# Determination of a High Potential Barrier Hindering Internal Rotation from the Microwave Ground State Spectrum The Methylbarrier of Antiperiplanar and Synclinal Normal Propyl Fluoride

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The microwave ground state spectra of antiperiplanar and synclinal normal propyl fluoride have been measured by microwave Fourier transform spectroscopy and analysed for methyl torsion fine structure. Additionally, the spectrum of the synclinal form in the first excited state of the methyl group has been investigated due to methyl torsion. The difference of the values determined for the barrier heights in the ground and first excited state of the synclinal form is discussed by an approximate treatment of the coupling of $CH_3$ and C–C torsional motions.

As high $J$ transitions were measured a centrifugal distortion analysis was necessary.

## I. Introduction

Some years ago Hirota [1] investigated the microwave spectrum of the antiperiplanar (trans) and synclinal (gauche) rotational isomers of normal propyl fluoride, $CH_3CH_2CH_2F$. He determined the rotational constants, the dipole moments and the barrier heights hindering methyl rotation using lines of the first excited state of methyl torsion since the barriers are too high to yield splittings in the ground state, which could be resolved by Stark spectroscopy.

We reinvestigated the spectra of the two rotational isomers of normal propyl fluoride with the higher resolution of microwave Fourier transform (MWFT) spectroscopy to resolve the methyl torsion fine structure in the ground state.

To verify some structural assumptions made by Hirota [1] to analyse the methyl torsion splittings, it was an important point of this work to determine not only the barrier height but also the moment of inertia of the methyl group and the angles between the internal rotation axis and the principal axes.

## II. Experimental

Normal propyl fluoride was prepared by the reaction of normal propyl bromide, $CH_3CH_2CH_2Br$, with silver fluoride, AgF, and used after vacuum destillation.

The spectra were recorded in the range of 8 to 26 GHz by use of the microwave Fourier transform spectrometers described in [2, 3, 4].

Sample pressure was around 0.3 mTorr and cell temperature was around – 60 °C.

## III. Ground State Spectra

A part of the measured frequencies and their assignments are listed in Table 1 a and 1 b for the antiperiplanar and synclinal rotamer of normal propyl fluoride in the ground state, respectively. Only a reduced set of lines could be reproduced in this publication. The complete list of measurements is available in the Universitätsbibliothek Kiel under the number TNA 1 *. Figure 1 gives an example of the recordings.

The measurement of narrow split multiplets ($\Delta\nu \leqq 200$ kHz) in the range 18 to 26 GHz (K-band)

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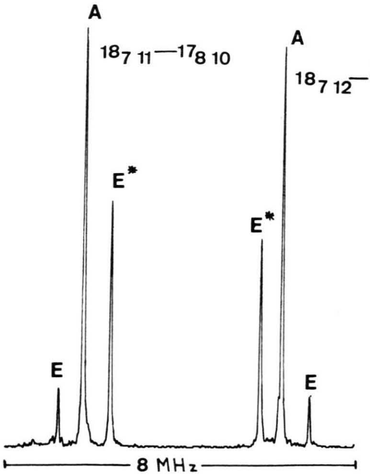


Fig. 1. $J_{K_-K_+} = 18_{7\,11} - 17_{8\,10}$ and $18_{7\,12} - 17_{8\,9}$ transition of synclinal normal propyl fluoride in the ground state with $CH_3$ torsion splitting. A section of 8 MHz out of a 25 MHz range of the power spectrum is given. The frequency increases from left to right. Sample interval 20 ns, 640 k cycles, 1024 data points supplemented by 3072 zeros, pressure 0.3 mTorr, temperature −60 °C.

were refined by line contour analyses [5]. Because the spectra in the range of 8 to 18 GHz were recorded some time ago, when no line contour analysis was possible in our laboratory, splittings with $\Delta\nu \leqq 200$ kHz in this range are not used for the fine structure analyses and indicated by "*n*" in Tables 1 a and 1 b.

The assignment was checked by the consistency of the analysis of centrifugal distortion and torsional fine structure. The two perturbation effects were calculated separately. The calculated spectra were refined by an iterative procedure to fit the measured ones.

The observed and by line contour analyses refined splittings between A and E species $\Delta\nu_{\text{obs}}$ were used to analyse the torsional fine structure by the internal axis method (IAM) by a program written by Woods [6, 7] and modified by W. Kasten (program – AC3IAM). For the two rotational isomers the Fourier coefficients $w_1(s)$ ($s$ the reduced barrier), the angles $\sphericalangle(g, i)$ between the $g = a, b, c$ inertia axes and the internal rotation axis $i$, and the moments of inertia $I_\alpha$ of the methyl group could be fitted.

No regular $\mu_c$-type transitions could be measured because the antiperiplanar form has a plane of symmetry perpendicular to the $c$-axis and the $\mu_c$-dipole moment of the synclinal form is small [1]. But by mixing of nearly degenerate K-doublets some $\mu_c$-type transitions of the symmetry species E become observable. The intensity of these lines increases with $K_-$, see Figure 1. An explanation of this effect is given by Herschbach [8]. These $\mu_c$-type transitions E* are connected with the regular $\mu_b$-type transitions A and E. Because $\mu_c$- and $\mu_b$-type transitions show a different centrifugal distortion effect, the program was modified to include centrifugal constants up to fourth order (Watson's A reduction is used [9]).

The results for the torsional analyses are given in Table 2 column 1 and 4 for the antiperiplanar and synclinal form, respectively, in comparison with Hirota's [1] values in column 2 and 5 of Table 2, determined with use of splittings of the first excited state of the methyl group. The internal rotation parameters were used to calculate the deviations from the rigid rotor lines (program FC3IAM). The deviations were added to the frequencies $\nu_{\text{obs}}$ in Table 1 a and 1 b. The hypothetical unsplit lines $\nu_{\text{unsplit}}$ were evaluated as a mean value.

The frequencies $\nu_{\text{unsplit}}$ were used in a least squares analysis to fit the constants in the following Hamiltonian (Watson's $A$-reduction is used [10, 11, 12], program ZFAP4 and ZFAP6):

$$
\begin{aligned}
H = {} & 1/2\,(B+C)\,P^2 + [A - 1/2\,(B+C)]\,P_z^2 \\
& + 1/2\,(B-C)\,(P_x^2 - P_y^2) \\
& - \Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\,\delta_J P^2 (P_x^2 - P_y^2) \\
& - \delta_K [P_z^2 (P_x^2 - P_y^2) + (P_x^2 - P_y^2)\,P_z^2] \\
& + \Phi_J P^6 + \Phi_{JK} P^4 P_z^2 + \Phi_{KJ} P^2 P_z^4 + \Phi_K P_z^6 \\
& + 2\,\varphi_J P^4 (P_x^2 - P_y^2) \\
& + \varphi_{JK} P^2 [P_z^2 (P_x^2 - P_y^2) + (P_x^2 - P_y^2)\,P_z^2] \\
& + \varphi_K [P_z^4 (P_x^2 - P_y^2) + (P_x^2 - P_y^2)\,P_z^4]\,. \qquad (1)
\end{aligned}
$$

For the antiperiplanar form only the centrifugal distortion constants up to fourth order could be determined.

The results for the centrifugal distortion analyses are given in Table 3 column 1 and 3 for the antiperiplanar and synclinal rotamer, respectively.

The internal rotation and centrifugal distortion analyses were repeated iteratively until no further changes in the derived parameters were observed.

