CENTRIFUGAL DISTURBANCE IN SPECTRUM TRANS-CONFORMER OF THE MOLECULE OF ETHYL ALCOHOL

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In this paper the rotary, quart, sixth and oct- centrifugal constants of A-reduction of Hamiltonian of *trans*-conformer of ethyl alcohol molecule in three axial representations have been established. The introduction in opposite spectroscopic task anew identified 33 rotary transitions, situated in range of 24,0-498,0 GGs frequencies with high $J(J=34)$ allow to decrease in three times mean-square inclination of above mentioned constants and because of this their combinations have been calculated more precisely.

The investigation of micro-waved rotary spectrum of ethanol molecule CH_3CH_2OH had been begun with identification of *Q*-branches of its *trans*-conformer [1]. Further, its isotope replaced analogues had been investigated in our country by Imanov, Kadjar, Abdurakhmanov, Ragimov and other [2-5], abroad – by Miliggen-Efinger [6], Kulot [7], Kakar [8], Lovas [9] and by others. Further, many serious works were dedicated to the investigation and identification of submillimeter rotary transitions trans- and gosh-conformers of this molecule [9-14,16-18]. Firstly on the base of the result analysis, obtained in these refs in 1975 in Sagittarius constellation (Sgr B2) the three rotary transitions have been revealed: $6_{06} - 5_{15}$ 82265,46 MHz, $4_{14} - 3_{03}$ 90117,51 MHz, $5_{15} - 4_{04}$ 104808,58 MHz [10]. After it, in constellation Hot Cores G34,3+0,15 the rotary transitions of this molecule had been revealed in big quantity [11, 12].

Table 1

The frequencies (MHz) of rotary transitions of molecule trans-ethanol

Transitions							ν_{exp}	$\Delta\nu$	Centrifugal deposit		
									Quart-	Sixth-	Oct-
1							2	3	4	5	6
4	0	4	-	3	0	3	69521,200	-0,017	-1,952	0,085	0,086
6	4	2	-	7	3	5	60136,578	0,102	-27,418	0,088	-0,013
7	5	3	-	8	4	4	94895,800	-8,249	-60,011	8,526	8,185
8	4	4	-	9	3	7	24789,250	-0,081	-8,794	0,086	-0,026
8	5	3	-	9	4	6	77235,048	-0,056	-57,330	0,289	-0,064
10	10	0	-	10	9	1	495876,700	0,113	-808,916	12,079	-2,559
10	10	1	-	10	9	2	495876,700	0,113	-808,916	12,079	-2,559
10	3	8	-	11	0	11	70336,001	-0,133	14,710	-0,069	0,009
11	3	9	-	12	0	12	61775,903	-0,022	14,521	-0,122	0,015
12	6	7	-	13	5	8	58889,529	0,008	-60,885	0,680	-0,383
14	3	12	-	13	4	9	62593,411	-0,079	-75,856	-0,082	0,069
16	4	12	-	15	5	11	50099,200	0,001	-118,431	0,044	0,291
16	4	13	-	17	1	16	64654,377	-0,050	140,553	-0,658	-0,017
17	4	14	-	18	1	17	52020,420	-0,172	138,707	-0,859	-0,016
18	1	17	-	17	2	16	297087,881	-0,099	-224,093	-0,220	-0,019
18	3	16	-	19	0	19	38769,436	0,096	-105,286	-1,538	0,054
19	4	16	-	20	1	19	31772,729	-0,143	108,427	-1,426	-0,030
23	6	18	-	22	7	15	68134,250	-0,054	-322,684	0,212	3,768
23	5	19	-	24	2	22	43838,449	-0,212	543,686	-4,017	-0,986
24	5	20	-	25	2	23	28697,089	-0,191	519,330	-4,562	-1,144
25	4	21	-	24	5	20	250150,722	-0,062	-1077,06	3,425	1,092
26	7	19	-	25	8	18	68657,454	0,021	-442,587	0,351	9,593
26	2	24	-	27	1	27	52171,970	0,015	-832,258	-8,196	-1,219
28	1	27	-	28	0	28	293453,889	-0,035	-656,144	-6,642	-0,832
28	2	26	-	28	1	27	253327,468	-0,010	-835,831	-6,377	-0,995
28	2	27	-	27	3	24	58778,250	-0,141	1154,863	3,762	0,876
29	2	27	-	28	3	26	492412,557	-0,036	-844,304	-2,411	-0,193
30	1	30	-	29	0	29	493256,377	-0,055	-579,460	-0,812	0,649
30	0	30	-	29	1	29	493238,503	-0,046	-580,100	-0,810	0,647
31	6	25	-	31	5	26	244342,608	0,208	853,466	-15,218	-7,420
32	3	29	-	32	2	30	249604,873	0,139	-1518,16	-6,441	-1,480
33	2	32	-	33	1	33	350959,413	-0,028	-1028,97	-13,215	-2,811
34	1	33	-	34	0	34	362257,701	0,021	-1124,83	-14,910	-3,472

