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Millimetre Wave Spectrum of Deutero-Derivatives of Formic Acid (*).

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Summary. — The rotational constant A of DCOOH, HCOOD and DCOOD have been determined by analysing the « a » type transitions in the range of frequencies from 120 000 MHz to 160 000 MHz. By assuming I_a and I_b as the equilibrium moments of inertia, the Kraitchman's method has been used to determine the co-ordinates of the two hydrogen atoms in the principal axis system of HCOOH. The centrifugal distortion constants of the three molecules are also given.

1. - Introduction.

Formic acid has been already studied by many investigators in microwave spectroscopy. Among them most recently ERLANDSSON⁽¹⁾ has been using millimetric techniques in order to study HCOOH and LERNER, DAILEY and FRIEND⁽²⁾ have been studying five isotopic species of the acid from 20 000 to 50 000 MHz. By using this range of frequencies it was impossible to determine the rotational constants A , and the molecular structure was obtained by use of the moments of inertia I_b and I_c ; therefore the position of the hydrogen atom attached to the carbon could not be directly determined because of zero-point vibrations.

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(¹) G. ERLANDSSON: *Journ. Chem. Phys.*, **28**, 71 (1958).

(²) G. LERNER, B. P. DAILEY and J. P. FRIEND: *Journ. Chem. Phys.*, **26**, 680 (1957).

The present work is an attempt of getting a better molecular structure by studying the spectra of the deuterio-derivatives of formic acid in the millimetre wave region; by examining millimetric transitions it is possible to determine the constant A for each molecular species. The lines used where « a » type transitions sufficiently sensitive to A ; but a complete centrifugal distortion analysis has been necessary to obtain the constants A with a reasonably good accuracy.

2. - Spectrum.

The measurements have been done at room temperature with a video-type spectrometer using harmonic generator and millimetre wave detector of the type developed in the Laboratory of Duke University⁽³⁾. In the harmonic generation a specially treated silicon crystal kindly supplied us by R.S. Ohl of Bell Telephone Laboratories, was used. The frequency measurements were made on the fundamental with a frequency standard monitored by Station WWV of the National Bureau of Standards.

DCOOD used was part of a sample kindly sent us by Dr. H. W. MORGAN of Oak Ridge National Laboratory; a sample of DCOOH was prepared from DCOOD by equilibrating it with H_2O and HCOOD by equilibrating commercial formic acid with D_2O .

For the localization of the spectrum, the constants B and C found by LERNER, DAILEY and FRIEND⁽²⁾ were used together with an approximate value of A , calculated by using the planarity relation $I_a - I_b - I_c = 0$, valid for rigid rotors. The observed lines were all « a » type transitions; an attempt to find « b » type transitions was unsuccessful. In particular all the transitions $J = 6 \rightarrow 7$ with $\Delta K_1 = 0$ and $\Delta K_{-1} = 1$ for DCOOH and HCOOD and all the transitions $J = 5 \rightarrow 6$ of the same kind for DCOOD were measured. For these transitions a rather large contribution of centrifugal distortion effects is to be expected. On the other hand the constant A is very strongly dependent on a even small shift of frequency (0.2 MHz corresponds to an uncertainty of about 5 MHz in A); consequently a complete centrifugal distortion analysis was required in order that the uncertainty on A should be due only to the experimental error.

The maximum experimental error on the average value of several measurements of each frequency was 0.03 MHz on the fundamental and about 0.2 MHz on the transition frequencies.

⁽³⁾ W. C. KING and W. GORDY: *Phys. Rev.*, **93**, 407 (1954).

3. - Centrifugal distortion analysis.

In order to determine the centrifugal distortion constants a convenient formula developed by JOHN G. BAKER⁽⁴⁾ was used, based on the use of the reduced energy « w » and of the asymmetry parameter b . If we denote by W' the centrifugal distortion energy, the formula reads:

$$(1) \quad W'/h = bR_{10}(J+1)J - \frac{5}{2}bwR_{10} - (D_J + \frac{1}{2}bR_{10})J^2(J+1)^2 - \\ - (D_{JK} - bR_{10})J(J+1)(w - b dw/db) - 2\delta_J J(J+1) dw/db + \\ + R_{10}w dw/db + (R_6 - \frac{1}{4}bR_{10})T_{JK},$$

with $R_{10} = (bD_K + 4R_5)/(1 - \frac{1}{2}b^2)$; all the constants are those defined by NIELSEN⁽⁵⁾.

