

# Ab initio computation of force constants. V. The theoretical anharmonic force fields and vibrational frequencies of methyl fluoride and methyl chloride<sup>a)</sup>

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The anharmonic force fields of methyl fluoride and methyl chloride have been calculated *ab initio*. The theoretical and experimental harmonic force fields agree fairly well, but certain small discrepancies are found for CH<sub>3</sub>F. Agreement between calculated and observed anharmonic frequencies is good. It is suggested that application of the theoretical anharmonicity corrections to the observed frequencies can lead to better estimates of the experimental harmonic frequencies and force constants.

## I. INTRODUCTION

Part IV of this series<sup>1</sup> was concerned with the theoretical vibrational spectra of the CH<sub>3</sub>X molecules methylamine, methanol, and methanethiol. The study of these systems was undertaken because of our particular interest in the phenomenon known as the Bohlmann bands.<sup>2,3</sup> Other CH<sub>3</sub>X molecules of interest include methyl fluoride and methyl chloride. Their vibrational spectra have attracted attention for many years.<sup>4</sup> As instrumental techniques have improved, additional details of the spectra have been resolved, with the result that unique harmonic force fields have finally been obtained.<sup>5,6</sup> Earlier work<sup>7</sup> was often frustrated by the absence of sufficient data pertaining to isotopically substituted molecules, especially Coriolis constants and centrifugal distortion constants. Thus, a number of different harmonic force fields, equally compatible with the experimental data, had been proposed for certain of the methyl halides. Because of the absence of data on combination and overtone bands, anharmonicity corrections continue to be made empirically<sup>5,6,8</sup>; these add further uncertainty to the harmonic force field.

The purpose of the present paper is to present the results of *ab initio* computations of the anharmonic force fields of methyl fluoride and methyl chloride, and to suggest ways in which these may be useful in the analysis of the experimental data.

## II. CALCULATIONS

The SCF wavefunctions were calculated with the GAUSSIAN 70 program system<sup>9a</sup> using the 4-31G basis set<sup>9b,c</sup>; forces on the atoms in the molecule were computed analytically.<sup>10,11</sup> Force constants were deter-

mined from the forces in the manner already described.<sup>1,2,10</sup>

The presence of C<sub>3</sub> axes in CH<sub>3</sub>F and CH<sub>3</sub>Cl causes some of the vibrational modes to be doubly degenerate. The calculation of vibrational frequencies for such systems therefore requires a slight modification of the approach used in the previous work.<sup>1,2</sup> In molecules that contain double degenerate vibrational modes, the vibrational energy can be expressed as

$$E(v) = \sum_s \omega_s (v_s + \frac{1}{2}) + \sum_t \omega_t (v_t + 1) + \sum_{s \geq s'} \chi_{ss'} (v_s + \frac{1}{2}) (v_{s'} + \frac{1}{2}) + \sum_{s,t} \chi_{st} (v_s + \frac{1}{2}) (v_t + 1) + \sum_{t \geq t'} \chi_{tt'} (v_t + 1) (v_{t'} + 1) + \sum_{t \geq t'} g_{tt'} 1_t 1_{t'}, \quad (2.1)$$

in which  $s, s'$  run over only those modes that are non-degenerate, and  $t, t'$  run over only those modes that are degenerate. Formulas for  $\chi_{ss'}$ ,  $\chi_{st}$ ,  $\chi_{tt'}$ , and  $g_{tt'}$  can be found in the literature.<sup>12</sup> Details of the calculations have been given in earlier papers in this series. In addition to this interaction between vibrational modes, Coriolis coupling<sup>12d,13</sup> occurs between vibrational and rotational levels. For doubly degenerate vibrational modes, Coriolis coupling constants can be determined directly from the rotational fine structure of the experimental vibrational bands. These constants are related directly to the normal modes of vibration, and provide an additional check on the accuracies of the calculated normal coordinates.