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

Table 2

The rotary and centrifugal constants of CH_3CH_2OH molecule in three axial representations

Parameter	Representation		
	I^r	II^r	III^r
X (MHz)	9350,676(1)	8135,488(1)	34891,765(4)
Y (MHz)	8135,234(1)	34891,788(3)	9350,927(1)
Z (MHz)	34891,783(4)	9350,410(3)	8134,994(1)
Δ_J (κHz)	8,530(5)	118,83(6)	122,32(6)
Δ_{JK} (κHz)	-28,63(3)	-359,78(19)	-370,25(19)
Δ_K (κHz)	252,87(11)	252,98(12)	253,01(12)
δ_J (κHz)	1,738(1)	-56,86(3)	55,12(3)
δ_K (κHz)	6,63(9)	120,30(5)	-132,03(5)
H_J (Hz)	-0,011(9)	12,2(8)	12,4(8)
H_{JK} (Hz)	0,90(21)	-68,6(38)	-70,7(39)
H_{KJ} (Hz)	-9,38(79)	97,4(49)	103,2(52)
H_K (Hz)	35,76(147)	-41(1)	-44,8(21)
h_J (Hz)	-0,002(2)	-6,1(3)	6,16(39)
h_{JK} (Hz)	0,11(22)	27,3(14)	-29,4(15)
h_K (Hz)	58,8(65)	-20,2(8)	22,8(9)
L_J (MHz)	0,003(5)	-27,6(33)	-28,1(33)
L_{JJK} (MHz)	0,30(25)	128(22)	134(23)
L_{JK} (MHz)	-44,8(83)	-161(43)	-175(46)
L_{KKJ}(MHz)	47(23)	61(33)	71(37)
L_K(MHz)	-69(16)	-0,7(93)	-2(10)
L_{LJ}(MHz)	-0,0007(13)	13,8(16)	-14(1)
l_{JK}(MHz)	-0,09(15)	-49,2(93)	54(10)
l_{LKJ}(MHz)	15,3(71)	29(11)	-35(13)
l_K (MHz)	-582(145)	-0,3(46)	1,1(55)

Table 3

The defined combinations of spectroscopic parameters of CH_3CH_2OH molecule in three axial representations

Parameter	Presentation		
	I^r	II^r	III^r
A (MHz)	34891,8002	34891,7936	34891,7940
B (MHz)	9350,6482	9350,6480	9350,6480
C (MHz)	8135,2397	8135,2391	8135,2392
T_{aa} (kHz)	-232,7683	-232,5662	-232,5811
T_{bb} (kHz)	-12,0070	-12,0320	-12,0660
T_{cc} (κHz)	-5,0533	-5,1073	-5,0838
T_1 (κHz)	3,0493	3,2764	3,2828
T_2 (κHz)	-3,5553	-3,4630	-3,4510
Φ_{aaa} (Hz)	27,2705	24,4982	24,7425
Φ_{bbb} (Hz)	-0,0167	-0,0004	0,0942
Φ_{ccc} (Hz)	-0,0062	0,0910	0,0177
Φ_1 (Hz)	-19,4751	-25,5021	-25,4089
Φ_2 (Hz)	-4,6031	-5,4553	-5,4198
Φ_3 (Hz)	0,0211	0,0986	0,1075
Φ_4 (Hz)	0,0025	0,0820	0,1140
θ_1 (MHz)	-67,0808	-55,3147	-56,3899
θ_2 (MHz)	0,0023	0,0026	0,0003
θ_3 (MHz)	0,0054	0,0062	0,0059
θ_4 (MHz)	-67,6859	-63,8631	-64,1170
θ_5 (MHz)	-0,0034	0,0145	0,0023
θ_6 (MHz)	-0,0175	-0,0556	-0,0609
θ_7 (MHz)	-756,0766	-707,7655	-711,4906
θ_8 (MHz)	1,8591	4,0902	-7,4367
θ_9 (MHz)	-4,4117	10,6619	5,8051

In Lovas's paper [9], the analytic review of all earlier obtained investigation results of molecule trans-ethanol and calculations of centimeter and millimeter spectrums of this molecule, representing the astrophysical interest are given. Further, Pearson and others identified 450 transitions with high $J \geq 33$ [13], situated mainly in submillimeter region of wave lengths.

