On the Emission Bands of CF_2

PUTCHA VENKATESWARLU* Department of Physics, University of Chicago, Chicago, Illinois (Received November 7, 1949)

A new band system attributed to a non-linear CF_2 molecule has been obtained by exciting the flowing vapor of carbon tetrafluoride. The symmetric stretching frequencies and the bending frequencies in the lower and upper states have been determined. From a study of the sub-band heads (K-structure), it is shown that the band system is of the parallel type, that is, the electric moment associated with the transition vibrates parallel to the line joining the fluorine atoms. The band system is identified with the transition $^{1}B_{2} \rightarrow ^{1}A_{1}$.

IN an earlier communication by the writer,¹ it was mentioned that the excitation of carbon tetrachloride vapor by an uncondensed transformer discharge gave CCl and Cl₂ bands, and that in the case of CBr₄ only Br₂ bands were obtained. The same kind of excitation, in the case of carbon tetrafluoride, gave an extensive band system attributed to the CF_2 molecule. This will be dealt with in the present paper.

The carbon tetrafluoride vapor was kept flowing at a low pressure, estimated to be about 0.1 mm, through a discharge tube fitted with aluminum electrodes and a quartz window. The gas was excited by an uncondensed transformer discharge ($\frac{1}{2}$ kw and 5000–10,000 volts). The color of the discharge was yellowish white. The spectrum obtained was photographed on Hilger medium quartz and E_1 -quartz spectrographs. The dispersion of the E_1 -quartz spectrograph is about 2.6A/mm at 2500A.

Part of the spectrum obtained is shown in Fig. 1. A

tained. The bands are degraded to longer wave-lengths. The wave-lengths and wave numbers along with the visually estimated relative intensities are given in Table I. The structure of the bands, each of which is made up of a series of sub-bands attributable to rotational structure, is similar to that of the NO₂ absorption bands† near 2500A. The presence of the sub-band heads rules out the diatomic molecule CF as the emitter of the band system. The similarity of this band system to the $\lambda 2500$ system of NO₂ strongly suggests that the emitter is an obtuse-angled non-linear triatomic molecule CF_2 . This idea is supported by the vibrational analysis discussed.

All the bands given in Table I can be fairly well represented by the formula

 $\nu = 39195 + 750v_1' \ddagger + (495.5v_2' - 0.5v_2'^2)$

FIG. 1. The spectra of CF_2 taken on the E_1 quartz spectrograph. (b) is from the original and (a) is three times enlarged. Wave-lengths of some of the bands are marked.

* Post-Doctoral Research Fellow, Molecular Spectra Research Project. Now with the Division of Physics, National Research Council, Ottawa, Canada.

P. Venkateswarlu, Phys. Rev. 77, 79 (1950).

† A good photograph of these bands is given in Mulliken's paper (see reference 4) referred to later. † This frequency 750 cm⁻¹ for v_1 is doubtful, as there are only two weak bands which are represented by this.

where v_1'' and v_2'' are vibrational quantum numbers here interpreted as those of the symmetric stretching and deformation frequencies in the lower state, while v_1' and v_2' are corresponding quantum numbers for the upper state.

The $(v_1'', v_2'', v_1', v_2')$ values and the corresponding wave numbers for the band heads are also given in Table I. To some of the observed bands alternative assignments of $(v_1'', v_2'', v_1', v_2')$ could be given with the same frequencies; probably experiments with higher resolution might show two bands instead of one in some of these cases. As all the bands can be well explained by formula (1), the analysis indicates that the emitter is a CF₂ molecule with a stretching frequency of 1162 cm⁻¹ and a deformation frequency of 666.5 cm⁻¹ in the lower state, and a deformation frequency of 495.5 cm⁻¹ (and also a probable stretching frequency of 750 cm⁻¹) in the upper state.¶

The idea that the CF_2 molecule is non-linear like NO_2 is supported by the following considerations. The allowed changes in the vibrational quantum numbers according to the selection rules and the most probable changes according to the Franck-Condon principle assuming moderate changes in the nuclear configurations are summarized in Table II.

From the analysis (Table I) it is evident that bands with Δv_2 values from zero to five as well as those with Δv_1 values from zero to seven are all present. Hence, from Table II it follows that the molecule is non-linear. Further, as discussed below, the rotational structure shows the existence of two rotational quantum numbers K and J, which is possible only for a non-linear molecule.

