Molecular $g_\perp$-value, Magnetic Susceptibility Anisotropy, and Deuterium Quadrupole Coupling Constant in Deuterodiacetylene

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To Professor Helmut Dreizler, Pioneer of NWFT-spectroscopy, on the Occassion of his 60th Birthday

The rotational Zeeman effect in the $J' \to J = 2 \to 1$ rotational transition and the deuterium quadrupole coupling effect in the $J' \to J = 1 \to 0$ transition have been observed for $D-C\equiv C-C\equiv C-H$ using a microwave Fourier transform (MWFT)-spectrometer.

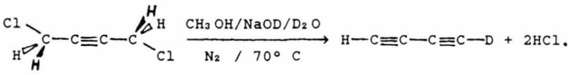
The molecular parameters determined are: rotational constant $B_0 = 4084.452$ MHz, deuterium quadrupole coupling constant $e\,q\,Q\,(D) = 217(6)$ kHz, molecular $g_\perp$-value = 0.0073(1) and molecular magnetic susceptibility anisotropy $(\chi_\perp - \chi_\parallel) = 11.5(7)\,10^{-6}$ erg G^{-2} mol^{-1}.

Introduction

Over the past few years the microwave spectrum of diacetylene and its deuterated isotopomers has been studied extensively by Tanaka and coworkers [1–5]. The molecule being non-polar in its equilibrium configuration, the pure rotational transitions observed here arise because of the minute dipole moment caused by the difference in the average internuclear distances of the C–H and C–D bond, respectively. For the experiments we have used the microwave Fourier transform (MWFT) spectrometers developed recently at the University of Kiel [6–9]. These spectrometers are exceptionally well suited for the study of molecules with very small electric dipole moments, and our present work is in fact the very first rotational Zeeman effect study carried out for an essentially non-polar molecule whose electric dipole moment is generated by partial deuteration.

Experimental Details

The sample was prepared by shaking an alkaline solution of 1,4-dichlorobutyne, methanol and heavy water under nitrogen for several hours at 70 °C followed by a distillation:



The rotational spectra were recorded at pressures in the range between 0.5 and 4 mTorr and at temperatures around 213 K, using the most advanced of the waveguide microwave Fourier transform spectrometers developed recently by the Kiel group. In such a spectrometer the molecules are exposed to short intense microwave pulses. These pulses coherently drive those molecular subensembles which are capable of electric dipole transitions, and are near resonant to the carrier frequency of the pulse, into non-eigenstates from which they afterwards emit their characteristic transition frequencies. Collisions, and to a lesser extent Doppler dephasing, destroy the coherence in the emission signal and cause it to decay within several microseconds. (For similar emissions the term 'free induction decay', FID, has been coined in NMR spectroscopy). The faint microwave FID-signals, which in fact are deeply buried in noise, are averaged and then numerically analyzed to obtain the frequency domain spectrum. Since originally the discrete Fourier transform method was used for this analysis, this type of time domain spectroscopy is still known as microwave Fourier transform spectroscopy, MWFT, even though the final analysis of the FID-signal is now performed by a least squares fit of the frequencies, amplitudes, relaxation times and phases to the observed decays [10]. A recent review on MWFT-spectrometry has been given in the comprehensive article by Dreizler [11].

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For the Zeeman measurements, in-band waveguide absorption cells were located in the gap of a powerful electromagnet [9]. For a detailed account of rotational Zeeman spectroscopy we refer to the review by Sutter and Flygare [12], which also contains the derivation of the effective Hamiltonian from first principles.

Analysis of the Spectra

We have used the triplet splitting of the $J' \to J = 1 \to 0$ rotational transition in zero magnetic field for accurate determination of the deuterium quadrupole coupling constant, $eqQ(D)$, and we have used the Zeeman-hfs-splitting of the $J' \to J = 2 \to 1$ transition for the determination of the molecular $g_\perp$-value and the molecular magnetic susceptibility anisotropy $(\chi_\perp - \chi_\parallel)$.

