

Microwave Spectrum and Structural Parameters of 4-Chlorobuten-3-yne

FRED KARLSSON, MATS GRANBERG and RAGNAR VESTIN

Department of Physical Chemistry, Arrhenius Laboratory, University of Stockholm, S-104 05 Stockholm, Sweden

The microwave spectra of the two natural species of 4-chlorobuten-3-yne: $\text{CH}_2\text{CHCC}^{35}\text{Cl}$ and $\text{CH}_2\text{CHCC}^{37}\text{Cl}$ together with the three possible monodeuterated species: $\text{CDHCHCC}^{35}\text{Cl}$, $\text{CHDCHCC}^{35}\text{Cl}$ and $\text{CH}_2\text{CDCC}^{35}\text{Cl}$, have been measured and assigned in the region 34 000—40 000 MHz. The rotational constants A, B and C for the ground state as well as the centrifugal distortion constants D_J and D_{JK} were determined. The centrifugal distortion constants were also calculated from a simple estimated valence force field.

The positions of the chlorine atom and the three hydrogen atoms in the principal axis system of the molecule $\text{CH}_2\text{CHCC}^{35}\text{Cl}$ were obtained with Kraitchman equations from the change in moments of inertia due to isotopic substitution. The nuclear quadrupole coupling constant χ_{aa} was calculated for the $\text{CH}_2\text{CHCC}^{35}\text{Cl}$ and $\text{CH}_2\text{CHCC}^{37}\text{Cl}$ species from the hyperfine splittings of the rotational lines.

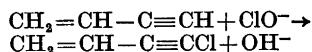
The substance 4-chlorobuten-3-yne was first described by Carothers *et al.*¹ Recently we have confirmed this identification with NMR, IR and mass spectroscopy,² and in order to obtain a detailed structure we have also started to investigate 4-chlorobuten-3-yne with microwave spectroscopy and electron diffraction in gas phase. The configuration with the chlorine atom in line with three of the four carbon atoms is very suitable for a study of the molecular structure with the electron diffraction method. However, since the hydrogen atoms have a low nuclear charge, their accurate positions in the molecule are sometimes very hard to determine by electron diffraction. Therefore it was convenient to substitute the different hydrogen atoms by deuterium and obtain their positions with Kraitchman's equations³ from

the changes in moments of inertia on isotopic substitution as recommended by Costain.⁴ The moments of inertia were obtained from the rotational constants measured by microwave spectroscopy.

4-Chlorobuten-3-yne is an important member of the series of highly unsaturated chlorohydrocarbons which we have been studying for some time.⁵⁻⁸

EXPERIMENTAL

4-Chlorobuten-3-yne was prepared by treating butenyne with hypochlorite solution:¹



The sample was isolated by distillation *in vacuo* and finally gas-liquid chromatography at a temperature of 100 °C. The column was packed with diethylhexylsebacete (15 %) absorbed on Chromosorb. Pure 4-chlorobuten-3-yne is unstable to polymerization but could be stored at -70 °C.

A mixture containing about 10 % of each of the three possible monodeuterated species of 4-chlorobuten-3-yne was obtained in the following way. We used the fact that acetylene is a very weak acid and prepared a mixture of normal and deuterated acetylene: C_2H_2 , C_2HD and C_2D_2 by leading ordinary acetylene free from acetone from a steel flask through a strong alkaline solution of KOH dissolved in a mixture of H_2O and D_2O . The D/H-ratio was held at 1/3 in this solution. The partly deuterated acetylene leaving the washing flask was then dimerized to butenyne in a liquid Cu(I) catalyst according to Nieuwland *et al.*⁵



The partly deuterated butenyne was purified by distillation *in vacuo* and used to synthesize