## III. GEOMETRY AND INTERNAL COORDINATES

The set of internal coordinates employed in the present calculation is given in Table I. These resemble the coordinate system used for methylamine, methanol, and methanethiol.<sup>1</sup> The usual set of redundant valence coordinates has not been employed, for the reasons outlined previously.<sup>1</sup>

The initial geometry for the force constant calcula-

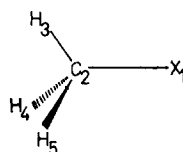
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TABLE I. Geometry and internal coordinates for methyl fluoride and methyl chloride.<sup>a</sup>

Coordinate	Description	CH <sub>3</sub> F			CH <sub>3</sub> Cl		
		Initial <sup>b</sup>	Relaxed	Exptl <sup>c</sup>	Initial <sup>b</sup>	Relaxed	Exptl <sup>c</sup>
1	r <sub>CX</sub>	1.385	1.411	1.382	1.781	1.864	1.778
2	r <sub>CH<sub>3</sub></sub>	1.109	1.073	1.095	1.110	1.068	1.086
3	r <sub>CH<sub>4</sub></sub>	1.109	1.073	1.095	1.110	1.068	1.086
4	r <sub>CH<sub>5</sub></sub>	1.109	1.073	1.095	1.110	1.068	1.086
5	H <sub>3</sub> CX	108.937	108.295	108.422	108.422	106.957	108.248
6	H <sub>4</sub> CX	108.937	108.295	108.422	108.422	106.957	108.248
7	H <sub>5</sub> CX	108.937	108.295	108.422	108.422	106.957	108.248
8	H <sub>4</sub> CXH <sub>3</sub> (dihedral)	120.0	120.0	120.0	120.0	120.0	120.0
9	H <sub>5</sub> CXH <sub>3</sub> (dihedral)	-120.0	-120.0	-120.0	-120.0	-120.0	-120.0

<sup>a</sup>Bond lengths in Å; dihedral angles measured about the CX axis.



<sup>b</sup>Reference 13.

<sup>c</sup>Reference 14.

tions was based on an earlier estimate.<sup>14</sup> The energy and forces were calculated at this geometry and small displacements from it ( $\pm 0.05$  Å for bond lengths and  $\pm 2.5^\circ$  for bond angles). The harmonic force constants computed from the forces and energies were then used to relax the molecules to their theoretical equilibrium geometry. In Table I, the relaxed geometrical parameters are compared to more recent experimental estimates of the equilibrium geometries of methyl fluoride and methyl chloride.<sup>15</sup> While the theoretical C-H bond lengths are in both cases shorter than the observed, the trend, C-H in CH<sub>3</sub>F longer than C-H in CH<sub>3</sub>Cl, is reproduced correctly. The change in the HCX angles is also in the correct direction, but it is overestimated considerably.

#### IV. FORCE CONSTANTS

The theoretical and experimental force fields of methyl fluoride and methyl chloride are listed in Table II-V. The theoretical force constants correspond to the more recent experimental geometry. The change of

origin of the force field was made with the aid of the anharmonic force constants computed about the initial geometry.

$$F_{ij}^{\text{new}} = F_{ij}^{\text{old}} + \sum_k F_{ijk} \Delta_k + \frac{1}{2} \delta_{ij} F_{iiii} \Delta_i^2,$$

$$F_{iii}^{\text{new}} = F_{iii}^{\text{old}} + F_{iiii} \Delta_i, \quad (4.1)$$

where  $\Delta_k$  is the change in geometry of the  $k$ th coordinate, and  $F^{\text{old}}$ ,  $F^{\text{new}}$  are the force constants at the original and the changed geometries, respectively.

In general, the computed force constants are higher than the observed. The C-F and C-Cl stretching force constants appear to be overestimated the most. However, most of the differences between methyl fluoride and methyl chloride are predicted correctly. In both the calculated and the experimental force fields, the change from fluorine to chlorine causes an increase in the C-H stretching force constant and a decrease in the HCX bending force constant. In addition, the C-X stretch/C-H stretch interaction constant increases while

TABLE II. Theoretical force constants of methyl fluoride.<sup>a</sup>

<i>i</i>	<i>j</i>								
	1	2	3	4	5	6	7	8	9
<i>F<sub>ij</sub></i>									
1	7.0094								
2	0.1904	5.3604							
3	0.1904	0.0480	5.3604						
4	0.1904	0.0480	0.0480	5.3604					
5	0.5842	-0.0426	-0.0530	-0.0530	1.3004				
6	0.5842	-0.0530	-0.0426	-0.0530	0.1795	1.3004			
7	0.5842	-0.0530	-0.0530	-0.0426	0.1795	0.1795	1.3004		
8	0.0000	0.1582	0.0000	-0.1582	-0.2218	0.0000	0.2218	0.9313	
9	0.0000	-0.1582	0.1582	0.0000	0.2218	-0.2218	0.0000	-0.4679	0.9313
<i>F<sub>iii</sub></i>									
	-38.9706	-31.7389	-31.7389	-31.7389	-0.4462	-0.4462	-0.4462	0.0	0.0

<sup>a</sup>Units: quadratic, cubic, and quartic bending force constants, mdyne-Å; stretch-bend and stretch-bend-bend force constants, mdyne; stretch-stretch and stretch-stretch-bend force constants, mdyne/Å; cubic stretching force constants, mdyne/Å<sup>2</sup>.