For the analysis of the zero field hfs multiplet we have used the first order energy expression in the coupled basis, $|J, I, F, M_F\rangle$. This expression is given in [13]. Division by Planck's constant leads to frequency units:

$$E_{F,J,I}/h = B_0 J(J+1) - D_J J^2 (J+1)^2 + 0.5\, C_\perp C \quad (1)$$
$$- eqQ(D)\, \frac{0.75\, C(C+1) - I(I+1)\, J(J+1)}{2I(2I-1)(2J-1)(2J+3)}.$$

In (1) B_0 is the rotational constant, D_J the centrifugal distortion constant, $C_\perp$ the spin-rotation coupling constant with the sign convention as in [13], $eqQ(D)$ the quadrupole coupling constant, I the deuterium spin quantum number, J the quantum number of the rotational angular momentum, F the quantum number of the overall angular momentum including spin, and $C = F(F+1) - I(I+1) - J(J+1)$.

The quadrupole coupling constant is related to the vibronic ground state expectation value of the electric field gradient by $eqQ(D) = |e| \langle |\delta^2 V/\delta z^2| \rangle Q/h$, where e is the electron charge, Q the nuclear quadrupole moment, and $\delta^2 V/\delta z^2$ the second derivative of the intramolecular field gradient at the deuterium nucleus in direction of the molecular axis.

The quadrupole coupling constant $eqQ(D)$ was determined from the three hyperfine components of the $J' \to J = 1 \to 0$ transition using

$$eqQ(D) = (3\nu_{1\to1} - 2\nu_{0\to1} - \nu_{2\to1})/1.8, \quad (2)$$

where $\nu_{F' \to F}$ is the hfs satellite frequency corresponding to a transition between the F'-sublevels in the $J = 1$ state and the F-sublevel in the $J = 0$ state. As was pointed out in [14], the frequency difference used in (2) is exclusively determined by the quadrupole coupling constant since contributions involving the other molecular parameters in (1) cancel. Our hfs-satellite frequencies are listed in Table 1. We have refrained from using the $J' \to J = 2 \to 1$ hfs pattern for the $eqQ(D)$ determination because the quintet could only be partly resolved even with the high resolution achieved in our present investigation.

Table 1. Zero field frequencies, ν_{exp}, for the $J' \to J = 1 \to 0$ and $J' \to J = 2 \to 1$ rotational transitions as determined from a least squares fit to the microwave FID-signal [10]. The listed frequencies are the mean values of three experiments, and as uncertainties we present the largest deviations from the average values. Also given are the hypothetical center frequencies, $\nu_{C_{J' \to J}}$, of the hfs multiplets, i.e. the rotational transition frequencies which would be observed in the absence of deuterium quadrupole coupling. The center frequencies are calculated from the observed satellite frequencies and from the deuterium quadrupole coupling constant fitted to the observed splittings of the $1 \to 0$ transition (2). The $\delta\nu$ values represent the shifts of the hfs-satellites with respect to this center frequency. The satellites are designated by the appropriate quantum numbers of the coupled representation. The frequencies are given in MHz. Even with the decay fit procedure the $J' \to J = 2 \to 1$ hfs-quintet could only be resolved into a triplet as indicated by * and **.

Rotational transition $J' \to J = 1 \to 0$

$\nu_{C_{1\to0}}$: 8168.906

F	F'	ν_{exp}	$\delta\nu_{\text{exp}}$	$\delta\nu_{\text{calc}}$	Int/%
1	0	8168.796(7)	−.110	−.108	11.1
1	1	8168.959(2)	.053	.054	33.3
1	2	8168.895(1)	−.011	−.011	55.5