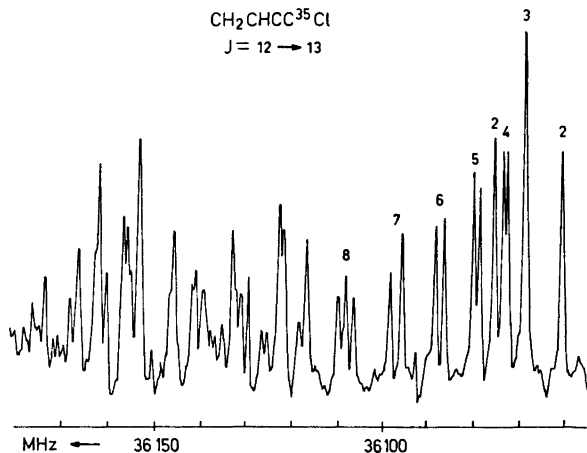


Fig. 1. Bandhead of the $J=12 \rightarrow 13$ transitions of $\text{CH}_2\text{CHCC}^{35}\text{Cl}$ near 36 100 MHz. Sweep rate 0.5 MHz/s.

4-chlorobuten-3-yne as described above. The amount of double and triple deuterated species of 4-chlorobuten-3-yne in this sample was found to be negligible. The rate of deuteration on acetylene and butenyne was controlled by IR-spectroscopy.

The microwave spectra were recorded on a Hewlett-Packard model 8460A R-band microwave spectrometer with a phase stabilized source oscillator. The upper part of the R-band (34 000–40 000 MHz) was used due to the better performance of the spectrometer in that region. The precision of the measured transitions was estimated to be 0.05 MHz.

MICROWAVE SPECTRUM

Most of the lines in the spectrum are gathered in bands at intervals of approximately 2770 MHz. Each band begins abruptly on the low frequency side and continues for 300–400 MHz with decreasing intensity. A characteristic bandhead is shown in Fig. 1. The line abundance of the bands and the repeated structure within the bands indicates the existence of several low lying excited vibrational modes, presumably states in which the skeletal bending modes are excited.

4-Chlorobuten-3-yne is expected to be an almost prolate symmetric rotor with the dipole moment lying close to the principal axis a: see Fig. 2. Therefore the microwave spectrum is expected to consist of R-branch a-type transitions with $\Delta J = +1$ and $\Delta K_{-1} = 0$. Conse-

quently, the regions of dense absorption are assigned to the transitions with $K_{-1} \geq 2$. The remaining transitions with $K_{-1} = 0$ and $K_{-1} = 1$ are found outside the bands and identified on the basis of their characteristic second order (but unresolved) Stark effects.

The individual transitions within the bands were identified by their relative intensities and nuclear quadrupole hyperfine splitting; see Table 1. This observable nuclear quadrupole splitting is due to transitions with $\Delta F = +1$. The splitting increases with K_{-1} . Thus for low values of K_{-1} , the four nuclear quadrupole components merge into one single peak. As K_{-1} increases the peak splits into two, and

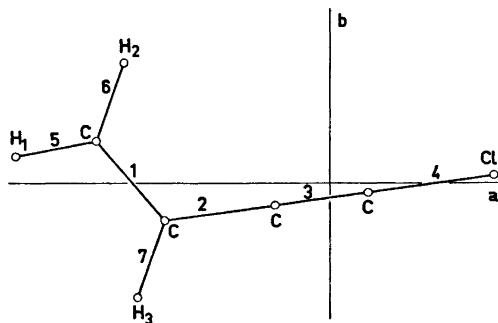


Fig. 2. Assumed structure of 4-chlorobuten-3-yne with principal axes of inertia.

Table 1. Observed rotational transitions and nuclear quadrupole hyperfine splitting in MHz for $\text{CH}_2\text{CHCC}^{35}\text{Cl}$ and $\text{CH}_2\text{CHCC}^{37}\text{Cl}$.

