The polarographic method is a simple one for determining rate constants of radicals but the absence of qualitative information about the radicals is, however, a great disadvantage.

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# Microwave Spectrum of Chlorobutatriene

FRED KARLSSON, RAGNAR VESTIN and ASTRID BORG

*Institute of Inorganic and Physical Chemistry, University of Stockholm, Box 6801, S-113 86 Stockholm, Sweden*

The simplest molecule containing three cumulated double bonds — butatriene — has been carefully studied by electron diffraction,[1] IR and Raman spectroscopy.[2] As butatriene itself has no permanent dipole moment it produces no pure rotational spectra. Chlorobutatriene, however, has a dipole moment and it is the only four carbon cumulene studied so far with microwave spectroscopy. The substance has been discovered by Vestin et al.[3] It is extremely unstable and difficult to handle.

The spectrum has been recorded in the region $25\,000 - 40\,000$ MHz. It is very complex but most of its lines are grouped together in bands at intervals of approximately $3\,000$ MHz. Each band begins abruptly on the low frequency side and continues for $500 - 600$ MHz with decreasing intensity. There is also a repeated structure within the band. A typical bandhead is shown in Fig. 1.

In order to solve the spectrum, a theoretical structure was proposed with butatriene $C-C$ and $C-H$ bond lengths,[1] vinylchloride $C-Cl$ bond length,[4] the $C-C-Cl$ angle $122°$ and all $C-C-H$ angles $120°$. See Fig. 2.

This gives an expected value of the asymmetry parameter $\varkappa = -0.992$ and from this chlorobutatriene is expected to be an almost prolate symmetric rotor. Consequently the regions of dense absorption are logically assigned to $\varDelta J = +1, \varDelta K_{-1} = 0$ transitions which are active through the $\mu_a$ dipole moment. CNDO calculations on the assumed structure give a theoretical dipole moment $\mu_a = -2.05$, $\mu_b = 0.44$ and $\mu_c = 0$ debye.

The line abundance of the bands and the repeated structure with decreasing intensity within the bands indicate a low lying successively excited vibrational mode.

In Fig. 1 the labeling indicates the main peaks of the rotational bands in the vibrational states $v = 0$ to $v = 5$. From fitting the relative intensities of the lines with those expected from the Boltzmann distribution law the fundamental frequency of the vibration was found to be $100 \pm 50$ cm$^{-1}$.[5] The great error is due to the uncertainty in the intensity measurements. These vibrational satellites are presumably states in which the skeletal bending mode is excited.

High resolution spectra of the bands give evidence for other vibrational satellites.

The lines from the ground state have been assigned. Outside each group, lines were found which could be identified as $K_{-1} = 0$, 1 and 2 transitions on the basis of their characteristic second-order (but unresolved) Stark effects. Within the band the transitions $K_{-1} > 3$ were detected by their relative intensities and quadrupole splittings, which increase with $K_{-1}$. It is necessary to include the centrifugal distortion terms $D_J$ and $D_{JK}$. The $D_{JK}$ term makes an important contribution and reverses the normal ordering of the $K_{-1}$ values.

The rotational constants are given in Table 1 together with those calculated from the hypothetical structure above.
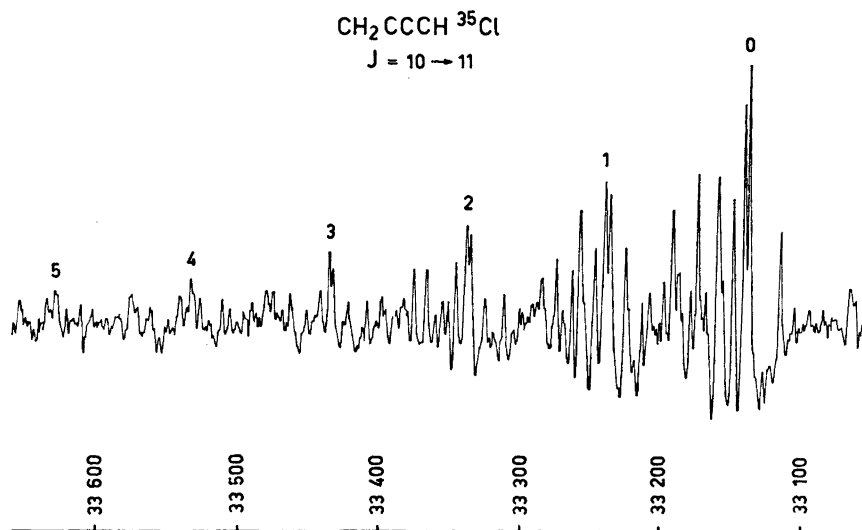
*Fig. 1.* Band of the J = 10 → 11 transitions of chlorobutatriene $CH_2CCCH^{35}Cl$ near 33 200 MHz. Sweep rate 2 MHz/sec.



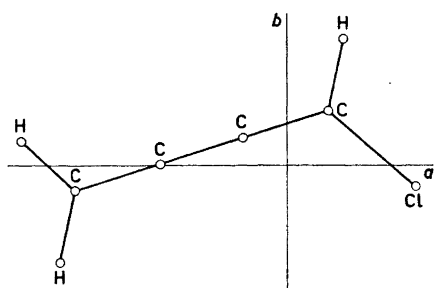*Fig. 2.* Theoretical structure of chlorobutatriene $CH_2CCCH^{35}Cl$ with principal axes of inertia.

*Table 1.* Rotational constants for chlorobutatriene $CH_2CCCH^{35}Cl$, in MHz.

| | From assumed structure | From observed spectra |
|---|---|---|
| A | 24 472 | 25 266 ± 14 |
| B | 1551.14 | 1551.153 ± 0.004 |
| C | 1458.68 | 1459.770 ± 0.004 |
| $D_J$ | — | 0.000357 ± 0.000009 |
| $D_{JK}$ | — | − 0.04536 ± 0.00003 |

The first vibrational bands as well as the $CH_2CCCH^{37}Cl$ species have been assigned but more refined data are being collected, which will enable a more detailed interpretation to be presented.

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