THE ENIGMATIC LOW FREQUENCY SPECTROSCOPY OF THE *PARA*- SUBSTITUTED TOLUENES

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The internal rotation of a methyl group attached to a quasi-rigid frame has been the subject of numerous spectroscopic and theoretical investigations. Yet despite the prolific attention focussed on these systems there have remained many unresolved matters concerning the spectroscopic manifestations of the internal rotor motion. A particularly frustrating observation has plagued our understanding of the S_1-S_0 spectroscopy of the *para*- substituted toluenes which are of G_{12} molecular symmetry species. The G_{12} family, which includes the parent toluene molecule, are found to display S_1-S_0 excitation spectra that are dominated by m' - m$''$ torsional transitions that abide by a $|m' \pm m''| = 0, \pm 3$ type selection rule, rather than the expected $|m' \pm m''| = 0, \pm 6$ selection rule which emerges rigorously for molecules of G_{12} symmetry.

We have undertaken a comprehensive investigation of the S_1-S_0 spectroscopy of the mono-substituted toluenes, with particular focus on toluene and its *para*- substituted derivatives. Jet cooled electronic excitation spectra are measured using 1C-R2PI - mass resolved spectroscopy to facilitate observation of the low frequency torsional structure and to ensure that complications due to cluster species are avoided.

The anomalous $|m' \pm m''| = 0, \pm 3$ selection rules observed for toluene and its *para*- substituted derivatives are found to be accounted for qualitatively by a model, introduced by Walker *et al* (Wisconsin) that permits a modulation of the transition dipole by the torsional motion. A prediction of the model is that the formally forbidden (but in fact dominant) torsional structure should display A-type rotational band contours. Our experimental measurements reveal, however, that in the region near the S_1-S_0 electronic origin, the torsional transitions observed for all the G_{12} toluenes display a diverse range of rotational contours, few of which even remotely resemble an A-type contour.

A partial answer to this conundrum emerges as a result of including internal-overall rotational coupling in the computation of the contours associated with torsional transitions. A further key lies in our ability to distinguish between Cl^{35} and Cl^{37} isotopomers in the spectra of the chlorotoluenes. Isotope effects allow us to identify that many of the transitions traditionally ascribed to purely torsional transitions, do in fact contain substantial degrees of vibronic excitation as well. The importance of internal-overall rotational coupling in the G_{12} substituted toluenes, and indeed the coupling to vibration is revealed as a result of our investigations.