Microwave Spectrum of Ethyl Iodid: Internal Rotation Analysis

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The rotational spectra of the first excited state of the methyl torsion and the CCI-in plane deformation of CH_3CH_2I have been studied. A Coriolis interaction between these two modes has been found. Splittings of transitions in the first excited torsional state show that the barrier hindering internal rotation of the methyl group is 3.62 kcal/mole. This value agrees quite well with the value previously reported from Raman studies. It is internally consistent and similar to the other ethyl halides.

It was empirically found [1] that the methyl barrier in substituted ethanes CH_3CH_2X slightly increases when the electronegativity of the substituent X decreases. Consequently the barrier in ethyl iodide would be expected to be greater than in ethyl fluoride where $V_3 = 3.30$ kcal/mole [2] and of the same order of magnitude as in ethyl bromide: $V_3 = 3.57$ kcal/mole [3]. From a microwave study it was in fact shown that $V_3 = 3.22$ kcal/mole [4], somewhat lower than expected from the above considerations. On the other hand a Raman investigation in gas phase [5] has given $V_3 = 3.67$ kcal/mole, which is considerably higher than the value previously reported from microwave studies but in good agreement with the values found for the other ethyl halides.

To clear up this discrepancy we have reinvestigated the microwave spectrum of CH_3CH_2I. The spectra were recorded in the region from 5 to 80 GHz with a conventional microwave spectrometer employing 25 kHz Stark-modulation. For the high resolution measurements a 8 m-absorption cell was used, the sample pressure was 5 m-Torr and the temperature approximately -50 °C. The analysis of the ground state spectrum is reported elsewhere [6].

$^aR_{01}$ transitions of two excited states of nearly equal intensity were easily identified, both at the low frequency side of the ground state transitions. No lines were found to be split. The $^bQ_{1,-1}$ lines were much more difficult to find because they were very far from the ground state lines. The $^bQ_{1,-1}$ lines of one excited state shows a doublet splitting while the other state has very sharp lines. The split lines probably belong to the first excited torsional state which was calculated at v_{18} $(a'') = 259\ \mathrm{cm}^{-1}$ [7] and the other state was most likely the in-plane CCI bend, measured in gas phase as v_{11} $(a') = 258\ \mathrm{cm}^{-1}$ [7]. The relative intensities are in agreement with this vibrational assignment.

The energy difference between these two vibrational levels is only about $1\ \mathrm{cm}^{-1}$. Hence, the rotational spectra of these two states are expected to be perturbed by a Coriolis interaction. Indeed, an attempt to fit these spectra to an appropriate centrifugal distorded Hamiltonian [8] gave a poor fit. On the other hand a fit without the $^bQ_{1,-1}$ lines was satisfactory but the A-rotational constants were very inaccurate. To overcome this difficulty we have used a weighted least squares method giving a weight 100 times lower to the $^bQ_{1,-1}$ lines. In this way the $^aR_{0,1}$ lines could be well reproduced (see Tables 1, 2 and 3) and the A-rotational constants were also determined (Table 4). These two constants deviate considerably from the ground state A constant in opposite directions. This indicates the existence of an a-type Coriolis interaction between the two states. The state with negative deviation of A is the lower frequency, it is the CCI in-plane deformation. So the torsion lies a few cm^{-1} above this state. This is in good agreement with the vibrational assignment of Ref. [7].

The A-E doublet splitting of the excited torsional state can be affected by the Coriolis interaction. A treatment of this perturbation has been given by Dreizler and coll. [9, 10, 11]. But for the case of a high barrier and small asymmetry, it was shown by Laurie [12] that the contribution from Coriolis

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Table 1. [a] R_{01} Transitions (MHz) of CH_3CH_2I in the first excited state of the methyl torsion.