Table 1 a. Part of the measured frequencies $\nu_{obs}$ of antiperiplanar normal propyl fluoride with $CH_3$ torsion fine structure in the ground state. The complete list is available in the Universitätsbibliothek Kiel under the number TNA 1, see text. $\Gamma$: symmetry species, $\nu_{unsplit}$: hypothetical frequency without torsion splitting, $\Delta\nu_{obs}$, $\Delta\nu_{calc}$: experimental and calculated torsional splittings, n: not used for the fine structure analysis, see text. Frequency in MHz.

| $J'$ | $K'_-$ | $K'_+$ | $J$ | $K_-$ | $K_+$ | $\nu_{obs}$ | $\Gamma$ | $\nu_{unsplit}$ | $\Delta\nu_{obs}$ | $\Delta\nu_{calc}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1a.1. A-transitions: | | | | | | | | | | |
| 1a.1.1. Q-branch: | | | | | | | | | | |
| 8 | 1 | 7 | - 8 | 1 | 8 | 8 578.818 | A, E | 8 578.812 | 0.0 | 0.038 |
| 9 | 1 | 8 | - 9 | 1 | 9 | 10 720.242 | A, E | 10 720.234 | 0.0 | 0.048 |
| 10 | 1 | 9 | -10 | 1 | 10 | 13 097.135 | A | 13 097.088 | | |
| | | | | | | 13 097.065 | E | | $0.070^{n}$ | 0.058 |
| 11 | 1 | 10 | -11 | 1 | 11 | 15 707.913 | A | 15 707.860 | | |
| | | | | | | 15 707.834 | E | | $0.079^{n}$ | 0.070 |
| 12 | 1 | 11 | -12 | 1 | 12 | 18 550.697 | A | 18 550.639 | | |
| | | | | | | 18 550.609 | E | | 0.089 | 0.083 |
| 13 | 1 | 12 | -13 | 1 | 13 | 21 622.977 | A | 21 622.914 | | |
| | | | | | | 21 622.882 | E | | 0.095 | 0.096 |
| 14 | 1 | 13 | -14 | 1 | 14 | 24 921.609 | A | 24 921.528 | | |
| | | | | | | 24 921.492 | E | | 0.117 | 0.111 |
| 1a.1.2. R-branch: | | | | | | | | | | |
| 2 | 0 | 2 | - 1 | 0 | 1 | 14 514.726 | A, E | 14 514.726 | 0.0 | 0.002 |
| 2 | 1 | 1 | - 1 | 1 | 0 | 14 754.998 | A, E | 14 754.998 | 0.0 | 0.003 |
| 2 | 1 | 2 | - 1 | 1 | 1 | 14 278.148 | A, E | 14 278.148 | 0.0 | 0.001 |
| 3 | 0 | 3 | - 2 | 0 | 2 | 21 767.476 | A, E | 21 767.476 | 0.0 | 0.003 |
| 3 | 1 | 3 | - 2 | 1 | 2 | 21 416.015 | A, E | 21 416.015 | 0.0 | 0.001 |
| 3 | 2 | 1 | - 2 | 2 | 0 | 21 782.150 | A | 21 782.148 | | |
| | | | | | | 21 781.551 | E | | 0.599 | 0.605 |
| 3 | 2 | 2 | - 2 | 2 | 1 | 21 774.848 | A | 21 774.846 | | |
| | | | | | | 21 775.447 | E | | -0.599 | -0.600 |
| 1a.2. B-transitions: | | | | | | | | | | |
| 1a.2.1. Q-branch: | | | | | | | | | | |
| 1 | 1 | 0 | - 1 | 0 | 1 | 23 476.768 | A | 23 476.627 | | |
| | | | | | | 23 476.556 | E | | 0.212 | 0.217 |
| 2 | 1 | 1 | - 2 | 0 | 2 | 23 717.036 | A | 23 716.888 | | |
| | | | | | | 23 716.814 | E | | 0.222 | 0.218 |
| 3 | 1 | 2 | - 3 | 0 | 3 | 24 080.850 | A | 24 080.706 | | |
| | | | | | | 24 080.634 | E | | 0.216 | 0.219 |
| 4 | 1 | 3 | - 4 | 0 | 4 | 24 572.293 | A | 24 572.149 | | |
| | | | | | | 24 572.077 | E | | 0.216 | 0.221 |
| 5 | 1 | 4 | - 5 | 0 | 5 | 25 196.761 | A | 25 196.617 | | |
| | | | | | | 25 196.545 | E | | 0.216 | 0.224 |
| 6 | 1 | 5 | - 6 | 0 | 6 | 25 960.946 | A | 25 960.799 | | |
| | | | | | | 25 960.725 | E | | 0.221 | 0.227 |
| 1a.2.2. R-branch: | | | | | | | | | | |
| 5 | 0 | 5 | - 4 | 1 | 4 | 14 066.490 | A | 14 066.633 | | |
| | | | | | | 14 066.704 | E | | -0.214 | -0.205 |
| 6 | 0 | 6 | - 5 | 1 | 5 | 21 864.605 | A | 21 864.735 | | |
| | | | | | | 21 864.800 | E | | -0.195 | -0.201 |
| 10 | 1 | 9 | - 9 | 2 | 8 | 8 924.891 | A | 8 925.292 | | |
| | | | | | | 8 925.492 | E | | -0.601 | -0.582 |
| 11 | 1 | 10 | -10 | 2 | 9 | 17 435.432 | A | 17 435.803 | | |
| | | | | | | 17 435.989 | E | | -0.557 | -0.574 |
| 14 | 1 | 14 | -13 | 2 | 11 | 16 210.052 | A | 16 210.491 | | |
| | | | | | | 16 210.709 | E | | -0.657 | -0.656 |
| 15 | 1 | 15 | -14 | 2 | 12 | 20 797.728 | A | 20 798.169 | | |
| | | | | | | 20 798.390 | E | | -0.662 | -0.661 |
| 18 | 2 | 17 | -17 | 3 | 14 | 11 335.953 | A | 11 336.562 | | |
| | | | | | | 11 336.855 | E | | -0.902 | -0.913 |
| 20 | 2 | 19 | -19 | 3 | 16 | 24 463.674 | A | 24 464.283 | | |
| | | | | | | 24 464.582 | E | | -0.908 | -0.907 |
| 1a.2.3. P-branch: | | | | | | | | | | |
| 5 | 2 | 4 | - 6 | 1 | 5 | 24 041.868 | A | 24 041.459 | | |
| | | | | | | 24 041.219 | E | | 0.649 | 0.644 |
| 6 | 2 | 5 | - 7 | 1 | 6 | 15 965.995 | A | 15 965.596 | | |
| | | | | | | 15 965.377 | E | | 0.618 | 0.621 |
| 6 | 2 | 4 | - 7 | 1 | 7 | 22 767.459 | A | 22 767.040 | | |
| | | | | | | 22 766.848 | E | | 0.611 | 0.616 |
| 12 | 3 | 10 | -13 | 2 | 11 | 20 611.968 | A | 20 611.336 | | |
| | | | | | | 20 610.926 | E | | 1.042 | 1.043 |
| 12 | 3 | 9 | -13 | 2 | 12 | 23 089.140 | A | 23 088.506 | | |
| | | | | | | 23 088.284 | E | | 0.856 | 0.855 |
| 13 | 3 | 11 | -14 | 2 | 12 | 12 775.699 | A | 12 775.067 | | |
| | | | | | | 12 774.692 | E | | 1.007 | 1.004 |
| 14 | 3 | 11 | -15 | 2 | 14 | 9 102.057 | A | 9 101.459 | | |
| | | | | | | 9 101.159 | E | | 0.898 | 0.903 |

Table 1 b. Part of the measured frequencies $\nu_{obs}$ of synclinal normal propyl fluoride with $CH_3$ torsion in the ground state, see also Table 1 a.
* indicates "dipole forbidden" transitions, see text.

