290. *The Vibrational Spectra and Thermodynamic Properties of Chlorofluoromethanes.*

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The infra-red absorption spectra of several chlorofluoromethanes have been measured. The results have been correlated with the Raman spectra and assignments of vibrational frequencies have been made. The contour of some of the vibrational bands has been correlated with the molecular structure. The values of some thermodynamic properties of these molecules have been calculated from the results.

PARTICULAR interest attaches to halogenated hydrocarbons containing fluorine, not only as regards their molecular structure, but also because of their particular physical and chemical

properties. In connexion with their practical uses, it would be valuable to compute the thermodynamic properties from the molecular vibration frequencies and structural parameters. This has been attempted already in some cases (Glockler, *J. Chem. Physics*, 1941, **9**, 527). In continuation of previous work (Torkington and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 236) we have recently measured the infra-red absorption spectra of a number of partly and fully fluorinated hydrocarbons, and of some mixed halogenated hydrocarbons. The present paper summarises the results for chlorotrifluoromethane, trichlorofluoromethane, dichlorodifluoromethane, and dichlorofluoromethane. The Raman spectra of some of these substances have been measured by previous workers and discussed with particular reference to the assignment of the vibration frequencies (Glockler and co-workers, *Physical Rev.*, 1938, **54**, 970; 1939, **55**, 669, 1273; *J. Chem. Physics*, 1939, **7**, 278, 382, 553; 1940, **8**, 125, 291, 699, 897; 1941, **9**, 527; Lecomte, *Ann. Physique*, 1941, **11**, 257; Bradley, *Physical Rev.*, 1932, **40**, 908).

The substances were supplied by Imperial Chemical Industries Ltd. (General Chemicals Division, Research Department), and had been prepared by the action of hydrogen fluoride on

FIG. 1.
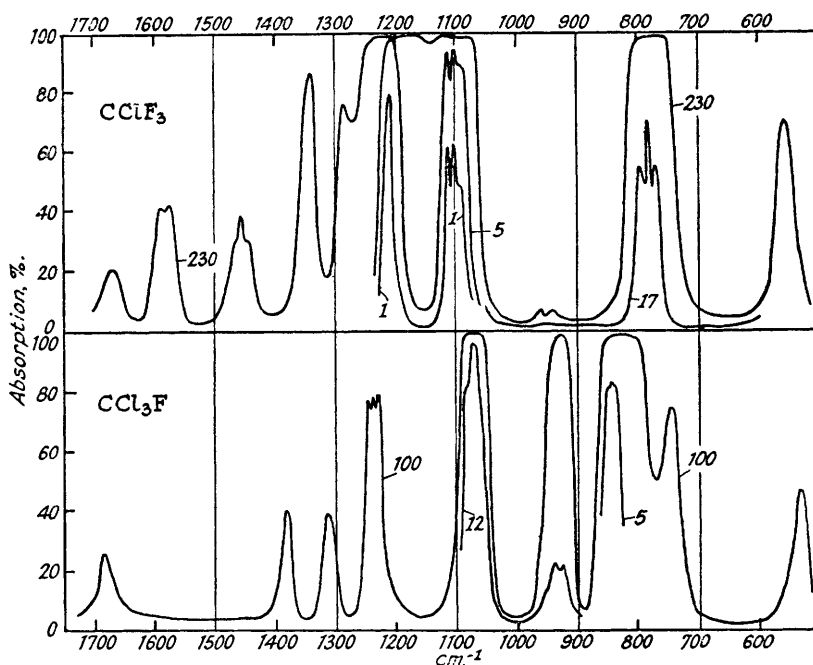
carbon tetrachloride or chloroform in presence of antimony pentafluoride. Although the recorded boiling points were close to those given in the literature, small amounts of impurities were detected and identified by the spectra, but these did not interfere with the main conclusions given below.

The spectra were measured between 5 and 14 μ on a single-beam recording spectrometer with rock-salt prism (Whiffen and Thompson, *J.*, 1945, 268), and also between 2 and 8 μ with a double-beam recorder having a large prism of synthetic calcium fluoride (Sutherland and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 178; Thompson, Whiffen, Richards, and Temple, in the press). The range 14—20 μ was examined with the single-beam recorder using a prism of potassium bromide, and a small non-automatic Wadsworth spectrometer with a prism of sylvine. The substances were measured in the vapour state at pressures between 1 and 300 mm. The absorption cells were cylindrical glass tubes 17 cm. in length with flanged ends, on to which windows of sodium chloride or potassium bromide were fixed with hard wax.

