

## HIGH AMPLITUDE VIBRATIONS IN THE DIHALOMETHANES

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The high amplitude vibrations of difluoro-, dichloro-, dibromo-, and diiodomethane are studied through an examination of the overtone spectra in the liquid phase from 6000 to 12000  $\text{\AA}$ . The principal absorption bands in the three latter molecules are assigned to  $\Delta v_{\text{CH}} = 3, 4, 5$  and 6 in a pure local mode CH-stretching oscillator. Combination bands are identified either between two CH-stretching local modes or between a CH local mode and a lower frequency normal mode. The transition energies for the pure local mode overtones are explained by the simple equation

$$\Delta E = v_1 \omega_1 + v_1^2 X_{11} \quad (1)$$

where  $v_1$  and  $\omega_1$  correspond to the vibrational quantum number and the local mode frequency associated with the CH-stretching oscillator.  $X_{11}$  is the diagonal local mode anharmonicity constant. From the spectra, and Eq. (1), these two parameters are obtained for all four molecules and are given in Table 1.

Table 1

Local mode frequencies and diagonal anharmonicity constants ( $\text{cm}^{-1}$ ).

	$\text{CH}_2\text{F}_2$	$\text{CH}_2\text{Cl}_2$	$\text{CH}_2\text{Br}_2$	$\text{CH}_2\text{I}_2$
$\omega_1$	3042	3069	3080	3059
$X_{11}$	-60.1	-61.1	-61.5	-61.0

The changes in  $\omega_1$  between molecules are discussed in terms of electro-negativity, hydrogen bonding, and steric considerations. Quantitative measures of the coupling between the two local CH oscillators and between the local mode and lower frequency normal modes are obtained in terms of

off-diagonal anharmonicity constants. These values are small in comparison to  $X_{11}$ . The effects of changing mass on the spectra are dramatic. The local mode character of the overtone spectrum increases from the chloro-, to the bromo-, to the iodo- compound. Indeed, the difluoromethane spectrum shows the structure expected on the basis of symmetry allowed normal mode components for  $\Delta v_{\text{CH}} = 3$ . The mass dependence of the spectra is interpreted in terms of coupling between the local CH oscillators through the nuclear kinetic energy. The photochemical consequences of such a non-normal mode vibrational pattern in the dihalomethanes is alluded to.