Internal Rotation Spectrum in the Ground State of cis Propionyl Fluoride

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Z. Naturforsch. **36a**, 1327–1333 (1981); received October 23, 1981

The microwave ground state spectrum of cis propionyl fluoride has been investigated expanding, with respect to a previous study, the range of the quantum numbers of the transitions, *J* up to 40 and *K* up to 18. At low *K* the spectrum resembles that of an asymmetric rigid rotor, except in a number of cases where the lines are split into A, E doublets. At intermediate and high *K* the mixing of the *K*-doublet rigid rotor wave functions makes forbidden transitions appear. The results of the analysis of the methyl top internal rotation ground state splittings are: $V_3 = 2350 \pm 11$ cal/mole, $\sphericalangle(i, a) = 32.7° \pm 2.0°$, and $I_\alpha = 3.18 \pm 0.03$ uÅ^2.

Introduction

The microwave spectrum of propionyl fluoride (CH_3CH_2COF) was first investigated by Stiefvater and Wilson [1]. Their study proved the existence of two stable rotameric conformations, cis and gauche. The cis form (planar heavy atom skeleton and methyl top eclipsing oxygen) was found to be energetically favoured by 1290 ± 50 cal/mole over the gauche form. Rotational constants in the ground and vibrational excited states of both the forms were determined. From the splittings of lines in the first excited state of the methyl top internal rotation of the cis conformer the V_3 barrier was calculated. The results were: $V_3(\text{cis}) = 2400 \pm 60$ cal/mole, $\sphericalangle(i, a) = 31.5° \pm 2.0°$, fixing $I_\alpha = 3.12 \pm 0.02$ uÅ^2.

The present work on cis propionyl fluoride has been undertaken with the aim of performing, in the ground state, a centrifugal distortion analysis and possibly determining the methyl top internal rotation barrier. It has been already demonstrated that the internal rotation barrier determination from the ground state spectrum is the most reliable [2]. This is related to the absence, in the Hamiltonian, of terms of the type $H_{IR,V}$ from the coupling of the internal rotation (IR) with some other close by vibration (V).

The recently in use Fourier transform microwave spectroscopy (FTMWS) provides a resolution high enough (~ 30 kHz) to make this determination feasible even in the case of high barrier [3]. Moreover, in cis propionyl fluoride a preliminary internal rotation calculation using the constants of Ref. [1] indicated that high *J*, high *K* transitions might be split far above the resolution of a conventional (Stark) spectrometer.

I. Experimental

The FTMW spectrometer used in the early stage of the investigation has been already described in Reference [4].

The 33 kHz modulated Stark spectrometer, with which most of the work was done, uses BWO's as stabilized sources [5, 6] and an absorption cell 8 m long. The Stark voltage, from the Stark generator, can be based to zero very precisely by an internal bias [7]. This feature resulted very useful since many spectra were recorded at Stark field below 10 V/cm, in the presence of first order Stark effect exhibited by the lines, see Section II.

The sample was supplied by Columbia Organic Co., USA. The cell was cooled to about −60 °C and the pressure of the sample was 10 or 1 mTorr, the lower limit referring to FTMWS.

Frequency measurements on the lines recorded by Stark spectroscopy are believed to be accurate to within 50 kHz, while to within 30 kHz on those recorded by FTMWS.

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II. Analysis of the Spectrum and Results

According to the value of K (throughout the paper K is used in place of K_{-1}) the measured transitions are divided into three groups: low K, intermediate K, and high K transitions, as in [8].

a) Low K Transitions

A number of low K transitions were measured in addition to those of [1]. Some were observed split into A, E components. The finding of these split lines, which was started with the help of FTMWS, produced evidence of the methyl top internal rotation affecting the ground state spectrum. On this basis, an internal rotation calculation predicted higher K transitions to be much more split. A centrifugal distortion analysis was carried out, in view also of the search for higher K transitions.

Table 1 lists the transitions which were used, in addition to those from Ref. [1], in the centrifugal distortion analysis. In the cases of split lines ($\leqq 1$ MHz) the average frequency of the two components was taken as pseudorigid rotor frequency. It was calculated, by internal rotation analysis, that this approximation introduces an error which is of the order of the experimental accuracy of the measurements.