| $J'$ | $K'_-$ | $K'_+$ | $J$ | $K_-$ | $K_+$ | $\nu_{obs}$ | $\Gamma$ | $\nu_{unsplit}$ | $\Delta\nu_{obs}$ | $\Delta\nu_{calc}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1b. 1. A-transitions: | | | | | | | | | | |
| 1b. 1. 1. Q-branch: | | | | | | | | | | |
| 5 | 1 | 4 | - 5 | 1 | 5 | 11 804.209 | A, E | 11 804.204 | 0.0 | 0.029 |
| 7 | 1 | 6 | - 7 | 1 | 7 | 21 753.902 | A | 21 753.860 | | |
| | | | | | | 21 753.839 | E | | 0.063 | 0.053 |
| 8 | 2 | 6 | - 8 | 2 | 7 | 8 383.416 | A, E | 8 383.416 | 0.0 | 0.030 |
| 9 | 2 | 7 | - 9 | 2 | 8 | 12 259.432 | A | 12 259.392 | | |
| | | | | | | 12 259.373 | E | | 0.059* | 0.043 |
| 10 | 2 | 8 | -10 | 2 | 9 | 16 953.872 | A | 16 953.824 | | |
| | | | | | | 16 953.800 | E | | 0.072* | 0.057 |
| 11 | 2 | 9 | -11 | 2 | 10 | 22 417.037 | A | 22 416.986 | | |
| | | | | | | 22 416.961 | E | | 0.076 | 0.072 |
| 13 | 3 | 10 | -13 | 3 | 11 | 10 717.377 | A | 10 717.334 | | |
| | | | | | | 10 717.312 | E | | 0.065* | 0.050 |
| 14 | 3 | 11 | -14 | 3 | 12 | 15 093.789 | A | 15 093.737 | | |
| | | | | | | 15 093.711 | E | | 0.078* | 0.067 |
| 1b. 1. 2. R-branch: | | | | | | | | | | |
| 1 | 0 | 1 | - 0 | 0 | 0 | 9 381.094 | A, E | 9 381.094 | 0.0 | 0.002 |
| 2 | 0 | 2 | - 1 | 0 | 1 | 18 714.319 | A, E | 18 714.319 | 0.0 | 0.005 |
| 2 | 1 | 1 | - 1 | 1 | 0 | 19 552.582 | A, E | 19 552.581 | 0.0 | 0.007 |
| 2 | 1 | 2 | - 1 | 1 | 1 | 17 971.673 | A, E | 17 971.673 | 0.0 | 0.003 |
| 1b. 2. B-transitions: | | | | | | | | | | |
| 1b. 2. 1. Q-branch: | | | | | | | | | | |
| 1 | 1 | 0 | - 1 | 0 | 1 | 10 208.459 | A, E | 10 208.457 | 0.0 | 0.009 |
| 2 | 1 | 1 | - 2 | 0 | 2 | 11 046.723 | A, E | 11 046.721 | 0.0 | 0.011 |
| 3 | 1 | 2 | - 3 | 0 | 3 | 12 391.298 | A, E | 12 391.295 | 0.0 | 0.015 |
| 4 | 1 | 3 | - 4 | 0 | 4 | 14 337.785 | A | 14 337.772 | | |
| | | | | | | 14 337.766 | E | | 0.019* | 0.020 |
| 5 | 1 | 4 | - 5 | 0 | 5 | 16 990.383 | A | 16 990.358 | | |
| | | | | | | 16 990.345 | E | | 0.038* | 0.028 |
| 6 | 1 | 5 | - 6 | 0 | 6 | 20 432.904 | A | 20 432.879 | | |
| | | | | | | 20 432.866 | E | | 0.038 | 0.037 |
| 7 | 1 | 6 | - 7 | 0 | 7 | 24 696.036 | A | 24 695.995 | | |
| | | | | | | 24 695.974 | E | | 0.062 | 0.049 |
| 5 | 2 | 3 | - 5 | 1 | 4 | 25 338.998 | A, E | 25 338.995 | 0.0 | 0.016 |
| 6 | 2 | 4 | - 6 | 1 | 5 | 24 692.114 | A, E | 24 692.111 | 0.0 | 0.017 |
| 7 | 2 | 5 | - 7 | 1 | 6 | 24 533.164 | A, E | 24 533.161 | 0.0 | 0.020 |
| 8 | 2 | 6 | - 8 | 1 | 7 | 25 019.981 | A, E | 25 019.977 | 0.0 | 0.025 |
| 1b. 2. 2. R-branch: | | | | | | | | | | |
| 1 | 1 | 1 | - 0 | 0 | 0 | 18 799.029 | A, E | 18 799.027 | 0.0 | 0.009 |
| 2 | 0 | 2 | - 1 | 1 | 1 | 9 296.387 | A, E | 9 296.387 | 0.0 | -0.003 |
| 3 | 0 | 3 | - 2 | 1 | 2 | 19 277.736 | A, E | 19 277.736 | 0.0 | 0.001 |
| 4 | 1 | 3 | - 3 | 2 | 2 | 11 903.644 | A, E | 11 903.644 | 0.0 | -0.005 |
| 5 | 1 | 4 | - 4 | 2 | 3 | 23 067.043 | A, E | 23 067.043 | 0.0 | 0.001 |
| 6 | 2 | 4 | - 5 | 3 | 3 | 9 706.976 | A, E | 9 706.978 | 0.0 | -0.016 |
| 7 | 1 | 7 | - 6 | 2 | 4 | 21 237.709 | A | 21 237.748 | | |
| | | | | | | 21 237.768 | E | | -0.059 | -0.050 |
| 7 | 2 | 5 | - 6 | 3 | 4 | 20 732.845 | A, E | 20 732.846 | 0.0 | -0.008 |
| 8 | 1 | 8 | - 7 | 2 | 5 | 24 842.013 | A | 24 842.062 | | |
| | | | | | | 24 842.087 | E | | -0.074 | -0.065 |
| 8 | 2 | 7 | - 7 | 3 | 4 | 23 530.592 | A, E | 23 530.597 | 0.0 | -0.031 |
| 9 | 3 | 6 | - 8 | 4 | 5 | 17 983.376 | A, E | 17 983.379 | 0.0 | -0.023 |
| 10 | 3 | 8 | - 9 | 4 | 5 | 25 773.432 | A, E | 25 773.437 | 0.0 | -0.030 |
| 11 | 4 | 7 | -10 | 5 | 6 | 16 495.583 | A | 16 495.613 | | |
| | | | | | | 16 495.682 | E | | -0.099* | -0.077 |
| 12 | 4 | 9 | -11 | 5 | 6 | 25 850.275 | A, E | 25 850.288 | 0.0 | -0.019 |
| 13 | 1 | 13 | -12 | 2 | 10 | 24 622.514 | A | 24 622.626 | | |
| | | | | | | 24 622.682 | E | | -0.168 | -0.175 |

Table 1 b (continued)

| $J'$ | $K'_-$ | $K'_+$ | $J$ | $K_-$ | $K_+$ | $\nu_{obs}$ | $\Gamma$ | $\nu_{unsplit}$ | $\Delta\nu_{obs}$ | $\Delta\nu_{calc}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 13 | 5 | 8 | -12 | 6 | 7 | 15 552.578 | A | | | |
| | | | | | | 15 552.877 | E | 15 552.607 | -0.299 | -0.294 |
| | | | | | | 15 486.400 | E* | | 66.178 | 66.173 |
| 13 | 5 | 9 | -12 | 6 | 6 | 15 485.344 | A | | | |
| | | | | | | 15 485.130 | E | 15 485.374 | -0.214 | -0.203 |
| | | | | | | 15 551.608 | E* | | -66.264 | -66.264 |
| 14 | 5 | 9 | -13 | 6 | 8 | 25 379.577 | A | 25 379.603 | | |
| | | | | | | 25 379.732 | E | | -0.155[n] | -0.151 |
| 14 | 5 | 10 | -13 | 6 | 7 | 25 239.381 | A | 25 239.409 | | |
| | | | | | | 25 239.301 | E | | 0.080 | 0.070 |
| 15 | 6 | 9 | -14 | 7 | 8 | 14 754.181 | A | | | |
| | | | | | | 14 754.742 | E | 14 754.215 | -0.561 | -0.567 |
| | | | | | | 14 752.887 | E* | | 11.294 | 11.290 |
| 15 | 6 | 10 | -14 | 7 | 7 | 14 742.240 | A | | | |
| | | | | | | 14 741.780 | E | 14 742.274 | 0.460 | 0.461 |
| | | | | | | 14 753.635 | E* | | -11.395 | -11.395 |
| 16 | 1 | 16 | -15 | 2 | 13 | 13 533.398 | A | 13 533.567 | | |
| | | | | | | 13 533.652 | E | | -0.254 | -0.248 |
| 16 | 6 | 10 | -15 | 7 | 9 | 24 501.225 | A | | | |
| | | | | | | 24 501.672 | E | 24 501.255 | -0.447 | -0.453 |
| | | | | | | 24 475.998 | E* | | 25.227 | 25.220 |
| 16 | 6 | 11 | -15 | 7 | 8 | 24 475.234 | A | | | |
| | | | | | | 24 474.881 | E | 24 475.263 | 0.353 | 0.358 |
| | | | | | | 24 500.552 | E* | | -25.318 | -25.315 |
| 17 | 7 | 10 | -16 | 8 | 9 | 13 992.059 | A | | | |
| | | | | | | 13 992.826 | E | 13 992.097 | -0.767 | -0.762 |
| | | | | | | 13 990.583 | E* | | 1.476 | 1.473 |
| 17 | 7 | 11 | -16 | 8 | 8 | 13 990.053 | A | | | |
| | | | | | | 13 989.409 | E | 13 990.091 | 0.644 | 0.643 |
| | | | | | | 13 991.643 | E* | | -1.590 | -1.592 |
| 18 | 7 | 11 | -17 | 8 | 10 | 23 697.292 | A | | | |
| | | | | | | 23 697.948 | E | 23 697.326 | -0.656 | -0.654 |
| | | | | | | 23 693.373 | E* | | 3.919 | 3.921 |
| 18 | 7 | 12 | -17 | 8 | 9 | 23 692.770 | A | | | |
| | | | | | | 23 692.216 | E | 23 692.804 | 0.554 | 0.547 |
| | | | | | | 23 696.799 | E* | | -4.029 | -4.028 |

