Determination of a High Potential Barrier Hindering Internal Rotation from the Analysis of the Ground State Spectrum: The Case of Ethyl Cyanide

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The ground state rotational spectrum of ethyl cyanide has been reinvestigated between 8 and 250 GHz. The barrier potential V_3 is calculated from 11 high J, ground state transitions which were found split into doublets. V_3 is 3007 cal/mole, assuming $I_\alpha = 3.167$ uÅ^2 and $\sphericalangle (i, a) = 48.65°$. The splittings of the K-doublet transitious have also been analyzed.

Introduction

Microwave spectroscopy is a very accurate method to determine the potential barrier restricting the rotation of a methyl group [1 – 3]. The finite barrier hindering internal rotation normally splits each rotational line into two components. This splitting depends strongly on the height of the barrier. Generally the barrier is determined from the splittings in the ground torsional state. But for a high barrier, these splittings may be too small to be resolved. In this case the barrier may be determined from the larger splittings of rotational lines in an excited torsional state. However the analysis may be much more difficult because of the possible interaction of the torsion with the other vibrations. In this respect ethyl cyanide, CH_3CH_2CN is a very interesting molecule: no internal rotation splitting could be observed up to now in the ground torsional state and an interaction between the CCN-bend in plane ($\nu_{13} = 206.9 \pm 0.5$ cm^{-1} [4]) and the first excited torsional state ($\nu_{23} = 210.5$ cm^{-1} [5]) affects significantly the internal rotation fine structure [4]. Dreizler and coworkers [6, 7] developed a simplified rotational Hamiltonian with five degrees of freedom (three of overall rotation, one of internal rotation, and one of vibration) and suceeded in explaining the excited states fine structure [4]. This Hamiltonian was successfully used for a lot of other molecules [8] where an interaction between torsion and a vibration also occurs. But the general conclusion of that work is that "barrier determination from the ground state spectra is the most reliable" [9].

For this reason and to investigate the possibility for the determination of high barriers from the ground state we decided to search for internal rotation splittings in the ground torsional state of ethyl cyanide. A preliminary calculation using the constants of Ref. [4] showed that some lines were probably sufficiently split to be resolved with a "conventional" spectrometer (i. e. splittings > 100 Hz). These lines are either of high J or of high K, so a centrifugal distortion analysis was first carried out and is reported in Reference [10].

Experimental

At Kiel a conventional spectrometer with 33 kHz Stark modulation was used [11, 12] for lines below 40 GHz. Above this frequency the lines were measured in Lille with a video spectrometer employing superheterodyne detection [13]. In both cases the cells were cooled to – 70 °C. The measured lines showing a resolved internal rotation splitting are reported in Tables 1 and 2.

Theory

Following the P. A. M. method the Hamiltonian may be written [1 – 3]:

$$H_{0\sigma} = H_{\mathrm{R}} + F \sum_{n=1}^{6} W_{0\sigma}^{(n)} (\varrho_{\mathrm{a}} P_{\mathrm{a}} + \varrho_{\mathrm{b}} P_{\mathrm{b}})^n , \qquad (1)$$

where H_{R} is the usual rotational Hamiltonian in-

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Table 1. Rotational transitions of ethyl cyanide (ground state).