Rotational transition $J' \to J = 2 \to 1$

$\nu_{C_{2\to1}}$: 16 337.7998

F	F'	ν_{exp}	$\delta\nu_{\text{exp}}$	$\delta\nu_{\text{calc}}$	Int/%
0	1	16 337.868 (5)	.068 *	.054	11.1
1	1	16 337.677 (9)	−.123	−.108	8.3
1	2	16 337.795 (1)	−.005 **	.000	25.0
2	2	16 337.868 (5)	.068 *	.065	8.3
2	3	16 337.795 (1)	−.005 **	−.004	46.7

For the determination of the satellite frequencies typically 10^7 free induction decays were averaged, and the result was analyzed by directly fitting the frequencies, intensities, phases and relaxation times to the observed decay. From (2) and the hfs frequencies listed in Table 1 our quadrupole coupling constant is $eqQ(D) = 217(6)$ kHz. The quoted uncertainty corresponds to one standard deviation, obtained by Gaussian error propagation from the noise limited accuracy in the satellite frequencies.

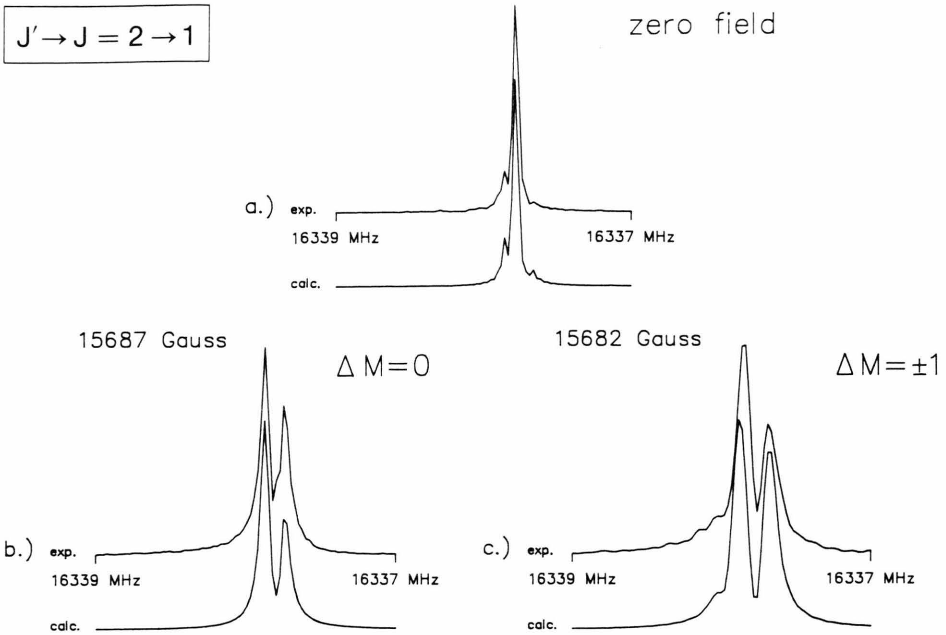

Fig. 1. Power spectra for the $J' \rightarrow J = 2 \rightarrow 1$ multiplets of monodeuterodiacetylene in zero magnetic field (trace *a*) and in fields close to 15.7 kG, observed under $\Delta M_J = 0$ (trace *b*) and $\Delta M_J = \pm 1$ (trace *c*) selection rule. The lower traces show power spectra calculated within the short pulse approximation [9] from the parameters listed in Table 3. Note that trace *a* is a composite of five, trace *b* a composite of nine, and trace *c* a composite of eighteen components. – The experimental conditions were: sample points: *a*, *b* 2048, *c* 1024; sample interval 10 ns; $T = 213$ K; pressures: *a* 0.7 mTorr, *b* 2 mTorr, *c* 4 mTorr; averaging cycles: *a*, *b* $60 \cdot 10^6$, *c* $4 \cdot 10^6$.