T_{JK} is important only in the following cases:

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

$$K = 1: \quad T_{JK} = \frac{8c_1R_5}{b}(w - 1 - c_1b),$$

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

The order of magnitude of the constants was first evaluated by various approximate methods. Initial values for D_J , D_{JK} and δ_J were calculated by the sum rules⁽⁴⁾ applied to the whole series of « a » type transitions.

The following two relations, valid for every molecule with a plane of symmetry, were also very helpful in the centrifugal analysis:

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

$$(3) \quad R_6 = \frac{[(I_c^2 - I_b^2)^2 - I_a^4]D_J - I_a^4(D_{JK} + D_K) + 2(I_c^4 - I_b^4)\delta_J}{2(I_c^4 + 6I_c^2I_b^2 + I_b^4)}.$$

A first approximate value for D_K was obtained by use of the relation: $D_J + D_{JK} + D_K \propto 1/I_a^4$ valid for a planar molecule, assuming the same proportionality constant as in HCOOH; in this case D_K was calculated by Erlandsen's data for D_J , D_{JK} , δ_J and R_6 using relation (3). R_5 and R_6 could be easily evaluated from (2) and (3). Final values for all the constants were obtained by an iteration method.

⁽⁴⁾ J. G. BAKER: *Bull. Am. Phys. Soc.*, **5**, 241 (1960); P. FAVERO, A. M. MIRRI e J. G. BAKER: *Nuovo Cimento*, **17**, 740 (1960).

⁽⁵⁾ H. H. NIELSEN: *Rev. Mod. Phys.*, **23**, 90 (1951).

TABLE I. - Frequency (MHz).

Transition	Observed	Calculated	Centrifugal shift
DCOOH			
$6_{06} \rightarrow 7_{07}$	150 345.06	150 345.07	— 8.76
$6_{15} \rightarrow 7_{16}$	160 392.07	160 392.12	— 12.04
$6_{16} \rightarrow 7_{17}$	145 882.95	145 882.76	— 6.93
$6_{24} \rightarrow 7_{25}$	157 241.48	157 241.60	— 10.10
$6_{25} \rightarrow 7_{26}$	153 521.68	153 521.47	— 7.82
$6_{33} \rightarrow 7_{34}$	154 757.18	154 757.27	— 6.09
$6_{34} \rightarrow 7_{35}$	154 571.17	154 570.95	— 5.87
$6_{42} \rightarrow 7_{43}$	154 431.13	154 431.16	— 2.26
$6_{43} \rightarrow 7_{44}$	154 427.84	154 427.91	— 2.40
$6_5 \rightarrow 7_5$	154 332.94	154 333.11	+ 2.49
$6_6 \rightarrow 7_6$	154 285.66	154 285.75	+ 8.29
$0_{00} \rightarrow 1_{01}$	22 011.3 (a)	22 011.47	— 0.03
$1_{10} \rightarrow 2_{11}$	46 122.6 (a)	46 122.95	— 0.25
$1_{11} \rightarrow 2_{12}$	41 923.0 (a)	41 922.71	— 0.30
$4_{14} \rightarrow 4_{13}$	20 989.6 (a)	20 989.82	— 0.75
HCOOD			
$6_{06} \rightarrow 7_{07}$	149 753.66	149 753.58	— 12.65
$6_{15} \rightarrow 7_{16}$	157 770.81	157 770.99	— 16.26
$6_{16} \rightarrow 7_{17}$	145 312.14	145 312.30	— 10.47
$6_{24} \rightarrow 7_{25}$	154 137.58	154 137.57	— 12.64
$6_{25} \rightarrow 7_{26}$	151 778.74	151 778.60	— 10.62
$6_{33} \rightarrow 7_{34}$	152 526.01	152 525.89	— 7.20
$6_{34} \rightarrow 7_{35}$	152 442.80	152 442.69	— 7.23
$6_{42} \rightarrow 7_{43}$	152 344.38	152 344.41	— 1.40
$6_{43} \rightarrow 7_{44}$	152 343.36	152 343.37	— 1.42
$6_5 \rightarrow 7_5$	152 288.87	152 288.83	+ 5.82
$6_6 \rightarrow 7_6$	152 264.95	152 265.14	+ 14.59
$0_{00} \rightarrow 1_{01}$	21 732.6 (a)	21 732.56	— 0.04
$1_{10} \rightarrow 2_{11}$	45 257.8 (a)	45 257.34	— 0.34
$1_{01} \rightarrow 2_{02}$	43 420.2 (a)	43 421.23	— 0.35
$1_{11} \rightarrow 2_{12}$	41 673.0 (a)	41 672.42	— 0.28
$5_{15} \rightarrow 5_{14}$	26 865.5 (a)	26 865.75	— 3.08

