A Contribution to the Microwave Spectrum of 1,2-Difluoroethane

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Z. Naturforsch. **36a**, 1239 – 1241 (1981); received September 25, 1981

The microwave spectrum of gauche 1,2-difluoroethane was investigated in the ground and five vibrationally excited states by a centrifugal distortion analysis.

1,2-difluoroethane has been found to be a possible candidate for Laser-Stark-Spectroscopy [1]. For this reason we extended the published investigation [2] of gauche 1,2-difluoroethane. The rotational spectrum of the ground state was remeasured, additional lines assigned, and analysed with a centrifugal distortion Hamiltonian [3, 4]. In addition the rotational spectra of five excited vibrational states were measured, assigned and analysed in the same way.

Experimental

The substance was prepared according to Edgell and Parts [5], measured at temperatures between − 73 and 29 °C under pressures of approximately 1 to 5 mT with conventional Starkmodulation Spectrometers [6, 7], using 100 kHz and 33 kHz modulation frequencies. The measured lines are given in Tables 1 – 3. The experimental uncertainty is 30 kHz except for Table 2 c (300 kHz). For the spectra in excited vibrational states intensity measurements were made.

Analysis of the Spectra

The assignment of the lines was checked by calculation of the Stark effect, by comparison of the Stark effect of excited and ground state transitions and through analysis with the rigid rotor [8] and centrifugal distorted rotor model [3, 4].

The results are given in Table 4. In the first column the constants are given for the fitting of 30 lines, in the remaining columns equal sets of 15 lines were fitted to allow comparison **. The correlation matrix for the groundstate is given in Table 5. It is typical for all states.

By intensity measurements and comparison with infrared and Laser-Raman (Table 6) measurements [9] the rotational spectrum of Table 2 a was assigned to the first excited state of the torsion ν_{10}

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* Part of Diplom-thesis, Kiel 1981.

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** With exception of Table 4, Column 5, see Table 2 c.

Table 1. Rotational transitions of gauche 1,2-difluoroethane in vibrational ground state. ν_{calc} calculated with constants of Table 4, Column 1. Mean square deviation 75 kHz.

$J'_{K_-'K_+'} \leftarrow J_{K_-K_+}$	ν_{exp} [MHz]	ν_{calc} [MHz]	$\Delta\nu$ [kHz]	$J'_{K_-'K_+'} \leftarrow J_{K_-K_+}$	ν_{exp} [MHz]	ν_{calc} [MHz]	$\Delta\nu$ [kHz]
$1_{10} \leftarrow 1_{01}$	12 939.574	12 939.552	− 22	$5_{14} \leftarrow 4_{23}$	13 673.357	13 673.325	− 32
$1_{11} \leftarrow 0_{00}$	21 705.127	21 705.035	− 92	$5_{14} \leftarrow 5_{05}$	17 991.939	17 991.901	− 38
$2_{11} \leftarrow 2_{02}$	13 593.640	13 593.633	− 7	$5_{23} \leftarrow 5_{14}$	34 064.930	34 064.999	+ 69
$2_{12} \leftarrow 1_{01}$	30 470.670	30 470.601	− 69	$6_{15} \leftarrow 6_{06}$	20 467.882	20 467.941	+ 59
$2_{20} \leftarrow 2_{11}$	36 950.093	36 950.053	− 40	$6_{24} \leftarrow 6_{15}$	33 065.611	33 065.737	+ 126
$2_{21} \leftarrow 2_{12}$	38 817.405	38 817.376	− 29	$7_{16} \leftarrow 7_{07}$	23 550.091	23 550.154	+ 63
$3_{03} \leftarrow 2_{12}$	16 389.977	16 389.930	− 47	$8_{26} \leftarrow 7_{35}$	15 540.373	15 540.292	− 81
$3_{12} \leftarrow 3_{03}$	14 618.331	14 618.338	+ 7	$10_{19} \leftarrow 10_{0,10}$	36 642.692	36 642.693	+ 1
$3_{13} \leftarrow 2_{02}$	38 930.103	38 930.027	− 76	$10_{56} \leftarrow 11_{47}$	9 527.220	9 527.255	+ 35
$3_{21} \leftarrow 3_{12}$	36 114.797	36 114.800	+ 3	$11_{29} \leftarrow 11_{1,10}$	33 055.898	33 055.925	+ 27
$3_{22} \leftarrow 3_{13}$	39 778.066	39 778.085	+ 19	$12_{2,10} \leftarrow 12_{1,11}$	34 723.945	34 723.837	− 108
$4_{13} \leftarrow 4_{04}$	16 063.851	16 063.879	+ 28	$13_{49} \leftarrow 12_{58}$	9 858.663	9 858.738	+ 75
$4_{22} \leftarrow 4_{13}$	35 120.089	35 120.122	+ 33	$16_{4,12} \leftarrow 15_{5,11}$	39 845.963	39 846.134	+ 171
$4_{32} \leftarrow 5_{23}$	15 457.228	15 457.272	+ 44	$18_{8,11} \leftarrow 19_{7,12}$	9 704.173	9 704.147	− 26
$5_{05} \leftarrow 4_{14}$	36 748.149	36 748.136	− 13	$21_{6,15} \leftarrow 20_{7,14}$	35 430.284	35 430.182	− 102

