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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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PHYSICS

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MICROWAVE SPECTRUM OF THE MOLECULE F_2HC—CDHF

(Presented by Academician V. N. Kondrat’ ev on 24 X 1962)

1. In studies on microwave spectroscopy of molecules with internal rotation, consisting of two asymmetric groups joined by a single bond, the following phenomena are of particular interest: the presence of several isomeric states with different energy levels, whose determination is of practical interest; the doubling of absorption lines of rotational transitions in the presence of two energetically identical configurations, owing to the tunneling effect in torsional vibrations about the axis of internal rotation. We have undertaken a study of a series of halogen-substituted ethane molecules belonging to the above-mentioned type of molecules. Molecules of this type have hardly been studied by others, with the exception of certain works in which replacement of H by D slightly disturbs the symmetry (^{1,2}).

Fig. 1

Fig. 2

2. The present work gives the results of an investigation of the molecule F_2HC—CDHF. In this molecule, owing to hindered internal rotation about the single C—C bond, the following isomeric states may occur:

Isomer I ($\alpha = 0$)–when the projections of the C—H (or C—D) and C—F bonds onto a plane perpendicular to the C—C axis do not obscure one another and are directed oppositely (Fig. 1*a*).

Isomer II (skew)—obtained from isomer I by rotating one of the groups by +120° or −120° (Fig. 1*b*).

The skew states ($\alpha = +120°$) and ($\alpha = -120°$) are not energetically identical. Replacement of H by D annuls the plane of symmetry of the CH_2F group, and therefore the moments of inertia in the positions (+120°) and (−120°) are different. As a result, the absorption lines of the rotational transitions of the skew isomer are not degenerate, as is the case for the molecule $F_2HC—CH_2F$, where removal of the twofold degeneracy as a result of the tunneling effect may lead to doubling of the lines.

3. The investigation was carried out with a gas radiospectroscope with electric molecular modulation in the range 7000-25000 MHz at two temperatures: room temperature and dry ice, and at pressures in the cell from 10^{-2} to 10^{-3} Hg. To avoid errors in measuring Stark components due to a certain inhomogeneity of the field, calibration was performed using the shifts of the Stark components of the $2_{1,1}—2_{1,2}$ transition of formaldehyde.

Table 1

$\alpha =$ +120° transitions	observed, MHz	calculated, MHz	$\alpha =$ −120° transitions	observed, MHz	calculated, MHz
$2_{0,2}-2_{1,1}$	6819.5	6819.5	$2_{0,2}-2_{1,1}$	6876.4	6876.6
$3_{0,3}-3_{1,2}$	8260.4	8260.4	$3_{0,3}-3_{1,2}$	8508.1	8508.3
$4_{0,4}-4_{1,3}$	10413.8	10414.0	$4_{0,4}-4_{1,3}$	10959.3	10959.8
$0_{0,0}-1_{1,1}$	11548.45	11548.45	$0_{0,0}-1_{1,1}$	11416.25	11416.25
$5_{0,5}-5_{1,4}$	13374.05	13374.5	$5_{1,4}-5_{2,3}$	13614.4	13615.8
$5_{1,4}-5_{2,3}$	13835.9	13837.1	$6_{1,5}-6_{2,4}$	14206.2	14208.3
$2_{1,2}-3_{0,3}$	14326.7	14326.7	$5_{0,5}-5_{1,4}$	14315.75	14316.4
$7_{1,6}-7_{2,5}$	15219.2	15222.0	$3_{1,2}-3_{2,1}$	14395.25	14395.7
$2_{1,1}-2_{2,0}$	15603.9	15603.9	$2_{1,2}-3_{0,3}$	14446.4	14446.6
$6_{0,6}-6_{1,5}$	17128.25	17127.5	$2_{1,1}-2_{2,0}$	15226.7	15226.7
$1_{0,1}-2_{1,2}$	17141.0	17141.2	$7_{1,6}-7_{2,5}$	15714.8	15717.8
$8_{1,7}-8_{2,6}$	17194.2	17197.8	$1_{0,1}-2_{1,2}$	16924.5	16924.9
$2_{1,2}-2_{2,1}$	17867.1	17867.1	$2_{1,2}-2_{2,1}$	17723.5	17723.5
$3_{1,3}-3_{2,2}$	19088.65	19088.6	$8_{1,7}-8_{2,6}$	18260.1	18264.1
$9_{1,8}-9_{2,7}$	20129.3	20133.5	$6_{0,6}-6_{1,5}$	18514.35	18515.0
$4_{1,4}-4_{2,3}$	20737.1	20737.2	$3_{1,3}-3_{2,2}$	19083.6	19083.7
$10_{2,8}-10_{3,7}$	21031.6	21039.6	$9_{2,7}-9_{3,6}$	20639.9	20646.2
$3_{1,6}-4_{0,4}$	21151.1	21151.2	$4_{1,4}-4_{2,3}$	20920.0	20920.4
$9_{2,7}-9_{3,6}$	21223.85	21230.1	$10_{2,8}-10_{3,7}$	20982.5	20990.8
$7_{0,7}-7_{1,6}$	21530.65	21530.7	$8_{2,6}-8_{3,5}$	21206.35	21211.0

