The Microwave Spectrum of the Bimolecule Trifluoroacetic Acid · · · Cyclopropanecarboxylic Acid

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Z. Naturforsch. **52a**, 803–806 (1997); received September 24, 1997

We have investigated the microwave spectrum of the bimolecule trifluoroacetic acid · · · cyclopropanecarboxylic acid in the region 1 to 4 GHz, where the low J transitions of this heavy complex appear. The measured μ_a–R branch transition frequencies were fitted to determine the rotational constants and three centrifugal distortion constants. With the assumption that the structures of the subunits remain unchanged upon complexation, the O · · · O distances of the hydrogen bridge bonds are determined as 2.62 Å.

Introduction

The first observation of the bimolecules formed by trifluoroacetic acid and formic, acetic and fluoroacetic acid by microwave (MW) spectroscopy was reported by Costain and Srivastava [1]. Later Bellott and Wilson [2] used the broad band scans of a Hewlett-Packard MW spectrometer to observe "band" spectra of a large number of bimolecules.

The present investigation deals with a high resolution MW spectrum of one of their examples: trifluoroacetic acid · · · cyclopropanecarboxylic acid, for which they reported a value of $B+C$, the sum of rotational constants, obtainable from a μ_a-type band spectrum.

It was shown by Martinache et al. [3] that molecular beam Fourier transform microwave (MB-FTMW) spectroscopy allows to record highly resolved rotational spectra of bimolecules. The advantage of the beam method is that due to the strong cooling in the supersonic expansion only rotational spectra in the ground vibrational state appear.

Experimental

As the bimolecules are units with large moments of inertia, the rotational spectra with low rotational quantum numbers are in a MW region typically not accessible with existing MB-FTMW spectrometers [4, 5] based on a Fabry-Perot cavity. Our recently constructed [6] MB-FTMW spectrometer with a TE_{01} (H_{01}) cavity, however, covers the region from 1 to 4 GHz and is ideally suited for such an investigation.

The monomers, trifluoroacetic acid, CF_3COOH, and cyclopropanecarboxylic acid, C_3H_5COOH, were purchased from Merck, Darmstadt, and Aldrich, Steinheim. They were used without further purification. Helium was used as carrier gas with a content of 1 to 2% CF_3COOH. The low vapour pressure of C_3H_5COOH did not allow to prepare a mixture of both substances in helium. Therefore, C_3H_5COOH was kept upstream the nozzle in a stainless steel vessel providing by its construction a good contact of helium and CF_3COOH with C_3H_5COOH. Even better signal to noise ratios were obtained with a mixture of both compounds in the vessel and pure helium as carrier gas.

By observation of the transition $J', K_a', K_c'-J'', K_a'', K_c''=2, 1, 1-2, 1, 2$ at the frequency 1270.7762 MHz of CF_3COOH we proved that the substance is in the beam. The hitherto not measured frequency was calculated from the rotational constants reported by Stolwijk and van Eijck [7]. Unfortunately, for C_3H_5COOH we could not observe the line 3, 1, 2–2, 2, 1 at the frequency 1122.608 MHz. Here the frequency was calculated with data published by Marstokk et al. [8]. But with the help of a MB-FTMW spectrometer [9] in a higher frequency region, we observed the up to now not reported transitions of C_3H_5COOH given in Table 1. So we are convinced that the substance is contained in the beam.

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Table 1. Observed transitions of the monomers trifluoracetic acid and cyclopropanecarboxylic acid hitherto not reported.

	J'	K_a'	K_c'	J''	K_a''	K_c''	ν/MHz
Trifluoroacetic acid	2	1	1	2	1	2	1 270.776
Cyclopropane-carboxylic acid	2	0	2	1	0	1	10 196.313
	2	1	2	1	0	1	14 771.176
	2	2	1	2	1	2	15 728.924

As Bellott and Wilson [2] derived a $B+C=539.6(20)$ MHz, we scanned in ranges of 6 to 27 MHz around the frequencies $(J+1)$ $(B+C)$, $J=1, \ldots, 6$, to locate the $K_a=0$ R-branch transitions. Typically 512 cycles per frequency point and a step width of 250 kHz were used for this search. Taking high resolution spectra with 8 k data points in the time domain at a sample interval of 10 ns and 1 to 16 k averaging cycles, we were able to measure nearly all μ_a-type lines from $J=2-1$ to $J=7-6$ in the region 1 to 4 GHz with sufficient signal to noise ratio. They are listed in Table 2. Figure 1 gives an example.

