Centrifugal Distortion and Internal Rotation Analysis in the Ground State of Trans N-Propanol

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The ground state rotational spectrum of the trans n-propanol ($CH_3CH_2CH_2OH$) has been reinvestigated expanding the frequency region, with respect to a previous study, from 8 to 40 GHz. A centrifugal distortion analysis has been carried out by measuring new transitions, including μ_a-transitions not observed before. The potential barrier V_3 to the methyl top internal rotation has been determined from fourteen transitions which were found split into doublets. V_3 is 2730 ± 60 cal/mole, $\sphericalangle (i, a) = 29° \pm 1°$, assuming $I_\alpha = 3.193$ uÅ^2.

I. Introduction

A previous microwave study of n-propanol confirmed the existence of two rotational isomers separated by 0.29 ± 0.15 kcal/mole, the gauche form being more stable than the trans form [1–5].

For both these conformers a set of ground state rotational constants were evaluated. The inertial quantity $I_a + I_b - I_c$ for the trans conformer resulted in agreement with the assumed structure having a plane of symmetry. From the splittings of lines in the first excited state of the methyl top internal rotation of both the gauche and the trans form, the V_3 barrier was calculated to be:

$$V_3(\text{gauche}) = 2876 \pm 50 \text{ cal/mole} \quad \text{and}$$
$$V_3(\text{trans}) = 3084 \pm 50 \text{ cal/mole}.$$

The determination of the electric dipole moment of the trans conformer indicated the existence of a small component $\mu_a = 0.21 \pm 0.07$ D, in addition to $\mu_b = 1.54 \pm 0.02$ D.

The low value of the μ_a dipole moment component prevented the detection of the corresponding μ_a-spectrum. Moreover, the high metyl top internal rotation barrier did not allow, for both the conformers, any observation of split lines in the ground state even if this possibility, for the trans form, was not theoretically ruled out [6].

In view of the microwave-microwave double resonance (MWMWDR) facilities in this laboratory and of the high resolution achievable by the recently in use Fourier transform microwave spectroscopy (FTMWS), a ground state reinvestigation of the trans form was undertaken. The following analyses were considered within our instrumental capabilities. First, a centrifugal distortion analysis following measurements of new lines, including μ_a-lines. Second, an internal rotation analysis from A–E splittings which could possibly be resolved. The importance of determining the internal rotation barriers in the ground state has been discussed elsewhere [7]. It is related to the absence, in the Hamiltonian, of terms of the type $H_{\text{IR, V}}$ from the coupling of the internal rotation (IR) with some other close by vibration (V).

II. Experimental

Different spectrometers and techniques were employed to record and interpret the spectrum of trans n-propanol.

A conventional microwave spectrometer with a 33 kHz Stark modulation and BWO's as stabilized sources from 8 to 40 GHz [8, 9] was extensively used throughout the investigation.

Microwave-radiofrequency double resonance, using a set up as in [10], failed to produce signals due to insufficient saturation of the K-doublet μ_a-pump transitions. On the other hand microwave-microwave double resonance was very successful. The instrumental configuration was the same as that described in [11], with an extended pump frequency range up to 26.4 GHz by a Hughes 1077H11000 TWT [12]. Experiments were performed either to check the assignment and/or to

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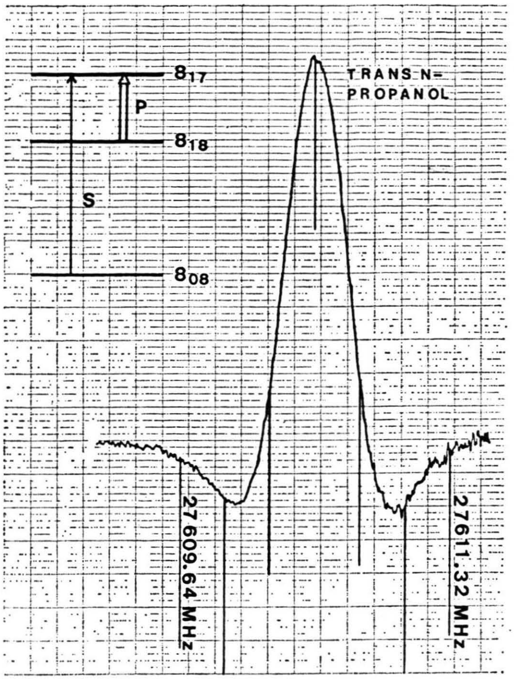

Fig. 1. Double resonance experiment with trans n-propanol. The transition pumped is the ground state $8_{1,7}-8_{1,8}$ at 9091.6 MHz and the monitored signal is the $8_{1,7}-8_{0,8}$ transition at 27610.48 MHz. The pumping power at the input of the cell was 8 W.