Transition						$\text{CH}_2\text{CHCC}^{35}\text{Cl}$		$\text{CH}_2\text{CHCC}^{37}\text{Cl}$	
J	K_{-1}	K_{+1}	J	K_{-1}	K_{+1}	ν_{obs}	$\Delta\nu_{\text{Qobs}}$	ν_{obs}	$\Delta\nu_{\text{Qobs}}$
13	1	13	12	1	12	35753.07		34926.75	
13	0	13	12	0	12	36045.52		35206.64	
13	2	12	12	2	11	36060.91		35220.86	
13	3	11	12	3	10	36068.88	0.42	35228.39	
13	4	10	12	4	9	36073.26	0.87	35232.74	0.66
13	2	11	12	2	10	36075.64		35234.31	
13	5	9	12	5	8	36079.60	1.31	35238.94	1.04
13	6	8	12	6	7	36087.56	1.93	35246.76	1.54
13	7	7	12	7	6	36097.09	2.56	35256.07	2.06
13	8	6	12	8	5	36108.06	3.40	35266.88	2.73
13	1	12	12	1	11	36361.73		35508.29	
14	1	14	13	1	13	38502.49		37612.68	
14	0	14	13	0	13	38815.51		37912.33	
14	2	13	13	2	12	38834.22		37929.59	
14	3	12	13	3	11	38843.55		37938.44	
14	4	11	13	4	10	38848.12	0.66	37942.93	0.48
14	2	12	13	2	11	38852.62		37946.41	
14	5	10	13	5	9	38854.87	1.07	37949.56	0.82
14	6	9	13	6	8	38863.42	1.52	37957.95	1.21
14	7	8	13	7	7	38873.63	2.08	37967.96	1.62
14	8	7	13	8	6	38885.49	2.64	37979.53	2.14
14	1	13	13	1	12	39157.94		38238.93	

Table 2. Observed rotational transition in MHz for the three monodeuterated species of 4-chlorobuten-3-yne.

Transition						$\text{CDHCHCC}^{35}\text{Cl}^a$	$\text{CHDCHCC}^{35}\text{Cl}^b$	$\text{CH}_2\text{CDCC}^{35}\text{Cl}$
J	K_{-1}	K_{+1}	J	K_{-1}	K_{+1}	ν_{obs}	ν_{obs}	ν_{obs}
13	1	13	12	1	12	34202.70	34893.54	35023.66
13	0	13	12	0	12	34472.51	35222.95	
13	2	12	12	2	11	34486.15	35244.57	35372.80
13	3	11	12	3	10	34493.63	35253.98	35381.37
13	4	10	12	4	9	34498.37	35256.51	35382.81
13	2	11	12	2	10	34498.71	35267.67	35395.55
13	5	9	12	5	8	34504.97	35260.88	35385.66
13	6	8	12	6	7	34513.28		
13	7	7	12	7	6	34523.17		
13	1	12	12	1	11	34762.86	35588.43	35715.70
14	1	14	13	1	13	36832.94	37576.42	37716.61
14	0	14	13	0	13	37121.92		
14	2	13	13	2	12	37138.39	37954.80	38093.00
14	3	12	13	3	11	37147.08	37966.09	38103.32
14	4	11	13	4	10	37152.03	37968.64	38104.60
14	2	12	13	2	11	37154.07	37983.65	38121.40
14	5	10	13	5	9	37159.09	37973.25	38107.53
14	6	9	13	6	8	37168.00	37979.25	38111.78
14	7	8	13	7	7	37178.65	37986.76	
14	1	13	13	1	12	37436.15	38324.83	38461.90

^aDeuterium *trans* to the chloroacetylene group. ^bDeuterium *cis* to the chloroacetylene group.

Table 3. Observed rotational constants in MHz for five isotopic species of 4-chlorobuten-3-yne.