Table 1. Measured low K transitions of cis propionyl fluoride, ground state. Frequencies are in MHz.

Transition	ν (exp.)	ν (calc.-exp.)[a]
$6_{4,3} - 5_{4,2}$[b]	39890.00	− 0.17
$6_{4,2} - 5_{4,1}$[b]	39901.48	− 0.18
$6_{5,2} - 5_{5,1}$[b]	39808.13	− 0.06
$6_{5,1} - 5_{5,0}$[b]	39808.13	0.09
$6_{2,4} - 6_{1,5}$	17097.37	− 0.08
$13_{5,8} - 12_{6,7}$	15047.79	0.01
$15_{5,10} - 14_{6,9}$	31240.63	0.03
$15_{4,11} - 15_{4,12}$	14248.17	− 0.04
$17_{6,11} - 16_{7,10}$	30071.77	0.05
$19_{7,12} - 18_{8,11}$	29553.70	− 0.05
$21_{5,16} - 21_{5,17}$	29863.93	− 0.06
$22_{5,17} - 22_{5,18}$	38248.69	− 0.02
$23_{6,17} - 23_{6,18}$	17346.62	− 0.03
$25_{6,19} - 25_{6,20}$	32176.24	0.00
$29_{7,22} - 29_{7,23}$	33997.26	− 0.01
$32_{8,24} - 32_{8,25}$	26519.26	0.02
$33_{8,25} - 33_{8,26}$	35381.14	0.01
$36_{9,27} - 36_{9,28}$	27198.13	− 0.03
$37_{9,28} - 37_{9,29}$	36373.82	0.02

[a] Calculated frequency using Hamiltonian (1) and the parameters of Table 2.

[b] These are not low K transitions, but have a similar behaviour, see Setion II.

Table 2. Results of the centrifugal distortion analysis for cis propionyl fluoride, ground state. The transitions used in the least squares fitting procedure are those from Table 1 of the present work and from Table XIV of Reference [1].

$A/\mathrm{MHz} = 10042.5425\,(56)$[a]
$B/\mathrm{MHz} = 3762.2088\,(21)$
$C/\mathrm{MHz} = 2832.6919\,(18)$
$(I_a + I_b - I_c)/\mathrm{u\AA}^2 = 6.2447$[b]
$\Delta_J/\mathrm{kHz} = 0.776\,(18)$
$\Delta_{JK}/\mathrm{kHz} = 3.474\,(66)$
$\Delta_K/\mathrm{kHz} = 4.20\,(36)$
$\delta_J/\mathrm{kHz} = 0.1832\,(29)$
$\delta_K/\mathrm{kHz} = 1.774\,(89)$

[a] Standard error in units of the last digit.

[b] Conversion factor 505376 MHz · uÅ².

The transition frequencies were least squares fitted to a Watson Hamiltonian [9, 10]:

$$\begin{aligned} H = {} & A P_a^2 + B P_b^2 + C P_c^2 - \Delta_J P^4 \\ & - \Delta_{JK} P^2 P_a^2 - \Delta_K P_a^4 \\ & - \delta_J \left[P^2 (P_b^2 - P_c^2) + (P_b^2 - P_c^2) P^2 \right] \\ & - \delta_K \left[P_a^2 (P_b^2 - P_c^2) + (P_b^2 - P_c^2) P_a^2 \right] \end{aligned} \tag{1}$$

and the determined parameters with their standard errors are shown in Table 2. The standard deviation of the fit resulted to be 83 kHz and the largest correlation coefficient 0.929, connecting Δ_J and Δ_{JK}.

The internal rotation split lines were analyzed together with the intermediate K lines.

b) Intermediate K Transitions

When passing from low K to intermediate K transitions the internal rotation spectrum changes almost abruptly. In fact a multiplet structure replaces the doublet structure of the low K transitions. This particular feature was observed only for perpendicular ($\Delta K = \pm 1$) transitions in $^{\mathrm{R}}\mathrm{P}$ and $^{\mathrm{P}}\mathrm{R}$ branches. Parallel transitions ($\Delta K = 0$) did not show, in the present analysis, any splitting due to the internal rotation. In the following discussion of this Section we will always refer to perpendicular transitions, if not otherwise specified.