1b.2.3. P-branch:

Table 1 b (continued)

| $J'$ | $K'_-$ | $K'_+$ | $J$ | $K_-$ | $K_+$ | $\nu_{obs}$ | $\Gamma$ | $\nu_{unsplit}$ | $\Delta\nu_{obs}$ | $\Delta\nu_{calc}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 3 | 3 | 1 | - 4 | 2 | 2 | 10 901.214 | A | 10 901.193 | | |
| | | | | | | 10 901.128 | E | | 0.086[n] | 0.074 |
| 3 | 3 | 0 | - 4 | 2 | 3 | 11 606.853 | A, E | 11 606.824 | 0.0 | -0.015 |
| 5 | 4 | 2 | - 6 | 3 | 3 | 11 915.066 | A | | | |
| | | | | | | 11 914.819 | E | 11 915.040 | 0.247 | 0.243 |
| | | | | | | 12 064.045 | E* | | -148.979 | -148.977 |
| 5 | 4 | 1 | - 6 | 3 | 4 | 12 064.794 | A | | | |
| | | | | | | 12 064.963 | E | 12 064.767 | -0.169 | -0.163 |
| | | | | | | 11 915.741 | E* | | 149.053 | 149.057 |
| 7 | 5 | 3 | - 8 | 4 | 4 | 12 701.260 | A | | | |
| | | | | | | 12 700.789 | E | 12 701.227 | 0.471 | 0.461 |
| | | | | | | 12 728.311 | E* | | -27.051 | -27.035 |
| 7 | 5 | 2 | - 8 | 4 | 5 | 12 728.866 | A | | | |
| | | | | | | 12 729.230 | E | 12 728.833 | -0.364 | -0.361 |
| | | | | | | 12 701.734 | E* | | 27.132 | 27.134 |
| 8 | 6 | 3 | - 9 | 5 | 4 | 22 976.449 | A | | | |
| | | | | | | 22 975.724 | E | 22 976.408 | 0.725 | 0.718 |
| | | | | | | 22 977.545 | E* | | -1.096 | -1.096 |
| 8 | 6 | 2 | - 9 | 5 | 5 | 22 978.026 | A | | | |
| | | | | | | 22 978.623 | E | 22 977.985 | -0.597 | -0.593 |
| | | | | | | 22 976.805 | E* | | 1.221 | 1.222 |
| 9 | 6 | 4 | -10 | 5 | 5 | 13 430.367 | A | | | |
| | | | | | | 13 429.748 | E | 13 430.329 | 0.619 | 0.621 |
| | | | | | | 13 434.532 | E* | | -4.165 | -4.164 |
| 9 | 6 | 3 | -10 | 5 | 6 | 13 435.096 | A | | | |
| | | | | | | 13 435.586 | E | 13 435.059 | -0.490 | -0.504 |
| | | | | | | 13 430.816 | E* | | 4.280 | 4.282 |
| 10 | 7 | 4 | -11 | 6 | 5 | 23 691.742 | A, E* | 23 691.702 | 0.0 | 0.014 |
| 10 | 7 | 3 | -11 | 6 | 6 | 23 692.007 | A | 23 691.960 | | |
| | | | | | | 23 691.897 | E* | | 0.110[n] | 0.129 |
| 11 | 7 | 5 | -12 | 6 | 6 | 14 145.938 | A | 14 145.894 | | |
| | | | | | | 14 146.309 | E* | | -0.371 | -0.361 |
| 11 | 7 | 4 | -12 | 6 | 7 | 14 146.710 | A | 14 146.666 | | |
| | | | | | | 14 146.207 | E* | | 0.503 | 0.495 |
| 13 | 8 | 6 | -14 | 7 | 7 | 14 857.339 | A | 14 857.291 | | |
| | | | | | | 14 857.238 | E* | | 0.101[n] | 0.093 |
| 13 | 8 | 5 | -14 | 7 | 8 | 14 857.474 | A | 14 857.413 | | |
| | | | | | | 14 857.408 | E* | | 0.066 | 0.055 |
| 14 | 9 | 6 | -15 | 8 | 7 | 25 108.164 | A | 25 108.109 | | |
| | | | | | | 25 108.008 | E* | | 0.156 | 0.162 |
| 14 | 9 | 5 | -15 | 8 | 8 | 25 108.164 | A, E* | 25 108.112 | 0.0 | 0.009 |

Table 1c. Part of the measured frequencies $\nu_{obs}$ of synclinal normal propyl fluoride with CH$_3$ torsion in the first excited torsion state, see also Table 1a.