For comparison the vibrational frequencies of some triatomic molecules² are given in Table III, and the frequencies obtained for the lower electronic state in the present band system of CF_2 are seen to be of about the right magnitudes for that molecule.

Mulliken³ has discussed quite extensively the spectra of triatomic molecules. Non-linear triatomic molecules of the type AB_2 fall into the asymmetric top class; that is, they have three unequal moments of inertia. However, the analysis of the band structure of such molecules can be carried out, to a considerable extent, as if they were the bands of symmetrical top molecules. The electronic as well as vibration-rotation bands of symmetric top molecules fall into parallel and perpendicular types. We call the bands parallel or perpendicular according as the electric moment associated with

ntensity	λ_{air}	^ν vac	v1", v2", v1', v2'	"calc
0	2399.24	41667	0,0,0,5	41660
0	2409.44	41491	0,1,0,6	41485
3	2428.32	41168	0,0,0,4	41169
2	2438.51	40996	0,1,0,5	40995
7	2457.64	40677	0,0,0,3	40677
2	2467.82	40509	0,1,0,4	40504
2	2472.31	40436	0,0,1,1	40440
9	2487.80	40184	0,0,0,2	40184
2	2502.60	39946	0,0,1,0	39945
9	2518.65	39692	0,0,0,1	39690
2	2530.0	39514	1,0,0,3; 0,1,0,2	39515; 39519
3	2541.34	39339	1,1,0,4	39342
8	2550.56	39195	0,0,0,0	39195
4	2561.81	39023	1,0,0,2; 0,1,0,1	39022; 39025
4	2573.17	38851	1,1,0,3; 0,2,0,2	38850; 38855
3	2583.56	38695	0,3,0,3	38687
9	2594.60	38530	0,1,0,0	38530
?	2594.96	38525	1.0.0.1	38528
2	2606.68	38352	2.0.0.3: 1.1.0.2	38354: 38357
3	2617.90	38187	1.2.0.3	38187
9	2628.51	38033	1.0.0.0	38033
6	2652.38	37691	1.2.0.2: 2.1.0.3	37694: 37690
4	2663.39	37535	1.3.0.3	37526
6	2675.47	36366	1.1.0.0: 2.0.0.1	37368: 37367
5	2688.14	37189	$1201 \cdot 2102$	37200 37197
3	2699.06	37039	1302	37033
ğ	2711.30	36872	2000	36872
Ŕ	2736 40	36534	2,0,0,0	36534
4	2749 09	36365	2,2,0,2	36367
5	2761 24	36205	2,0,0,0	36208 · 36208
5	2774 16	36036	2,1,0,0,0,0,0,0,0,0	36040 . 36038
3	2787 07	35869	2,2,0,1,0,1,0,2 $2,3,0,2 \cdot 3,2,0,3$	35874 35869
8 8	2799.81	35706	3000	35713
ž	2812.92	35540	$3101 \cdot 4002$	35544 . 35544
2	2839 41	35208	3303	35200
6	2852 47	35047	3100.4001	35049 . 35050
6	2866 14	34880	3201.4102	34882 · 34881
ă ă	2870 73	34715	3302	34716
7	2803 54	34550	4000	34555
3	2007 51	34384	4101	34387
6	2921 28	34222	4202	34219
3	2935 17	34060	4303	34053
2	2040 82	33801	4100	33892
2	2978 92	33559	4302	33560
2	2003 60	33304	5,0,0,0	33400
3	3007 53	33240	5,0,0,0	33737
š	3022 76	33073	5,2,0,2	33065
5	3038.00	32006	5 3 0 3	32800
š	3053.66	32738	5100	32737
3	3060 61	32568	5 2 0 1	32571
ž	3084 57	32410	5302	32406
ĩ	3164.6	31500	6100	31585
2	3181.0	31428	6201	31420
ĩ	3107 5	31265	6302	31265
6	3214 1	31104	7000	31008
ž	3231 1	30040	7101	30031
1	3240 5	30765	7 2 0 2	30765
T	5449.3	30703	1,2,0,2	30703

TABLE I. Experimental data and the vibrational analysis.

the transition in question vibrates parallel or perpendicular to the symmetry or quasi-symmetry axis.** The selection rule for parallel bands is $\Delta K=0$ and for perpendicular bands $\Delta K=\pm 1$, where K is the quantum number of rotation around the symmetry or quasisymmetry axis. The structure for parallel-type bands

[¶] It may be mentioned that the bands can also be explained with a deformation frequency in the lower state of 340 cm⁻¹ instead of 667 cm⁻¹. But the calculated values for the band heads in general agree better with the observed values if we use 667 cm⁻¹. Further, a comparison with the frequencies of the triatomic molecules NO₂ and O₃ (Table III) suggests that 667 cm⁻¹ is of about the right magnitude.

