Determination of Dipole Moments by Microwave Fourier Transform Spectroscopy. Trifluoropropine, Tert. Butylisocyanide, and Cyanoacetylene

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We report the measurements of dipole moments by Microwave Fourier Transform Spectroscopy. Hereby we indicate that it is worth to supplement this type of microwave spectroscopy to increase its capability.

As an application of our recently developed Stark cell for Microwave Fourier Transform (MWFT) Spectroscopy [1, 2] we investigated Trifluoropropine, $CF_3C\equiv C-H$ and $CF_3C\equiv C-D$ [3], tert. Butylisocyanide, $(CH_3)_3CNC$ [4], and Cyanoacetylene, $H-C\equiv C-C^{14}N$ [5, 6] and $H-C\equiv C-C^{15}N$. In [3] and [5, 6] the dipole moment μ was given for the normal species together with B_0 for both species. The assignment of tert. Butylisocyanide is reported in [4]. The Stark cell was calibrated with Carbonylsulfide, OCS, $\mu = 0.71512(3)$ [7].

The measurements are given in Tables 1–5. Figure 1 shows the measurements for $HC\equiv C-C^{14}N$.

With the exception of $H-C\equiv C-C^{14}N$ the Stark shifts were evaluated by the usual symmetric top formalism [8]. The rotational constant B_0 was determined from the zero field transition frequency ν_0. Second order has to be used as $K = 0$ (or $M = 0$) satellites were measured. The dipole moment was

Table 1. Measurement of the dipole moment μ [D] of $CF_3C\equiv CH$ for $J = 2 \leftarrow 1$, $\nu_0 = 11\,511.798$ MHz, E [V/cm] field strength, ν_1 [MHz], frequency of satellite: $K = 0$, $|M| = 1$; $|K| = 1$, $M = 0$, ν_2: $K = M = 0$. Standard deviation in brackets.

E	ν_1	ν_2	μ
117.701	11512.196	11511.308	2.296
141.223	11512.382	11511.073	2.323
164.806	11512.601	11510.840	2.309
188.291	11512.832	11510.499	2.326
211.874	11513.144	11510.171	2.334
235.397	11513.429	11509.825	2.313

$B_0 = 2877.950$ MHz; $\mu = 2.317(13)$ D,
for comparison [3]; $\mu = 2.36(4)$ D

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Table 2. Measurement of the dipole moment μ [D] of $CF_3C\equiv CD$ for $J = 2 \leftarrow 1$, $\nu_0 = 10\,784.271$ MHz. See also Table 1.

E	ν_1	ν_2	μ
94.117	10784.554	10783.939	2.312
117.701	10784.699	10783.731	2.320
141.223	10784.883	10783.491	2.318
164.806	10785.118	10783.197	2.334
188.291	10785.370	10782.873	2.329
211.874	10785.684	10782.537	2.324
235.397	10785.990	10782.085	2.330

$B_0 = 2696.068$ MHz $\mu = 2.324(7)$ D

Table 3. Measurement of the dipole moment of $(CH_3)_3CNC$ for $J = 2 \leftarrow 1$, $\nu_0 = 11\,728.699$ MHz, ν_1: frequency of satellite: $K = 0$, $M = 0$. See also Table 1.

E	ν_1	μ	
70.703	11729.112	3.929	
94.117	11729.492	4.090	
117.701	11729.851	3.942	
141.223	11730.372	3.959	
164.806	11731.105	4.068	$B_0 = 2932.175$ MHz
188.291	11731.810	4.049	$\mu = 4.01(7)$ D

Table 4. Measurement of the dipole moment μ [D] of $HC\equiv CC^{14}N$, for $J = 1 \leftarrow 0$, $\nu_{10} = 9100.269$, $\nu_{20} = 9098.329$, $\nu_{30} = 9097.029$ MHz, ν_1: $F = 0 \leftarrow 1$, $K = 0 \leftarrow 0$, $M = 0 \leftarrow 0$; ν_2: $F = 2 \leftarrow 1$, $K = 0 \leftarrow 0$, $M = 1 \leftarrow 1$; ν_3: $F = 1 \leftarrow 1$, $K = 0 \leftarrow 0$, $M = 1 \leftarrow 1$. See also Table 1. The last two lines result from one Stark voltage by the inequality of the four sections of the Stark cell.