The backing pressure was kept at 1.2 to 2 bar, with lower pressures the lines disappeared.

Spectrum Analysis

The spectrum was analysed with a centrifugally distorted asymmetric top Hamiltonian using Watson's *A*-reduction [10] in I^r representation. Typke's program ZFAP4 [11] was used in this context.

The rotational and centrifugal distortion constants are given in Table 3.

As only μ_a-transitions could be observed for this near prolate top, the *A* rotational constant was determined with a larger uncertainty.

The centrifugal distortion constants of the A-reduction are less by an order of magnitude as compared to the corresponding values for $CF_3COOH \cdots HCOOH$ and $CF_3COOH \cdots CH_3COOH$ given in Table 2 and 4 of [3]. The highest correlation coefficients are $|(B, \delta_J)| = |(C, \delta_J)| = 0.89$.

With the rotational constants of Table 3, we predicted the μ_b-spectrum. Due to the presumably very low μ_b dipole moment, we were not able to find the 1, 1, 1 – 0, 0, 0 and 3, 1, 3 – 2, 0, 2 lines, even though we scanned with 4096 averaging cycles and higher polarization power.

Partial r_0-structure

The experimental rotational constants were used to calculate a partial r_0-structure [12] for the bimolecule. With only three experimental values available at present, at most three structural parameters could be determined. Correlation reduced this number to two. They were chosen as the C_1-C_9 distance and the

Table 2. Observed and calculated transition frequencies (in MHz) of $CF_3COOH \cdots C_3H_5COOH$.

J'	K_a'	K_c'	J''	K_a''	K_c''	exp	calc-exp
2	0	2	1	0	1	1075.333	.001
2	1	2	1	1	1	1062.486	−.001
2	1	1	1	1	0	1088.306	.000
3	0	3	2	0	2	1612.847	−.001
3	1	3	2	1	2	1593.689	.000
3	1	2	2	1	1	1632.417	.003
3	2	2	2	2	1	1613.091	.001
3	2	1	2	2	0	1613.339	.000
4	0	4	3	0	3	2150.176	−.001
4	1	4	3	1	3	2124.845	.002
4	1	3	3	1	2	2176.485	.001
4	2	3	3	2	2	2150.744	−.002
4	2	2	3	2	1	2151.356	.001
4	3	2	3	3	1	2150.914	−.002
4	3	1	3	3	0	2150.914	−.001
5	0	5	4	0	4	2687.254	.001
5	1	5	4	1	4	2655.942	.001
5	1	4	4	1	3	2720.490	.000
5	2	4	4	2	3	2688.349	.000
5	2	3	4	2	2	2689.580	.000
5	3	3	4	3	2	2688.698	−.003
5	3	2	4	3	1	2688.698	.001
6	0	6	5	0	5	3224.028	.000
6	1	6	5	1	5	3186.965	.000
6	1	5	5	1	4	3264.414	.000
6	2	5	5	2	4	3225.903	.001
6	2	4	5	2	3	3228.059	−.002
6	3	4	5	3	3	3226.518	−.004
6	3	3	5	3	2	3226.518	.006
6	4	3	5	4	2	3226.391	−.003
6	4	2	5	4	1	3226.391	−.003
7	0	7	6	0	6	3760.433	.000
7	1	7	6	1	6	3717.897	−.001
7	1	6	6	1	5	3808.241	−.001
7	2	6	6	2	5	3763.397	−.001
7	2	5	6	2	4	3766.840	.000
7	3	5	6	3	4	3764.378	−.003
7	3	4	6	3	3	3764.396	.002
7	4	4	6	4	3	3764.177	.003
7	4	3	6	4	2	3764.177	.003

