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# Intensity distribution in the overtone spectra of methyl halides: A local mode analysis of the spectra of methyl halides and methyl cyanide

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The CH-stretching overtone spectra of CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CH<sub>3</sub>I, and CH<sub>3</sub>CN are measured at room temperature in the liquid phase in the regions of  $\Delta\nu_{\text{CH}} = 2-6$ . We successfully analyze these spectra with a harmonically coupled local mode model. The local mode parameters  $\omega$ ,  $\omega x$ , and  $\gamma'\omega$ , the coupling parameter between the methyl CH bonds, are determined. Oscillator strengths are obtained from the spectra of the three methyl halides. We demonstrate that these oscillator strengths fit the simple intensity distribution law derived by Medvedev. A parameter determined from this fit is used to discuss the sensitivity of the CH bond potential to the successive replacement of one, two, or three hydrogen atoms of methane by halogens.

## I. INTRODUCTION

The usefulness of the local mode model is well established for the interpretation and understanding of XH-stretching overtone spectra ( $X = \text{C, O, N, or S}$ ).<sup>1-5</sup> In this model, zeroth order vibrational states are constructed on the basis of the assumption that the XH oscillators behave anharmonically, but essentially independently.<sup>6-8</sup> High energy overtone spectra ( $\Delta\nu_{\text{XH}} \geq 3$ ) are dominated by transitions to states whose components have all of the vibrational energy localized in one of a set of equivalent XH oscillators.

Vibrational analysis within the local mode description has been greatly facilitated by the use of a harmonically coupled local mode model.<sup>8-15</sup> In this model off-diagonal matrix elements between local mode product states are calculated on the basis of the harmonic oscillator approximations. In particular, this model has been applied to the dihalomethanes CH<sub>2</sub>X<sub>2</sub><sup>8</sup> and CD<sub>2</sub>X<sub>2</sub>,<sup>10</sup> and to a number of molecules with local C<sub>3v</sub> symmetry: (CH<sub>3</sub>)<sub>4</sub>C,<sup>9</sup> and CH<sub>3</sub>D, CHD<sub>3</sub>, SiH<sub>3</sub>D, and SiHD<sub>3</sub>.<sup>15</sup> Here we utilize this model in the analysis of the liquid phase overtone spectra of the methyl halides CH<sub>3</sub>Cl, CH<sub>3</sub>Br, and CH<sub>3</sub>I, and of CH<sub>3</sub>CN.

The local mode approach has also been used to understand sources of overtone intensity. We have demonstrated that an approach which uses SCF theory for the calculation of the dipole moment function in terms of local coordinates and a harmonically coupled local mode model for the calculation of the vibrational wave functions can account for the oscillator strengths in the CH-stretching overtone spectrum of CH<sub>2</sub>Cl<sub>2</sub>.<sup>16,17</sup> More recently we have shown that in some circumstances vibronic coupling of the excited vibrational state to a low lying electronic state can contribute to CH-stretching overtone intensity.<sup>18</sup> Recently, Medvedev has developed a totally different theoretical approach to XH-stretching overtone intensities.<sup>19-21</sup> This approach treats highly excited vibrational states quasiclassically, and leads to a surprisingly simple expression for the dependence of overtone intensity on upper state vibrational energy, i.e.,

$$\log f_{\text{ov}} = -a(E_{\text{v}}/\hbar\omega)^{1/2} + B, \quad (1)$$

where  $f_{\text{ov}}$  is the oscillator strength of the  $v \leftarrow 0$  transition and  $\omega$  is the harmonic frequency.  $E_{\text{v}}$  is obtained from the diatomic-like equation

$$E_{\text{v}} = \hbar[\omega(v + \frac{1}{2}) - \omega x(v + \frac{1}{2})^2], \quad (2)$$

where  $\omega x$  is the anharmonicity. The slope "a" of Eq. (1) is given by

$$a = (10.51/\beta)(\bar{M}\bar{\omega})^{1/2}, \quad (3)$$

where  $\bar{M}$  and  $\bar{\omega}$  are the reduced mass of the XH fragment and the harmonic frequency in units of  $10^3 \text{ cm}^{-1}$ , respectively. The molecular parameter  $\beta$  in units  $\text{\AA}^{-1}$  describes the repulsive part of the potential  $V(r)$  at large negative displacements from the equilibrium position, where  $V(r)$  exceeds the dissociation energy  $D$  of the diatomic entity [ $V(r) = Ce^{-2\beta r}$  at  $r < r_e$  and  $V(r) > D$ ]. Medvedev's analysis leads to the conclusion that overtone intensities are relatively insensitive to the form of the dipole moment function  $\mu(r)$ . Rather, these intensities are primarily governed by the repulsive portion of the vibrational potential which can be successfully approximated as  $V(r) = Ce^{-2\beta r}$ . An application of Eqs. (1)–(3) to overtone intensity data yields values for the parameter  $\beta$  which can be used to discuss the form of the bond potential for various series of molecules.

