Journal of Fluorine Chemistry, 3 (1973/74) 125–131
© Elsevier Sequoia S.A., Lausanne — Printed in Switzerland

VIBRATIONAL ANALYSIS OF THE 1,1,1-TRIFLUOROETHYL HALIDES*

G. A. CROWDER

Department of Chemistry and Killgore Research Center, West Texas State University, Canyon, Texas 79015 (U.S.A.)

(Received July 17, 1972)

SUMMARY

Normal coordinate calculations have been carried out for CF_3CH_2Cl using a 30-parameter valence force field. The resulting force constants for the CF_3 group have been transferred to CF_3CH_2F, CF_3CH_2Br and CF_3CH_2I with excellent results. Previous vibrational assignments have been revised, the calculations showing that several of the normal modes are highly mixed.

INTRODUCTION

Infrared and Raman spectra have been determined for CF_3CH_2F[1,2], CF_3CH_2Cl[3,4], CF_3CH_2Br[1] and CF_3CH_2I[1], and vibrational assignments have been proposed for all four compounds. However, on the basis of current knowledge of the theory of group vibrations, several of the band assignments do not seem reasonable. For this reason, normal coordinate calculations have been undertaken in order to derive some information about the vibrational frequencies and force constants, and add to the theory of group vibrations for the groups involved.

EXPERIMENTAL

The calculations were carried out with an IBM 360/40 computer and utilized programs written by Schachtschneider[5,6] for the calculation of the G matrix, the solution of the vibrational secular equation and for the least-squares refinement of the force constants to fit the observed frequencies. The programs were modified slightly to run on our computer.

---

* This work was supported by The Robert A. Welch Foundation, Houston, Texas.

NORMAL COORDINATE CALCULATIONS

The trifluoroethyl halide molecules belong to the C_s point group, giving rise to $11a' + 7a''$ vibrations. Symmetry coordinates were constructed from the 20 internal coordinates in order to take advantage of the molecular symmetry in the calculations. The bond lengths and angles of the CF_3CH_2 group were assumed to be the same in all four molecules. The values used were C–F = 1.33 Å, C–C = 1.54 Å, C–H = 1.093 Å; all angles were assumed to be 109° 28′. The carbon–halogen bond lengths of the CH_2X groups were taken to be C–F = 1.385 Å, C–Cl = 1.782 Å, C–Br = 1.938 Å and C–I = 2.140 Å, respectively.

CF_3CH_2Cl

Calculations were first carried out for trifluoroethyl chloride because a force field has been published for ethyl chloride[7] from which initial values for the CH_2Cl group may be transferred. Initial values of force constants for the CF_3 group were transferred from CF_3CHO[8].

The calculated potential-energy distribution showed that the interaction constant between the two HCCl angles was hindering the calculation, and for this reason it was set equal to zero as had been done for $ClCH_2CN$[9]. It was also obvious that H_α and K_X were too small. In addition, either K_S was too large or F_S was too small, or both, because the CF_3 asymmetric stretching frequencies were calculated to be above 1400 cm^{-1} (F_S makes a negative contribution to the potential energy). These values were therefore changed manually until more reasonable values for the frequencies were calculated. Then refinements of some of the force constants were made by the method of least-squares discussed by Schachtschneider[5,6]. Some of the band assignments of Nielsen, Liang and Smith[3] were changed prior to the refinement of the force constants but their frequency values were used.

In the final adjustment, the following force constants were refined: K_r, F_r, F_{RS}, F_S, $F_{X\delta}$, H_α, H_γ, H_β, $F_{\beta\gamma}$, H_δ, H_θ, F_θ, H_ω and H_τ. Values for some of the force constants that were held fixed were obtained by prior refinement or were estimated from the resulting potential-energy distribution. The observed and calculated fundamental frequencies for CF_3CH_2Cl are listed in Table 1, together with the approximate normal coordinate description of the vibrations in terms of the symmetry coordinates.

Nielsen, Liang and Smith[3] assigned bands observed at 905, 1110, 1339 and 1443 cm^{-1} to the CH_2 wag, rock, bend and twisting vibrations, respectively. The normal order of these frequencies is that shown in Table 1. These authors also assigned a weak infrared band at 455 cm^{-1} to the a'' CF_3 deformation and the C–C stretch to a band at 855 cm^{-1}. It appears unlikely that the asymmetric CF_3 deformations will differ by 96 cm^{-1}, and in the present calculations these vibrations were assumed to be accidentally degenerate at 541 cm^{-1}. The major contribution to the 855 cm^{-1} band is from the CF_3 symmetric stretch, and the C–C stretch makes its major contribution to the band at 1339 cm^{-1}. These calculations are in agreement with those made for other fluorine-containing molecules, a number of which have been discussed by Tuazon, Fateley and Bentley[10].

