THE ROTATION SPECTRUM OF TRANSCONFORMER OF $(CD_3)_2CDOH$ MOLECULE. THE FORBIDDEN TRANSITIONS

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The rotational spectrum of trans-conformer of deuteroreplaced izopropanol molecule $(CD_3)_2CDOH$, which is registered by hybrid spectrometer with Stark modulation and modulation on double quantum RF-MW resonances with absorbing cell on the base of flute waveguide system in frequency range 17500–79050MHz is investigated. 105 new authorized and 12 forbidden rotation transitions are identified. The theoretical treatment of spectrum is carried out by rotation Watson Hamiltonian of A-reduction. The spectroscopic parameters of molecule are essentially specified.

Key words: microwave rotation spectrum, Watson Hamiltonian, hybrid spectrometer.

Introduction

First, the investigation of rotation spectrum of deuterated sample of isopropyl alcohol molecule $(CD_3)_2CDOH$ trans-conformer is carried out in the work [1]. The determination accuracy of spectroscopic constants in this work is comparatively inferior one. Henceforth the molecule investigation in centimeter and millimeter wave band is continued in the works [2-3], where the identification accuracy is confirmed by double RF-MW resonances up to J=25. However, all transitions with $J>10$ anew included in calculation are related only to Q-arms. The information for essential precise definition of values of spectroscopic constants isn't enough.

In the present work the problem of noticeable precise definition of rotation and spectroscopic constants of deutero-replaced isopropanol molecule $(CD_3)_2CDOH$ transconformer at the expense of inclusion of transitions relating to R-arms with high J into reverse spectroscopic problem (RSP) solution is set.

The search and identification of such transitions are carried out on modified hybrid spectrometer with Stark modulation and modulation on double quantum RF-MW resonances with absorbing cell on the base of flute waveguide system in frequency range 17500–79050 MHz [4].

Calculation

The theoretical treatment of spectrum is carried out by rotation Watson Hamiltonian of A-reduction, including only quartic centrifugal constants:

$$\tilde{H} = \tfrac{1}{2}\left(\tilde{X} - \tilde{Y}\right)J^2 + \left[\tilde{Z} - \tfrac{1}{2}\left(\tilde{X} + \tilde{Y}\right)\right]J^2 - \Delta_J J^4 - \Delta_{JK} J^2 J_Z^2 - \Delta_K J_Z^4 + \\ + \tfrac{1}{2}\left(\tilde{X} - \tilde{Y}\right)J^2 J_{XY}^2 - 2\delta_J J^2 J_{XY}^2 - \delta_K\left(J_Z^2 J_{XY}^2 + J_{XY}^2 J_Z^2\right),$$

where X, Y, Z are rotation constants; Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K are quartic constants of centrifugal distortion; J_X, J_Y, J_Z are components of total angular momentum J in arbitrary co-ordinates x, y, z; $J^2 = J(J+1)$, $J_{XY}^2 = J_X^2 + J_Y^2$.

The calculations are carried out in the second axial representation, when $x \to c$, $y \to a$, $z \to b$, where a, b, c are axes of reference, connected with main molecule axes.

As it is known, the several forbidden transitions in rotation spectrums are removed in the result of strong rotation-smoking-vibration interaction of energy levels which have similar k_1 and k_2 for both levels appear [5]. The purposeful search of these transitions leads to positive results. The revealing and inclusion of such transitions into RST solution simplify the interpretation of spectrum for high J, widen the possibility of further investigation of millimeter rotational spectrum of trans-conformer molecule $(CD_3)_2CDOH$ and help to unambiguously identify the transitions with high J. The identification of spectrum is carried out by consistent inclusion of frequency transitions into RST solution, beginning from the transitions with low J, the calculation errors of which are minimal ones and the reverse spectroscopic task is solved. The direct spectroscopic task is solved every time after inclusion of new frequencies into calculation and the transitions, the frequencies of which are calculated with minimal error, are chosen for the further treatment.

The calculation, carried out by this way, gives the possibility to identify 12 forbidden transitions.

Only 105 allowed transitions up to $J=35$, 32 of which are related to R-arms, are succeeded to identify. The frequencies of again identified allowed transitions with the values of experimentally measured frequencies by their differences with calculated values of transition frequencies in the second axial representation are given in the table 1. The frequencies of identified forbidden transitions, which are marked by star, are given in the same table.