A typical spectrum of multiplet structure is displayed in Fig. 1, corresponding to the $26_{10} - 25_{11}$ transition. The level scheme of Fig. 2 illustrates how the multiplet originates. The following asymmetric rigid rotor (ARR) selection rules apply for the indicated transitions:

$$\left.\begin{aligned} |\Delta K_-| &= 1 \\ |\Delta K_+| &= 1, 3 \end{aligned}\right. \quad \text{allowed transitions: A, E,}$$

$$\left.\begin{aligned} |\Delta K_-| &= 1 \\ |\Delta K_+| &= 2 \end{aligned}\right. \quad \text{forbidden transitions: E}^{\times},$$

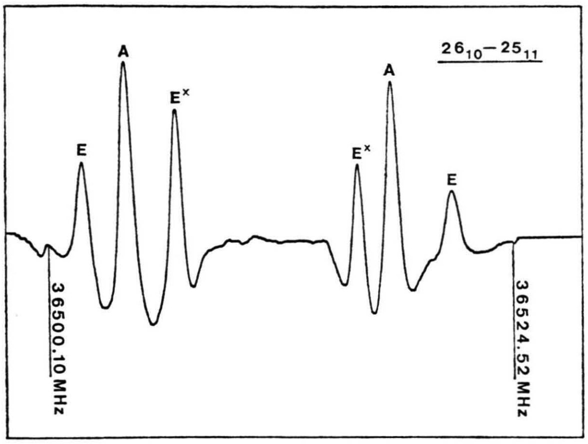

Fig. 1. Ground state Stark spectrum of cis propionyl fluoride showing the $26_{10}-25_{11}$ intermediate K multiplet. Stark field = 4 V/cm, gas pressure = 2 mTorr, cell temperature = − 60 °C.

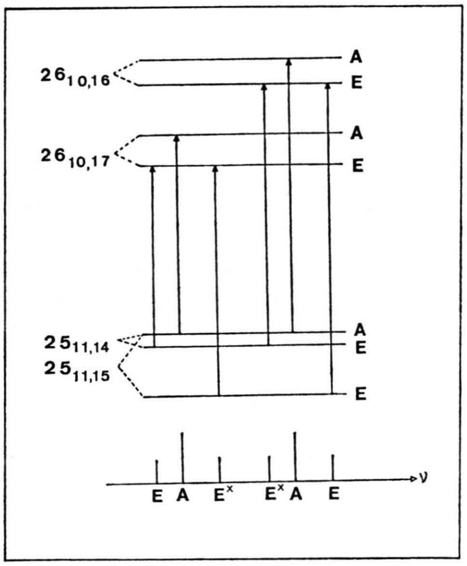

Fig. 2. Level scheme (not to scale) of the ground state 26_{10} and 25_{11} intermediate K doublets of cis propionyl fluoride. The transitions corresponding to the spectrum of Fig. 1 are indicated. The E-species forbidden transitions are labelled by $E^{\times}$.

where the symmetry species A and E refer to the C_3 group. The forbidden transitions, labelled by $E^{\times}$, are only of E-species. They are ARR dipole moment forbidden, in fact $\mu_c = 0$, but, as explained in Sect. III, may appear due to the mixing of the K-doublet ARR wave functions.