$J_{K_- K_+} \rightarrow J'_{K'_- K'_+}$	Γ	$F \rightarrow F'$	ν_{exp}	$\nu_{\text{A-E}}$ exp	$\nu_{\text{A-E exp}}$ $- \nu_{\text{A-E cal}}$
$17_{0,17} \rightarrow 17_{1,16}$	E	18 → 18 16 → 16	74 901.194	0.185	− 0.015
	A E	18 → 18 16 → 16 17 → 17	74 901.379		
$23_{1,22} \rightarrow 23_{2,21}$	E	24 → 24 22 → 22	78 436.747	0.131	0.013
	A E	24 → 24 22 → 22 23 → 23	78 436.871		
$28_{1,28} \rightarrow 27_{2,25}$	A	29 → 28 27 → 26	11 244.203	0.491	− 0.026
	E	29 → 28 27 → 26	11 243.712		
$29_{1,29} \rightarrow 28_{2,26}$	A	29 → 28	17 534.711	0.560	0.015
	A	30 → 29 28 → 27	17 534.382		
	E	29 → 28	17 534.148		
	E	30 → 29 28 → 27	17 533.824		
$30_{1,30} \rightarrow 29_{2,27}$	A	30 → 29	24 105.663	0.564	− 0.05
	A	31 → 30 29 → 28	24 105.341		
	E	30 → 29	24 105.099		
	E	31 → 30 29 → 28	24 104.776		
$31_{1,31} \rightarrow 30_{2,28}$	A	31 → 30	30 896.375	0.619	0.024
	A	31 → 31 30 → 29	30 896.065		
	E	31 → 30	30 895.786		
	E	32 → 31 30 → 29	30 895.430		
$32_{1,32} \rightarrow 31_{2,29}$	A	32 → 31	37 845.907	0.621	0.03
	A	33 → 32 31 → 30	37 845.592		
	E	32 → 31	37 845.307		
	E	33 → 32 31 → 30	37 844.961		
$35_{3,32} \rightarrow 36_{2,35}$	A	35 → 36	38 855.761	− 0.485	0.006
		36 → 37 34 → 35	38 856.019		
	E	35 → 36	38 856.249		
		36 → 37 34 → 35	38 856.502		
$36_{3,33} \rightarrow 37_{2,36}$	A	36 → 37	32 599.473	− 0.516	− 0.002
		37 → 38 35 → 37	32 599.753		
	E	36 → 37	32 600.011		
		37 → 38 35 → 37	32 600.258		
$37_{3,34} \rightarrow 38_{2,37}$	A	37 → 38	25 896.166	− 0.528	0.009
		38 → 39 36 → 37	25 896.418		
	E	37 → 38	25 896.711		
		38 → 39 36 → 37	25 896.937		
$38_{3,35} \rightarrow 39_{2,38}$	A	38 → 39	18 807.014	− 0.547	0.009
		39 → 40 37 → 38	18 807.260		
	E	38 → 39	18 807.546		
		39 → 40 37 → 38	18 807.814		

Table 2. Internal rotation multiplets of the K-doublet transitions of ethyl cyanide.

$J_{K_-K_+} \rightarrow J'_{K_-'K_+'}$	Torsional[a] species	ν_{exp}[MHz]	V_3 calculated[b] [cal/mole]
$7_{35} \rightarrow 7_{44}$	E_a	162 189.675	3080
	A	162 190.383	
$8_{36} \rightarrow 8_{45}$	E_a	162 166.920	3125
$8_{36} \rightarrow 8_{45}$	A	162 167.445	
$8_{36} \rightarrow 8_{44}$	E_f		
$9_{37} \rightarrow 9_{46}$	E_a	162 136.591	3125
$9_{37} \rightarrow 9_{46}$	A	162 136.988	
$9_{37} \rightarrow 9_{45}$	E_f		
$10_{47} \rightarrow 10_{56}$	A	208 445.383	3185
	E_a	208 444.751	
$11_{48} \rightarrow 11_{57}$	A	208 414.703	3190
	E_a	208 414.029	
$11_{47} \rightarrow 11_{56}$	A	208 410.987	3180
$11_{47} \rightarrow 11_{56}$	E_a		
$11_{47} \rightarrow 11_{57}$	E_f	208 410.000	
$12_{49} \rightarrow 12_{58}$	A	208 373.223	3140
	E_a	208 372.451	
$13_{4,10} \rightarrow 13_{5,9}$	A	208 319.280	3190
	E_a	208 318.717	
$18_{5,14} \rightarrow 17_{6,11}$	A E_a	93 104.267	3240
$18_{5,14} \rightarrow 17_{6,12}$	E_f	93 103.500	
mean (σ)			3162 (48)

[a] a = ARR allowed; f = ARR forbidden.
[b] I_α and θ assumed as in Table 4.

cluding centrifugal distortion and where the remaining quantities have their conventional meaning.

The denominator correction [14, 15] was not taken into account after having checked that it does not influence the splittings *.

The internal rotation and the quadrupole splittings are of the same order of magnitude. So a coupling between these two interactions is possible [16]. To test this point we have diagonalized the Hamiltonian (1) including the nuclear quadrupole interaction term [17]. For the lines we have measured it could be concluded that the internal rotation and quadrupole interaction splittings are simply additive. So the nuclear quadrupole interaction was treated by the usual first order perturbation theory [18] using the nuclear quadrupole coupling constants of [19].

