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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE MICROWAVE SPECTRUM OF THE MOLECULE $F_2HC–CH_2F$

(Presented by Academician V. N. Kondrat' ev on 4 February 1963)

The molecule $F_2HC–CH_2F$ consists of two asymmetric groups with hindered internal rotation about the single C–C bond. Molecules of this type were studied by us earlier ([1,2]). In the present case the considerations concerning the isomeric states presented in ([1,2]) remain valid, with, however, the fundamental difference that the rotational constants in the folded states $a = +120°$ and $a = -120°$ of the $F_2HC–CH_2F$ molecule are identical owing to the presence of planes of symmetry in the groups. In this case the Hamiltonian of the molecule (only 4 degrees of freedom are taken into account: rotation as a whole and internal rotation) is invariant with respect to a certain operation ξ, consisting in replacing $a \to -a$ and C_{2y} (Fig. 1), the choice of the axes x and y being to a considerable extent made by virtue of arbitrariness in the choice of the variables $\psi, \theta, \varphi, \alpha$: $\psi = \lambda_1\varphi_1 + \lambda_2\varphi_2$, $\alpha = \varphi_1 - \varphi_2$, $\lambda_1 + \lambda_2 = 1$. ψ and θ determine the position in space of the axis of internal rotation, and φ_1 and φ_2 are the angles of rotation of the first and second groups, respectively, relative to this axis. The indicated symmetry property leads to a classification of the states $\xi\psi_\pm = \pm\psi_\pm$ and to the selection rule for dipole transitions $+ \leftrightarrow -$.

Fig. 1. The xy plane is perpendicular to the C–C axis and passes through the center of mass O of the molecule. O_1, O_2, and C are the projections of the centers of mass of the first and second groups and of the C′–C axis onto this plane.

In the case when the part of the Hamiltonian corresponding to rotation as a whole may be treated as a perturbation, and, consequently, the states may be specified by the quantum numbers of a rigid asymmetric top I, τ and by certain torsional quantum numbers n, the energy difference of the states $\psi_+^{nI\tau}$ and $\psi_-^{nI\tau}$ is to a considerable extent determined by the difference of the energies E_+^n and E_-^n of the corresponding torsional states $H_{\text{kr}}\varphi_\pm^n = E_\pm^n\varphi_\pm^n$, where $\varphi_+^n(\alpha)$ and $\varphi_-^n(\alpha)$ are even and odd eigenfunctions of the internal-rotation Hamiltonian $H_{\text{kr}}(\alpha)$. Figure 2 shows the approximate form of the potential of internal

rotation ([1,2]). Obviously, at low torsional energies the difference $E_+^n - E_-^n$ is determined by the penetrability of the barrier between the minima near $a = 120^\circ$ and $a = -120^\circ$, and is small when the penetrability is small. Since rotational transitions are possible between the states $\psi_\pm^{nI\tau}$ and $\psi_\mp^{nI'\tau'}$, where I', τ' are determined by the selection rules of the rigid asymmetric top, each line with given I, τ and I', τ' will be doubled, with a spacing between the components of order $2(E_+^n - E_-^n)$. This spacing increases with increasing torsional energy. Therefore one may expect that, if in rotational transitions belonging to the ground torsional state the doubling of the lines is small and unobservable, in excited torsional states it will be larger and, possibly, observable. It is precisely such a situation that occurs in our case.