Equation (1) appears to account reasonably well for what little experimental data are available.<sup>19-21</sup> Such a novel approach, as opposed to more conventional analyses,<sup>16,17,22-24</sup> is certainly worthy of further study. In this work, we measure the intensities in the liquid phase overtone spectra of the methyl halides CH<sub>3</sub>Cl, CH<sub>3</sub>Br, and CH<sub>3</sub>I and attempt to analyze our data with Medvedev's approach. We arrive at a value for the molecular parameter  $\beta$  and relate this value for the methyl halides to values reported by Medvedev for the di- and trihalomethanes.<sup>20,21</sup>

## II. EXPERIMENTAL

Research grade methyl chloride and methyl bromide were obtained from Pfaltz and Bauer, Inc. Methyl iodide (99.9%) was obtained from Fisher Scientific Co. and meth-

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yl cyanide (99% + ) was obtained from Aldrich Chemical Co. All compounds were used without further purification.

The liquid phase overtone spectra were recorded on a Beckman 5270 spectrophotometer at room temperature with the near-IR light source in the regions of  $\Delta\nu_{\text{CH}} = 2, 3$ , and 4 and the visible light source in the regions of  $\Delta\nu_{\text{CH}} = 5$  and 6. For the liquids  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{CN}$ , the overtone spectra in the regions corresponding to  $\Delta\nu_{\text{CH}} = 2$  and 3 were measured with cells of path lengths 0.1 and 1 cm, respectively. For these two molecules, the overtone spectra in the regions corresponding to  $\Delta\nu_{\text{CH}} = 4-6$  were measured with 5 cm path length cells.

Both  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  are gaseous at room temperature. The liquid phase overtone spectra of these molecules were measured in a Beckman high pressure cell (F-076). The cell was evacuated, and then the gas was condensed into the cell by cooling it with liquid nitrogen. The cell had an effective path length of 5 cm. The relatively weak spectra of the higher overtones ( $\Delta\nu_{\text{CH}} = 4-6$ ) were measured with a fully filled cell. The spectra in the regions of  $\Delta\nu_{\text{CH}} = 2$  and 3 were measured with a reduced path length of 0.1 and 1 cm, respectively. Reduction in cell path length was achieved by

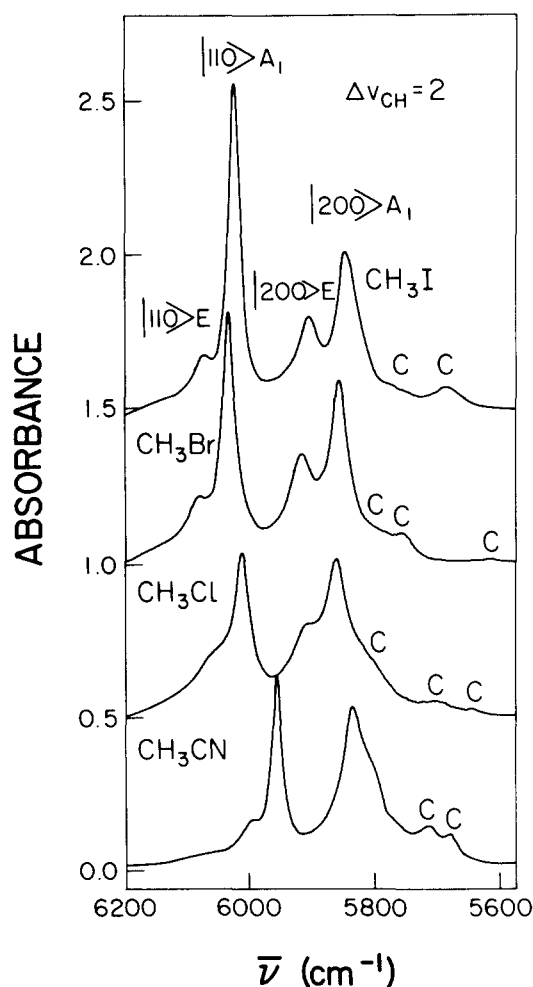


FIG. 1. Liquid phase overtone spectra of  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  in the region of  $\Delta\nu_{\text{CH}} = 2$ . Spectra were measured at room temperature with a path length of 0.1 cm. Absorbances of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  have been offset by 0.5, 1.0, and 1.5 absorbance units, respectively.

