

The Submillimeter-Wave Rotational Spectrum of Isopropyl Alcohol (*trans*-form)

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Abstract

The submillimeter-wave spectrum of the *trans* isopropyl alcohol was studied in the frequency range from 240 to 480 GHz. More than 170 lines were assigned to ground state transition. The identification of the high J transitions was checked by centrifugal distortion analysis. The frequencies of all transitions were least squares fitted to the Watson's Hamiltonian, including two P^8 terms. The ground-state rotational constants are (in MHz) $A = 8489.0150$, $B = 8041.9182$, $C = 4765.2326$, which yield an asymmetry parameter $\kappa = 0.75986663$.

1. Introduction

In recent years, significant attention has been focused on the study of molecules containing the hydroxyl group. One of the main interest in these investigations was observation of rotational isomers. Preliminary study of microwave spectra of isopropyl alcohol $(CH_3)_2CHOH$ has shown the existence two stable conformers, the *trans*- and *gauche* variations of this molecule [1]. These conformers were investigated in detail Hirota [2]. Later, the spectroscopic constants of *gauche* isopropyl alcohol molecule have been considerably corrected by O. Ulenikov et.al. [3].

The microwave rotational spectrum of *trans* isopropyl alcohol $(CH_3)_2CHOH$ has been studied by a number of investigators [2, 4-6]. However, obtained spectroscopic constants uncertainties were too large. The frequencies of higher J transitions calculated by using these constants gives a large discrepancy with measured frequencies.

This paper reports further studies of the ground-state rotational spectrum of *trans* isopropyl alcohol. The investigations have been extended into the submillimeter region within the range 240-480 GHz. Various Q -, R -, and P -branch high J transitions (b - and c -type) have been measured. More than 170 lines were assigned to ground state

transition. All that permitted to determine more accurate values of the spectroscopic constants.

2. Experimental

The spectrum of isopropyl alcohol was recorded at room temperature at pressure below 2 mTorr by using a video spectrometer at the University of Kharkov [7]. The frequency measurement's accuracy is believed to be better than $\pm 50 \text{ kHz}$, except for very weak or overlapping lines.

The sample of $(\text{CH}_3)_2\text{CHOH}$ was obtained from BDH Chemical Co. and used without further purification.

3. Results and Discussions

The submillimeter transitions together with the lines recorded earlier [2, 4-6] were least squares fitted to the following A-reduced Watson Hamiltonian in I' -representation, including two P^8 terms:

$$\begin{aligned} \tilde{H} = & \frac{1}{2}(\tilde{X} - \tilde{Y})J^2 + [\tilde{Z} - \frac{1}{2}(\tilde{X} + \tilde{Y})]J^2 - \Delta_J J^4 - \Delta_{JK} J^2 J_z^2 - \Delta_R J_z^4 \\ & + H_{KJ} J^2 J_z^4 + L_{JK} P^4 P_z^4 + \frac{1}{2}(\tilde{X} - \tilde{Y})J^2 J_{XY}^2 - 2\delta_J J^2 J_{XY}^2 - \delta_K (J_z^2 J_{XY}^2 + J_{XY}^2 J_z^2) \\ & + h_{JK} J^2 (J_z^2 J_{XY}^2 + J_{XY}^2 J_z^2) + h_K (J_z^4 J_{XY}^2 + J_{XY}^2 J_z^4) + \ell_{KJ} J^2 (J_z^4 J_{XY}^2 + J_{XY}^2 J_z^4) \end{aligned}$$

where \tilde{X}, \tilde{Y} and \tilde{Z} are the effective rotational constants; and where $\Delta_J, \Delta_{JK}, \Delta_K, \delta_J, \delta_K$ are the effective quartic, H_{KJ}, h_{JK}, h_K the effective sextic and L_{JK}, ℓ_{KJ} are the effective octic distortion coefficients. $J_{XY}^2 = J_X^2 + J_Y^2$ and J_X, J_Y, J_Z are components of the total angular momentum, J .

The lists of assigned transition of *trans* isopropanol in the ground vibrational state are shown in Table 1.

