InfraRed and Raman Spectra of Fluorinated Ethanes II: 1,1,1Trifluoroethane

J. Rud Nielsen, Howard H. Claassen, and D. C. Smith

Infra-Red and Raman Spectra of Fluorinated Ethanes II: 1,1,1-Trifluoroethane*

J. Rud Nielsen and Howard H. Claassen
Department of Physics, University of Oklahoma, Norman, Oklahoma

AND

D. C. Smith
Naval Research Laboratory, Washington, D. C.

(Received July 21, 1950)

The infra-red absorption spectrum of gaseous 1,1,1-trifluoroethane between 2 and 23μ has been investigated with a prism spectrometer of high resolution. The Raman spectrum of CF_3-CH_3 in the gaseous state has been photographed with a three-prism glass spectrograph of linear dispersion 15A/mm at 4358A. The 12 fundamental frequencies have been assigned, and the spectra have been interpreted in detail. Thermodynamic functions have been calculated. A value of 3290 cal./mole has been obtained for the potential barrier opposing internal rotation.

INTRODUCTION

THE Raman spectrum of CF_3-CH_3 in the liquid state at $-75°C$ has been studied by Hatcher and Yost.[1] Some corrections to their data were given by Russell, Golding and Yost.[2] The infra-red spectrum of CF_3-CH_3 has been studied by Thompson and Temple.[3] Attempts at the assignment of fundamentals have been made by Kohlrausch,[4] Russell, Golding and Yost,[2] Thompson and Temple,[3] and Herzberg.* There is wide divergence among the assignments proposed by these workers, and none has attempted to determine the twisting frequency. Recently, Daily, Minden and Shulman,[5] have derived a value for the twisting frequency from the relative intensities at different temperatures of certain microwave absorption lines.

EXPERIMENTAL

The sample of 1,1,1-trifluoroethane was prepared and purified in the Jackson Laboratory of E. I. du Pont de Nemours and Company. No information was available about its purity. However, some of the very weak infra-red bands observed appear to be caused by impurities.

The infra-red absorption spectrum of gaseous CF_3-CH_3 was measured over the range from 2 to 23μ by means of a prism spectrometer of high resolution.[6] The Raman spectrum of the compound in the gaseous state was photographed by means of a three-prism glass spectrograph of linear dispersion 15A/mm at 4358A. This instrument and the irradiation apparatus used have been briefly described elsewhere.[7]

RESULTS

The infra-red absorption of CF_3-CH_3 gas between 2 and 23μ is shown in Fig. 1. The wave numbers of the observed absorption maxima are given in the first column of Table I. In the second column relative intensities are indicated and for some bands unusual sharpness. The observed Raman shifts for gaseous CF_3-CH_3 are listed in the first column of Table II. In the second column are given rough estimates of the relative intensities of the bands, as well as indication about unusual sharpness or diffuseness. The following abbreviations are used in both tables: *vs* very strong, *s* strong, *m* medium, *w* weak, etc., *sh* sharp, *d* diffuse.

A comparison of the infra-red data with those of Thompson and Temple[3] is made difficult by the great difference in resolution. It shows, however, that the bands observed by them at 684 and 900 cm^{-1} must have been caused by impurities. All of the Raman bands observed by Hatcher and Yost in liquid CF_3-CH_3 were here in the gas, most of the bands being shifted a few cm^{-1} toward greater wave numbers. One new Raman band at 1232 cm^{-1} was observed and also rotational branches of two bands.

ASSIGNMENT OF FUNDAMENTALS

Electron diffraction work of Brockway and Livingston[8] has given the $C-C$ distance $=1.45\pm0.05A$, $C-F$ distance $1.33\pm0.03A$, FCF angle $=108\frac{1}{2}\pm2°$. Assuming a $C-H$ distance of 1.09A and tetrahedral angles for the methyl group, the following moments of inertia were calculated

$$I_A=I_B=155\times10^{-40}, \quad I_C=152\times10^{-40} \text{ g cm}^2.$$

Thus, the molecule is very nearly spherical and the parallel and perpendicular bands may be expected to have similar contours.