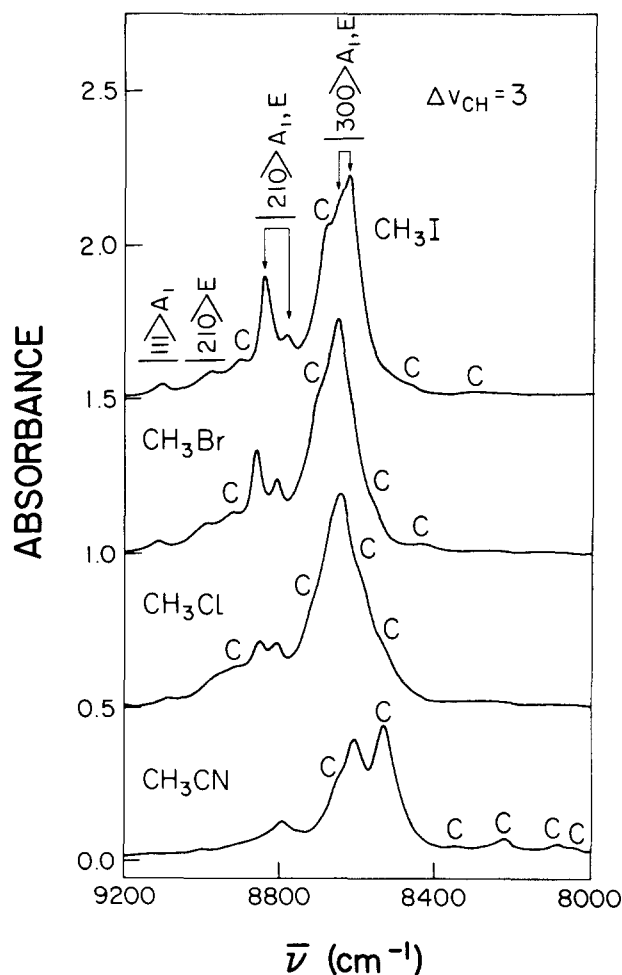


FIG. 2. Liquid phase overtone spectra of  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  in the region of  $\Delta\nu_{\text{CH}} = 3$ . Spectra were measured at room temperature with a path length of 1.0 cm. Absorbances of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  have been offset by 0.5, 1.0, and 1.5 absorbance units, respectively.

fitting the cell with fire polished glass cylinders of appropriate lengths.

All of the spectra, in a digital format, were transferred to a Nicolet 1280 computer and converted to a linear energy scale. The spectra were plotted in wave number units with a Nicolet Zeta 160 plotter. All of the overtone spectra were decomposed with a FORTRAN 77 curve analysis program, NIRCAP,<sup>25</sup> which fitted Lorentzian peaks to the experimental bands. The experimental and fitted spectra were plotted and compared to check the quality of the deconvolution fit.

The oscillator strength  $f$  of an absorption band can be calculated from the standard formula<sup>26</sup>

$$f = \left( \frac{4m_e c \epsilon_0}{Le^2} \right) A \quad \text{or} \quad f = 6.257 \times 10^{-19} (\text{m}^{-2} \text{mol s}) A, \quad (4)$$

where  $A$  is the integrated absorption coefficient. The integrated absorption coefficient  $A$  and the absorbance  $\mathcal{A}$  are related through

$$A = \int \alpha \, d\nu = \left( \frac{2.303}{Cl} \right) \int \mathcal{A} \, d\nu \quad (5)$$

where  $\alpha$  is the absorption coefficient,  $C$  is the concentration of the sample, and  $l$  is the length of the cell. Oscillator

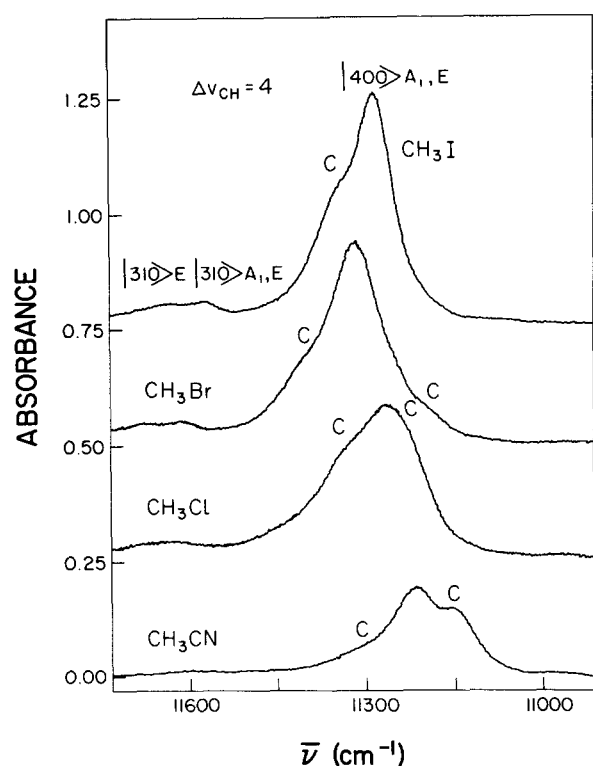


FIG. 3. Liquid phase overtone spectra of  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  in the region of  $\Delta\nu_{\text{CH}} = 4$ . Spectra were measured at room temperature with a path length of 5.0 cm. Absorbances of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  have been offset by 0.27, 0.53, and 0.78 absorbance units, respectively.

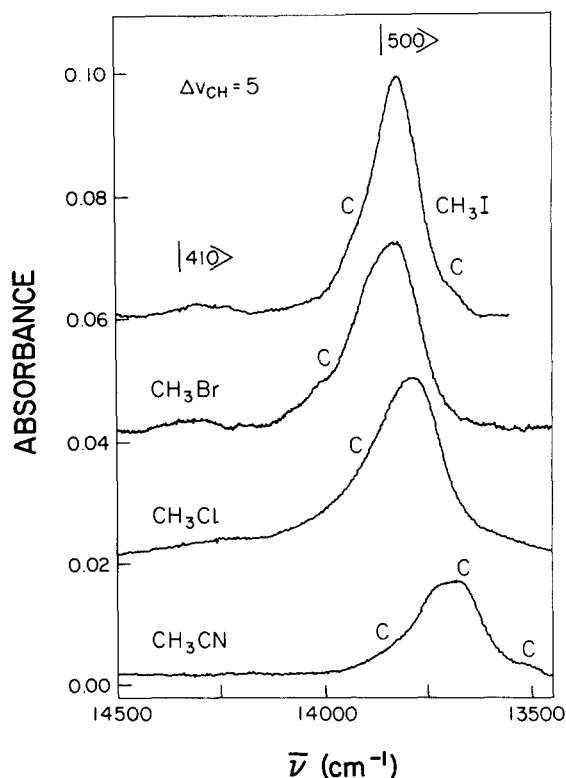


FIG. 4. Liquid phase overtone spectra of  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  in the region of  $\Delta\nu_{\text{CH}} = 5$ . Spectra were measured at room temperature with a path length of 5.0 cm. Absorbances of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  have been offset by 0.02, 0.04, and 0.06 absorbance units, respectively.