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Table 2a—c. Rotational transitions of gauche 1,2-difluoroethane in the first torsional excited (ν_{10}) and first and second CCF-bending excited (ν_9, $2\nu_9$) states, ν_{calc} is calculated with the constants of Table 4 column 3, 4 and 5. Mean square deviation 9, 10 and 94 kHz respectively. $2\nu_9$ measuring accuracy 300 kHz.

$J'_{K_-'K_+'} \leftarrow J_{K_-K_+}$	ν_{10}			ν_9			$2\nu_9$		
	ν_{exp} [MHz]	ν_{calc} [MHz]	$\Delta\nu$ [kHz]	ν_{exp} [MHz]	ν_{calc} [MHz]	$\Delta\nu$ [kHz]	ν_{exp} [MHz]	ν_{calc} [MHz]	$\Delta\nu$ [kHz]
$1_{10} \leftarrow 1_{01}$	13 090.064	13 090.068	+ 4	12 894.737	12 894.756	− 19	12 847.67	12 847.744	+ 74
$1_{11} \leftarrow 0_{00}$	21 843.447	21 843.441	− 6	21 658.413	21 658.421	+ 8	21 609.86[b]	21 609.909	+ 49
$2_{11} \leftarrow 2_{02}$	13 737.464	13 737.477	+ 13	13 557.895	13 557.886	− 9	13 520.60	13 520.603	+ 3
$2_{12} \leftarrow 1_{01}$	30 596.896	30 596.891	− 5	30 422.175	30 422.177	+ 2	30 372.475	30 372.356	− 119
$2_{20} \leftarrow 2_{11}$	37 418.589	37 418.588	− 1	36 791.265	36 791.267	+ 2	36 625.56[b]	36 625.560	0
$3_{03} \leftarrow 2_{12}$	16 176.887	16 176.891	+ 4	16 467.478	16 467.472	− 6	16 549.93[b]	16 549.957	+ 27
$3_{12} \leftarrow 3_{03}$	14 750.858	14 750.854	− 4	14 597.508	14 597.520	+ 12	14 576.25	14 576.165	− 85
$3_{13} \leftarrow 2_{02}$	39 046.874	39 046.878	+ 4	38 875.885	38 875.886	+ 1	38 820.80	38 820.852	+ 52
$3_{21} \leftarrow 3_{12}$	36 588.931	36 588.928	− 3	35 946.811	35 946.813	+ 2			
$4_{13} \leftarrow 4_{04}$	16 178.962	16 178.956	− 6	16 065.317	16 065.320	+ 3	16 067.58[a]	16 067.628	+ 48
$4_{22} \leftarrow 4_{13}$	35 598.103	35 598.113	+ 10	34 943.474	34 943.471	− 3			
$5_{05} \leftarrow 4_{14}$	36 497.033	36 497.032	− 1	36 848.786[b]	36 848.787	+ 1	36 955.94[b]	36 955.930	− 10
$5_{14} \leftarrow 5_{05}$	18 081.826	18 081.829	+ 3	18 024.575	18 024.572	− 3	18 060.00	18 059.995	− 5
$5_{23} \leftarrow 5_{14}$	34 542.289	34 542.280	− 9	33 883.100	33 883.099	− 1	33 693.20[a]	33 693.200	0
$6_{24} \leftarrow 6_{15}$	33 534.685	33 534.688	+ 3	32 885.118	32 885.119	+ 1			