The CF_3-CH_3 molecule undoubtedly has the symmetry C_{3v}, the fluorine atoms being either "eclipsed"

* This work has been supported by the ONR under Contract N7onr-398, Task Order I.
[1] J. B. Hatcher and D. M. Yost, J. Chem. Phys. **5**, 992 (1937).
[2] Russell, Golding, and Yost, J. Am. Chem. Soc. **66**, 16 (1944).
[3] H. W. Thompson and R. B. Temple, J. Chem. Soc. **90**, 1428 (1948).
[4] K. W. F. Kohlrausch, *Ramanspektren* (Akademische Verlagsgesellschaft Becker & Erler, Leipzig, 1943), p. 173.
* Private communication to J. Rud Nielsen.
[5] Dailey, Minden, and Shulman, Phys. Rev. **75**, 1319 (1949).
[6] Nielsen, Crawford, and Smith, J. Opt. Soc. Am. **37**, 296 (1947).
[7] Smith, Nielsen, and Claassen, J. Chem. Phys. **18**, 326 (1950).
[8] L. O. Brockway and R. L. Livingston, Abstracts, Am. Chem. Soc. Meeting, Buffalo, New York, 1942.

or "staggered" with respect to the hydrogen atoms. In either case, the normal vibrations divide into symmetry species in the following manner: $5A_1+1A_2+6E$. The fundamentals of species A_1 and E are active both in infra-red absorption and in the Raman effect. The torsional oscillation of species A_2, on the other hand, is inactive both in the infra-red and in the Raman effect.

Since the mass of a methyl group is not much smaller than that of a fluorine atom, the problem of assigning the fundamental vibration frequencies for CF_3-CH_3 may be conveniently attacked by taking the vibration spectrum of CF_4 as a starting point. This spectrum consists[9] of a doubly degenerate fundamental at 437 cm⁻¹, a triply degenerate at 635, a totally symmetrical at

904, and a triply degenerate fundamental near 1265 cm⁻¹. Consideration of the correlations between CF_4 and molecules of type XCF_3 leads to the conclusion that the "skeletal vibrations" of CF_3-CH_3 consist of a doubly degenerate fundamental near 400 cm⁻¹, a fundamental of species E and another of species A_1 in the neighborhood of 900 cm⁻¹, and E and A_1 fundamentals near 1250 cm⁻¹.