The rotation and quartic centrifugal constants, defined by the fit of method of least squares (MLS), calculated on Watson Hamiltonian of A-reduction in the second axial representation of frequencies and their ratio to ones experimentally defined are given in table 2. The same constants, defined on frequencies of 163 transitions in work [3] are included in this table for the comparison. It is seen from the table, that inclusion of frequency spectrum of R-arm transitions into treatment allows to decrease the errors of definition of rotation constants approximately in 3-4 times, and centrifugal ones decrease almost on the one order.

Table 1.
The frequencies (MHz) of identified rotation transitions of $(CD_3)_2CDOH$ molecule.

Transition	$\nu_{exp.}$	$\nu_{calc.}$	$\Delta\nu = \nu_{exp} - \nu_{calc.}$
$2_{1\,1} - 1_{0\,1}$	25054.83	25054.70	0.12
$3_{2\,2} - 2_{1\,1}$	32853.51	32853.37	0.14
$3_{1\,2} - 2_{2\,1}$	28414.86	28414.89	-0.03
$4_{4\,1} - 3_{3\,1}$	54688.53	54688.33	0.20
$4_{2\,2} - 3_{1\,3}$	62131.50	62131.67	-0.17
$4_{1\,3} - 4_{0\,4}$	17483.64	17483.56	0.08
$5_{3\,3} - 4_{2\,2}$	54209.26	54209.21	0.05
$5_{4\,2} - 4_{3\,1}$	62429.54	62429.39	0.15
$5_{4\,1} - 4_{3\,1}$	64462.57	64462.49	0.08
$5_{2\,3} - 4_{1\,3}$	63671.26	63671.14	0.11
$6_{1\,6} - 5_{1\,4}$	26767.00*	26766.99	0.01
$6_{2\,5} - 5_{1\,4}$	54712.43	54712.30	0.13
$6_{3\,3} - 5_{4\,2}$	59227.82	59227.79	0.03
$6_{1\,5} - 5_{2\,4}$	54623.09	54623.05	0.03
$6_{6\,1} - 6_{5\,2}$	19284.97	19284.98	-0.01
$6_{6\,0} - 6_{5\,2}$	19327.45	19327.37	0.08
$7_{6\,1} - 6_{6\,1}$	74500.06*	74499.89	0.17
$7_{5\,2} - 6_{6\,1}$	58766.61	58766.57	0.04
$7_{5\,3} - 6_{6\,0}$	54664.34	54664.25	0.09
$7_{5\,3} - 7_{4\,4}$	19111.59	19111.40	0.19
$7_{5\,2} - 6_{6\,0}$	58724.04	58724.17	-0.13
$7_{3\,4} - 6_{4\,2}$	64408.56	64408.48	0.08
$7_{3\,4} - 6_{6\,0}$	34378.69	34378.76	-0.07
$8_{3\,5} - 8_{2\,6}$	27179.85	27180.05	-0.20
$8_{2\,6} - 8_{1\,7}$	32842.26	32842.22	0.04
$8_{5\,3} - 7_{6\,2}$	74287.24	74287.25	-0.01
$8_{1\,7} - 7_{2\,6}$	70313.66	70313.81	-0.15
$8_{6\,3} - 7_{7\,1}$	62382.71	62382.58	0.13
$8_{5\,4} - 7_{6\,1}$	64091.34	64091.22	0.12
$9_{7\,3} - 8_{8\,0}$	69653.29	69653.43	-0.14
$9_{6\,3} - 9_{3\,6}$	57227.92	57227.81	0.11
$9_{7\,2} - 9_{4\,5}$	47740.78	47740.58	0.20
$9_{4\,5} - 9_{3\,6}$	26315.55	26315.50	0.05
$10_{3\,8} - 9_{3\,6}$	58586.24	58586.36	-0.12
$10_{5\,6} - 9_{7\,2}$	54477.98*	54477.91	0.07
$10_{5\,6} - 10_{4\,7}$	32223.02*	32223.19	-0.17
$10_{9\,2} - 10_{8\,2}$	28364.34	28364.43	-0.09
$10_{5\,6} - 10_{2\,8}$	69948.07	69948.01	0.06
$10_{8\,3} - 10_{7\,4}$	25072.21	25072.28	-0.07
$10_{9\,2} - 10_{8\,3}$	28877.64	28877.49	0.15
$10_{3\,8} - 9_{4\,6}$	5852.08	58520.07	0.01
$11_{4\,7} - 10_{8\,3}$	32914.05*	32914.06	-0.01
$11_{9\,2} - 11_{8\,3}$	25990.85	25990.81	0.04
$11_{8\,3} - 11_{7\,4}$	17725.03	17724.99	0.04
$12_{8\,5} - 12_{5\,7}$	59517.21	59517.24	-0.03
$12_{8\,5} - 11_{11\,1}$	31138.42	31138.38	0.04
$12_{6\,6} - 12_{5\,7}$	29747.83	29747.82	0.01
$12_{7\,5} - 12_{6\,6}$	20477.52	20477.47	0.05
$12_{9\,4} - 12_{8\,4}$	21030.90	21030.90	0.00
$12_{11\,2} - 12_{10\,2}$	35943.54	35943.42	0.12
$13_{7\,6} - 13_{6\,7}$	27668.44	27668.42	0.02
$13_{11\,3} - 13_{10\,3}$	34426.88	34426.76	0.12
$14_{11\,3} - 14_{10\,4}$	31892.34	31892.44	-0.10
$14_{10\,5} - 13_{13\,1}$	31783.27	31783.15	0.12
$14_{5\,9} - 14_{4\,10}$	47363.31	47363.24	0.07
$15_{9\,7} - 15_{8\,8}$	35640.84	35640.66	0.18
$15_{2\,14} - 15_{1\,15}$	73943.32	73943.40	-0.08