TABLE 1

OBSERVED AND CALCULATED WAVE NUMBERS (cm^{-1}) AND ASSIGNMENT FOR CF_3CH_2Cl

Obs.	Calc.	Description[a] (approx. PED[b])
a′		
2994	2994	CH_2 ss(99)
1443	1443	CH_2 δ(81); C–C s(14)
1339	1339	C–C s(39); CF_3 sδ(30); CF_3 ss(28); CH_2 w(11)
1267	1265	CF_3 as(43); CH_2 w(21); CF_3 aδ(17); CF_3 r(11)
1159	1159	CH_2 w(59); CF_3 as(17); CF_3 ss(11)
855	855	CF_3 ss(44); C–C s(30)
801	800	C–Cl s(84)
639	640	CF_3 sδ(50); C–C s(18)
541	542	CF_3 aδ(68); CF_3 as(18)
330	325	CF_3 r(56); C–Cl s(14)
180	182	C–C–Cl δ(59); CF_3 r(26)
a″		
3044	3044	CH_2 as(99)
1277	1279	CF_3 as(47); CF_3 aδ(18); CH_2 tw(17); CH_2 r(11)
1110	1111	CH_2 tw(77); CH_2 r(10)
905	905	CH_2 r(71); CF_3 as(20)
541	541	CF_3 aδ(70); CF_3 as(17)
355	358	CF_3 r(85); CF_3 as(15)
109	109	C–C τ(89); CH_2 r(6); CF_3 r(4)

[a] Abbreviations used: ss = symmetric stretch, δ = deformation, s = stretch, w = wag, as = asymmetric stretch, r = rock, sδ = symmetric deformation, aδ = asymmetric deformation, tw = twist, τ = torsion.

[b] Only potential energy contributions of 10 % or greater are given, except for torsion.

CF_3CH_2Br

The final force constant values obtained for CF_3CH_2Cl were used as the initial values for CF_3CH_2Br. The zero-order calculated frequencies were used to revise the vibrational assignment given by Edgell, Riethof and Ward[1] who assigned the bands observed at 843, 868, 1082, 1140 and 1308 cm^{-1} to the C–C stretch, CH_2 wag, CH_2 rock, C–F stretch and CH_2 twist, respectively.

In order to support the present assignments and to check the transferability of the force constants of the CF_3 group, only those force constants of the CH_2X group were initially adjusted while those of the C–CF_3 group were constrained to the chloride value. However, there seemed to be small differences in the calculated value of K_R and H_ω among the halides. For this reason, the 10 force constants K_r, F_r, K_R, K_X, H_α, H_β, H_γ, H_δ, H_ω and $F_{\beta\gamma}$ were refined while constraining the other 20 constants to the trifluoroethyl chloride values.

CF_3CH_2I

The final force constant values obtained for CF_3CH_2Br were used as the initial ones for CF_3CH_2I, and as a result five of the band assignments given by Edgell, Riethof and Ward had to be changed. They assigned the bands at 142, 289, 844, 1127 and 1286 cm^{-1} to the *a′* CF_3 rock, CH_2I rock, C–C stretch, C–F stretch and CH_2 wag respectively. The same 10 force constants as listed for the bromide were refined while constraining the other 20 constants to the chloride value.

CF_3CH_2F

The final force constant values obtained for CF_3CH_2Cl were used as the initial set for the fluoride. Several changes also had to be made in the band assignments of this compound. Two bands in the region 1050–1100 cm^{-1} were assigned as fundamentals, but when the frequencies of all four halides were compared it was obvious that only the C–F stretch of the CH_2F group should lie in this region. In addition, it seems likely that only one of the two bands at 908 and 972 cm^{-1} should be assigned as a fundamental. The 908 cm^{-1} infrared band is weak and there is no corresponding Raman band, and for this reason the 972 cm^{-1} band was chosen as the CH_2 rock. The chloride value was then equal to 905 cm^{-1} while the fluoride frequency should be higher than this.

