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Microwave Spectrum of Ethyl Iodide

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The microwave spectrum of ethyl iodide C_2H_5I was observed in the frequency range from 5 to 30 kMc/sec. About fifty lines were assigned to the a-type transitios, and other twenty to the b-type transitions.

This molecule is a slightly asymmetric rotor with $b_p \fallingdotseq -0.003$, having a very large quadrupole coupling constant, and the calculated frequencies could not satisfactorily be fitted to the observed spectrum with the first order quadrupole treatment alone.

The second order quadrupole effect was calculated using the wave function expanded in the power series of b_p [1]. With the parameters listed in Table II, the discrepancies between the calculated and observed frequencies were less than 1 Mc/sec (Table I).

The hyperfine anomalies in $K=1$ lines reported by Wagner and Dailey in the case of C_2H_5Br [2]

Table I. Spectroscopic parameters of ethyl iodide.

A	29109.2±5 Mc/sec	$(eqQ)_{aa}$	−1481.9±0.5 Mc/sec
B	2979.2 ±0.5	$\eta=(\chi_{bb}-\chi_{cc})/\chi_a$	=0.22 (assumed)
C	2797.1 ±0.5	$\xi=\chi_{bc}/\chi_{aa}$	=0.60 (〃)

were also observed in this molecule. For example, the hyperfine component corresponding to 7/2→9/2 of $2_{12}\rightarrow3_{13}$ transition was found to show the splitting of 1.09 Mc/sec. This splitting was explained by taking into account of the internal rotation of CH_3 group (Table II).

Table II. An example of hyperfine anomaly.

$2_{12}\rightarrow3_{13}$	obs.	calc.
9/2→11/2	17096.08	17095.84
7/2→ 9/2	17034.84	17035.30 (E)
	17035.75	17034.21 (A)
3/2→ 5/2	16976.8	16976.6
1/2→ 3/2	17007.76	17007.14

The quadrupole interaction term averaged by the rigid asymmetric rotor wave function is known to be

$$eqQ=\frac{(eqQ)_{aa}}{(J+1)(2J+3)}\left[\{3K^2-J(J+1)\}+(-1)^{\gamma}\frac{J(J+1)\eta}{2}\delta_{K,1}+\text{asymmetry correction}\right]^{3)}.$$

The second term $\pm[J(J+1)\eta]/2$ which does not vanish for $K=1$ must be multiplied by a factor ε, owing to the coupling of internal and overall rotation[4].

For A-state of internal rotation ε is one, but for E-state it is dependent sensitively on potential, which can be used to evaluate the barrier height[5]. Treating the internal rotation problem by the Hamiltonian developed by Kilb, Lin and Wilson[6], the potential value of about 2.4 kcal/mole was obtained. This should be compared with that of C_2H_5Cl and C_2H_5Br [7]*.

From the parameters listed in Table I, the structural constants were determined as follows

Table III. Microwave spectrum of ethyl iodide.

a-type transition				b-type transition	
$0_{00}\rightarrow1_{01}$		9/2→ 9/2	17070.40	$3_{03}\rightarrow3_{12}$	
5/2→ 3/2	5988.1	3/2→ 3/2	17382.34	11/2→11/2	26744
5/2→ 5/2	5542.08	$3_{30}\rightarrow4_{31}$, $3_{31}\rightarrow4_{32}$		9/2→ 9/2	26845
5/2→ 7/2	5852.44	11/2→13/2	23214.30	7/2→ 7/2	26837
$2_{10}\rightarrow3_{21}$		9/2→11/2	22968.75	5/2→ 5/2	26796
9/2→11/2	17443.60	7/2→ 9/2	22978.44	7/2→ 5/2	26928
7/2→ 9/2	17155.92	5/2→ 7/2	23116.56	5/2→ 3/2	26900
5/2→ 7/2	17227.84	$3_{21}\rightarrow4_{22}$		$4_{04}\rightarrow4_{13}$	
$2_{21}\rightarrow3_{22}$		11/2→13/2	23167.05	13/2→13/2	27108
9/2→11/2	17438.08	9/2→11/2	23059.77	11/2→11/2	27196
7/2→ 9/2	17152.32	7/2→ 9/2	23050.34	7/2→ 7/2	27166
$2_{02}\rightarrow3_{03}$		5/2→ 7/2	23090.64	5/2→ 5/2	27096
9/2→11/2	17342.28	$3_{22}\rightarrow4_{23}$		$5_{05}\rightarrow5_{14}$	
7/2→ 9/2	17354.96	11/2→13/2	23158.50	15/2→15/2	27595
5/2→ 7/2	17283.82	9/2→11/2	23050.34	13/2→13/2	27638
3/2→ 5/2	17212.40	7/2→ 9/2	23042.24	11/2→11/2	27663
		5/2→ 7/2	23083.38	5/2→ 5/2	27565

assuming the C–C bond length to be 1.555±0.005Å[2]
C–I 2.207±0.005Å, ∠CCI 112°1′±30″

More precise analysis especially of the b-type transition lines is now in progress considering the internal rotation effect.

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* 3560±12 cal/mole for C_2H_5Cl and 3567±30 cal-mole for C_2H_5Br.