In Musayev's paper [14] 56 rotary transitions of this molecule, situated in 25,0-496,0 GHz range of wave length. The introduction in opposite spectroscopic task the new identified frequencies allow firstly to define the oct-spectroscopic constants, and also to define the rotary, quart and sixth spectroscopic constants of this molecule. Besides, in this paper the defined combinations of rotary and centrifugal constants (with the introduction of oct- terms) [15] in three axial representations [16,17] are calculated.

At the solution of opposite spectroscopic task the Vatson Hamiltonian of A-reduction was used [19-21]. Because of the strong centrifugal ethanol spectrum distortion further in solution of opposite spectroscopic task the oct- terms of centrifugal distortion had been introduced, that gave the possibility to identify 33 transitions, relating to millimeter and submillimeter region of wave lengths.

626 rotary transitions, 92 of which rotary transitions, identified in ref [9], 450 rotary transitions, identified in ref [13], 51 millimeter and submillimeter transitions, identified in ref [14] and 33 rotary transitions, identified by us, 20 from which relate to millimeter and 13 relate to submillimeter range of wave lengths, have been introduced into opposite spectroscopic problem. The rotary and centrifugal constants till decimal terms of rotary Hamiltonian in three axial representations are obtained.

The introduction in opposite spectroscopic task of anew identified 33 rotary transitions, situated in range of 24,0-498,0 GHz frequency with high $J(J=34)$ allow to decrease in three times the mean-square inclination of above-mentioned constants and because of it their defined combinations had been calculated more precisely.

The frequencies of rotary transitions, identified by us, and also the centrifugal deposits of separately quart, sixth and oct- terms of these transitions are given in the table 1. The rotary and centrifugal constants of CH_3CH_2OH molecule in three axial representations are given in table 2. The defined combinations of spectroscopic constants of molecule *trans*-conformer of ethyl alcohol, defined on the base of the constants given on the base of table 2, are given in the table 3.

The rotary and centrifugal constants, obtained at the solution of the opposite spectroscopic task and their correlation matrix in representation II^r are given in the table 4.

[1] *L.M. Imanov, Ch.O. Kadzhar.* "Q-Vetv vrashatelnoqo mikrovolnovogo spektra molekuli CH_3CH_2OH. Izv. AN Azerb. SSR, seriya FTMN 2, 51. (1961).

[2] *L.M. Imanov and Ch.O. Kadzhar.* "Superhigh – Frequency Spectrum and Dipole Moment of the Ethyl alcohol Molecule. Opt. Spectrosc. 14, 156. (1963).

[3] *L.M. Imanov, Ch.O. Kadzhar, and I.D. Isaev.* "Microwave Rotational Spectrum of the CH_3CH_2OH and CH_3CHDOH Molecules. Opt. Spectrosc. 18, 194, 1965.

[4] *L.M. Imanov, A.A. Abduraxmanov, R.A. Ragimova.* Mikrovolnoviy spektr i effektivniye postoyanniye molekuli CD_3CH_2OH. Optika i spektroskopiya, t. 19, №2, 306.,1965.

[5] *Ch.O. Kadzhar, I.D. Isaev, and L.M. Imanov.* "Radio-Spectroscopis Structure Determination of the Ethanol Molecule. J. Struct. Chem. 9, 375. (1968).

[6] Michelsen-Efinger P.J., Le, Jour, DE Phys. Spectre de rotation en microondes de la molecule d'alcool etylique *CH_3CH_2OH*. v, 30, avr 11, p. 336. (1969).

[7] *A.P. Culot.* Contribution a l'etude de la molecule d'alcool ethylique en spectroscopic hertzienne. Ann, Soc, Scient, Brux., v, 83, N 1, p. 65. (1969).

[8] *R.K. Kakar, P.J. Seibit.* Microwave Rotational Spectrum of *gauche*-Ethyl Alcohol. J.Chem. Phys, v, 57, N 9, p, 4060. (1972).

[9] *F.J. Lovas.* Microwave Spectra of Molecules of Astrophysical Interest, XXI, Ethanol *(C_2H_5OH)* and Propionitril *(C_2H_5NH)*. J. Chem, Phys., v.11, N2, p.251-300. (1982).