All the measured intermediate K transitions, see Table 3, present the same appearance as the case discussed above, whenever the complete spectrum could be recorded. The close degeneracy of the K-doublet levels involved in these transitions make them exhibit a first order Stark effect. Consequently they are modulated at very low electric field. Due to this the spectral region, where these transitions are searched for, appear in general clear from extraneous lines and the multiplet structure is readily recognizable. Moreover, frequency relationships must hold as in the case of Fig. 1, where for the E-species transitions is:

$$(26_{10,17} - 25_{11,15}) - (26_{10,17} - 25_{11,14})$$
$$= (26_{10,16} - 25_{11,15}) - (26_{10,16} - 25_{11,14})$$

and the sum of the intensity of the E-species allowed line (E) and of the E-species forbidden line ($E^{\times}$) has to be equal to the intensity of the corresponding A-species line (A). Figure 3 shows another multiplet from the $23_9 - 22_{10}$ transition. Here the two triplets are separated by 25 MHz, but the identification was quite straightforward. Table 3 presents the measured and calculated internal rotation splittings of low K transitions (doublet structure) and of intermediate K transitions (multiplet structure). The above described frequency and intensity sum rule was applied to all the measured intermediate K multiplets.

In the PAM the following effective rotational Hamiltonian was used [11, 12]:

$$H_{0\sigma} = H_R + F \sum_n W_{0\sigma}^{(n)} \left(\lambda_a \frac{I_\alpha}{I_a} P_a + \lambda_b \frac{I_\alpha}{I_b} P_b \right)^n , \tag{2}$$

Table 3. Observed split transitions of cis propionyl fluoride, ground state. Low and intermediate K transitions. Frequencies are in MHz.

Transition	ν (exp.)	Γ	$\Delta\nu$ (exp.)^a	$\Delta\nu$ (calc.)^b
a) Low K transitions				
$6_{2,4} - 6_{1,5}$	17097.42	A		
	17097.31	E	− 0.11	− 0.08
$13_{5,8} - 12_{6,7}$	15047.48	A		
	15048.08	E	0.60	0.57
$15_{5,10} - 14_{6,9}$	31240.47	A		
	31240.79	E	0.32	0.35
$17_{6,11} - 16_{7,10}$	30071.51	A		
	30072.02	E	0.51	0.52
$19_{7,12} - 18_{8,11}$	29553.19	A		
	29554.21	E	1.02	1.08
$20_{7,13} - 19_{8,12}$	37332.70	A		
	37333.38	E	0.68	0.69
$23_{6,17} - 23_{6,18}$	17346.56	A		
	17346.69	E	0.13	0.09

Table 3. (continued).

