Investigation of the Microwave Spectrum of Cyclopropyl Isocyanate. An Example for the Failure of Centrifugal Distortion Theory

C. Heldmann and H. Dreizler
Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

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The vibrational ground state microwave spectrum of cyclopropyl isocyanate was investigated in the region from 8.4 to 40 GHz by microwave Fourier transform (MWFT) spectroscopy. The quadrupole hyperfine structure was resolved and assigned. The quadrupole coupling constants are given. With respect to the data given in the literature up to now, this work led to a more profound description of the pure rotational spectrum. Furthermore, some interesting and surprising results concerning the effect of centrifugal distortion are presented. Compared to hitherto existing investigations, these results indicate a more complicated conformational behaviour of cyclopropyl isocyanate.

Introduction

The first investigations of cyclopropyl isocyanate in 1988 by microwave, infrared and Raman spectroscopy were carried out by Durig, Berry and Wurrey [1]. They presented data about the conformational stability, structure, dipole moment, as well as the vibrational assignment of cyclopropyl isocyanate. From known structural parameters of cyclopropyl isothiocyanate [2], Durig et al. evaluated sets of rotational constants for various assumed conformers and compared them with the rotational constants obtained from the assignment of the microwave spectrum in the region from 18.5 to 40 GHz. The cis and trans conformation corresponded best with the observed values.

The results of our reinvestigation, and in particular the failure of the centrifugal distortion analysis, indicate a more complicated conformational behaviour of cyclopropyl isocyanate. Especially, there are some doubts about the existence of a cis conformation. Thus, the expression "cis" is set in quotation marks in this paper.

Another important item concerning this investigation is the resolution and assignment of the quadrupole hyperfine structure of the spectrum of cyclopropyl isocyanate since no quadrupole coupling constants were determined up to now.

Reprint requests to Prof. Dr. H. Dreizler, Institut für Physikalische Chemie der Universität Kiel, Ludewig-Meyn-Str. 8, D-2300 Kiel.

Experimental Methods

Cyclopropyl isocyanate was prepared according to a method of Kricheldorf and Regel [3, 4] by a two-step procedure. In the first step dichloro diphenyl silane **1** (Aldrich) reacts with sodium azide in quinoline to yield diphenyl diazido silane **2**:

$$\underset{\mathbf{1}}{(C_6H_5)_2SiCl_2} + 2\,NaN_3 \xrightarrow[10\,h/120\,^\circ C]{\text{quinoline}} 2\,NaCl + \underset{\mathbf{2}}{(C_6H_5)_2Si(N_3)_2}\,.$$

The solvent was dried with calcium hydride for about two hours to remove traces of water. Cyclopropyl isocyanate **4** is formed by a reaction according to Curtius of cyclopropyl carbonyl chloride **3** (Aldrich) with the intermediate product **2**:

$$\underset{\mathbf{2}}{(C_6H_5)_2Si(N_3)_2} + \underset{\mathbf{3}}{2\,C_4H_5OCl} \xrightarrow[30\,min]{80\,^\circ C} \underset{\mathbf{4}}{2\,C_3H_5NCO} + 2\,N_2 + \underset{\mathbf{1}}{(C_6H_5)_2SiCl_2}\,.$$

The product **4** was purified under vacuum in a fraction column. The purity was checked by NMR and gaschromatography. No impurities were found with these methods. Cyclopropyl isocyanate is a colourless liquid (b.p.: 78–79 °C). The substance can immediately be identified by its irritating effect and provocation of lacrimation. The compound is sensitive to traces of water and was stored in a sample tube at −178 °C (liq. nitrogen).

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The investigations of cyclopropyl isocyanate were carried out with our standard microwave Fourier transform spectrometers combined with double-resonance techniques in the region from 8.4 to 40 GHz [5–9]. Sample pressures in the waveguide spectrometers were often <0.3 mTorr (<0.04 Pa) and temperatures were about -50 °C.

The transition frequencies of the multiplet components were evaluated by a least squares fit of the time domain signal [10] to avoid overlapping effects.

In addition, some results were obtained with a beam spectrometer described in [11]. For the measurements we used argon containing ca. 1% cyclopropyl isocyanate at a stagnation pressure of 380 Torr ($5 \cdot 10^4$ Pa).

Results and Analysis

Figure 1 shows the conformers trans and cis cyclopropyl isocyanate in their principal axes system. The notation cis/trans characterizes the relative orientation of the cyclopropyl frame and the N=C=O group with respect to the N–C bond. The trans conformer possesses an a, c-, the cis conformer an a, b-plane of symmetry. Furthermore, the polar NCO group lies approximately in the direction of the *a*-axis. Thus, a-type transitions should be the most intense ones in the microwave spectrum. The remaining components μ_c (trans) and μ_b ("cis") are expected to be smaller, whereas the μ_b (trans) and μ_c ("cis") components are zero because of symmetry properties. The microwave investigation of Durig et al. leads to the dipole moments: $\mu_a = 2.56(2)$ D, $\mu_c = 0.71(3)$ D, $\mu_b = 0$ D for the trans and $\mu_a = 2.720(4)$ D, $\mu_b = 0.17(1)$ D, $\mu_c = 0$ D for the "cis" isomer.

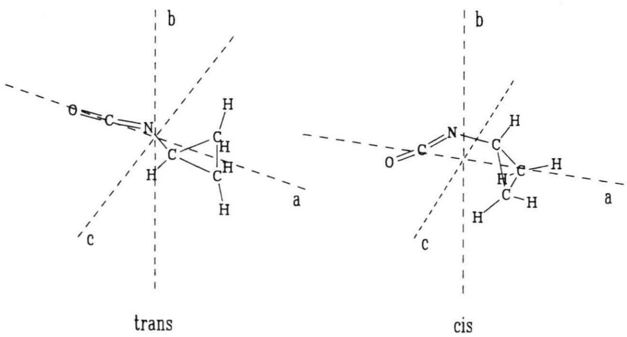

Fig. 1. Schematic diagram of trans and cis cyclopropyl isocyanate in their principal axes system. The molecular structure is take from the data in [1].

For the reason of intensity we tried to resolve and assign the quadrupole hyperfine structure of the a-type spectrum. We started with the trans conformer and obtained the quadrupole coupling constants $\chi^+ = (\chi_{bb} + \chi_{cc})$ by an iterative measurement and fit procedure of R-branch series with low J. $\chi^- = (\chi_{bb} - \chi_{cc})$ was not accessible, the observed transitions being nearly independent of this constant. Thus, we attempted to measure c-type transitions. Because of the large uncertainty of the rotational constant A [1], we used double-resonance techniques with the pump/signal combination in the V/Ku band. We found the Q-branch series $J_{1J}-J_{0J}$ with $J=3$ to $J=12$, which enabled us to gradually evaluate the A and χ^- constants. Subsequently, the value of χ^- was refined by measurements of the $J'-J=3-2$ transitions with a beam spectrometer using its high capability for resolution and sensitivity.