strengths for the overtones of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  were determined with the same procedure used in our previous work on dichloromethane.<sup>16</sup> Briefly, the integrated absorbance ( $\int \mathcal{A} d\nu$ ) was obtained by weighing the total area under the curve for a given overtone  $\Delta\nu_{\text{CH}}$ . The total oscillator strength follows straightforwardly from Eqs. (4) and (5).

### III. RESULTS AND DISCUSSION

#### A. Spectral analysis

The liquid phase overtone spectra of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$ , and  $\text{CH}_3\text{CN}$  in the regions of  $\Delta\nu_{\text{CH}} = 2-6$  are shown in Figs. 1-5. The observed peak positions are listed in Tables I and II. These positions correspond to the maxima of the individual Lorentzian components which were obtained from curve decomposition.

The overtone spectra are dominated by purely CH-stretching peaks. The spectra can be assigned through an application of the local mode Hamiltonian of three coupled Morse oscillators<sup>9</sup> to symmetrized states with components  $|v_1, v_2, v_3\rangle$ . Here  $v_1$ ,  $v_2$ , and  $v_3$  denote the vibrational quanta in each of the three methyl CH bonds, respectively, and

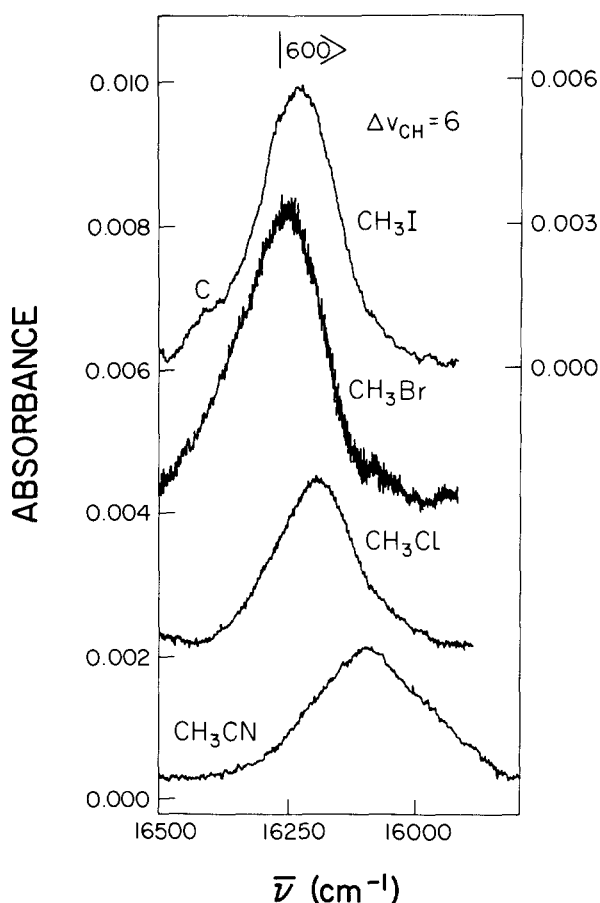


FIG. 5. Liquid phase overtone spectra of  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  in the region of  $\Delta\nu_{\text{CH}} = 6$ . These spectra are the sum of four base line corrected scans. Individual scans were measured at room temperature with a path length of 5.0 cm. The right-hand ordinate scale represents the absorbance of  $\text{CH}_3\text{I}$ . Absorbances of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  have been offset by 0.002 and 0.004 absorbance units, respectively, with respect to the absorbance of  $\text{CH}_3\text{CN}$ .

TABLE I. Observed and calculated CH-stretching peak positions ( $\text{cm}^{-1}$ ) in the overtone spectra of methyl halides and methyl cyanide.