Under these circumstances, however, it was not possible to assign a band to the CH_2 twist. For this reason, the values for H_β, H_γ and $F_{\beta\gamma}$ were determined by refining these constants to fit those frequencies other than the CH_2 twist to which they make a significant contribution to the potential energy. These are mainly the bands at 1374, 1296, 1187 and 972 cm^{-1}. When this was done, the CH_2 twist frequency was calculated as 1184 cm^{-1}, only 4 cm^{-1} lower than the calculated value for the wag, although it should be borne in mind that the wagging mode mixes significantly with other modes.

During the refinement of the 10 force constants listed previously for the bromide, the C–C stretching constant oscillated between 4.60 and 4.65 N cm^{-1} without converging to a final value. Therefore, K_R was constrained to the chloride value, 4.626 N cm^{-1}, and the other nine constants were refined.

DISCUSSION

The observed and calculated wave numbers and fundamental vibrational assignments of the trifluoroethyl halides are given in Table 2. Only the major contribution is listed in the assignment but a number of the normal modes are highly mixed, as shown for the chloride in Table 1. The amount of mixing is approximately the same in all four compounds but there are some differences, usually in the percentage contributions. One big difference lies in the two smallest *a′* frequencies. For the chloride, bromide and iodide, these two frequencies

TABLE 2

OBSERVED AND CALCULATED WAVE NUMBERS (cm^{-1}) AND BAND ASSIGNMENTS FOR THE 1,1,1-TRIFLUOROETHYL HALIDES

Assignment	CF_3CH_2F		CF_3CH_2Cl		CF_3CH_2Br		CF_3CH_2I	
	Obs.[a]	Calc.	Obs.[b]	Calc.	Obs.[c]	Calc.	Obs.[c]	Calc.
CH_2 sym. str.	2984	2984	2994	2994	2992	2992	2991	2991
CH_2 bend	1431	1431	1443	1443	1433	1433	1430	1429
C–C str.	1374	1371	1339	1339	1308	1306	1286	1291
CF_3 asym. str.	1296	1298	1267	1265	1250	1258	1223	1244
CH_2 wag	1189	1191	1159	1159	1140	1141	1127	1120
CF_3 sym. str.	843	853	855	855	843	846	844	840
C–X str.	1096	1096	801	800	723	725	671	672
CF_3 sym. def.	666	661	639	640	633	632	632	622
CF_3 asym. def.	550	546	541	542	528	528	537	521
CF_3 rock	409	385	330	325	314	291	289	275
CCX bend	225	246	180	182	161	157	142	134
CH_2 asym. str.	3015	3015	3044	3044	3025	3025	3044	3044
CF_3 asym. str.	1296	1302	1277	1279	1280	1276	1275	1276
CH_2 twist	1189	1199	1110	1111	1082	1080	1060	1062
CH_2 rock	972	967	905	905	868	869	880	881
CF_3 asym. def.	541	545	541	541	528	527	516	521
CF_3 rock	350	358	355	358	355	357	355	357
Torsion	120	139	109	109	101	97	94	91

[a] From Refs. 1 and 2.
[b] From Refs 3 and 4.
[c] From Ref. 1.

represent mixtures of CF_3 rock (~60%) and C–X stretch (~20%, with this contribution increasing from 14% in the chloride to 27% in the iodide) for the next to the smallest frequency, and the smallest frequency representing about 60% C–C–X bend and 20% CF_3 rock. However, in the fluoride, the two smallest *a'* frequencies both represent approximately equal mixtures of the CF_3 rock and C–C–F bend. These two frequencies show the largest differences between observed and calculated values of all the frequencies for the fluoride. This behavior suggests that some interaction constant which has been neglected is considerably more important in the fluoride than in the other halides. The torsional force constant does not reproduce the fluoride torsional frequency as well as for the other halides, suggesting that the CH_2F fluorine must affect this force constant more so than does the corresponding bromine or iodine.

The force constants used to calculate the frequencies given in Tables 1 and 2 are listed in Table 3. The good agreement between calculated and observed frequencies for CF_3CH_2F, CF_3CH_2Br and CF_3CH_2I, using CF_3 force constant values transferred from CF_3CH_2Cl, support the present vibrational assignments and indicate that these force constants are at least very nearly the same in all four molecules, although there is nothing unique about the set derived here.