The Raman band at 365 cm⁻¹, which has the diffuse appearance typical of doubly degenerate bands, must be the lowest E fundamental. It may be roughly characterized as a rocking of the methyl group. Of the next two skeletal frequencies the totally symmetrical is lower for both $ClCF_3$ and Cl_3CF, according to Kahovec
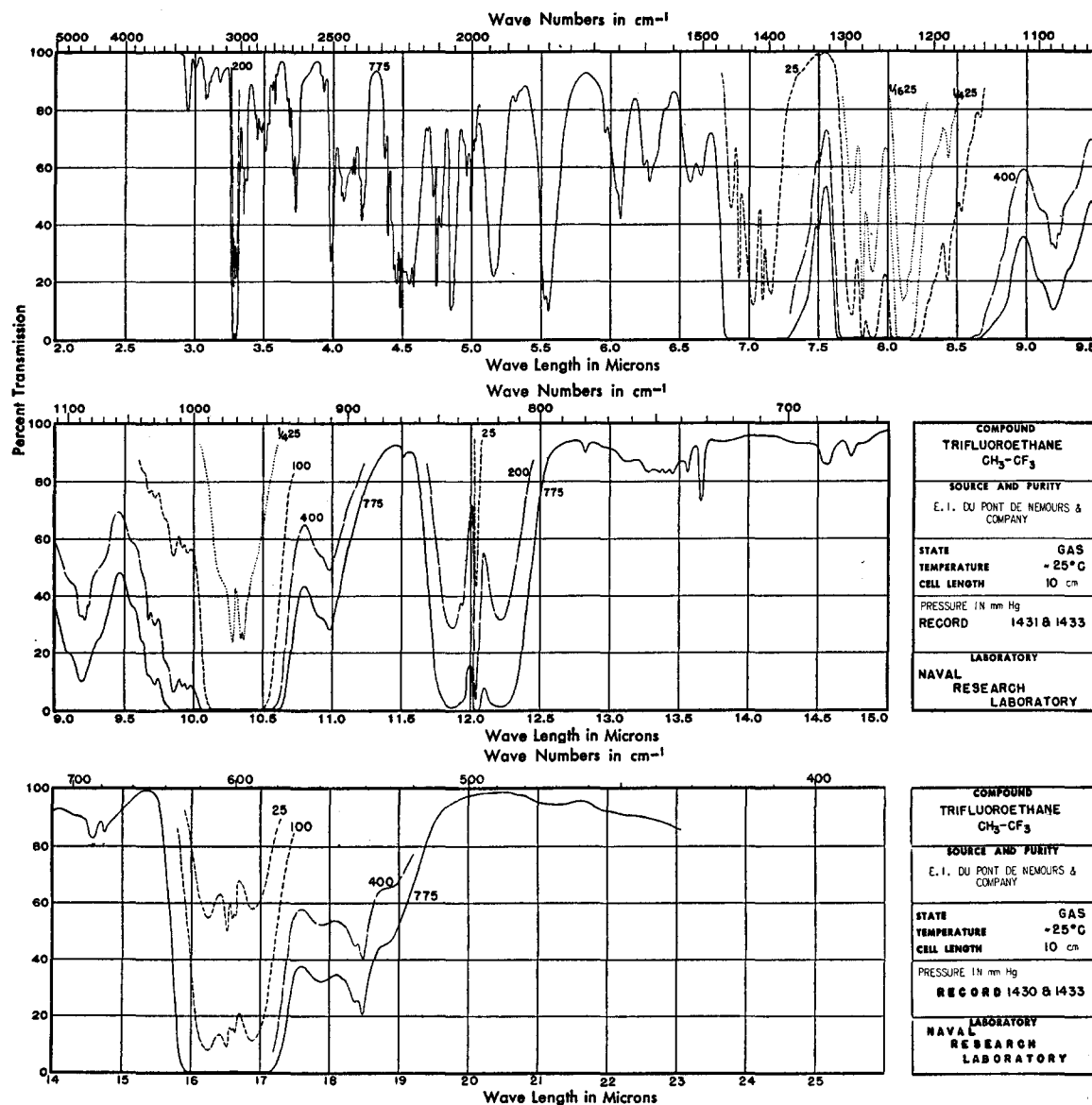

FIG. 1. Infra-red absorption spectrum of gaseous 1,1,1-trifluoroethane.

9 See reference 4, p. 151.

TABLE I. Infra-red spectrum of $CF_3 \cdot CH_3$ (gas).

