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NORMAL COORDINATE ANALYSIS OF CF_3CH_3

G. A. CROWDER

Department of Chemistry
West Texas State University
Canyon, Texas 79016 (USA)

SUMMARY

Normal coordinate calculations were made for CF_3CH_3, using a twenty-two parameter modified valence force field. Thirteen force constants were constrained to the CF_3CH_2X values and nine were adjusted to fit the twelve frequencies, resulting in an average error of 2.3 cm^{-1}. The CF_3 group force constants should be useful in calculations for other compounds containing this group.

INTRODUCTION

Ideal gas thermodynamic properties of CF_3-CH_3 have recently been published by Chen, et al (1). These authors stated that drastically conflicting assignments for some vibrational modes have been published (2-4), but that later assignments by Nielsen, et al (5,6) appear consistent and reliable. Several years later, Bucker and Nielsen made normal coordinate calculations for this molecule, using a Urey-Bradley force field that included nineteen force constants (7). Those calculations included an error in the symmetry coordinates, and they were redone by Lafon and Nielsen (8), using the same force field, except that the five primed force constants were constrained to the values of minus one-tenth of the corresponding unprimed force constant. All fourteen unprimed constants were adjusted to provide the best fit of twenty-two frequencies of CF_3CH_3 and CF_3CD_3.

Normal coordinate calculations have recently been made for CF_3CH_2X molecules (X = F, Cl, Br, I) which showed excellent transferability of the force constants of the CF_3 group among these molecules (9). The calculations have now been repeated for CF_3CH_3 in order to obtain a modified valence force field for this molecule and to check the transferability of the CF_3 force constants from the CF_3CH_2X molecules to CF_3CH_3. The resulting force field should be useful for other hydrocarbons that contain a terminal CF_3 group. The MVFF has been used to a greater extent than the UBFF in recent years.

NORMAL COORDINATE CALCULATIONS

The calculations were made with a PDP-10 computer and utilized programs written by Schachtschneider (10,11) for calculation of the G matrix (gmat), solution of the vibrational secular equation (vsec), and for the least-squares refinement of designated force constants to fit the calculated frequencies to the observed values (fpert). The molecular parameters used were: C-C = 1.53Å, C-H = 1.90Å, C-F = 1.33Å, and all angles were assumed to be tetrahedral.

RESULTS AND DISCUSSION

In the initial calculation, the force constants were taken from CF_3CH_2I (9), except for H_β and F_β, which were taken from a hydrocarbon force field (11), and H_τ, which was taken from propyl bromide (12). F_τ was not used for CF_3CH_2X. The resulting calculated wavenumbers were reasonable, except for two values (obs., 1408, 970; calc., 1476, 927). The average error for the other ten frequencies was 9.7 cm^{-1}.

In the next calculation, five constants of the CH_3 group (K_r, F_r, H_α, H_β, F_β) were refined by the fpert program, resulting in an average error of 8.0 cm^{-1}, with the largest error being 21 cm^{-1} for the 1408 cm^{-1} value. Several more runs were made, and in the next to the final run, twelve constants were refined, resulting in an average error of 2.0 cm^{-1}. However, five of the constants that were refined differed from the transferred values by less than 0.01 unit. These five were K_r, H_β, $F_{R\theta}$, $F_{\omega\theta}$, and H_τ. The constants K_r and F_r solely determine the two CH_3 stretching frequencies, and H_τ alone determines the torsional frequency, and these three constants must be refined in order to fit those three frequencies exactly. Therefore, K_r and H_τ were allowed to vary in the final calculation, but the other three were added to the list of constants constrained to the transferred values. In the final calculation, nine force constants were refined, resulting in an average error of 2.3 cm^{-1}. The observed and calculated wavenumbers are listed in Table 1, along with the approximate potential energy distribution in terms of the symmetry coordinates. The resulting force constants are listed in Table 2.

The potential energy distributions given in Table 1 show considerable mixing of the coordinates for most of the frequencies, as was found by Bucker and Nielson (8). However, the relative contributions of different coordinates differ in the two sets of calculations. Table 2 shows that six of the eight diagonal force constants were constrained to the transferred values, and the other two differ by only 0.01 and 0.05 units from the transferred values. Only one force constant ($F_{S\omega}$) differs from the transferred value by more than 0.1 unit. This shows the excellent transferability of these constants and also provides support for the correctness of the vibrational assignment.

