Investigation of the Stark Shift of the Benzene-d$_1$ $1_{01} - 0_{00}$ Rotational Transition by Microwave Fourier Transform Spectroscopy

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Z. Naturforsch. **42 a,** 72–78 (1987); received September 9, 1986

The Stark shift of the $J'_{K'_- K'_+} - J''_{K''_- K''_+} = 1_{01} - 0_{00}$ transition of benzene-d$_1$ was investigated to determine the dipole moment caused by deuterium substitution. A modified set-up of the microwave Fourier transform spectrometer was used to be able to apply the necessary Stark voltage and to increase the sensitivity of the instrument. The resulting permanent dipole moment is $\mu_a = 0.00810(28)$ D corresponding to an absorption coefficient of $\gamma_{\max} = 2.8 \cdot 10^{-12}\ \mathrm{cm}^{-1}$, determined at a sample pressure of 1.5 mTorr, for that line.

Introduction

The weak rotational spectrum of benzene-d$_1$, C_6H_5D, was first measured and assigned by Oldani and Bauder [1] with the help of microwave Fourier transform (MWFT) spectroscopy. We investigated the $1_{01} - 0_{00}$ transition with our MWFT spectrometer applying DC voltages to get information about the dipole moment, which equals the difference between the C–H and C–D bond moments.

Experimental

As the spectrum is very weak and is further weakened by inserting a Stark septum into our X-band sample cell, we had to enhance the sensitivity of the MWFT spectrometer. For that reason and in order to be able to work with Stark voltages up to 6 kV, we modified the scheme of the hitherto used configuration [2–5]. The new set-up is outlined in Figure 1.

The changes are: The local MW oscillator (LO) (1 a)* is phase-stabilized to a synthesizer (1 c) and the signal oscillator (SO) (1 b) is phase-stabilized 160 MHz above or below the LO frequency. By this scheme the superhet system can be kept active when the SO part of the spectrometer is modified during a search for coherent perturbations [2, 6] which disturb weak molecular signals. As the spectrometer works by averaging molecular signals with a fixed phase relation to the master frequency (23), coherent perturbations of comparable intensity will reduce its sensitivity.

Two modifications were implemented to reduce the leakage of signal microwave to the detection mixer (3 a), i.e., to reduce the coherent disturbing signal at the position of the polarizing microwave frequency, i.e., at 30 MHz intermediate frequency (IF). The track for a leakage from the SO (1 b) to the detection mixer (3 a) during the "pulse off", i.e., the molecular signal detection period, was blocked by an additional PIN switch 3 b (4 c″) working in the same on-off rythm as PIN switch 3 a (4 c′). The on-off sequence is given as trace PS 3 in Fig. 2 of [5]. So the leakage during the detection period is reduced by additional 80 dB. By the insertion of more coaxial isolators between the mixer (3 c) and the directional coupler (13 e) the leakage of signal microwave to the mixer (3 a) was reduced further by about 80 dB.

In addition part of the detection system, PIN switch 4 (4 d), MW amplifier (9 b), isolator (6 c), mixer (3 a) and IF amplifier (9 d) were enclosed in a shielding box filled with microwave absorbing foam. Moreover the windows of the sample cell (27) were shielded very carefully.

After taking all these MW shielding and blocking measures within and around the coaxial and wave-

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* Numbers in round brackets refer to Figure 1.