Wave number	Description	Interpretation
$\sim$ 470 cm^{-1}	vvw	$2 \times 238 = 476$ (A_1); $830 - 365 = 465$ (E)
530	w	
541	m sh	E fundamental
546	m	
560	w	
594	s	
600	s	
602	s	$238 + 365 = 603$ (E)
605	s sh	A_1 fundamental
616	s	
678	vvw	$1280 - 604 = 676$ (A_1), or impurity
$\sim$ 686	vw	$1233 - 541 = 692$ $(A_1 + A_2 + E)$, or impurity
732	w sh	$2 \times 365 = 730$ $(A_1 + E)$, or impurity
737	vw sh	$1280 - 541 = 739$ (E)
743	vw	
746	vw	
749	vw	
$\sim$ 754	vw	
762	vw	
780	vvw	$238 + 541 = 779$ (E)
$\sim$ 818	s	
831	s sh	A_1 fundamental
838	w	$1443 - 604 = 839$ (E)
$\sim$ 842	s	
869	vvw	Impurity
911	m	$365 + 541 = 906$ $(A_1 + A_2 + E)$
918	w	$1280 - 365 = 915$ (E)
965	vs sh	
967	vs sh	$365 + 604 = 969$ (E)
973	vs sh	E fundamental
1005	m	
1008	m	Impurity (C_3F_8)
1015	m	
1029	m	
1034	m	$604 + 970 - 541 = 1033$ $(A_1 + A_2 + E)$
$\sim$ 1045	w	$1408 - 365 = 1043$ (E)
$\sim$ 1070	w	
1082	m	$1443 - 365 = 1078$ $(A_1 + A_2 + E)$
1086	m sh	$2 \times 541 = 1082$ $(A_1 + E)$
1089	m	
$\sim$ 1100	w	
1155		Impurity
1172	w sh	$365 + 830 = 1195$ (E)
1186	m sh	$2 \times 604 = 1208$ (A_1); $238 + 970 = 1208$ (E)
1208		$1443 - 238 = 1205$ (E)
1233	vs	E fundamental
1267		
1280	vs sh	A_1 fundamental
1292		
1333	vw	$365 + 970 = 1335$ $(A_1 + A_2 + E)$
1397	s	
1408	s sh	A_1 fundamental
1422	s	
1443	s sh	E fundamental
1456	s	
1504	w	$541 + 970 = 1511$ $(A_1 + A_2 + E)$
1522	w	$830 + 1233 - 541 = 1522$ $(A_1 + A_2 + E)$

TABLE I.—(Continued)

Wave number	Description	Interpretation
$\sim$ 1570	vvw	$604 + 970 = 1574$ (E)
1592	w	$365 + 1233 = 1598$ $(A_1 + A_2 + E)$
1603	vw	
1647	m	$365 + 1280 = 1645$ (E)
$\sim$ 1660	w	$2 \times 830 = 1660$ (A_1)
1678	w	$238 + 1443 = 1681$ (E)
1802	s	$830 + 970 = 1800$ (E)
1808	s	$365 + 1443 = 1808$ $(A_1 + A_2 + E)$
1883	vvw	$604 + 1280 = 1884$ (A_1)
1938	m	$2 \times 970 = 1940$ $(A_1 + E)$
1992	vw	$541 + 1443 = 1984$ $(A_1 + A_2 + E)$?
1997	vw	Impurity?
2002	w sh	Impurity?
2006	vw	$2 \times 365 + 1280 = 2010$ $(A_1 + E)$
2015	vw	$604 + 1408 = 2012$ (A_1)
2061	m	$830 + 1233 = 2063$ (E)
2093	m	
2106	m sh	$830 + 1280 = 2110$ (A_1)
2117	m	
2137	vvw	
2183	m sh	$365 + 541 + 1280 = 2186$ $(A_1 + A_2 + E)$
2197	m	$970 + 1233 = 2203$ $(A_1 + A_2 + E)$
2215	m	
2231	m sh	$830 + 1408 = 2238$ (A_1)
2242	m	
2251	w	$970 + 1280 = 2250$ (E)
2273	m sh	$830 + 1443 = 2273$ (E)
2286	w sh	
2369	w	
2376	w sh	$970 + 1408 = 2378$ (E)
$\sim$ 2386	w	
2406	vw	$970 + 1443 = 2413$ $(A_1 + A_2 + E)$
2415	vw	
2451	w sh	$2 \times 1233 = 2466$ $(A_1 + E)$
2460	w	
2509	w sh	$1233 + 1280 = 2513$ (E)
2542	vvw	$2 \times 1280 = 2560$ (A_1)
2615	vvw	$2975 - 365 = 2610$ (E)
2630	vvw	$1233 + 1408 = 2641$ (E)
2681	w sh	$1233 + 1443 = 2676$ $(A_1 + A_2 + E)$
2694	vw	$1280 + 1408 = 2688$ (A_1)
2714	vw	$604 + 830 + 1280 = 2714$ (A_1)
2725	vvw	$1280 + 1443 = 2723$ (E)
2784	vvw	
2794	vvw sh	$3035 - 238 = 2797$ (E)
2807	vvw	$2 \times 1408 = 2816$ (A_1)
2833	vvw	$604 + 830 + 1408 = 2842$ (A_1)
2849	w sh	$1408 + 1443 = 2851$ (E)
2860	vw	
2874	vw	$604 + 830 + 1443 = 2877$ (E)
2882	vw	$2 \times 1443 = 2886$ $(A_1 + E)$
2897	w sh	$3 \times 970 = 2910$ $(A_1 + A_2 + E)$
2910	vvw	$365 + 2 \times 1280 = 2925$ (E)
2967	vw	
2978	w sh	A_1 fundamental
2987	vw	

