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Short Communication

Force field for CF_3CHO and CF_3CDO *

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In a continuing study of the vibrational spectra of fluorinated hydrocarbons, infrared spectra have been obtained in this laboratory for several fluorinated compounds containing the $C{=}O$ or $C{=}CH_2$ group. These compounds include 1-alkenes such as $CF_3CH{=}CH_2$[1], esters such as CF_3COOCH_3[2] and $CF_3COOCH{=}CH_2$[3], and most recently, 1,1,1-trifluoroacetone[4]. In order to aid in making vibrational assignments for some of the compounds such as CF_3COCH_3, normal coordinate calculations have been carried out for trifluoroacetaldehyde and trifluoroacetaldehyde-d in order to obtain a force field to use as a starting point for such compounds. This force field should be reasonably transferable to trifluoroacetone or other CF_3COX compounds because the compounds differ only in the replacement of the H by CH_3 or some other group. A force field for acetone is available, which will provide initial values of force constants for the CH_3–C group[5].

Infrared spectra have been obtained for CF_3CHO and CF_3CDO, most recently by Berney, and he has made vibrational assignments for both compounds[6]. These assignments were used in the normal coordinate calculations reported here.

Normal coordinate calculations

In its most symmetrical configuration, a molecule of CF_3CHO belongs to the C_s point group, giving rise to $10a' + 5a''$ vibrations. An electron diffraction study by Schwendeman[7] yielded the following molecular parameters, which were used in the calculations: C–F = 1.332 Å, C–C = 1.540 Å, C=O = 1.204 Å, C–H = 1.09 Å, $\widehat{FCF} = 108.7°$, $\widehat{CCO} = 121.8°$, $\widehat{HCO} = 120°$. The 17 internal coordinates were used to construct 17 symmetry coordinates identical to those given by Schachtschneider and Snyder for acetaldehyde[8]. The vibrational calculations were done with an IBM 360/40 computer, and utilized programs written by Schachtschneider[8,9] modified slightly to run on our computer.

A search of the literature yielded modified valence force fields for molecules containing the CF_3 group only of the type $CF_3C{\equiv}X$. Force constants of the

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C–CF$_3$ group in CF$_3$CHO were transferred from CF$_3$C≡CH[10] and those involving the –CHO group from CH$_3$CHO[5].

The transferred force constants resulted in reasonably good agreement between observed and calculated frequencies for most of the vibrations, as shown in Table 1. The largest difference between observed and calculated frequencies in the initial calculation was for the C=O stretch. This difference was to be expected because of the increase in double-bond character of the C=O bond compared to acetone with introduction of the fluorine atoms, so the C=O force constant should be larger in the fluorinated compounds than in acetaldehyde.

TABLE 1

OBSERVED AND CALCULATED WAVE NUMBERS (cm^{-1}) FOR CF$_3$CHO AND CF$_3$CDO

CF$_3$CHO				CF$_3$CDO		
Calc. (zero order)	Calc. (final)	Obs.[a]	Assignment	Obs.[a]	Calc. (final)	Calc. (zero order)
a′				*a′*		
2800	2863	2864	ν(CH)	2150	2151	2100
1695	1797	1788	ν(CO)	1770	1760	1661
1441	1378	1384	ρ(CH)ν(CC)	1033	1047	1086
1253	1287	1310	ρ(CH)ν(CC)δ(CF$_3$)ν(CF$_3$)	1302	1316	1269
1212	1206	1202	ν(FCF$_2$)	1244	1213	1234
857	841	840	ν(CF$_3$)ν(CC)	811	808	822
699	723	706	δ(CF$_3$)δ(CCO)	693	682	667
602	554	580	δ(FCF$_2$)	580	550	596
433	427	431	δ(CCO)ρ(CF$_3$)ν(CF$_3$)ν(C–C)	428	425	430
257	252	256	ρ(CF$_3$)	253	250	255
a″				*a″*		
1216	1197	1183	ν(FCF$_2$)	1174	1189	1210
952	963	958	ρ(CH)*op*	842	832	824
606	550	531	δ(FCF$_2$)	521	545	601
345	334	322	ρ(CF$_3$)	318	310	319
—	55	~55	τ(CF$_3$)	~52	51	—

[a] From Ref. 6.