Transition	ν (exp.)	Γ	$\Delta\nu$ (exp.)[a]	$\Delta\nu$ (calc.)[b]
b) Intermediate K transitions				
$8_{6,3} - 9_{5,4}$	13792.78	A		
	13790.53	E	− 2.25	− 2.35
$8_{6,3} - 9_{5,5}$	13806.76	E$^{\times}$	13.98	13.72
$8_{6,2} - 9_{5,5}$	13808.59	A		
	13810.19	E	1.60	1.71
$8_{6,2} - 9_{5,4}$	13793.95[c]	E$^{\times}$	− 14.64	− 14.36
$15_{6,9} - 14_{7,8}$	14730.44	A		
	14731.74	E	1.30	1.33
$15_{6,9} - 14_{7,7}$	14726.39	E$^{\times}$	− 4.05	− 4.14
$17_{7,10} - 16_{8,9}$	14604.49	A		
	14606.67	E	2.18	2.32
$17_{7,10} - 16_{8,8}$	14602.24	E$^{\times}$	− 2.25	− 2.33
$19_{8,12} - 18_{9,9}$	14533.50	A		
	14531.45	E	− 2.05	− 2.22
$19_{8,12} - 18_{9,10}$	14536.12	E$^{\times}$	2.62	2.63
$19_{8,11} - 18_{9,10}$	14549.62	A		
	14552.52	E	2.90	3.06
$19_{8,11} - 18_{9,9}$	14547.84	E$^{\times}$	− 1.78	− 1.80
$21_{8,13} - 20_{9,12}$	29309.42	A		
	29311.45	E	2.03	2.11
$21_{8,13} - 20_{9,11}$	29306.54	E$^{\times}$	− 2.88	− 2.93
$22_{8,14} - 21_{9,13}$	36896.39	A		
	36897.79	E	1.40	1.47
$22_{8,14} - 21_{9,12}$	36891.56	E$^{\times}$	− 4.83	− 4.90
$23_{9,15} - 22_{10,12}$	29153.98	A		
	29152.06	E	− 1.92	− 2.18
$23_{9,15} - 22_{10,13}$	29156.90	E$^{\times}$	2.92	2.73
$23_{9,14} - 22_{10,13}$	29176.89	A		
	29179.73	E	2.84	3.02
$23_{9,14} - 22_{10,12}$	29174.93	E$^{\times}$	− 1.96	− 1.90
$24_{9,16} - 23_{10,13}$	36613.93	A		
	36612.42	E	− 1.51	− 1.57
$24_{9,16} - 23_{10,14}$	36617.32	E$^{\times}$	3.39	3.37
$24_{9,15} - 23_{10,14}$	36662.97	A		
	36665.42	E	2.45	2.44
$24_{9,15} - 23_{10,13}$	36660.51	E$^{\times}$	− 2.46	− 2.51
$25_{10,16} - 24_{11,13}$	29087.22	A		
	29084.38	E	− 2.84	− 2.77
$25_{10,16} - 24_{11,14}$	29089.47	E$^{\times}$	2.25	2.18
$25_{10,15} - 24_{11,14}$	29093.62	A		
	29097.31	E	3.69	3.67
$25_{10,15} - 24_{11,13}$	29092.27	E$^{\times}$	− 1.35	− 1.29
$26_{10,17} - 25_{11,14}$	36503.95	A		
	36501.70	E	− 2.25	− 2.34
$26_{10,17} - 25_{11,15}$	36506.65	E$^{\times}$	2.70	2.54
$26_{10,16} - 25_{11,15}$	36517.93	A		
	36521.10	E	3.17	3.21
$26_{10,16} - 25_{11,14}$	36516.16	E$^{\times}$	− 1.77	− 1.67
$28_{11,18} - 27_{12,15}$	36412.96	A		
	36409.85	E	− 3.11	− 2.98
$28_{11,18} - 27_{12,16}$	36414.85	E$^{\times}$	1.89	1.83
$28_{11,17} - 27_{12,16}$	36416.88	A		
	36420.93	E	4.05	3.89
$28_{11,17} - 27_{12,15}$	36415.94	E$^{\times}$	− 0.94	− 0.93

[a] $\Delta\nu = (\nu_{\mathrm{E}} - \nu_{\mathrm{A}})$ or $(\nu_{\mathrm{E}^{\times}} - \nu_{\mathrm{A}})$.

[b] Calculated splitting using Hamiltonian (2) and the parameters of Table 4.

[c] Overlapped by unassigned line.

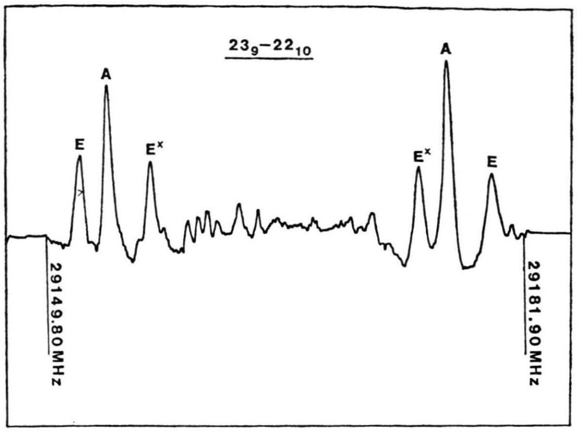

Fig. 3. Ground state Stark spectrum of cis propionyl fluoride showing the $23_9 - 22_{10}$ intermediate K multiplet. Stark field = 10 V/cm, gas pressure = 2 mTorr, cell temperature = − 60 °C.