Results.—(1) *Chlorotrifluoromethane.* The absorption spectrum is shown in Fig. 1, and the positions of the absorption bands in wave-number units are listed in Table I together with the Raman frequencies found by Kahovec and Wagner (*Z. physikal. Chem.*, 1941, *B*, **48**, 190). The pressures (mm.) used are shown on the curves. Several of the infra-red bands show a

TABLE I.

Raman.	Infra-red.	Interpretation.
356 (4) *dp*	—	Fundamental
478 (8) *p*	—	,,
561 (2) *dp*	560 medium)	,,
	772⎫	
784 (8) *p*	783 ⎬(strong)	,,
	793⎭	
—	948⎫(very weak)	(2 × 478)
	957⎭	
	1092⎫	
1092 (0) *p*	1102 ⎬(very strong)	Fundamental
	1112⎭	
	1125 (strong)	(2 × 560) (356 + 783)
1205 (0) *dp*	1210 (very strong)	Fundamental
	1288 (weak)	((2 × 356) + 560)
	1340 (medium)	(561 + 783)
	1443⎫	
	1455 ⎬(weak)	(356 + 1102)
—	1463⎭	
	1580 (weak)	Several combinations
	1670 (very weak)	,, ,,

well-defined contour. Although the substance has not been examined by electron diffraction, it is possible to estimate the bond lengths and angles satisfactorily from measurements on closely related molecules given by Brockway (*J. Physical Chem.*, 1937, **41**, 747) and Wheland (" Theory of Resonance ", Wiley, 1944), and very plausible values are C–Cl = 1·74 A., C–F = 1·36 A., F–$\hat{\text{C}}$–F = 110°. The moments of inertia are then 158, 256, and 256 × 10⁻⁴⁰ g.-cm.², the molecule being a symmetrical rotator with least axis of inertia along the C–Cl bond. The parallel-type bands will have three submaxima, the outer spacing of which is calculated by the method of Gerhard and Dennison (*Physical Rev.*, 1933, **43**, 197) to be about 20 cm.⁻¹. The perpendicular-type bands will have a fairly strong central branch flanked by shoulders about 14 cm.⁻¹ apart.

The molecule falls in the symmetry point group C_{3v}. There will be three vibrations in the A_1 class, polarised in the Raman effect and giving parallel-type bands in the infra-red spectrum. These can be described as the symmetrical stretching vibration of the CF_3 group, the stretching vibration of the C–Cl bond, and the symmetrical deformation of the CF_3 group. There will be three twofold degenerate vibrations, depolarised in the Raman effect and giving perpendicular-type bands in the infra-red spectrum, namely, the antisymmetrical CF_3 stretching mode, and two rocking or bending modes.

An assignment of all six fundamentals can be made at once, for there are just three polarised Raman lines, of which the two observable in the infra-red are found to give bands with a parallel-type contour, and the other three degenerate modes are also clearly identified with the Raman displacements of 356, 561, and 1205 cm.⁻¹. The last of these corresponds to a very intense infra-red band at 1210 cm.⁻¹. We shall therefore take as the fundamentals : 356(2), 478, 560(2), 783, 1102, 1210(2). The last two correspond to the symmetrical and antisymmetrical stretching vibrations of the CF_3 group, and are particularly intense in the infra-red ; 478 must be correlated with the symmetrical deformation of the CF_3 group, that at 783 with the stretching of the C–Cl link, and those at 356 and 560 with the remaining degenerate deformational modes. The remaining infra-red bands can be explained satisfactorily as combination tones or overtones.

By using the above vibrational assignment, the moments of inertia already given, and a symmetry number σ = 3, some values of thermodynamic properties have been calculated, and are given in Table II. The tables of Wilson (*Chem. Reviews*, 1940, **27**, 17) have been used, and

TABLE II.

