

On the Force Field and Mean Amplitudes of Vibration of Germanium Dichloride

JON BRUNVOLL and ISTVÁN HARGITTAI *

Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway

In a recent communication¹ a preparation technique, mass spectrometric and infrared (matrix isolation) spectroscopic studies and electron diffraction investigation of germanium dichloride, GeCl_2 , were reported. The vapour sample of the electron diffraction investigation, in fact, consisted of approximately equal amounts of GeCl_2 and GeCl_4 . The earlier results² for the tetrachloride structure have been reproduced, and the bond angle in GeCl_2 was determined to be $107 \pm 5^\circ$. Whereas the non-bond distances for the two molecular species were treated independently, only mean values for the Ge-Cl bond length and amplitude of vibration could be determined. The results are summarized in Table 1. That the mean values for $r(\text{Ge}-\text{Cl})$ and $l(\text{Ge}-\text{Cl})$ referring to the two molecular species were essentially the same as found for GeCl_4 by Morino *et al.* suggested that the r_g and l values for the Ge-Cl bond in GeCl_2 are little different from those in GeCl_4 . We found it of interest to examine how different the bond strength is in these molecules, and accordingly, decided to determine the bond stretching force constant for GeCl_2 . The bond stretching force constant in GeCl_4 has been reported earlier (2.79 mdyn/Å).³ By establishing the force field for GeCl_2 , it was also possible to see whether a difference in the $l(\text{Ge}-\text{Cl})$ values for GeCl_2 and GeCl_4 could be detected in the calculations. For this purpose, the available information in the literature^{2,3} was extended calculating the l values for GeCl_4 at the temperature of the electron diffraction experiment of the mixture, *viz.* 80 °C (see below).

* Permanent address: Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1088 Budapest, Puskin utca 11-13, Hungary.

Table 1. Structural parameters (Å) determined by electron diffraction¹ for a mixture of GeCl_2 and GeCl_4 .

$r_g(\text{Ge}-\text{Cl})_{\text{av}}$	2.110 ± 0.004
$l(\text{Ge}-\text{Cl})_{\text{av}}$	0.048 ± 0.001
$r_g(\text{Cl}\cdots\text{Cl})_{\text{GeCl}_2}$	3.387 ± 0.096
$l(\text{Cl}\cdots\text{Cl})_{\text{GeCl}_2}$	0.095 ± 0.010
$r_g(\text{Cl}\cdots\text{Cl})_{\text{GeCl}_4}$	3.447 ± 0.014
$l(\text{Cl}\cdots\text{Cl})_{\text{GeCl}_4}$	0.098 ± 0.010

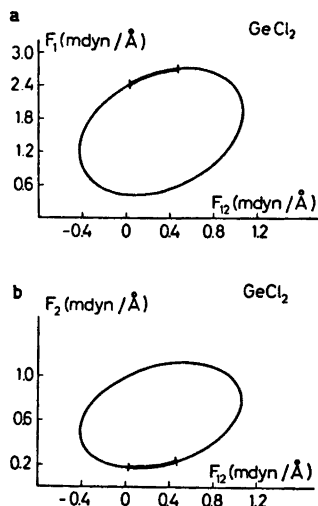


Fig. 1. Force constants for germanium dichloride, consistent with observed frequencies. The thicker portions of the graphs are consistent with the electron diffraction results. *a*, F_1 vs. F_{12} ; *b*, F_2 vs. F_{12} .

The secular equation technique described by Cyvin⁴ was used for establishing the force field of GeCl_2 . The three frequencies were taken from the following sources:

ν_1 398.6 cm^{-1} , argon matrix infrared spectroscopy;^{1,5} ν_2 159 cm^{-1} , gas phase Raman spectroscopy;³ ν_3 373.4 cm^{-1} , argon matrix infrared spectroscopy.^{1,5}

The force field of the A_1 species was varied within such limits that all force constants take real values. The results are presented graphically in Fig. 1. For each set of F values (F_{11} , F_{12} , F_2) expressions given by Cyvin⁴ for the bent symmetrical XY_2 molecular model were used to find the l values. These calculated mean amplitudes of vibration were compared with the electron diffraction results. Computed l and F values consistent with the electron diffraction $l(\text{Cl}\cdots\text{Cl})$ value for GeCl_2 are given in Table 2 and Fig. 2 (see also the thick portions

Table 2. Force fields and mean amplitudes of vibration for some combinations of force constants of GeCl_2 .

