Microwave Spectrum of 2-Chloro-1,3-butadiene

FRED KARLSSON and ZUZANA SMITH

Department of Physical Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

The microwave spectrum of 2-chloro-1,3-butadiene (Chloroprene) was recorded in order to supply additional information for a detailed analysis of the molecular structure with electron diffraction in the gas phase. The preliminary structure data from the electron diffraction experiments made it possible to predict the rotational constants accurately enough for an assignment of the microwave transitions.

The substance was prepared according to Carothers *et al.*[1] A sample with two deuterated species was prepared by using deuterated instead of normal hydrochloric acid. Deuterium only appeared in either of the two positions *cis* or *trans* to chlorine in the chlorovinyl part of 2-chloro-1,3-butadiene.

The spectral region 18 – 40 GHz was investigated at low resolution in order to assign the spectral transitions. It was obvious that the spectrum was dominated by strong Q-branch transitions, active through the μ_b-dipole moment. The strongest Q_b-lines were first identified and this information together with the expected planarity of the molecule made it possible to find the R-branch transitions.[2] The strongest Q-branch and R-branch b-type transitions and the strongest lines yielded by the weak R-branch a-type transitions were measured in high resolution in the region 18 – 26.5 GHz. The rotational constants and centrifugal distortion constants were fitted to the observed spectrum by the least squares method: See Table 1. About twenty transitions were included in the fit for each isotopic species. It was not possible to refine all five centrifugal distortion constants for the deuterated species.

The effect of nuclear quadrupole coupling between the chlorine nucleus and the rotation of the molecule is observable as a splitting of the rotational lines. The quadrupole coupling constants χ_{aa} and χ_{bb} were fitted to the observed splittings with the least squares method. The values obtained for ^{35}Cl in $CH_2CH^{35}ClCHCH_2$ are: $\chi_{aa} = 5.2(2)$ and $\chi_{bb} = -37.5(2)$ MHz. The transition $2_{2,1} \leftarrow 1_{1,0}$ was split into six observable peaks, and this observation was important for the accuracy of the constants. Accurate values for the less abundant ^{37}Cl-species were not obtained.

The determination of a complete substitution structure would at least require measurements of all possible monosubstituted species of 2-chloro-1,3-butadiene. In fact, two enriched samples have been prepared: one containing the three remaining deuterated species and one with the four ^{13}C-species. The concentration of each of the monosubstituted species was about 20 mol % in the deuterated sample and about 10 mol % in the ^{13}C sample. However, the spectra of these samples turned out to be very complex due to the frequently occurring overlap with the more abundant normal species and the complicated character of the 2-chloro-1,3-butadiene spectrum.

1. Carothers, W. H., Berchet, G. J. and Collins, A. M. *J. Am. Chem. Soc. 54* (1932) 4066.
2. Karlsson, F., Granberg, M. and Vestin, R. *Acta Chem. Scand. A 29* (1975) 855.

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Table 1. Rotational constants, centrifugal distortion constants and inertial defect for four isotopic species of 2-chloro-1,3-butadiene.

	$CH_2CH^{35}ClCHCH_2$	$CH_2CH^{37}ClCHCH_2$	$CDCH^{35}ClCHCH_2$[a]	$CHDCH^{35}ClCHCH_2$[b]
A/MHz	5438.865(8)	5359.4(1)	5262.77(4)	5045.62(2)
B/MHz	3743.080(8)	3685.57(1)	3647.39(1)	3742.10(1)
C/MHz	2216.321(8)	2182.94(1)	2153.52(1)	2147.74(1)
Δ_J/kHz	0.83(8)	0.5(2)	–	–
Δ_{JK}/kHz	−1.80(9)	−2.7(6)	−4.8(2)	−6.4(1)
Δ_K/kHz	3.3(1)	4.3(7)	7.0(6)	7.8(3)
δ_J/kHz	0.50(1)	0.44(5)	–	–
δ_K/kHz	0.96(6)	1.3(4)	3.5(1)	3.5(1)
Δ/u Å^2	0.089(1)[c]	0.092(2)[c]	0.087(2)[c]	0.093(2)[c]

[a] Deuterium *cis* to chlorine. [b] Deuterium *trans* to chlorine. [c] Conversion factor: 505374 (MHz) (u Å^2).

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