1	2	3	4
$6_{10\ 6} - 16_{9\ 7}$	21177.22	21177.12	0.10
$16_{9\ 7} - 16_{8\ 8}$	29972.11	29972.13	-0.02
$16_{12\ 5} - 16_{11\ 6}$	36245.02	36244.97	0.05
$17_{7\ 11} - 17_{6\ 12}$	57369.89	57369.84	0.05
$17_{12\ 6} - 17_{11\ 7}$	35939.60	35939.75	-0.15
$18_{9\ 10} - 18_{8\ 11}$	51093.20	51093.38	-0.18
$18_{6\ 12} - 18_{5\ 13}$	62555.91	62556.00	-0.09
$19_{6\ 13} - 18_{10\ 9}$	28974.31*	28974.74	-0.14
$19_{7\ 12} - 19_{6\ 13}$	62160.71	62160.81	-0.10
$19_{9\ 10} - 19_{8\ 11}$	50202.94	50202.76	0.18
$19_{19\ 0} - 19_{18\ 1}$	65627.28	65627.24	0.04
$19_{11\ 8} - 19_{10\ 9}$	31860.83	31860.92	-0.09
$20_{20\ 0} - 20_{19\ 2}$	69208.15	69208.06	0.09
$20_{17\ 4} - 20_{16\ 4}$	55628.33	55628.45	-0.12
$20_{18\ 2} - 20_{17\ 3}$	60391.93	60391.82	0.11
$21_{8\ 13} - 20_{12\ 9}$	58824.72*	58824.61	0.11
$21_{18\ 3} - 21_{17\ 4}$	59305.20	59305.31	-0.11
$21_{18\ 4} - 21_{17\ 4}$	59305.20	59305.09	0.11
$21_{17\ 4} - 20_{20\ 0}$	28955.48	28955.36	0.12
$21_{19\ 2} - 21_{18\ 4}$	64010.21	64010.21	0.00
$22_{9\ 13} - 22_{8\ 14}$	66436.55	66436.41	0.14
$22_{18\ 4} - 22_{17\ 5}$	57979.61	57979.73	-0.12
$22_{13\ 9} - 22_{12\ 11}$	78351.15	78351.06	0.09
$22_{18\ 5} - 21_{21\ 1}$	28560.28	28560.44	-0.16
$22_{12\ 11} - 22_{11\ 12}$	54252.15	54252.26	-0.11
$22_{10\ 13} - 22_{9\ 14}$	66438.90	66438.97	-0.07
$23_{0\ 23} - 22_{2\ 21}$	72926.30*	72926.38	-0.08
$23_{19\ 4} - 22_{22\ 0}$	28188.11	28188.01	0.10
$23_{15\ 8} - 23_{14\ 9}$	28922.53	28922.69	-0.16
$23_{17\ 6} - 23_{16\ 7}$	49589.07	49589.08	-0.01
$23_{11\ 13} - 23_{10\ 14}$	65856.08	65856.06	0.02
$23_{9\ 14} - 23_{8\ 15}$	71700.08	71699.94	0.14
$23_{14\ 9} - 23_{13\ 11}$	71684.83	71684.94	-0.11
$24_{1\ 24} - 23_{1\ 22}$	75645.73*	75645.71	0.02
$24_{13\ 11} - 24_{12\ 12}$	50409.85	50409.68	0.17
$24_{18\ 7} - 23_{21\ 3}$	57765.51	57765.35	0.16
$24_{9\ 16} - 23_{11\ 12}$	34268.16*	34268.28	-0.12
$24_{10\ 15} - 23_{13\ 11}$	57713.46	57713.58	-0.12
$25_{10\ 15} - 24_{14\ 11}$	73167.90*	73167.91	-0.01
$25_{16\ 10} - 25_{15\ 10}$	18026.13	18026.15	-0.02
$26_{19\ 8} - 26_{18\ 9}$	56585.43	56585.48	-0.05
$26_{13\ 14} - 26_{12\ 15}$	69862.80	69862.71	0.09
$26_{22\ 5} - 25_{25\ 1}$	27146.51	27146.58	-0.07
$26_{9\ 18} - 25_{11\ 14}$	17884.35*	17884.15	0.20
$27_{12\ 15} - 27_{11\ 16}$	75261.80	75261.73	0.07
$27_{13\ 15} - 27_{12\ 16}$	75265.88	75265.98	-0.10
$27_{9\ 18} - 26_{12\ 14}$	32575.42	32575.46	-0.04
$29_{19\ 11} - 29_{18\ 11}$	31865.30	31865.31	-0.01
$29_{18\ 11} - 29_{17\ 12}$	34331.95	34332.10	-0.15
$30_{20\ 10} - 30_{19\ 12}$	59208.96	59208.95	0.01
$31_{15\ 16} - 31_{14\ 17}$	78349.97	78349.93	0.04
$31_{21\ 10} - 31_{20\ 11}$	51000.48	51000.59	-0.11
$32_{22\ 11} - 32_{21\ 11}$	56537.87	56537.82	0.05
$32_{20\ 13} - 32_{19\ 14}$	58802.91	58802.97	-0.06
$32_{18\ 15} - 32_{17\ 16}$	70572.06	70572.17	-0.11
$32_{22\ 10} - 32_{21\ 12}$	62802.36	62802.30	0.06
$33_{23\ 11} - 33_{22\ 11}$	62751.02	62750.97	0.05
$34_{22\ 13} - 34_{21\ 14}$	60675.99	60675.89	0.10
$34_{23\ 11} - 34_{22\ 12}$	57136.77	57136.67	0.10
$35_{25\ 10} - 35_{24\ 11}$	72951.43	72951.48	-0.05