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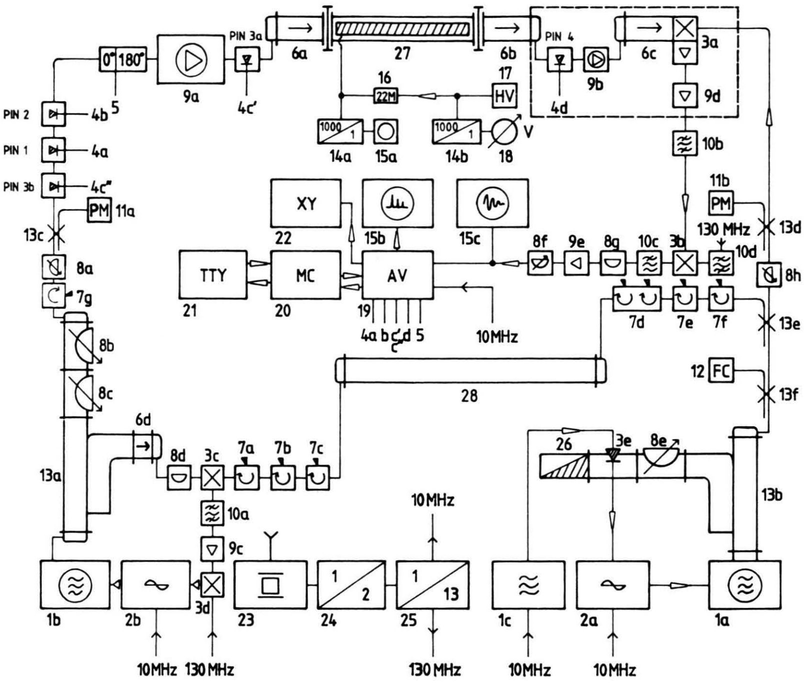

Fig. 1. Set-up of a MWFT spectrometer for Stark effect measurements.