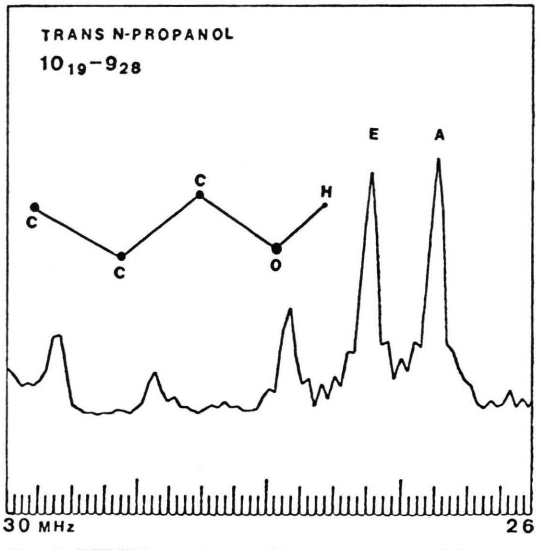

Fig. 2. FTMW spectrum of trans n-propanol in a range of 4 MHz out of a 50 MHz scan. Measuring time 210 sec for 50 MHz, MW signal at 12124.50 MHz, $p = 1$ mTorr, $T = -50$ °C, 1024 data points incremented by 1024 zeros. The doublet shown corresponds to the ground state $10_{1,9}-9_{2,8}$ transition, $\nu_A = 12125.34$ MHz, and $(\nu_E - \nu_A) = 0.49$ MHz. The C—C—C—O—H planar skeleton of the molecule is drawn.

find new transitions. In Fig. 1 an example is shown, where the weak μ_a-transition (pump) was stepwise located by on-off resonance effect on the swept μ_b-transition (signal). The same μ_a-transition could not be detected by any other technique, here described.

A Fourier transform microwave spectrometer, as described in [13], was used in the frequency region between 8 and 18 GHz, and Fig. 2 shows a well resolved doublet with components having a FWHM of 140 kHz.

The sample of n-propanol was supplied by Merck. The cell was cooled to −40 or −50°C and the pressure of the gas was 20 or 1 mTorr, the lower limits referring to FTMWS.

Frequency measurements on the μ_b-lines are believed to be accurate to within 50 kHz, while for the weak μ_a-lines the error is probably a few times these values.

III. Centrifugal Distortion Analysis

The transitions reported in Ref. [2] were remeasured with one order of magnitude higher accuracy and new μ_b-transitions were measured. With respect to the previous measurements the transition $11_{3,9}-12_{2,10}$ was assigned to the line at 23850.21 MHz, and the transition $5_{2,3}-6_{1,6}$ was not confirmed and, in consideration of the intensity, not reassigned. Some lines were found split into doublets due to the internal rotation of the methyl top.

A few μ_a-transitions were observed by Stark spectroscopy in the frequency region between 26.4 and 40 GHz. In the 8 to 26.4 GHz region the μ_a-transitions were measured by stepwise locating them as pumps in MWMWDR experiments or by FTMWS. The observation of these μ_a-lines provided evidence for the small non vanishing μ_a dipole moment component and allowed the application of frequency sum rules involving μ_b-transitions.

Table 1 lists all the transitions which were used in the centrifugal distortion analysis. In cases of split lines (< 1 MHz) the average frequency of the two components was taken as pseudo rigid rotor frequency. It was calculated by internal rotation analysis that this approximation introduces an error which is within the experimental accuracy of the measurements. The double resonance connections are given in Table 2.

The measured transitions were least squares fitted to the following Watson Hamiltonian [14, 15]:

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

and the determined parameters, with their standard errors, are shown in Table 3. The standard deviation of the fit resulted to be 195 kHz. The largest, still acceptable, correlation coefficient is 0.906, connecting Δ_J and Δ_{JK}. A tentative fit of the measured transitions to a Hamiltonian including terms up to the sixth order made the standard deviation drop to 89 kHz, but introduced a somewhat larger correlation among the parameters. It indicates, however, that terms beyond the fourth order give a contribution to the centrifugal distortion of this conformer, as to be expected by the rather large value of the A rotational constant.