where H_{R} is the usual rotational Hamiltonian, F is the reduced rotational constant for the internal rotation, $W_{0\sigma}^{(n)}$ are the nth order perturbation coefficients, which are dependent on the reduced barrier s, and λ_a and λ_b are the direction cosines of the internal rotation axis with respect to the corresponding principal axis. Since this conformer has a plane of symmetry, then $\lambda_c = 0$ and λ_a is correlated to λ_b. Herschbach's expression for the denominator correction, Eq. (43) of Ref. [13], was added to the Hamiltonian (2). Terms up to the fourth order were retained, which resulted particularly necessary for the intermediate K transitions. The truncation was justified by an IAM method calculation [14] of the internal rotation splittings. The strong dependance of the lines on the different terms of the Hamiltonian (2), see also Sect. III, made it possible to fit simultaneously the three internal rotation parameters, V_3, $\sphericalangle(i, a)$, and I_α. The standard deviation of the fit was 112 kHz, being the mean observed splitting $|\overline{\Delta\nu}|_{\exp} = 2.94$ MHz. The largest correlation coefficient between the fitted parameters is 0.924, connecting V_3 and $\sphericalangle(i, a)$. The results are shown in Table 4.

c) *High K Transitions*

The multiplet structure characteristic of the intermediate K transitions changes into close doublets for the high K transitions, which resemble the A, E doublets of the low K case. Moreover, for the measured transitions, they result almost

Table 4. Results of the ground state internal rotation analysis for cis propionyl fluoride. For comparison the parameters of the first excited internal rotation state, Ref. [1], are also reported.

	Present work	Ref. [1]
$I_\alpha/\mathrm{u\AA}^2$	3.18 ± 0.03	$(3.12 \pm 0.02)^{a,b}$
$\sphericalangle\,(i, a)$/degr.	32.7 ± 2.0	31.5 ± 2.0
s	65.2 ± 0.3	65.5 ± 1.6
V_3/cal/mole	2350 ± 11	2400 ± 60
V_3/kJ/mole	9.83 ± 0.05	10.04 ± 0.25
F/GHz	168.0 ± 1.7	170.78

[a] Assumed value.

[b] The internal rotation parameters of Ref. [1] are reproduced, within their quoted uncertainties, even with the presently obtained value of $I_\alpha = 3.18\ \mathrm{u\AA}^2$.

equally split. Figure 4 reports one of these doublets from the $34_{14} - 33_{15}$ transition. The associated level scheme is illustrated in Figure 5. It appears that the observed doublet actually consists of two coinciding A-species lines (A + A) and two coinciding E-species forbidden lines ($E^\times + E^\times$). In propylene oxide, for the high K transitions, in addition to an analogous doublet structure, a triplet structure was found, where the two forbidden transitions do not coincide [8]. Table 5 lists the measured high K transitions and the observed and calculated internal rotation splittings. The observed spectrum is better reproduced in the IAM than in the PAM. In fact for the high K transitions the internal and over-all rotation coupling terms become too large in the PAM to be treated by the perturbation method. In the IAM the doublet structure is fully accounted for within the linewidth, which typically is 300 kHz FWHM. The calculated splittings in Table 5 are according the IAM, using the parameters previously obtained, see Table 4.

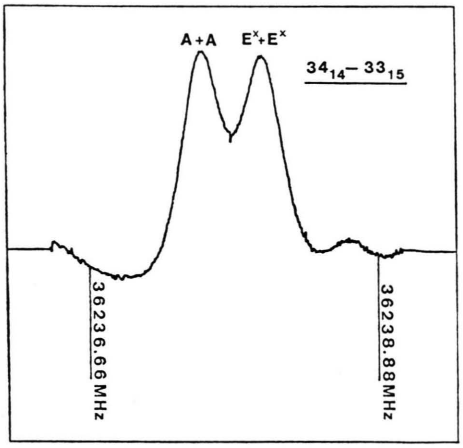

Fig. 4. Ground state Stark spectrum of cis propionyl fluoride showing the $34_{14} - 33_{15}$ high K doublet. Stark field = 20 V/cm, gas pressure = 6 mTorr, cell temperature = − 60 °C.