| $J'$ | $K'_-$ | $K'_+$ | | $J$ | $K_-$ | $K_+$ | $\nu_{obs}$ | $\Gamma$ | $\nu_{unsplit}$ | $\Delta\nu_{obs}$ | $\Delta\nu_{calc}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1c.1. A-transitions: | | | | | | | | | | | |
| 1c.1.1. Q-branch: | | | | | | | | | | | |
| 6 | 1 | 5 | - | 6 | 1 | 6 | 16 316.722 | A | 16 317.887 | | |
| | | | | | | | 16 318.461 | E | | -1.739 | -1.730 |
| 7 | 1 | 6 | - | 7 | 1 | 7 | 21 589.157 | A | 21 590.656 | | |
| | | | | | | | 21 591.427 | E | | -2.270 | -2.259 |
| 8 | 2 | 6 | - | 8 | 2 | 7 | 8 228.498 | A | 8 229.358 | | |
| | | | | | | | 8 229.801 | E | | -1.303 | -1.317 |
| 9 | 2 | 7 | - | 9 | 2 | 8 | 12 047.581 | A | 12 048.814 | | |
| | | | | | | | 12 049.431 | E | | -1.850 | -1.829 |
| 11 | 2 | 9 | - | 11 | 2 | 10 | 22 081.642 | A | 22 083.710 | | |
| | | | | | | | 22 084.744 | E | | -3.102 | -3.072 |
| 13 | 3 | 10 | - | 13 | 3 | 11 | 10 411.501 | A | 10 412.931 | | |
| | | | | | | | 10 413.665 | E | | -2.164 | -2.145 |
| 14 | 3 | 11 | - | 14 | 3 | 12 | 14 693.981 | A | 14 695.885 | | |
| | | | | | | | 14 696.849 | E | | -2.868 | -2.851 |
| 15 | 3 | 12 | - | 15 | 3 | 13 | 19 868.123 | A | 19 870.547 | | |
| | | | | | | | 19 871.759 | E | | -3.636 | -3.619 |
| 1c.1.2. R-branch: | | | | | | | | | | | |
| 2 | 1 | 1 | - | 1 | 1 | 0 | 19 486.826 | A | 19 487.014 | | |
| | | | | | | | 19 487.093 | E | | -0.267 | -0.271 |
| 2 | 0 | 2 | - | 1 | 0 | 1 | 18 656.015 | A | 18 656.157 | | |
| | | | | | | | 18 656.228 | E | | -0.213 | -0.194 |
| 2 | 1 | 2 | - | 1 | 1 | 1 | 17 918.671 | A | 17 918.761 | | |
| | | | | | | | 17 918.823 | E | | -0.152 | -0.131 |
| 1c.2. B-transitions: | | | | | | | | | | | |
| 1c.2.1. Q-branch: | | | | | | | | | | | |
| 1 | 1 | 0 | - | 1 | 0 | 1 | 10 270.181 | A | 10 270.460 | | |
| | | | | | | | 10 270.625 | E | | -0.444 | -0.405 |
| 2 | 1 | 1 | - | 2 | 0 | 2 | 11 100.992 | A | 11 101.314 | | |
| | | | | | | | 11 101.483 | E | | -0.491 | -0.482 |
| 3 | 1 | 2 | - | 3 | 0 | 3 | 12 432.498 | A | 12 432.927 | | |
| | | | | | | | 12 433.141 | E | | -0.643 | -0.628 |
| 4 | 1 | 3 | - | 4 | 0 | 4 | 14 358.362 | A | 14 358.938 | | |
| | | | | | | | 14 359.226 | E | | -0.864 | -0.857 |
| 5 | 1 | 4 | - | 5 | 0 | 5 | 16 981.344 | A | 16 982.134 | | |
| | | | | | | | 16 982.529 | E | | -1.185 | -1.177 |
| 6 | 1 | 5 | - | 6 | 0 | 6 | 20 385.391 | A | 20 386.461 | | |
| | | | | | | | 20 386.996 | E | | -1.605 | -1.591 |
| 7 | 1 | 6 | - | 7 | 0 | 7 | 24 603.514 | A | 24 604.929 | | |
| | | | | | | | 24 605.637 | E | | -2.123 | -2.091 |
| 5 | 2 | 3 | - | 5 | 1 | 4 | 25 541.660 | A | 25 542.112 | | |
| | | | | | | | 25 542.379 | E | | -0.719 | -0.721 |
| 6 | 2 | 4 | - | 6 | 1 | 5 | 24 878.324 | A | 24 878.793 | | |
| | | | | | | | 24 879.048 | E | | -0.724 | -0.727 |
| 7 | 2 | 5 | - | 7 | 1 | 6 | 24 690.851 | A | 24 691.403 | | |
| | | | | | | | 24 691.690 | E | | -0.839 | -0.835 |
| 8 | 2 | 6 | - | 8 | 1 | 7 | 25 136.301 | A | 25 137.001 | | |
| | | | | | | | 25 137.358 | E | | -1.057 | -1.051 |
| 1c.2.2. R-branch: | | | | | | | | | | | |
| 1 | 1 | 1 | - | 0 | 0 | 0 | 18 837.451 | A | 18 837.722 | | |
| | | | | | | | 18 837.834 | E | | -0.383 | -0.376 |
| 3 | 0 | 3 | - | 2 | 1 | 2 | 19 119.509 | A | 19 119.545 | | |
| | | | | | | | 19 119.571 | E | | -0.062 | -0.057 |
| 5 | 1 | 4 | - | 4 | 2 | 3 | 22 683.846 | A | 22 683.895 | | |
| | | | | | | | 22 684.026 | E | | -0.180 | -0.167 |
| 7 | 1 | 7 | - | 6 | 2 | 4 | 21 004.863 | A | 21 003.444 | | |
| | | | | | | | 21 002.714 | E | | 2.149 | 2.138 |
| 8 | 1 | 8 | - | 7 | 2 | 5 | 24 651.805 | A | 24 649.961 | | |
| | | | | | | | 24 649.036 | E | | 2.769 | 2.745 |
| 6 | 2 | 4 | - | 5 | 3 | 3 | 9 153.675 | A | 9 153.236 | | |
| | | | | | | | 9 155.963 | E | | -2.288 | -2.291 |
| 7 | 2 | 5 | - | 6 | 3 | 4 | 20 121.836 | A | 20 121.638 | | |
| | | | | | | | 20 122.561 | E | | -0.725 | -0.724 |
| 8 | 2 | 7 | - | 7 | 3 | 4 | 23 026.325 | A | 23 025.471 | | |
| | | | | | | | 23 024.637 | E | | 1.688 | 1.681 |
| 12 | 4 | 8 | - | 11 | 5 | 7 | 25 536.340 | A | 25 535.542 | | |
| | | | | | | | 25 548.974 | E | | -12.634 | -12.622 |
| 12 | 4 | 9 | - | 11 | 5 | 6 | 24 883.207 | A | 24 882.273 | | |
| | | | | | | | 24 867.976 | E | | 15.231 | 15.227 |
| 14 | 5 | 9 | - | 13 | 6 | 8 | 24 204.050 | A | | | |
| | | | | | | | 24 224.721 | E | 24 202.966 | -20.671 | -20.649 |
| | | | | | | | 24 090.724 | E* | | 113.326 | 113.336 |
| 14 | 5 | 10 | - | 13 | 6 | 7 | 24 072.658 | A | | | |
| | | | | | | | 24 048.658 | E | 24 071.523 | 24.000 | 23.971 |
| | | | | | | | 24 182.656 | E* | | -109.998 | -110.013 |

Table 2. Internal rotation parameters of normal propyl fluoride in the ground and first excited methyl torsion state. A fitting calculation of the constants of this table leads with the reduced set of lines of Table 1 a, b and c only approximately to the given values. To get the constants the complete set of measurements available in the Universitätsbibliothek Kiel under the number TNA 1 is used, see text. Column 1: Parameters of the antiperiplanar rotamer in the ground state fitted with splittings of Table 1 a. Column 2: Parameters of the antiperiplanar rotamer in the first excited methyl torsion state determined by Hirota [1]. Column 3: Parameters of the antiperiplanar rotamer in the first excited methyl torsion state fitted with splittings given in Table 1 b of [1]. Only transitions with $K_- = 2$ are used. $I_\alpha$ and $\sphericalangle(g,i)$ are taken from column 1 and kept fixed. Column 4: Parameters of the synclinal rotamer in the ground state fitted with splittings of Table 1 b. Column 5: Parameters of the synclinal rotamer in the first excited methyl torsion state determined by Hirota [1]. Column 6: Parameters of the synclinal rotamer in the first excited methyl torsion state fitted with splittings of Table 1 c. $w_1(s)$: Fourier coefficient, $s$: reduced barrier height; $I_\alpha$: moment of inertia of the methyl group. $\sphericalangle(g,i)$: angle between the inertia axes $g = a, b, c$ and the internal rotation axis $i$; $F$: reduced internal rotation constant $V_3$: barrier height to internal rotation; $\lambda_+ = \cos^2 \sphericalangle(a,i) + \cos^2 \sphericalangle(b,i) = 1 - \cos^2 \sphericalangle(c,i)$; $\lambda_- = \cos^2 \sphericalangle(a,i) - \cos^2 \sphericalangle(b,i)$. $\sigma$: standard deviation of the fit; $\overline{\Delta\nu}$: mean experimental methyl torsion splitting. Assumptions in square brackets. Standard errors in units of the last digit in brackets.

| Column | | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| $w_1(s)$ | = | $-0.7010(29) \cdot 10^{-5}$ | | $0.380(47) \cdot 10^{-3}$ | $-0.2810(26) \cdot 10^{-5}$ | | $0.12108(54) \cdot 10^{-3}$ |
| $I_\alpha$ [amu Å$^2$] | = | 3.157(6) | [3.194] | [3.157] | 3.168(35) | [3.194] | 3.170(24) |
| $\sphericalangle(a,i)$ [°] | = | 26.71(23) | [27.0] | [26.71] | 55.54(40) | [57.23] | 56.04(20) |
| $\sphericalangle(b,i)$ [°] | = | 63.29(23) | [63.0] | [63.29] | 38.74(38) | [37.66] | 38.47(19) |
| $\sphericalangle(c,i)$ [°] | = | [90.00] | [90.0] | [90.00] | 74.49(92) | [73.61] | 74.11(52) |
| $F$ [GHz] | = | 186.00(48) | [184.1] | [186.00] | 168.0(19) | [166.46] | 167.8(13) |
| $s$ | = | 67.926(33) | 68(1) | 68.1(13) | 76.505(95) | 80.2(5) | 79.840(43) |
| $V_3$ [kcal/mol] | = | 2.7104(84) | 2.69(4) | 2.719(53) | 2.758(35) | 2.865(17) | 2.874(24) |
| $V_3$ [kJ/mol] | = | 11.340(35) | 11.25(17) | 11.37(22) | 11.54(15) | 11.987(71) | 11.03(10) |
| $\sigma$ [kHz] | = | 7.2 | | 402.7 | 6.6 | | 26.0 |
| $\overline{\Delta\nu}$ [MHz] | = | 0.704 | | 9.604 | 8.482 | | 7.216 |