The investigation of the "cis" conformer was more difficult. At the beginning, no consistent assignment of the quadrupole hyperfine structure, even for the a-type spectrum, was possible. The A constant was not well determined by Durig et al., and there were no suitable double-resonance combinations which could simplify the search for the b-type transitions. After some unsuccessful attempts with conventional continuous-wave Stark modulation techniques and continuous-wave double-resonance methods in the Ku/K band (pump/signal) we refrained from measurements of b-type transitions and evaluation of the A constant. An explanation of this unsuccessful experimental result may be the lower theoretical line strength in comparison with a-type transitions (factor: ≈ 260).

Moreover, it was not possible to observe any transitions of "cis" cyclopropyl isocyanate in the beam spectrometer. Thus, the trans must be more stable than the "cis" conformation. This corresponds with the data of Durig et al. The impossibility of the observation of "cis"-transitions in a beam spectrometer leads to another fact: during the short time of cooling down in the molecular beam, the majority of the "cis-molecules" is apparently transformed into the trans conformation. Thus, the energy barrier should be low between the two conformational states.

On account of the above mentioned difficulties of the "cis" conformer we measured a-type R-branch J-series ($J_{K_- K'_+} - (J-1)_{K_- K_+}$) for the "cis" ($J=5, 6, 7, 8, 9$) and trans ($J=8, 9, 10, 11$) isomer in the K and V band. We started for each J value with the $K_-=0$ transition, then searched for the $K_-=1$ lines and so on. The transitions were assigned by means of their quadrupole hyperfine splittings. This is corroborated by Fig. 2 representing the $K_- = 3$ transitions for $J = 7$, 8, 9. The quadrupole hyperfine structure is not resolvable for $K_- = 0, 1$ transitions. In general, the splitting of the $K_- = 2$ transitions can be observed, but they are very small. Therefore, the extrapolation to larger splittings could lead to uncertainties and incorrect assignments. For this reason the typical pattern of the $K_- = 3$ lines (Fig. 2) is of particular importance for this investigation. The $K_- = 3$ lines are characterized by a small K-doublet splitting combined with a sufficient quadrupole hyperfine splitting ensuring a correct extrapolation. A comparison of Figs. 2a, 2b, and 2c indicates that according to theory the asymmetry splitting increases and the quadrupole splitting decreases with increasing J value. For all measured transitions a consistent assignment with respect to the fit of the quadrupole coupling constants could be evaluated in combination with double-resonance techniques.

Table 1 contains the evaluated values of the quadrupole coupling constants for trans and "cis" cyclopropyl isocyanate.

Carrying out the measurement procedure by following increasing K_- as described above, we obtained a very surprising result. The frequencies of the $K_- = 0$, 1, 2 transitions correspond (within the standard error) with the prediction of the spectrum including centrifugal distortion effects. The frequencies of the lines with

Table 1. Quadrupole coupling constants of trans and "cis" cyclopropyl isocyanate. Numbers in parentheses represent single standard errors in units of the last quoted digit.

trans cyclopropyl isocyanate	Correlation matrix	
	χ^+	χ^-
$\chi^+ = -2.6306(26)$ MHz	1.00	
$\chi^- = -0.1372(36)$ MHz	0.07	1.00
Standard deviation of the fit: 3 kHz	$\chi_{aa} = 2.6306(26)$ $\chi_{bb} = -1.3839(31)$ $\chi_{cc} = -1.2467(31)$	
"cis" cyclopropyl isocyanate	Correlation matrix	
	χ^+	χ^-
$\chi^+ = -2.5647(49)$ MHz	1.00	
$\chi^- = 0.440\ (10)$ MHz	0.00	1.00
Standard deviation of the fit: 5 kHz	$\chi_{aa} = 2.5647(49)$ $\chi_{bb} = -1.0624(75)$ $\chi_{cc} = -1.5022(75)$	

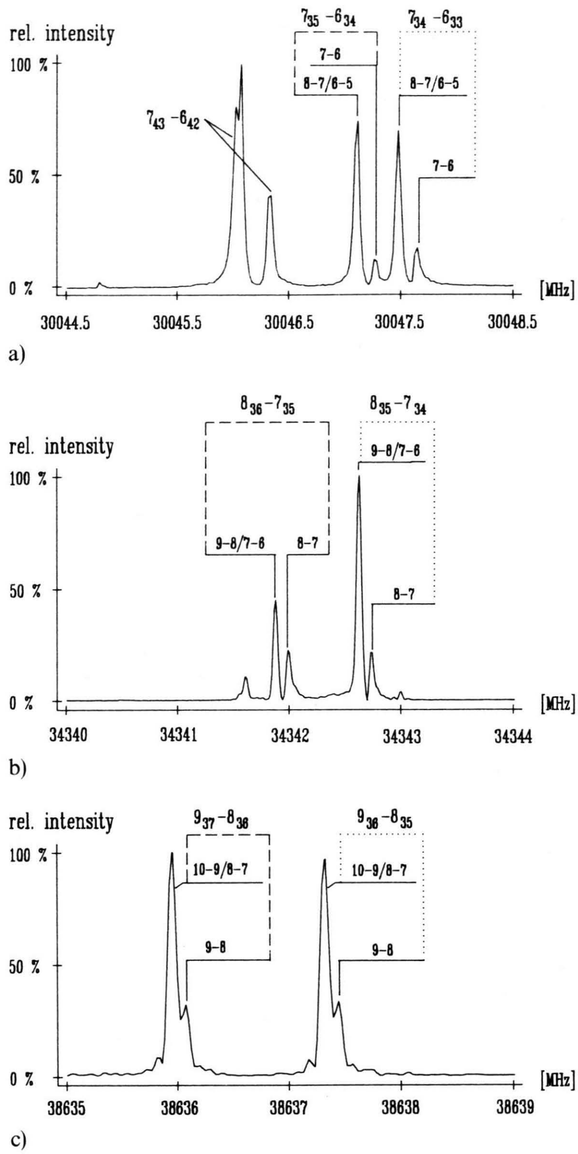

Fig. 2a–c. The $K_- = 3$ transition for $J = 7$, 8, 9. The $K_- = 3$ transitions are characterized by a small K-doublet splitting in combination with a quadrupole hyperfine splitting. This typical pattern was important for the confirmation of the assignment. a) Transitions $7_{35}-6_{34}$ and $7_{34}-6_{33}$ (and $7_{43}-6_{42}$): 0.2 mTorr, −50 °C, polarisation frequency: 30 048.5 MHz, sample interval: 10 ns, 1024 data points supplemented by 3072 zeros before Fourier transformation, 76 800 k experiment cycles (1 k = 1024). b) Transitions $8_{36}-7_{35}$ and $8_{35}-7_{34}$: 0.2 mTorr, −50 °C, polarisation frequeny: 34 343 MHz, sample interval: 10 ns, 1024 data points supplemented by 3072 zeros before Fourier transformation, 45 440 k experiment cycles. c) Transitions $9_{37}-8_{36}$ and $9_{36}-8_{35}$: 0.2 mTorr, −50 °C, polarisation frequency: 38 637 MHz, sample interval: 10 ns, 1024 data points supplemented by 3072 zeros before Fourier transformation, 16 600 k experiment cycles.

