

## ANOMALOUS CH STRETCH INTENSITY EFFECTS IN HALOMETHYL RADICALS: THE ROLE OF “CHARGE-SLOSHING” VS. BOND-DIPOLE CONTRIBUTIONS TO IR TRANSITION MOMENTS

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Fundamental IR transition strengths arise from vibrationally induced non-zero dipole moment derivatives along a specific normal mode coordinate. A conventional picture of what leads to strong vs. weak intensities in these fundamental vibrations is the bond dipole model, in essence arising from vibrational displacements of partially charged atoms. Additional transition moment intensity can arise from vibrationally induced changes in bond polarization (which we figuratively call “charge-sloshing”) that can either interfere constructively or destructively with the bond dipole contributions. This “charge-sloshing” effect proves to be remarkably strong in the series of halomethyl radicals  $\text{CH}_2\text{F}$  and  $\text{CH}_2\text{Cl}$ , high resolution IR spectra of which have been acquired in the  $\text{CH}_2$  symmetric and asymmetric stretch regions. Theoretical analysis of the data indicates competition between bond-dipole and “charge-sloshing” contributions, which results in i) greatly enhanced symmetric vs. asymmetric stretch intensities, ii) a near vanishing of the  $\text{CH}_2$  asymmetric stretch transition moment in  $\text{CH}_2\text{Cl}$ , and iii) even a sign reversal of the symmetric and asymmetric stretch transition moments from simple bond dipole expectations.