 ^a R. S. Mulliken, Rev. Mod. Phys. 14, 204 (1942); see also reference 7.

^{**} In asymmetric top molecules like AB_2 the quasi-symmetry axis is the axis of smallest moment of inertia. The other two moments of inertia, which are roughly equal, are much larger in the case that the asymmetric simulates a symmetric top molecule. The quasi-symmetry axis in CF_2 is the line joining the two fluorine atoms.

TABLE II.[•] The allowed changes in the vibrational quantum numbers according to the selection rules, and the most probable changes according to the Franck-Condon principle.

rules	Franck-Condon principle		
Non-linear molecule	Linear molecule	Non-linear molecule	
$\Delta v_{ss} = any$ $\Delta v_{sd} = any$	$\begin{array}{l} \Delta v_{ss} = \mathrm{any} \\ \Delta v_d = 0 \end{array}$	$\Delta v_{ss} = \text{any}$ $\Delta v_{sd} = \text{any}$	
	rules Non-linear molecule $\Delta v_{ss} = any$ $\Delta v_{sd} = any$	rulesFranck-CondNon-linear moleculeLinear molecule $\Delta v_{ss} = any$ $\Delta v_{sd} = any$ $\Delta v_{ad} = 0$ $\Delta v_{ss} = any$ $\Delta v_{ad} = 0$	

• In this table, Δv_{**} and Δv_{**} are the changes in the quantum numbers of the symmetric and antisymmetric stretching frequencies, $\Delta v_{\pi d}$ and $\Delta v_{\pi d}$ are the changes in the deformation frequency quantum numbers for linear and non-linear molecules, respectively.

TABLE III. Comparison of the vibrational frequencies.

	ν1	ν2	¥3
CF ₂ (bent)	1162	667	
NO_2 (bent) ⁴	1306	755	1621
O_3 (bent) ⁴	1110	705	1043
SO ₂ (bent)	1151	524	1361
CO ₂ (linear)	1337	667	2349

consists of a series of sub-bands (K-structure) each characterized by a definite value of K. These follow the parabolic formula

$$\nu = \nu_0 + (C' - C'')K^2, \qquad (2)$$

where C' and C'' are related^{††} to the moments of inertia in the upper and lower states, respectively. Further, each sub-band has fine structure, called J-structure, consisting of Q, R, and P branches corresponding to changes $\Delta J=0, \pm 1$ in the over-all rotational quantum number J.

A complete study of the rotational structure of CF_2 could be made only by using high dispersion. But the dispersion of the instrument used at present is enough to analyze the K-structure for some of the higher frequency bands and this, as we shall see, gives the proof that the present band system of CF_2 corresponds to a parallel-type transition. Each band, as stated, consists of a series of sub-bands each of which has a definite K value. The K-structure is shaded toward shorter wave-lengths, but the J-structure of each subband, and so the band as a whole, is shaded toward longer wave-lengths.^{‡‡} That is, C' > C'' and B' < B'', B' and B'' being the constants \P of the *J*-structure in the upper and lower states. From considerations of Metropolis,⁵ which need not be repeated here, this shows that the apex angle α' in the upper state is larger than α'' in the lower state, but leaves open the question as to whether r'-r'' is positive or negative, where r'and r'' correspond to the CF distances in the upper and lower states, respectively. The existence of a long v_1'' series, but with maximum intensity for Δv_1 perhaps about one or two, indicates that |r'-r''| is appreciably different from zero, but not large.

As an example, the wave numbers of the sub-band heads of the band at 2487A are given in Table IV with the assigned values for K.

The sub-heads or in other words the K-structure can be well represented for this band by the parabolic formula

$$\nu = 40185 + 2.35K^2, \tag{3}$$

which shows that the transition involved for the band system is of a parallel type.