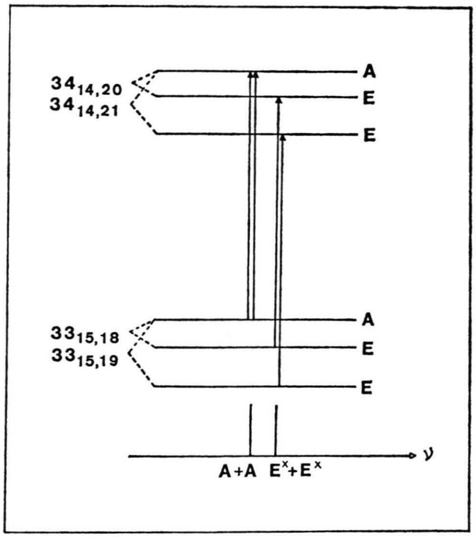

Fig. 5. Level scheme (not to scale) of the ground state 34_{14} and 33_{15} high K doublets of cis propionyl fluoride. The transitions corresponding to the spectrum of Fig. 4 are indicated. The E-species forbidden transitions are labelled by $E^\times$.

Table 5. Observed split transitions of cis propionyl fluoride, ground state. High K transitions. Frequencies are in MHz.

Transition	ν (exp.)	Γ	$\Delta\nu$ (exp.)[a]	$\Delta\nu$ (calc.)[b]
$23_{14} - 24_{13}$	20769.09	A + A		
	20768.60	$E^\times + E^\times$	− 0.49	− 0.56
$28_{12} - 27_{13}$	21714.80	A + A		
	21715.23	$E^\times + E^\times$	0.43	0.50
$31_{13} - 30_{14}$	28961.92	A + A		
	28962.38	$E^\times + E^\times$	0.46	0.50
$33_{14} - 32_{15}$	28938.38	A + A		
	28938.85	$E^\times + E^\times$	0.47	0.51
$34_{14} - 33_{15}$	36237.52	A + A		
	36237.99	$E^\times + E^\times$	0.47	0.50
$35_{15} - 34_{16}$	28921.01	A + A		
	28921.49	$E^\times + E^\times$	0.48	0.49
$36_{15} - 35_{16}$	36201.38	A + A		
	36201.86	$E^\times + E^\times$	0.48	0.48
$38_{16} - 37_{17}$	36172.87	A + A		
	36173.28	$E^\times + E^\times$	0.41	0.47
$40_{17} - 39_{18}$	36150.48	A + A		
	36150.88	$E^\times + E^\times$	0.40	0.45

[a] $\Delta\nu = \nu_{E^\times} - \nu_A$.

[b] Calculated with the IAM, using the parameters of Table 4.

III. Forbidden Transitions. Theory

It is well known that in an asymmetric rigid rotor as K increases the K-doubling decreases and for sufficiently high K the pairs of levels having the same value of K become nearly degenerate. In the presence of an internal and over-all rotation coupling the behaviour of the A-species K-doublet levels is still ARR-like, while the E-species K-doublet levels are affected by the odd order terms in the Hamiltonian (2), particularly the linear terms. The result is that, for intermediate and high K, the ARR original pair of E-species wave functions mix together and the ARR selection rules break down. Following the treatment of [8], the new internal rotation perturbed wave functions can be written as:

$$\begin{aligned} \psi'_+ &= \psi_+ \cos\omega - \psi_- \sin\omega\,, \\ \psi'_- &= \psi_+ \sin\omega + \psi_- \cos\omega\,, \end{aligned} \tag{3}$$

where ω quantifies the extent of the mixing ($0 \leqq \omega \leqq \pi/4$) and is defined by the Eq. (24) of [8]. Using the expressions (3) for the initial and final states of the observed transitions, see Fig. 2 and Fig. 5, line strengths (S) can be calculated, with reference to the ARR. It turns out that for perpendicular transitions ($\Delta K = \pm 1$):

$$\begin{aligned} S_{\mathrm{E}^\times} &= S_{\mathrm{ARR}}[\sin(\omega_{\mathrm{i}} + \omega_{\mathrm{f}})]^2\,, \\ S_{\mathrm{E}} &= S_{\mathrm{ARR}}[\cos(\omega_{\mathrm{i}} + \omega_{\mathrm{f}})]^2\,. \end{aligned} \tag{4}$$

By these expressions it can be seen that when no mixing occurs, $\omega_{\mathrm{i}} = \omega_{\mathrm{f}} = 0$, the forbidden transitions ($\mathrm{E}^\times$) have no intensity, while the allowed transitions (E) have all the intensity: this is the low K case. As the mixing increases the forbidden transitions gain intensity at expense of the allowed transitions. In the limit of complete mixing, $\omega_{\mathrm{i}} = \omega_{\mathrm{f}} = \pi/4$, the forbidden transitions have all the intensity: this is the high K case.