TABLE 3

FORCE CONSTANTS FOR THE 1,1,1-TRIFLUOROETHYL HALIDES[a]

Force constant	Coordinate(s) involved	CF_3CH_2F	CF_3CH_2Cl	CF_3CH_2Br	CF_3CH_2I
Stretch					
K_r	C–H	4.897	4.968	4.936	4.966
K_R	C–C	4.626[b]	4.626[b]	4.386	4.251
K_S	C–F	5.417[b]	5.417	5.417[b]	5.417[b]
K_X	C–X	6.045	3.700	3.358	2.951
Stretch–stretch					
F_r	C–H, C–H	0.078	0.046	0.072	0.041
F_S	C–F, C–F	1.597[b]	1.597	1.597[b]	1.597[b]
F_{RS}	C–C, C–F	0.425[b]	0.425	0.425[b]	0.425[b]
F_{RX}	C–C, C–X	0.550[b]	0.550[b]	0.550[b]	0.550[b]
Bend					
H_α	HCH	0.400	0.454	0.457	0.443
H_β	HCC	0.755	0.688	0.693	0.716
H_γ	HCX	0.905	0.727	0.635	0.633
H_δ	CCX	1.112	0.927	1.064	0.933
H_θ	CCF	0.761[b]	0.761	0.761[b]	0.761[b]
H_ω	FCF	1.810	1.774	1.657	1.603
Stretch–bend					
$F_{R\delta}$	C–C, CCX	0.084[b]	0.084[b]	0.084[b]	0.084[b]
$F_{R\theta}$	C–C, CCF	0.199[b]	0.199[b]	0.199[b]	0.199[b]
$F_{R\omega}$	C–C, FCF	−0.209[b]	−0.209[b]	−0.209[b]	−0.209[b]
$F_{X\gamma}$	C–X, HCX	0.333[b]	0.333[b]	0.333[b]	0.333[b]
$F_{X\delta}$	C–X, CCX	0.325[b]	0.325	0.325[b]	0.325[b]
$F_{S\theta}$	C–F, CCF (C–C common)	−0.100[b]	−0.100[b]	−0.100[b]	−0.100[b]
$F'_{S\theta}$	C–F, CCF (C common)	0.100[b]	0.100[b]	0.100[b]	0.100[b]
$F_{S\omega}$	C–F, FCF (C–F common)	−0.102[b]	−0.102[b]	−0.102[b]	−0.102[b]
$F'_{S\omega}$	C–F, FCF (C common)	0.332[b]	0.332[b]	0.332[b]	0.332[b]
Bend–bend					
F_θ	CCF, CCF	−0.274[b]	−0.274	−0.274[b]	−0.274[b]
$F_{\beta\gamma}$	HCC, HCX (H–C common)	0.252	0.144	0.106	0.135
$F'_{\beta\gamma}$	HCC, HCX (C common)	0.019[b]	0.019[b]	0.019[b]	0.019[b]
$F_{\theta\omega}$	CCF, FCF (C–F common)	−0.359[b]	−0.359[b]	−0.359[b]	−0.359[b]
$F'_{\theta\omega}$	CCF, FCF (C common)	−0.259[b]	−0.259[b]	−0.259[b]	−0.259[b]
F_ω	FCF, FCF	0.059[b]	0.059[b]	0.059[b]	0.059[b]
Torsion					
H_τ	C–C	0.0217[b]	0.0217	0.0217[b]	0.0217[b]

[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).

[b] Constrained.

REFERENCES

1 W. F. Edgell, T. R. Riethof and C. Ward, *J. Mol. Spectroscopy, 11* (1963) 92.
2 A. Danti and J. L. Wood, *J. Chem. Phys., 30* (1959) 582.
3 J. R. Nielsen, C. Y. Liang and D. C. Smith, *J. Chem. Phys., 21* (1953) 1060.
4 E. Catalano and K. S. Pitzer, *J. Phys. Chem., 62* (1958) 838.
5 J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta, 19* (1963) 117.
6 J. H. Schachtschneider, *Shell Development Co. Tech. Repts.*, Nos. 231–264 (1964) and 57–65 (1965).
7 A. B. Dempster and G. Zerbi, *J. Mol. Spectroscopy, 39* (1971) 1.
8 G. A. Crowder, *J. Fluorine Chem., 2* (1972/73) 107.
9 G. A. Crowder, *Mol. Phys., 23* (1972) 707.
10 E. C. Tuazon, W. G. Fateley and F. F. Bentley, *Appl. Spectroscopy, 25* (1971) 374.