$\alpha =$ $+120°$ transitions	observed, MHz	calculated, MHz	$\alpha =$ $-120°$ transitions	observed, MHz	calculated, MHz
$11_{2,9}-11_{3,8}$	21741.2	21751.3	$3_{1,3}-4_{0,4}$	21233.65	21233.7
$8_{2,6}-8_{3,5}$	22107.6	22112.1	$9_{1,8}-9_{2,7}$	21866.20	21871.0
$2_{02}-3_{13}$	22376.0	22376.3	$2_{0,2}-3_{1,3}$	22041.2	22041.6
$5_{15}-5_{24}$	22816.0	22816.4	$11_{2,9}-11_{3,8}$	22430.8	22441.1
$12_{2,10}-12_{3,9}$	23491.4	23503.3	$5_{1,5}-5_{2,4}$	23234.2	23234.7
$10_{1,9}-10_{2,8}$	23988.6	23993.3	$7_{0,7}-7_{1,6}$	23342.6	23343.0
$6_{24}-6_{33}$	24810	24812.2	$6_{2,4}-6_{3,3}$	23858	23859.8

guide. The frequency was measured with an accuracy of 0.1 MHz by means of markers from harmonics of a 10-megahertz quartz oscillator controlled by a 100-kHz frequency standard.

4. Experimentally, more than 200 absorption lines of rotational transitions of the molecule $F_2HC-CDHF$ were found. From the Stark splitting, a number of lines of the Q- and RP-branches were identified, corresponding to the folded isomeric states ($\alpha = +120°$ and $\alpha = -120°$) (Table 1).

1) From the experimental values of the transition frequencies $0_{0,0}-1_{1,1}$, $2_{1,1}-2_{2,0}$, and $2_{1,2}-2_{2,1}$, the values of the rotational constants A, B, and C were obtained (Table 2).

From these values, the frequencies of the lines of other transitions were calculated in the representation of a rigid asymmetric top. As is seen from the data of Table 1, the calculated frequency values are in good agreement with the experimental ones. The small discrepancies are apparently associated with centrifugal perturbation.

Table 2

	$\alpha = +120°$	$\alpha = -120°$
A	8752.07	8662.04
B	3578.13	3620.59
C	2796.37	2754.21
μ_a^2	0.06 ± 0.01	0.08 ± 0.01
μ_b^2	2.40 ± 0.05	2.39 ± 0.05
μ_c^2	0.13 ± 0.01	0.10 ± 0.01
$\Sigma\mu_g^2$	2.59 ± 0.05	2.57 ± 0.05

2) From the shifts of the Stark components of the transitions $2_{1,1}$—$2_{2,0}$; $2_{1,2}$—$2_{2,1}$ and $3_{0,3}$—$3_{1,2}$, $4_{0,4}$—$4_{1,3}$, the values of the squares of the components of the molecular dipole moment along the principal axes, μ_a^2, μ_b^2, μ_c^2 (Table 2), were calculated. The shifts of the Stark components of other transitions calculated from these values are in good agreement with the measured ones. The obtained value of the square of the dipole moment is approximately 1.4 times smaller than that calculated from the electronegativities of the atoms in the molecule F_2HC—CDHF.

According to a preliminary calculation, the square of the dipole moment of isomer I should be approximately 3.5 times larger than that for isomer II. Accordingly, assuming equal stability of isomers II and I, the intensity of the lines of the latter should be significantly greater than that of the lines of isomer II. However, the observed lines of isomer II have a sufficiently high intensity, whereas at our temperatures no lines of isomer I were observed. On this basis it may be assumed that the folded isomeric state for this molecule is more stable than state I, and accordingly the internal-rotation potential $V(\alpha)$ has the form shown in Fig. 2.

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