TABLE I.—*Continued*

Wave number	Description	Interpretation
3025	m	
3036	$m\ sh$	E fundamental
3049	m	
3143	vw	$541+2975-365=3151\ (A_1+A_2+E)$
3234	vw	
3249	vw	$238+3035=3273\ (E)$
3336	vvw	$365+2975=3340\ (E)$
3397	vw	$365+3035=3400\ (A_1+A_2+E)$

and Wagner,[10] but in neither case is the difference in frequency great. For CCl_3-CH_3 Wagner,[11] on the basis of a valence force model and considering the methyl group as a mass point, calculated almost equal values for these two frequencies but found from polarization measurements that the E fundamental lies somewhat lower than the A_1 fundamental. In the case of CF_3-CH_1 the frequencies in question are undoubtedly 541 and 602 cm⁻¹, of which the former has medium and the latter high intensity in the infra-red. The Raman band at 541 cm⁻¹ is diffuse, whereas the Raman band at 602 cm⁻¹ is sharp. Thus, there can be little doubt that 541 cm⁻¹ is an E and 602 cm⁻¹ an A_1 fundamental. These skeletal fundamentals may be characterized roughly as CF_3 deformations.

The frequency at 830 cm⁻¹, which is observed as an intense infra-red absorption band and as a strong and sharp Raman band, must be the skeletal fundamental of species A_1 corresponding to the "breathing vibration" of CF_4. It may be designated very roughly as largely a $C-C$ stretching frequency.

The very intense infra-red bands at 1233 and 1280 cm⁻¹ must represent the remaining two skeletal fundamentals. Both of them may be roughly characterized as $C-F$ stretching modes. According to Kahovec and Wagner,[10] the E fundamental lies lower than the A_1 fundamental for the Cl_3CF, whereas the A_1 fundamental is the lower for $ClCF_3$. For CF_3-CF_3 the average value of the highest frequencies belonging to species A_{1g} and A_{2u} is higher than the average of the corresponding frequencies belonging to E_g and E_u.[12] The infra-red band at 1280 cm⁻¹ has a typical PQR-structure, while the stronger band at 1233 has less regular appearance and resembles the E fundamental at 541 cm⁻¹, and also the perpendicular band at 1250 cm⁻¹ in CF_3-CF_3.[12] In the Raman spectrum of CF_3-CH_3 both bands are very faint. However, the band of lower frequency is diffuse, whereas the other appears to be sharp. For these reasons it seems most probable that the band at 1233 cm⁻¹ is an E fundamental and the band at 1280 cm⁻¹ an A_1 fundamental. This conclusion

could be tested by polarization measurements. However, because of the very low intensities of the Raman bands at 1233 and 1280 cm⁻¹, and their proximity to 2975 and 3035 cm⁻¹ excited by the 4047A mercury line, such measurements would be extremely difficult with gaseous CF_3-CH_3. Since this was the only assignment problem requiring polarization data, no such measurements were made.

To the skeletal vibrations must be added an A_1 and an E C—H stretching frequency near 3000 cm⁻¹, an A_1 and an E methyl deformation frequency in the region 1400 to 1460 cm⁻¹, a doubly degenerate CH_3 rocking frequency near 1000 cm⁻¹, and finally the low twisting frequency of species A_2. The order of these frequencies follows uniquely from Wagner's work[13] on molecules of type XCH_3.

