

OVERTONE SPECTROSCOPY AND DYNAMICS OF HCFC COMPOUNDS

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Photoacoustic spectra of the second, third and fourth overtones of methyl C-H stretches of $\text{CH}_3\text{CF}_2\text{Cl}$ and CH_3CFCl_2 and of the $N = 3$, $N = 7/2$ and $N = 4$ C-H stretch-bend polyads of CHFCl_2 were measured at room temperature. For the last two compounds also the action spectra were obtained via photodissociation of the jet-cooled vibrationally excited molecules combined with mass spectroscopic detection of the photofragments. In the action spectra fragments of H, $\text{Cl}(^2\text{P}_{3/2})$ [Cl] and $\text{Cl}(^2\text{P}_{1/2})$ [Cl^*] were detected, due to enhanced C-Cl and C-H bond breaking indicating energy flow out of the initially prepared states. A simplified local mode model for C-H stretching, including the stretch-deformation Fermi resonances, was used to interpret the multi-peak structure of the spectra of $\text{CH}_3\text{CF}_2\text{Cl}$ and CH_3CFCl_2 . The action spectra are significantly narrower than the room temperature photoacoustic spectra due to reduction of the rotational inhomogeneous structure. In CHFCl_2 the action spectra enabled to resolve the components arising from the different isotopomers of the precursor and the resonance splitting attributed to a local resonance of the $7/2_1$ polyad component with a combination of the $7/2_3$ component and the CClCl bending. This splitting reflects an oscillation period of ~ 3 ps for the vibrational redistribution and indicates that the coupling of the stretch-bend mixed state to the rest of the molecule is weaker than the stretch-bend coupling itself. The yield of Cl^* photofragments was found to be about half that of Cl for ~ 235 nm photolysis of vibrationally excited CH_3CFCl_2 and CHFCl_2 . The initial vibrational state preparation increases the Cl^*/Cl branching ratio, as compared to the nearly isoenergetic one-photon 193 nm photolysis of vibrationless ground state CH_3CFCl_2 , implying that it alters the photodissociation dynamics. Possible reasons for this enhancement are discussed.