The difference $v_{obs.} - v_{calc.}$ is given in the third column of the Table 1. The largest deviation is 130 kHz. The highest contribution due to P^8 terms is about 4.81 MHz for the transition $59_{23,36} - 59_{22,37}$ ($59_{24,36} - 59_{23,37}$ and due to P^6 term is about 38.86 MHz for the transition $60_{24,36} - 60_{23,37}$ ($60_{24,36} - 60_{23,37}$). The three rotational constants, ten centrifugal distortional constants, and correlation matrix of isopropyl alcohol are given in Table 2a and Table 2b.

Including two P^8 terms in the Hamiltonian made the standard deviation drop to 0.050 kHz, but introduce somewhat larger correlation among the spectroscopic parameters. The largest correlation coefficient is 0.95 connecting Δ_J and δ_J and 0.96 for terms L_{JK} and ℓ_{KJ} . The rotational constants obtained are two orders of magnitude more accurate of those reported formerly [2].

Table 1. Assigned Submillimeter Transitions $J_{k-1,k_1} \rightarrow J'_{k'-1,k'_1}$ (Frequencies in MHz) of the *trans* form of Isopropyl Alcohol in the Ground Vibrational State

Transition	v_{obs}	$v_{obs.} - v_{calc.}$	Transition	v_{obs}	$v_{obs.} - v_{calc.}$
15 _{15 0} - 14 _{14 1}	253278.47	-0.02	21 _{8 13} - 20 _{7 13}	346404.80	0.03
15 _{15 1} - 14 _{14 0}	253262.82	-0.04	21 _{9 13} - 20 _{8 13}	346404.80	0.03
15 _{15 0} - 14 _{14 0}	253268.30	-0.04	21 _{18 3} - 20 _{17 3}	346476.15	-0.03
16 _{12 5} - 15 _{9 6}	300711.21	0.16	21 _{18 4} - 20 _{17 4}	347350.08	-0.02
17 _{16 1} - 16 _{15 2}	284667.38	-0.01	21 _{16 5} - 20 _{15 5}	342342.66	-0.09
18 _{17 2} - 17 _{16 1}	301481.26	-0.02	21 _{3 18} - 20 _{2 18}	346664.37	0.02
18 _{17 1} - 17 _{16 1}	301518.59	-0.03	21 _{4 18} - 20 _{3 18}	346664.37	0.02
21 _{13 8} - 20 _{12 8}	345665.47	-0.11	21 _{17 4} - 20 _{16 4}	343067.38	-0.02
21 _{16 6} - 20 _{15 6}	345158.72	-0.03	21 _{10 11} - 20 _{9 11}	346223.48	-0.01
21 _{16 6} - 20 _{15 5}	316737.92	0.02	21 _{11 10} - 20 _{10 10}	346094.03	-0.02
21 _{15 7} - 20 _{14 7}	345360.71	0.00	21 _{8 13} - 20 _{7 13}	346404.80	0.03
21 _{15 6} - 20 _{14 6}	344061.06	-0.01	21 _{12 10} - 20 _{11 10}	346094.03	-0.05
21 _{10 12} - 20 _{9 12}	346323.95	0.00	21 _{7 14} - 20 _{6 14}	346471.84	0.02
21 _{9 12} - 20 _{8 12}	346323.95	0.00	21 _{9 13} - 20 _{8 13}	346404.80	0.03
21 _{14 7} - 20 _{13 7}	345209.48	0.00	21 _{16 5} - 20 _{15 5}	342342.66	-0.09
21 _{10 11} - 20 _{9 11}	346223.48	-0.01	21 _{8 14} - 20 _{7 14}	346471.84	0.02
21 _{5 16} - 20 _{4 16}	346578.96	-0.03	29 _{9 20} - 28 _{10 19}	342503.88	-0.02