Twelve force constants were simultaneously adjusted to give the best least-squares fit of calculated to observed frequencies for both compounds. Several others were adjusted but no improvement in agreement was obtained, so these force constants were constrained to the transferred values in the final calculation. The C–C stretching force constant was also adjusted initially, but the final value was too large to be reasonable (>6). This behavior resulted from the correlation between C=O and C–C force constants. Therefore, $K_{\mathrm{C-C}}$ was constrained to the transferred value. Both values of $K_{\mathrm{C-C}}$ resulted in approximately the same potential energy distributions for the vibrations involving this force constant.

Berney assigned the CF_3 asymmetric deformation vibrations to bands at *ca.* 580 and 531 cm^{-1} in CF_3CHO and *ca.* 580 and 521 cm^{-1} in CF_3CDO. In all the calculations made here, the calculated values of these two frequencies differed by no more than 5 cm^{-1}. The interaction constants involving the FCF angle were adjusted one or two at a time along with the FCF bending force constant, but the asymmetric deformation frequencies could not be reproduced. All nearest-neighbor interaction constants involving the C–F bond, FCF angle, or CCF angle are included in the force field, and next-nearest-neighbor interactions should not be of such magnitude as to make the calculated frequencies differ by 50 cm^{-1}. We are, therefore, unable to explain the difference of 50 cm^{-1} between the two asymmetric CF_3 deformations unless the very weak band observed at *ca.* 580 cm^{-1} is not a fundamental.

One question raised by Gallasso and Bigotto[10] about assignments of the CF_3–C≡X molecules concerned the bands previously assigned to the C–C stretch at around 800 cm^{-1}. Their potential energy distributions showed this frequency to have the largest character of C–F stretch of any of the frequencies. The calculations also showed the largest contribution of C–C stretch to be to the vibrational frequencies at 1254 and 535 cm^{-1} in $CF_3C{\equiv}CH$. These frequencies have been discussed in more detail by Tuazon, Fateley and Bentley[11].

TABLE 2

FINAL ADJUSTED FORCE CONSTANTS FOR CF_3CHO AND CF_3CDO

Coordinates	Force constant[a]	Coordinates	Force constant[a]
Stretching		*Interaction*	
C–H	4.436 ± 0.017	CF, CF	0.894 ± 0.060
C=O	11.890 ± 0.208	CF, CC	0.247
C–F	5.942 ± 0.061	CF, FCF (C common)	—0.102
C–C	4.626	CF, FCF (CF common)	0.332
Bending		CF, CCF (C common)	—0.328 ± 0.035
F–C–F	1.683 ± 0.038	CF, CCF (CF common)	0.322
C–C–F	0.810 ± 0.020	CC, FCF	—0.209
C–C–H	0.435	CC, CCF	0.199
C–C=O	1.006	CO, HCO	0.259 ± 0.082
H–C=O	0.692 ± 0.021	FCF, FCF	0.059 ± 0.038
C–H *o–p*	0.391 ± 0.005	FCF, CCF (C common)	—0.359
CF_3 τ	0.00181 ± 0.0003	FCF, CCF (CF common)	—0.259
		CCF, CCF	—0.022

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[a] Stretching constants in units of millidynes per angstrom (or newtons per centimeter). Stretch–bend interaction constants in units of millidynes per radian (or 10^{-8} newtons per radian). Bending constants in units of millidyne angstroms per square radian (or 10^{-16} newton centimeters per square radian). Errors were estimated from estimated accuracy of 5 cm^{-1} in all frequencies. All values for which an uncertainty is not given were held constant.

The calculated potential energy distributions for CF_3CHO and CF_3CDO also indicate that the CF_3 symmetric stretch makes its largest contribution to the vibrations at 840 and 811 cm^{-1}, respectively, assigned by Berney to the C–C stretch. The contributions of the CF_3 symmetric stretch and C–C stretch are about 60% and 20%, respectively. The frequencies assigned to the CF_3 symmetric stretch [1310 (H) and 1302 cm^{-1} (D)] have calculated major contributions from the C–H in plane wag, CF_3 symmetric deformation, CF_3 stretch and C–C stretch. There also seems to be considerable mixing of vibrations that give rise to the bands previously assigned to the CF_3 symmetric deformation and C–C=O deformation. There is not much mixing of the other normal modes, especially in the a'' species. The CF_3 torsion is about 99% pure, so mixing of this mode with some others is probably not the reason for the discrepancy between the infrared-determined torsional barrier[6] and the microwave-determined barrier[12].

The frequencies calculated with the final set of force constants are listed in Table 1 and the force constants are given in Table 2.

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