(a) Frequencies measured by LERNER, DAILEY and FRIEND.

TABLE I (continued).

Transition	Observed	Calculated	Centrifugal shift
DCOOD			
$5_{05} \rightarrow 6_{06}$	124 685.34	124 685.16	--- 5.73
$5_{14} \rightarrow 6_{15}$	133 623.69	133 623.70	--- 8.67
$5_{15} \rightarrow 6_{66}$	120 407.60	120 407.47	--- 4.36
$5_{23} \rightarrow 6_{24}$	130 411.85	130 411.68	--- 7.11
$5_{24} \rightarrow 6_{25}$	127 342.80	127 342.91	--- 5.40
$5_{32} \rightarrow 6_{33}$	128 336.34	128 336.39	--- 4.28
$5_{33} \rightarrow 6_{34}$	128 203.04	128 203.19	--- 4.13
$5_{41} \rightarrow 6_{42}$	128 077.64	128 077.74	--- 1.57
$5_{42} \rightarrow 6_{43}$	128 075.90	128 075.82	--- 1.43
$5_5 \rightarrow 6_5$	127 996.80	127 996.65	--- 1.90
$0_{00} \rightarrow 1_{01}$	21 293.9 (a)	21 293.93	--- 0.02
$1_{10} \rightarrow 2_{11}$	44 813.4 (a)	44 813.22	--- 0.33
$4_{14} \rightarrow 4_{13}$	22 237.5 (a)	22 237.63	--- 1.99

(a) Frequencies measured by LERNER, DAILEY and FRIEND.

All the calculated transitions (Table I) are in very good agreement with the observed ones including those measured by LERNER, DAILEY and FRIEND. For some of these, the $4_{14} \rightarrow 4_{13}$ of DCOOH and DCOOD and the $5_{15} \rightarrow 5_{14}$ of HCOOD the centrifugal distortion contribution is very considerable (of the

TABLE II. - Rotational and centrifugal constants in MHz.

	HCOOH (a)	DCOOH	HCOOD	DCOOD
<i>A</i>	77 520.07	57 710 ± 5	66 110 ± 5	50 815 ± 5
<i>B</i>	12 054.98	12 055.80	11 762.55	11 759.8
<i>C</i>	10 416.16	9 955.71	9 970.05	9 534.15
<i>D_J</i>	+0.009 28	+0.008 45	+0.010 42	+0.008 37
<i>D_{JK}</i>	-0.083 0	-0.036 6	-0.057 5	-0.030 9
<i>D_K</i>	+3.12	+1.21	+1.77	+0.75
<i>δ_J</i>	-0.002 02	-0.001 9	-0.002 1	-0.002 3
<i>R₆</i>	-0.000 23	-0.000 20	-0.000 18	-0.000 22
<i>R₅</i>	---	-0.004 0	+0.001 4	+0.006 5
<i>R₁₀</i>	---	-0.040	-0.023	+0.006

(a) ERLANDSSON (1).

order of 1 MHz), such effects being especially due to δ_J and R_{10} ; they have therefore been of help in the evaluation of R_{10} . In Table II are listed the rotational and centrifugal distortion constants of the various isotopic species of formic acid. The centrifugal distortion constants of each isotopic species are comparable in magnitude and of the same order as those determined by ERLANDSSON for HCOOH.

