UNDERSTANDING INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION BY THE ROVIBRATIONAL ANALYSIS OF HIGH RESOLUTION INFRARED SPECTRA: THE CASE OF CHD_2I

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In our group we pursue two experimental approaches to investigate Intramolecular Vibrational Redistribution (IVR)[a]: this process can be studied by time-resolved femtosecond pump-probe experiments, or the corresponding time-dependent quantum dynamics can be obtained from stationary spectra in the IR at high frequency resolution by a time-dependent analysis using the underlying Hamiltonian and time evolution operator[a]. Recent work in our group[b] has shown that CH_3I and its deuterated isotopomers have different IVR-times, revealing different intramolecular coupling schemes for the initially excited vibrational levels. The present work is part of a larger effort to understand IVR in these molecules on the basis of high resolution spectra in the 500-12000 cm^{-1} region. In previous work we have analyzed the strong Fermi-resonance coupling between the CH-stretching and bending modes in CHD_2I at modest resolution, demonstrating very fast redistribution times on the order of 100 fs[c]. We refer to this recent paper for the past literature on the topic. Here we present detailed rovibrational analysis of ν_1 and several other fundamentals of CHD_2I recorded with our high resolution FTIR spectrometer Bruker ZP2001[d] with resolutions up to 0.0008 cm^{-1}. We discuss our new results in relation to our recent work on the overtone spectra and dynamics and to the femtosecond pump-probe results.

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