Here $\Delta\nu = \nu_{exp} - \nu_{calc.}$.

The correlation matrix of Watson Hamiltonian constants of A-reduction, and also asymmetry parameter of χ molecule are given in table 3. The spectrum identification is confirmed by good fit by MLS in all three axial representations (table 4).

Result discussion

The values of rotation and centrifugal constants, presented in the table 4, are used at the calculation of defined combinations of spectroscopic constants, not depending on the choice of axial representation [6]. As it is expected, the values of calculated defined combinations of spectroscopic constants don't depend on the choice of axial representation and the degree of their equality to each other in all three axial representations is the criteria of objective estimation of quality of fit procedure of spectroscopic parameters in different axial representations. The value interval of defined combinations of spectroscopic parameters in all three axial representations is minimal one (table 5) in the result of inclusion of big number of R-arm transitions and ones with high *J* into fit procedure.

Conclusion

The spectroscopic parameters, specified in the present work allow us to describe the rotation spectrum of the given molecule with high accuracy. These constants can be used at the specification of monohydric alcohol structures, definition of intramolecular potential functions, electric and relaxation characteristics of molecule for prediction of transition frequencies which haven't been revealed yet experimentally by any reasons.

The obtaining of frequencies calculated on specified spectroscopic constants at local and remote sensings of atmosphere and space has the essential value.

Table 2.
The rotation and centrifugal constants of $(CD_3)_2CDOH$ molecule.

Constants	Work [3]	Present paper
A (MHz)	7035.7587 (0.0040)	7035.7701 (0.0012)
B (MHz)	6006.3329 (0.0040)	6006.3450 (0.0015)
C (MHz)	3915.4308 (0.0040)	3915.4438 (0.0012)
Δ_J (kHz)	2.8000 (0.0354)	2.8854 (0.0015)
Δ_{JK} (kHz)	-1.8033 (0.0106)	- 1.8139 (0.0015)
Δ_K (kHz)	2.8158 (0.0081)	2.8271 (0.0013)
δ_J (kHz)	-0.9410 (0.0016)	-0.9401 (0.0004)
δ_K (kHz)	-0.3352 (0.0031)	- 0.3314 (0.0007)

Table 3.
The rotation and centrifugal constants of $(CD_3)_2CDOH$ molecule and their correlation matrix.