CH <sub>3</sub> Cl		CH <sub>3</sub> Br		CH <sub>3</sub> I		CH <sub>3</sub> CN		Assignment
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
2 956 <sup>a</sup>	2 956	2 961 <sup>a</sup>	2 957	2 948 <sup>b</sup>	2 943	2 944 <sup>a</sup>	2 944	$ 100\rangle_{A_1}$
3 033 <sup>a</sup>	3 034	3 048 <sup>a</sup>	3 044	3 045 <sup>b</sup>	3 039	3 000 <sup>a</sup>	3 001	$ 100\rangle_E$
5 861	5 845	5 858	5 852	5 845	5 826	5 800	5 819	$ 200\rangle_{A_1}$
5 914	5 882	5 920	5 897	5 911	5 880	5 837	5 841	$ 200\rangle_E$
6 014	6 009	6 034	6 028	6 028	6 016	5 958	5 953	$ 110\rangle_{A_1}$
6 061	6 049	6 080	6 069	6 082	6 059	6 003	5 988	$ 110\rangle_E$
8 647	8 625	8 622	8 648	8 620	8 617	8 608	8 579	$ 300\rangle_{A_1}$
8 647	8 632	8 653	8 659	8 650	8 632	8 608	8 582	$ 300\rangle_E$
8 809	8 808	8 808	8 824	8 785	8 794	8 753	8 760	$ 210\rangle_{A_1}$
8 855	8 862	8 856	8 883	8 840	8 848	8 793	8 800	$ 210\rangle_E$
8 968	8 950	8 996	8 982	8 982	8 956	8 858	8 865	$ 210\rangle_E$
...	8 976	...	9 009	...	8 996	...	8 885	$ 210\rangle_{A_2}$
9 079	9 059	9 109	9 086	9 103	9 070	8 996	8 969	$ 111\rangle_{A_1}$
11 265	11 265	11 319	11 308	11 287	11 273	11 217	11 209	$ 400\rangle_{A_1,E}$
...	...	...	11 309	...	11 274	...	...	...
11 605	11 568	11 614	11 589	11 575	11 543	11 491	11 517	$ 310\rangle_{A_1}$
11 605	11 606	11 614	11 635	11 575	11 596	11 491	11 540	$ 310\rangle_E$
11 654	11 656	11 684	11 693	11 647	11 662	11 600	11 575	$ 310\rangle_E$
...	11 682	...	11 723	...	11 696	...	11 592	$ 310\rangle_{A_2}$
...	11 794	...	11 903	...	11 877	...	11 701	$ 220\rangle_{A_1}$
...	11 830	...	11 875	...	11 854	...	11 721	$ 220\rangle_E$
...	11 866	...	11 830	...	11 801	...	11 771	$ 211\rangle_{A_1}$
...	11 975	...	12 016	...	11 995	...	11 858	$ 211\rangle_E$
13 777	13 788	13 825	13 857	13 817	13 819	13 743	13 719	$ 500\rangle_{A_1,E}$
16 191	16 171 <sup>c</sup>	16 261	16 264 <sup>c</sup>	16 243	16 218 <sup>c</sup>	16 082	16 117 <sup>c</sup>	$ 600\rangle_{A_1,E}$

<sup>a</sup> Reference 27.<sup>b</sup> Measured in our laboratory.<sup>c</sup> Calculated from Eq. (7) (see the text).

$\nu_1 + \nu_2 + \nu_3 = \Delta\nu_{\text{CH}}$ . The states are symmetrized under the point group  $C_{3v}$ . Peaks corresponding to pure local mode states of the type  $|v,0,0\rangle_{A_1,E}$  whose components have all of the vibrational quanta localized in a single methyl CH bond

dominate the spectra in the regions of  $\Delta\nu_{\text{CH}} = 3-6$ . Transitions to local mode combination states of the type  $|v-1,1,0\rangle_{A_1,E}$ ,  $|v-2,1,1\rangle_{A_1,E}$ , etc., whose components have vibrational quanta distributed over two or all three

TABLE II. Position ( $\text{cm}^{-1}$ ) and tentative assignments for the combination peaks in the overtone spectra of methyl halides and methyl cyanide.

CH <sub>3</sub> Cl	CH <sub>3</sub> Br	CH <sub>3</sub> I	CH <sub>3</sub> CN	Assignment <sup>a</sup>
5 643	...	...	5 678	$ 100\rangle_{A_1} + 2\delta_A$
5 697	5 615	...	5 716	$ 100\rangle_E + 2\delta_A$
...	5 756	5 685	...	$ 100\rangle_E + \delta_A + \delta_E$
5 809	5 801	5 776	...	$ 100\rangle_{A_1} + 2\delta_E$
8 531	8 440	8 265	8 529	$ 200\rangle_{A_1} + 2\delta_A$
8 589	8 559	8 476	...	$ 200\rangle_{A_1} + \delta_A + \delta_E$
8 707	8 697	8 681	8 651	$ 200\rangle_{A_1} + 2\delta_E$
8 916	8 923	8 914	...	$ 110\rangle_E + 2\delta_E$
...	...	...	8 045	$ 200\rangle_{A_1} + \nu_{\text{CN}}$
...	...	...	8 085	$ 200\rangle_E + \nu_{\text{CN}}$
...	...	...	8 218	$ 200\rangle_{A_1} + \delta_A + \rho$
...	...	...	8 339	$ 200\rangle_E + \delta_E + \rho$
11 225	11 203	...	11 143	$ 300\rangle_{A_1,E} + 2\delta_A$
11 346	11 410	11 351	11 314	$ 300\rangle_{A_1,E} + 2\delta_E$
...	...	...	13 505	$ 400\rangle_{A_1,E} + \nu_{\text{CN}}$
...	...	13 690	13 667	$ 400\rangle_{A_1,E} + 2\delta_A$
13 873	13 987	13 899	13 852	$ 400\rangle_{A_1,E} + 2\delta_E$
...	...	16 358	...	$ 500\rangle_{A_1,E} + 2\delta_E$

<sup>a</sup>  $\delta_A$  and  $\delta_E$  are methyl deformation modes of  $A_1$  and  $E$  symmetries;  $\nu_{\text{CN}}$  is a CN-stretching mode of  $A_1$  symmetry;  $\rho$  is a methyl rocking mode of  $E$  symmetry. Fundamental assignments and frequencies are from Ref. 27.

methyl oscillators also appear in the spectra, particularly at lower overtones.