$K_- > 2$ showed considerable deviations from the prediction depending on the value of K_-. In general, the deviations increase with K_-, but there are also some differences in the K_--dependence of the deviations for the trans and "cis" conformer. Figures 3a and 3b present the dependence of the deviation $\Delta\nu$ (difference between the calculated central frequency and the observed value) on the quantum number K_- for different J values for the trans conformer. Figure 3a is based on a fit using Van Eijck's fourth order centrifugal distortion Hamiltonian, Fig. 3b implies terms of Van Eijck's sixth order Hamiltonian. In Fig. 3a transitions with $K_- > 3$ are weighted with the factor 1/1000 in the fit (which actually means: excluded from the fit) to get an acceptable standard deviation for the fit. This is indicated by the arrow ↓ in the picture. Figure 3a shows that the deviation $\Delta\nu$ gets large with increasing K_- (e.g. for $K_- = 10$: $\Delta\nu = 22$ MHz) but in a way indicating a functional continuity. $\Delta\nu$ is extremely decreased by consideration of the sixth order centrifugal distortion Hamiltonian (the $\Delta\nu$-axis is spread by the factor 2 in Figure 3b). In addition, it is possible to consider a greater number of transitions in the fit. Transitions with $K_- > 6$ are still weighted with the factor 1/1000. Hopefully, an eighth order centrifugal distortion Hamiltonian will eliminate the remaining deviations.

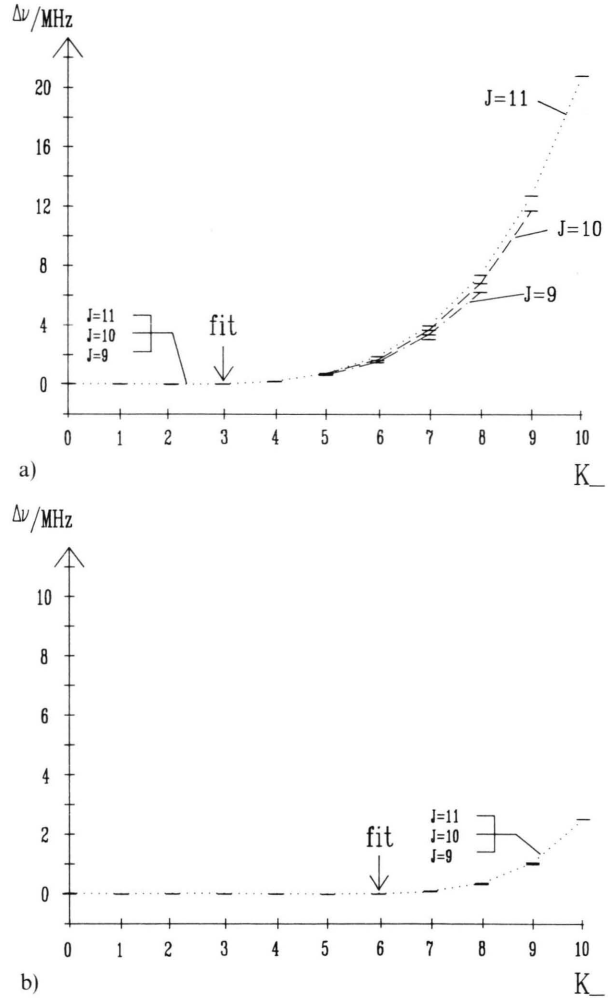

Fig. 3a and b. Deviations $\Delta\nu$ from a fit using Van Eijck's centrifugal distortion Hamiltonian for trans cyclopropyl isocyanate. The deviations strongly depend on the angular momentum projection quantum number K_- (in this figure only presented for $J = 9, 10, 11$). Table 3 contains the evaluated spectroscopic constants for the different fits. a) Deviations from a *fourth* order centrifugal distortion fit. Transitions with $K_- > 3$ are weighted with the factor 1/1000 in the fit. This is indicated by the arrow ↓. b) Deviations from a *sixth* order centrifugal distortion fit. Transitions with $K_- > 6$ are weighted with the factor 1/1000 in the fit. This is indicated by the arrow ↓. In comparison to a), the axis concerning $\Delta\nu$ is spread by the factor 2.

Table 2 contains all measured transition frequencies of the trans conformer including the quadrupole hyperfine structure, the (hypothetical) central frequency ν_0 and the calculated central frequencies resulting from a fourth ($^4\nu_0$) and sixth ($^6\nu_0$) order centrifugal distortion fit. The evaluated sets of the rotational as well as Van Eijck's centrifugal distortion constants for the different fit procedures (according to Figs. 3a and 3b) are given in Table 3.

The deviations from a Van Eijck fourth order centrifugal distortion fit for the "cis" isomer is illustrated by Figure 4. The fit includes all measured transition frequencies for K_- values up to $K_- = 2$. The relatively

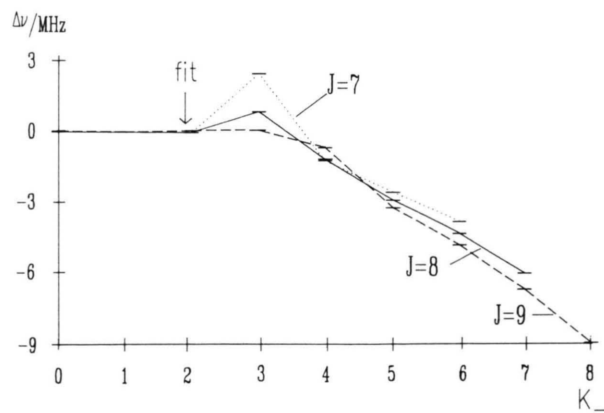

Fig. 4. Deviations $\Delta\nu$ from a fourth order centrifugal distortion fit in dependence on K_- for "cis" cyclopropyl isocyanate. Transitions with $K_- > 2$ are weighted by the factor 1/100. This is indicated by the arrow ↓.