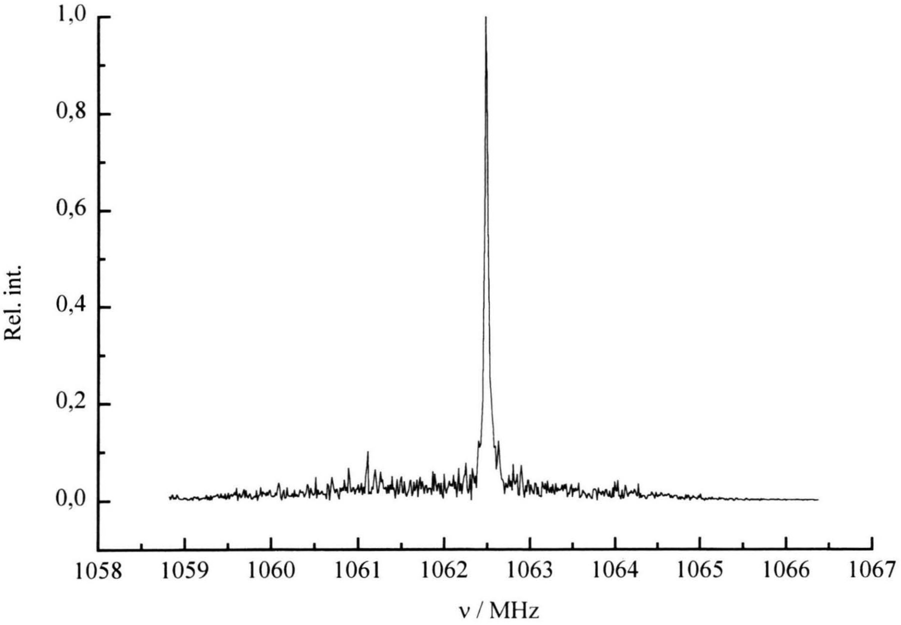

Fig. 1. Transition $J', K_a', K_c' - J'', K_a'', K_c'' = 2, 1, 2 - 1, 1, 1$ at 1062.486 MHz of the bimolecule trifluoroacetic acid · · · cyclopropanecarboyxlic acid. Amplitude spectrum recorded with 8 k data points with 10 ns sample interval in the time domain, 16 k experiment cycles, polarization frequency 1062.6 MHz, polarization power 1.2 mW, MW pulse width 1.2 μs, backing pressure 1.2 bar He with 1% CF_3COOH. Cyclopropanecarboxylic acid in a vessel upstream the nozzle. The Doppler splitting, of approximately 10 kHz, is not visible.

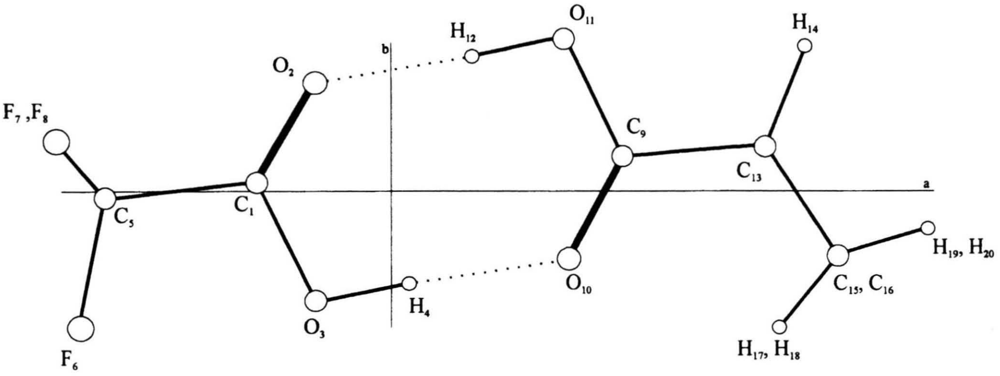

Fig. 2. $CF_3COOH \cdots C_3H_5COOH$ bimolecule in its principal axis system with atom numbering.

$C_1-C_9-C_{13}$ angle (compare Figure 2). Typkes program MWSTR1 [11] was used for the corresponding least squares fitting procedure.