	A	B	C
CH ₂ CHCC ³⁵ Cl	41927. ± 50	1410.388 ± 0.004	1363.563 ± 0.004
CH ₂ CHCC ³⁷ Cl	41907. ± 50	1377.027 ± 0.004	1332.289 ± 0.004
CDHCHCC ³⁵ Cl ^a	41705. ± 50	1347.939 ± 0.004	1304.846 ± 0.004
CHDCHCC ³⁵ Cl ^b	35145. ± 50	1382.398 ± 0.006	1328.929 ± 0.006
CH ₂ CDCC ³⁵ Cl	35341. ± 60	1387.239 ± 0.008	1333.992 ± 0.008

^a Deuterium *trans* to the chloroacetylene group. ^b Deuterium *cis* to the chloroacetylene group.

finally into four, observable peaks. Only splitting into doublets was observed since the transitions with $K_{-1} \geq 9$ were obscured by the very dense vibrational satellite bands: see Fig. 1. The observable splitting is mainly determined by only one nuclear quadrupole coupling constant χ_{aa} .⁶ For ³⁵Cl in CH₂CHCC³⁵Cl this value was determined to be $\chi_{aa} = -76.9 \pm 0.4$ MHz and for ³⁷Cl in CH₂CHCC³⁷Cl $\chi_{aa} = -60.9 \pm 0.4$.

The assignment of the microwave transitions from the three possible monodeuterated species: CDHCHCC³⁵Cl, CHDCHCC³⁵Cl and CH₂CDCC³⁵Cl, was very complicated for two of them due to band overlapping with the more abundant CH₂CHCC³⁷Cl species. The lines

Table 4. Measured and calculated centrifugal distortion constants for five isotopic species of 4-chlorobuten-3-yne in kHz.

		Observed	Calculated
CH ₂ CHCC ³⁵ Cl	D_J	0.12 ± 0.01	0.12
	D_{JK}	-28.55 ± 0.02	-26.43
CH ₂ CHCC ³⁷ Cl	D_J	0.11 ± 0.01	0.12
	D_{JK}	-27.94 ± 0.02	-25.93
CDHCHCC ³⁵ Cl ^a	D_J	0.13 ± 0.01	0.12
	D_{JK}	-29.65 ± 0.02	-27.44
CHDCHCC ³⁵ Cl ^b	D_J	0.13 ± 0.02	0.13
	D_{JK}	-21.05 ± 0.03	-19.74
CH ₂ CDCC ³⁵ Cl	D_J	0.13 ± 0.02	0.11
	D_{JK}	-14.85 ± 0.05	-13.25

^a Deuterium *trans* to the chloroacetylene group.
^b Deuterium *cis* to the chloroacetylene group.

outside with $K_{-1} = 1$ were weaker than expected due to incomplete Stark modulation. The problem was solved by making high resolution sweeps at low pressure and low temperature of the $J = 12 \rightarrow 13$ and $J = 13 \rightarrow 14$ bands from the CH₂CHCC³⁷Cl molecules in samples with and without deuterated species. A close comparison between these spectra revealed the contributions from the deuterated species. Once these bandheads were found it was rather easy to find the $K_{-1} = 1$ transitions outside the bands: see Table 2.

Corresponding lines in the spectra of the deuterated species CDHCHCC³⁵Cl, CHDCHCC³⁵Cl and CH₂CDCC³⁵Cl showed the same nuclear quadrupole hyperfine structure as the CH₂CHCC³⁵Cl species. The rotational constants A, B and C for the natural and deuterated species of 4-chlorobuten-3-yne are given in Table 3.

CENTRIFUGAL DISTORTION

It was necessary to include the centrifugal distortion terms D_J and D_{JK} in the least squares fit of the rotational constants A, B and C to the observed spectra. The term D_{JK} makes an important contribution and reverses the normal order of the K_{-1} values. However, these centrifugal distortion constants could be adequately predicted with theoretical calculations from a simple estimated diagonal force field:¹⁰ see Table 4. In fact these calculations turned out to be a very valuable aid in the assignment of the overlapped deuterium spectral bands. The bandheads of the species CH₂CDCC³⁵Cl were in the most dense regions of the vibrational satellites from another deuterated species CHDCHCC³⁵Cl as well as from the natural

Table 5. The absolute values of the coordinates for the chlorine atom and the hydrogen atoms calculated with Kraitchman's equations and the distances between these atoms. Conversion factor 505 376 (MHz) ($\text{au}\text{\AA}^2$).