Table 1

Transitions	Calculated frequency values, MHz	Observed frequency values, MHz	Transitions	Calculated frequency values, MHz	Observed frequency values, MHz
$3_{0,3}$—$3_{1,2}$	8747.8	8747.55	$8_{1,7}$—$8_{2,6}$	18242.9	18238.2
$4_{0,4}$—$4_{1,3}$	11042.9	11042.45	$3_{1,3}$—$3_{2,2}$	20179.4	20179.3
$0_{0,0}$—$1_{1,1}$	11909.7	11909.7	$3_{1,3}$—$4_{0,4}$	21203.6	21202.9
$5_{0,5}$—$5_{1,4}$	14197.3	14196.75	$9_{1,8}$—$9_{2,7}$	23388.3	21384.8
$2_{1,2}$—$3_{0,3}$	14280.5	14281.6	$4_{1,4}$—$4_{2,3}$	21934	21933.8
$5_{1,4}$—$5_{2,3}$	14612.5	14610.65	$10_{2,8}$—$10_{3,7}$	22229.9	22219.65
$4_{1,3}$—$4_{2,2}$	14916.9	14916.0	$9_{2,7}$—$9_{3,6}$	22406.4	22
$6_{1,5}$—$6_{2,4}$	14952.9	14950.2	$2_{0,2}$—$3_{1,3}$	22762.6	22761.65
$3_{1,2}$—$3_{2,1}$	15628.4	15627.95	$7_{0,7}$—$7_{1,6}$	22875.8	22875.65
$7_{1,6}$—$7_{2,5}$	16119.4	16115.7	$11_{2,9}$—$11_{3,8}$	23026.0	23013.4
$2_{1,1}$—$2_{2,0}$	16472.2	16472.2	$8_{2,6}$—$8_{3,5}$	23315.8	23310
$1_{0,1}$—$2_{1,2}$	17526.3	17525.75	$5_{1,5}$—$5_{2,4}$	24146.7	24145.7
$6_{0,6}$—$6_{1,5}$	18193.2	18192.7	$12_{2,10}$—$12_{3,9}$	24933.3	24918.6

In the range 7000–30,000 MHz, more than 400 absorption lines of rotational transitions of the molecule F_2HC—CH_2F were found. The observed lines can be divided into three groups:

1. A large group of intense single lines, whose frequencies and Stark splittings agree well with calculation in the representation of a rigid asymmetric rotor. Some of them are given in Table 1. All these transitions have analogues in the spectra of the skew isomers $\alpha = 120^\circ$ and $\alpha = -120^\circ$ of the molecules F_2HC—CDHF and F_2DC—CDHF ([1,2]). These lines belong to the ground torsional state.

Fig. 2

2. A number of single lines, approximately three times weaker in intensity,

identified from Stark splittings as satellites of the lines of the first group, belong to the first excited torsional state.

3. Doubled lines of very low intensity; as a result, it has not yet been possible to identify them. From the considerations given above, it may be assumed that these are rotational transitions in higher excited torsional states.

From the experimental frequency values of the transitions in the ground torsional state $0_{0,0}$—$1_{1,1}$, $2_{1,1}$—$2_{2,0}$, and $2_{1,2}$—$2_{2,1}$, the values of the rotational constants A, B, C were calculated. The transition frequencies calculated from these values are given in Table 1. The small discrepancies between the calculated and experimental frequency values are associated with rotational-vibrational interaction.

From the shifts of the Stark components of the transitions $3_{0,3}$—$3_{1,2}$, $4_{0,4}$—$4_{1,3}$, $2_{1,1}$—$2_{2,0}$, and $2_{1,2}$—$2_{2,1}$, the values of the squares of the components of the dipole moment along the principal axes of the molecule were calculated (see below). The Stark-component shifts of other transitions calculated from these values agree well with the measured ones.

Table 2

A, MHz	B, MHz	C, MHz	μ_a^2	μ_b^2	μ_c^2	$\Sigma\mu_d^2$
9101.4	3640.0	2808.3	0.06 ± 0.01	2.12 ± 0.05	0.31 ± 0.01	2.49 ± 0.05

The obtained value of the square of the dipole moment is close to those obtained earlier for the molecules F_2HC—CDHF and F_2DC—CDHF ([1,2]), and is also 1.4 times larger than that calculated from the electronegativities of the atoms in the molecule. The considerations regarding the stability of the isomers presented in ([1,2]) are confirmed.

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References Cited

[1] I. A. Mukhtarov, DAN, **148**, No. 3 (1963). [2] I. A. Mukhtarov, *Optics and Spectroscopy*, **15**, issue 3 (1963).

Note: Figure translations are in progress. See original paper for figures.