The Hamiltonian (1) up to $n = 4$ was diagonalized numerically. The $n = 5$ terms were neglected since the $n = 3$ terms are already insignificant and the $n = 6$ terms were handled by a perturbation treatment using the formal equivalence between the internal rotation and the centrifugal distortion. The sextic correction form internal rotation is:

$$F\,W^{(6)}_{0\sigma}(\varrho_a P_a + \varrho_b P_b)^6 \qquad (2)$$

$$= F\,W^{(6)}_{0\sigma}\sum_{k=0}^{6}\frac{6!}{k!\,(6-k)!}\,\varrho_a^{\,k}\,\varrho_b^{\,6-k}\,P_a^{\,k}\,P_b^{\,6-k}$$

while the sextic correction from the centrifugal distortion may be written [20].

$$[\alpha\,\beta\,\gamma\,\delta\,\varepsilon\,\eta]\,P_\alpha P_\beta P_\gamma P_\delta P_\varepsilon P_\eta\,. \qquad (3)$$

The Centrifugal distortion coefficients $[\alpha\,\beta\,\gamma\,\delta\,\varepsilon\,\eta]$ are identified with $F\,W^{(6)}_{0\sigma}\,\varrho_a^{\,k}\,\varrho_b^{\,6-k}$ and after some algebra the pseudocentrifugal distortion coefficients are found and given in Table 3 for the Watson's asymmetric reduction [21].

Table 3. Pseudocentrifugal distortion coefficients for sixth-order internal rotation effects (in the A reduced Hamiltonian and for the I^r representation) *.

$$A = 31\,\alpha^2\beta^4 - 3\,\alpha^4\beta^2$$

$$B = -\,3\,\alpha^2\beta^4 + 31\,\alpha^4\beta^2$$

$$C = -\,30(\alpha^2\beta^4 + \alpha^4\beta^2)$$

$$\Delta_J = 5\,\alpha^2\beta^4$$

$$\Delta_{JK} = -\,\frac{45}{2}\,\alpha^2\beta^4 - \frac{15}{2}\,\alpha^4\beta^2$$

$$\Delta_K = \frac{35}{2}\,(\alpha^4\beta^2 + \alpha^2\beta^4)$$

$$\delta_J = \frac{5}{2}\,\alpha^2\beta^4$$

$$\delta_K = \frac{20 + 55\,\sigma}{4}\,\alpha^2\beta^4 + \frac{75}{4}\,\alpha^4\beta^2$$

$$\phi_J = \frac{1}{2}\,\beta^6$$

$$\phi_{JK} = \frac{\sigma - 9}{4}\,\beta^6 + \frac{15}{2}\,\alpha^2\beta^4$$

$$\phi_{KJ} = \frac{5}{2}\left(1 - \frac{\sigma}{3}\right)\beta^6 - \frac{35}{2}\,\alpha^2\beta^4 + \frac{15}{2}\,\alpha^4\beta^2$$

$$\phi_K = \left(\frac{7\,\sigma}{12} - \frac{3}{4}\right)\beta^6 + 10\,\alpha^2\beta^4 - 15\,\alpha^4\beta^2 + \alpha^6$$

$$\varphi_J = \frac{1}{4}\,\beta^6$$

$$\varphi_{JK} = \frac{3\,\sigma - 5}{8}\,\beta^6 + \frac{15}{4}\,\alpha^2\beta^4$$

$$\varphi_K = \left(\frac{3 - \sigma}{8} + \frac{\sigma^2}{6}\right)\beta^6 + \frac{15}{4}\,\alpha^4\beta^2 - \frac{15}{4}\left(1 - \frac{\sigma}{3}\right)\alpha^2\beta^4$$

* with $\alpha^n = F\,W^{(6)}_{v\sigma}\,\varrho_a^n$; $\beta^n = F\,W^{(6)}_{v\sigma}\,\varrho_b^n$ and $\sigma = \dfrac{2A - B - C}{B - C}$

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Determination of the Potential

1. Analysis of the High J Lines

Two types of lines could be resolved: I) For the high J lines of Table 1 the splittings depend only on the even order terms of (1). II) The splittings of the K doublet transitions of Table 2 are mainly due to the linear term $F \varrho_a W_{01}^{(1)} P_a$. So, in principle the three internal rotation parameters (V_3, I_α and $\sphericalangle(i, a)$) are separately determinable [22]. But an attempt to simultaneously fit all the lines of Table 1 and 2 to (1) converged to an unreasonably high $I_\alpha > 3.3$ uÅ². A similar behavior was already found in dimethylallene and dimethylsulfide [23] and may be attributed to higher order effects which are not taken into account in the Hamiltonian (1) and to which the K doublet transitions are particularily sensitive.