BW	band width
IS	isolation
IF	intermediate frequency
NF	noise figure
MW	microwave
1a	Local oscillator, 8–16 GHz, Carcinotron CSF CO 521 A with power supply, FXR Z 817 A
1b	Signal oscillator, sweeper 8–12.5 GHz, Hewlett-Packard 8690 B + 8694 A or klystron generator, 7–11 GHz, Polarad 1208 E
2a, b	Synchronizer, IF 30 MHz, Schomandl FDS 30
3a	Mixer with integrated preamplifier, RHG, WMP12C06EC
3b	IF-Mixer, Mini Circuits ZAD 1
3c	Mixer, Watkins Johnson M17C
3d	IF-Mixer, Mini Circuits ZAY 3
3e	Waveguide mixer with diode 1N23, Schomandl FMDR 8/12
4a–d	PIN-switch with TTL-driver, Hewlett-Packard 33144 A + 33190 B
5	Biphase modulator with TTL-driver, RHG DMK2-18
6a–c	Waveguide isolator, selected for VSWR 1:1.1
6d	Waveguide isolator
7a–c, e–g	Coaxial isolator, IS = 17 dB
7d	Coaxial isolator, IS = 34 dB
8a, f, h	Coaxial variable attenuator
8b, c, e	Waveguide variable attenuator
8d, g	Coaxial attenuator 50, 20 dB
9a	Travelling wave tube amplifier, 8–18 GHz, Hughes 1177H04
9b	MW amplifier, NF = 4 dB, gain = 37dB, Avantek AMT-12435
9c	IF amplifier, gain NF = 2.5 dB, gain = 40 dB, Amplica 401 USL
9d	IF amplifier, NF = 1.5 dB, gain = 38 dB, RHG ICFH 160 LN
9e	IF amplifier, NF = 4.5 dB, gain = 34 dB, Avantek GPD461, 462, 463, with 5 MHz high-pass filter
10a	Band-pass filter 160 MHz, 10 MHz BW
10b	Band-pass filter 160 MHz, 20 MHz BW
10c	Low-pass filter 55 MHz
10d	Band-pass filter 130 MHz, 2.6 MHz BW
11a, b	Powermeter, Hewlett-Packard 432 A + 8478 B
12	MW frequency counter, EIP 548
13a	Waveguide directional coupler, 20 dB
13b	Waveguide directional coupler, 10 dB
13c–e	Coaxial directional coupler, 10 dB
13f	Coaxial directional coupler, 20 dB
14a	High voltage probe, 1000:1, Tektronix P6015
14b	High voltage divider, Fluke 80 E
15a–c	Oscilloscope
16	Current-limiting series resistor 22 MΩ
17	High voltage power supply, 0–6000 V, Heinzinger HN 6000-10
18	Digitalvoltmeter, 5 1/2 digits, Data Precision 3600
19	Analogue to digital converter, averager and experiment control [7], 10, 20, 50, 100 ns sampling interval, 1024 data points, 25 kHz maximum repetition rate
20	Mini computer, Texas 990/10
21	Teletype
22	XY-recorder
23	Frequency standard, 5 MHz, and receiver, Rhode und Schwarz XSD 2, XKE 2
24	Frequency doubler, 5 to 10 MHz, and amplifier
25	Frequency multiplier, 10 to 130 MHz, and amplifier
26	Waveguide termination
27	Stark cell, with MW-shielded windows, 3.05 m long X-band waveguide with 5 × 20 mm septum, tapered, attenuation 10 to 20 dB including isolators and coax transitions
28	Waveguide transmission line
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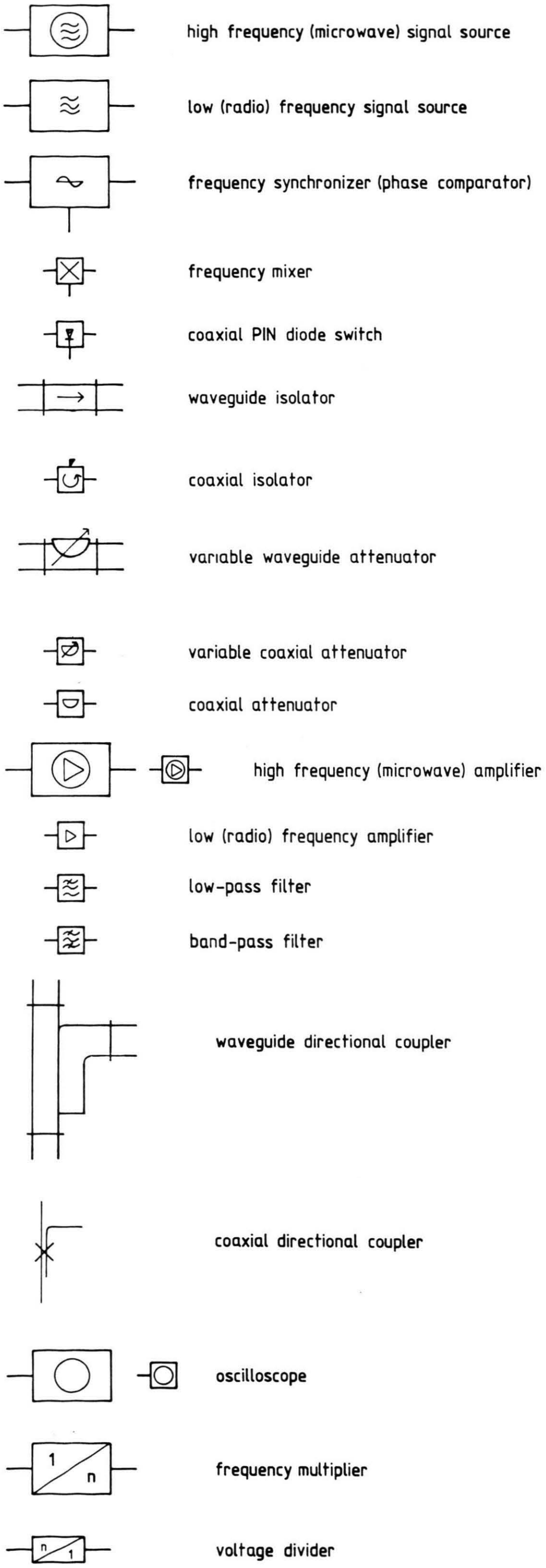

guide lines, even for 10^8 averaging cycles no perturbing signal at 30 MHz IF could be detected, which had been the main perturbation before.