[10] *B. Zuckerman, B. Turner, D.Jonson, F. Clarc, F.Lovas, N. Fourikis, P. Palmer, Morris., A. Lilley, I. Ball, C.Gottlieb, M. Litvak, H. Penfield.* Detection of Interstellar *Trans*-Ethyl Alcohol. Astrophys, J., v, 196, N1, p, 99-102. (1975).

[11] *T.J. Millar, H.Olafsson, A. Hjalmarson, P.D.Brown.* "The detection of Ethanol in W51M," Astron, Astrophys, 205, L5. (1988).

[12] *T.J. Millar, G.H. Macdonald, and R.J. Habing,* "The detection of hot ethanol in G34,3+0,15," Mon. Not. R.Astron, Soc, 25, 273. (1995).

[13] *J.C. Pearson, K.V.L.N. Sastry, M. Winnewisser, E.Herbst, F.C.D. Lusia.* The Millimeter- and Submillimeter-Wave Spectrum of *transe*-Ethyl Alcohol. J. Mol. Spectrosc., v. 24, N1, p.246-261. (1995).

[14] *S.A. Musaev.* Sentrobejnoe vozmushenie trans-konformera molekuli etanola (oktichnie termi). Dokl, NAN Azerbaijana, , t, 57, № 4-6, s, 111. (2001).

[15] *Rao Ch,V,S.* Centrifugal-Distortion Coefficients of Asymmetric-Top Molecules, Reduction of the Octic Terms of, Rotational Hamiltonian. J, Mol, Spectrosc, v102, N1, p, 79. (1983).

[16] *S.A. Musaev.* Dissertasiya d.f.m.nauk. Sentrobejnoe vozmushenie i vnutrennee vrashenie v molekulax etilovogo i izopropilovogo spirtov .BAKU – 2003.

[17] *O.I.Baskakov, Ch.O. Kadjar, S.A. Musaev, D.A. Rzaev, E.Yu. Salaev.* Submillimetroviy spektr molekuli *trans*-etanola, Trudi VII Vsesoyuznogo simpoziuma po molekulyarnoy spektroskopii visokogo i sverxvi-sokogo razresheniya. Tomsk, chast 3, s, 84. (1986).

[18] *J.C. Pearson, K.V.L.N. Sastry, E. Herbst, and Frank C. De Lusia.* The Millimeter- and Submillimeter-Wave Spectrum of *gauche*-Ethyl Alcohol. J. Mol. Spectrosc., v. 175, N 1, p. 246. (1996).

[19] *J.K.G. Watson.* Determination of Centrifugal Distortion of Asymmetric-Top Molecules. J.Chem. Phys., v. 46, N 5, p.1935-1949. (1967).

[20] *J.K.G.Watson.* Determination of centrifugal-Distortion Coefficietts of Asymmetric-Top Molecules. III. Sextic Coefficients. J. Mol.,Spectrosc.,v.48, N10, p.4517-4524. 1968.

[21] *J.K.G. Watson*. Mass Derivatives of Molecular Parameters and Distortions in $r^{(2)}_m$ Structures J. Mol. Spectrosc., v.207, N 1, p.16-24. (2001).

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ETİL SPİRTİ MOLEKULUNUN TRANS - KONFORMERİNİN SPEKTRİNDƏ MƏRKƏZƏQAÇMA HƏYƏCANLANMASI

Etil spirti molekulunun trans – konformerinin fırlanma homiltoniyanın kvartik, sekstik və oktik spektral sabitləri təyin olunmuşdur. Bu molekulun misalında, ilk dəfə olaraq, reduksiya olunmuş fırlanma homiltaniyanın $J=34$ qiymətlərində oktik spektral sabitlərinin təyin olunan kombinasiyası hesablanmışdır.

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ЦЕНТРОБЕЖНОЕ ВОЗМУЩЕНИЕ В СПЕКТРЕ ТРАНС-КОНФОРМЕРА МОЛЕКУЛЫ ЭТИЛОВОГО СПИРТА

В этой работе уточнены вращательные, квартичные, секстичные и октичные центробежные постоянные гамильтониана А – редукции транс-конформера молекулы этилового спирта в трех осевых представлениях. Включение в обратную спектроскопическую задачу заново идентифицированные 33 вращательных перехода, попадающих в диапазон частот 24,0-498,0 ГГц с высокими *J (J=34)*, позволило в среднем в 3 раза уменьшить среднеквадратичное отклонение вышеуказанных постоянных и, благодаря этому, более точно вычислить их определяемые комбинации.

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