

Centrifugal Effects in Millimetre Wave Spectra: Formyl Fluoride (*).

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Summary. — The three rotational and six distortion constants of both formyl and d-formyl fluoride have been determined from their millimetre wave absorption spectra, using an improved method of calculation of centrifugal effects. The rotational constants are: for HCOF, $A=91\,156.56$ MHz, $B=11\,760.23$ MHz, $C=10\,396.72$ MHz; for DCOF, $A=65\,096.59$ MHz, $B=11\,761.74$ MHz, $C=9\,941.71$ MHz. Taken with electron diffraction data these yield the parameters $r_{\text{CH}}=(1.087 \pm 0.01)$ Å, $r_{\text{CO}}=(1.182 \pm 0.003)$ Å, $r_{\text{CF}}=(1.341 \pm 0.003)$ Å, and $\beta_{\text{FCO}}=(123.04 \pm 0.02)^\circ$. Comparisons are made with the structure of the formyl grouping in similar molecules.

1. — Introduction.

Although rotational constants of molecules are now readily obtained by microwave spectroscopy to seven significant figures, this high precision does not carry over into the determination of internuclear distances and bond angles. The main cause of this is the presence of zero-point vibrations, which shift the molecular parameters from their equilibrium values by large and uncertain

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amounts. For example, KIVELSON, WILSON, and LIDE⁽¹⁾ studied a large number of isotopic forms of vinyl chloride but were not able to fix values of the bond lengths to better than 0.01 Å. Corrections for these vibration-rotation effects have been carried out for diatomic and some triatomic molecules, but the problem has become excessively difficult in more complicated cases. However little attention has been paid to centrifugal effects, although these depend on the molecular vibrations in a markedly similar manner.

In addition to the fundamental difficulty above, it is often necessary to assume values for some molecular bond lengths because of the lack of sufficient data to determine them all. These values are chosen by comparison with the parameters in similar molecules for which a full determination exists. A particularly common practice is to take a C-H bond length of 1.11 Å, as determined for the methyl halides⁽²⁾, but recently COSTAIN⁽³⁾ has pointed out that studies by isotopic substitution in these halides support a bond length of only 1.096 Å. Another recent change in an accepted bond length is shown by the C=C bond in ethylene, which formerly was given by an infrared study⁽⁴⁾ as 1.353 Å. Three new determinations, by electron diffraction⁽⁵⁾, infrared spectroscopy⁽⁶⁾, and Raman spectroscopy⁽⁷⁾, agree in setting this length in the vicinity of 1.335 Å. It would seem that many of the rotational analyses of complicated molecules are based on data that are, at best, uncertain, and there is great need of a detailed analysis of the behaviour of simple chemical groupings in changing molecular surrounding.

The formyl grouping, HCO—, is particularly well adapted to such a study. Detailed measurements are available for formaldehyde⁽⁸⁾, formic acid^(9,10), methyl formate⁽¹¹⁾, formamide⁽¹²⁾, and acetaldehyde⁽¹³⁾. However, in several of these molecules there are further complications due to internal rotation. Formyl fluoride, for which no microwave studies have previously appeared in

(1) D. KIVELSON, E. B. WILSON and D. R. LIDE: *Journ. Chem. Phys.*, **32**, 205 (1960).

(2) S. L. MILLER, L. C. AAMODT, G. DOUSMANIS, C. H. TOWNES and J. KRAITCHMAN: *Journ. Chem. Phys.*, **20**, 1112 (1952).

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(7) J. M. DOWLING and B. P. STOICHEFF: *Ann. Rev. Phys. Chem.*, **10**, 33 (1959).

(8) R. B. LAWRENCE and M. W. P. STRANDBERG: *Phys. Rev.*, **83**, 363 (1951).

(9) R. TRAMBARULO, A. CLARK and C. HEARNS: *Journ. Chem. Phys.*, **28**, 736 (L) (1958).

