Deuterium Quadrupole Coupling Constants in Deuteriochloroacetylene

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The deuterium and chlorine nuclear quadrupole coupling constants have been determined for both of the chlorine isotopomers of deuteriochloroacetylene (DCCCl), along with the rotational, centrifugal distortion, and chlorine spin-rotation coupling constants. The values are $B = 5186.97631(22)$ MHz, $D_J = 1.13(2)$ kHz, $eQq(\text{Cl}) = -79.7358(19)$ MHz, $c_f(\text{Cl}) = 1.10(31)$ kHz, and $eQq(\text{D}) = 207.0(28)$ kHz for DCCCl-35, and $B = 5084.17839(30)$ MHz, $D_J = 0.99(2)$ kHz, $eQq(\text{Cl}) = -62.8451(27)$ MHz, $c_f(\text{Cl}) = 0.76(43)$ kHz, and $eQq(\text{D}) = 205.8(39)$ kHz for DCCCl-37.

Introduction

Recently we reported on the deuterium quadrupole coupling constants of deuteriohaloacetylenes [1] with the exception of deuteriochloroacetylene. To fill the gap we now investigated the microwave spectra of the ^{35}Cl - and ^{37}Cl -isotopomers of this molecule as well. We used our microwave Fourier transform (MWFT) spectrometers in X-band (8.0–12.4 GHz) [2], K-Band (18.0–26.4 GHz) [3], and V-band (26.4–40 GHz) [4]. The high resolution of these instruments was essential for the investigations. A comparison of our results with the beam maser data of Tack and Kukolich [5] shows that static gas MWFT spectroscopy approaches the accuracy of molecular beam spectroscopy.

Experimental

Deuteriochloroacetylene (DCCCl) was prepared by dehydrohalogenation of cis-1,2-dichloroethylene with excess molten KOD. The ratio of the yields of DCCCl and HCCCl was approximately 1 : 3 (as determined by microwave spectroscopy). The sample was stored at liquid N_2 temperature in a dark place.

The recordings covered the rotational transitions $J=1-0$, $J=2-1$, and $J=3-2$, in the frequency range 8–33 GHz. We used the spectrometers men-

tioned above. The temperature of the sample was around 230 K, and the pressure around 0.2 Pa (1–2 mTorr). The determination of the frequencies was performed by a fit procedure [6] using the time domain signals. The results are given in Tables 1 and 2.

Analysis

For the analysis we used only resolved components of the multiplets of the rotational transitions $J=1-0$ through $3-2$. The procedure was similar to that given in [1] for DCCBr, and is based on the complete Hamiltonian including matrix elements off-diagonal in J [7]. Our programme SYM2QS [8] was used. The results are enclosed in Tables 1 and 2. In Table 3 we compare our results with older data. Table 4 of [1], which summarizes the deuterium quadrupole coupling constants of the other haloacetylenes, should also be considered: Systematic trends with varying halogen mass cannot be ruled out, but the experimental accuracy so far achievable does not allow us to be more definitive.

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Table 1. Observed and calculated frequencies and derived molecular constants of deuteriochloro(35)acetylene.