Transition $J'_{K'_p K'_0} \leftarrow J_{K_p K_0}$	$F' \leftarrow F$	ν (obs.)	ν (unsplit)[a]	ν (calc.)-ν (unsplit)
$2_{02} \leftarrow 1_{01}$	3/2 ← 3/2	11 432.39	11 535.20	− 0.45
	5/2 ← 3/2	11 225.75		
	5/2 ← 5/2	11 672.29		
	5/2 ← 7/2	11 346.24		
	7/2 ← 5/2	11 592.31		
	7/2 ← 7/2	11 280.82		
	9/2 ← 7/2	11 568.28		
$2_{12} \leftarrow 1_{11}$	3/2 ← 1/2	11 620.80	11 353.12	1.61
	5/2 ← 5/2	11 201.49		
	7/2 ← 5/2	11 156.47		
	7/2 ← 7/2	11 280.10		
	9/2 ← 7/2	11 452.12		
$2_{11} \leftarrow 1_{10}$	3/2 ← 1/2	11 967.26	11 721.48	− 0.33
	5/2 ← 5/2	11 538.95		
	7/2 ← 5/2	11 510.67		
	7/2 ← 7/2	11 703.98		
	9/2 ← 7/2	11 811.20		
$3_{03} \leftarrow 2_{02}$	11/2 ← 9/2	17 318.99	17 300.74	− 0.24
$4_{14} \leftarrow 3_{13}$	3/2 ← 1/2	22 699.50	22 700.51	− 0.39
	5/2 ← 3/2	22 661.26		
	7/2 ← 5/2	22 654.80		
	9/2 ← 7/2	22 674.24		
	9/2 ← 9/2	22 675.55		
	11/2 ← 9/2	22 704.84		
	13/2 ← 11/2	22 724.52		
$5_{15} \leftarrow 4_{14}$	5/2 ← 3/2	28 369.22	28 374.01	− 0.14
	11/2 ← 9/2	28 362.00		
	13/2 ← 11/2	28 381.78		
$5_{14} \leftarrow 4_{13}$	5/2 ← 3/2	29 299.29	29 299.91	− 0.18
$6_{15} \leftarrow 5_{14}$	7/2 ← 5/2	35 154.20	35 156.46	− 0.18
	9/2 ← 7/2 } 11/2 ← 9/2 }	35 143.12		
	13/2 ← 11/2	35 151.00		
	15/2 ← 13/2	35 161.36		
	17/2 ← 15/2	35 167.00		
$7_{17} \leftarrow 6_{16}$	9/2 ← 7/2	39 711.63	39 716.31	− 0.20
	11/2 ← 9/2	39 702.22		
	13/2 ← 11/2	39 704.00		
	15/2 ← 13/2	39 712.32		
	17/2 ← 15/2	39 722.98		
	19/2 ← 17/2	39 724.06		
$12_{0,12} \leftarrow 11_{0,11}$	19/2 ← 17/2	68 941.01	68 942.55	2.76
	21/2 ← 19/2	68 938.27		
	23/2 ← 21/2	68 939.40		
	25/2 ← 23/2	68 942.47		
	27/2 ← 25/2 } 29/2 ← 27/2 }	68 945.08		
$12_{1,11} \leftarrow 11_{1,10}$	19/2 ← 17/2	70 250.04	70 252.80	1.18
	21/2 ← 19/2	70 248.27		
	23/2 ← 21/2	70 252.21		
	25/2 ← 23/2	70 253.61		
	27/2 ← 25/2			
	29/2 ← 27/2	70 255.11		

[a] Calculated with the quadrupole coupling constants of the ground state (Ref. [6]).

Table 2. [b]Q Transitions (MHz) of CH_3CH_2I in the first excited state of the methyl torsion.