In fact, it is known that I_α is most reliably determined using the inertial defects of the normal and the deuteriated species [22, 24]:

$$I_\alpha = -[\Delta(\mathrm{CD_3CH_2CN}) - \Delta(\mathrm{CH_3CH_2CN})] = 3.167\ \mathrm{u\AA^2}. \qquad (4)$$

So we have adopted fixed values $I_\alpha = 3.167$ uÅ² (from (4) and $\sphericalangle(i, a) = 48.65°$ (from the r_s structure [25]) while least-squares fitting only the reduced potential s to the experimental splittings of Table 1. The results are reported in Table 4 (fit I). We have repeated the fit for different values of the two fixed parameters I_α and $\sphericalangle(i, a)$ for the comparison with the literature and for studying the influence of the assumptions. The errors of V_3 and s in Table 4 make an estimated allowance for the uncertainty of I_α (0.1 uÅ²) and $\sphericalangle(i, a)$ (1°). One can notice that the uncertainty on V_3 is mainly due to the error on I_α.

2. Analysis of the K-doublet transitions

While the first-order terms of the effective Hamiltonian (1) could be neglected in the analysis of the splittings of Table 1, they are the most important for explaining the splitting pattern of the K-doublet transitions of Table 2. For the A species no linear term exists ($W_{0A}^{(1)} = 0$). Their behavior is not different from that of other A-species lines. For the E-species, on the other hand, the K-doublet levels are connected by a large off-diagonal element due to P_a in the ARR basis. A large frequency shift and a breakdown of the ARR selection rules can be observed. Similar observations have already been made for several other molecules [26].

To gain more insight into the problem, we have determined the potential from each line splitting separately. With the same assumptions on I_α and $\sphericalangle(i, a)$ of Table 4, the values of the barrier potential V_3 are shown in Table 2. Inspection of Table 2 shows that the potential determined from the K-doublet transitions is significantly higher than that obtained from the other lines and that the difference increases with K. These facts probably indicate that the effective Hamiltonian (1) is not appropriate to explain satisfactorily the splittings of the K-doublet transitions. Similar conclusions have already been obtained for some other molecules [22] and a centrifugal distortion effect on the methyl top was proposed as explanation [27]. It is in principle possible to introduce in the Hamiltonian additional terms to account for the nonrigidity effects [28]. But as we dispose only of a few lines such an analysis was not attempted.

When one is interested only in the determination of V_3 it should be noted that the potential from the K-doublet transitions is only 5% higher than that of Table 4. For many purposes this difference may be acceptable.

Table 4. Internal rotation parameters of CH_3CH_2CN.

	Fit I	Fit II	Fit III	Fit IV
s	79.72 ± 0.15[a]	79.70	79.43	79.95
V_3/cal/mole	3007 ± 90[a]	3013	3009	3003
I_α/u Å²	3.167[b]	3.159[c]	3.167[b]	3.167[b]
$\sphericalangle(i, a)$/degr.	48.65[c]	48.65[c]	47	50
F/GHz	175.809	176.209	176.611	175.163
σ/kHz	13.7	13.8	13.5	14.0

[a] Allowance for uncertainty of I_α and $\sphericalangle(i, a)$ included (see text).
[b] Calculated from the inertial defect Eq. (4).
[c] Calculated from the r_s structure [25].

Discussion

The previous determinations of the barrier are reported in Table 5. Laurie [29] first obtained the barrier from the splittings of the first excited torsional state, but without taking into account the interaction. Li and Durig [30] determined the barrier in CD_3CD_2CN from the splittings of some μ_a transitions in the 3rd excited torsional state. We believe that their value cannot be compared to ours for two reasons: I) it is known that the barrier can change significantly upon deuteration of the methyl group (Table 6) and II) it is very unlikely that the 3rd excited torsional state does not interact with other vibrations.

Heise, Mäder, and Dreizler [4] obtained a value for V_3 from the simultaneous analysis of the splittings of the rotational transitions in the two lowest excited vibrational states of torsion and CCN in plane-bend of three isotopic molecules: CH_3CH_2CN; $CH_3CH_2C^{15}N$ and CH_3CD_2CN. Their I_a differs from

Table 5. Internal rotation parameters of CH_3CH_2CN. Comparison with earlier work.

