

THE ILLUSIVE ν_1 FUNDAMENTAL AT 1070 cm^{-1} IN THE IR SPECTRUM OF $^{12}\text{CF}_3\text{I}$ AND $^{13}\text{CF}_3\text{I}$

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Trifluoromethyl halides have been successfully subjected to IR multiphoton dissociation experiments. These are closely related to rovibrational energy levels, and some of the most relevant levels have now been studied. High resolution FTIR spectra of $\text{CF}_3^{79}\text{Br}$, $^{12}\text{CF}_3\text{I}$ and $^{13}\text{CF}_3\text{I}$ have been recorded and analyzed in the region of the ν_1 CF_3 symmetric stretching fundamental which is accessible to CO_2 -laser pumping. Spectra with a resolution of 0.01 cm^{-1} have been obtained at different temperatures. J clusters were resolved and analysed by polynomial and simulation methods. In $^{13}\text{CF}_3\text{I}$ a Fermi resonance between ν_1 ($\nu_{\text{eff}} = 1047.60\text{ cm}^{-1}$) and $4\nu_6^0$ ($\nu_{\text{eff}} = 1049.51\text{ cm}^{-1}$) has been established, $W = 0.94\text{ cm}^{-1}$. For $\text{CF}_3^{35}\text{Cl}$, $^{12}\text{CF}_3^{79}\text{Br}$ and $^{12}\text{CF}_3\text{I}$ the Fermi resonance between ν_1 and $2\nu_5^0$ has been analyzed semi-quantitatively. Further rotational resonances occur in $^{12}\text{CF}_3\text{I}$, which could not be assigned unambiguously, but are likely to be due in part to $\nu_3 + 3\nu_6$. The spectra of the ν_5 fundamental near 550 cm^{-1} have been obtained for CF_3Br and CF_3I at a resolution of 0.05 cm^{-1} . Whereas ν_5 appears to be unperturbed for $\text{CF}_3^{79}\text{Br}$, for CF_3I a Fermi resonance between ν_5 and $\nu_3 + \nu_6$ and a rotational resonance of ν_5 with $2\nu_6$ have been assigned. A set of recommended vibrational frequencies for $^{12}\text{CF}_3\text{I}$ and $^{13}\text{CF}_3\text{I}$ is given, and several effective rotational constants and anharmonic constants including Fermi resonance are quoted. The implications of the results for the IR-multiphoton excitation of these molecules are discussed.