

## Measured and Calculated Vibration-rotation Constants in the Microwave Spectrum of Chlorobutatriene

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The inertial defects for the ground state and three excited vibrational states have been measured with microwave spectroscopy and calculated from an estimated diagonal valence force field for chlorobutatriene,  $\text{CH}_2\text{CCCH}^{35}\text{Cl}$ , in order to test the significance of a transformation of inertial moments from the effective structure to the average structure. The measured inertial moments are  $I_b^0 = 325.82$  and  $I_c^0 = 346.20$  au  $\text{\AA}^2$ . The calculated  $r_z$ -parameters are  $I_b^z = 326.01$  and  $I_c^z = 346.20$  au  $\text{\AA}^2$ .

The excited vibrational states correspond to a single excited out-of-plane vibration at  $220 \pm 50$   $\text{cm}^{-1}$  and to a single excited in-plane vibration at  $100 \pm 50$   $\text{cm}^{-1}$ . The vibration-rotation constants,  $\alpha_b$  and  $\alpha_c$ , are  $-0.12 \pm 0.02$  and  $-1.58 \pm 0.02$  MHz and  $-5.72 \pm 0.02$  and  $3.25 \pm 0.02$  MHz, respectively.

The inertial moments of a molecule in the ground vibrational state, obtained by microwave spectroscopy, are related to the effective structure  $r_0$ . This is a different structure than that observed in electron diffraction experiments,<sup>1</sup> because of the internal vibrations. However, both these methods are comparable in the average structure,  $r_z$ , which can be calculated if the harmonic potentials are known.<sup>2,3</sup> In contrast to the  $r_0$  structure, the  $r_z$  structure has a physically well-defined meaning.

Since we have used both electron diffraction and microwave spectroscopy to obtain structural information from three isomeric chlorobutenynes; *cis*-1-chlorobuten-3-yne, *trans*-1-chlorobuten-3-yne,<sup>4</sup> and 2-chlorobuten-3-yne, and chlorobutatriene,<sup>5</sup> we are interested to see if it is possible to carry out this kind of corrections for these molecules with a rather simple estimated force field.

In the microwave spectrum of chlorobutatriene it is possible to observe satellite spectra of two low-lying vibrational states. We have used this information to test the validity of the method on this kind of molecule. The result is probably of significant value even for the chlorobutenynes, since they have the same atoms,  $\text{C}_4\text{H}_3\text{Cl}$ , and symmetry.

### MICROWAVE SPECTRUM

The microwave spectrum of chlorobutatriene,  $\text{CH}_2\text{CCCH}^{35}\text{Cl}$ , is that of a near prolate symmetric rotor and has been described previously.<sup>5</sup> These measurements have been improved and the standard deviations of the rotational constants have been given more realistic values.

The strong  $K_{-1} = 1 \rightarrow 1$  transitions and the strongest and best resolved band,  $J = 12 \rightarrow 13$ , have been used for the assignment of the vibrational satellites; see Table 1. Three vibrational states have been examined; the first excited state of a vibrational mode  $\nu_2$  and the first and second excited state of a vibrational mode  $\nu_1$ . The rotational constants are listed in Table 2. Only  $\alpha$ -type  $R$ -lines have been observed so far which accounts for the low precision in the  $A$  constants which have to be obtained from the deviation of the observed lines from the symmetric top pattern.

The vibration-rotation coupling constants are listed in Table 3. It is not possible to calculate these constants from the force field due to the large contribution from the anharmonicity.

Due to the near degeneracy to a symmetric rotor with  $\kappa = -0.992$ , the observable quad-

Table 1. Observed rotational transitions and nuclear quadrupole hyperfine splitting in MHz for the ground state and low-lying vibrational states of chlorobutatriene  $\text{CH}_2\text{CCCH}^{35}\text{Cl}$ .