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(11) R. F. CURL: *Journ. Chem. Phys.*, **30**, 1529 (1959).

(12) C. C. COSTAIN and J. M. DOWLING: *Journ. Chem. Phys.*, **32**, 158 (1960).

(13) R. W. KILB, C. C. LIN and E. B. WILSON: *Journ. Chem. Phys.*, **26**, 1695 (1957).

the literature, is conveniently simple and possesses the advantage of having a dipole moment not orientated along any principal axis, so that it is possible to observe rotational transitions originating in low energy states to determine the rotational constants and in high energy states to measure centrifugal effects. Both types of transition can be observed in the 2-3 mm wavelength region.

2. - Experimental.

Formyl fluoride was made from formic acid, KF and benzoyl chloride, as described by MORGAN, STAATS, and GOLDSTEIN⁽¹⁴⁾. It was found that even traces of water greatly lowered the yield, and rigorous drying of the reagents, by means of anhydrous Cu SO₄ for the liquids and strong heating for the KF, was necessary to bring the yield to the 20 % quoted by the above authors. d-Formyl fluoride, DCOF, was prepared in the same way from a 5 ml sample of 97 % DCOOD, sent to us by Dr. H. W. MORGAN of Oak Ridge National Laboratory, to whom we are deeply indebted. The gas, with boiling point -26°C , was collected at dry ice temperature and stored under liquid nitrogen after distillation with retention of the middle fraction. All microwave studies were carried out at dry ice temperature to avoid decomposition to CO and HF at room temperature; even at dry ice temperature this change becomes noticeable after some weeks.

Millimetre waves were generated by using a harmonic generator of the type described by KING and GORDY⁽¹⁵⁾ to multiply up the output of a 2K33 K band klystron. The output was fed from fourth harmonic waveguide ((0.075×0.034) in.) to a two metre K band absorption cell with mica windows and detected by a fourth harmonic or sixth harmonic (guide dimensions: (0.045×0.022) in.) detector. Lines were observed on a cathode ray oscilloscope by video detection; Stark patterns were studied by means of a conventional one metre K band Stark cell, using 4000 Hz field modulation and a lock-in amplifier. Frequency measurements were made at the fundamental frequency by means of a frequency standard monitored by Station WWV, whose input at 5 MHz was correct to a few parts in 10^9 . The limiting accuracy of frequency measurement was set by the rather large line width and is estimated as ± 0.04 MHz at the fundamental frequency. Final identification of the correct harmonic at which a line appeared was made by tuning this line with a stub at the detector and finding its wavelength in the guide from the

⁽¹⁴⁾ H. W. MORGAN, P. A. STAATS and J. H. GOLDSTEIN: *Journ. Chem. Phys.*, **25**, 337 (1956).

⁽¹⁵⁾ W. C. KING and W. GORDY: *Phys. Rev.*, **93**, 407 (1954).

separation of its successive disappearances. It was readily possible to distinguish between the first three harmonics transmitted by the detector guide in this way, but more difficult for higher harmonics.

3. - Analysis of spectra.

Although neither gas showed lines with a resolvable hyperfine structure, a very large number of lines without any regular pattern occurred due to the presence of *b*-type transitions of much greater intensity than *a*-type transitions. The method of analysis was to search for *Q* branch transitions, which were readily identifiable by their strength and their characteristic Stark pattern. When sufficient of these had been found it was possible to compare their frequencies with those predicted from the crude molecular model used by MORGAN, STAATS, and GOLDSTEIN (14) and to modify the rotational constants to get better agreement; only the assignments in Tables I and II gave close agreement.