Reference	This work	This work	[4]	[29]	[30]
s	79.72	83.92	85	81.5	153.15(76.6)[b]
V_3/cal/mole	3007 ± 90	3166 ± 100	3226 ± 10	3005 ± 150	3002 ± 150
V_6/cal/mole	0	− 172[a]	-172 ± 0.5	0	0
V'_{3c} cal/(mole. rad)	0	0	-1421 ± 134	0	0
θ/degr.	48.65	48.65	47.3	48.1	c
I_α/u Å^2	3.167	3.167	3.159	3.197	c

[a] Fixed to the value of [4]. [b] Mass corrected by m_D/m_H.
[c] These values cannot be compared because they do not correspond to same isotopic species.

Table 6. Influence of the deuteration on the potential.

Parent molecule	$V_N(CH_3)$ in cal/mole	Reference	Isotopic species	$V_N(CD_3)$ in cal/mole	Reference
CH_3OH	1073.98 (6)	[31]	CD_3OH	1063.14 (26)	[31]
CH_3NO	1137 (5)	[27]	CD_3NO	1095 (7)	[27]
CH_3NO_2	5.961 (6)	[32]	CD_3NO_2	5.19 (3)	[33]
CH_3NH_2	1955.99	[34]	CD_3ND_2	1920.54	[34]
CH_3CH_2CN	3007 (90)	this work	CD_3CD_2CN	3002 (150)	[30]
CH_3CHO	1233 (20)	[35]	CD_3CHO	1228 (100)	[35]
CH_3COOH	480.8 (5)	[36]	CD_3COOH	468 (2)	[36]
CH_3CHS	1572 (30)	[37]	CD_3CHS	1501 (20)	[37]
CH_3CHCH_2	1963.4	[38]	CD_3CDCD_2	1967	[38]
CH_3GeH_2F	941 (20)	[39]	CD_3GeH_2F	921 (20)	[39]
CH_3OPF_2	422 (5)	[40]	CD_3OPF_2	404 (5)	[40]
CH_3OSiH_3	557	[41]	CD_3OSiH_3	510	[41]
$(CH_3)_2S$	2136 (2)	[42]	$(CD_3)_2S$	2097.3 (4)	[42]
$(CH_3)_2Se$	1500	[43]	$(CD_3)_2Se$	1493 (9)	[44]
$(CH_3)_2CO$	757.1 (25)	[45]	$(CD_3)_2CO$	732.3 (25)	[45]
CH_3CHN_2	773.9 (10)	[46]	CD_3CHN_2	770.4 (10)	[46]
$CH_3NC_4H_4$	133.5	[47]	$CD_3NC_4H_4$	113.0	[47]
$CH_3C_6H_5$	13.95 (2)	[48]	$CD_3C_6H_5$	11.79 (2)	[48]
CH_3BF_2	13.77 (3)	[49]	CD_3BF_2	12.12 (3)	[50]
CH_3CHNCH_3	1741.55	[51]	CD_3CHNCH_3	1703.81	[51]
$\overline{CH_3}CHNCH_3$	2197.55	[51]	$\overline{CH_3}CHNCD_3$	2151.57	[51]
$CH_3CO\overline{CH_2}CH_2$	517.6 (10)	[52]	$CD_3CO\overline{CH_2}CH_3$	497.1 (10)	[52]
$\overline{CH_3}SCN$	1589	[53]	$\overline{CD_3}SCN$	1553 (12)	[54]
CH_3SeCN	1241 (50)	[55]	CD_3SeCN	1228 (50)	[55]
$CH_3CHCHCH_3$ cis	747.6 (41)	[56]	$CD_3CHCHCD_3$	777 (30)	[57]
$(CH_3)_2O$	2618 (4)	[58]	$(CD_3)_2O$	2572 (6)	[58]

Conversion factors used: $1\ cm^{-1} = 2.85922$ cal/mole; $1\ MHz = 9.53731 \times 10^{-5}$ cal/mole.

this work but the results of Table 4 show that the difference is not very significant. However they use two further potential coefficients: V_6 and V'_{3c}. Introduction of their $V_6 = -172$ cal/mol in our analysis leads to $s = 83.92$. The remaining discrepancy may be eliminated by the introduction of V'_{3c} which is strongly correlated to V_3.

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