The energies of these methyl CH-stretching states can be obtained through an application of the harmonically coupled local mode model for an  $\text{XH}_3$  system.<sup>8,9,15</sup> The Hamiltonian is written in the form

$$H = E_0 + (v_1 + v_2 + v_3)\omega - (v_1^2 + v_2^2 + v_3^2 + v_1 + v_2 + v_3)\omega x + \gamma\omega(p_1 p_2 + p_1 p_3 + p_2 p_3) + \phi\omega(q_1 q_2 + q_1 q_3 + q_2 q_3). \quad (6)$$

Here  $E_0$  is the wave number energy of the ground state and  $\gamma$  and  $\phi$  characterize the off-diagonal kinetic and potential energy coupling, respectively. These parameters are defined in terms of Wilson  $G$  and  $F$  matrix elements [ $\gamma = -(1/2)G_{ij}/G_{ii}$ ;  $\phi = (1/2)F_{ij}/F_{ii}$ ,  $i, j = 1, 2, 3$ ].  $p_i$  and  $q_i$  are normalized momentum and coordinate variables, and are conveniently expressed in terms of creation  $a^+$  and annihilation  $a$  operators ( $p = a^+ - a$ ;  $q = a^+ + a$ ).

The details of this model have been described in our previous work on the overtone spectra of the dihalomethanes<sup>8</sup> and neopentane.<sup>9</sup> The model accounts for all of the anharmonicity that is diagonal in a single CH oscillator. However, coupling between the simple product basis states is restricted to a given vibrational manifold and to the harmonic limit, i.e., states couple only when their respective bond excitations differ by a single quantum. A calculation of the CH-stretching vibrational state energies requires the harmonic frequency  $\omega$ , the anharmonicity constant  $\omega x$ , and the effective coupling parameter  $\gamma'\omega$  ( $\gamma' = \gamma - \phi$ ) which appears in the intramanifold coupling matrices<sup>9</sup> of Eq. (6).

The parameters  $\omega$  and  $\omega x$  are evaluated by fitting the observed energies of the pure local mode peaks  $|v, 0, 0\rangle_{A_1, E}$  to the energy equation of a diatomic Morse oscillator, with a least mean squares analysis:

$$\Delta E = v\omega - (v^2 + v)\omega x. \quad (7)$$

For those spectra where the pure local mode peaks  $|v, 0, 0\rangle_{A_1}$  and  $|v, 0, 0\rangle_E$  are resolved, the weighted mean, i.e.,  $(2/3)E(|v, 0, 0\rangle_E) + (1/3)E(|v, 0, 0\rangle_{A_1})$ , is taken as the peak energy in the fit to Eq. (7). The parameters  $\omega$  and  $\omega x$  are given in Table III.

The effective interoscillator coupling parameter  $\gamma'\omega$  is also listed in Table III. This parameter is obtained from the observed splitting<sup>27</sup> between the fundamental CH-stretching modes of  $A_1$  and  $E$  symmetries<sup>9</sup> ( $3\gamma'\omega = E(|1, 0, 0\rangle_E) - E(|1, 0, 0\rangle_{A_1})$ ).

TABLE III. Local mode parameters ( $\text{cm}^{-1}$ ) of methyl halides and methyl cyanide.

Molecule	$\omega$	$\omega x$	$\gamma'\omega$
$\text{CH}_3\text{Cl}$	$3133 \pm 3$	$62.5 \pm 0.8$	26
$\text{CH}_3\text{Br}$	$3136 \pm 12$	$60.8 \pm 3.0$	29
$\text{CH}_3\text{I}$	$3129 \pm 5$	$60.8 \pm 1.1$	32
$\text{CH}_3\text{CN}$	$3101 \pm 4$	$59.2 \pm 1.1$	19

Substitution of the local mode parameters of Table III into the intramanifold coupling matrices<sup>9</sup> of the Hamiltonian [Eq. (6)] followed by diagonalization of these matrices gives the calculated energies of the peaks corresponding to the methyl CH bonds. The calculated and observed energies of these methyl CH-stretching peaks are given in Table I, along with the peak assignments. The agreement between calculated and observed peak energies is very good.

The assignments of the pure local mode and the local mode combination peaks for  $\text{CH}_3\text{I}$  are indicated in Figs. 1–5. The assignments for the corresponding peaks of the other molecules are analogous. The discussion in the following paragraphs applies to the spectra of all four molecules.

The spectra at  $\Delta v_{\text{CH}} = 2$  (Fig. 1) display four major peaks which are particularly well resolved for  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{Br}$ . From low to high energy, these peaks correspond to transitions to the states  $|2, 0, 0\rangle_{A_1}$ ,  $|2, 0, 0\rangle_E$ ,  $|1, 1, 0\rangle_{A_1}$ , and  $|1, 1, 0\rangle_E$ . The splitting of the  $|2, 0, 0\rangle_{A_1}$  and  $|2, 0, 0\rangle_E$  peaks is evident for the methyl halides. This splitting arises from the harmonic coupling of the  $|2, 0, 0\rangle_{A_1, E}$  states with the  $|1, 1, 0\rangle_{A_1, E}$  states of the same symmetry. As in the case of neopentane,<sup>9</sup> this splitting is not resolved in  $\text{CH}_3\text{CN}$ .