Quantum numbers						Frequencies		
J'	$2F'_1$	$2F'$	J	$2F_1$	$2F$	$\nu_{\text{obs.}}/\text{MHz}$	$\nu_{\text{calc.}}/\text{MHz}$	$\Delta\nu/\text{kHz}$
1	1	1	0	3	3	10 393.892	10 393.892	0
1	1	3	0	3	5	10 393.892	10 393.892	0
1	3	1	0	3	1	10 358.051	10 358.051	0
1	3	3	0	3	3	10 357.976	10 357.977	-1
1	3	5	0	3	5	10 358.017	10 358.018	-1
1	5	3	0	3	1	10 377.912	10 377.913	-1
1	5	5	0	3	3	10 377.975	10 377.975	0
1	5	7	0	3	5	10 377.931	10 377.932	-1
2	1	1	1	1	1	20 747.867	20 747.867	0
2	1	3	1	1	3	20 747.867	20 747.867	0
2	1	1	1	3	3	20 783.782	20 783.782	0
2	1	3	1	3	5	20 783.738	20 783.741	-3
2	3	3	1	1	1	20 727.947	20 727.948	-1
2	3	5	1	1	3	20 727.947	20 727.947	0
2	3	1	1	3	1	20 763.791	20 763.788	+3
2	3	3	1	3	3	20 763.864	20 763.863	+1
2	3	5	1	3	5	20 763.823	20 763.821	+2
2	5	3	1	5	3	20 729.648	20 729.660	*
2	5	5	1	5	5	20 729.648	20 729.630	*
2	5	7	1	5	7	20 729.648	20 729.651	*
2	5	3	1	3	1	20 749.580	20 749.522	*
2	5	5	1	3	3	20 749.580	20 749.628	*
2	5	7	1	3	5	20 749.580	20 749.565	*
2	7	5	1	5	3	20 749.580	20 749.579	*
2	7	7	1	5	5	20 749.580	20 749.591	*
2	7	9	1	5	7	20 749.580	20 749.577	*
3	3	1	2	3	1	31 137.627	31 137.628	-1
3	3	3	2	3	3	31 137.704	31 137.703	+1
3	3	5	2	3	5	31 137.663	31 137.661	+2
3	5	3	2	5	3	31 131.999	31 131.986	*
3	5	5	2	5	5	31 131.999	31 132.004	*
3	5	7	2	5	7	31 131.999	31 131.992	*
3	5	3	2	7	5	31 112.070	31 112.068	*
3	5	5	2	7	7	31 112.070	31 112.043	*
3	5	7	2	7	9	31 112.070	31 112.066	*
3	3	3	2	1	1	31 117.748	31 117.783	*
3	3	5	2	1	3	31 117.748	31 117.742	*
3	3	3	2	3	1	31 117.748	31 117.720	*
3	5	5	2	3	3	31 117.748	31 117.769	*
3	5	7	2	3	5	31 117.748	31 117.735	*
3	7	5	2	5	3	31 122.693	31 122.676	*
3	7	7	2	5	5	31 122.693	31 122.702	*
3	7	9	2	5	7	31 122.693	31 122.680	*
3	9	7	2	7	5	31 122.693	31 122.688	*
3	9	9	2	7	7	31 122.693	31 122.692	*
3	9	11	2	7	9	31 122.693	31 122.685	*
Molecular parameters:						Standard deviation:		
B (MHz)						5186.97631(22)		
D_J (MHz)						0.00113(2)		
eQq (Cl) (MHz)						-79.7358(19)		
C_I (Cl) (MHz)						0.00110(31)		
eQq (D) (MHz)						0.2070(28)		

* not used for fit; only $\Delta F = \Delta F_1$ considered.

Table 2. Observed and calculated frequencies and derived molecular constants of deuteriochloro(37)acetylene.