Table 2. Measured transition frequencies ν_{obs} of trans cyclopropyl isocyanate including the quadrupole hyperfine splitting. The hyperfine components are characterized by their overall angular momentum quantum number $F-F'$. δ_{HFS}: quadrupole hyperfine splitting referred to the strongest component. ≪: not resolvable hyperfine components. n.r. not resolvable quadrupole hyperfine structure of the transition. $\Delta(\delta_{HFS})$: deviation of the experimental and calculated splitting. ν_0: hypothetical unsplit ("central") line frequency calculated with the quadrupole hyperfine splitting δ_{HFS} for each component. ν_0 is the arithmetic mean of these values. ${}^4\nu_0$: calculated (hypothetical) unsplit line frequencies using Van Eijck's fourth order centrifugal distortion Hamiltonian. This corresponds to Figure 3a. ${}^4\Delta\nu_0 = {}^4\nu_0 - \nu_0$. ${}^6\nu_0$: calculated (hypothetical) unsplit line frequencies using Van Eijck's sixth order centrifugal distortion Hamiltonian. This corresponds to Figure 3b. ${}^6\Delta\nu_0 = {}^6\nu_0 - \nu_0$. In addition, see Table 3 for the conditions of the centrifugal distortion fits. In the table caption it should be: $F-F'$.

$J\ K_-\ K_+$	$J'K_-'K_+'$	$F'-F$	ν_{obs} [MHz]	δ_{HFS} [MHZ]	$\Delta(\delta_{HFS})$ [kHz]	ν_0, ${}^4\nu_0$, ${}^6\nu_0$ [MHz]	${}^4\Delta\nu_0$, ${}^6\Delta\nu_0$ [MHz]
3 1 3	3 0 3	4-4	14987.550			14987.491	
		3-3	14987.310	0.240	2	14987.502	0.011
		2-2	14987.636	-0.086	1	14987.487	-0.004
4 1 4	4 0 4	5-5	14852.589			14852.540	
		4-4	14852.431	0.158	0	14852.559	0.019
		3-3	14852.624	-0.035	6	14852.547	0.007
5 1 5	5 0 5	6-6	14685.221			14685.187*)	
		4-4	≪	0.0	-	14685.178	0.009
		5-5	14685.102	0.119	5	14865.170	-0.017
6 1 6	6 0 6	7-7	14486.247			14486.221	
		5-5	≪	0.0	-	14486.225	0.004
		6-6	14486.158	0.089	0	14486.222	0.001
7 1 7	7 0 7	8-8	14256.767			14256.746*)	
		6-6	≪	0.0	-	14256.742	-0.004
		7-7	14256.692	0.075	2	14256.743	-0.003
8 1 8	8 0 8	9-9	13997.958			13997.938*)	
		7-7	≪	0.0	-	13997.943	0.005
		8-8	13997.901	0.057	-5	13997.948	0.010
9 1 9	9 0 9	10-10	13711.235			13711.222*)	
		8-8	≪	0.0	-	13711.215	-0.007
		9-9	13711.182	0.053	1	13711.223	0.001
10 1 10	10 0 10	11-11	13398.141			13398.126*)	
		9-9	≪	0.000	-	13398.116	-0.010
		10-10	13398.089	0.052	4	13398.125	-0.001
11 1 11	11 0 11	12-12	13060.385			13060.369*)	
		10-10	≪	0.000	-	13060.366	-0.003
		11-11	13060.339	0.046	2	13060.374	0.005
12 1 12	12 0 12	13-13	12699.864			12699.853	
		11-11	≪	0.000	-	13699.847	-0.006
		12-12	12699.823	0.041	1	13699.852	-0.001
18 2 17	18 1 17	19-19	39806.201			39806.191	
		17-17	≪	0.000	-	39806.196	0.005
		18-18	39806.151	0.050	0	39806.196	0.005
19 2 18	19 1 18	20-20	39180.859			39180.850	
		18-18	≪	0.000	-	39180.849	-0.001
		19-19	39180.813	0.046	-1	39180.849	-0.001
20 2 19	20 1 19	21-21	38526.439			38526.430	
		19-19	≪	0.000	-	38526.426	-0.004
		20-20	38526.394	0.045	0	38526.426	-0.004
21 2 20	21 1 20	22-22	37843.673			37843.664	
		20-20	≪	0.000	-	37843.663	-0.001
		21-21	37843.632	0.041	-2	37843.662	-0.002
22 2 21	22 1 21	23-23	37133.379			37133.370	
		21-21	≪	0.000	-	37133.370	0.000
		22-22	37133.339	0.040	0	37133.369	-0.001
23 2 22	23 1 22	24-24	36396.441			36396.432	
		22-22	≪	0.000	-	36396.434	0.002
		23-23	36396.403	0.038	-1	36396.436	0.004

$J\ K_-\ K_+$	$J'K_-'K_+'$	$F'-F$	ν_{obs} [MHz]	δ_{HFS} [MHZ]	$\Delta(\delta_{HFS})$ [kHz]	ν_0, ${}^4\nu_0$, ${}^6\nu_0$ [MHz]	${}^4\Delta\nu_0$, ${}^6\Delta\nu_0$ [MHz]
3 0 3	2 0 2	4-3	10500.354			10500.386	
		3-2	10500.384	-0.030	1	10500.386	-0.000
		2-1	10500.518	-0.164	-1	10500.384	-0.002
		3-3	10501.231	-0.877	0		
8 0 8	7 0 7		n. r.			27983.938	
						27938.946	0.008
						27938.934	-0.004
9 0 9	8 0 8		n. r.			31476.005	
						31476.017	0.012
						31475.999	-0.006
11 0 11	10 0 10		n. r.			38453.698	
						38453.724	0.026
						38453.690	-0.008
3 1 2	2 1 1	4-3	10603.053			10603.123	
		3-2	10603.289	-0.236	0	10603.120	-0.003
		2-1	10603.062	-0.009	0	10603.122	-0.001
		3-3	10603.732	-0.679	2		
		2-2	10602.371	0.682	2		
3 1 3	2 1 2	4-3	10398.506			10398.574	
		3-2	10398.739	-0.234	0	10398.573	-0.001
		3-3	10399.141	-0.635	0	10398.575	0.001
		2-2	10397.881	0.624	2		
8 1 7	7 1 6		n. r.			28270.413	
						28270.409	-0.004
						28270.416	0.003
8 1 8	7 1 7		n. r.			27725.142	
						27725.148	0.006
						27725.139	-0.003
9 1 8	8 1 7		n. r.			31802.606	
						31802.596	-0.010
						31802.605	-0.001
9 1 9	8 1 8		n. r.			31189.279	
						31189.290	0.011
						31189.274	-0.005
10 1 9	9 1 8		n. r.			35334.210	
						35334.199	-0.011
						35334.211	0.001
10 1 10	9 1 9		n. r.			34652.896	
						34652.916	0.020
						34652.891	-0.005
11 1 10	10 1 9		n. r.			38865.157	
						38865.147	-0.010
						38865.161	0.004
11 1 11	10 1 10		n. r.			38115.947	
						38115.974	0.027
						38115.940	-0.007
3 2 1	2 2 0	4-3	10500.783			10500.970	
		3-3	≪			10500.965	-0.005
		3-2	10501.628	-0.845	0	10500.969	-0.001
		2-2	≪				