Transition			G.S.			$\nu_2$	$\nu_1$	$2\nu_1$			
$J$	$K_{-1}$	$K_{+1}$	$J$	$K_{-1}$	$K_{+1}$	$\nu_{\text{obs}}$	$\Delta\nu_{\text{Qobs}}$	$\nu_{\text{obs}}$	$\Delta\nu_{\text{Qobs}}$	$\nu_{\text{obs}}$	$\Delta\nu_{\text{Qobs}}$
9	1	9	8	1	8	26679.46					
9	0	9	8	0	8	27065.57					
9	2	8	8	2	7	27095.61					
9	1	8	8	1	7	27501.15					
10	1	10	9	1	9	29641.60		29666.35		29718.50	
10	0	10	9	0	9	30064.10					29795.08
10	2	9	9	2	8	30104.60					
10	1	9	9	1	8	30554.35		30564.45		30655.80	30756.96
11	1	11	10	1	10	32603.02		32630.37		32687.50	32771.57
11	0	11	10	0	10	33060.13					
11	2	10	10	2	9	33113.09					
11	1	10	10	1	9	33606.81		33617.97		33718.30	33829.38
12	1	12	11	1	11	35563.72		35593.55		35655.71	35747.30
12	0	12	11	0	11	36053.23					
12	2	11	11	2	10	36120.94					
12	1	11	11	1	10	36658.35		36670.63		36779.82	36900.83
13	1	13	12	1	12	38523.50		38555.75		38623.05	38772.16
13	0	13	12	0	12	39043.19				39155.12	39266.71
13	2	12	12	2	11	39128.15		39151.05			39359.30
13	3	11	12	3	10	39161.27		39183.57			39394.82
13	3	10	12	3	9	39162.69		39184.95		39279.85	39396.42
13	4	10	12	4	9	39164.65		39187.37		39281.30	39397.33
13	5	9	12	5	8	39172.89	0.35	39172.89	0.35	39289.24	0.45
13	6	8	12	6	7	39184.62	0.60	39208.28	0.77	39300.70	0.61
13	7	7	12	7	6	39199.17	0.90			39314.99	0.84
13	8	6	12	8	5	39216.25	1.13	39240.93	1.15	39331.76	1.12
13	2	11	12	2	10	39223.60		39243.95		39344.15	39464.04
13	9	5	12	9	4	39235.80	1.42			39350.95	1.45
13	10	4	12	10	3	39257.58	1.72			39372.40	1.80
13	1	12	12	1	11	39708.90		39722.32		39840.35	39971.25

Table 2. Observed rotational constants in MHz for the ground state and low-lying vibrational states of chlorobutatriene  $\text{CH}_2\text{CCCH}^{35}\text{Cl}$ .

	G.S.		$\nu_2$		$\nu_1$		$2\nu_1$	
$A$	25181	$\pm 50$	25200	$\pm 50$	25304	$\pm 50$	25475	$\pm 50$
$B$	1551.10	$\pm 0.02$	1551.22	$\pm 0.02$	1556.82	$\pm 0.02$	1562.52	$\pm 0.02$
$C$	1459.80	$\pm 0.02$	1461.38	$\pm 0.02$	1463.05	$\pm 0.02$	1466.30	$\pm 0.02$
$D_J$	0.00034	$\pm 0.00005$	0.00035	$\pm 0.00005$	0.00034	$\pm 0.00005$	0.00035	$\pm 0.00005$
$D_{JK}$	-0.0454	$\pm 0.0001$	-0.0474	$\pm 0.0001$	-0.0447	$\pm 0.0001$	-0.0437	$\pm 0.0001$

Table 3. Vibration-rotation coupling constants for the  $\nu_1$  and  $\nu_2$  states (in MHz).

	$\nu_1$	$\nu_2$
$\alpha^a$	$-130 \pm 50$	$-20 \pm 50$
$\alpha^b$	$-5.72 \pm 0.02$	$-0.12 \pm 0.02$
$\alpha^c$	$-3.25 \pm 0.02$	$-1.58 \pm 0.02$

rupole hyperfine splitting is only dependent on the constant  $\chi_{aa}$ , which is, for the  $^{35}\text{Cl}$  nucleus,  $\chi_{aa} = -25.8 \pm 0.5 \text{ MHz}^4$

## FORCE FIELD

The main difficulty with vibrational problems arises in the determination of an appropriate

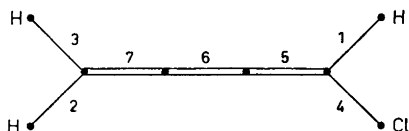


Fig. 1. Estimated diagonal force constants for chlorobutatriene in  $\text{md}/\text{\AA}$  and  $\text{md \AA}$ ;  $K_1=5.6$ ,  $K_2=K_3=5.5$ ,  $K_4=3.8$ ,  $K_5=K_7=9.4$ ,  $K_6=10.1$ ,  $K_{15}=0.50$ ,  $K_{27}=K_{37}=0.56$ ,  $K_{45}=0.85$ ,  $K_{56}=K_{67}=0.35$ ,  $\rho_6^{14}=0.312$ ,  $\rho_7^{23}=0.250$ ,  $\chi_{23}^{14}=0.35$ .