The observed splitting between the $F' = 1 \rightarrow F = 1$ satellite and the $F' = 2 \rightarrow F = 1$ satellite, 64 kHz, is slightly smaller than that calculated from our $e\,q\,Q\,(D)$ value neglecting spin rotation, i.e. 65.1 kHz. In contrast, the observed splitting between the $F' = 2 \rightarrow F = 1$ and the $F' = 0 \rightarrow F = 1$ satellites, 99 kHz, is slightly larger than that which is calculated from the quadrupole coupling constant, i.e. 97.7 kHz. From these differences, which according to (1) should be equal to $-2C_\perp$ for the former splitting and $+3C_\perp$ for the latter splitting, one could conclude that the deuterium spin-rotation coupling constant has a value of 0.5 kHz. The experimental uncertainty, however, exceeds the absolute value and we have set $C_\perp$ to zero for all further evaluations.

For the Zeeman patterns we have used the first order expressions in the uncoupled basis $|J, M_J\rangle \cdot |I, M_I\rangle$:

$$\begin{aligned} E_{J,I,M_I,M_J}/h = {} & B_0\,J(J+1) - D_J\,J^2(J+1)^2 + C_\perp\,M_I\,M_J \\ & - e\,q\,Q\,(D)\,\frac{\{3\,M_I^2 - I(I+1)\}\,\{3\,M_J^2 - J(J+1)\}}{4\,I(2\,I-1)\,(2\,J-1)\,(2\,J+3)} \\ & - \mu_N\,g_D\,M_I\,H/h - \mu_N\,g_\perp\,M_J\,H/h \\ & - (1/2\,N)\,\chi_{\text{bulk}}\,H^2/h \\ & - \frac{3\,M_J^2 - J(J+1)}{3(J-1)\,(J+3)}\,\frac{(\chi_\perp - \chi_\parallel)}{N}\,H^2/h. \end{aligned} \tag{3}$$

In (3) M_I and M_J are the quantum numbers for the projections of the deuterium spin and the rotational angular momentum on the magnetic field axis. μ_N is the nuclear magneton, $g_D = 0.8574$ [15] is the nuclear g-value of deuterium, $g_\perp$ the molucular g-value, $\chi_\perp$ and $\chi_\parallel$ are the molecular magnetic susceptibilities perpendicular and parallel to the carbon carbon chain, $\chi_{\text{bulk}} = (\chi_\parallel + 2\chi_\perp)/3$ is the bulk susceptibility, N Avogadro's number, and H the magnetic field strength.

The Zeeman-hfs-FID-signals were observed for three magnetic fields following the $\Delta M_J = 0$ selection rule (electric vector of the incident microwave radiation parallel to the applied magnetic field), and for two magnetic fields following the $\Delta M_J = \pm 1$ selection rule (microwave perpendicular to the magnetic field).

To demonstrate the quality of the observed spectra, we reproduce in Fig. 1 zero field and high field Fourier

Table 2. Zeeman-hfs-frequencies of the $J' \rightarrow J = 2 \rightarrow 1$ rotational transition observed under $\Delta M_J = 0$ and $\Delta M_J = \pm 1$ selection rule at different values of the exterior magnetic field H. The $\delta\nu_{\text{exp}}$ values represent the shifts of the satellites with respect to the hypothetical center frequency at zero field (see Table 1). The satellites are designated with the appropriate quantum numbers of the uncoupled representation. $\delta\nu_{\text{calc}}$ was calculated from the parameters listed in Table 3 according to the energy expression given in (3). All frequencies are given in MHz.

Selection rule ΔM_J: 0

Magnetic field strength H: 15 682 Gauss

M_I	$M_{J'}$	M_J	$\delta\nu_{\text{exp}}$	$\delta\nu_{\text{calc}}$	Int/%
−1	−1	−1	.100	.099	10.0
−1	0	0	−.031	−.033	13.3
−1	1	1	.100	.099	10.0
0	−1	−1		0.44	10.0
0	0	0	−.031	−.014	13.3
0	1	1		.044	10.0
1	−1	−1	.100	.099	10.0
1	0	0	−.031	−.033	13.3
1	1	1	.100	.099	10.0