Kraitchman's coordinates (\AA)			
Atom	$ a $	$ b $	
Cl	2.1090	0.1000	
H ₁	4.0858	0.2731	
H ₂	2.6988	1.5582	
H ₃	2.4429	1.5141	
Chlorine-hydrogen and hydrogen-hydrogen distances (\AA).			
Cl—H ₁	6.197	H ₁ —H ₂	1.891
Cl—H ₂	5.024	H ₁ —H ₃	2.428
Cl—H ₃	4.830	H ₂ —H ₃	3.083

species $\text{CH}_2\text{CHCC}^{37}\text{Cl}$, but the general appearance of the bandheads from $\text{CH}_2\text{CDCC}^{35}\text{Cl}$ were well predicted from the theoretical calculation of the D_{JK} distortion constant. This D_{JK} -value turned out to be considerable less than the values obtained from the other species: see Table 4.

The following symbols are used for the force constants.¹¹ K_i is the force constant for the stretching of the bond i , K_{ij} is the bending of the angle between the bonds i and j , ρ_k^{ij} is the bending of the bond k out of the plane spanned by the bonds i and j , χ_{kl}^{ij} finally is the torsion between the planes spanned by the bonds i and j , and k and l , respectively. The values for the constants are, with the bond numbers of Fig. 2: $K_5 = K_6 = 5.53$, $K_7 = 5.38$, $K_1 = 7.69$, $K_2 = 7.12$, $K_3 = 16.49$, $K_4 = 5.16$, $K_{12} = 1.08$, $K_{15} = K_{16} = 0.59$, $K_{17} = 0.42$, $K_{23} = 0.32$, $K_{34} = 0.28$, $\delta_1^{27} = 0.273$, $\delta_1^{56} = 0.223$ and $\chi_{56}^{27} = 0.577$ in $\text{mdyn}/\text{\AA}$ and $\text{mdyn}/\text{\AA}$ for stretching and bending constants, respectively. We have assumed the same force constants for bending in plane and out of plane for the acetylenic group. The agreement between measured and calculated centrifugal distortion parameters is of course no direct proof of the validity of this simple force field.

MOLECULAR STRUCTURE

The measured inertial defect for $\text{CH}_2\text{CHCC}^{35}\text{Cl}$ is $0.25 \pm 0.02 \text{ au}\text{\AA}^2$ which can be compared with the value $0.29 \text{ au}\text{\AA}^2$ obtained from theoretical

calculations using the previous mentioned valence force field assuming planar configuration.^{10,12} Thus there is no reason to expect the molecular structure to deviate from planarity.

The absolute values of the Cartesian coordinates for the chlorine atom and the hydrogen atoms were calculated in the principal axis system of the $\text{CH}_2\text{CHCC}^{35}\text{Cl}$ molecule from the changes in the moments of inertia I_b and I_c on isotopic substitution:^{3,4} see Table 5. We have also calculated the distances between these atoms to combine with later information from electron diffraction measurements. However, great care must be taken in the use of these structural parameters due to several sources of uncertainties. Primarily, these uncertainties arise from the vibrational effects. It was not possible to obtain the moments of inertia I_a accurate enough so we used I_b and I_c assuming no change in inertial defect due to substitution. However, theoretical calculations for the different isotopic species with the force field above suggest that the inertial defect increases by as much as $0.01 \text{ au}\text{\AA}^2$ for the hydrogens H₂ and H₃. This alone leads to an uncertainty in the b -coordinates of H₂ and H₃ of about 0.005\AA .

There is also the well known effect of change in effective bond length with isotopic substitution especially for the hydrogen-deuterium substitution.^{10,13} This effect might be of the magnitude 0.01\AA for the hydrogen-hydrogen distances and 0.005\AA for the hydrogen-chlorine distances.