TABLE I. - *Transitions of HCOF.*

Assignment	Frequency Observed	Δf Calc. - Obs.	Centrifugal Shift
<i>a</i> -type transitions			
6 ₀₆ → 7 ₀₇	154 120.02 MHz	+ 0.45 MHz	- 12.37 MHz
6 ₁₆ → 7 ₁₇	150 098.73	- 0.99	- 8.78
6 ₁₅ → 7 ₁₆	159 618.91 (*)	- 0.02	- 14.58
6 ₂₄ → 7 ₂₅	155 923.97	+ 3.66	- 8.59
6 ₂₅ → 7 ₂₆	154 955.55	+ 0.55	- 7.08
6 ₃₃ → 7 ₃₄	155 251.93	- 0.08	- 0.30
6 ₃₄ → 7 ₃₅	155 234.17	+ 0.26	+ 0.24
6 ₄ → 7 ₄	155 195.15	+ 0.14	+ 10.03
6 ₅ → 7 ₅	155 183.56	+ 0.10	+ 23.24
6 ₆ → 7 ₆	155 186.37	+ 0.34	+ 39.37
<i>b</i> -type transitions			
0 ₀₀ → 1 ₁₁	101 550.36 MHz	- 0.05 MHz	- 2.97 MHz
1 ₀₁ → 2 ₁₂	122 343.95	- 0.04	- 2.75
2 ₀₂ → 3 ₁₃	142 462.44	- 0.07	- 2.63
3 ₀₃ → 4 ₁₄	161 927.56	- 0.12	- 2.68
5 ₁₄ → 4 ₂₃	119 298.55	+ 0.07	- 34.93
6 ₁₅ → 5 ₂₄	93 164.04	- 0.04	- 26.52
8 ₁₈ → 9 ₀₉	138 988.38	+ 0.13	- 37.07
5 ₀₅ → 5 ₁₄	90 786.64	+ 0.17	- 2.09
6 ₀₆ → 6 ₁₅	95 339.16	+ 0.37	- 2.99
7 ₀₇ → 7 ₁₆	100 838.05	+ 0.13	- 5.13
8 ₀₈ → 8 ₁₇	107 362.11	- 0.63	- 9.13
9 ₀₉ → 9 ₁₈	114 993.80	- 1.54	- 15.77
10 _{0,10} → 10 ₁₉	123 812.35	+ 0.08	- 25.96

(*) Calculated by combining other transition frequencies.

TABLE II. — *Transitions of DCOF.*

Assignment	Frequency Observed	Δf Calc. — Obs.	Centrifugal Shift
<i>a</i> -type transitions			
$6_{06} \rightarrow 7_{07}$	149 439.56 MHz	— 0.33 MHz	— 10.56 MHz
$6_{16} \rightarrow 7_{17}$	144 988.68	— 0.15	— 8.53
$6_{15} \rightarrow 7_{16}$	157 633.14	— 0.02	— 13.89
$6_{24} \rightarrow 7_{25}$	154 029.84	0.00	— 11.56
$6_{25} \rightarrow 7_{26}$	151 558.74	— 0.03	— 9.63
$6_{33} \rightarrow 7_{34}$	152 343.06	+ 0.16	— 7.59
$6_{34} \rightarrow 7_{35}$	152 253.06	— 0.06	— 7.55
$6_{42} \rightarrow 7_{43}$	152 147.81	+ 1.15	— 3.73
$6_{43} \rightarrow 7_{44}$	152 147.81	+ 0.06	— 3.72
$6_5 \rightarrow 7_5$	152 088.00	— 0.24	+ 1.13
$6_6 \rightarrow 7_6$	152 059.08	+ 0.29	+ 7.05
<i>b</i> -type transitions			
$1_{01} \rightarrow 2_{12}$	94 920.60 MHz	— 0.09 MHz	— 1.19 MHz
$2_{02} \rightarrow 3_{13}$	113 911.30	— 0.04	— 1.41
$3_{03} \rightarrow 4_{14}$	132 067.57	+ 0.27	— 1.91
$4_{04} \rightarrow 5_{15}$	149 483.49	+ 0.21	— 3.22
$3_{12} \rightarrow 2_{21}$	92 176.92	— 0.16	— 16.41
$6_{25} \rightarrow 5_{32}$	141 567.45	+ 0.08	67.25
$2_{12} \rightarrow 2_{21}$	165 448.32	— 1.17	— 17.49
$3_{13} \rightarrow 3_{22}$	168 210.00	— 5.00	— 17.95
$3_{12} \rightarrow 3_{21}$	157 515.96	— 0.14	— 16.48
$4_{13} \rightarrow 4_{22}$	154 391.16	+ 0.19	— 15.19
$5_{14} \rightarrow 5_{23}$	150 856.20	+ 0.15	— 13.43
$6_{15} \rightarrow 6_{24}$	147 150.05	+ 0.43	— 11.29
$7_{16} \rightarrow 7_{25}$	143 547.24	— 0.05	— 8.95
$8_{17} \rightarrow 8_{26}$	140 340.46	+ 0.07	— 6.82
$8_{68} \rightarrow 8_{17}$	93 881.72	+ 0.19	— 12.89
$9_{09} \rightarrow 9_{18}$	105 584.79	+ 0.27	— 21.50
$10_{0,10} \rightarrow 10_{19}$	119 163.65	+ 0.21	— 33.94
$11_{0,11} \rightarrow 11_{1,10}$	134 614.08	— 0.12	— 50.96
$12_{0,12} \rightarrow 12_{1,11}$	151 855.87	— 0.09	— 73.04

