Rotation-Torsion Interaction in the Ground State Microwave Spectrum of Trans-gauche Ethylnitrite

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We investigated a small rotation-torsion interaction in the microwave spectrum of trans-gauche ethylnitrite, $\text{CH}_3\text{CH}_2\text{ONO}$. We found the difference between the two lowest energy levels of the torsion around the $\text{C}-\text{O}$ bond axis to be 24.8(8) kHz. The high resolution of microwave Fourier transform (MWFT) spectroscopy was necessary to measure the resulting small splittings.

Introduction

Several investigations were made on the microwave spectrum of ethylnitrite in recent years. Turner [1] assigned the spectra of three conformers called cis-trans, cis-gauche, and trans-gauche ethylnitrite. They are shown in Figure 1. Endo et al. [2] recorded the spectra of some isotopomers and determined partial structures. In 1988 we published the ground state quadrupole coupling constants of all three conformers [3] determined by microwave Fourier transform (MWFT) spectroscopy. We found an additional splitting of the *c*-type transitions of trans-gauche ethylnitrite. Turner [1] found a similar, but much larger splitting of the *c*-type transitions of the named conformer in an excited state of the torsion around the $\text{C}-\text{O}$ bond axis. This splitting is caused by the interaction between the overall rotation and the tunneling motion through the barrier separating the two equivalent gauche-conformations. The splitting in the ground torsional state should have the same reason. To confirm this hypothesis, further research had to be done.

Experimental

Ethylnitrite was purchased from Fa. Merck-Schuchardt, Darmstadt, in a purity of 85% and distilled under low pressure for further purification. The measurements were made with waveguide MWFT spectrometers in the frequency range from 3.8 to

40 GHz [4–8] at pressures between 0.025 and 0.2 Pa and temperatures between -30 and -55°C . We focused our attention on recording additional *c*-type transitions to gain more information on the rotation-torsion interaction.

The Fourier transformation of a transient emission signal into the frequency domain causes line shape deformations, especially in the case of narrow multiplets [9]. To eliminate these overlap effects, the frequencies of the transitions were determined by a least squares fit of the time domain signal [10]. Because this fit program was improved since our last publication on ethylnitrite [3], all transitions given there were refitted to gain more accurate hyperfine frequencies. We focused our attention on measuring additional *c*-type transitions with their torsional hyperfine structure. A total of 5 *a*- and 29 *c*-type transitions was measured. A list of all transitions is given in Table 1. For an example see Fig. 3 of [3]. To calculate the hypothetical center frequencies we used the quadrupole coupling

Fig. 1. Rotational isomers of ethylnitrite.

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Table 1. Rotational transitions of trans-gauche ethylnitrite. ν_{obs} : measured frequency [MHz], ν_c : hypothetical unsplit line frequency [MHz] calculated by adding the hfs-splittings to the frequencies of the components, δ_c : deviation of the centrifugal distortion calculation [MHz].