Selection rule ΔM_J: 0

Magnetic field strength H: 17 861 Gauss

M_I	$M_{J'}$	M_J	$\delta\nu_{\text{exp}}$	$\delta\nu_{\text{calc}}$	Int/%
−1	−1	−1	.123	.123	10.0
−1	0	0	−.044	−.041	13.3
−1	1	1	.123	.123	10.0
0	−1	−1		0.68	10.0
0	0	0	−.044	−.023	13.3
0	1	1		.068	10.0
1	−1	−1	.123	.123	10.0
1	0	0	−.044	−.041	13.3
1	1	1	.123	.123	10.0

Selection rule ΔM_J: 0

Magnetic field strength H: 19 592 Gauss

M_I	$M_{J'}$	M_J	$\delta\nu_{\text{exp}}$	$\delta\nu_{\text{calc}}$	Int/%
−1	−1	−1	.140	.145	10.0
−1	0	0	−.054	−.049	13.3
−1	1	1	.140	.145	10.0
0	−1	−1		0.89	10.0
0	0	0	−.054	−.030	13.3
0	1	1		.089	10.0
1	−1	−1	.140	.145	10.0
1	0	0	−.054	−.049	13.3
1	1	1	.140	.145	10.0

Selection rule ΔM_J: ± 1

Magnetic field strength H: 15 682 Gauss

M_I	$M_{J'}$	M_J	$\delta\nu_{\text{exp}}$	$\delta\nu_{\text{calc}}$	Int/%
−1	−1	−2	.062	.062	10.0
−1	−1	0	.062	.053	1.7
−1	0	−1	.062	.012	5.0
−1	0	1	−.103	−.162	5.0
−1	1	0	.234	.229	1.7
−1	1	2	−.103	−.112	10.0
0	−1	−2	.062	.076	10.0
0	−1	0		−.025	1.7
0	0	−1	.062	.054	5.0
0	0	1	−.103	−.120	5.0
0	1	0		.150	1.7
0	1	2	−.103	−.098	10.0
1	−1	−2	.062	.062	10.0
1	−1	0	.062	.053	1.7
1	0	−1	.062	.012	5.0
1	0	1	−.103	−.162	5.0
1	1	0	.234	.229	1.7
1	1	2	−.103	−.112	10.0

Selection rule ΔM_J: ± 1

Magnetic field strength H: 17 861 Gauss

M_I	$M_{J'}$	M_J	$\delta\nu_{\text{exp}}$	$\delta\nu_{\text{calc}}$	Int/%
−1	−1	−2	.071	.069	10.0
−1	−1	0	.071	.075	1.7
−1	0	−1		.007	5.0
−1	0	1	−.138	−.192	5.0
−1	1	0		.275	1.7
−1	1	2	−.138	−.131	10.0
0	−1	−2	.071	.082	10.0
0	−1	0		−.003	1.7
0	0	−1	.071	.048	5.0
0	0	1	−.138	−.151	5.0
0	1	0		.196	1.7
0	1	2	−.138	−.117	10.0
1	−1	−2	.071	.069	10.0
1	−1	0	.071	.075	1.7
1	0	−1		.007	5.0
1	0	1	−.138	−.192	5.0
1	1	0		.275	1.7
1	1	2	−.138	−.131	10.0

transform power spectra of the $J' \rightarrow J = 2 \rightarrow 1$ transition of monodeuterodiacetylene in its vibronic ground state.

The decay fit routine, rather than the Fourier transform method, was used to obtain the final frequencies. Our observed frequencies are listed in Table 2. The $g_\perp$ value and the susceptibility anisotropy $(\chi_\perp - \chi_\parallel)$ were fitted according to (3) to the observed changes with respect to the zero field FID-signal. Spin-rotation interaction was neglected (see above). In Table 2 we also list the complete Zeeman-hfs patterns including the relative intensities which would be observed in a standard CW-spectrometer if this were possible. These patterns were calculated from our optimized $g_\perp$-value, susceptibility anisotropy and deuterium quadrupole coupling constant as given in Table 3.