For the measurement of the Stark effect a 3.05 m long waveguide cell (27), made of precision X-band waveguide with a 20 mm broad and 5 mm thick brass septum, was used. The septum was smoothed over the whole length to a precision better than 0.01 mm as regards its thickness. It is tapered on both ends and approaches the cell windows to 5 mm. Thereby MW pulse reflections are reduced and quickly damped by the waveguide isolators (6a) and (6b). The septum is positioned by Teflon spacers at the narrow walls of the waveguide. Additionally a 0.5 mm thick Teflon foil was inserted between the spacers and the narrow walls along the waveguide. All connections and the septum are shaped to stand 6000 V, which gives a field of approximately 24000 V/cm. The DC voltage is supplied by a power supply (17) via a 22 MΩ resistor (16) and measured with a digital voltmeter (18) after division by 1000 with (14b). By the oscilloscope (15a) with a high voltage probe (14a) the DC voltage is monitored allowing the detection of possible sparking during measurements. The other features of the spectrometer are analogous to those described formerly [2–5, 7].

To sum up, the most helpful modification implemented with the present experimental set-up is a shift of the function of the reference oscillator, i.e., the oscillator directly phase-stabilized with reference to the master oscillator (23), from the SO (1b) as in former set-ups to the LO (1a). Thus a higher phase-stability of the system and additional means for the detection and elimination of coherent perturbations are reached.

The sample was purchased from Aldrich-Chemie, Steinheim, with 98% isotopic purity and used without further purification. The cell (27) was filled with some ten mTorrs 10 hours before starting the measurements. The spectra were recorded at about 2 mTorr (0.27 Pa) and −64 °C.

The applied DC voltages, corresponding field strengths, and the Stark-shifted frequencies of the $M_J = 0$ component are listed in Table 1. A typical recording is given in Figure 2. It may be noticed from Fig. 3 that the frequency of the only Stark component $M_J = 0$ varies linearly with the square of the field strength ε.