$J_{K_+K_-} \leftarrow J'_{K'_+K'_-}$	$v \leftarrow v'$	$F \leftarrow F'$	ν_{obs}	ν_c	δ_c
$3_{21} \leftarrow 2_{20}$	$0 \leftarrow 0$ $1 \leftarrow 1$	$4 \leftarrow 3$	16 103.018	16 103.057	-0.004
		$3 \leftarrow 2$	16 103.203		
		$2 \leftarrow 1$	16 102.927		
$3_{22} \leftarrow 2_{21}$	$0 \leftarrow 0$ $1 \leftarrow 1$	$4 \leftarrow 3$	16 099.808	16 099.850	0.002
		$3 \leftarrow 2$	16 100.004		
		$2 \leftarrow 1$	16 099.714		
$4_{04} \leftarrow 3_{03}$	$0 \leftarrow 0$ $1 \leftarrow 1$		21 454.494	21 454.494	0.003
$4_{04} \leftarrow 3_{12}$	$1 \leftarrow 0$	$5 \leftarrow 4$	6 112.748	6 113.049	-0.004
		$4 \leftarrow 3$	6 113.942		
		$3 \leftarrow 2$	6 112.359		
	$0 \leftarrow 1$	$5 \leftarrow 4$	6 112.700	6 113.001	0.000
		$4 \leftarrow 3$	6 113.892		
		$3 \leftarrow 2$	6 11.306		
$4_{14} \leftarrow 3_{13}$	$0 \leftarrow 0$ $1 \leftarrow 1$	$5 \leftarrow 4$	21 208.315	21 208.350	0.002
		$4 \leftarrow 3$	21 208.366		
		$3 \leftarrow 2$	21 208.413		
$5_{15} \leftarrow 4_{14}$	$0 \leftarrow 0$ $1 \leftarrow 1$	$6 \leftarrow 5$	26 508.382	26 508.410	-0.002
		$5 \leftarrow 4$			
		$4 \leftarrow 3$	26 508.446		
$7_{17} \leftarrow 7_{07}$	$1 \leftarrow 0$	$8 \leftarrow 8$	13 267.201	13 267.506	-0.004
		$7 \leftarrow 7$	13 268.247		
		$6 \leftarrow 6$	13 267.048		
	$0 \leftarrow 1$	$8 \leftarrow 8$	13 267.148	13 267.452	-0.005
		$7 \leftarrow 7$	13 268.194		
		$6 \leftarrow 6$	13 266.994		
$7_{07} \leftarrow 6_{15}$	$1 \leftarrow 0$	$8 \leftarrow 7$	21 176.484	21 176.851	-0.002
		$7 \leftarrow 6$	21 177.763		
		$6 \leftarrow 5$	21 176.278		
	$0 \leftarrow 1$	$8 \leftarrow 7$	21 176.433	21 176.800	0.002
		$7 \leftarrow 6$	21 177.712		
		$6 \leftarrow 5$	21 176.227		
$8_{18} \leftarrow 8_{08}$	$1 \leftarrow 0$	$9 \leftarrow 9$	12 815.276	12 815.579	-0.001
		$8 \leftarrow 8$	12 816.302		
		$7 \leftarrow 7$	12 815.144		
	$0 \leftarrow 1$	$9 \leftarrow 9$	12 815.221	12 815.525	-0.002
		$8 \leftarrow 8$	12 816.248		
		$7 \leftarrow 7$	12 815.089		
$9_{19} \leftarrow 9_{09}$	$1 \leftarrow 0$	$10 \leftarrow 10$	12 322.745	12 323.040	0.003
		$9 \leftarrow 9$	12 323.742		
		$8 \leftarrow 8$	12 322.633		
	$0 \leftarrow 1$	$10 \leftarrow 10$	12 322.670	12 322.985	0.002
		$9 \leftarrow 9$	12 323.688		
		$8 \leftarrow 8$	12 322.581		
$10_{110} \leftarrow 10_{010}$	$1 \leftarrow 0$	$11 \leftarrow 11$	11 794.981	11 795.274	0.000
		$10 \leftarrow 10$	11 795.952		
		$9 \leftarrow 9$	11 794.882		
	$0 \leftarrow 1$	$11 \leftarrow 11$	11 794.926	11 795.218	-0.001
		$10 \leftarrow 10$	11 795.898		
		$9 \leftarrow 9$	11 794.827		
$11_{111} \leftarrow 11_{011}$	$1 \leftarrow 0$	$12 \leftarrow 12$	11 237.834	11 238.115	0.003
		$11 \leftarrow 11$	11 238.768		
		$10 \leftarrow 10$	11 237.749		
	$0 \leftarrow 1$	$12 \leftarrow 12$	11 237.780	11 238.059	0.002
		$11 \leftarrow 11$	11 238.712		
		$10 \leftarrow 10$	11 237.691		

Table 1 (continued)