Table 1. Measured transitions for trans n-propanol, ground state. Frequencies are in MHz.

Transition	ν(exp.)	ν(calc.-exp.)[a]
$1_{1,1} - 0_{0,0}$	29950.80	0.19
$1_{1,0} - 1_{0,1}$	22851.91	0.12
$2_{1,2} - 1_{0,1}$	37049.77	0.10
$2_{1,1} - 2_{0,2}$	23106.75	0.07
$3_{1,3} - 2_{1,2}$	21674.32	0.13
$3_{1,2} - 3_{0,3}$	23492.92	0.04
$3_{2,2} - 4_{1,3}$	37510.46	0.24
$4_{3,1} - 3_{3,0}$	29410.17	− 0.24
$4_{3,2} - 3_{3,1}$	29410.17	− 0.30
$4_{2,3} - 3_{2,2}$	29404.65	− 0.26
$4_{1,4} - 3_{1,3}$	28896.65	0.00
$4_{0,4} - 3_{0,3}$	29385.11	0.16
$4_{1,3} - 4_{0,4}$	24015.15	0.00
$4_{2,3} - 5_{1,4}$	29535.12	0.03
$5_{1,4} - 4_{1,3}$	37379.94	0.01
$5_{1,5} - 4_{1,4}$	36116.65	− 0.02
$5_{0,5} - 4_{1,4}$	15227.39	0.10
$5_{0,5} - 4_{0,4}$	36715.44	0.05
$5_{1,4} - 5_{0,5}$	24679.66	− 0.06
$5_{2,4} - 6_{1,5}$	21438.25	− 0.05
$6_{0,6} - 5_{1,5}$	23145.85	0.07
$6_{1,5} - 6_{0,6}$	25494.11	− 0.08
$6_{2,5} - 7_{1,6}$	13221.71	− 0.21
$7_{0,7} - 6_{1,6}$	31153.97	− 0.01
$7_{1,6} - 7_{0,7}$	26467.72	− 0.21
$8_{0,8} - 7_{1,7}$	39240.56	− 0.37
$8_{1,7} - 8_{0,8}$	27610.48	− 0.14
$9_{1,8} - 9_{0,9}$	28933.93	− 0.07
$10_{1,9} - 9_{2,8}$	12125.59	0.28
$10_{1,9} - 10_{0,10}$	30450.24	− 0.09
$10_{3,8} - 11_{2,9}$	31632.34	0.10
$11_{1,10} - 10_{2,9}$	20798.28	0.22
$11_{1,10} - 11_{0,11}$	32171.72	− 0.02
$11_{3,9} - 12_{2,10}$	23850.21	0.01
$12_{1,11} - 11_{2,10}$	29577.25	0.04
$12_{1,11} - 12_{0,12}$	34110.84	0.10
$12_{3,10} - 13_{2,11}$	15959.59	− 0.04
$13_{1,12} - 12_{2,11}$	38458.31	− 0.22
$13_{1,12} - 13_{0,13}$	36279.34	0.40
$14_{1,13} - 14_{0,14}$	38688.56	0.25
$15_{1,14} - 15_{1,15}$	30114.10	− 0.26
$16_{1,15} - 16_{1,16}$	34062.00	− 0.43
$16_{2,14} - 15_{3,13}$	8490.92	0.02
$17_{1,16} - 17_{1,17}$	38228.53	0.32
$17_{2,15} - 16_{3,14}$	16936.57	− 0.01

[a] The calculated frequency is according to Hamiltonian (1) up to the fourth order terms.

Table 2. Observed double resonance connections in trans n-propanol, ground state. Frequencies are in MHz.