Table 3. Summary of the most important molecular parameters determined here.
B_0 = rotational constant in MHz, determined as $\nu_{C_{1\to 0}}/2$.
$e\,q\,Q\,(D)$ = deuterium quadrupole coupling constant in kHz.
$g_\perp$ = molecular g-value. Only its absolute value is determined in the present investigation. In view of the excess positive charge at both hydrogen nuclei we assume $g_\perp$ to be positive.
$\chi_\perp - \chi_\parallel$ = molecular susceptibility anisotropy in units of 10^{-6} erg G^{-2} mol^{-1}.
$Q_\parallel$ = molecular electric quadrupole moment as defined in (4) in units of 10^{-26} esu cm^2. Note that a second definition of $Q_\parallel$ is also used in the literature which differs by a factor of two from the one used here.

B_0	4084.452	± 0.002
$e\,q\,Q\,(D)$	217.0	± 6.0
$g_\perp$	.00734	± 0.00010
$\chi_\perp - \chi_\parallel$	11.5	± 0.7
$Q_\parallel$	17.4	± 0.7

Discussion

The deuterium coupling constant observed here (217 ± 6 kHz) is about 10 kHz more positive than in cyanoacetylene (204 ± 2 kHz) [16] and in the halogenoacetylenes, where it ranges from 205 ± 1 kHz in FCCD to 210 ± 3 kHz in ICCD [14]. This came as a surprise to us since we had expected the electronegative substitutents to pull negative charge from the carbon atom adjacent to the deuterium nucleus and thus to make the coupling constant in the substituted acetylenes more positive than in diacetylene. The opposite is observed. Certainly an extensive comparative ab initio analysis such as was carried out by Huber [17] for some related molecules would be of great interest here.

The magnetic susceptibility anisotropy $(\chi_\perp - \chi_\parallel) = 11.5(7)\,10^{-6}$ erg $G^{-2}\,$mol^{-1} is in close agreement with the susceptibility anisotropy observed earlier for the isoelectronic cyanoacetylenes, where an average value of $11.9(8)\,10^{-6}$ erg $G^{-2}\,$mol^{-1} was observed [18]. This observation will be of use for setting up additivity rules for the molecular magnetic susceptibility tensor from tensors of typical molecular subunits [19].

We finally note that the vibronic ground state expectation value for the molecular electric quadrupole moment of diacetylene can be derived from our experimental rotational constant, $g_\perp$-value and susceptibility anisotropy using the equation [18]

$$Q_\parallel = 0.5\,|e| \cdot \left\{ \sum_n^{\text{nuclei}} (2\,Z_n z_n^2) - \langle 0 | \sum_i^{\text{electrons}} (2 z_i^2 - x_i^2 - y_i^2) | 0 \rangle \right\}$$

$$= \frac{|e|\,h}{8\pi^2 m_p} \frac{g_\perp}{B_0} + \frac{4 m c^2}{|e|} \frac{(\chi_\perp - \chi_\parallel)}{N} \tag{4}$$

with: m_p = proton mass, m = electron mass,
c = velocity of light.

The resultant value is: $Q_\parallel = 17.5(7)\,10^{-26}$ esu cm^{-2}.

The value of $Q_\parallel$ is of interest not only for comparison with quantum chemical results but also for the theoretical understanding of rotational relaxation pathways in the gas phase. The presence of a sizeable molecular quadrupole moment effectively opens pathways for rotational transitions which obey the $|\Delta J| = 2$ propensity rule, as was observed earlier in the case of cyanoacetylene by Bomsdorf [20]. In fact in diacetylene with its larger molecular quadrupole moment and near zero dipole moment such propensity rules should be even more pronounced. A comparison of results might also clarify the relative contributions of molecular shape and electrical moments in rotational relaxation.

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