TABLE III. Experimental force constants of methyl fluoride.<sup>a</sup>

<i>i</i>	<i>j</i>								
	1	2	3	4	5	6	7	8	9
1	5.692								
2	0.222	5.267							
3	0.222	-0.009	5.267						
4	0.222	-0.009	-0.009	5.267					
5	0.535	0.178	0.065	0.065	1.136				
6	0.535	0.065	0.178	0.065	0.159	1.136			
7	0.535	0.065	0.065	0.178	0.159	0.159	1.136		
8	0.000	0.110	0.000	-0.110	-0.176	-0.000	0.176	0.801	
9	0.000	-0.110	0.110	0.000	0.176	-0.176	0.000	-0.400	0.801

<sup>a</sup>Reference 4; units: see Table II.TABLE IV. Theoretical force constants for methyl chloride.<sup>a</sup>

<i>i</i>	<i>j</i>								
	1	2	3	4	5	6	7	8	9
<i>F<sub>ij</sub></i>									
1	4.4455								
2	0.0541	5.6944							
3	0.0541	0.0350	5.6944						
4	0.0541	0.0350	0.0350	5.6944					
5	0.5260	-0.0977	-0.0623	-0.0623	1.1783				
6	0.5260	-0.0623	-0.0977	-0.0623	0.1611	1.1783			
7	0.5260	-0.0623	-0.0623	-0.0977	0.1611	0.1611	1.1783		
8	0.0000	0.1433	0.0000	-0.1433	-0.2333	0.0000	0.2333	0.9218	
9	0.0000	-0.1433	0.1433	0.0000	0.2333	-0.2333	0.0000	-0.4481	0.9218
<i>F<sub>iii</sub></i>									
	-17.5481	-33.8129	-33.8129	-33.8129					

<sup>a</sup>Units: see Table II.TABLE V. Experimental force constants of methyl chloride.<sup>a</sup>

<i>i</i>	<i>j</i>								
	1	2	3	4	5	6	7	8	9
1	3.500								
2	0.100	5.407							
3	0.100	0.043	5.407						
4	0.100	0.043	0.043	5.407					
5	0.418	-0.014	-0.012	-0.012	0.950				
6	0.418	-0.012	-0.014	-0.012	0.128	0.950			
7	0.418	-0.012	-0.012	-0.014	0.128	0.128	0.950		
8	0.000	0.111	-0.000	-0.111	-0.199	0.000	0.199	0.760	
9	0.000	-0.111	0.111	0.000	0.199	-0.199	0.000	-0.380	0.760

<sup>a</sup>Reference 5; units: see Table II.

the C-X stretch/HCX bend constant decreases. The changes in the bend/bend interaction constants are also in the correct direction.

The change in the C-H stretch/C-H stretch interaction does not agree with the experimental results. A decrease in this constant is predicted on going from F to Cl (0.048 and 0.035 mdyn/Å, respectively), and is consistent with the trend observed for methyl halides, other than CH<sub>3</sub>F (0.043, 0.033, and 0.024 mdyn/Å for CH<sub>3</sub>Cl, CH<sub>3</sub>Br, and CH<sub>3</sub>I, respectively). The experimental value of -0.09 mdyn/Å for CH<sub>3</sub>F therefore appears to be anomalous. The experimental C-H stretch/

HCF bending interactions also fail to follow the trend found in the other halides and do not agree in sign with the computed values. These points of disagreement can possibly be associated with the empirical anharmonicity correction used in the experimental work. This view might be tested by using the present theoretical data to make the anharmonicity corrections (see below).

## V. FREQUENCIES

The calculated and observed anharmonic frequencies are presented in Tables VI and VII. Theoretical har-

TABLE VI. Calculated and observed fundamental vibrational frequencies and coriolis constants for methyl fluoride.<sup>a</sup>