$J_{K_+K_-} \leftarrow J'_{K'_+K'_-}$	$v \leftarrow v'$	$F \leftarrow F'$	ν_{obs}	ν_c	δ_c
$12_{112} \leftarrow 12_{012}$	$1 \leftarrow 0$	$13 \leftarrow 13$	10 657.434	10 657.709	0.002
		$12 \leftarrow 12$	10 658.331		
		$11 \leftarrow 11$	10 657.359		
	$0 \leftarrow 1$	$13 \leftarrow 13$	10 657.379	10 657.652	0.001
		$12 \leftarrow 12$	10 658.274		
$13_{113} \leftarrow 13_{013}$	$1 \leftarrow 0$	$14 \leftarrow 14$	10 060.178	10 060.437	-0.001
		$13 \leftarrow 13$	10 061.030		
		$12 \leftarrow 12$	10 060.116		
	$0 \leftarrow 1$	$14 \leftarrow 14$	10 060.116	10 060.382	0.000
		$13 \leftarrow 13$	10 060.974		
$14_{114} \leftarrow 14_{014}$	$1 \leftarrow 0$	$15 \leftarrow 15$	9 452.531	9 452.780	0.000
		$14 \leftarrow 14$	9 453.340		
		$13 \leftarrow 13$	9 452.472		
	$0 \leftarrow 1$	$15 \leftarrow 15$	9 452.472	9 452.722	-0.002
		$14 \leftarrow 14$	9 453.280		
$15_{115} \leftarrow 15_{015}$	$1 \leftarrow 0$	$16 \leftarrow 16$	8 840.924	8 841.159	-0.002
		$15 \leftarrow 15$	8 841.686		
		$14 \leftarrow 14$	8 840.869		
	$0 \leftarrow 1$	$16 \leftarrow 16$	8 840.869	8 841.104	0.001
		$15 \leftarrow 15$	8 841.629		
$16_{116} \leftarrow 16_{016}$	$1 \leftarrow 0$	$17 \leftarrow 17$	8 231.587	8 231.808	0.001
		$16 \leftarrow 16$	8 232.297		
		$15 \leftarrow 15$	8 231.532		
	$0 \leftarrow 1$	$17 \leftarrow 17$	8 231.532	8 231.753	0.004
		$16 \leftarrow 16$	8 232.240		
$16_{215} \leftarrow 16_{115}$	$1 \leftarrow 0$	$17 \leftarrow 17$	36 558.829	36 559.177	-0.004
		$16 \leftarrow 16$	36 660.021		
		$15 \leftarrow 15$	36 558.908		
	$0 \leftarrow 1$	$17 \leftarrow 17$	36 558.744	36 559.092	0.001
		$16 \leftarrow 16$	36 559.934		
$17_{117} \leftarrow 17_{017}$	$1 \leftarrow 0$	$18 \leftarrow 18$	7 630.393	7 630.598	-0.002
		$17 \leftarrow 17$	7 631.056		
		$16 \leftarrow 16$	7 630.354		
	$0 \leftarrow 1$	$18 \leftarrow 18$	7 630.334	7 630.540	-0.002
		$17 \leftarrow 17$	7 630.998		
$18_{118} \leftarrow 18_{018}$	$1 \leftarrow 0$	$19 \leftarrow 19$	7 042.741	7 042.931	-0.002
		$18 \leftarrow 18$	7 043.359		
		$17 \leftarrow 17$	7 042.708		
	$0 \leftarrow 1$	$19 \leftarrow 19$	7 042.682	7 042.873	-0.001
		$18 \leftarrow 18$	7 043.298		
$19_{119} \leftarrow 19_{019}$	$1 \leftarrow 0$	$20 \leftarrow 20$	6 473.417	6 473.592	0.000
		$19 \leftarrow 19$	6 473.983		
		$18 \leftarrow 18$	6 473.386		
	$0 \leftarrow 1$	$20 \leftarrow 20$	6 473.358	6 473.533	-0.001
		$19 \leftarrow 19$	6 473.923		
$19_{218} \leftarrow 19_{118}$	$1 \leftarrow 0$	$20 \leftarrow 20$	33 265.585	33 625.922	0.002
		$19 \leftarrow 19$	33 626.671		
		$18 \leftarrow 18$	33 625.521		
	$0 \leftarrow 1$	$20 \leftarrow 20$	33 625.486	33 625.827	0.006
		$19 \leftarrow 19$	33 626.578		
		$18 \leftarrow 18$	33 625.430		

Table 1 (continued)