T, °K.	$-(F° - E_0^0)/T$, transl.-rot.	vib.	total.	$(H° - E_0^0)/T$, vib.	total.	$(H° - E_0^0)$, kcals.	$S°$, transl.-rot.	vib.	total.	C_p, vib.	total.
250	54·47	0·88	55·35	2·28	10·23	2·56	62·42	3·17	65·59	6·54	14·49
300	55·94	1·37	57·31	3·10	11·05	3·31	63·89	4·47	68·36	8·10	16·05
400	58·22	2·48	60·70	4·69	12·64	5·05	66·17	7·17	73·34	10·62	18·57
500	59·98	3·72	63·70	6·06	14·01	7·00	67·93	9·78	77·71	12·41	20·36
600	61·40	4·91	66·31	7·24	15·19	9·11	69·35	12·15	81·50	13·62	21·63

the values refer to one mole of the ideal gas under standard conditions of one atmosphere pressure. Unless otherwise stated, the units are cals./°K./mole.

(2) *Trichlorofluoromethane.* The Raman spectrum has been discussed by Glockler and Leader (*J. Chem. Physics*, 1939, **7**, 278), by Kohlrausch and Wagner (*Z. physikal. Chem.*, 1939, B, **45**, 93), by Volkringer, Lecomte, and Tchakirian (*J. Chem. Physics*, 1940, **8**, 126) and by Lecomte (*Ann. Physique*, 1941, **11**, 257). The absorption spectrum is shown in Fig. 1, and the positions of the bands are given in Table III.

TABLE III.

Raman.	Infra-red.	Interpretation.
244 (5)	—	Fundamental
349 (5)	—	Fundamental
397 (4)	—	Fundamental
535 (10)	532 (weak)	Fundamental
	744 (weak)	(349 + 397)
837 (2b)	845 (very strong)	Fundamental
	930 (weak)	(397 + 535)
1067 (0b)	1072 (very strong)	Fundamental
—	1085 (strong)	(244 + 845)
	1234 (medium)	(397 + 845)
	1310 (weak)	(1072 + 244)
	1377 (weak)	(535 + 845)
	1685 (weak)	(2 × 845)
	1825 (weak)	(1072 + 349 + 397)
	2135 (medium)	(2 × 1072)

The molecular dimensions given by Brockway (*J. Physical Chem.*, 1937, **41**, 747), namely, $C-F = 1\cdot40$ A., $C-Cl = 1\cdot76$ A., and $F-\widehat{C}-Cl = 107°\ 30'$, being used, the moments of inertia are 502, 352, and 352 × 10^{-40} g.-cm.². The molecule is a symmetrical top and the spacing of the outer maxima in the parallel type bands will be about 17 cm.$^{-1}$. Although several of the bands show a partly resolved contour, the spacings of the sub-maxima cannot be determined very exactly. It is certain, however, that we can take for the fundamentals the following values : 244, 349, 397, 532, 845, and 1072 cm.$^{-1}$. Moreover, the intense infra-red bands at 845 and 1072 will be the twofold degenerate antisymmetrical stretching mode of the CCl_3 group and the stretching mode of the C–F bond, and the intense Raman interval 535 will be due to the symmetrical stretching mode of the CCl_3 group. The other three values will be due to deformations. By analogy with the frequencies found for chloroform (260 and 363) we can take 244 as due to the degenerate bending vibration mainly controlled by the CCl_3 group, and 349 as due to the symmetrical deformation of this group. The stretching modes at 532 and 845 cm.$^{-1}$ are paralleled in chloroform by the values 672 and 760. The Raman interval 397 is then assigned to the other skeletal deformation. The remaining infra-red bands can be satisfactorily explained as overtones or combinations.

Osborne, Garner, Doescher, and Yost (*J. Amer. Chem. Soc.*, 1941, **63**, 3496) have measured the entropy of this substance and have compared it with the values calculated, using a vibrational assignment essentially the same as that now adopted. The small changes in the values of the frequencies do not significantly affect their conclusions or computations. In Table IV calculated values are summarised for several thermodynamic properties over a wider range of temperature, the above vibrational assignment and moments of inertia, and a symmetry number $\sigma = 3$, being used.

TABLE IV.