These *Q* branch frequencies depend on only two rotational constants, but the third was estimated by assuming planarity of the molecule and a search carried out for *R* branch transitions of low *J* in the vicinity of the predicted frequencies. These transitions were also identified by their Stark patterns, which consist of only a few components. The best rotational constants without taking account of centrifugal distortion were derived from the low *J* transitions and used to locate transitions needed to complete the centrifugal distortion fitting.

Rotational transition frequencies were fitted to the expression of King,

Hainer, and Cross:

$$W/h = \frac{1}{2}(A + C)J(J + 1) + \frac{1}{2}(A - C)E_r$$

using published tables of E_r . These are described in reference (16). For centrifugal effects a convenient new formula (17) was devised, based on the molecular « reduced energy » w and asymmetry parameter b , also described in reference (16).

$$\begin{aligned} W'/h = & b R_{10} J(J + 1) - \frac{5}{2} b w R_{10} - (D_J + \frac{1}{2} b R_{10}) J^2 (J + 1)^2 - \\ & - (D_{JK} - b R_{10}) J(J + 1) (w - b dw/db) - 2 \delta_J J(J + 1) dw/db + \\ & + R_{10} w dw/db + (R_6 - \frac{1}{4} b R_{10}) T_{JK}. \end{aligned}$$

Here R_{10} has the value $(b D_K + 4 R_5)/(1 - \frac{1}{2} b^2)$ in terms of constants defined by NIELSEN (18). The correction term T_{JK} is only important in the following cases:

$$K = 0 \quad T_{JK} = \frac{1}{16} b^2 (J - 3)(J - 2)(J - 1) J(J + 1)(J + 2)(J + 3)(J + 4),$$

$$K = 1 \quad T_{JK} = \frac{8c_1 R_5}{b} (w - 1 - c_1 b),$$

$$K = 2 \quad (E^\pm) \quad T_{JK} = \pm (J - 1) J(J + 1)(J + 2).$$

All these coefficients may be calculated from the tables of E_r by means of suitable interpolation and the algebraic relations between w and E_r . The calculations were programmed onto the Mathematics Department IBM 650 computer, with a resultant great saving of time. Initial values of the constants were obtained by Erlandsson's method (19) from the a -type transitions and were then refined by iteration. The transition frequencies were rather insensitive to R_5 and R_6 which were instead estimated from the following relations, true for any molecule with one plane of symmetry:

