THE WEAK HYDROGEN BOND IN THE FLUOROBENZENE-AMMONIA VAN DER WAALS COMPLEX: INSIGHTS INTO THE EFFECTS OF ELECTRON WITHDRAWING SUBSTITUENTS ON PI VS IN-PLANE BONDING

MARTIN C. R. COCKETT, NICOLA M. TONGE, EWAN C. MACMAHON and IGOR PUGLIESI, *Department of Chemistry, University of York, Heslington, York YO10 5DD, UK..*

The fluorobenzene-ammonia van der Waals complex has been studied using a combination of two-colour resonance enhanced multiphoton ionisation spectroscopy (REMPI), high-level ab initio calculations of both ground and first excited electronic states and multidimensional Franck-Condon calculations. The experimental REMPI spectrum is characterised by a dominant, blue-shifted band origin, with weak activity in intermolecular vibrational modes. Second order approximate coupled cluster with singles and doubles (RICC2) geometry optimisations and numerical vibrational frequency calculations have been performed on a number of different structural isomers of the complex. Ground state counterpoise-corrected zero point binding energies show the in-plane complex, forming a pseudo-six membered ring connecting the fluorine atom and ortho hydrogen, to be consistently the most stable of all six conformations considered, at all levels of theory. Comparison of computed zero-point excitation energies for the most stable π and in-plane conformers with fluorobenzene show that the in-plane complex is the only conformer predicted to exhibit a spectral blue-shift upon electronic excitation. The pattern of computed shifts in fluorobenzene S_1 state intramolecular modes were also found to be unique for each conformer, thereby providing an additional aid to assignment of the experimental spectrum. The computed ground and first excited state geometries and frequencies were used to perform multidimensional Franck-Condon simulations of the S_1-S_0 vibronic spectrum for each of the most stable conformers. The simulations yielded a null spectrum for the π complex but showed remarkable agreement with experiment for the in-plane complex, allowing an almost complete vibrational assignment. Molecular electrostatic potential calculations show that, in comparison to benzene, the effect of the fluorine substituent in fluorobenzene is to withdraw electron density from the aromatic π-system, thereby destabilising the π-bound conformer with respect to the in-plane conformer.[a]

---

[a] Nicola M. Tonge, Ewan C. MacMahon, Igor Pugliesi and Martin C. R. Cockett *J. Chem. Phys.* accepted for publication, 2007.