As input data we have used the structures for the monomers as proposed in Table 1 of [7] for CF_3COOH, and Table 8 column 1 of [8] for C_3H_5COOH unchanged. Furthermore, a coplanar configuration was assumed for the two carboxylic groups, and equality of the O · · · O distances in the two hydrogen bridges was imposed as an additional constraint. The result is shown in Fig. 2 and Table 4. The numbers of given digits do not indicate the accuracy of the structure determination. They are necessary to reproduce the moments of inertia.

Table 3. Rotational and Watson centrifugal distortion constants of the bimolecule $CF_3COOH \cdots C_3H_5COOH$.

Watson A-reduction	
A [MHz]	2298.82 (80)[a]
B	275.3040 (3)
C	262.3938 (3)
Δ_J [kHz]	0.0062 (13)
Δ_{JK}	0.0129 (67)
Δ_K	[0.][b]
δ_J	0.0012 (22)
δ_K	[0.]
$\varkappa$[c]	−0.98732
N[d]	40
σ[e] [kHz]	2

[a] Numbers in brackets: standard error in units of the last digit.
[b] In squared brackets: centrifugal distortion constants fixed to zero.
[c] Asymmetry parameter.
[d] Number of lines.
[e] Standard deviation.

We note that the O ··· O distance in the bridges, which is obtained that way, $r_{(O \cdots O)} = 2.62$ Å, is by 0.1 Å smaller than the value reported by Bauder and coworkers [3] for the related complex $CF_3COOH \cdots CH_3COOH$. This finding of a shortened O ··· O distance correlates with the smaller centrifugal distortion constants. Both findings indicate considerably stronger hydrogen bridges in the title compound. To check this, one needs more detailed experimental information on the structure. The microwave spectra of the isotopomers of the complex, but also of the two subunits will have to be studied. It would also be of interest to investigate the intermolecular vibrations of the complex in the far infrared in order to look for complementary information on the strength of the hydrogen bonds.

Table 4. Atom r_0-coordinates (in Å) with respect to the principal inertia axis system of the bimolecule $CF_3COOH \cdots C_3H_5COOH$. Six decimals are given for the sake of reproducibility of the calculated rotational constants (in MHz): $A_{calc} = 2298.901$, $B_{calc} = 275.359$, $C_{calc} = 262.333$. (Conversion factor: 505 376 MHz amu Å^2; estimated uncertainties on the order of 0.01 Å for the bond distances and 1° for the bond angles, respectively).

	n	$a(n)$	$b(n)$	$c(n)$	$M(n)$/amu
CF_3COOH	1	−1.390494	0.089995	0.000000	12.000000
	2	−0.787664	1.118324	0.000000	15.994915
	3	−0.765325	−1.109910	0.000000	15.994919
	4	0.178538	−0.934631	0.000000	1.007825
	5	−2.926799	−0.082877	0.000000	12.000000
	6	−3.226657	1.373501	0.000000	18.998405
	7	−3.436150	0.488249	−1.081666	18.998405
	8	−3.436150	0.488249	1.081666	18.998405
	9	2.400009	0.376065	0.000000	12.000000
C_3H_5COOH	10	1.821035	−0.690980	0.000000	15.994915
	11	1.791440	1.579994	0.000000	15.994915
	12	0.825927	1.385033	0.000000	1.007825
	13	3.872786	0.457019	0.000000	12.000000
	14	4.292536	1.472701	0.000000	1.007825
	15	4.620340	−0.636959	−0.748500	12.000000
	16	4.620340	−0.636959	0.748500	12.000000
	17	3.993947	−1.395382	1.247535	1.007825
	18	3.993947	−1.395382	−1.247535	1.007825
	19	5.546469	−0.363573	1.281560	1.007825
	20	5.546469	−0.363573	−1.281560	1.007825

Acknowledgements

We thank the members of our groups for help and discussions. For funds we thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemie, the Land Schleswig-Holstein and a FPI grant from Ministerio de Educatión y Ciencia. S. A. thanks for the hospitality during a stay in Kiel.

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