Table 2 (continued)

$J\ K_-\ K_+$	$J'\ K_-'\ K_+'$	$F'-F$	ν_{obs} [MHz]	δ_{HFS} [MHz]	$\Delta(\delta_{HFS})$ [kHz]	ν_0, $^4\nu_0$, $^6\nu_0$' [MHz]	$^4\Delta\nu_0$, $^6\Delta\nu_0$' [MHz]
5 2 3	4 2 2	6-5	17504.050			17504.106	
		4-3	<<			17504.102	-0.004
		5-4	17504.240	-0.190	-2	17504.111	0.005
5 2 4	4 2 3	6-5	17499.480			17499.536	
		4-3	<<			17499.531	-0.005
		5-4	17499.671	-0.191	-3	17499.539	0.003
6 2 4	5 2 3	7-6	21006.951			21006.993	
		5-4	<<			21006.979	-0.014
		6-5	21007.069	-0.117	-6	21006.991	-0.002
6 2 5	5 2 4	7-6	20998.958			20998.992	
		5-4	<<			20998.981	-0.011
		6-5	20999.067	-0.109	2	20998.990	-0.002
8 2 6	7 2 5		n. r.			28016.292	
						28016.274	-0.018
						28016.293	0.001
8 2 7	7 2 6		n. r.			27997.106	
						27997.093	-0.013
						27997.105	-0.001
9 2 7	8 2 6		n. r.			31523.071	
						31523.056	-0.015
						31523.079	0.008
9 2 8	8 2 7		n. r.			31495.681	
						31495.672	-0.009
						31495.686	0.005
10 2 8	9 2 7		n. r.			35031.521	
						35031.495	-0.026
						35031.524	0.003
10 2 9	9 2 8		n. r.			34993.891	
						34993.878	-0.013
						34993.894	0.003
11 2 10	10 2 9		n. r.			38491.685	
						38491.669	-0.016
						38491.687	0.002
5 3 2	4 3 1	6-5	17498.080			17498.189	
		5-4	17498.487	-0.407	-2	17498.211	0.022
		4-3	17497.980	0.100	1	17498.192	0.003
8 3 5	7 3 4	9-8	27998.435			27998.472	
		7-6	<<			27998.491	0.019
		8-7	27998.542	-0.107	1	27998.474	0.002
8 3 6	7 3 5	9-8	27998.318			27998.357	
		7-6	<<			27998.371	0.014
		8-7	27998.428	-0.110	-2	27998.354	-0.003
9 3 6	8 3 5	10-9	31498.943			31498.965	
		8-7	<<			31498.983	0.018
		9-8	31499.014	-0.071	3	31498.970	0.005
9 3 7	8 3 6	10-9	31498.725			31498.746	
		8-7	<<			31498.763	0.017
		9-8	31498.796	-0.071	3	31498.750	0.040
10 3 7	9 3 6	11-10	34999.702			34999.720	
		9-8	<<			34999.728	0.008
		10-9	34999.756	-0.054	0	34999.723	0.003
10 3 8	9 3 7	11-10	34999.325			34999.343	
		9-8	<<			34999.352	0.009
		10-9	34999.379	-0.054	0	34999.346	0.003
11 3 8	10 3 7	12-11	38500.750			38500.763	
		10-9	<<			38500.764	0.001
		11-10	38500.790	-0.040	1	38500.768	0.005
11 3 9	10 3 8	12-11	38500.138			38500.153	
		10-9	<<			38500.153	-0.000
		11-10	38500.180	-0.042	-1	38500.156	0.003
5 4 2	4 4 1	6-5	17493.959			17494.131	
		5-4	17494.663	-0.704	5	17494.267	0.136
		4-3	17493.752	0.207	-5	17494.131	-0.000
8 4 4	7 4 3	9-8	27991.196			27991.248	
		8-7	27991.374	-0.178	1	27991.432	0.184
		7-6	27991.166	0.029	9	27991.244	-0.004
9 4 5	8 4 4	9-8	31490.550			31490.463**)	
		10-9	31490.422	0.129	2	31490.658	0.195
		8-7	31490.415	0.135	-2	31490.460	-0.003
10 4 6	9 4 5	11-10	34989.755			34989.789	
		9-8	<<			34989.988	0.199
		10-9	34989.853	-0.098	0	34989.787	-0.002
11 4 7	10 4 6	12-11	38489.209			38489.230	
		10-9	<<			38489.435	0.205
		11-10	38489.278	-0.069	2	38489.235	0.005
8 5 3	7 5 2	8-7	27982.994			27982.798**)	
		9-8	27982.718	0.276	0	27983.413	0.615
		7-6	27982.678	0.316	-1	27983.791	-0.007
9 5 4	8 5 3	9-8	31480.964			31480.827**)	
		10-9	31480.768	0.196	0	31481.489	0.662
		8-7	31480.744	0.220	-1	31480.814	-0.013
10 5 5	9 5 4	10-9	34979.006			34978.907**)	
		11-10	34978.864	0.142	-2	34979.619	0.712
		9-8	34978.846	0.160	4	34978.899	-0.008
11 5 6	10 5 5	12-11	38477.024			38477.062	
		10-9	<<			38477.807	0.745
		11-10	38477.137	-0.113	-5	38477.052	-0.010
7 6 1	6 6 0	8-7	24475.666			24475.838	
		7-6	24476.260	-0.594	-9	24477.159	1.321
		6-5	24475.551	0.115	-5	24475.841	0.003
8 6 2	7 6 1	9-8	27972.357			27972.470	
		8-7	27972.752	-0.395	0	27973.953	1.483
		7-6	27972.292	0.065	-1	27972.476	0.006
9 6 3	8 6 2	9-8	31469.337			31469.140**)	
		10-9	31469.060	0.277	-2	31470.771	1.631
		8-7	31469.021	0.316	-1	31469.145	0.005
11 6 5	10 6 4	11-10	38462.708			38462.600**)	
		12-11	38462.550	0.158	3	38464.486	1.886
		10-9	38462.535	0.173	4	38462.604	0.004
8 7 1	7 7 0	9-8	27959.742			27959.893	
		8-7	27960.277	-0.535	0	27962.926	3.033
		7-6	27959.646	0.096	1	27959.972	0.079
9 7 2	8 7 1	10-9	31454.853			31454.961	
		9-8	31455.230	-0.377	2	31458.319	3.358
		8-7	31454.798	0.055	-1	31455.048	0.087
10 7 4	9 7 3	11-10	34949.983			34950.063	
		10-9	34950.258	-0.275	3	34953.723	3.660
		9-8	34949.949	0.034	-1	34950.151	0.088