$J_{K_-K_+} \leftarrow J'_{K'_-K'_+}$	$v \leftarrow v'$	$F \leftarrow F'$	ν_{obs}	ν_c	δ_c
$20_{120} \leftarrow 20_{020}$	1 $\leftarrow$ 0	21 $\leftarrow$ 21	5 926.508	5 926.668	0.000
		20 $\leftarrow$ 20	5 927.023		
		19 $\leftarrow$ 19	5 926.481		
		21 $\leftarrow$ 21	5 926.449		
$20_{219} \leftarrow 20_{119}$	0 $\leftarrow$ 1	20 $\leftarrow$ 20	5 926.965	5 926.608	0.002
		19 $\leftarrow$ 19	5 926.422		
		21 $\leftarrow$ 21	32 538.124		
		20 $\leftarrow$ 20	32 539.191		
$20_{219} \leftarrow 20_{119}$	1 $\leftarrow$ 0	19 $\leftarrow$ 19	32 538.071	32 538.461	0.001
		21 $\leftarrow$ 21	32 538.028		
		20 $\leftarrow$ 20	32 539.097		
		19 $\leftarrow$ 19	32 537.970		
$21_{121} \leftarrow 21_{021}$	0 $\leftarrow$ 1	22 $\leftarrow$ 22	5 405.340	5 405.485	0.001
		21 $\leftarrow$ 21	5 405.810		
		20 $\leftarrow$ 20	5 405.317		
		22 $\leftarrow$ 22	5 405.281		
$21_{121} \leftarrow 21_{021}$	1 $\leftarrow$ 0	21 $\leftarrow$ 21	5 405.752	5 405.426	0.000
		20 $\leftarrow$ 20	5 405.259		
		23 $\leftarrow$ 23	4 912.464		
		22 $\leftarrow$ 22	4 912.888		
$22_{121} \leftarrow 22_{021}$	0 $\leftarrow$ 1	21 $\leftarrow$ 21	4 912.444	4 912.595	0.000
		23 $\leftarrow$ 23	4 912.406		
		22 $\leftarrow$ 22	4 912.830		
		21 $\leftarrow$ 21	4 912.386		
$22_{221} \leftarrow 22_{121}$	1 $\leftarrow$ 0	23 $\leftarrow$ 23	30 269.910	30 270.237	-0.008
		22 $\leftarrow$ 22	30 270.959		
		21 $\leftarrow$ 21	30 269.862		
		23 $\leftarrow$ 23	30 269.806		
$22_{221} \leftarrow 22_{121}$	0 $\leftarrow$ 1	22 $\leftarrow$ 22	30 270.856	30 270.133	-0.006
		21 $\leftarrow$ 21	30 269.753		
		25 $\leftarrow$ 25	27 904.838		
		24 $\leftarrow$ 24	27 905.842		
$24_{223} \leftarrow 24_{123}$	1 $\leftarrow$ 0	23 $\leftarrow$ 23	27 904.769	27 905.152	0.003
		25 $\leftarrow$ 25	27 904.735		
		24 $\leftarrow$ 24	27 905.732		
		23 $\leftarrow$ 23	27 904.692		
$24_{223} \leftarrow 24_{123}$	0 $\leftarrow$ 1	26 $\leftarrow$ 26	26 697.339	26 697.644	0.002
		25 $\leftarrow$ 25	26 698.315		
		24 $\leftarrow$ 24	26 697.296		
		26 $\leftarrow$ 26	26 697.225		
$25_{224} \leftarrow 25_{124}$	1 $\leftarrow$ 0	25 $\leftarrow$ 25	26 698.202	26 697.531	0.004
		24 $\leftarrow$ 24	26 697.183		
		27 $\leftarrow$ 27	25 479.733		
		26 $\leftarrow$ 26	25 480.689		
$26_{225} \leftarrow 25_{125}$	0 $\leftarrow$ 1	25 $\leftarrow$ 25	25 479.695	25 480.031	0.003
		27 $\leftarrow$ 27	25 479.619		
		26 $\leftarrow$ 26	25 480.572		
		25 $\leftarrow$ 25	25 479.580		
$26_{225} \leftarrow 25_{125}$	1 $\leftarrow$ 0	28 $\leftarrow$ 28	24 257.192	24 257.481	0.001
		27 $\leftarrow$ 27	24 257.156		
		26 $\leftarrow$ 26	24 258.119		
		28 $\leftarrow$ 28	24 257.071		
$27_{226} \leftarrow 27_{126}$	0 $\leftarrow$ 1	27 $\leftarrow$ 27	24 257.035	24 257.360	-0.001
		26 $\leftarrow$ 26	24 257.997		
		29 $\leftarrow$ 29	23 035.009		
		28 $\leftarrow$ 28	23 035.903		
$28_{227} \leftarrow 28_{127}$	1 $\leftarrow$ 0	27 $\leftarrow$ 27	23 034.977	23 035.288	-0.001
		29 $\leftarrow$ 29	23 034.881		
		28 $\leftarrow$ 28	23 035.779		
		27 $\leftarrow$ 27	23 034.847		