	CH <sub>3</sub> F		CD <sub>3</sub> F		CH <sub>2</sub> DF		CHD <sub>2</sub> F		
	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	
$\nu_1$	2878 <sup>b</sup>	2910.0	2114	2110	$\nu_1$	2204	2197	2132 <sup>d</sup>	2174
$\nu_2$	1562	1460.4	1241	1134.8	$\nu_2$	1461	1364	1193	1092
$\nu_3$	1164	1048.6	1076	992.3	$\nu_3$	992	938	1027	965
$\nu_4'$	2970 <sup>b</sup>	3006.2	2286(2336) <sup>c</sup>	2258.5	$\nu_4$	2951	2950	2995	2976
$\nu_5'$	1577	1467.8	1149	1071.3	$\nu_5$	1575	1466	1432	1330
$\nu_6'$	1247	1182.3	960	911.3	$\nu_6$	1168	1052	1136	1050
					$\nu_7$	3001	3016	2246	2259
$\zeta_4$	0.040	0.089	0.181	0.182	$\nu_8$	1383	1299	1417	(1337)
$\zeta_5$	-0.248	-0.28	-0.299	-0.293	$\nu_9$	1202	1133	961	(897)
$\zeta_6$	0.292	0.284	0.252	0.240					

<sup>a</sup>Frequencies in cm<sup>-1</sup>, zetas dimensionless; Ref. 4.

<sup>b</sup>Perturbed by a strong interaction with overtone and combination bands of  $\nu_2$  and  $\nu_5$ .

<sup>c</sup>Before correction for resonance between  $\nu_4$  and  $2\nu_5$ .

<sup>d</sup>Perturbed by a strong interaction with  $\nu_2 + \nu_6$ .

monic frequencies and anharmonicity constants for methyl fluoride (CH<sub>3</sub>F, CD<sub>3</sub>F, and <sup>13</sup>CH<sub>3</sub>F) and methyl chloride (CH<sub>3</sub>Cl, CD<sub>3</sub>Cl, and <sup>13</sup>CH<sub>3</sub>Cl) are tabulated in the supplementary material.<sup>16</sup> Overall, the agreement with experiment seems quite good. It is better for the C-H (C-D) stretches (average deviation 38 cm<sup>-1</sup> for 20 frequencies) than for the lower frequency modes (average deviation 86 cm<sup>-1</sup> for 40 frequencies). The latter are mainly C-H (C-D) bends and, as in our earlier calculations, are expected to be overestimated by 5%–10% by basis set defects. Because of the neglect of certain cubic force constants of the type  $F_{ijk}$ ,  $i$ ,  $j$ , and  $k$  not equal, the anharmonic corrections to individual modes of a degenerate set of vibrations are not necessarily equal. This difficulty has been circumvented by taking an average of the two frequencies (or anharmonicity constants).

The experimental spectra of methyl fluoride and methyl chloride are complicated by Fermi resonances. Because of the overestimation of the bending frequencies and their overtones, these resonances are not reproduced by the theoretical calculations. However, other resonances do appear in the theoretical calcula-

tions, and lead to a breakdown in the usual second order expansion of the vibrational energies (cf. Tables VI, VII).

When this occurs, the offending interaction can be removed from the perturbational treatment. Then, as a first approximation, the two unperturbed levels are allowed to interact directly via the appropriate anharmonic force constant, and the associated 2×2 eigenvalue problem is solved explicitly. The resulting level shifts are then added to the anharmonic frequencies calculated by perturbation theory.

In addition to frequencies, Tables VI and VII also contain values for the Coriolis constants of CH<sub>3</sub>X and CD<sub>3</sub>X. Since these constants depend directly on the normal coordinates, the good agreement between the calculated and observed values provides a further subtle demonstration of the quality of the theoretical force fields. The fact that the agreement of the  $\zeta$ 's is better for the fully deuterated species suggests that anharmonicity corrections to the Coriolis constants and, in the case of  $\zeta_4$ , Fermi resonance effects on these constants may have to be considered.

TABLE VII. Calculated and observed fundamental vibration frequencies and coriolis constants of methyl chloride.<sup>a</sup>

	CH <sub>3</sub> Cl		CD <sub>3</sub> Cl		CH <sub>2</sub> DCl		CHD <sub>2</sub> Cl		
	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	
$\nu_1$	2987	2967.8	2128(2046) <sup>b</sup>	2160.2	$\nu_1$	2292	2224	2233(2409) <sup>b</sup>	2194
$\nu_2$	1468	1355.0	1114	1028.7	$\nu_2$	1375	1269	1122	1050
$\nu_3$	822	732.8	787	701.4	$\nu_3$	799	713	791	705
$\nu_4$	3099	3039.3	2324	2283.3	$\nu_4$	3082	2990	3061	3012
$\nu_5$	1548	1452.1	1129	1059.9	$\nu_5$	1544	1436	1351	1249
$\nu_6$	1109	1017.3	840	767.6	$\nu_6$	906	827	947	870
					$\nu_7$	3083	3035	2331	2279
$\zeta_4$	0.054	0.065	0.186	0.187	$\nu_8$	1347	1260	1392	1300
$\zeta_5$	-0.253	-0.272	-0.324	-0.336	$\nu_9$	1067	986	843	768
$\zeta_6$	0.243	0.238	0.209	0.219					

<sup>a</sup>Frequencies in cm<sup>-1</sup>, zetas dimensionless; Ref. 5.