Table 2 (continued)

J K_- K_+	J'K_-'K_+'	F'-F	ν_{obs} [MHz]	δ_{HFS} [MHZ]	$\Delta(\delta_{HFS})$ [kHz]	ν_0 / ${}^4\nu_0$ / ${}^6\nu_0$ [MHz]	${}^4\Delta\nu_0$ / ${}^6\Delta\nu_0$ [MHz]
11 7 4	10 7 3	12-11	38445.117			38445.182	
		11-10	38445.335	-0.218	-8	38449.138	3.956
		10-9	18445.090	0.027	5	38445.285	0.103
9 8 1	8 8 0	10-9	31437.716			31437.859	
		9-8	31438.210	-0.494	-1	31444.063	0.6204
		8-8	31437.639	0.077	1	31438.191	0.332
10 8 2	9 8 1	11-10	34930.946			34931.050	
		10-9	34931.305	-0.359	2	34937.847	6.797
		9-8	34930.892	0.054	6	34931.405	0.355
11 8 3	10 8 2	12-11	38424.196			38424.273	
		11-10	38424.464	-0.268	5	38431.630	7.357
		10-9	38424.158	0.038	7	38424.646	0.373
10 9 1	9 9 0	11-10	34908.105			34908.237	
		10-9	34908.560	-0.455	1	34919.940	11.703
		9-8	34908.041	0.064	0	34909.237	1.000
11 9 2	10 9 1	12-11	38399.090			38399.191	
		11-10	38399.433	-0.343	2	38411.902	12.711
		10-9	38399.047	0.043	0	38400.259	1.068
11 10 1	10 10 0	12-11	38369.023			38369.142	
		11-10	38369.448	-0.425	0	38389.924	20.782
		10-9	38368.968	0.055	2	38371.676	2.534

* The assignment was confirmed with the following double-resonance combinations:

Signal transition (Ku band)	Pump transition (V band)
5 1 5 − 5 0 5	6 1 5 − 5 0 5
7 1 7 − 7 0 7	8 0 8 − 7 0 7
8 1 8 − 8 0 8	9 1 9 − 8 1 8
	9 0 9 − 8 0 8
9 1 9 − 9 0 9	9 0 9 − 8 0 8
10 1 10 − 10 0 10	10 0 10 − 9 0 9
11 1 11 − 11 0 11	11 1 11 − 10 1 10

** δ_{HFS} is referred to the component with the largest hfs offset from ν_0.

large deviation for the $J'-J=2-1$ transitions may be due to the fact that K_- reaches the value $K_{-,max}$ (see Table 4). Transitions with $K_->2$ were weighted with 1/100. It is remarkable to notice that the $K_-=3$ transitions show a positive deviation whereas transitions with $K_->3$ are characterized by negative $\Delta\nu$'s. Thus, no obvious functional continuity can be constructed, in contrast to the trans conformer. A centrifugal distortion fit using Van Eijck's sixth order Hamiltonian yields only a gradual improvement.

Figure 5 leads to a slightly modified result. In this case, transitions with $K_-=2$, 3, 4 were weighted with the factor 1/1000 in a sixth order centrifugal distortion fit (transitions with $K_->4$ were fully included in the fit). The small deviations for transitions with K_- values $K_-<2$ and $K_->4$ suggest that only a few transitions (which means in particular the corresponding energy levels) are perturbed by some effects which have to be discussed hereafter. The frequency data of "cis" cyclopropyl isocyanate are given in Table 4. Table 4 is constructed in the same way as Table 2. ${}^4\nu_0$ corresponds

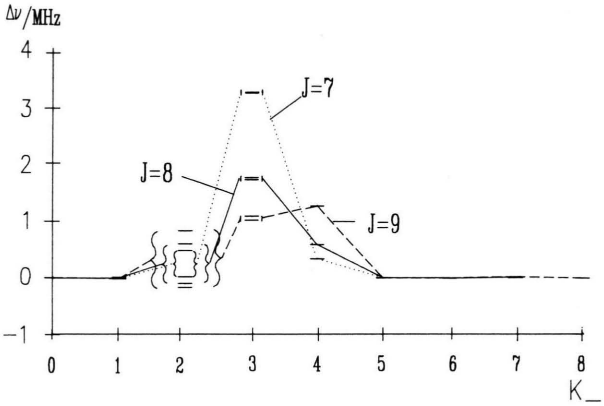

Fig. 5. Deviations $\Delta\nu$ from a sixth order centrifugal distortion fit in dependence on K_- for "cis" cyclopropyl isocyanate. Transitions with $K_-=2$, 3, 4 are weighted with the factor 1/1000. The braces indicate the related K_--doublet transitions for each J.

Table 3. Comparison of the rotational and Van Eijck's centrifugal distortion constants of trans cyclopropyl isocyanate for a fourth and sixth order centrifugal distortion fit. The conditions of the fit are given at the bottom of the Table. Numbers in parentheses represent single standard errors in units of the last quoted digit.

	Fourth order		Sixth order	
A	16 941.889(8)	MHz	16 941.865(3)	MHz
B	1 784.3121(6)	MHz	1 784.3117(2)	MHz
C	1 716.1278(6)	MHz	1 716.1281(3)	MHz
$\tilde{D}_J$	0.153(2)	kHz	0.159(1)	kHz
$\tilde{D}_{JK}$	52.28(3)	kHz	51.72(2)	kHz
$\tilde{D}_K$	−6(3)	kHz	−7(1)	kHz
$\tilde{\delta}_J$	0.027(1)	kHz	0.0176(4)	kHz
$\tilde{R}_6$	−0.019(1)	kHz	−0.0179(4)	kHz
$\tilde{H}_{JK}$	–		1.80(7)	Hz
$\tilde{H}_{KJ}$	–		−92.8(3)	Hz
Weight of the transitions in the fit:				
	$K_->3$: 1/1000		$K_->7$: 1/1000	
Standard deviation of the fit:				
	14 kHz		5 kHz	
Highest correlation:				
	$\tilde{R}_6/\tilde{\delta}_J$: 0.982		$\tilde{R}_6/\tilde{\delta}_J$: 0.854	

Table 4. Measured transition frequencies ν_{obs} of "cis" cyclopropyl isocyanate including the quadrupole hyperfine splitting. The hyperfine components are characterized by their overall angular momentum quantum number $F-F'$. δ_{HFS}, $\Delta(\delta_{HFS})$, $\ll$, n.r., ν_0: see Table 2. $^4\nu_0$: calculated (hypothetical) unsplit line frequencies using Van Eijck's fourth order centrifugal distortion Hamiltonian. This corresponds to Figure 4. $^4\Delta\nu_0 = {}^4\nu_0 - \nu_0$. $^6\nu_0'$: calculated (hypothetical) unsplit line frequencies using Van Eijck's sixth order centrifugal distortion Hamiltonian. This corresponds to Figure 5. $^6\Delta\nu_0' = {}^6\nu_0' - \nu_0$. In addition, see Table 5 for the conditions of the centrifugal distortion fits. In the table caption it should be: $F-F'$.