Table 1 (continued)

$J_{K_-K_+} \leftarrow J'_{K'_-K'_+}$	$v \leftarrow v'$	$F \leftarrow F'$	ν_{obs}	ν_c	δ_c
$29_{228} \leftarrow 29_{128}$	1 $\leftarrow$ 0	30 $\leftarrow$ 30	21 818.558	21 818.824	-0.002
		29 $\leftarrow$ 29	21 819.418		
		28 $\leftarrow$ 28	21 818.525		
		30 $\leftarrow$ 30	21 818.419		
$29_{228} \leftarrow 29_{128}$	0 $\leftarrow$ 1	29 $\leftarrow$ 29	21 819.285	21 818.689	0.002
		28 $\leftarrow$ 28	21 818.388		
		31 $\leftarrow$ 31	20 613.203		
		30 $\leftarrow$ 30	20 614.040		
$30_{229} \leftarrow 30_{129}$	1 $\leftarrow$ 0	29 $\leftarrow$ 29	20 613.174	20 613.460	-0.002
		31 $\leftarrow$ 31	20 613.065		
		30 $\leftarrow$ 30	20 613.903		
		29 $\leftarrow$ 29	20 613.034		

constants from [3]. Since they are determined with sufficient accuracy, no effort was made to improve them further.

Theoretical Background

To fit the rotation-torsion interaction we assumed the molecule to be rigid with exception of the large amplitude internal torsion around the C–O bond axis. In Fig. 2 one can see that this bond axis is nearly parallel to the a -principal inertia axis. To simplify the setup of the Hamiltonian we made the approximation that the torsional angular momentum couples with the a -component P_a of the total angular momentum only. It is then possible to fit the spectra of the hypothetical center frequencies to a Hamiltonian [1] in the so called reduced axis system. The potential function of the torsion is a double minimum potential shown in Figure 3. The Hamiltonian in a II' -representation ($a=y$, $b=z$, $c=x$) can be written as follows:

$$\hat{H} = \begin{pmatrix} \hat{H}_{00} & \hat{H}_{01} \\ \hat{H}_{01} & \hat{H}_{11} \end{pmatrix}, \quad (1a)$$

$$\hat{H}_{00} = A_0 \hat{P}_a^2 + B_0 \hat{P}_b^2 + C_0 \hat{P}_c^2 + \hat{H}_{cd00}, \quad (1b)$$

$$\hat{H}_{11} = A_1 \hat{P}_a^2 + B_1 \hat{P}_b^2 + C_1 \hat{P}_c^2 + \hat{H}_{cd11} + \Delta E_{01}, \quad (1c)$$

$$\hat{H}_{01} = F_{01} (\hat{P}_b \hat{P}_c + \hat{P}_c \hat{P}_b). \quad (1d)$$

$A_0, B_0, C_0, A_1, B_1, C_1$: rotational constants in the torsional states $v=0, 1$, respectively,

$\hat{H}_{cd}$: Hamiltonian of the centrifugal distortion up to sixth order according to Watson's A reduction,

ΔE_0 : energy difference of the two torsional states $v=0$ and $v=1$ (see Fig. 3),

F_{01} : fit parameter of the rotation-torsion interaction.

Fig. 2. Trans-gauche ethylnitrite in a projection on the a, b -principal inertia axis plane.

Fig. 3. Potential energy function of the symmetric double minimum potential. Q : torsional coordinate, V : potential energy.

Fig. 4. Some energy levels and possible transitions of trans-gauche ethylnitrite.