	$- (F° - E_0^0)/T$,			$(H° - E_0^0)/T$,		$(H° - E_0^0)$,	$S°$,			C_p,	
T, °K.	transl.-rot.	vib.	total.	vib.	total.	kcals.	transl.-rot.	vib.	total.	vib.	total.
298·16	58·43	2·79	61·22	4·97	12·92	3·86	66·38	7·75	74·13	10·76	18·71
300	58·47	2·81	61·28	4·99	12·94	3·88	66·42	7·80	74·22	10·83	18·78
500	60·79	4·48	65·27	6·73	14·68	5·87	68·74	11·21	79·95	12·94	20·89
500	62·56	6·16	68·72	8·12	16·07	8·03	70·51	14·29	84·80	14·34	22·29
600	64·04	7·69	71·73	9·22	17·17	10·30	71·99	16·91	88·90	15·22	23·10

(3) *Dichlorodifluoromethane.* The Raman spectrum was measured by Bradley (*Physical Rev.*, 1932, **40**, 908) and discussed by Wu (" Vibrational Spectra and Structure of Polyatomic Molecules ", Shanghai, 1939) and by Lecomte (*loc. cit.*). The infra-red spectrum is shown in Fig. 2 and the positions of the bands are given in Table V. This molecule falls into the symmetry
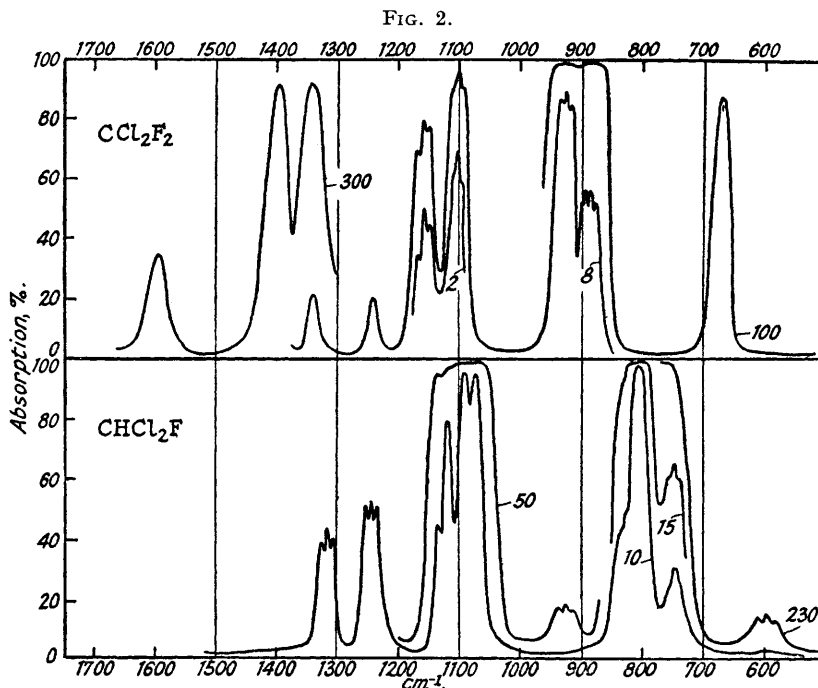
Fig. 2.

TABLE V.

Raman.	Infra-red.		Interpretation.	Raman.	Infra-red.		Interpretation.
260 (5)	—		Fundamental		1091 ⎤		
320 (3)	—		Fundamental	1082 (3)	1095 ? ⎬ (very strong)		Fundamental
433 (5)	—		Fundamental		1098 ⎟		?(433 + 669)
455 (7)	—		Fundamental		1105 ⎦		
664 (10)	669	(strong)	Fundamental		1148 ⎤		
	877 ⎤			1147 (1)	1155 ⎬ (strong)		Fundamental
	882 ⎟				1167 ⎦		
877 (1)	888 ⎬ (very strong)		Fundamental		1235	(medium)	(920 + 320)
	892 ⎦				1337	(medium)	(2 × 669)
	914 ⎤				1395	(medium)	(1095 + 320)
919 (2)	920 ⎬ (very strong)		Fundamental		1592	(weak)	(920 + 669)
	929 ⎦				1765	(weak)	(2 × 885)
					1797	(medium)	(885 + 920)

point group C_{2v} and the nine fundamental vibrations form four groups, indicated in Table VI. In discussing the assignment of frequencies, Wu suggested that the Raman interval 919 was a

TABLE VI.