Correlation coefficient matrix:

| | | | |
|---|---|---|---|
| $w_1(s)$ | 1.00 | | |
| $I_\alpha$ | −0.87 | 1.00 | |
| $\sphericalangle(a,i)$ | −0.96 | 0.85 | 1.00 |

| | | | | |
|---|---|---|---|---|
| $w_1(s)$ | 1.00 | | | |
| $I_\alpha$ | −0.82 | 1.00 | | |
| $\lambda_+$ | −0.12 | −0.25 | 1.00 | |
| $\lambda_-$ | −0.89 | 0.81 | −0.24 | 1.00 |

| | | | | |
|---|---|---|---|---|
| $w_1(s)$ | 1.00 | | | |
| $I_\alpha$ | 0.98 | 1.00 | | |
| $\lambda_+$ | −0.91 | −0.95 | 1.00 | |
| $\lambda_-$ | 0.99 | 0.98 | −0.94 | 1.00 |

## IV. Spectrum of Synclinal Normal Propyl Fluoride in the First Excited State of the Methyl Group

A comparison between the values for the hindering potentials determined by us using ground state splittings, see Table 2 column 1 and 4, and determined by Hirota using splittings of the first excited state of the methyl group, see Table 2 column 2 and 5, shows that for the antiperiplanar form the agreement is good but for the synclinal form there is a difference of 107 cal/mol.

Because Hirota has made some structural assumptions and because it is possible that the structure in the ground state and first excited state differs, we reinvestigated the spectrum of the synclinal form in the first excited state of the methyl group torsion to determine not only the hindering potential but also the angles $\sphericalangle(g,i)$ between the principal inertia axes $g = a, b, c$ and the internal rotation axis $i$, and the moment of inertia of the methyl group $I_\alpha$.

A part of the measured frequencies and their assignment are listed in Table 1 c. As for the ground state lines, the complete list of measurements is available in the Universitätsbibliothek Kiel under the number TNA 1.

Using the same procedure as for the ground state spectra we get for the torsional and centrifugal distortion analysis the results given in Table 2 column 6 and Table 3 column 5, respectively.

Because the sixth order centrifugal distortion constants are not well determined and the correlation coefficients are high and a centrifugal distortion analysis up to fourth order is insufficient for high $J$ transitions, we performed an analysis using the ground state sixth order centrifugal distortion constants of Table 3 column 3 as fixed values, see Table 3 column 5.

As one result of the torsional analysis we can verify the value for the hindering potential determined by Hirota [1], although his structural assumptions for $\sphericalangle(g,i)$ and $I_\alpha$ are somewhat different from our fitted parameters.

Table 3. Rotational and centrifugal distortion constants of normal propyl fluoride in the ground and first excited methyl torsion state. A fitting calculation of the constants of this table leads with the reduced set of lines of Table 1 a, b and c only approximately to the given values. To get the constants the complete set of measurements available in the Universitätsbibliothek Kiel under the number TNA 1 is used, see text. Column 1: Constants of the antiperiplanar rotamer in the ground state fitted with the hypothetical unsplit frequencies of Table 1 a. Column 2: Constants of the antiperiplanar rotamer in the ground state determined by Hirota [1]. Column 3: Constants of the synclinal rotamer in the ground state fitted with the hypothetical unsplit frequencies of Table 1 b. Column 4: Constants of the synclinal rotamer in the ground state determined by Hirota [1]. Column 5: Constants of the synclinal rotamer in the first excited methyl torsion state fitted with the hypothetical unsplit frequencies of Table 1 c. The sixth order centrifugal constants are taken from column 3 and kept fixed. Column 6: Constants of the synclinal rotamer in the first excited methyl torsion state determined by Hirota [1]. Watsons A-reduction is used. Conversion factor: 505 376 amu Å$^2$; $\sigma$: standard deviation of the fit. Standard errors in units of the last digit in brackets. Assumptions in square brackets.

| Column | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $A$ [MHz] = | 26 986.6160(25) | 26 986.73 | 14 503.76303(76) | 14 503.69 | 14 554.1057(30) | 14 553.97 |
| $B$ [MHz] = | 3 748.36348(39) | 3 748.32 | 5 085.83422(28) | 5 085.71 | 5 067.8570(10) | 5 067.74 |
| $C$ [MHz] = | 3 509.92740(35) | 3 509.88 | 4 295.27013(23) | 4 295.28 | 4 283.6197(8) | 4 283.65 |
| $\Delta_J$ [kHz] = | 0.8743(25) | | 6.3184(17) | | 5.9569(62) | |
| $\Delta_{JK}$ [kHz] = | −2.735(49) | | −30.226(12) | | −28.869(42) | |
| $\Delta_k$ [kHz] = | 67.28(22) | | 78.4732(20) | | 75.952(48) | |
| $\delta_J$ [kHz] = | 0.074823(71) | | 1.86063(18) | | 1.75016(62) | |
| $\delta_K$ [kHz] = | 0.598(22) | | 13.3093(47) | | 12.867(32) | |
| $\Phi_J$ [Hz] = | | | 0.0116(23) | | [0.0116] | |
| $\Phi_{JK}$ [Hz] = | | | 0.212(32) | | [0.212] | |
| $\Phi_{KJ}$ [Hz] = | | | −1.225(41) | | [−1.225] | |
| $\Phi_K$ [Hz] = | | | 2.733(23) | | [2.733] | |
| $\varphi_J$ [Hz] = | | | 0.00349(29) | | [0.00349] | |
| $\varphi_{JK}$ [Hz] = | | | −0.040(25) | | [−0.040] | |
| $\varphi_K$ [Hz] = | | | 0.57(19) | | [0.57] | |
| $\varkappa$ = | −0.979687 | | −0.845116 | | −0.847283 | |
| $I_a$ [amu Å$^2$] = | 18.726913(2) | | 34.844474(18) | | 34.723947(7) | |
| $I_b$ [amu Å$^2$] = | 134.825772(14) | | 99.369342(55) | | 99.721835(20) | |
| $I_c$ [amu Å$^2$] = | 143.984745(14) | | 117.658723(63) | | 117.978727(22) | |
| $\sigma$ [kHz] = | 9.0 | | 5.0 | | 14.0 | |
| highest correlations: | | | | | | |
| | $\lvert(\Delta_J, \Delta_{JK})\rvert = 0.997$ | | $\lvert(A, B)\rvert = 0.985$ | | $\lvert(B, C)\rvert = 0.951$ | |
| | $\lvert(\Delta_K, \Delta_{JK})\rvert = 0.990$ | | $\lvert(\Delta_J, \Delta_{JK})\rvert = 0.985$ | | $\lvert(A, B)\rvert = 0.872$ | |
| | $\lvert(\Delta_J, \Delta_K)\rvert = 0.980$ | | $\lvert(A, C)\rvert = 0.974$ | | $\lvert(A, C)\rvert = 0.787$ | |

Because the angles $\sphericalangle(g, i)$ and the moment of inertia $I_\alpha$ determined for the synclinal rotamer in the ground state and first excited state, see Table 2 column 4 and 6, are similar, we believe that it is a good approximation to assume the same for the antiperiplanar form. So we use the splittings of Table IV in [1] and the values of $\sphericalangle(g, i)$ and $I_\alpha$ of Table 2 column 1 in this work to calculate a presumably better value for the hindering potential of the antiperiplanar rotamer in the first excited methyl torsion state. We get: $V_3 = 2719(53)$ cal/mol, see Table 2 column 3.