Table 2. Rotational and centrifugal distortion constants written in the notation of sums and differences explained in the text. A, B, C : rotational constants, $\Delta_J, \Delta_{JK}, \Delta_K, \delta_J, \delta_K, \Phi_J, \Phi_{JK}, \Phi_{KJ}, \Phi_K, \phi_J, \phi_{JK}, \phi_K$: fourth and sixth order centrifugal distortion constants according to Watson's A-reduction, rotation-torsion interaction constants $\Delta E_{01}, F_{01}$; explanation see text, α : asymmetry parameter, σ : standard deviation of the fit, standard errors in brackets, $\Delta \bar{\nu}_{\text{exp}}$: mean experimental torsion splitting, largest correlation coefficient: $(|\Delta_J, \Delta_K|) = -0.992$.

A	17 639.500(10) MHz	Φ_{KJ}	$-1.14(30)$ kHz
B	2 745.031 (6) MHz	Φ_K	$0.55(17)$ kHz
C	2 620.852 (5) MHz	ϕ_J	$43.8 (52)$ Hz
Δ_J	$628.4 (29)$ kHz	ϕ_{JK}	$-279. (71)$ Hz
Δ_{JK}	$-1 979.2 (80)$ kHz	ϕ_K	$271. (83)$ Hz
Δ_K	$1 357.0 (48)$ kHz	ΔE_{01}	$24.8 (8)$ kHz
δ_J	$-313.7 (15)$ kHz	F_{01}	$7.2 (18)$ kHz
δ_K	$673.7 (30)$ kHz	ΔC	$12. (2)$ Hz
Φ_J	$-92. (11)$ Hz	ΔB	$54. (6)$ Hz
Φ_{JK}	$0.683(15)$ kHz	$\Delta(\Delta_K)$	$0.007(9)$ Hz
σ :	5 kHz	$\Delta \bar{\nu}_{\text{exp}}$:	77 kHz

We assume that only the first two torsional states ($v=0, 1$ in Fig. 3) take part in the rotation-torsion interaction. The Hamiltonian (1 b), (1 c) includes the usual centrifugal distortion $\hat{H}_{cd}$ according to Watson [12]. This implies that the rigidity for vibrational degrees of freedom has been lifted by allowing small amplitude vibrations.

Only a short sketch of the development of this Hamiltonian is outlined in [11]. We therefore performed a careful step by step development of the Hamiltonian and confirmed especially that the transformation from the principal axis system of inertia to the reduced axis system is in fact a contact transformation. That means that the angular momenta components in the reduced axis system obey the normal commutation relations of quantum mechanical angular momenta and can be treated in the usual manner. Details of these rather extended considerations are given in [13].

The c -dipole moment μ_c is an odd function of the C–O torsional angle, hence c -type transitions connect the $v=0$ and $v=1$ torsional states and show a splitting of approximately twice the energy difference ΔE_{01} (see Figure 4).

The fit of the measured transitions to the Hamiltonian was carried out with a modified version of the program MALON*.

* Original written by L. Halonen, P. H. Turner, and J. Randell.

Results and Discussion

From the splittings of the *c*-type transitions (ca. 45–140 kHz) one expects the torsional energy difference ΔE_{01} to be in the range between 20 and 70 kHz. This small difference entails that the rotational and centrifugal distortion constants for both torsional states are nearly equal. The following notation is employed. For example:

$$A = \frac{A_0 + A_1}{2}, \quad \Delta A = \frac{A_0 - A_1}{2}. \quad (2)$$

When performing a centrifugal distortion analysis according to Watson up to sixth order, we have 15 independent rotational and centrifugal distortion constants for each torsional state, or, with the just given notation, 15 sums and 15 differences of them. In addition we must fit ΔE_{01} and F_{01} . Because we could not fit 32 parameters to 68 transitions independently and simultaneously, some fixing of common rotational

and centrifugal distortion constants for the two torsional states was necessary. Therefore a first fit was carried out with all differences of constants fixed to zero. We then tried to improve the reproduction of the measured spectrum with different combinations of differences allowed to be nonzero and included in the fit. The best reproduction was achieved with inclusion of ΔB_v , ΔC_v , and $\Delta(\Delta_K)_v$. The results are summarized in Table 2. One can see from this Table that the energy difference ΔE_{01} is only 24.8(8) kHz. The high resolution of MWFT spectroscopy was necessary to determine such a small effect with sufficient accuracy.

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