RESONANCE RAMAN INTENSITIES BY MEANS OF THE TRANSFORM THEORY

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The transform theory of Hizhnyakov and Tehver [1] provides an efficient approach to calculate resonance Raman (RR) intensities for large molecules possessing many vibrational degrees of freedom. The approach avoids the summation over the manifold of vibrational states by using experimental information from the electronic absorption spectrum. It only requires the quantum mechanical calculation of the geometries of the ground state and of the electronically excited state that is in resonance with the exciting laser line. Using the approximations introduced by Peticolas and Rush [2], we have calculated the RR spectra of hexamethyl pyrromethene, a model compound representing a building block of many biologically important linear and cyclic tetrapyrroles. The force field of the ground state was derived by density functional theory using the B3LYP functional and the 6-31G* basis set and scaled according to Pulay et al. [3]. The geometry changes upon electronic excitation were obtained within the Hartree-Fock approximation by means of the single-excitation configuration interaction approach. The calculated RR spectra and their wavelength dependence show a good agreement with the experimental results.

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