For the methyl halides, the most intense peaks in the spectra at  $\Delta v_{\text{CH}} = 3$  (Fig. 2) correspond to transitions to the pure local mode states  $|3, 0, 0\rangle_{A_1}$  and  $|3, 0, 0\rangle_E$ . These peaks appear as two unresolved peaks in the spectra of  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{Br}$ , and as totally unresolved single peaks in the spectra of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{CN}$ . The symmetry splitting is much smaller here than at  $\Delta v_{\text{CH}} = 2$  because of the absence of first order harmonic coupling.<sup>8</sup> However, transitions to the local mode combination states  $|2, 1, 0\rangle_{A_1}$ , two  $|2, 1, 0\rangle_E$  states, and  $|1, 1, 1\rangle_{A_1}$  are clearly resolved in the spectra of the methyl halides. This splitting is comparatively larger than the  $|3, 0, 0\rangle_{A_1}$ ,  $|3, 0, 0\rangle_E$  splitting because the various product states  $|2, 1, 0\rangle$ ,  $|2, 0, 1\rangle$ ,  $|1, 1, 1\rangle$ , etc., undergo substantial first order harmonic couplings.<sup>8</sup>

In the regions of  $\Delta v_{\text{CH}} = 4$ –6 (Figs. 3–5), the intensities of local mode combination peaks are greatly diminished, and

TABLE IV. Integrated oscillator strengths for the overtones of methyl halides.

$\Delta v_{\text{CH}}$	$\text{CH}_3\text{Cl}$ $\log f_{\text{ov}}$	$(E_v/\hbar\omega)^{1/2}$	$\text{CH}_3\text{Br}$ $\log f_{\text{ov}}$	$(E_v/\hbar\omega)^{1/2}$	$\text{CH}_3\text{I}$ $\log f_{\text{ov}}$	$(E_v/\hbar\omega)^{1/2}$
2	– 6.62	1.541	– 6.59	1.542	– 6.56	1.542
3	– 7.47	1.804	– 7.40	1.806	– 7.44	1.806
4	– 8.46	2.024	– 8.43	2.027	– 8.38	2.026
5	– 9.52	2.213	– 9.48	2.217	– 9.44	2.216
6	– 10.24	2.379	– 10.21	2.384	– 10.13	2.383

the spectra are largely dominated by the pure local mode peaks.

The peaks marked "C" in Figs. 1–5 are combination peaks. They are particularly noticeable in the spectral regions of  $\Delta\nu_{\text{CH}} = 3$  and 4 for all four molecules. The most prominent of these peaks involve transitions to states with  $\nu - 1$  quanta in CH stretching and two quanta of a methyl deformation<sup>27</sup>  $\delta_A$  or  $\delta_E$ . [ $\delta_A$  ( $\delta_E$ ) = 1346(1444), 1297(1434), 1245(1429), and 1374(1441)  $\text{cm}^{-1}$  for  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$ , and  $\text{CH}_3\text{CN}$ , respectively.<sup>27</sup>] Such peaks are commonly observed in the overtone spectra of several molecules.<sup>8,28–36</sup>

Tentative assignments of these combination peaks are given in Table II and are based on fundamental frequencies obtained by Glass and Pullin.<sup>27</sup> The combinations can steal intensity from the pure local mode peaks through resonant or near-resonant interactions. Intensity stealing is particularly pronounced for the  $|\nu - 1, 0, 0\rangle_{A_1} + 2\delta_A$  or  $|\nu - 1, 0, 0\rangle_{A_1, E} + 2\delta_A$  peaks in the spectra of  $\text{CH}_3\text{CN}$  at  $\Delta\nu_{\text{CH}} = 3, 4$ , and 5 (Figs. 2–4), where these combinations are comparable in intensity to the pure local mode peaks. In the spectral regions of  $\Delta\nu_{\text{CH}} = 3, 4$ , and 5, the most intense combination peaks in the spectra of the methyl halides correspond to transitions to the states  $|\nu - 1, 0, 0\rangle_{A_1} + 2\delta_E$  or  $|\nu - 1, 0, 0\rangle_{A_1, E} + 2\delta_E$ .

