VIBRATIONAL SPECTRA AND *AB-INITIO* CALCULATIONS FOR THE STUDY OF INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION IN THE CH-CHROMOPHORE IN CHD_2I

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Intramolecular vibrational energy redistribution (IVR) on the femto- to picosecond time scale is a central primary process in unimolecular chemical reaction dynamics. There are two main approaches towards its understanding. One is the analysis of the highly resolved vibrational spectra of polyatomic molecules[a,b] combined with *ab initio* calculations. Another approach consists in time resolved femtosecond (fs) pump-probe experiments, which we have recently carried out for a series of alkyliodides[c] including CHD_2I. For the latter molecule we present here results for IVR processes within the CH-chromophore. The infrared absorption spectrum of CHD_2I from 500 to 12000 cm^{-1} has been recorded with a Bomem Fourier transform infrared spectrometer equipped with a White type multi reflection cell and resolutions of 0.10 and 0.15 cm^{-1}. The CH-chromophore bands dominate the vibrational overtone spectrum of CHD_2I and we have assigned 24 of them. Vibrational variational calculations were carried out for the overtone spectrum of the CH-chromophore based on a 3-dimensional *ab initio* potential energy and electric dipole moment surface in normal coordinates. The anharmonic resonance structure between the CH-stretching and bending modes was investigated via an effective Hamiltonian for both experimental and theoretical spectra. Finally, we have calculated the time dependent dynamics on the fs time scale[d].

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