For parallel transitions ($\Delta K = 0$) the result is quite different:

$$\begin{aligned} S_{\mathrm{E}^\times} &= S_{\mathrm{ARR}}[\sin(\omega_{\mathrm{i}} - \omega_{\mathrm{f}})]^2\,, \\ S_{\mathrm{E}} &= S_{\mathrm{ARR}}[\cos(\omega_{\mathrm{i}} - \omega_{\mathrm{f}})]^2\,. \end{aligned} \tag{5}$$

The forbidden transitions vanish at both the limits $\omega_{\mathrm{i}} = \omega_{\mathrm{f}} = 0$ and $\omega_{\mathrm{i}} = \omega_{\mathrm{f}} = \pi/4$ and, in general, have little intensity.

By group theory considerations the intermediate and high K spectra can be accounted for in the following way. The A-species eigenstates of the effective rotational Hamiltonian (2), after elimination or neglect of cross terms, are classified under the V group and consequently the A-species transitions obey the ARR selection rules. On the other hand for the E-species eigenstates the effective rotational Hamiltonian (2) is no longer invariant to the V group but only to the trivial group E, and ARR forbidden transitions may occur.

IV. Discussion and Conclusion

The present investigation has extended the measurements of the transitions of cis propionyl fluoride to higher J and higher K, with respect to a previous study [1]. A centrifugal distortion analysis, up to the fourth order terms, has been performed. The obtained rotational constants are still within the uncertainty range of those previously reported [1], but are one order of magnitude more accurate.

The methyl top internal rotation barrier has been determined from the ground state spectrum. The value obtained here is in agreement with that obtained in Ref. [1], from the first excited methyl top internal rotation state. A test calculation has reproduced with the present value of $I_\alpha = 3.18$ uÅ^2 the internal rotation parameters of [1], within their quoted uncertainties. The agreement which has been found in cis propionyl fluoride between ground and excited state barrier determinations is not generally observed, as the internal rotation may interact with other vibrations. In cis propionyl fluoride the second excited state of the torsion around the C—C (carbonyl) bond, at 163 cm^{-1}, is the closest to the first excited methyl top internal rotation state, at 194 cm^{-1} [1]. The results produce evidence for this coupling being below the experimental sensitivity. The present analysis contributes to the effort of this and other laboratories to determine high internal rotation barriers from the ground state spectra, for reasons already discussed [2, 13, 15].

A particular finding of the work are the forbidden transitions. The same kind of transitions has been extensively studied by Herschbach and Swalen [8], and much of our understanding of the complex spectral features of cis propionyl fluoride came from their paper. The theoretical arguments of Sect. III are taken from it. Recently the multiplet structure of intermediate K transitions has been observed in the ground state of ethyl cyanide [15] and ethyl vinyl ether [16]. The forbidden transitions in the internal rotation spectra are of importance for two main reasons. First, they provide additional experimental data and in the intermediate K case facilitate the assignment of the transition. Moreover, they are the only E-species transitions observable at high K. The second reason has to be viewed in connection with the far infrared (FIR) region becoming now more accessible [17]. From population distribution considerations it appears that the most intense rotational and/or rovibrational transitions involve high quantum numbers. In the high resolution internal rotation FIR spectra forbidden transitions will presumably be numerous. In this respect microwave investigations, like the present and the referenced ones, provide experimental material and useful background for the interpretation of the FIR spectra.

Acknowledgements

We thank Dipl. Phys. G. Bestmann for technical help with the FTMW spectrometer. The assistence in the computing by Dipl. Chem. E. Fliege and Dipl. Chem. D. Hübner is also acknowledged. We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemie for funds. Calculations were carried out at the Rechenzentrum der Universität Kiel.

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