## B. Overtone intensities in methyl halides

The logarithms of the experimental oscillator strength  $f_{\text{ov}}$  for the overtones of the methyl halides are given in Table IV, along with the square roots of the upper state vibrational

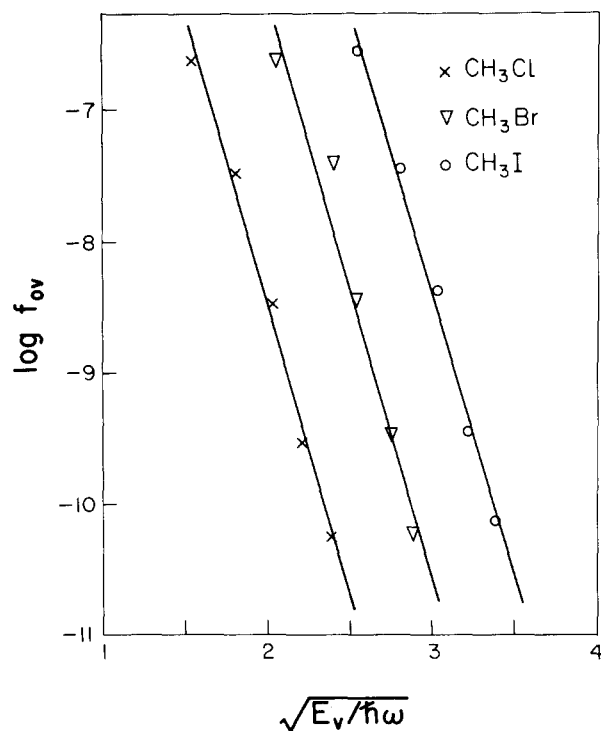


FIG. 6. The correlation between integrated oscillator strengths for the CH-stretching overtones of methyl halides for  $\Delta\nu_{\text{CH}} = 2$ –6 and reduced upper state vibrational energy [Eq. (1)].

TABLE V. Slopes and the parameter  $\beta$  ( $\text{\AA}^{-1}$ ) associated with Medvedev's intensity distribution law for methyl halides.

Molecule	$a$	$\beta$
$\text{CH}_3\text{Cl}$	$4.43 \pm 0.25$	$4.05 \pm 0.2$
$\text{CH}_3\text{Br}$	$4.42 \pm 0.26$	$4.06 \pm 0.2$
$\text{CH}_3\text{I}$	$4.34 \pm 0.23$	$4.13 \pm 0.2$
$\text{CH}_2\text{X}_2^a$	$4.80^b$	$3.76 \pm 0.07^b$
$\text{CHX}_3^a$	$5.80^b$	$3.10 \pm 0.05^b$

<sup>a</sup> X = Cl, Br.

<sup>b</sup> Reference 21.

energies from Eq. (2) in units of  $\hbar\omega$ . From these data, the Medvedev intensity distribution law<sup>19–21</sup> [Eq. (1)] is plotted in Fig. 6. From a least squares fit of Eq. (1), the slope " $a$ " and the molecular parameter  $\beta$  are obtained. Values of  $a$  and  $\beta$  are given in Table V. The parameter  $\beta$  is obtained straightforwardly by substituting  $\bar{M} = 0.930$ ,  $\bar{\omega}$  values ( $\bar{\omega} = 10^{-3} \omega$ ) from Table III, and  $a$  values from Table V into Eq. (3). In Table V, we have also listed values of  $a$  and  $\beta$  obtained by Medvedev for dihalomethanes and trihalomethanes.<sup>21</sup>

Medvedev has also applied his intensity distribution law to the CH-stretching overtones of relatively large polyatomic molecules.<sup>21</sup> He used average overtone intensity data for ten liquid phase polyatomic molecules,<sup>37,38</sup> which included both aromatic and aliphatic CH bonds (benzene, xylenes, tetramethylsilane, hexane, etc.). His analysis led him to conclude that there is a common value of  $\beta = 3.81 \text{ \AA}^{-1}$  for all of these molecules. This value is also within experimental error of the value obtained by Medvedev for the two dihalomethanes  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{Br}_2$  ( $\beta = 3.76 \text{ \AA}^{-1}$ ). Thus it appears that the repulsive parts of the vibrational potential are similar for all of these molecules. On this basis Medvedev<sup>19</sup> predicted the same value of  $\beta$  for the methyl halides, for which no intensity data were available.

A common value of  $\beta$  was obtained for the two trihalomethanes  $\text{CHCl}_3$  and  $\text{CHBr}_3$  ( $\beta = 3.10 \text{ \AA}^{-1}$ ).<sup>21</sup> On the basis of these results and the results for the dihalomethanes, Medvedev concluded that although the CH bond potential is sensitive to whether there are two or three halogen substituents, it is insensitive to the type of halogen substituent.

It is evident from Fig. 6 that the intensities of methyl halide overtones fit very well to Medvedev's intensity distribution law [Eq. (1)]. In agreement with Medvedev's results for the dihalomethanes and trihalomethanes, our results indicate that  $\beta$  is insensitive to the type of halogen substituent for the methyl halides. However, contrary to the prediction of Medvedev,<sup>19</sup> our results appear to indicate a difference between the  $\beta$  values of the methyl halides and the dihalomethanes.<sup>39</sup> Thus it appears that successive replacement of the hydrogen atoms of methane by halogen atoms successively decreases the value of  $\beta$ , and that the repulsive part of the CH bond potential rises more steeply for the less substituted halomethanes.

Amrein *et al.*<sup>40</sup> have studied fundamental and overtone intensities in a series of molecules of the type  $\text{C}_n\text{F}_m\text{Cl}_k\text{H}$ . They find that although there are large differences in intensities at the fundamental level, the intensities converge to similar values for higher overtones. This result would appear to

be quite general. As Medvedev has pointed out,<sup>21</sup> it is in accord with his analysis for the dihalomethanes and the trihalomethanes. It is also in accord with our data for the methyl halides.

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