Spectroscopic constants	Correlation matrix						
A = 7035.7701 MHz							
B = 6006.3450 MHz	0.89						
C = 3915.4438 MHz	0.89	0.94					
Δ_J = 2.8854 kHz	0.59	0.73	0.71				
Δ_{JK} = - 1.8139 kHz	0.20	0.07	0.23	-0.03			
Δ_K = 2.8271 kHz	-0.25	-0.07	-0.13	0.15	-0.91		
δ_J = -0.9401 kHz	-0.31	-0.60	-0.53	-0.86	-0.07	-0.07	
δ_K = - 0.3314 kHz	0.32	0.33	0.28	0.35	0.64	-0.67	-0.48

Table 4.
The rotation and centrifugal constants of $(CD_3)_2CDOH$ molecule in three axial representations.

Spectroscopic parameters	Axial representation		
	I^r	II^r	III^r
X (МГц)	6006.3503(0.0012)	3915.4438(0.0012)	7035.7659 (0.0015)
Y (МГц)	3915.4421(0.0012)	7035.7701(0.0015)	6006.3517 (0.0013)
Z (МГц)	7035.7668(0.00015)	6006.3450(0.0013)	3915.4416 (0.0011)
Δ_J (кГц)	2.4522 (0.0013)	2.8854(0.0015)	4.3326 (0.0020)
Δ_{JK} (кГц)	-0.5135 (0.0017)	- 1.8139(0.0015)	- 6.1544 (0.0019)
Δ_K (кГц)	2.8275 (0.0013)	2.8271(0.0013)	2.8268 (0.0013)
δ_J (кГц)	0.7233 (0.0003)	- 0.9401(0.0004)	0.2168 (0.0002)
δ_K (кГц)	1.1917 (0.0012)	- 0.3314(0.0006)	- 1.8639 (0.0015)

Table 5.
Defined combinations of spectroscopic parameters of $(CD_3)_2CDOH$ molecule.

Parameters	Axial representation		
	I^r	II^r	III^r
A (MHz)	7035.77168	7035.77148	7035.771755
B (MHz)	6006.35084	6006.35074	6006.350910
C (MHz)	3915.45030	3915.45027	3915.450236
T_{aa} (kHz)	-4.76622	-4.76558	4.766308
T_{bb} (kHz)	3.89890	- 3.89861	- 3.898930
T_{cc} (kHz)	-1.00551	- 1.00528	- 1.005023
T_1 (kHz)	-6.84313	- 6.84234	-6.843405
T_2 (kHz)	-2.06585	- 2.06574	- 2.065901

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$(CD_3)_2CDOH$ MOLEKULUNUN TRANS-KONFORMERİNİN FIRLANMA SPEKTRİ. QADAĞAN OLUNMUŞ KEÇİDLƏR

$(CD_3)_2CDOH$ molekulunun trans-konformerinin fırlanma spektri tədqiq edilmiş, 12 qadağan olunmuş keçid identifikasiya edilmişdir. 105 μ_b və μ_c keçidi identifikasiya olunmuşdur. Fırlanma spektrinin nəzəri təsvirində Vatsonun A-reduksiyalı fırlanma hamiltonianından istifadə edilib. Molekulun fırlanma və mərkəzəqaçma sabitləri dəqiqləşdirilmişdir.

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ВРАЩАТЕЛЬНЫЙ СПЕКТР ТРАНС-КОНФОРМЕРА МОЛЕКУЛЫ $(CD_3)_2$ CDOH. ЗАПРЕЩЕННЫЕ ПЕРЕХОДЫ

Исследован вращательный спектр транс-конформера молекулы дейтерозамещенного изопропанола – $(CD_3)_2CDOH$, который регистрировался гибридным спектрометром со штарковской модуляцией и модуляцией по двойным квантовым РЧ-МВ резонансам с поглощающей ячейкой на базе желобковой волноводной системы в диапазоне частот 17500-79050 МГц. Идентифицировано 105 новых разрешенных и 12 запрещенных вращательных переходов. Теоретическая обработка спектра осуществлялась вращательным гамильтонианом Ватсона А–редукции. Существенно уточнены спектроскопические параметры молекулы.

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