J	K_-	K_+	J'	K_-'	K_+'	F'-F	ν_{obs} [MHz]	δ_{HFS} [MHz]	$\Delta(\delta_{HFS})$ [kHz]	ν_0, $^4\nu_0$, $^6\nu_0'$ [MHz]	$^4\Delta\nu_0$, $^6\Delta\nu_0'$ [MHz]
4	0	4	3	0	3	5-4	17165.518			17165.539	
						4-3	<<			17165.557	0.018
						3-2	17165.595	-0.077	-3	17165.538	-0.001
5	0	5	4	0	4		n. r.			21452.073	
										21452.061	-0.012
										21452.040	-0.033
6	0	6	5	0	5		n. r.			25735.307	
										25735.327	0.020
										25735.307	0.000
7	0	7	6	0	6		n. r.			30014.721	
										30014.737	0.016
										30014.721	0.000
8	0	8	7	0	7		n. r.			34289.692	
										34289.701	0.009
										34289.691	-0.001
9	0	9	8	0	8		n. r.			38559.665	
										38559.668	0.003
										38559.669	0.004
2	1	1	1	1	0	3-2	8666.490			8666.640	
						2-1	8667.282	-0.792	0	8666.554	-0.086
						1-0	8665.609	0.881	15	8666.572	-0.068
						2-2	8666.839	-0.349	-7		
						1-1	8666.753	-0.263	-2		
2	1	2	1	1	1	3-2	8505.138			8505.296	
						2-1	8505.939	-0.801	1	8505.200	-0.096
						1-0	8504.393	0.745	-1	8505.216	-0.080
						2-2	8505.610	-0.472	11		
						1-1	8505.188	-0.050	1		
5	1	4	4	1	3		n. r.			21662.737	
										21662.734	-0.004
										21662.763	0.026
5	1	5	4	1	4		n. r.			21259.673	
										21259.672	-0.001
										21259.702	0.029
6	1	5	5	1	4		n. r.			25992.966	
										25992.963	-0.003
										25992.989	0.023
6	1	6	5	1	5		n. r.			25509.554	
										25509.541	-0.013
										25509.571	0.017
7	1	6	6	1	5		n. r.			30321.913	
										30321.901	-0.012
										30321.921	0.008
7	1	7	6	1	6		n. r.			29758.317	
										29758.313	-0.004
										29758.338	0.021
8	1	7	7	1	6		n. r.			34649.328	
										34649.315	-0.013
										34649.325	-0.003
8	1	8	7	1	7		n. r.			34005.844	
										34005.829	-0.015
										34005.841	-0.003
9	1	8	8	1	7		n. r.			38974.968	
										38974.958	-0.010
										38974.957	-0.011
9	1	9	8	1	8		n. r.			38251.947	
										38251.940	-0.007
										38251.931	-0.016
4	2	3	3	2	2	5-4	17169.993			17170.087	
						4-3	17170.344	-0.351	-1	17170.157	0.070
						3-2	17169.903	0.089	-1	17170.399	0.312
5	2	3	4	2	2	6-5	21473.667			21473.720	
						4-3	<<			21473.771	0.051
						5-4	21473.845	-0.178	3	21473.925	0.205
5	2	4	4	2	3	6-5	21461.446			21461.466	
						4-3	<<			21461.553	0.087
						5-4	21461.631	-0.185	1	21461.874	0.408
6	2	4	5	2	3	7-6	25773.505			25773.538	
						5-4	<<			25773.540	0.002
						6-5	25773.609	-0.104	3	25773.660	0.122
6	2	5	5	2	4	7-6	25752.157			25752.193	
						5-4	<<			25752.189	-0.004
						6-5	25752.268	-0.111	-2	25752.601	0.408
7	2	5	6	2	4	8-7	30076.016			30076.037	
						6-5	<<			30076.004	-0.033
						7-6	30076.085	-0.069	-1	30076.054	0.017
7	2	6	6	2	5	8-7	30041.929			30041.947	
						6-5	<<			30041.911	-0.036
						7-6	30041.993	-0.064	6	30042.430	0.483
8	2	6	7	2	5	9-8	34381.588			34381.600	
						7-6	<<			34381.561	-0.039
						8-7	34381.631	-0.043	-5	34381.500	-0.100
8	2	7	7	2	6	9-8	34330.606			34330.616	
						7-6	<<			34330.573	-0.043
						8-7	34330.646	-0.040	9	34331.216	0.600
9	2	7	8	2	6		n. r.			38690.518	
										38690.567	0.049
										38690.348	-0.169
9	2	8	8	2	7		n. r.			38617.978	
										38618.021	0.043
										38618.808	0.830
7	3	4	6	3	3	8-7	30047.452			30047.500	
						6-5	<<			30049.949	2.449
						7-6	30047.606	-0.154	-6	30050.771	3.271
7	3	5	6	3	4	8-7	30047.084			30047.131	
						6-5	<<			30049.576	2.445
						7-6	30047.235	-0.151	-3	30050.417	3.286
8	3	5	7	3	4	9-8	34342.632			34342.664	
						7-6	<<			34343.501	0.837
						8-7	34342.731	-0.099	1	34344.401	1.737

Table 4 (continued)