Transition $J'_{K'_p K'_0} \leftarrow J_{K_p K_0}$	$F' \leftarrow F$	Torsional species	ν (obs.)	Internal rotation splitting measured	Internal rotation splitting calculated	ν (unsplit) [a]	ν (calc.)-ν (unsplit)
$8_{17} \leftarrow 8_{08}$	11/2 ← 11/2	A	29 943.379	0.620	0.638	29 982.00	−137.14
		E	29 943.999				
	13/2 ← 13/2	A	29 975.333	0.619			
		E	29 975.952				
	15/2 ← 15/2	A	29 998.890	0.621			
		E	29 999.511				
	17/2 ← 17/2	A	30 006.936	0.630			
		E	30 007.566				
	19/2 ← 19/2	A	29 992.941	0.626			
		E	29 993.567				
	21/2 ← 21/2	A	29 953.666	0.618			
		E	29 954.284				
$9_{18} \leftarrow 9_{09}$	13/2 ← 13/2	A	30 951.225	0.675	0.670	30 987.496	− 51.39
		E	30 951.900				
	17/2 ← 17/2	A	31 005.948	0.673			
		E	31 006.621				
	19/2 ← 19/2	A	31 012.992	0.667			
		E	31 013.657				
	21/2 ← 21/2	A	30 998.658	0.673			
		E	30 999.332				
	23/2 ← 23/2	A	30 960.665	0.663			
		E	30 961.328				
$10_{1,9} \leftarrow 10_{0,10}$	15/2 ← 15/2	A	32 083.991	0.716	0.707	32 120.046	− 37.33
		E	32 084.707				
	17/2 ← 17/2	A	32 116.331	0.717			
		E	32 117.048				
	19/2 ← 19/2	A	32 138.932	0.711			
		E	32 139.643				
	21/2 ← 21/2	A	32 145.142	0.711			
		E	32 145.853				
	23/2 ← 23/2	A	32 130.044	0.709			
		E	32 130.753				
	25/2 ← 25/2	A	32 093.317	0.713			
		E	32 094.030				
$11_{1,10} \leftarrow 11_{0,11}$	17/2 ← 17/2	A	32 358.308	0.762	0.750	33 393.132	136.02
		E	32 359.070				
	19/2 ← 19/2	A	32 389.895	0.764			
		E	32 390.659				
	21/2 ← 21/2	A	33 408.994	0.743			
		E	33 409.737				
	25/2 ← 25/2	A	33 404.217	0.772			
		E	33 404.989				

[a] Calculated with the quadrupole coupling constants of the ground state (Ref. [6]) and with $\nu_0 = (\nu_A + 2\nu_E)/3$.

coupling to the A-E splittings is small. This conclusion is furthermore strengthened by the fact that only the torsional excited state shows a splitting due to internal rotation. So the barrier to internal rotation of the methyl group was calculated from the splittings with the conventional principal axis method [13, 14], the calculation used second and fourth order perturbation. The imput data for this computation includes, in addition to the observed splittings, the moment of inertia of the methyl top, taken to be $I_a = 3.18$ u. Å^2, the rotational constants and the angle Θ (methyl top to a axis) $= 48.5°$. This latter quantity was obtained from an assumed structure [15]. The derivatives shown in Table 4

Table 3. Rotational Transitions (MHz) of CH_3CH_2I in the first excited state of the in plane-CCI deformation.