Class.	C_2^z.	Symmetry w.r.t. σ_x.	σ_y.	Raman.	Infrared.	No. of modes.	Nature of vibration.
A_1	s	s	s	p	M_z	4	Symm. CCl_2 stretching Symm. CF_2 stretching Symm. CCl_2 deformation Symm. CF_2 deformation
A_2	s	$-\ as$	as	dp	ia	1	Twisting
B_1	as	as	s	dp	M_x	2	Antisymm. CCl_2 stretching Rocking
B_2	as	s	as	dp	M_y	2	Antisymm. CF_2 stretching Rocking

combination (664 + 260), but adopted the other eight Raman intervals as fundamentals. Lecomte on the other hand regarded the interval 919 as a fundamental but considered that at 1147 as some combination tone.

According to Brockway (*loc. cit.*) the molecular dimensions are C–F = 1·35 A., C–Cl = 1·74 A., Cl–C͡–Cl = 112°, F–C͡–F = 110°, and the calculated moments of inertia are close to 206, 324,

and 375×10^{-40} g.-cm.^{2}. The molecule is thus an asymmetrical rotator. Vibrations in class A_1 will involve a changing electric moment parallel to the intermediate axis of inertia (B-type bands), those in class B_1 will give rise to A-type bands, and those in class B_2 to C-type contour. Interpolation from the curves of Badger and Zumwalt (*J. Chem. Physics*, 1938, **6**, 711), and from more detailed computations very kindly sent to us by Dr. R. S. Rasmussen, suggests that the B-type bands will have four sub-maxima, with central spacing about 5 cm.$^{-1}$ and outer spacing about 13 cm.$^{-1}$. The A- and C-type bands will each have three sub-maxima with outer spacings of about 15 cm.$^{-1}$ and 20 cm.$^{-1}$.

The most satisfactory explanation of the results seems to be to assume for the fundamental frequencies the values 260, 320, 433, 455, 669, 885, 920, 1095, and 1155 cm.$^{-1}$. The last four are intense in the infra-red absorption. Further, adoption of the frequency 920 cm.$^{-1}$ helps in the interpretation of several combinations, and the frequencies 1095 and 1155 cm.$^{-1}$ agree well with the values found for stretching vibrations of other compounds containing two or three fluorine atoms attached to carbon.

As regards the assignment of these magnitudes to the different normal modes, the bands at 885 appears to have a contour expected for a B-type band, and in this case would be assigned to the A_1 class, and presumably to the symmetrical stretching mode of the CCl_2 group. In this case it would follow that the band at 920 cm.$^{-1}$ should be assigned to the antisymmetrical stretching mode of the CCl_2 group, and indeed this band appears to have the A-type contour required. The bands at 1095 and 1155 cm.$^{-1}$ are assigned to the symmetrical and antisymmetrical stretching modes of the CF_2 group, and again the contours appear to conform the former probably having four sub-maxima (Table V) and the latter three. By analogy with the frequencies in other molecules such as CH_2Cl_2 (283) or chloroform (262), the Raman interval 260 cm.$^{-1}$ can be assigned to the symmetrical deformation of the CCl_2 group. The most probable assignment of the remaining four fundamentals is 320 for the twisting vibration frequency, 433 and 455 for the two rocking vibration frequencies, and 669 for the symmetrical deformation of the CF_2 group.

The unexpected feature of this assignment is the rather high values adopted for the two stretching modes of the CCl_2 group. On the other hand, it may be noted that on passing from CH_2Cl_2 (where the two frequencies concerned are 704 and 737 cm.$^{-1}$) to CF_2Cl_2, there is a shortening of the C–Cl linkages, implying a rather stronger binding. It may also be observed that in other cases such as CH_3Cl and $CHCl_3$, replacement of hydrogen by fluorine in chlorinated hydrocarbons leads to an increase in the stretching vibration frequency of the C–Cl bonds; and in other compounds such as $CH_3 \cdot CCl_3$ the corresponding stretching frequencies are high.

If the above assignment is incorrect, the alternative would be to assign the band at 669 cm.$^{-1}$ to the symmetrical stretching mode of the CCl_2 group, this band being intense in the Raman effect. It would then be difficult to reconcile the contour of the infra-red band at 885 cm.$^{-1}$ with any plausible fundamental, unless the molecular dimensions assumed are in error and the principal axes of inertia can be interchanged. Also, it would then be necessary to assign one very high value to a deformational mode.