J	K_-	K_+	J'	K_-'	K_+'	F'-F	ν_{obs} [MHz]	δ_{HFS} [MHZ]	$\Delta(\delta_{HFS})$ [kHz]	ν_0, $^4\nu_0$, $^6\nu_0$ [MHz]	$^4\Delta\nu_0$, $^6\Delta\nu_0$ [MHz]
8	3	6	7	3	5	9-8	34341.884			34341.916	
						7-6	<<			34342.756	0.840
						8-7	34341.984	-0.100	0	34343.693	1.777
9	3	6	8	3	5	10-9	38637.307			38637.332	
						8-7	<<			38637.392	0.060
						9-8	38637.380	-0.073	-2	38638.352	1.020
9	3	7	8	3	6	10-9	38635.940			38635.964	
						8-7	<<			38636.029	0.065
						9-8	38636.011	-0.071	0	38637.056	1.092
6	4	2	5	4	1	7-6	25753.900			25754.011	
						6-5	25754.302	-0.402	2	25752.845	-1.166
						5-4	25753.815	0.085	-2	25754.227	0.216
7	4	3	6	4	2	8-7	30046.032			30046.109	
						7-6	30046.293	-0.261	-4	30044.865	-1.244
						6-5	30045.995	0.037	-3	30046.452	0.343
8	4	4	7	4	3	9-8	34337.958			34338.010	
						8-7	34338.130	-0.172	2	34336.828	-1.182
						7-6	34337.939	0.019	-1	34338.608	0.598
9	4	5	8	4	4	10-9	38629.364			38629.411	
						8-7	<<			38628.726	-0.685
						9-8	38629.496	-0.132	-9	38630.687	1.276
6	5	1	5	5	0	7-6	25751.173			25751.341	
						6-5	25751.797	-0.624	2	25749.124	-2.217
						5-4	25751.018	0.155	3	25751.350	0.009
7	5	2	6	5	1	8-7	30042.751			30042.863	
						7-6	30043.147	-0.396	2	30040.293	-2.570
						6-5	30042.674	0.077	2	30042.863	0.000
8	5	3	7	5	2	9-8	34334.124			34334.202	
						8-7	34334.390	-0.266	3	34331.301	-2.901
						7-6	34334.085	0.039	-1	34334.202	0.000
9	5	4	8	5	3	10-9	38625.285			38625.341	
						9-8	38625.471	-0.186	4	38622.122	-3.219
						8-7	38625.265	0.020	-2	38625.339	-0.002
7	6	1	6	6	0	8-7	30038.955			30039.113	
						7-6	30039.524	-0.569	1	30035.310	-3.803
						6-5	30038.839	0.116	-1	30039.106	-0.007
8	6	2	7	6	1	9-8	34329.642			34329.753	
						8-7	34330.030	-0.388	-3	34325.448	-4.305
						7-6	34329.578	0.064	0	34329.744	-0.009
9	6	3	8	6	2	10-9	38620.043			38620.123	
						9-8	38620.314	0.271	2	38615.336	-4.787
						8-7	38620.007	0.036	-1	38620.116	-0.007
8	7	1	7	7	0	9-8	34324.763			34324.909	
						8-7	34325.280	-0.517	5	34318.929	-5.980
						7-6	34324.671	0.092	-1	34324.913	0.004
9	7	2	8	7	1	10-9	38614.433			38614.537	
						9-8	38614.796	-0.363	6	38607.884	-6.653
						8-7	38614.374	0.059	4	38614.555	0.018
9	8	1	8	8	0	10-9	38608.359			38608.497	
						9-8	38608.836	-0.477	3	38599.576	-8.921
						8-7	38608.285	0.074	-1	38608.490	-0.007

Table 5. The rotational and Van Eijck's centrifugal distortion constants of "cis" cyclopropyl isocyanate for different fit procedures using a fourth (first column) and sixth order (second column) centrifugal distortion Hamiltonian. Furthermore, different sets of transitions are included in the fits (according to Figures 4 and 5). The conditions of the fits are given at the bottom of the Table. Numbers in parentheses represent single standard errors in units of the last quoted digit. n.d.: not derminable, set to zero.

	Fourth order		Sixth order	
A	10 215(6)	MHz	10 235(3)	MHz
B	2 186.859(6)	MHz	2 186.856(3)	MHz
C	2 106.172(6)	MHz	2 106.168(3)	MHz
$\tilde{D}_J$	2.01(1)	kHz	2.06(1)	kHz
$\tilde{D}_{JK}$	29.5(3)	kHz	21.87(7)	kHz
$\tilde{D}_K$	n.d.		n.d.	
$\tilde{\delta}_J$	0.31(2)	kHz	0.32(1)	kHz
$\tilde{R}_6$	0.14(1)	kHz	n.d.	
$\tilde{H}_{JK}$	–		−1.1(5)	Hz
$\tilde{H}_{KJ}$	–		8(1)	Hz
Weight of the transitions in the fit:				
	$K_- > 2$: 1/100		$K_- = 2, 3, 4$: 1/1000	
Standard deviation of the fit:				
	53 kHz		26 kHz	
Highest correlation:				
	$\tilde{\delta}_J/B$: 0.888		$\tilde{\delta}_J/B$: 0.884	

to the fit procedure indicated by Fig. 4, wheras $^6\nu_0'$ corresponds to Figure 5. Table 5 contains the rotational as well as Van Eijck's centrifugal distortion constants. The "conditions" of the fit are summarized at the bottom of the Table.

Attempt at Explanation

The experimental results of the "cis" isomer indicate that the spectrum of cyclopropyl isocyanate cannot be described completely by application of a centrifugal distortion Hamiltonian. To find an explanation for these effects we have to go back to the basic assumptions of conventional centrifugal distortion theory. In addition to the rigid asymmetric rotor Hamiltonian, centrifugal distortion effects are considered in the total Hamiltonian by a potential energy term [12].
The potential energy is formulated as a harmonic potential function [13]. The elements of the inverse moment of inertia tensor are approximated by a series expansion in the internal displacement coordinates

considering only the linear term. Thus, the theory only regards small displacements of the internal coordinates from their equilibrium values [14]. These conditions are obviously not fulfilled for "cis" cyclopropyl isocyanate. Because of the rigidity of the cyclopropyl frame and of the NCO group especially the torsion around the $C_{frame}-N$ bond allows for flexibility of the molecule. If we assume a very flat and anharmonic potential near the "cis" conformation with a low barrier to the trans conformation, the failure of the centrifugal distortion analysis is plausible and the mentioned observation with the beam spectrometer can be explained. This agrees with the statement of Durig et al. who found four excited vibrational states for the trans but only one for the "cis" isomer. They concluded that higher excited states lie above the barrier of internal rotation.

To strengthen the above assumption we tried to calculate the potential function with Gaussian 86 [15]. With a STO-3G basis set a trans and a gauche/gauche minimum potential result by varying the torsion angle in steps of 15°. With an extended 4-31 G* basis set we obtained a cis and a trans minimum potential when starting the computation of the potential energy function from a cis conformation. This clearly indicates the need of further extended quantum chemical calculations (which we cannot perform presently), and of additional microwave investigations of cyclopropyl isocyanate to obtain a proper understanding of the conformational behaviour and the effects concerning centrifugal distortion.

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