## V. Discussion

At first we give a summary of the hindering potentials $V_3$ determined in the ground state $v_\alpha = 0$ and first excited state of the methyl torsion $v_\alpha = 1$ for antiperiplanar and synclinal normal propyl fluoride:

$V_3$ (antiperiplanar, $v_\alpha = 0$): 2710(8) cal/mol,

$V_3$ (antiperiplanar, $v_\alpha = 1$): 2719(53) * cal/mol,

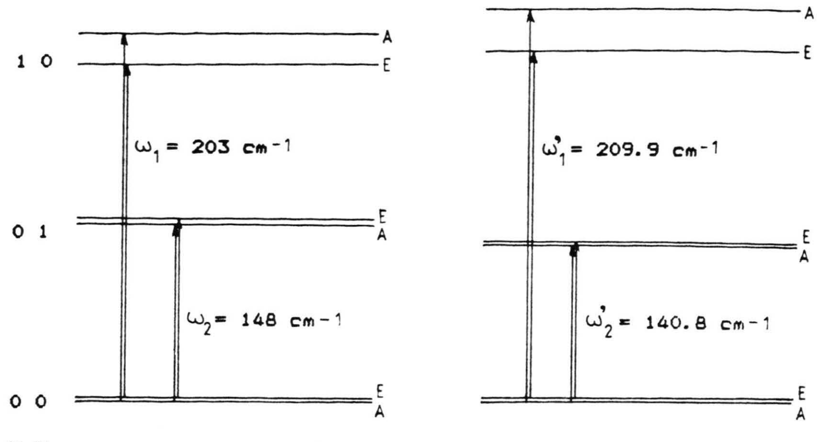
$V_3$ (synclinal, $v_\alpha = 0$): 2758(35) cal/mol,

$V_3$ (synclinal, $v_\alpha = 1$): 2874(24) cal/mol.

As mentioned above, the agreement is only good for the antiperiplanar form. For the synclinal form there is a difference we want to discuss now.

Because the parameters $\sphericalangle(g, i)$ and $I_\alpha$ show no essential changes for $v_\alpha = 0$ in comparison with $v_\alpha = 1$, see Table 2 column 4 and 6, we believe structural reasons can be excluded.

* Error reflects only uncertainty of $s$.



without interaction

with interaction

Fig. 2. Energy level pattern with and without interaction between the first excited $CH_3$ torsion state $v_\alpha v_\tau = 10$ and the first excited C–C torsion state 01. The A–E splitting is enlarged.

The discrepancy may be explained in the following way:

Using the ground state values of $F$ and $s$, see Table 2 column 4, a calculation of the torsion energy levels $E_{v_\alpha \sigma}$ yields

$$E_{0\sigma} = 107.0 \text{ cm}^{-1} \quad \text{and} \quad E_{1\sigma} = 313.8 \text{ cm}^{-1} .$$

By comparison a calculation of $E_{v_\alpha \sigma}$, using the values determined for the first excited methyl torsion state, see Table 2 column 6, yields

$$E'_{1\sigma} = 320.9 \text{ cm}^{-1} .$$

The difference between $E_{1\sigma}$ and $E'_{1\sigma}$ of 7.1 $\text{cm}^{-1}$ may be interpreted by interaction of the first excited methyl torsion level with some other low lying vibrations, as the central C–C torsion changing the angle $\tau$ appears to be.

In the vibrational spectrum the $v_\alpha = 1-0$ transition was found to be at $\omega'_1 = 209.9 \text{ cm}^{-1}$ and the $v_\tau = 1-0$ transition at $\omega'_2 = 140.76 \text{ cm}^{-1}$ [13].

In the following we assume that by interaction between the $v_\alpha v_\tau = 10$ and 01 level the 10 level is shifted by 7.1 $\text{cm}^{-1}$ to higher and the 01 level to lower energies, respectively, see Figure 2.

Hirota [14], see also Butcher [15], Kuhler [16, 17] and Kasten [18], have discussed the Hamiltonian for a molecular model containing, as degrees of vibrational freedom, a methyl torsion ($\alpha$) and a heavy top torsion, as the C–C torsion ($\tau$) in this molecule.

Following Hirota the kinetic energy is given by

$$T = \tfrac{1}{2} \sum_g I_g \cdot \omega_g^2 + \tfrac{1}{2} I_\alpha \cdot \dot{\alpha}^2 + I_\alpha \cdot \dot{\alpha} \sum_g \lambda_g \cdot \omega_g + S \cdot \dot{\alpha} \cdot \dot{\tau} + \tfrac{1}{2} G^{-1} \dot{\tau}^2 , \qquad (2)$$

where $I_g$ ($g = a, b, c$) are the components of the inertia tensor, $\omega_g$ are the components of angular velocity of overall rotation, $I_\alpha$ is the moment of inertia of the methyl top, $\dot{\alpha}$ the angular velocity of the methyl torsion, $\lambda_g = \cos(g, i)$, $i$ is the internal rotation axis, $\dot{\tau}$ the angular velocity of the C–C torsion, and S and $G^{-1}$ are given by

$$S = \sum_j m_j (\boldsymbol{\sigma}_j \times \boldsymbol{r}'_j) \cdot \boldsymbol{e}_\alpha \qquad (3)$$

and

$$G^{-1} = \sum_k m_k \boldsymbol{r}'^2_k + \sum_j m_j \boldsymbol{r}'^2_j , \qquad (4)$$

where "$k$" indicates the frame and "$j$" the methyl top atoms, $m_l$, $l = j, k$ are the atomic masses, $\boldsymbol{\sigma}_j$ is the vector between the jth methyl top atom and the center of gravity of the three methyl top atoms, $\boldsymbol{e}_\alpha$ is the unit vector of the internal rotation axis, and $\boldsymbol{r}'_l$ is given by

$$\boldsymbol{r}'_l = (\boldsymbol{r}_l - \boldsymbol{r}^0_l)/\tau , \quad l = j, k , \qquad (5)$$

where $\boldsymbol{r}_l$ is the instantaneous and $\boldsymbol{r}^0_l$ the equilibrium vector.

The $\boldsymbol{r}'_l$ of (5) are determined by the Eckart condition:

$$\sum_k m_k (\boldsymbol{r}^0_k \times \boldsymbol{r}'_k) + \sum_j m_j (\boldsymbol{r}^0_j \times \boldsymbol{r}'_j) = 0 . \qquad (6)$$

With use of (2) the following Hamiltonian results:

$$\begin{aligned} H = {} & H_R + F_0 p_\alpha^2 + (1/2) M p_\tau^2 \\ & - 2 L p_\alpha p_\tau - 2 (F_0 p_\alpha - L p_\tau) \mathscr{P} \\ & + 1/2 \, V_3 (1 - \cos 3\alpha) + V_S \tau \sin 3\alpha + V(\tau) \end{aligned} \qquad (7)$$

with

$$F_0 = \frac{1}{2 r_0 I_\alpha}; \quad r_0 = r - \frac{S^2}{I_\alpha G^{-1}}; \quad r = 1 - \sum_g \lambda_g^2 \frac{I_\alpha}{I_g},$$

$$M = \frac{r}{r_0 G^{-1}}; \quad L = \frac{S F_0}{G^{-1}}; \quad \mathscr{P} = \sum_g \lambda_g \frac{I_\alpha}{I_g} P_g,$$

where $H_R$ is the rigid rotor Hamiltonian, $p_\alpha$ and $p_\tau$ are the angular momentum operators of the $CH_3$ and C−C torsion, respectively, $P_g$ ($g = a, b, c$) are the components of the angular momentum operator of the overall rotation, $V_3$ is the threefold expansion coefficient of the hindering barrier of the methyl top, $V(\tau)$ is the potential of the C−C torsion, and $V_S$ is the interaction potential between the $CH_3$ and C−C torsion. The determination of $V_S$ is the aim of this interpretation.