The value of C'-C'' from Eq. (3) is 2.35 cm⁻¹, not far different in magnitude from the value⁶ -3.78 cm⁻¹ in the case of NO₂. An accurate determination of B'-B'' would require higher dispersion. However, by measuring the second differences in the *J*-structure for a few higher frequency bands, a rough value of -0.13 ± 0.03 cm⁻¹ is obtained, as compared with the value -0.06 cm⁻¹ in the case of NO₂ ($\lambda 2500$) and -0.03 cm⁻¹ for ClO₂.⁷

Besides the main band system discussed, there are additional weak bands on the longer wave-length side (3300-3700A) which appear to be of a different structure. These may probably form a second CF₂ system. However, it is not yet certain whether these bands belong to CF₂, and further work is needed to determine definitely the nature of these bands.

Following are some comments by Professor R. S. Mulliken on the probable electronic states responsible for the band system and relative to certain states of CH_2 . These are included with his kind permission.

[The foregoing results on CF_2 have a bearing on the

TABLE IV. K-structure of the band at 2487A.

K	^v obs	νΔ	^ν cale
0	40184.0	2.4	40185.0
1	40187.1	3.1	40187.4
2	40194.2	7.1	40194.4
2	40207 8	13.6	40206.2
	40207.8	17.3	40200.2
4	40225.1	21.2	40222.6
5	40246.3	25.8	40243.8
6	40272.1	30.0	40269.6
7	40303.0	30.9	40300.2
8	40335.5	32.5	40335.4
9	40375.3	39.8	40375.4

⁶ L. Harris and G. W. King, J. Chem. Phys. 8, 775 (1940).

⁷ J. B. Coon, J. Chem. Phys. 14, 665 (1946).

⁴ M. Kent Wilson and R. M. Badger, Phys. Rev. **76**, 472 (1949) and J. Chem. Phys. **16**, 741 (1948). $\dagger \dagger C' = h/(8\pi^2 c) [1/I_a' - \frac{1}{2}(1/I_b' + 1/I_c')]$, where I_a' , I_b' , and I_c'

 $[\]uparrow C' = h/(8\pi^2 c) [1/I_a' - \frac{1}{2}(1/I_b' + 1/I_c')]$, where I_a' , I_b' , and I_c' are the three moments of inertia of the molecule in the upper state, with $I_a < I_b' < I_c'$; C'' stands for a similar expression in the lower state.

the lower state. $\ddagger Here the CF_2$ bands differ from the bands of NO₂ at 2500A, where the K-structure and the J-structure are both shaded toward longer wave-lengths.

toward longer wave-lengths. $\P B' = (h/8\pi^2 c) \frac{1}{2}(1/I_b'+1/I_c')$, with a similar relation for B''. ⁵ N. C. Metropolis, Phys. Rev. **60**, 283 (1941).

question of the structure of the CH2 radical.8,9 From general considerations of valence theory it is fairly certain that CH₂ is a non-linear symmetrical molecule with a singlet ground electronic state. For an s^2p^2 carbon atom, CH₂ would have the same type of electronic and geometrical structure as H₂O, except for the absence of two non-bonding p electrons from the central atom. For an sp^3 carbon atom, CH₂ would be a linear molecule with a triplet ground state. The actual condition of the carbon atom must certainly be intermediate between s^2p^2 and sp^3 , but probably nearer the former. This leads to the prediction of an apex angle in the range 110° -130° (or possibly somewhat more) with in all probability a singlet ground state. A triplet ground state would occur if the angle sufficiently approached 180°, but it is improbable that this happens.

For an obtuse-angled model in the range $110^{\circ}-130^{\circ}$ or somewhat more, the electronic structure of the ground state and probable lowest excited states of CH₂ may be described as follows:

$$\begin{array}{l} (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2, {}^{1}A_1 \\ (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1), {}^{3}B_1 \text{ and } {}^{1}B_1 \\ (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(2b_2), {}^{3}B_2 \text{ and } {}^{1}B_2. \end{array}$$

$$(4)$$

The electron configurations are stated here in terms of MO's (molecular orbitals) classified according to the appropriate symmetry group (C_{2v}) , with z axis bisecting the HCH angle and x axis taken as perpendicular to the plane of the nuclei. The y axis, parallel to the H-H line, is the quasi-symmetry axis for the rotation of CH₂ as a quasi-symmetric top—a valid approximation for apex angles in the indicated range. The forms of the various MO's may be described approximately, in LCAO approximation, as follows:

$$1a_{1}=1s_{C}; \quad 2a_{1}\approx s_{H}h_{C}s_{H}; \quad 3a_{1}\approx h_{C}'(?); \\ 1b_{2}\approx s_{H}y_{C}\bar{s}_{H}; \quad 2b_{2}\approx \bar{s}_{H}y_{C}s_{H}; \\ 1b_{1}=x_{C}.$$
(5)