21 _{6 16} - 20 _{5 16}	346578.96	-0.03	29 _{10 20} - 28 _{9 19}	342503.88	-0.02
21 _{6 16} - 20 _{5 16}	346578.96	-0.03	29 _{1 28} - 28 _{2 27}	286736.80	0.02
22 _{10 12} - 21 _{11 11}	282959.52	-0.02	29 _{2 28} - 28 _{1 27}	286736.80	0.02
22 _{5 18} - 21 _{4 17}	241025.18	0.01	30 _{9 22} - 29 _{8 21}	345041.14	-0.09
22 _{4 18} - 21 _{5 17}	241025.18	0.01	30 _{8 22} - 29 _{9 21}	345041.14	-0.09
22 _{16 7} - 21 _{15 6}	321267.43	-0.02	31 _{8 24} - 30 _{7 23}	347582.74	-0.07
22 _{11 12} - 21 _{10 11}	282959.52	-0.02	31 _{7 24} - 30 _{8 23}	347582.74	-0.07
23 _{19 4} - 22 _{20 3}	301307.82	0.09	32 _{5 27} - 31 _{6 26}	343161.02	-0.01
24 _{17 8} - 23 _{16 7}	345831.19	-0.03	32 _{2 30} - 31 _{3 29}	322257.83	0.04
24 _{8 17} - 23 _{7 16}	280994.64	-0.00	32 _{3 30} - 31 _{2 29}	322257.83	0.04
24 _{7 17} - 23 _{8 16}	280994.64	-0.00	33 _{5 29} - 32 _{4 28}	345706.62	-0.01
24 _{18 6} - 23 _{19 5}	345163.75	-0.07	33 _{4 29} - 32 _{5 28}	345706.62	-0.01
24 _{16 8} - 23 _{17 7}	344622.66	0.01	35 _{1 34} - 34 _{2 33}	343829.57	-0.00
24 _{12 12} - 23 _{13 11}	316003.35	0.04	35 _{2 34} - 34 _{1 33}	343829.57	-0.00
24 _{13 12} - 23 _{12 11}	316003.35	0.02	36 _{17 19} - 35 _{18 18}	464803.60	-0.06
25 _{1 25} - 24 _{0 24}	241680.85	0.02	36 _{1 36} - 35 _{0 35}	346372.87	0.00
25 _{0 25} - 24 _{1 24}	241680.85	0.02	36 _{0 36} - 35 _{1 35}	346372.87	0.00
25 _{16 10} - 24 _{15 9}	346848.94	0.07	38 _{2 36} - 38 _{2 37}	254658.18	-0.04
25 _{6 19} - 24 _{7 18}	283533.32	0.03	38 _{2 36} - 38 _{1 37}	254658.18	-0.04
25 _{7 19} - 24 _{6 18}	283533.32	0.03	39 _{13 26} - 38 _{14 25}	465353.87	0.00
26 _{5 21} - 25 _{6 20}	286075.72	0.04	39 _{14 26} - 38 _{13 25}	465353.87	0.00
26 _{6 21} - 25 _{5 20}	286075.72	0.04	40 _{5 36} - 40 _{4 37}	254498.50	0.08
27 _{13 15} - 26 _{12 14}	344457.34	-0.00	40 _{4 36} - 40 _{3 37}	254498.45	0.03
27 _{12 15} - 26 _{13 14}	344457.34	-0.00	42 _{10 33} - 41 _{9 32}	466025.11	0.03
27 _{9 19} - 26 _{8 18}	316510.94	0.04	42 _{9 33} - 41 _{9 32}	466025.11	0.03
27 _{8 19} - 26 _{9 18}	316510.94	0.04	42 _{6 36} - 42 _{5 37}	254326.92	0.05
27 _{5 23} - 26 _{4 22}	288619.95	0.03	42 _{7 36} - 42 _{6 37}	254326.92	0.05
27 _{4 23} - 26 _{5 22}	288619.95	0.03	43 _{8 36} - 43 _{7 37}	254236.53	0.02
27 _{4 24} - 26 _{3 23}	281647.30	0.03	43 _{7 36} - 43 _{6 37}	254236.53	0.02
27 _{3 24} - 26 _{4 23}	281647.30	0.03	43 _{8 35} - 42 _{9 34}	468571.61	-0.02
28 _{27 1} - 27 _{26 1}	470831.03	0.13	43 _{9 35} - 42 _{8 34}	468571.61	-0.02
28 _{11 17} - 27 _{12 16}	346957.61	-0.08	44 _{8 36} - 44 _{7 37}	254143.01	0.01