F_1	F_2	F_{12}	$l(\text{Ge}-\text{Cl})$	$l(\text{Cl}\cdots\text{Cl})$
2.439	0.182	0.026	0.0532	0.1112
2.581	0.183	0.174	0.0532	0.1037
2.676	0.204	0.322	0.0543	0.0960
2.726	0.244	0.470	0.0563	0.0881

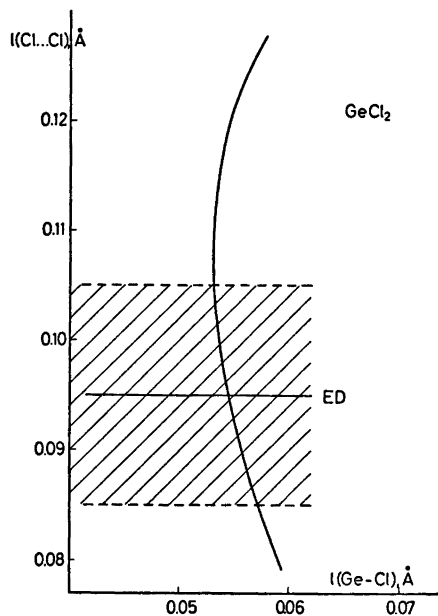


Fig. 2. Part for the mean amplitude of vibration ellipse for germanium dichloride at 80 °C. The electron diffraction value (ED) with error limit (shaded area) is also shown.

of the graphs in Fig. 1). As $l(\text{Ge}-\text{Cl})$ is plotted against $l(\text{Cl}\cdots\text{Cl})$ in Fig. 2, it is seen that $l(\text{Cl}\cdots\text{Cl})=0.095$ Å, i.e. the electron diffraction value, corresponds to $l(\text{Ge}-\text{Cl})=0.054$ Å. The calculated l (and K) values for GeCl_2 using $F_1=2.676$, $F_{12}=0.322$, and $F_3=0.204$ mdyn/Å are given for three temperatures in Table 3.

If the contribution of the $\text{Ge}-\text{Cl}$ bond of GeCl_2 is subtracted from the composite maximum of the radial distribution curve of the mixture, using $l(\text{Ge}-\text{Cl})=0.054$ Å, the remaining part corresponding to GeCl_4 yields $l(\text{Ge}-\text{Cl})=0.046$ Å. This is then in excellent

agreement with the calculated $l(\text{Ge}-\text{Cl})$ value for GeCl_4 , viz. 0.0468 Å at 80 °C.*

As for the force constants, the electron diffraction result for GeCl_2 , $l(\text{Cl}\cdots\text{Cl})=0.095 \pm 0.010$ Å, is consistent with $2.58 < F_1 < 2.73$ mdyn/Å and $F_3=1.79$ mdyn/Å. The bond stretching force constant for GeCl_2 , $f_r = \frac{1}{2}(F_1 + F_3)$ will then be between 2.18 and 2.26 mdyn/Å.

The bond stretching force constants indicate a weaker bond in GeCl_2 than in GeCl_4 , while the bond lengths seemed to be little if any different from the electron diffraction results. The weaker bond is consistent with the calculated larger l value for the $\text{Ge}-\text{Cl}$ bond in GeCl_2 vs. that in GeCl_4 .

One of the authors (I.H.) expresses appreciation to Professors O. Bastiansen, S. J. Cyvin and H. Viervoll for an invitation to Norway and to Norges almenvitenskapelige forskningsråd for a fellowship (October – December, 1975).

1. Vajda, E., Hargittai, I., Kolonits, M., Ujszászy, K., Tamás, J., Maltsev, A. K., Mikaelian, R. G. and Nefedov, O. M. *J. Organometal. Chem. In press.*
2. Morino, Y., Nakamura, Y. and Iijima, T. *J. Chem. Phys.* 32 (1960) 643.
3. Bürger, H. and Ruoff, A. *Spectrochim. Acta* 24 A (1968) 1863.
4. Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo, and Elsevier, Amsterdam 1968.
5. See also Ozin, G. A. and Van der Voet, A. *J. Chem. Phys.* 56 (1972) 4768.
6. Beattie, I. R. and Perry, R. O. *J. Chem. Soc. A* (1970) 2429.

Received December 5, 1975.

* The other calculated values for GeCl_4 include $l(\text{Cl}\cdots\text{Cl})=0.1056$ Å, $K(\text{Ge}-\text{Cl})=0.0034$ Å, and $K(\text{Cl}\cdots\text{Cl})=0.0027$ Å.

Table 3. Mean amplitudes of vibration (l) and K values^a for GeCl_2 .

	$T=0$ K	$T=298$ K	$T=353$ K
$l(\text{Ge}-\text{Cl})$	0.0433	0.0514	0.0543
$l(\text{Cl}\cdots\text{Cl})$	0.0608	0.0893	0.0960
$K(\text{Ge}-\text{Cl})$	0.0012	0.0033	0.0039
$K(\text{Cl}\cdots\text{Cl})$	0.0002	0.0002	0.0003

^a $K = [\langle (\Delta x)^2 \rangle + \langle (\Delta y)^2 \rangle] / 2r$