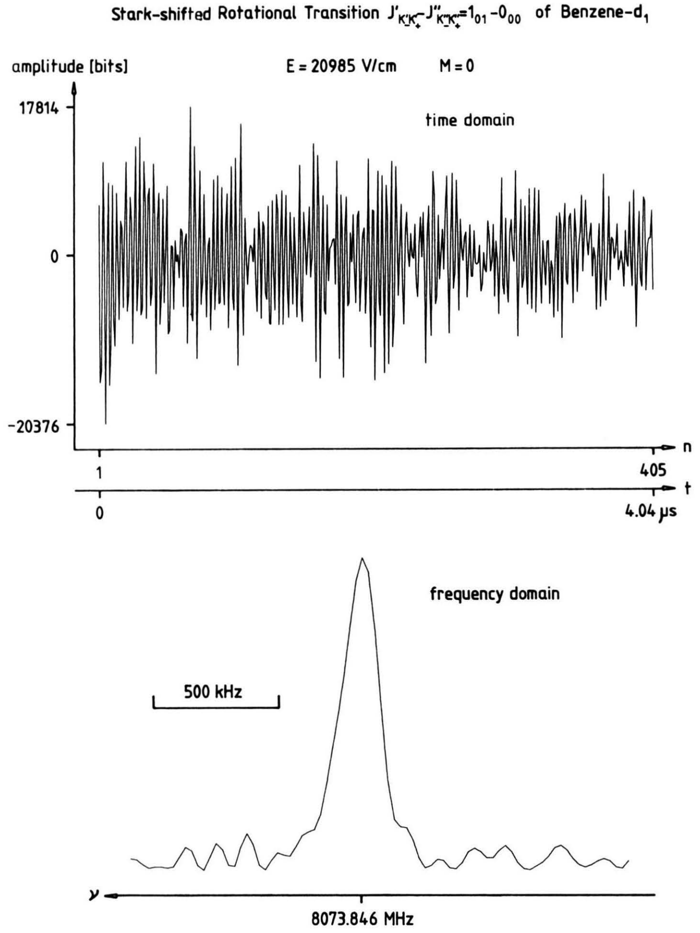

Fig. 2. A typical Stark effect measurement. The Stark-shifted $1_{01}-0_{00}$-line of benzene-d_1 at an electric field strength of $\varepsilon = 20\,985$ V/cm.
Upper chart: The first 405 data points of the molecular signal in the time domain. Sample interval: 10 nsec, $7.21 \cdot 10^7$ averaging cycles, microwave polarizing frequency: 8073.780 MHz, sample gas pressure: 2.3 mTorr, temperature in the waveguide cell: – 64 °C.
Lower chart: The upper chart molecular signal after Fourier transformation in the frequency domain. A 2 MHz-section of the 50 MHz scan, power spectrum, 1024 data points supplemented by 3072 zeros prior to Fourier transformation.

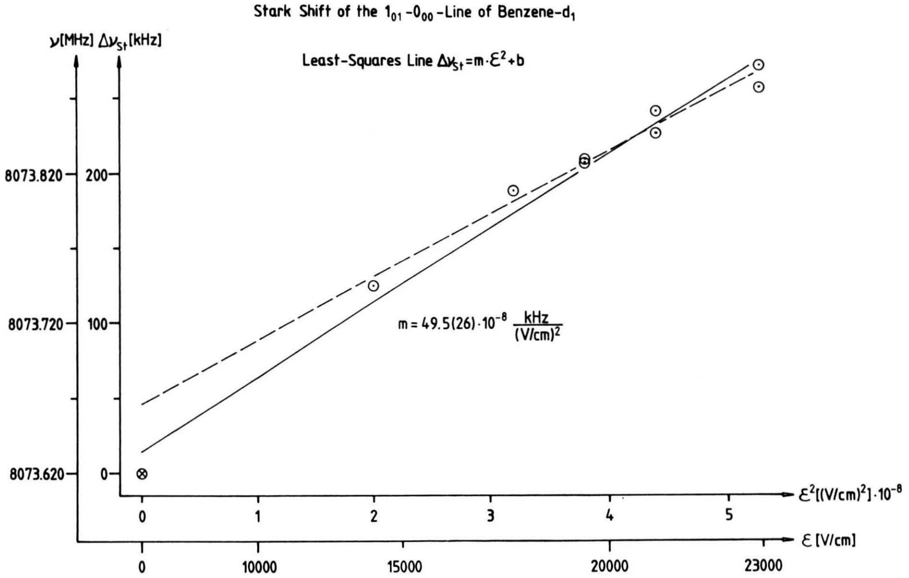

Fig. 3. Least-squares straight line $\Delta\nu_{St} = m \cdot \varepsilon^2 + b$, fitted to the measured Stark shifts $\Delta\nu_{St}$ of the $1_{01}-0_{00}$ rotational line of benzene-d_1 dependent on the square of the electrical field strength ε. – ⊙ and ⊗: our measurements, dashed line: straight line, least-squares fitted to our measurements omitting the zero-field line (⊗), for an estimation of the experimental error. – The slope m is given for the solid straight line.

Analysis

Because of the high electric fields (up to 23000 V/cm) applied in our experiment, besides the permanent dipole moment μ_a also the polarizability α contributes to the Stark shift which in our case shows a quadratic dependence on the field strength ε.

