PERTURBATION TREATMENT OF STARK EFFECT ON TORSIONAL ENERGY LEVELS

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When a uniform electric field is applied to nonrigid molecules with an internal rotor, the Stark pattern of the energy levels obtained is dependent upon the torsional motion. These effects are small but observable and require that appropriate corrections be made to theoretical expressions in order to obtain an accurate and meaningful dipole moment from Stark effect measurements. Emilsson et al. have reported the Stark spectral analysis of benzene-water dimer. [a] The dipole moment values reported by them for the dimer are 1.65 D and 2.0 D in the torsional states m = 0 and m = 1, respectively. The expressions they have used in deriving the dipole moments are based on standard semirigid rotor model. The expressions do not contain the torsional contribution which appears to be important in the spectral analysis of these complexes. We have derived the corresponding first and second order energy corrections with torsional degree of freedom in the presence of Stark field by using simple Rayleigh-Schrodinger perturbation theory to a general vibrational-rotational-torsional Hamiltonian. We have also used them to simulate the spectra as well as fit experimental spectra to re-derive the constants.

[a] T. Emilsson, H. S. .Gutowsky, G. de Oliveira, C. E. .Dykstra, J. Chem. Phys. 112, 1287 (2000)