4. - Molecular structure.

The Kraitchman's method ⁽⁶⁾ of the isotopic substitution was used. By this method it should be possible to obtain exactly the co-ordinates of the substituted atom in the principal axis system of HCOOH if the equilibrium moments of inertia were known. Applying Kraitchman's method to the effective moments of inertia one obtains co-ordinates that are not the equilibrium ones but, as COSTAIN ⁽⁷⁾ shows, differ from them less than the r_0 defined by:

$$I_{\text{eff}} = \sum_i m_i r_{0i}^2 = \frac{1}{(1/\sum m_i r_i^2)_{\text{av}}},$$

where r_i are the instantaneous co-ordinate of the atom i and they are nearly independent on the isotopic species used. The combination HCOOH, HCOOD, DCOOH has been used for the localization of the two hydrogen atoms, taking I_a and I_c , among the three possible couples of moments of inertia, as those of equilibrium; in fact use of I_b gives an imaginary co-ordinate for the hydrogen atom attached to the carbon because it is very near to the b axis and the zero point vibrations make impossible the evaluation of the distance between the hydrogen and the b axis; using I_a and I_c this problem does not arise. For the localization of the C atom, I_b and I_c of HCOOH and H¹³C OOH have been used as obtained by ERLANDSSON and DAILEY respectively; on the other hand, use of a particular couple of moments of inertia should be unimportant for the localization of this atom because it is very near to the center of gravity. For the calculation of the oxygen atoms co-ordinates have been used the equations for the center of gravity: $\sum m_i x_i = 0$, etc., and for the moments of inertia $\sum m_i x_i^2 = I_y$, etc. In Table III are listed the results obtained for the angles and bond lengths and the calculated rotational constants of DCOOD, that were determined treating the molecule as a rigid rotor and subtracting from the calculated value of I_b the experimental inertial defect. Taking in

⁽⁶⁾ J. KRAITCHMANN: *Am. Journ. Phys.*, **21**, 17 (1953).

⁽⁷⁾ C. C. COSTAIN: *Journ. Chem. Phys.*, **29**, 864 (1958).

account the fact that DCOOD was not used for the determination of the molecular structure the agreement between the experimental and the calculated

TABLE III. - *Structural parameters.*

	This work	LERNER, DAILEY and FRIEND
C-H	1.092 Å ± 0.01 Å	1.085 Å ± 0.025 Å
C=O	1.237 Å ± 0.002 Å	1.245 Å ± 0.002 Å
C-O	1.312 Å ± 0.002 Å	1.312 Å ± 0.002 Å
O-H	0.961 Å ± 0.01 Å	0.95 Å ± 0.020 Å
< OCO	124° 57' ± 15'	124° 18' ± 10'
< HC=O	120° 58' ± 15'	---
< COH	170° 50' ± 10'	107° 48' ± 1°

Rotational constants of DCOOD (MHz)

	Observed	Calculated
<i>A</i>	50 815 ± 5	50 840
<i>B</i>	11 759.80	11 758.44
<i>C</i>	9 534.15	9 534.07

rotational constants is satisfactorily good. The molecular structure obtained is in good agreement with the model *D* chosen by LERNER, DAILEY and FRIEND, except for the C=O bond length and the two HCO angles.

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RIASSUNTO

Sono state determinate le costanti rotazionali *A* di DCOOH, HCOOD e DCOOD analizzando le transizioni di tipo «*a*» nell'intervallo di frequenze fra 120 000 MHz e 160 000 MHz. Assumendo *I_a* e *I_b* come momenti d'inerzia di equilibrio, è stato usato il metodo di Kraitchman per determinare le coordinate dei due atomi di idrogeno nel sistema degli assi principali di HCOOH. È stata anche fatta l'analisi degli effetti di distorsione centrifuga per le tre molecole.