Table 1. (continued)

Transition	v_{obs}	$v_{obs.} - v_{calc.}$	Transition	v_{obs}	$v_{obs.} - v_{calc.}$
28 ₂ 26 – 27 ₃ 25	284192.26	0.03	44 ₉ 36 – 44 ₈ 37	254143.01	0.01
28 ₃ 26 – 27 ₂ 25	284192.26	0.03	44 ₆ 38 – 43 ₇ 37	464170.87	-0.00
28 ₂₆ 2 – 27 ₂₅ 3	468245.33	0.00	44 ₇ 38 – 43 ₆ 37	464170.87	-0.00
28 ₂₆ 3 – 27 ₂₅ 2	468236.74	0.01	45 ₉ 36 – 45 ₈ 37	254046.27	0.00
28 ₂₅ 3 – 27 ₂₄ 4	465671.01	-0.04	45 ₁₀ 36 – 45 ₉ 37	254046.27	0.00
28 ₂₃ 5 – 27 ₂₂ 6	466256.87	0.06	45 ₅ 40 – 44 ₆ 39	466718.20	-0.02
28 ₁₂ 17 – 27 ₁₁ 16	346957.61	-0.08	45 ₆ 40 – 44 ₅ 39	466718.20	-0.02
28 ₂₆ 3 – 27 ₂₅ 2	468236.74	0.01	46 ₁₀ 36 – 46 ₉ 37	253946.20	-0.05
28 ₂₇ 1 – 27 ₂₆ 2	470831.03	-0.04	46 ₁₁ 36 – 46 ₁₀ 37	253946.20	-0.05
29 ₆ 23 – 28 ₇ 22	321591.86	0.04	47 ₁₁ 36 – 47 ₁₀ 37	253842.79	-0.05
29 ₇ 23 – 28 ₆ 22	321591.86	0.04	47 ₁₂ 36 – 47 ₁₁ 37	253842.79	-0.05
47 ₇ 41 – 47 ₆ 42	289068.67	0.03	54 ₁₀ 45 – 54 ₈ 46	316459.96	0.07
47 ₆ 41 – 47 ₅ 42	289068.67	0.03	54 ₁₈ 36 – 54 ₁₇ 37	253017.57	0.00
47 ₃ 45 – 46 ₂ 44	464858.87	0.02	54 ₁₉ 36 – 54 ₁₈ 37	253017.57	0.00
47 ₂ 45 – 46 ₃ 44	464858.87	0.02	55 ₁₉ 36 – 55 ₁₈ 37	252884.12	-0.01
48 ₁₂ 36 – 48 ₁₁ 37	253736.01	0.03	55 ₂₀ 36 – 55 ₁₉ 37	252884.12	-0.01
48 ₁₃ 36 – 48 ₁₂ 37	253736.01	0.03	56 ₂₀ 36 – 56 ₁₉ 37	252746.49	-0.04
49 ₁₄ 36 – 49 ₁₃ 37	253625.57	-0.01	56 ₂₁ 36 – 56 ₂₀ 37	252746.49	-0.04
49 ₀ 49 – 48 ₁ 48	469944.20	-0.00	56 ₁₁ 45 – 56 ₁₀ 46	316194.11	0.01
49 ₁₃ 36 – 49 ₁₃ 36	253625.57	-0.01	56 ₁₂ 45 – 56 ₁₁ 46	316194.11	0.01
49 ₁ 49 – 48 ₀ 48	469944.20	0.00	57 ₁₃ 45 – 57 ₁₂ 46	316056.37	-0.02
50 ₁₄ 36 – 50 ₁₃ 37	253511.58	0.01	57 ₂₁ 36 – 57 ₂₀ 37	252604.69	0.03
50 ₁₅ 36 – 50 ₁₄ 37	253511.58	0.01	57 ₂₂ 36 – 57 ₂₁ 37	252604.69	0.03
51 ₇ 45 – 51 ₆ 46	316835.14	-0.04	57 ₁₇ 40 – 57 ₁₆ 41	280805.86	0.02
51 ₁₅ 36 – 51 ₁₄ 37	253393.85	0.00	57 ₁₂ 45 – 57 ₁₁ 46	316056.37	-0.02
51 ₁₆ 36 – 51 ₁₅ 37	253393.85	0.00	57 ₁₈ 40 – 57 ₁₇ 41	280805.86	0.02
51 ₁₀ 41 – 51 ₉ 42	288622.03	-0.01	58 ₂₂ 36 – 58 ₂₁ 37	252458.45	0.02
51 ₁₁ 41 – 51 ₁₀ 42	288622.03	-0.01	58 ₂₃ 36 – 58 ₂₂ 37	252458.45	0.02
51 ₆ 45 – 51 ₆ 46	316815.14	-0.04	59 ₁₄ 45 – 59 ₁₃ 46	315771.15	0.03
52 ₈ 45 – 52 ₇ 46	316713.13	-0.02	59 ₂₄ 36 – 59 ₂₃ 37	252307.79	0.06
52 ₇ 45 – 52 ₆ 46	316713.13	-0.02	59 ₂₃ 36 – 59 ₂₂ 37	252307.79	0.06
53 ₁₇ 36 – 53 ₁₆ 37	253146.93	-0.01	59 ₁₅ 45 – 59 ₁₄ 46	315771.15	0.03
53 ₁₈ 36 – 53 ₁₇ 37	253146.93	-0.01	60 ₂₄ 36 – 60 ₂₃ 37	252152.42	-0.04
53 ₈ 45 – 53 ₇ 46	316588.06	-0.01	60 ₁₇ 43 – 60 ₁₆ 44	301521.14	-0.05
53 ₉ 45 – 53 ₈ 46	316588.06	-0.01	60 ₁₈ 43 – 60 ₁₇ 44	301521.14	-0.05
54 ₉ 45 – 54 ₈ 46	316459.96	0.07	60 ₂₅ 36 – 60 ₂₄ 37	252152.42	-0.05