force field. We have used a simple diagonal valence force field with force constants estimated from similar bonds in simpler molecules such as butatriene<sup>6</sup> and vinyl chloride;<sup>7</sup> see Fig. 1. We have used the same symbols as Gribov.<sup>7</sup>  $K_i$  is the force constant for stretching the bond  $i$ ,  $K_{ij}$  is the force constant for bending the angle between the bonds  $i$  and  $j$ ,  $\rho_k^{ij}$  is the bending of the bond  $k$  out of the plane spanned by the bonds  $i$  and  $j$ , and  $\chi_{kl}^{ij}$  finally, is the torsion between the planes spanned by the bonds  $i$  and  $j$ , and  $k$  and  $l$ , respectively. We have assumed the same force constants for bending in plane and out of plane for the linear  $\text{C}=\text{C}=\text{C}$  groups. The calculated fundamental frequencies were compared with the observed IR-spectrum in the region  $4000-400 \text{ cm}^{-1}$ . We have not been able to make a complete assignment of this spectrum yet but some of the eighteen fundamentals are readily observed. The most characteristic transition is the strong line at  $2070$

$\text{cm}^{-1}$  which is identified as a  $\text{C}=\text{C}$  stretch  $\nu_{15}$ . This characteristic frequency is also observed for the simple butatriene at  $2079 \text{ cm}^{-1}$  but, due to the butatriene symmetry, this  $\text{C}=\text{C}$  stretch is only Raman active there.<sup>8</sup> Another  $\text{C}=\text{C}$  stretch,  $\nu_{14}$ , for chlorobutatriene is probably observed at  $1610 \text{ cm}^{-1}$ .

The low-lying fundamental vibrations make an important contribution to the transformation of the  $r_0$  to  $r_z$  parameters but the corresponding transitions are not observable with an ordinary IR-spectrometer. However, we have obtained the frequency of the two lowest fundamentals,  $\nu_1=100 \pm 50 \text{ cm}^{-1}$  and  $\nu_2=200 \pm 50 \text{ cm}^{-1}$  by intensity measurements on the corresponding vibrational satellites observed with microwave spectroscopy.<sup>9</sup> These fundamentals are characterized as skeletal bending modes,  $\nu_1$  in plane and  $\nu_2$  out of plane; see Fig 2. The calculated frequencies were  $\nu_1=113 \text{ cm}^{-1}$  and  $\nu_2=198 \text{ cm}^{-1}$ .

#### VIBRATION - ROTATION

The moments of inertia from the average structure are given by

$$I_{\alpha^2} = I_{\alpha^v} - \sum_s \left( v_s + \frac{d_s}{2} \right) \epsilon_s^2 (\text{har}) + \delta I_{\alpha} (\text{cent}) \quad (1)$$

$\alpha = a, b \text{ or } c$

where  $I_{\alpha^v}$  is one of the three principal moments of inertia for the effective structure in the

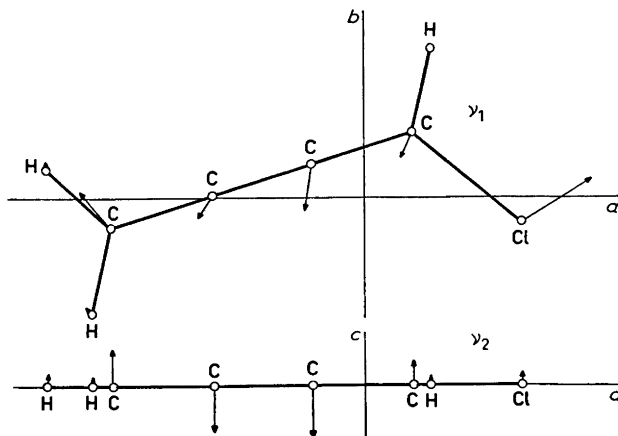


Fig. 2. The two lowest fundamental vibrations of chlorobutatriene  $\text{CH}_2\text{CCCH}^{35}\text{Cl}$  with principal axes of inertia. The vectors are obtained from the matrix of transformation from Cartesian to normal coordinates. Each component of a vector has been divided by the mass of the atom for appropriate scaling.

Table 4. Vibration-rotation correction for the moments of inertia in the ground vibrational state (in au  $\text{\AA}^2$ ) for chlorobutatriene  $\text{CH}_2\text{CCCH}^{35}\text{Cl}$ . Conversion factor 505376 au  $\text{\AA}^2$  MHz.

	$r_0$ -parameters	vibration correction	centrifugal distortion correction	$r_z$ -parameters
$I_b$	325.818	0.1908	0.0004	326.009
$I_c$	346.196	-0.0002	-0.0006	346.195

ground state or some excited vibrational state.<sup>10</sup> The sum includes all vibrations with degeneracy  $d_s$ .

The vibration-rotation correction term  $\epsilon_s^\alpha$  (har) is only dependent on the harmonic potentials and can be obtained from the transformation matrix from the Cartesian displacements to the normal coordinates and the fundamental frequencies.<sup>11</sup> So it is possible to calculate the parameters  $\epsilon_s^\alpha$ (har) when the geometry and force field of the molecule are known.