$$\begin{aligned} R_5 = & \frac{1}{2}(D_J + \delta_J - \frac{1}{2} D_{JK}) - I_b^2/2I_a^2 \times (D_J + 6R_6) - \\ & - I_a^2/I_c^2 \times (D_J^2 + D_{JK} + D_K) + I_b^4/2I_a^2 I_c^2 \times (D_J - 2\delta_J - 2R_6), \end{aligned}$$

$$R_6 = \frac{[(I_c^2 - I_b^2)^2 - I_a^4] D_J - I_a^4 (D_{JK} + D_K) + 2(I_c^4 - I_b^4) \delta_J}{2(I_c^4 + 6I_c^2 I_b^2 + I_b^4)}.$$

(16) C. H. TOWNES and A. L. SCHAWLOW: *Microwave Spectroscopy* (New York, 1955).

(17) J. G. BAKER: *Bull. Am. Phys. Soc.*, **5**, 241 (1960).

(18) H. H. NIELSEN: *Rev. Mod. Phys.*, **23**, 213 (1951).

(19) G. ERLANDSSON: *Journ. Chem. Phys.*, **28**, 71 (1958).

The constants obtained are shown in Table III. A most significant point is the very large value of D_K , which contributes even to the low J transitions. Neglect of this leads to an error in A of the order of D_K , and so it appears that determinations of the largest rotational constants of near-prolate rotors are not to be trusted unless corrected for centrifugal effects. Another interesting fact is the almost threefold change in D_{JK} between the two isotopes; this is probably associated with the closeness of the light H atom to the b axis of inertia.

TABLE III. - *Constants of formyl fluoride.*

	HCOF	DCOF
A MHz	91 156.56	65 096.59
B MHz	11 760.23	11 761.74
C MHz	10 396.72	9 941.71
z	- 0.966 233 0	- 0.934 002 9
D_J kHz	9.85	8.82
D_{JK} kHz	- 105.5	- 38.1
D_K kHz	3 150	1 207
δ_J kHz	- 2.13 ₅	- 2.00
R_5 kHz	25	4
R_6 kHz	- 0.135	- 0.162
R_{10} kHz	73	- 4
I_a a.m.u. Å^2	5.545 7 ₅	7.765 8 ₅
I_b a.m.u. Å^2	42.986 5	42.981 0
$I_c - I_a - I_b$ a.m.u. Å^2	0.091 8 ₅	0.1027

It will be seen that the lines of Tables I and II have been fitted within the experimental error of 0.04 MHz at 25 kHz, except for a few isolated and unexplained cases, and it appears that the formula given accounts rather well for centrifugal effects in an asymmetric molecule.

4. - Molecular structure.

It is possible to locate the H atom in the centre-of-gravity co-ordinates of HCOF by using Kraitchman's method of isotopic substitution⁽²⁰⁾. COSTAIN⁽³⁾ recommends the use of the two in-plane moments of inertia so long as the inertial defects of the two (planar) molecules are not too different. However, use of I_b leads to an imaginary co-ordinate because the H atom is very close

⁽²⁰⁾ J. KRAITCHMAN: *Amer. Journ. Phys.*, **21**, 17 (1953).

to the b axis and zero-point vibrations make this quantity smaller for DCOF than for HCOF. This problem does not arise if I_a and I_c are treated as the equilibrium moments of inertia, as will be done here. The result is shown in Table IV.

TABLE IV. - *Centre-of-gravity coordinates in HCOF.*

	H	C	O	F
$b(A)$	1.5007	0.4150	-0.1749	-0.1945
$a(A)$	0.0713	0.1325	1.1573	-1.0620
$r_{\text{CH}}(1.087 \pm 0.01) A$			$\beta_{\text{FCO}}(123.04 \pm 0.02)^\circ$	
$r_{\text{CO}}(1.182 \pm 0.003) A$			$\beta_{\text{FCH}} 114^\circ$	
$r_{\text{CF}}(1.341 \pm 0.003) A$			$\beta_{\text{OCH}} 123^\circ$	