Table 2a. Rotational constants and centrifugal distortion coefficients of the *trans* isopropyl alcohol

Parameters	Values
$\tilde{X}(MHz)$	4765.2326 (3)
$\tilde{Y}(MHz)$	8489.0150 (5)
$\tilde{Z}(MHz)$	8041.9182 (7)
$\Delta_J(KHz)$	4.6160 (3)
$\Delta_{JK}(KHz)$	-2.901 (2)
$\Delta_K(KHz)$	5.606 (1)
$\delta_J(KHz)$	-1.7478 (2)
$\delta_K(KHz)$	-1.5495 (7)
$H_{KJ}(Hz)$	0.064 (1)
$h_{JK}(Hz)$	0.0037 (3)
$h_K(Hz)$	-0.0272 (7)
$L_{JK}(mHz)$	-0.0014 (2)
$\ell_{KJ}(mHz)$	-0.0017 (3)

Table 2b. Correlation matrix for the ground state *trans* isopropyl alcohol

Parameters	Correlation Matrix											
\tilde{X}												
\tilde{Y}	0.30											
\tilde{Z}	0.34	0.66										
Δ_J	0.21	0.53	0.11									
Δ_{JK}	0.18	0.26	0.56	0.51								
Δ_K	0.03	0.10	0.20	0.68	-0.63							
δ_J	0.08	-0.46	-0.04	-0.95	0.66	-0.49						
δ_K	0.05	-0.13	-0.28	0.45	-0.67	0.42	-0.59					
H_{KJ}	0.33	0.55	0.81	0.11	0.58	0.19	-0.01	-0.43				
h_{JK}	0.35	0.35	0.35	0.12	0.31	-0.10	0.04	0.28	0.41			
h_K	-0.02	-0.01	-0.03	0.03	-0.10	0.00	-0.12	0.26	-0.30	-0.40		
L_{JK}	0.34	-0.38	-0.60	-0.09	-0.40	-0.15	0.05	0.11	-0.62	-0.10	-0.52	
ℓ_{KJ}	0.10	0.00	0.00	0.03	-0.06	-0.03	-0.08	0.35	-0.26	-0.19	0.96	-0.57

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