EFFECTIVE VIBRATIONAL-ROTATIONAL-TORSIONAL HAMILTONIAN IN THE PRESENCE OF A STARK FIELD

B. RAM PRASAD, MANGALA SUNDER KRISHNAN, *DEPARTMENT OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY MADRAS, CHENNAI, 600 036 INDIA*.

The standard theory for analyzing high resolution Vibrational-Rotational-Torsional (VRT) spectra of semi-rigid and nonrigid molecules is based on perturbation theory, which leads to the concept of effective Hamiltonians in molecular spectroscopy. Though there are several ways of obtaining effective Hamiltonians, the method proposed by van Vleck, also known as the contact transformation method has proven to be quite useful in the area of molecular spectroscopy. Several excellent reviews exist [a] which describe the method of obtaining effective Hamiltonians from the Watson Hamiltonian. In the present work we extend the above formalism to derive effective Hamiltonians in the presence of static electric fields. In our calculations we have considered the effective Hamiltonian for VRT systems recently given by Yun Bo Duan et al.[b] as the unperturbed field-free Hamiltonian and the interaction of effective dipole moment operator with static electric field as a perturbation and arrived at an effective Stark Hamiltonian. This is block diagonal for each polyad of interacting vibrational states, and gives rise to analytic expressions for molecular parameters, which might be used to fit transition intensities.

[a] M. R. Aliev and J. K. G. Watson, Molecular Spectroscopy, Modern Research Vol. III, Academic Press, (1985) Ed. K. Narahari Rao, and P. Jensen; P. R. Bunker, Computational Molecular Spectroscopy, John Wiley, (2000)

[b] Yun-Bo Duan, Hui-Min Zhang, and Kojiro Takagi, J. Chem. Phys. 104, 3914 (1996)