Thus, the very strong infra-red band at 966 cm⁻¹ is evidently the methyl rocking frequency of species E. It is observed as a medium diffuse band in the Raman effect. The two strong infra-red bands at 1408 and 1443 cm⁻¹ must be the A_1 and E methyl deformation frequencies, respectively. The former was not observed in the Raman effect, as is commonly the case for compounds containing methyl groups. The E methyl deformation was observed in the Raman effect as a very diffuse band with a broad maximum near 1450 cm⁻¹. The band at 2975 cm⁻¹, which is very strong and sharp in the Raman effect, must be the totally symmetric C—H stretching frequency. The band at 3035 cm⁻¹ must be the corresponding fundamental of species E.

There remains the torsional frequency of species A_2 which is inactive as well in the infra-red as in the Raman effect. The first attempt to determine this fundamental from infra-red combination bands led to a value, 180 cm⁻¹, which agreed within the experimental error with the frequency, 165 ± 25 cm⁻¹, obtained by Dailey, Minden, and Shulman[5] from intensity measurements at different temperatures in the microwave absorption spectrum of CF_3-CH_3.

TABLE II. Raman spectrum of $CF_3 \cdot CH_3$ (gas).

Wave number	Description	Interpretation
365	$w\ d$	E fundamental
541	$w\ d$	E fundamental
603	$m\ sh$	A_1 fundamental
830.3	$vs\ sh$	A_1 fundamental
969	$m\ vd$	E fundamental
1232	$vw\ d$	E fundamental
1278	vw	A_1 fundamental
~1450	$m\ vd$	E fundamental
2796	vw	$2\times1408=2816\ (A_1);\ 3035-238=2797\ (E)$
2833	vvw	$604+830+1408=2842\ (A_1)?$
2890	$vvw\ d$	$2\times1443=2886\ (A_1+E)$
2965	$vw\ d$	$P,\ O$ branches
2974.6	vs	A_1 fundamental
3022	$vw\ d$	$P,\ O$ branches
3035	m	E fundamental
3049	vwd	$R,\ S$ branches

[10] L. Kahovec and J. Wagner, Zeits. f. physik. Chemie **B48**, 188 (1940).

[11] J. Wagner, Zeits. f. physik. Chemie **B45**, 341 (1940).

[12] Nielsen, Richards, and McMurry, J. Chem. Phys. **16**, 67 (1948).

[13] J. Wagner, Zeits. f. physik. Chemie **B40**, 36 (1938).

The evidence for this value, however, was not very strong. Moreover, when thermodynamic properties were calculated and compared with the calorimetric data of Russell, Golding, and Yost[2] it became fairly clear that the torsional fundamental must lie somewhat higher. A renewed study was made of the infra-red spectrum and the value, 238 cm^{-1}, was obtained for the A_2 fundamental.* As may be judged from Table I and Fig. 1, the spectroscopic evidence for this value, while stronger than the evidence for the previously assumed value, can hardly be regarded as conclusive. It will be shown below, however, that the value 238 cm^{-1} for the torsional frequency, in conjunction with the values assigned for the active fundamentals, gives good agreement between calculated and observed thermodynamic properties.

The assigned fundamental vibration frequencies for CF_3-CH_3 are listed in Table III. The characterizations of the various vibration modes given in the second column are fairly meaningful for the vibrations involving primarily the atoms of the methyl group. For the skeletal vibrations they have only rough significance.