Pump transition	Pump frequency	Signal frequency	Signal transition
$8_{1,7} - 8_{1,8}$	9091.6[a]	27610.48	$8_{1,7} - 8_{0,8}$
$9_{1,8} - 9_{1,9}$	11360.7[a]	28933.93	$9_{1,8} - 9_{0,9}$
$10_{1,9} - 9_{2,8}$	12125.59	30450.24	$10_{1,9} - 10_{0,10}$
$4_{1,3} - 4_{0,4}$	24015.15	37379.94	$5_{1,4} - 4_{1,3}$
$5_{1,4} - 5_{0,5}$	24679.66	37510.46[b]	$3_{2,2} - 4_{1,3}$
$3_{1,3} - 2_{1,2}$	21674.32	28896.65	$4_{1,4} - 3_{1,3}$
		29535.12[b]	$4_{2,3} - 5_{1,4}$

[a] Not used in the centrifugal distortion analysis, but calculated within three standard deviations.
[b] Doublet average frequency, see Table 4.

Table 3. Results of the centrifugal distortion analysis for trans n-propanol, ground state.

A/MHz = 26401.671 (50)[a]
B/MHz = 3802.154 (11)
C/MHz = 3549.543 (20)
$(I_a + I_b - I_c)$/uÅ^2 = 9.682
Δ_J/kHz = 1.672 (73)
Δ_{JK}/kHz = 9.57 (99)
Δ_K/kHz = 141.5 (47)
δ_J/kHz = 0.0943 (45)
δ_K/kHz = − 29.6 (69)

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

IV. Internal Rotation Analysis

Since a number of μ_b-transitions were observed as doublets, see Table 4, an internal rotation analysis was possible in the ground state of the trans conformation.

In the PAM method the following effective rotational Hamiltonian was used [16]:

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

where H_{R} is the usual rotational Hamiltonian, F is

Table 4. Observed split transitions of trans n-propanol, ground state. Frequencies are in MHz.

Transition	Observed frequency	Γ	Obs. $(\nu_E - \nu_A)$	Calc. $(\nu_E - \nu_A)$[a]
$3_{2,2} - 4_{1,3}$	37510.12	E		
	37510.80	A	− 0.68	− 0.65
$4_{2,3} - 5_{1,4}$	29534.83	E		
	29535.40	A	− 0.57	− 0.54
$5_{0,5} - 4_{1,4}$	15227.45	E		
	15227.33	A	0.12	0.15
$5_{2,4} - 6_{1,5}$	21438.02	E		
	21438.48	A	− 0.46	− 0.51
$6_{2,5} - 7_{1,6}$	13221.51	E		
	13221.97	A	− 0.46	− 0.50
$10_{1,9} - 9_{2,8}$	12125.83	E		
	12125.34	A	0.49	0.48
$10_{3,8} - 11_{2,9}$	31631.84	E		
	31632.83	A	− 0.99	− 1.02
$11_{1,10} - 10_{2,9}$	20798.53	E		
	20798.03	A	0.50	0.45
$11_{3,9} - 12_{2,10}$	23849.76	E		
	23850.65	A	− 0.89	− 0.96
$12_{1,11} - 11_{2,10}$	29577.49	E		
	29577.00	A	0.49	0.47
$12_{3,10} - 13_{2,11}$	15959.16	E		
	15960.02	A	− 0.86	− 0.90
$13_{1,12} - 12_{2,11}$	38458.54	E		
	38458.07	A	0.47	0.42
$16_{2,14} - 15_{3,13}$	8491.32	E		
	8490.52	A	0.80	0.78
$17_{2,15} - 16_{3,14}$	16936.97	E		
	16936.17	A	0.80	0.87

[a] Calculated using Hamiltonian (2) up to the second order terms.

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 axes. Since this conformer has a plane of symmetry, then $\lambda_c = 0$ and λ_a is correlated to λ_b. Only terms up to the second order were retained, since the higher order terms contribution was found negligible. in the present case. The truncation was further justified by an IAM method calculation [17] of the internal rotation splittings.

Table 5. Results of internal rotation analysis for trans n-propanol, ground state.

$I_\alpha/\mathrm{u\AA^2} = 3.193$[a]
$\sphericalangle(i,a)/\mathrm{degr.} = 29 \pm 1$
$\lambda_a = 0.8746 \pm 0.0086$
$s = 69.6 \pm 1.5$[b]
$V_3/\mathrm{cal/mole} = 2730 \pm 60$[b]
$V_3/\mathrm{kJ/mole} = 11.43 \pm 0.25$[b]
$F/\mathrm{GHz} = 182.6$

[a] Structure assumed value from Ref. [3].

[b] The quoted errors allow for 0.1 uÅ² uncertainty on I_α, see text.