We assumed that the rotational energy, perturbed by the Stark field, is given by

$$E_{J\tau M_J} = E_{J\tau}^{(0)} + [E_a(\mu_a)^{(2)}]_{J\tau M_J} + [E(\alpha)^{(1)}]_{J\tau M_J}\,. \tag{1}$$

$E_{J\tau}^{(0)}$ is the unperturbed energy of an asymmetric rotor with the angular momentum quantum number J and the pseudo quantum number $\tau = K_- - K_+$. $E_{J\tau}^{(0)}$ is independent of the orientation quantum number M_J. $[E_a(\mu_a)^{(2)}]_{J\tau M_J}$ is the part of the perturbation due to the permanent dipole moment μ_a in second order approximation [8],

$$\begin{aligned}
&[E_a(\mu_a)^{(2)}] \\
&= \mu_a^2 \varepsilon^2 \left[\frac{J^2 - M_J^2}{4J^2(4J^2-1)} \sum_{\tau'} \frac{|(J,\tau|\Phi_{Za}|J-1,\tau')|^2}{E_{J\tau}^{(0)} - E_{J-1,\tau'}^{(0)}} \right. \\
&\quad + \frac{M_J^2}{4J^2(J+1)^2} \sum_{\tau' \neq \tau} \frac{|(J,\tau|\Phi_{Za}|J,\tau')|^2}{E_{J\tau}^{(0)} - E_{J\tau'}^{(0)}} \\
&\quad + \frac{(J+1)^2 - M_J^2}{4(J+1)^2(2J+1)(2J+3)} \\
&\quad \left. \cdot \sum_{\tau'} \frac{|(J,\tau|\Phi_{Za}|J+1,\tau')|^2}{E_{J\tau}^{(0)} - E_{J+1,\tau'}^{(0)}} \right].
\end{aligned} \tag{2}$$

$[E(\alpha)^{(1)}]_{J\tau M_J}$ is the part of the perturbation due to the polarizability α in first order approximation [9],

$$\begin{aligned}
&[E(\alpha)^{(1)}]_{J\tau M_J} = -\tfrac{1}{2} \sum_{g=a,b,c} \alpha_{gg} \varepsilon^2 \\
&\quad \cdot \left[\frac{J^2 - M_J^2}{4J^2(4J^2-1)} \sum_{\tau'} |(J,\tau|\Phi_{Zg}|J-1,\tau')|^2 \right. \\
&\quad + \frac{M_J^2}{4J^2(J+1)^2} \sum_{\tau'} |(J,\tau|\Phi_{Zg}|J,\tau')|^2 \\
&\quad + \frac{(J+1)^2 - M_J^2}{4(J+1)^2(2J+1)(2J+3)} \\
&\quad \left. \cdot \sum_{\tau'} |(J,\tau|\Phi_{Zg}|J+1,\tau')|^2 \right].
\end{aligned} \tag{3}$$

Because of the selection rule $\Delta M_J = 0$ the $1_{01}-0_{00}$ rotational transition has only one Stark component. Hence the contributions of the permanent dipole moment μ_a and the polarizability α to the Stark shift of the line cannot be separated. Additional measurements of higher J-lines would have provided this possibility, but we failed to resolve the M-patterns of such lines in the frequency range 8–12.4 GHz of our Stark cell.

But nevertheless we wanted to get information about the permanent dipole moment μ_a. So we took the polarizabilities $\alpha_\parallel = \alpha_{aa} = \alpha_{bb} = 11.73 \cdot 10^{-24}\,\text{cm}^3$ and $\alpha_\perp = \alpha_{cc} = 6.54 \cdot 10^{-24}\,\text{cm}^3$ determined by Alms, Burnham, and Flygare [10] from depolarization ratio and refractive index measurements in the visible light region for gas phase benzene, C_6H_6, extrapolated to infinite wavelength – wavelengths in the microwave region being approximately infinite when comparing them with wavelengths in the visible light region – to calculate with (3) the contribution of the polarizability. The result of this calculation is a quadratic dependence of the frequency on the electric field strength $m_\alpha = -5.810 \cdot 10^{-7}\,\text{kHz/(V/cm)}^2$. With the slope of the experimental straight line, least-squares fitted to our measurements, $m_{\text{exp}} = 4.949 \cdot 10^{-7}\,\text{kHz/(V/cm)}^2$ (see Fig. 3), reflecting the gross effect of both polarizability and permanent dipole moment, the net contribution of the permanent dipole moment is $m_{\mu_a} = m_{\text{exp}} - m_\alpha = 10.759 \cdot 10^{-7}\,\text{kHz/(V/cm)}^2$. Thus the contribution of the permanent dipole moment to the frequency displacement of the $M_J = 0$ Stark component is about twice as large as that of the polarizability, but with the opposite sign. The slope m_{μ_a} and Eq. (2)* yield a dipole moment $\mu_a =$