Table 4. Partial $r_0$-structure of synclinal normal propyl fluoride in the first excited methyl torsion state calculated with the rotational constants of Table 3 column 5. The angle ∢ CCH($CH_3$) is determined from $I_\alpha$ of Table 2 column 6 and not fitted. Assumptions in square brackets are taken from Table 3 of [1]. Additional the angles ∢ $(g, i)$ between the inertia axes $g$ and the C−$CH_3$ bond axis, assumed to be the internal rotation axis $i$, are derived from the fitted structure for comparison with the corresponding values of Table 2 column 6.

| | |
|---|---|
| [$r$(C−C): 1.534 Å] | ∢ CCH ($CH_3$): 110.65° |
| [$r$(C−F): 1.379 Å] | [∢ CCH ($CH_2$): 109.64°] |
| [$r$(C−H): 1.094 Å] | [∢ CCF: 110.0°] |
| | ∢ CCC: 111.4° |
| derived parameters: | dihedral angle: 62.6° |
| ∢ $(a, i)$: 56.53° | |
| ∢ $(b, i)$: 38.16° | |
| ∢ $(c, i)$: 73.84° | |

Table 5. Some elements of the extended tensor of inertia and its inverse tensor of synclinal normal propyl fluoride in the first excited methyl torsion state, using the assumption, that the max. change of the C−C torsion angle $\tau$ is about 10°. Only the elements important to calculate the perturbation correction, see text, are given.

| | |
|---|---|
| $I_\alpha$ = 3.169 amu Å$^2$ | $F_0$ = 175.87 GHz |
| $S$ = 1.146 amu Å$^2$ | $L$ = 21.55 GHz |
| $G^{-1}$ = 9.349 amu Å$^2$ | $M$ = 113.32 GHz · rad$^2$ |

At first it is necessary to assume a presumable structure to calculate the parameters $F_0$, $M$ and $L$.

Because there is no $r_S$-structure known, we use Hirota's structure assumption [1] with three exceptions.

For the angle ∢ CCH($CH_3$) we believe 110.65° is a better value than 110.14° given in [1], because our torsional analyses yields for the inertia moment of the methyl group a mean value of about 0.03 amu Å$^2$ lower than assumed in [1]. Additionally, we use the rotational constants of the first excited torsional state of the synclinal form, see Table 3 column 5, to fit the angle ∢ CCC and the dihedral angle (program MWSTR). The results are given in Table 4.

To calculate the parameters $F_0$, $M$ and $L$ (program KU1) we assume additionally that in the 01 state the maximum change of the C−C torsion angle $\tau$ is about 10°, because the wavefunction, using the approximation of a harmonic oscillator [19], has a maximum at $\tau = 9.2°$. The results are given in Table 5.

Next the $(V_S \tau \sin 3\alpha - 2 L p_\alpha p_\tau)$-term may be treated as a perturbation on the hindered rotor energy levels of the methyl top and the C−C torsional levels, which are approximated as those of a harmonic oscillator. The basis functions used are the Mathieu functions for the $CH_3$ torsion and the Hermite functions for the C−C torsion. The second order perturbation correction to the $v_\alpha v_\tau$ level is

$$E'_{v_\alpha \sigma v_\tau} = \sum_{v'_\alpha v'_\tau} \frac{|V_S \langle v_\alpha \sigma | \sin 3\alpha | v'_\alpha \sigma \rangle \langle v_\tau | \tau | v'_\tau \rangle - 2 L \langle v_\alpha \sigma | p_\alpha | v'_\alpha \sigma \rangle \langle v_\tau | p_\tau | v'_\tau \rangle|^2}{E_{v_\alpha \sigma v_\tau} - E_{v'_\alpha \sigma v'_\tau}} \tag{8}$$

because there are no matrix elements connecting states of different $\sigma$ (= A or E).

Using the approximation that the 10 level is only perturbed by the 01 level, the difference between the perturbation energies of the A and E species $\Delta E'_1 = E'_{1A0} - E'_{1E0}$ is

$$\Delta E'_1 = \frac{|V_S \langle 1A | \sin 3\alpha | 0A \rangle \langle 0 | \tau | 1 \rangle - 2L \langle 1A | p_\alpha | 0A \rangle \langle 0 | p_\tau | 1 \rangle|^2}{E_{1A0} - E_{0A1}} - \frac{|V_S \langle 1E | \sin 3\alpha | 0E \rangle \langle 0 | \tau | 1 \rangle - 2L \langle 1E | p_\alpha | 0E \rangle \langle 0 | p_\tau | 1 \rangle|^2}{E_{1E0} - E_{0E1}}. \tag{9}$$

Because the magnitude of the matrix elements in the nominators of (9) is nearly independent of the symmetry species:

$$\langle 1\mathrm{A} | \sin 3\alpha | 0\mathrm{A} \rangle \approx \mathrm{i} \cdot \langle 1\mathrm{E} | \sin 3\alpha | 0\mathrm{E} \rangle \quad (10)$$

and

$$\langle 1\mathrm{A} | p_\alpha | 0\mathrm{A} \rangle \approx \mathrm{i} \cdot \langle 1\mathrm{E} | p_\alpha | 0\mathrm{E} \rangle , \quad (11)$$

one gets the difference between the reduced perturbation energies of the A and E species $\Delta b_1'$:

$$\Delta b_1' = (\Delta b_0 - \Delta b_1) \frac{| V_\mathrm{S} \langle 1\mathrm{A} | \sin 3\alpha | 0\mathrm{A} \rangle \langle 0 | \tau | 1 \rangle - 2L \langle 1\mathrm{A} | p_\alpha | 0\mathrm{A} \rangle \langle 0 | p_\tau | 1 \rangle |^2}{(E_{1\mathrm{A}0} - E_{0\mathrm{A}1}) \cdot (E_{1\mathrm{E}0} - E_{0\mathrm{E}1})} , \quad (12)$$

where

$$\Delta b_{v_\alpha} = \frac{4}{9F} (E_{v_\alpha \mathrm{A} v_\tau} - E_{v_\alpha \mathrm{E} v_\tau}) ; \quad v_\alpha = 0, 1 .$$

To calculate the interaction potential $V_\mathrm{S}$ we use

$$E_{1\mathrm{A}0} - E_{0\mathrm{A}1} \approx E_{1\mathrm{E}0} - E_{0\mathrm{E}1} \approx \omega_1 - \omega_2$$
$$= 55\ \mathrm{cm}^{-1} = 1649\ \mathrm{GHz} , \quad \text{see Fig. 2} ,$$

$\langle 1\mathrm{A} | \sin 3\alpha | 0\mathrm{A} \rangle = 0.4345$ [20],

$\langle 1\mathrm{A} | p_\alpha | 0\mathrm{A} \rangle = i \cdot 3.041$ [20],

$\langle 0 | \tau | 1 \rangle = (M/2\omega_2)^{1/2} = 0.1130$ rad [21],

$\langle 0 | p_\tau | 1 \rangle = -i (\omega_2/2M)^{1/2} = -i \cdot 4.425\ \mathrm{rad}^{-1}$ [21],

$\Delta b_0 = -4.215\ 10^{-6}$ [20],

$\Delta b_1 = 2.503\ 10^{-4}$ [20],

$\Delta b_1' = -0.687\ 10^{-4}$ [20],

and get

$$V_{\mathrm{S}_1} = 2.93\ 10^4\ \mathrm{GHz/rad} = 2.79\ \mathrm{kcal/mol \cdot rad} = 11.67\ \mathrm{kJ/mol \cdot rad} ,$$

$$V_{\mathrm{S}_2} = -5.64\ 10^3\ \mathrm{GHz/rad} = -0.54\ \mathrm{kcal/mol \cdot rad} = -2.26\ \mathrm{kJ/mol \cdot rad} .$$

Unfortunately there are two results without a possibility to exclude one.

Next we prove that the ground state is really unperturbed by the 01 level. Using (8) and the matrix elements given in [20] we get the result that the perturbation of the ground state $v_\alpha v_\tau = 00$ in comparison with the 10 state is lower by a factor $10^{-10}$.

At last we check if there are some other vibrational levels to interact with the 10 level. In the vibrational spectrum the 02 level was found to be at 276.8 cm$^{-1}$ [13], near enough to interact, but nevertheless it can be excluded because the matrix elements $\langle 0 | \tau | 2 \rangle$ and $\langle 0 | p_\tau | 2 \rangle$ are zero.

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