Quantum numbers						Frequencies		
J'	$2F'_1$	$2F'$	J	$2F_1$	$2F$	$\nu_{\text{obs.}}/\text{MHz}$	$\nu_{\text{calc.}}/\text{MHz}$	$\Delta\nu/\text{kHz}$
1	1	1	0	3	3	10 184.071	10 184.070	+1
1	1	3	0	3	5	10 184.071	10 184.071	0
1	3	1	0	3	1	10 155.831	10 155.830	+1
1	3	3	0	3	3	10 155.756	10 155.756	0
1	3	5	0	3	5	10 155.798	10 155.798	0
1	5	3	0	3	1	10 171.471	10 171.471	0
1	5	5	0	3	3	10 171.534	10 171.533	+1
1	5	7	0	3	5	10 171.490	10 171.489	+1
2	1	1	1	1	1	20 336.680	20 336.681	-1
2	1	3	1	1	3	20 336.680	20 336.680	0
2	1	1	1	3	3	20 364.998	20 364.995	+3
2	1	3	1	3	5	20 364.954	20 364.953	+1
2	3	3	1	1	1	20 320.979	20 320.978	+1
2	3	5	1	1	3	20 320.979	20 320.978	+1
2	3	1	1	3	1	20 349.215	20 349.218	-3
2	3	3	1	3	3	20 349.288	20 349.293	-5
2	3	5	1	3	5	20 349.249	20 349.251	-2
2	5	3	1	5	3	20 322.320	20 322.333	*
2	5	5	1	5	5	20 322.320	20 322.302	*
2	5	7	1	5	7	20 322.320	20 322.324	*
2	5	3	1	3	1	20 338.030	20 337.973	*
2	5	5	1	3	3	20 338.030	20 338.079	*
2	5	7	1	3	5	20 338.030	20 338.016	*
2	7	5	1	5	3	20 338.030	20 338.029	*
2	7	7	1	5	5	20 338.030	20 338.040	*
2	7	9	1	5	7	20 338.030	20 338.027	*
3	3	1	2	3	1	30 517.486	30 517.483	+3
3	3	3	2	3	3	30 517.555	30 517.557	-2
3	3	5	2	3	5	30 517.515	30 517.516	-1
3	5	3	2	5	3	30 513.045	30 513.040	*
3	5	5	2	5	5	30 513.045	30 513.057	*
3	5	7	2	5	7	30 513.045	30 513.045	*
3	5	3	2	7	5	30 497.346	30 497.344	*
3	5	5	2	7	7	30 497.346	30 497.319	*
3	5	7	2	7	9	30 497.346	30 497.342	*
3	3	3	2	1	1	30 501.814	30 501.855	*
3	3	5	2	1	3	30 501.814	30 501.814	*
3	5	3	2	3	1	30 501.814	30 501.795	*
3	5	5	2	3	3	30 501.814	30 501.843	*
3	5	7	2	3	5	30 501.814	30 501.809	*
3	7	5	2	5	3	30 505.711	30 505.702	*
3	7	7	2	5	5	30 505.711	30 505.728	*
3	7	9	2	5	7	30 505.711	30 505.706	*
3	9	7	2	7	5	30 505.711	30 505.713	*
3	9	9	2	7	7	30 505.711	30 505.717	*
3	9	11	2	7	9	30 505.711	30 505.711	*
3	3	1	2	5	3	30 528.757	30 528.728	*
3	3	3	2	5	5	30 528.757	30 528.770	*
3	3	5	2	5	7	30 528.757	30 528.751	*
3	7	5	2	7	5	30 490.000	30 490.006	*
3	7	7	2	7	7	30 490.000	30 489.990	*
3	7	9	2	7	9	30 490.000	30 490.003	*
Molecular parameters:						Standard deviation:		
B (MHz)						5084.17839(30)		
D_J (MHz)						0.00099(2)		
eQq (Cl) (MHz)						-62.8451(27)		
C_I (Cl) (MHz)						0.00076(43)		
eQq (D) (MHz)						0.2058(39)		

* not used for fit; only $\Delta F = \Delta F_1$ considered.

Table 3. Comparison of the molecular parameters of DCCCl as determined in this work with earlier data.

Constant	DCCCl-35		DCCCl-37	
	this work	[5]	this work	[9]
B (MHz)	5186.97631 (22)	—	5084.17839 (30)	—
D_J (MHz)	0.00113 (2)	—	0.00099 (2)	—
$B-2D_J$ (MHz)	5186.97405 (22)	5186.9739 (10)	5084.17641 (30)	5084.24 (1)
eQq (Cl) (MHz)	−79.7358 (19)	−79.7395 (10)	−62.8451 (27)	−63.12 (1)
c_I (Cl) (kHz)	1.10 (31)	1.3 (5)	0.76 (43)	—
eQq (D) (kHz)	207.0 (28)	208.5 (15)	205.8 (39)	—

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