Even though the H atom is definitely located there remain only two moments of inertia to locate the remaining three atoms. It is necessary to use the most accurate electron diffraction data ⁽²¹⁾ ($r_{\text{CO}} = (1.192 \pm 0.011) A$; $r_{\text{CF}} = (1.351 \pm 0.013) A$; $r_{\text{CF}}/r_{\text{CO}} = (1.134 \pm 0.005) A$) to choose a final structure. Fortunately these restrictions are sufficient to locate the other three atoms with considerable accuracy; the best centre-of-gravity co-ordinates and a final structure are given in Table IV. This agrees very well with the results obtained by LEBLANC, LAURIE, and GWINN ⁽²²⁾ from studies at lower frequencies. It should be emphasized that the error limits given do not take account of zero-point vibration corrections; these will probably not affect the bond lengths significantly but will produce an uncertainty of several degrees in the angles

TABLE V. - *The formyl group in some simple molecules.*

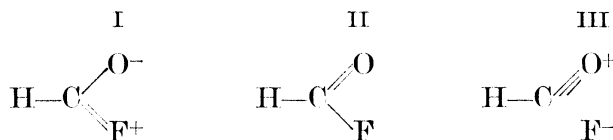
	C—H	C=O
HCOF	1.087 A	1.182 A
H ₂ CO ⁽⁸⁾	1.12	1.21
HCOOH ^(9,10)	1.092	1.237
HCONH ₂ ⁽¹²⁾	1.102	1.19 ₃
HCOOCH ₃ ⁽¹¹⁾	1.10	1.20

involving the C—H bond. One of us (J.G.B.) has devised a method of using centrifugal constants to estimate these corrections, details of which will be

⁽²¹⁾ M. E. JONES, K. HEDBERG and V. SCHOMAKER: *Journ. Amer. Chem. Soc.*, **77**, 5278 (1955).

⁽²²⁾ D. LEBLANC, V. W. LAURIE and W. D. GWINN: to be published.

published elsewhere, but further isotopic studies are required before they can be made for formyl fluoride. It is safe to conclude that the formyl fluoride molecule is exceptionally compact, for the C=O length is shorter than in all the molecules of Table V while the C—F bond is much shorter than the single bond length (1.385 Å) found in CH₃F⁽²³⁾. It appears that there are significant contributions from all three structures below:



5. — Conclusion.

A rotational and centrifugal analysis of the millimetre wave absorption spectra of HCOF and DCOF has led to a determination of all nine constants involved for each molecule and the conclusion that it is not safe to neglect centrifugal effects even for low J transitions. The molecular parameters obtained are in good agreement with those of earlier workers, and show that the formyl grouping undergoes large changes even in the simplest formyl compounds.

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⁽²³⁾ O. R. GILLIAM, H. D. EDWARDS and W. GORDY: *Phys. Rev.*, **75**, 1014 (1949).

RIASSUNTO

Sono state determinate le tre costanti rotazionali e le sei costanti di distorsione centrifuga del fluoruro di formile e del deutero fluoruro di formile studiandone gli spettri di assorbimento nella regione millimetrica e usando un metodo perfezionato di calcolo degli effetti centrifughi. Le costanti rotazionali sono: per HCOF, $A=91156.56$ MHz, $B=11760.23$ MHz, $C=10396.72$ MHz; per DCOF, $A=65096.59$ MHz, $B=11761.74$ MHz, $C=9941.71$ MHz. Tenendo conto dei dati di diffrazione elettronica, queste costanti rotazionali forniscono i seguenti valori per i parametri molecolari: $r_{\text{CH}}=1.087 \pm 0.01$ Å, $r_{\text{CO}}=(1.182 \pm 0.003)$ Å, $r_{\text{CF}}=(1.341 \pm 0.003)$ Å e $\beta_{\text{FCO}}=(123.04 \pm 0.02)^\circ$.