Although therefore the choice of fundamentals adopted is not completely proved, it seems very probable, and in any case may be in error only as regards assignment to the particular normal modes and not as regards their numerical values. None of the vibrations is degenerate. Since the thermodynamic properties of this substance are of some importance, values have been computed and are listed in Table VII. If later analysis should prove that one of the infra-red bands near 1000 cm.$^{-1}$ should be interpreted as a combination or overtone, and that a new fundamental around 600 cm.$^{-1}$ should be introduced, the values of C_p given here will be low by a few units %.

TABLE VII.

T, °K.	$(F° − E_0^0)/T$, transl.-rot.	vib.	total.	$(H° − E_0^0)/T$, vib.	total.	$(H° − E_0^0)$, kcals.	S°, transl.-rot.	vib.	total.	C_p, vib.	total.
250	55·93	1·25	57·18	2·74	10·69	2·67	63·88	3·99	67·87	7·08	15·03
300	58·04	1·82	59·86	3·60	11·54	3·46	65·99	5·42	71·41	8·63	16·57
400	60·33	3·09	63·42	5·17	13·12	5·25	68·28	8·26	76·54	11·08	19·03
500	62·11	4·39	66·50	6·54	14·48	7·24	70·06	10·92	80·98	12·82	20·77
600	63·55	5·84	69·39	7·84	15·78	9·47	71·50	13·68	85·18	14·14	22·09

(4) *Dichlorofluoromethane.* The Raman spectrum was measured by Bradley (*loc. cit.*), and also by Glockler, Leader, and Edgell (*J. Chem. Physics*, 1940, **8**, 897). The infra-red spectrum is shown in Fig. 2, and the positions of the bands are given in Table VIII. There are signs that a

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TABLE VIII.

Raman.	Infra-red.	Interpretation.
	—	Fundamental
277 (8)	—	Fundamental
366 (4)	—	Fundamental
457 (10)	—	Fundamental
	594 (very weak	? Impurity
729 (8)		(277 + 457) (2 × 366) or ? fundamental
739 (5)	739, 844, 750 (medium)	Fundamental
794 (2)	805 (very strong)	Fundamental
	823 (medium)	(366 + 457)
	911, 920, 929 (very weak)	(2 × 457)
1067 (0)	1072 (very strong)	Fundamental
	1085 (very strong)	(277 + 805)
	1115 (strong)	(744 + 366) or ? fundamental
	1131 (weak)	? Impurity
	1233	? Fundamental
1255 (0)	1241, 1248 (strong)	? Fundamental
1310 (1)	1305, 1315, 1323 (strong)	Fundamental
3020 (6)	3036 (strong)	Fundamental

small amount of impurity may have been present, although this does not obscure the main absorption bands. The molecule has a plane of symmetry, and the nine fundamentals, which are all active in both Raman effect and infra-red absorption, fall into two groups symmetrical or antisymmetrical respectively to the plane, and polarised or depolarised in the Raman effect. Polarisation measurements on the Raman spectrum have not been made. Several of the infra-red bands show interesting contour, but unfortunately all will be hybrid as regards the direction of change of electric moment. Comparison of the Raman and infra-red results, and also reference to related molecules suggests that seven fundamentals have the following approximate values : 277, 366, 457, 800, 1072, 1315, 3030. The value 277 will be associated with the vibration largely controlled by deformation of the CCl_2 group, 1072 and 3030 by the stretching of C–F and C–H bonds, and 800 by the antisymmetrical stretching of the CCl_2 group. The other three values just listed will be associated with deformational modes. There remain the symmetrical stretching frequency of the CCl_2 group, and one other skeletal deformation. It seems certain that there is a fundamental around 740 cm.$^{-1}$, but the last rocking mode cannot be clearly identified. It is possible that it has a value of 1241 cm.$^{-1}$ corresponding to the weak Raman line at 1255, but this value seems rather high. Alternatively it may be that there is another fundamental in the region of 740 or 800 cm.$^{-1}$ leading to the complex contour found in these regions, or that the strong infra-red band at 1115 cm.$^{-1}$ is due to the missing fundamental.