The assignment of fundamentals given here differs greatly from those made by Russell, Golding, and Yost[2] and by Thompson and Temple.[3] The former workers assigned the Raman bands observed at 368 and 968 cm^{-1} to A_1 and 1279 cm^{-1} to E. Assuming that a Raman band, here ascribed to excitation by the mercury line 4047A, is caused by Hg 4358A, they obtained a frequency, 1025 cm^{-1}, which they regarded as an E fundamental. They did not have the frequency 1233 cm^{-1}, which had not been observed in the Raman effect by Hatcher and Yost,[1] and assigned six fundamentals to A_1 and five to E, rather than the opposite. Thompson and Temple[3] assigned 541 to A_1 and 606, as well as both 1412 and 1450 cm^{-1}, to E. They took 1135 cm^{-1}, which was undoubtedly caused by an impurity in their sample, to be an A_1 fundamental.

The assignment given here confirms Kohlrausch's assignment[4] of nine of the fundamentals and agrees with an assignment of the active fundamentals by Herzberg,† except for an interchange of 1233 and 1280 cm^{-1}.

INTERPRETATION OF THE SPECTRA

On the basis of the fundamental vibration frequencies listed in Table III it has been possible to interpret all of the Raman bands and all but about a dozen of the 120 infra-red absorption maxima observed. The interpretations of the bands are given in the third columns of Tables I and II.

Some of the intense infra-red bands interpreted as fundamentals have extra zero branches and abnormal contours. In some cases this seems caused by overlap-

ping combination bands, listed in Table I. The interpretation of the infra-red bands is on the whole satisfactory. Except for bands that are masked by stronger bands or lie outside the range of observation, all active binary sum bands have been observed, as well as a few binary difference bands. In several cases two interpretations appear equally plausible. A few bands, mostly of very low intensity, are interpreted as ternary combination bands. Because of the large number of such active combinations, there are many cases, especially at high wave numbers, in which alternative interpreta-

TABLE III. Fundamental vibration frequencies for $CF_3 \cdot CH_3$.

Species	Approximate character*	Wave number
A_1	CH stretching	2975 cm^{-1}
A_1	CH_3 deformation	1408
A_1	CF stretching	1280
A_1	C–C stretching	830
A_1	CH_3 deformation	604
A_2	Twisting	238
E	CH stretching	3035
E	CH_3 deformation	1443
E	CF stretching	1233
E	CH_3 rocking	970
E	CF_3 deformation	541
E	CF_3 rocking	365

* The designations in this column have only very rough meaning, especially for vibration involving the CF_3 group.

tions can be made. No attempt has been made to indicate all such alternatives in the table.

Certain peculiarities and difficulties should be pointed out. The infra-red band at 541 cm^{-1}, interpreted as an E fundamental, has an irregular contour and an intensity that is somewhat lower than that of what appears to be its overtone at 1086 cm^{-1}. The absorption maxima at 600 and 602 cm^{-1}, ascribed in Table I to a combination band of species E, may also be interpreted as zero branches of upper-stage bands corresponding to the A_1 fundamental at 605 cm^{-1}. The very strong absorption maxima at 965, 967, and 937 cm^{-1} appear to arise from coupling of the combination 365+604 of species E with an E fundamental, the frequency of which has been assumed to be 970 cm^{-1}. The difference between calculated and observed frequencies is rather large for the infra-red bands at 1172 and 1186 cm^{-1}. This may be caused by their proximity to the fundamental at 1233 cm^{-1}.

The interpretation of the Raman bands given in Table II is satisfactory, although for the very faint bands at 2796 and 2833 cm^{-1} the difference between the observed and calculated wave numbers is rather high. The diffuse maxima at 2965, 3022, and 3049 cm^{-1} apparently are rotational branches belonging to the fundamentals at 2975 and 3035 cm^{-1}.

IMPURITIES

It has not been possible to find plausible interpretations for all of the faint absorption maxima around 750 cm^{-1}. They are probably caused by impurities. In

* After completion of the present paper, it has been reported by R. Karplus and R. S. Halford (J. Chem. Phys. 18, 912 (1950)) that a new microwave study by Dailey and Minden has given the value 230±40 cm^{-1}.

† Private communication to J. Rud Nielsen.

TABLE IV. Calculated thermodynamic functions for CF_3-CH_3 at one atmos. (in cal./deg. mole).