Table 3a, b. Rotational transitions of gauche 1,2-difluoroethane in unassigned vibrational states. ν_{calc} calculated with the constants of Table 4, Column 6 and 7, mean square deviation 38 and 16 kHz.

$J'_{K_-'K_+'} \leftarrow J_{K_-K_+}$	ν_x			ν_y		
	ν_{exp} [MHz]	ν_{calc} [MHz]	$\Delta\nu$ [kHz]	ν_{exp} [MHz]	ν_{calc} [MHz]	$\Delta\nu$ [kHz]
$1_{10} \leftarrow 1_{01}$	13 071.751	13 071.770	+ 19	13 029.328	13 029.305	− 23
$1_{11} \leftarrow 0_{00}$	21 801.183	21 801.196	+ 13	21 784.120	21 784.124	+ 4
$2_{11} \leftarrow 2_{02}$	13 710.650	13 710.665	+ 15	13 689.817	13 689.820	+ 3
$2_{12} \leftarrow 1_{01}$	30 530.660	30 530.674	+ 14	30 539.037	30 539.029	− 8
$2_{20} \leftarrow 2_{11}$	37 387.107[b]	37 387.052	− 55	37 201.017	37 201.038	+ 21
$3_{03} \leftarrow 2_{12}$	16 086.377[a]	16 086.387	+ 10	16 297.355	16 297.349	− 6
$3_{12} \leftarrow 3_{03}$	14 710.280	14 710.264	− 16	14 724.716	14 724.721	+ 5
$3_{13} \leftarrow 2_{02}$	38 960.451	38 960.421	− 30	38 984.830	38 984.842	+ 12
$3_{21} \leftarrow 3_{12}$	36 566.622	36 566.682	+ 60	36 358.003	36 357.981	− 22
$4_{13} \leftarrow 4_{04}$	16 118.200	16 118.197	− 3	16 184.837	16 184.839	+ 2
$4_{22} \leftarrow 4_{13}$	35 585.496	35 585.512	+ 16	35 254.391	35 354.384	− 7
$5_{05} \leftarrow 4_{14}$	36 329.661	36 329.664	+ 3	36 659.922	36 659.921	− 1
$5_{14} \leftarrow 5_{05}$	17 993.218[a]	17 993.217	− 1	18 132.549	18 132.549	0
$5_{23} \leftarrow 5_{14}$	34 537.504[b]	34 537.475	− 29	34 290.431	34 290.441	+ 10
$6_{24} \leftarrow 6_{15}$	33 533.396[b]	33 533.404	+ 8	33 283.838	33 283.836	− 2

[a] Stark effect not investigated. [b] Stark effect not clearly resolved.

Table 4. Rotational, centrifugal distortion constants and moments of inertia of gauche 1,2-difluoroethane in the ground and five vibrational excited states. $G[30]$, $G[15]$ 30 or 15 lines included. Standard errors are given in units of the last digit.