Bucker and Nielsen obtained a C-C force constant considerably higher than the value in ethane and they concluded that fluorine substitution strengthens the C-C bond. The C-C force constant used in the present work is a little lower than that in ethane (10). The JZ matrix shows that the C-C constant has only a small effect on the frequencies, and therefore a relatively large change in this constant is required to effect a small change in frequency. This was also undoubtedly the case during Bucker and Nielsen's work, and no conclusion about the bond strength can be drawn from the magnitude of the force constant.

It should be pointed out that the agreement between observed and calculated wavenumbers could be improved even beyond the average error of 2.3 cm^{-1} by refining additional constants and by including additional constants in the force field, e.g., $f^{t}_{\beta\theta}$ and $f^{g}_{\beta\theta}$. However, it seems more important to have a transferrable force field that gives an acceptable error than to try to obtain the lowest average error by refining as many constants as possible. The average error for CF_3CH_3 obtained by Lafon and Nielsen was 9.1 cm^{-1}. However, the fit for both hydrogen and deuterium compounds could not be expected to be as good as for only one of them.

TABLE 1

Observed and calculated wavenumbers and approximate potential energy distribution for CF_3-CH_3

Obs.[a] cm^{-1}	Calc. cm^{-1}	Normal coordinate description (approximate P.E.D.)[b]
		A_1 species
2975	2975	CH_3ss(100)
1408	1413	CH_3sδ(51),C-Cs(36),CF_3sδ(14),CF_3ss(13)
1280	1274	CH_3sδ(39),CF_3ss(36),CF_3sδ(28).
830	826	CF_3ss(46),C-Cs(34),CF_3sδ(10)
602	600	CF_3sδ(52),C-Cs(27)
		A_2 species
220	220	torsion(100)
		E species
3035	3035	CH_3as(99)
1443	1442	CH_3aδ(77),CH_3r(21)
1233	1236	CH_3r(38),CF_3as(32),CH_3aδ(17),CF_3aδ(10), CF_3r(10)
970	967	CF_3as(54),CH_3r(39),CF_3aδ(13)
541	539	CF_3aδ(85)
365	362	CF_3r(89),CF_3as(17)

[a] Observed values are from ref. 7 and 12 (torsion).

[b] Contributions less than 10% are excluded. Abbreviations used: ss=symmetric stretch, sδ=symmetric deformation, s=stretch, as=antisymmetric stretch, aδ=antisymmetric deformation, r=rock.

TABLE 2

Force constants for CF_3-CH_3

Force constant	Coordinate(s) involved	Common atom(s)	Initial value[a]	Final value[a]	Standard error[b]
Stretch					
K_r	C-H	-	4.966	4.958	0.008
K_R	C-C	-	4.251	4.251	-
K_S	C-F	-	5.417	5.417	-
Stretch-stretch					
F_r	C-H,C-H	C	0.041	0.067	0.005
F_S	C-F,C-F	C	1.597	1.597	-
F_{RS}	C-C,C-F	C	0.425	0.425	-
Bend					
H_α	H-C-H	-	0.540	0.502	0.002
H_β	C-C-H	-	0.716	0.716	-
H_θ	C-C-F	-	0.761	0.761	-
H_ω	F-C-F	-	1.603	1.603	-
Stretch-bend					
$F_{R\omega}$	CC,FCF	C	-0.209	-0.209	-
$F_{R\theta}$	CC,CCF	C-C	0.199	0.199	-
$F_{S\omega}$	CF,FCF	C-F	-0.102	-0.361[c]	-
$F'_{S\omega}$	CF,FCF	C	0.322	0.306	0.022
$F_{S\theta}$	CF,CCF	C-F	-0.100	-0.100	-
$F'_{S\theta}$	CF,CCF	C	0.100	0.100	-
Bend-bend					
F_β	CCH,CCH	C-C	-0.017	-0.113	0.005
F_ω	FCF,FCF	C-F	0.059	0.014	0.018
F_θ	CCF,CCF	C-C	-0.274	-0.231	0.016
$F_{\omega\theta}$	FCF,CCF	C-F	-0.359	-0.359	-
$F'_{\omega\theta}$	FCF,CCF	C	-0.259	-0.194	0.029
Torsion					
H_τ	C-C	-	0.00950	0.00977	0.00035

[a] Stretching constants are in units of millidynes per angstrom. Stretch-bend interaction constants are in units of millidynes per radian. Bending constants are in units of millidyne angstroms per square radian.

[b] Constants for which no standard error is given were constrained to the transferred values.

[c] This constant was refined in a prior run, but held fixed in the final run.

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