T		$C_p{}^\circ$	S°	$-(F^\circ-H_0{}^\circ)/T$	$(H^\circ-H_0{}^\circ)/T$
250°K	Translational	4.97	38.34	33.36	4.97
	Rotational	2.98	22.32	19.41	2.91
	Vibrational	6.67	2.98	0.80	2.18
	Torsional	2.01	1.27	0.21	1.06
	Total	16.63	64.91	53.78	11.12
298	Translational	4.97	39.21	34.23	4.97
	Rotational	2.98	22.84	19.93	2.91
	Vibrational	8.68	4.32	1.26	3.06
	Torsional	2.12	2.10	0.87	1.23
	Total	18.75	68.47	56.29	12.17
400	Translational	4.97	40.67	35.69	4.97
	Rotational	2.98	23.72	20.81	2.91
	Vibrational	12.65	7.46	2.44	5.02
	Torsional	2.18	2.75	1.34	1.41
	Total	22.78	74.60	60.28	14.31
600	Translational	4.97	42.69	37.71	4.97
	Rotational	2.98	24.93	22.02	2.91
	Vibrational	18.53	13.77	5.17	8.61
	Torsional	1.96	2.58	0.91	1.67
	Total	28.44	83.97	65.81	18.16

particular, the sharp band at 732 cm⁻¹, and also the weaker maxima or shoulders at 780, 1008, 1155, 1200, and 1205, and near 1350 cm⁻¹, all correspond to positions of strong $CF_3-CF_2-CF_3$ absorption and are undoubtedly caused by the presence of a small amount of this compound (b.p.= −38° vs. −47.5°C for CF_3-CH_3). Likewise, the very weak band at 869 cm⁻¹ and the weak absorption at 1155 and near 470 cm⁻¹ are probably caused by a small amount of contamination with CF_2H-CH_3 (b.p.= −24.7°C). The bands at 678 and 686 cm⁻¹ are considerably weaker than those observed by Thompson and Temple[3] in this region and may be caused by an impurity, although they can be interpreted satisfactorily as difference bands. The absorption maximum at 1997 cm⁻¹ has been left uninterpreted, and the interpretations of some of the neigh-boring maxima are not very plausible. Since similar absorption maxima occur at these wave numbers in $CF_2=CH_2$, and in part in C_2F_4, they too are probably caused by impurities.

CALCULATED THERMODYNAMIC FUNCTIONS

From the known molecular dimensions[8] and the fundamental frequencies listed in Table III the heat capacity, entropy, free energy function, and heat content function, have been calculated for gaseous CF_3-CH_3 at one atmosphere and temperatures 250 (b.p.), 298, 400, and 600°K. The translational, rotational, vibrational and torsional (hindered rotational) contributions are listed separately in Table IV. The potential barrier V_0 opposing the rotation of the methyl group relatively to the CF_3 group was calculated from the formula[14] $\nu=(\sigma_i/2\pi)(V_0/2I_r)^{\frac{1}{2}}$, where ν is the torsional frequency, $\sigma_i=3$ the internal symmetry number, and I_r the reduced moment of inertia, and the value 3290 cal./mole was obtained. For the remaining calculations the equations and tables given by Hougen and Watson[15] were used. The molecular symmetry number was taken to be three.

Russell, Golding, and Yost[2] have made calorimetric measurements on CF_3-CH_3 and have obtained the value 63.95±0.10 cal./deg. mole for the entropy of the ideal gas at 224.40°K and 0.9330 atmos. Calculation on the basis of the present spectroscopic data gives 63.77 cal./deg. mole, in good agreement with the calorimetric value.

ACKNOWLEDGMENT

[14] See S. Glasstone, *Theoretical Chemistry* (D. Van Nostrand Company, Inc., New York, 1944), p. 421.
[15] O. A. Hougen and K. M. Watson, *Chemical Process Principles* (John Wiley and Sons, Inc., New York, 1947), Part II, Chapter XVII.