Here $1s_{C}$, x_{C} (meaning $2p_{x}$ of carbon), y_{C} (meaning $2p_{y}$), h_{C} (meaning a hybrid of $2s_{C}$ and $2p_{z}$ of C), and $h_{C'}$ (another hybrid of $2s_{C}$ and $2p_{z}$ of C) are carbon atom AO's; s_{H} is a 1s hydrogen atom AO. A symbol such as $s_{H}h_{CSH}$ indicates a linear combination of the three AO's named, all with positive signs; a bar over s_{H} means that this AO is to be taken with negative sign in the linear combination. The MO's $2a_{1}$ and $1b_{2}$ are C-H bonding MO's. The MO $3a_{1}$ as described in (5) is nearly non-bonding; however, for pure $s^{2}p^{2}$ carbon, $2a_{1}$ would be non-bonding of the form $2s_{C}$, and $3a_{1}$ would be bonding of the form s_{HZCSH} ; the actual forms of $2a_{1}$, $3a_{1}$, and $4a_{1}$ are subject to considerable uncertainty. The excited MO's $2b_{2}$ and $1b_{1}$ are C-H

antibonding and non-bonding, respectively; for this reason, $2b_2$ should be considerably higher than $1b_1$ in energy, making the ${}^{3}B_2$ and ${}^{1}B_2$ excited states in (4) higher than the ${}^{3}B_1$ and ${}^{1}B_1$, respectively.

On the basis of (4) and what has just been said, the known visible emission bands^{*} which are attributed to CH₂ most probably represent the transition ${}^{1}B_{1} \rightarrow {}^{1}A_{1}$.¹⁰ Although it has not been proved that their lower state is the ground state of CH₂, the conditions of excitation of this spectrum in comets, as well as the fact that the best known spectra of molecules possessing fairly low excited electronic levels are usually transitions from these to the ground state, make this probable. The observed structures of the bands seems to be consistent¹⁰ with the indicated transition in an obtuse-angled CH₂ molecule.

Although the CF₂ molecule contains additional electrons, an examination of its expected MO's indicates that its normal and low excited states are probably similar to those of CH₂. In the bonding MO's, a linear combination of $2p_y$ and $2p_z$ of fluorine plays the role that $1s_{\rm H}$ has in CH₂. There are also various interactions involving the fluorine non-bonding electrons, of which perhaps the most significant is one between the carbon $2p_x$ and the fluorine $2p_x$ AO's. This should give some added stability to the ground state (partial C-F double-bond formation), and at the same time makes the excited b_1 MO now somewhat C-F antibonding. This should raise the energy of the 3B_1 and 1B_1 excited states of (5) but still probably leave them somewhat below the 3B_2 and 1B_2 excited states, respectively.

The parallel-type CF₂ emission band system described earlier in this paper can now probably be identified with the transition ${}^{1}B_{2} \rightarrow {}^{1}A_{1}$ involving states analogous to those in (4). The only other allowed types of transitions to the assumed ${}^{1}A_{1}$ ground state $({}^{1}B_{1} \rightarrow {}^{1}A_{1})$ and ${}^{1}A_{1} \rightarrow {}^{1}A_{1}$) would give perpendicular-type bands. (A transition of the type ${}^{1}A_{2} \rightarrow {}^{1}B_{1}$, ${}^{1}B_{1} \rightarrow {}^{1}A_{2}$, ${}^{3}A_{2} \rightarrow {}^{3}B_{1}$, or ${}^{3}B_{1} \rightarrow {}^{3}A_{2}$ would give parallel-type bands, but would involve two excited states.) It might be hoped that the appreciable though not large decrease in apex angle and change in interatomic distance during the emission process in the observed parallel-type transition would throw light on the electron configurations involved. However, in view of the qualitative nature of the information available and the uncertainty as to the exact form of the (CF₂ analog of the) $3a_1$ MO, all that can be said at present is that there seems to be no obvious inconsistency with the $\cdots (3a_1)(2b_2), B_2 \rightarrow (3a_1)^2, A_1$ interpretation.

The possible second system of CF_2 bands at longer wave-lengths than the main system, if confirmed by further work, should according to the preceding dis-

⁸ For a review and discussion, see, e.g., R. G. W. Norrish and G. Porter, Discussions Faraday Soc. No. 2, 97 (1947); C. A. McDowell, *ibid.*, p. 143. Discussions Faraday Soc. No. 2, 143 (1947).

