOSs leads to levels whose motions are more delocalized across the molecule. This has implications for photo-stability and chemical control. Assignment of the spectra is aided by recording ZEKE spectra at different energies through a REMPI feature that corresponds to couple ZOSs. In this way, we can see activity move in and out of resonance through the feature. By plotting these spectra together, we obtain a two-dimensional ZEKE spectrum. Quantum chemical calculations are used to aid in the assignments. The treatment of the torsional levels requires the use of molecular symmetry groups: G_{12} for toluene and para-fluorotoluene; G_{72} for para-xylene.



Biography

Tim G Wright has been working in the field of Spectroscopy covering electronic and photoelectron spectroscopy since 1988. He has used both conventional and laser-based methods. His work has always been underpinned by appropriate quantum chemical calculations and these often provide the foothold that allows the assignment of the spectra.

Tim.Wright@nottingham.ac.uk

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