Transition $J'_{K'_p K'_0} \leftarrow J_{K_p K_0}$	$F' \leftarrow F$	ν (obs.)	ν (unsplit)	ν (calc.)-ν (unsplit)
$2_{02} \leftarrow 1_{01}$	3/2 ← 1/2	11 609.89	11 520.07	0.37
	3/2 ← 3/2	11 417.35		
	5/2 ← 3/2	11 211.84		
	5/2 ← 5/2	11 656.28		
	3/2 ← 5/2	11 861.70		
	7/2 ← 5/2	11 576.60		
	5/2 ← 7/2	11 346.24		
	7/2 ← 7/2	11 266.57		
	9/2 ← 7/2	11 552.74		
$2_{12} \leftarrow 1_{11}$	9/2 ← 7/2	11 440.77	11 341.91	− 0.05
	7/2 ← 5/2	11 146.96		
	7/2 ← 7/2	11 268.97		
$2_{11} \leftarrow 1_{10}$	7/2 ← 5/2	11 489.55	11 699.63	0.25
	5/2 ← 5/2	11 517.81		
	9/2 ← 7/2	11 699.67		
$3_{03} \leftarrow 2_{02}$	11/2 ← 9/2	17 295.95	17 277.70	0.52
$4_{14} \leftarrow 3_{13}$	3/2 ← 1/2	22 681.15	22 682.29	0.40
	5/2 ← 3/2	22 643.15		
	7/2 ← 5/2	22 636.73		
	9/2 ← 7/2	22 656.05		
	11/2 ← 9/2	22 686.56		
	13/2 ← 11/2	22 706.18		
$5_{15} \leftarrow 4_{14}$	11/2 ← 9/2	28 339.21	28 351.22	0.75
	13/2 ← 11/2	28 358.95		
	15/2 ← 13/2	28 366.26		
$5_{14} \leftarrow 4_{13}$	5/2 ← 3/2	29 243.78	29 244.40	0.55
	11/2 ← 9/2	29 235.64		
	13/2 ← 11/2	29 248.80		
	15/2 ← 13/2	29 265.62		
$6_{15} \leftarrow 5_{14}$	7/2 ← 5/2	35 088.19	35 090.25	0.54
	9/2 ← 7/2	35 076.85		
	11/2 ← 9/2			
	13/2 ← 11/2	35 084.80		
	15/2 ← 13/2	35 095.22		
	17/2 ← 15/2	35 100.59		
$7_{17} \leftarrow 6_{16}$	9/2 ← 7/2	39 680.26	39 684.38	0.73
	11/2 ← 9/2	39 669.90		
	13/2 ← 11/2	39 671.62		
	15/2 ← 13/2	39 680.90		
	17/2 ← 15/2	39 690.95		
	19/2 ← 17/2	39 692.04		
$9_{18} \leftarrow 9_{09}$	23/2 ← 23/2	30 370.11	30 396.81	129.48
$10_{19} \leftarrow 10_{0,10}$	15/2 ← 15/2	31 279.67	31 316.17	42.65
	17/2 ← 17/2	31 311.45		
	19/2 ← 19/2	31 334.77		
	21/2 ← 21/2	31 342.73		
	23/2 ← 23/2	31 328.88		
	25/2 ← 25/2	31 289.85		
$11_{1,10} \leftarrow 11_{0,11}$	17/2 ← 17/2	32 323.97	32 359.44	− 45.88
	19/2 ← 19/2	32 355.51		
	21/2 ← 21/2	32 378.01		
	23/2 ← 23/2	32 384.97		
	25/2 ← 25/2	32 370.93		
	27/2 ← 27/2	32 333.20		
$12_{0,12} \leftarrow 11_{0,11}$	19/2 ← 17/2	68 853.58	68 855.07	− 1.26
	21/2 ← 19/2	68 850.78		
	23/2 ← 21/2	68 851.94		
	25/2 ← 23/2	68 855.01		
	27/2 ← 25/2	68 857.71		
	29/2 ← 27/2			
$13_{1,12} \leftarrow 12_{1,11}$	31/2 ← 29/2	75 950.05	75 948.04	− 0.31

Table 4. Rotational constants of CH_3CH_2I [a].

	Ground state [b]	CH_3-torsion [c]	CCI-bend [c]
A	29 116.321 (8)	29 515 (41)	28 596 (40)
B	2 979.564 (1)	2976.74 (7)	2969.52 (4)
C	2 796.452 (1)	2791.59 (6)	2790.81 (5)
α^A		−399	+520
α^B		2.82	10.04
α^C		4.86	5.64

[a] All values in MHz. The uncertainties shown in parentheses are in units of the last digit and are standard errors.

[b] From Ref. [6].

[c] The ground state centrifugal distortion constants of Ref. [6] were used in the fit.

Table 5. Internal rotation parameters of CH_3CH_2I.

$s = 96.46\ (12)$ [a] $\quad V_3 = 3\,623 \pm 150$ cal/mole [b]

[with $I_\alpha = 3.18$ u.Å^2 and $\sphericalangle(i, a) = 48.5°$ assumed]

$\partial V_3/\partial\theta = -22$ cal/mole deg;

$\partial V_3/\partial I_a = -872$ cal/mole u.Å^2;

$\partial V_3/\partial A = 3.32 \cdot 10^{-2}$ cal/mole MHz

[a] One standard error in units of the last digit.

[b] Allowance of uncertainty of I_α, $\sphericalangle(i, a)$ and A and for the Coriolis effect included.

indicate the dependence of V_3 on the two fixed parameters I_a and Θ and on the rotational constant A, which is not accurately determined. The error of V_3 in Table 5 makes an estimated allowance for the uncertainty of I_a, Θ and A and for the possible Coriolis effect.

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