⁹ Molecular orbital theory of CH₂, see R. S. Mulliken, Phys. Rev. 41, 751 (1932); J. E. Lennard-Jones, Trans. Faraday Soc. 30, 70 (1934).

^{*} The emitter of these bands has now, however, become doubtful because of the recently reported results of Monfils and Rosen (Nature 164, 713 (1949)).

¹⁰ G. Herzberg, Rev. Mod. Phys. 14, 195 (1942); Astrophys. J. 96, 314 (1942).

cussion be identified with the transition ${}^{1}B_{1} \rightarrow {}^{1}A_{1}$ and should consist of perpendicular-type bands.

The preceding probable identification of the CF_2 bands lends support to the obtuse-angled model with ${}^{1}A_1$ ground state for CH_2 . The presence of partial double-bond formation in CF_2 does not alter this

PHYSICAL REVIEW

conclusion, since the strength of π (i.e., $2p_x$) bonding in an AB_2 molecule is readily seen to be insensitive to the apex angle.]

The writer wishes to express his thanks to Professor Robert S. Mulliken for his kind interest and suggestions during the course of the work.

VOLUME 77, NUMBER 5

MARCH 1, 1950

Internal Conversion in Ni⁶⁰

MARTIN DEUTSCH* AND KAI SIEGBAHN Nobel Institute for Physics, Stockholm, Sweden (Received November 1, 1949)

The coefficients of internal conversion for the two gamma-rays accompanying the decay of Co⁶⁰ have been measured. For the 1.17-Mev gamma-ray we find $\alpha = 2.3 \times 10^{-4}$, for the 1.33-Mev ray $\alpha = 1.8 \times 10^{-4}$. Comparison with theoretical values indicates that the parity change must be the same in both transitions and that the two gamma-rays are probably electric quadrupoles.

LTHOUGH the decay of Co⁶⁰ has been studied in A considerable detail, no measurement of the coefficients of internal conversion of the two well-known gamma-rays has been published. We have used a large, double-focusing spectrometer of 50-cm radius of curvature to measure these coefficients. This instrument admits a solid angle of about 0.12 steradian and, with the extended sources used in these experiments, permits a resolution of about one percent. The magnetic field is measured by balancing the induced e.m.f. of a rotating coil against that of another coil rotating on the same shaft in the field of a set of Helmholz coils. The current through the latter is measured with a precision ammeter. The precision of the field measurements is estimated to be about ± 0.1 percent. An absolute momentum calibration was obtained by the measurement of several well-known electron lines from ThB and of secondary electrons produced by annihilation radiation.



* On leave from Massachusetts Institute of Technology, Cambridge, Massachusetts.

Figure 1 shows a momentum spectrum of the electrons from Co⁶⁰. A counter window of about 3 mg/cm² thickness was used. The two internal conversion lines are shown again in the insert, with the ordinate multiplied by 100. Although the number of conversion electrons is only of the order of 10^{-4} of the number in the primary spectrum, the peaks are well resolved since they appear beyond the end point of the continuum. The low intensity continuous high energy "tail" on the distribution is due to Compton electrons ejected from the source and parts of the spectrometer. The conversion coefficients were determined by comparing the area under each of the peaks with that under the continuous spectrum. The integration of the latter is made difficult by the effect of the counter window, which seriously distorts the spectrum below about 0.15 Mev. Above this energy the observed spectrum is well represented by an allowed Fermi plot and we assumed that the low energy part also follows the allowed shape. The effect of source thickness is probably to cause us to underestimate the number of beta-rays since retardation in the source will reduce the relative number of high energy particles on which our extrapolation is based. The two sources used in our experiments were 8 mg/cm^2 and 2 mg/cm² thick, respectively, which may cause some error in this direction. Another factor which may cause us to overestimate the conversion coefficients is the production of photo-electrons in the cobalt of the source material. These could not be resolved from the conversion electrons from the nickel product nucleus. From the known source thickness we estimate that this error should be only a few percent. This was confirmed by the fact that the area under the two peaks remained practically unchanged when the source was covered with 18 mg/cm² of copper. If the peaks were largely due



FIG. 1. The spectra of CF_2 taken on the E_1 quartz spectrograph. (b) is from the original and (a) is three times enlarged. Wave-lengths of some of the bands are marked.