

VIBRATION AND VIBRATION-TORSION LEVELS OF THE $\rm S_1$ AND GROUND CATIONIC $\rm D_0^+$ STATES OF PARAFLUOROTOLUENE AND PARA-XYLENE BELOW $\rm 1000~cm^{-1}$

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We have employed resonance-enhanced multiphoton ionisation (REMPI) spectroscopy and zero-kinetic-energy (ZEKE) spectroscopy to investigate the first excited electronic singlet (S_1) state and the cationic ground state (D_0^+) of para-fluorotoluene (pFT) and para-xylene (pXyl). Spectra have been recorded via a large number of selected intermediate levels, to support assignment of the vibration and vibration-torsion levels in these molecules and to investigate possible couplings.

The study of levels in this region builds upon previous work on the lower energy regions of pFT and $pXyl^{a,b,c}$ and here we are interested in how vibration-torsion (vibtor) levels might combine and interact with vibrational ones, and so we consider the possible couplings which occur. Comparisons between the spectra of the two molecules show a close correspondence, and the influence of the second methyl rotor in para-xylene on the onset of intramolecular vibrational redistribution (IVR) in the S_1 state is a point of interest. This has bearing on future work which will need to consider the role of both more flexible side chains of substituted benzene molecules, and multiple side chains.

^aA. M. Gardner, W. D. Tuttle, L. Whalley, A. Claydon, J. H. Carter and T. G. Wright, J. Chem. Phys., 145, 124307 (2016).

^bA. M. Gardner, W. D. Tuttle, P. Groner and T. G. Wright, J. Chem. Phys., (2017, in press).

^cW. D. Tuttle, A. M. Gardner, K. O'Regan, W. Malewicz and T. G. Wright, *J. Chem. Phys.*, (2017, in press).