Deuterium Quadrupole Coupling Constants in Deuterochloroacetylene

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The deuterium and chlorine nuclear quadrupole coupling constants have been determined for both of the chlorine isotopomers of deuterochloroacetylene (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, $eQq(\mathrm{Cl}) = -79.7358(19)$ MHz, $c_l(\mathrm{Cl}) = 1.10(31)$ kHz, and $eQq(\mathrm{D}) = 207.0(28)$ kHz for DCCCl-35, and $B = 5084.17839(30)$ MHz, $D_J = 0.99(2)$ kHz, $eQq(\mathrm{Cl}) = -62.8451(27)$ MHz, $c_l(\mathrm{Cl}) = 0.76(43)$ kHz, and $eQq(\mathrm{D}) = 205.8(39)$ kHz for DCCCl-37.

Introduction

Recently we reported on the deuterium quadrupole coupling constants of deuterohaloacetylenes [1] with the exception of deuterochloroacetylene. 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

Deuterochloroacetylene (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 mentioned 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.

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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 deuterochloro(35)acetylene.

Quantum numbers						Frequencies		
J'	$2F_1'$	$2F'$	J	$2F_1$	$2F$	$\nu_{obs.}$/MHz	$\nu_{calc.}$/MHz	$\Delta\nu$/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	5	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)	1.471 kHz
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 deuterochloro(37)acetylene.

Quantum numbers						Frequencies		
J'	$2F_1'$	$2F'$	J	$2F_1$	$2F$	$\nu_{obs.}$/MHz	$\nu_{calc.}$/MHz	$\Delta\nu$/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)	2.056 kHz
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_1(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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