Table 1. Measurement of the Stark effect of the $1_{01}-0_{00}$ transition of benzene-d$_1$. DC Stark voltage U, DC Stark field strength ε, frequency ν of the Stark component $M_J = 0$.

U [V]	ε [V/cm]	ν [MHz]
0	0	8073.620
3636.6	14 145.8	8073.744
4600.0	17 894.0	8073.808
5011.2	19 492.8	8073.827
5011.4	19 493.5	8073.829
5394.6	20 984.1	8073.861
5394.8	20 984.9	8073.846
5901.7	22 956.7	8073.877
5901.9	22 957.4	8073.892

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* Program KONABI.

Table 2. Results of the Stark effect analysis, fitting a straight line $\Delta\nu_{St} = m \cdot \varepsilon^2 + b$ (see Fig. 3) with the fitting parameters m and b to the measured Stark shifts $\Delta\nu_{St}$ of the $M_J = 0$ component of the $1_{01}-0_{00}$-line of benzene-d_1.

$\alpha_\parallel, \alpha_\perp$	components of the polarizability tensor parallel and perpendicular to the molecular plane,
A, B, C	rotational constants,
$\vert(m, b)\vert$	correlation coefficient between m and b.

Single standard deviations in units of the last digit in round brackets.

A [MHz]	5689.144(6)	[1]
B [MHz]	5323.934(6)	[1]
C [MHz]	2749.674(6)	[1]
$\alpha_\parallel$ [cm^3] $\cdot 10^{24}$	11.73	[10]
$\alpha_\perp$ [cm^3] $\cdot 10^{24}$	6.54	[10]

	Solid line of Fig. 3	Dashed line of Fig.3
m [kHz/(V/cm)^2] $\cdot 10^7$	49.5(26)	42.1(27)
b [MHz]	8073.635	8073.666
$\vert(m, b)\vert$	0.914	0.969
μ_a [D]	0.00810(10)	0.00782(10)

The results in the left column (solid line) are preferred. The right column analysis (dashed line; zero-field rotational line omitted) has only been performed for an estimation of the experimental error in the permanent dipole moment component leading to $\mu_a = 0.00810(28)$ D (see text).

0.00810 D with a single standard deviation of ± 0.00010 D. For an estimation of the error we repeated the least-squares fit of our measurements omitting the zero-field line and arrived at a dipole moment $\mu_a = 0.00782(10)$ D. Taking the difference of both values as the error of the permanent dipole moment, $\mu_a = 0.00810(28)$ D ($2.70(9) \cdot 10^{-32}$ Asecm).

The results of our analysis are comprised in Table 2.

The Stark cell was calibrated with OCS, $J' - J'' = 1-0$ using the dipole moment $\mu = 0.71519(3)$ D [11]. By resolving the M_J-patterns of $J' - J'' = 2-1$ rotational transitions in the Ku-band (12.5−18 GHz) we hope to be able to determine μ_a and α_{aa}, α_{bb} and α_{cc} independently. Presently there is no hope to fix the direction of the dipole moment.

Absorption Coefficient of the $1_{01}-0_{00}$ Transition

It is now interesting to calculate the absorption coefficient of the measured transition to judge the sensitivity of the spectrometer.