If an atom is close to a principal axis there is a corresponding uncertainty in the obtained distance to that axis. Therefore the b -coordinate of the chlorine atom is rather uncertain due to its position near the a -axis: see Fig. 2. However, even if we assume such a large error as 0.1\AA in this coordinate the error in the Cl—H₁ distance becomes only 0.004\AA and in the Cl—H₂ and Cl—H₃ distances 0.03\AA . From this discussion we expect the deviation of the r_s -distances obtained to be about $\pm 0.005 \text{\AA}$ for the hydrogen-chlorine distances and about $\pm 0.01 \text{\AA}$ for the hydrogen-hydrogen distances. The best determined value is probably the molecular length given by the distance Cl—H₁ to 6.197\AA .

The distance parameters from the substitution structure r_s are actually not directly com-

parable with the distances obtained with electron diffraction due to vibrational effect.^{12,14} However, both methods are comparable in the average structure r_z and this can be calculated from the effective parameters obtained by microwave spectroscopy.^{12,15} We have done that using the force field given above but the magnitude of these corrections falls within the uncertainty of the r_s -distances. Moreover, even for the average structure the deuterium substitution causes an error in the coordinates.¹³ However, if the effective principal moments of inertia are to be used directly for a comparison with the principal moments of inertia calculated from an average structure it would be advisable to calculate the correction from effective to average parameters. Using the force field above the effective moments of inertia $I_b^0=358.324$ and $I_c^0=370.629$ au \AA^2 for $\text{CH}_2\text{CHCC}^{35}\text{Cl}$ were transformed to the corresponding average parameters $I_b^z=358.486$ and $I_c^z=370.595$ au \AA^2 . No attempts were made to look for ^{13}C -substituted species in natural abundance due to the frequent occurrence of vibrational satellites in the expected spectral regions.

Acknowledgements. We thank all those who have contributed to this paper and especially Dr. Stig Ljunggren, Dr. Allan Rupprecht and Dr. Harald Møllendal for pleasant cooperation and valuable discussions.

REFERENCES

1. Carothers, W. H., Jacobson, R. A. and Berechet, G. J. *J. Amer. Chem. Soc.* 55 (1933) 4665.
2. Granberg, M., Karlsson, F. and Vestin, R. *Acta Chem. Scand. B* 28 (1974) 580.
3. Kraitchman, J. *Amer. J. Phys.* 21 (1953) 17.
4. Costain, C. C. *J. Chem. Phys.* 29 (1958) 864.
5. Karlsson, F., Borg, A. and Vestin, R. *Acta Chem. Scand.* 26 (1972) 3394.
6. Karlsson, F. and Vestin, R. *Acta Chem. Scand.* 27 (1973) 3033.
7. Karlsson, F., Granberg, M. and Vestin, R. *Acta Chem. Scand. A* 28 (1974) 201.
8. Karlsson, F., Granberg, M. and Vestin, R. *Acta Chem. Scand. A* 28 (1974) 206.
9. Nieuwland, J. A. and Vogt, R. *The Chemistry of Acetylene*, New York 1945.
10. Gordy, W. and Cook, R. L. *Microwave Molecular Spectra*, Interscience, New York 1970.
11. Gribov, L. A. *Vvedenie v teoriyu i raschet kolebatelnykh spektrov mnogoatomnykh molekul*, Istatelstvo Leningradskogo Universita, 1965.
12. Herschbach, D. R. and Laurie, V. W. *J. Chem. Phys.* 37 (1962) 1668.
13. Laurie, V. W. and Herschbach, D. R. *J. Chem. Phys.* 37 (1962) 1687.
14. Morino, Y., Kuchitsu, K. and Oka, T. *J. Chem. Phys.* 36 (1962) 1108.
15. Oka, T. and Morino, Y. *J. Mol. Spectrosc.* 8 (1962) 300.

Received August 12, 1974.