<sup>b</sup>Before correction for resonance between  $\nu_1$  and  $2\nu_2$ .

TABLE VIII.  $^{13}\text{C}$  shifts in methyl fluoride and chloride. <sup>a</sup>

	$^{13}\text{CH}_3\text{F}$				$^{13}\text{CH}_3\text{Cl}$			
	Harmonic		Anharmonic		Harmonic		Anharmonic	
	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs
$\Delta\nu_1$	2.5	4.0	3.7	4.0	2.5	3.04	7.1	3.04
$\Delta\nu_2$	7.9	5.64	7.1	5.42	6.2	5.76	5.7	5.53
$\Delta\nu_3$	23.3	21.53	22.8	21.10	20.8	18.23	20.5	17.88
$\Delta\nu_4$	10.6	11.43	7.4	10.52	12.4	11.99	9.8	11.05
$\Delta\nu_5$	2.9	2.49	2.7	2.39	3.1	2.68	2.6	2.58
$\Delta\nu_6$	8.5	8.13	8.2	7.81	6.2	5.67	6.0	5.45
$\Delta\xi_4$	0.012	0.007			0.011	0.005		
$\Delta\xi_5$	-0.004				-0.006	-0.009		
$\Delta\xi_6$	-0.006	-0.004			-0.004	-0.003		

<sup>a</sup>Frequencies in  $\text{cm}^{-1}$ , zetas dimensionless; Refs. 4, 5.

The  $^{13}\text{C}$  shift data are collected in Table VIII. Agreement with experiment is fairly good. Except for C-H stretching modes, anharmonicity corrections affect the theoretical values by less than  $1\text{ cm}^{-1}$ . The theoretical shifts in the Coriolis constants are all in the correct direction; however, because these shifts are so small, there is probably considerable uncertainty associated with both the calculated and observed differences.

In the derivation of the harmonic force fields, the experimental harmonic frequencies were estimated by the application of empirical corrections to the observed frequencies.<sup>5,6</sup> For example, one can define  $\tilde{\chi}_i = (\nu_i - \omega_i)/\omega_i$ , wherein  $\nu_i$  and  $\omega_i$  are the anharmonic (observed) and harmonic frequencies, respectively. For the analysis of experimental stretching modes,  $\tilde{\chi} = 0.04$  was used, whereas the theoretical calculations indicate a somewhat larger value,  $\tilde{\chi}_1 = 0.060$ ,  $\tilde{\chi}_4 = 0.054$  for  $\text{CH}_3\text{F}$  and  $\tilde{\chi}_1 = 0.051$ ,  $\tilde{\chi}_4 = 0.046$  for  $\text{CH}_3\text{Cl}$ . For the analysis of the experimental C-X stretching modes,  $\tilde{\chi} = 0.01$  was employed while  $\tilde{\chi}_3 = 0.019$  for  $\text{CH}_3\text{F}$  and  $\tilde{\chi}_3 = 0.014$  for  $\text{CH}_3\text{Cl}$  is calculated. The value of  $\tilde{\chi} = 0.02$  used for bending modes is in reasonable agreement with the computed results. The  $\tilde{\chi}$  for  $\text{CD}_3\text{X}$  can be calculated from the tables, if needed, rather than with Dennison's rule.<sup>17</sup>

## VI. CONCLUSIONS

The good agreement found for the C-H and C-D stretches suggests that the theoretical anharmonic corrections for these frequencies are reliable and could be used instead of the empirical corrections. The resulting differences in the experimental harmonic frequencies would affect the force field and could possibly account for the discrepancies found in methyl fluoride. A reinvestigation of the methyl fluoride and methyl chloride force fields using the present calculations as a guide might clarify the situation.

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<sup>16</sup>See AIP document No. PAPS JCPA-67-4194-6 for six pages of tables of theoretical force constants, harmonic frequencies, and anharmonicity constants of methyl fluoride and methyl chloride. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is \$1.50 for each microfiche, or \$5 for photocopies. Airmail additional. Make checks payable to the American Institute of Physics. This material also appears in *Current Physics Microfilm*, the monthly microfilm edition of the complete set of journals published by AIP, on the frames immediately following this journal article.

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