According to Townes and Schawlow [12] an absorption coefficient (peak absorption) $\gamma_{max} = 2.8 \cdot 10^{-12}\,\mathrm{cm}^{-1}$ results. In the course of its calculation we approximated the vibrational partition function of benzene-d_1 with that of benzene-h_6, C_6H_6, taking the fundamental vibrations from [13]. We got $Q_v = 1.22$ assuming the ground vibrational level to be $E_0 = 0$ Hz. The line-breadth parameter for the zero-field line was estimated from our measurement to be $\Delta\nu = 46$ kHz at a sample gas pressure of 1.52 mTorr. Subtracting Doppler broadening and dividing by the pressure, the pressure broadening coefficient is 27.2 kHz/mTorr. This value has to be checked by a more detailed study. A nuclear spin weight of 20/16 was included.

Our experience shows that a MWFT spectrometer equipped with a Stark cell is less sensitive than one with a waveguide cell of equal length without septum. We think that the high, frequency dependent, attenuation of 10−20 dB of the Stark cell, compared with 3 to 4 dB attenuation of a normal cell including isolators and coax transitions, is one reason. A second reason may be the reduced number of sample molecules in the cell because the septum occupies half of the volume.

With a normal Stark modulation microwave spectrometer it would be nearly impossible to investigate the reported Stark effect.

Discussion

We could not find any comparable nonpolar molecules in the literature, for which isotopic substitution of one atom provides a dipole moment, which was measured. The only similar cases are CH_3CD_3 [14], $CH_2{=}CD_2$ [15], and $CH_2{=}C{=}CD_2$ [16], for which $\mu = 0.01078(9)$ D, 0.0091(4) D, and 0.0031(3) D were determined.

But one can estimate the effect of substitution from polar molecules. In Table 3 we give some examples. A more detailed list is given in [21]. The order of magnitude of the variation of the dipole moment with deuterium substitution is in those cases equal to the dipole moment, we determined.

Acknowledgement

We thank the members of our group for help and discussions, Mr. H. Michaelis and H. Kaehler for the

Table 3. Variation of dipole moments under hydrogen to deuterium substitution in the vibrational ground state. MW microwave, MWFT microwave Fourier transform, LaSt Laser Stark.

Molecule	Transition	Method	μ [D]	$\Delta\mu$ [D]	Citation
CH_3CH_3					
CH_3CD_3	$J'-J''=2-1,\ K=1$	MW	0.01078(9)	+ 0.01078(5)	[14]
$CH_2{=}CH_2$					
$CH_2{=}CD_2$	$J'_{K'_- K'_+}-J''_{K''_- K''_+} = 3_{22}-2_{21},\ 3_{21}-2_{20}$	MW	0.0091(4)	+ 0.0091(4)	[15]
$CH_2{=}C{=}CH_2$					
$CH_2{=}C{=}CD_2$	$J'-J''=4-3,\ K=3$	MW	0.0031(3)	+ 0.0031(3)	[16]
C_6H_6					
C_6H_5D	$J'_{K'_- K'_+}-J''_{K''_- K''_+} = 1_{01}-0_{00}$	MWFT	0.0081(3)	+ 0.0081(3)	this work
HCN		?	2.984594(1500)		
DCN		?	2.990198(1500)	+ 0.005604	[17]
HCP		?	0.390		
DCP		?	0.397	+ 0.007	[18]
HC=CF		LaSt	0.7207(3)		[19]
DC=CF		LaSt	0.73292(22)	+ 0.01222	[20]
$CH_3C{\equiv}CH$	$J'-J''=1-0$	MW	0.7804		[21]
	$2-1$		0.7809		
$CH_3C{\equiv}CD$	$J'-J''=1-0$	MW	0.7689	− 0.0115	
	$2-1$		0.7668	− 0.0141	

elaborate and precise manufacturing of the Stark cell, Prof. Dr. W. Hüttner, Ulm, and Mr. F. Hegelund, Aarhus, for hints concerning literature. The work was funded by the Deutsche Forschungsgemeinschaft and the Fonds der Chemie. Part of the calculations was made at the Computer Center of the Christian-Albrechts-Universität zu Kiel.

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