The term  $\delta I_\alpha(\text{cent})$  is the correction for the centrifugal distortion, and can also be calculated if the force field and geometry are known;<sup>11</sup> see Table 4. The effect of the centrifugal distortion is negligible in this case. It is also interesting to note that the  $I_c^0$  constant is very little affected by these corrections as compared to  $I_b^0$ . The inertial defect is defined as

$$\Delta = I_c - I_a - I_b \quad (2)$$

For the moments of inertia corresponding to an average planar structure,  $\Delta$  vanishes as it would for a hypothetical rigid planar rotor. This implies that the inertial defect for the effective structure in the ground state or some vibrationally excited state can be calculated from the harmonic terms,  $\epsilon_s^\alpha$ (har), and the centrifugal distortion terms  $\delta I_\alpha$ .<sup>12,13</sup> Thus the combination of (1) and (2) gives

$$\Delta^v = \sum \left( v_s + \frac{d_s}{2} \right) [\epsilon_s^c(\text{har}) - \epsilon_s^a(\text{har}) - \epsilon_s^b(\text{har})] - \delta I_c(\text{cent}) + \delta I_a(\text{cent}) + \delta I_b(\text{cent})$$

Since  $\Delta^v$  can be obtained from the measured rotational constants, it is possible to control the vibration-rotation parameters used in the transformation from  $r_0$  to  $r_z$  parameters; see Table 5.

It is interesting to see that the inertial defect decreases for out of plane vibrations and in-

Table 5. Inertial defect for the ground state and low-lying vibrational states of chlorobutatriene  $\text{CH}_2\text{CCCH}^{35}\text{Cl}$  in au  $\text{\AA}^2$ .

	From observed microwave spectra	From normal coordinate analysis
G.S.	$0.31 \pm 0.05$	0.35
$\nu_a$	$-0.03 \pm 0.05$	0.02
$\nu_1$	$0.83 \pm 0.05$	0.85
$2\nu_1$	$1.39 \pm 0.05$	1.35

creases for in plane vibrations compared with the ground state.<sup>14</sup>

## CENTRIFUGAL DISTORTION

If the force field and geometry are known it is possible to calculate the centrifugal distortion constants.<sup>6</sup> A planar asymmetric rotor has four independent centrifugal distortion constants  $\tau_{aaaa}$ ,  $\tau_{bbbb}$ ,  $\tau_{aabb}$  and  $\tau_{abab}$ .<sup>10</sup> Due to the near degeneracy to a symmetric rotor it is not possible to fit these four constants to the observed spectra.<sup>15</sup> The spectrum is only dependent on two centrifugal distortion constants and we have used  $D_J$  and  $D_{JK}$  according to Kivelson and Wilson.<sup>16</sup> However, if the constants  $\tau_{aaaa}$ ,  $\tau_{bbbb}$ ,  $\tau_{aabb}$ , and  $\tau_{abab}$  are obtained from theoretical calculations, it is possible to calculate  $D_J$  and  $D_{JK}$ ;<sup>10,16</sup> see Table 6.

It is interesting to see that the unusually large and negative value of the  $D_{JK}$  term arises quite naturally from the theoretical calculations. This kind of  $D_{JK}$  value has been observed for some other molecules of about the same size and form.<sup>17</sup> We have observed the same effect for *trans*-1-chlorobuten-3-yne.<sup>4</sup>

It has been pointed out that the centrifugal distortion constants are mostly dependent on the diagonal force constants.<sup>18</sup> This might be

Table 6. Calculated and measured centrifugal distortion constants for chlorobutatriene  $\text{CH}_2\text{CCCH}^*\text{Cl}$  (in MHz).

Calculated constants from estimated force field		Measured constants	
$\tau_{aaaa} = -7.730$	$D_J = 0.00033$	$D_J = 0.00034$	$\pm 0.00005$
$\tau_{bbbb} = -0.001804$	$D_{JK} = -0.0405$	$D_{JK} = -0.0454$	$\pm 0.0001$
$\tau_{aabb} = 0.1028$			
$\tau_{abab} = -0.003531$			

the reason for the good agreement between calculated and measured constants despite the fact that a very simple diagonal force field was used.

## DISCUSSION

The critical point in the measured inertial defect is of course the contribution from the  $I_a$  moment since that is obtained from the rather uncertain rotational constant,  $A$ . However, the significance is enough to show that the corrections from  $r_0$  to  $r_z$  parameters are meaningful although a very simple force field is used. Great care must be taken if these  $r_z$  parameters are to be used in the evaluation of the average structure, but they are valuable in showing the expected magnitude of the corrections and how the different inertial moments are affected.

As for calculation of the contribution from centrifugal distortion, it is immediately clear that they do not affect the corrections significantly for this molecule.

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