	$G\,[30]$	$G\,[15]$	ν_{10}	ν_9	$2\,\nu_9$	ν_x	ν_y
A [GHz]	17.32236 (1)	17.32241 (1)	17.466832 (5)	17.276647 (6)	17.22873 (8)	17.43656 (2)	17.406792 (9)
B [GHz]	5.013148 (4)	5.01313 (2)	5.001151 (9)	5.02060 (1)	5.0300 (3)	4.98115 (4)	5.01398 (2)
C [GHz]	4.382700 (5)	4.38275 (2)	4.376638 (9)	4.38180 (1)	4.3797 (3)	4.36475 (4)	4.37734 (2)
$\Delta_J \cdot 10^5$ [GHz]	0.734 (4)	0.75 (1)	0.767 (6)	0.767 (7)	1.5 (1)	0.73 (3)	0.77 (1)
$\Delta_{JK} \cdot 10^4$ [GHz]	– 0.525 (5)	– 0.49 (1)	– 0.527 (6)	– 0.516 (7)	– 1.4 (2)	– 0.45 (3)	– 0.55 (1)
$\Delta_K \cdot 10^3$ [GHz]	0.1551 (2)	0.156 (2)	0.167 (1)	0.155 (1)	0.16 (1)	0.154 (5)	0.171 (2)
$\delta_J \cdot 10^5$ [GHz]	0.208 (1)	0.192 (5)	0.208 (3)	0.209 (3)	0.31 (4)	0.19 (1)	0.214 (5)
$\delta_K \cdot 10^4$ [GHz]	0.241 (7)	0.11 (8)	0.28 (4)	0.27 (4)	7 (1)	– 0.2 (2)	0.36 (7)
$\varkappa$	– 0.902556 (3)	– 0.902566 (8)	– 0.904583 (3)	– 0.900922 (4)	– 0.8988 (1)	– 0.90569 (2)	– 0.902277 (7)
I_a [amu · Å^2]	29.17478 (2)	29.17469 (2)	28.933467 (8)	29.25197 (1)	29.3333 (1)	28.98370 (3)	29.03327 (2)
I_b [amu · Å^2]	100.81011 (8)	100.8105 (4)	101.0519 (2)	100.6605 (2)	100.472 (6)	101.4577 (8)	100.7934 (4)
I_c [amu · Å^2]	115.3116 (1)	115.3103 (5)	115.4713 (2)	115.3353 (3)	115.391 (8)	115.786 (1)	115.4528 (5)

Table 5. Correlation matrix for the rotational spectrum in the ground state $G\,[15]$.

A	1.00							
B	– 0.46	1.00						
C	0.46	– 0.92	1.00					
Δ_J	– 0.39	0.80	– 0.54	1.00				
Δ_{JK}	0.52	– 0.92	0.95	– 0.58	1.00			
Δ_K	0.43	0.16	0.35	– 0.22	– 0.37	1.00		
δ_J	– 0.15	0.76	0.67	0.65	– 0.52	0.04	1.00	
δ_K	– 0.48	0.96	0.98	0.63	– 0.98	0.31	0.64	1.00

Table 6. Relative intensities I_v/I_g of excited state spectra refered to groundstate spectra. Mean for the lines $1_{10} \leftarrow 1_{01}$, $2_{11} \leftarrow 2_{02}$, $3_{12} \leftarrow 3_{03}$ and $5_{14} \leftarrow 5_{05}$. Temperature 26 °C. Estimated error 10 to 20%. $\nu_{JR\mathrm{calc}}$ [cm^{-1}] is calculated from I_v/I_g. $\nu_{JR\mathrm{exp}}$ [cm^{-1}] from [9]. — not assigned in [9] —— unassigned.

	ν_{10}	ν_9	$2\,\nu_9$	ν_x	ν_y
I_v/I_g	0.49	0.2	0.05	0.1	0.12
$\nu_{JR\mathrm{calc}}$	148	335	623	479	441
$\nu_{JR\mathrm{exp}}$	148	327	—	——	——

(148 cm^{-1}), those of Tables 2 b and 2 c to the A-symmetry type CCF-bending ν_9 vibration (327 cm^{-1}) in its first and second excited state. The regularity of the change of the rotational constants from the ground state to ν_9 and $2\,\nu_9$ indicates, that both spectra belong to the same vibration.

We thank the members of our group for help and discussions, especially Mr. M. Andolfatto for the preparation of the substance, the Deutsche Forschungsgemeinschaft and Fonds der Chemie for funds. The calculations were made with the PDP10 computer of the University Computer Center.

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[9] W. C. Harris, J. R. Holtsclaw, and V. F. Kalasinsky, J. Chem. Phys. **67**, 3330 (1977), Table II and Table III.