E	ν_1	ν_2	ν_3
23.593	9100.337	9098.418	9097.112
47.115	9100.554	9098.673	9097.348
70.703	9100.953	9099.118	9097.694
94.653	9101.583	9099.856	9098.203
115.680	9102.256	9100.639	–
118.371	9102.448	9100.828	9098.751

$B_0 = 4549.0579(4)$ [6], $eQq = -4.306(17)$ MHz, $\mu = 3.729(7)$ D; for comparison [5, 6]: $eQq = -4.319(3)$ MHz, $\mu = 3.724(30)$ D.

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Table 5. Measurement of the dipole moment μ [D] of $HC\equiv C-C^{15}N$ for $J = 1 \leftarrow 0$, $\nu_0 = 8833.501$ MHz, ν_1 frequency of satellite: $K = 0$, $M = 0$. See also Table 1.

E	ν_1	μ	
23.593	8833.618	3.706	
47.115	8833.965	3.695	
70.703	8834.554	3.710	
94.653	8835.400	3.721	$B_0 = 4416.752$ MHz
118.371	8836.489	3.733	$\mu = 3.713(13)$ D

Table 6. Dipole moments of isonitriles.

Molecule	μ [D]	
CH_3NC	3.83(6)	[11]
CH_3CH_2NC	4.01(3)	[12]
$CH_3CH_2CH_2NC$ antiperiplanar	4.16(2)	[13]
synclinal	4.10(9)	[13]
$(CH_3)_3CNC$	4.01(7)	this work

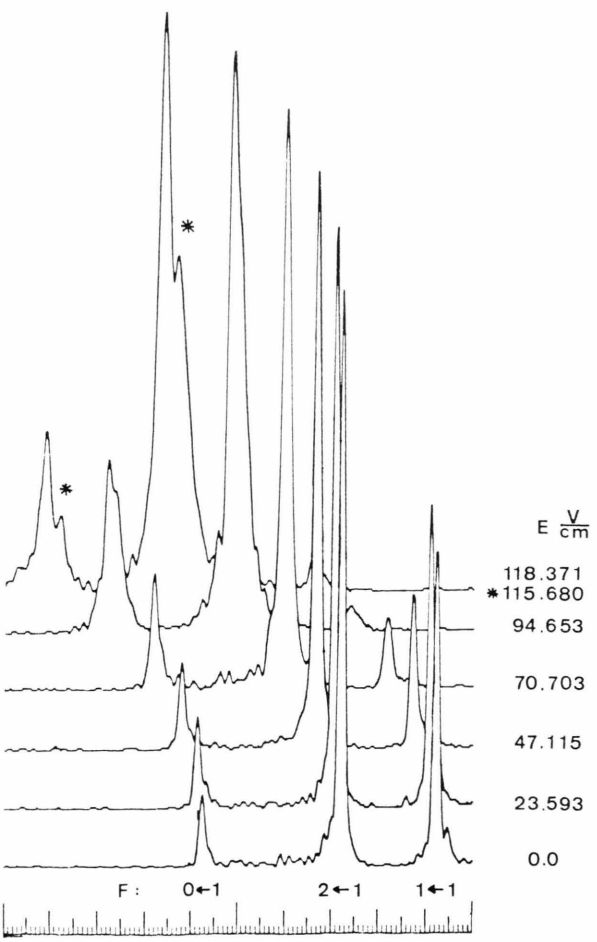

Fig. 1. Stark effect of $HC\equiv CC^{14}N$ $J = 1 \leftarrow 0$. Section of 6.5 MHz out of a 50 MHz scan. E [V/cm] field strength. Frequency increases from right to left. 1.0 mTorr, −60 °C. 10 ns sample interval. Up to $60 \cdot 2^{16}$ averaging cycles, 1024 data points supplemented by 3072 zeros prior to Fourier transformation. The splitting of the satellites at the highest field results from inequalities of the four sections of the Stark cell [1]. Different field strengths result for one Stark voltage. The influence was corrected by different calibration factors. Zero field line width at half height about 50 kHz.

calculated for each field strength. The mean value was taken as final.

For $H-C\equiv C-C^{14}N$ the N-hfs interferes with the Stark effect. A program * was used which includes Stark effect and quadrupole coupling [10]. The coupled basis is used and M_F-submatrices are diagonalized. eqQ and μ are fitted. B_0 was taken from [6]. It is indicated by the errors and comparison with reported values that the precision is higher, which may be due to the smaller line width of the MWFT-spectra. Still higher precision may be reached if a more precise Stark cell [1] of increased length is available to give more sensitivity.

As there are only few measurements of dipole moments of Isonitriles we give in Tab. 6 a comparison.

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