The observed A–E splittings made it possible to fit both the reduced barrier s and the direction cosine λ_a, fixing I_α at the structure assumed value [3]. The standard deviation of the fit was 42 kHz and the correlation coefficient between the parameters 0.816. Results are shown in Table 5. The calculated angle $\sphericalangle\ (i, a)$ is only slightly different from the structure assumed value 25.5°, which was used in the previous barrier calculation [6]. The barrier determined in this work is 350 cal/mole lower than that from Ref. [6], and the small change in the angle allows for only 10% of the difference. The discussion of this point is deferred to part V. It was shown that the main source of error in the barrier determination comes from the uncertainty on I_α [18]. For trans n-propanol to a variation of 0.1 uÅ² in I_α a 2% variation in the barrier value was calculated.

V. Conclusions

The present work has succeeded in performing those analyses which have been proposed in the Introduction as possible ones.

The rotational constants obtained are still within the uncertainty range of those previously reported [2], but they are one order of magnitude more accurate.

The set of centrifugal distortion constants might undergo some change if higher J and higher K transitions were measured, but the weakness and crowdness of the spectrum make this extension look very time consuming.

The discrepancy between the value of the internal rotation barrier obtained from the ground state and that obtained from the first excited state of the methyl top internal rotation [6] may be explained in the following way. It is likely that this latter state, at 230 cm⁻¹ [3], interacts with some other low lying vibration, as the central C–C torsion appear to be. In trans propyl fluoride the second excited state of the central C–C torsion was found to be at 211 cm⁻¹ [19]. The arising coupling term $H_{\mathrm{IR,V}}$, in the Hamiltonian, has to be properly accounted for in order to make the barrier free from state dependency. In this respect the barrier determined in Ref. [6] has to be considered as an effective excited state barrier.

The above conclusion is extendible to several other cases and it provides the motivation why some effort is spent, in this and other laboratories, to determine high internal rotation barriers from the ground state spectra [20, 21].

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[1] L. M. Imanov, A. A. Abdurakhmanov, and R. A. Ragimova, Opt. Spectrosc. **22**, 456 (1967).
[2] A. A. Abdurakhmanov, R. A. Ragimova, and L. M. Imanov, Izv. Akad. Nauk. Azerb. SSR **3**, 15 (1968).
[3] L. M. Imanov, A. A. Abdurakhmanov, and R. A. Ragimova, Opt. Spectrosc. **25**, 528 (1968).
[4] A. A. Abdurakhmanov, R. A. Ragimova, and L. M. Imanov, Opt. Spectrosc. **26**, 75 (1969).
[5] A. A. Abdurakhmanov, R. A. Ragimova, and L. M. Imanov, Phys. Lett. **32 A**, 123 (1970).
[6] A. A. Abdurakhmanov, R. A. Ragimova, and L. M. Imanov, Izv. Akad. Nauk. Azerb. SSR, **2**, 3 (1972).
[7] H. Dreizler, in "Molecular Spectroscopy: Modern Research", Vol. I, pag. 59, K. N. Rao and C. W. Mathews eds., Academic Press, New York 1972.
[8] H. D. Rudolph, Z. Angew. Physik **13**, 401 (1961).
[9] U. Andresen and H. Dreizler, Z. Angew. Physik **30**, 204 (1970).
[10] F. Scappini and A. Guarnieri, Z. Naturforsch. **27a**, 1011 (1972).
[11] G. K. Panday and H. Dreizler, Z. Naturforsch. **31a**, 357 (1976).
[12] Experimental details will be published.
[13] G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, Z. Naturforsch. **35a**, 392 (1980).
[14] J. K. Watson, J. Chem. Phys. **46**, 1935 (1967).
[15] Computing program by V. Typke, Z. Naturforsch. **26a**, 1775 (1971).
[16] C. C. Lin and J. D. Swalen, Rev. Mod. Phys. **31**, 841 (1959).
[17] R. C. Woods, J. Mol. Spectrosc. **21**, 4 (1966).
[18] H. Dreizler in "Critical Evaluation of Chemical and Physical Structural Information", pag. 352, National Academy of Sciences, Washington, D.C., 1974.
[19] E. Hirota, J. Chem. Phys. **37**, 283 (1962).
[20] D. Boucher, A. Dubrulle, J. Demaison, and H. Dreizler, Z. Naturforsch. **35a**, 1136 (1980).
[21] F. Scappini and H. Dreizler, to be published.