

THE SECTOR-VISUAL METHOD OF ELECTRON DIFFRACTION: THE MOLECULAR STRUCTURE OF TETRACHLOROETHENE

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RECENTLY, in this laboratory,¹ a comparative study has been made of various methods of electron diffraction for molecular structure determinations. The potentialities of the visual method using sectored patterns have also been studied with several molecules.² We have now investigated the molecular structure of tetrachloroethene by the sector-visual method. Since the molecular structure of this molecule has been studied independently by the visual method using non-sectored patterns³ and by the sector-microphotometer method,⁴ it seemed interesting to be able to compare the results of the sector-visual method with those by the other two methods. Of further interest was the carbon-chlorine distance in this molecule in order to test Pauling's proposal⁵ regarding the double-bond character of the C-Cl bonds in the chloroethenes.

Tetrachloroethene, obtained by Matheson and Company, was purified by fractional distillation under vacuum before use. Electron diffraction patterns were taken using an r^3 -rotating sector in the new Purdue apparatus.⁶ Electrons of wavelength 0.05452 \AA were used with Kodak Lantern Slide Medium plates. The photographs were taken at camera distances of 10.19 and 25.04 cm .

A visual intensity curve was obtained, making use of six patterns, three taken at the long camera distance and three at the short camera distance. These sector-visual data extended from $q = 15$ to $q = 87$.

A radial distribution curve was calculated by equation⁷

$$r D(r) = \sum_{q=1,2,3,\dots}^{q_{\max}} I_m(q) \exp(-bq^2) \frac{\sin \pi q r}{10}$$

using I.B.M. punched cards. The value of b was chosen so that $\exp(-bq^2) = 0.1$ at $q = 90$. The data for the range $q = 0$ to $q = 14$ were supplied from a theoretical curve. The radial distribution curve thus obtained is shown in Fig. 1

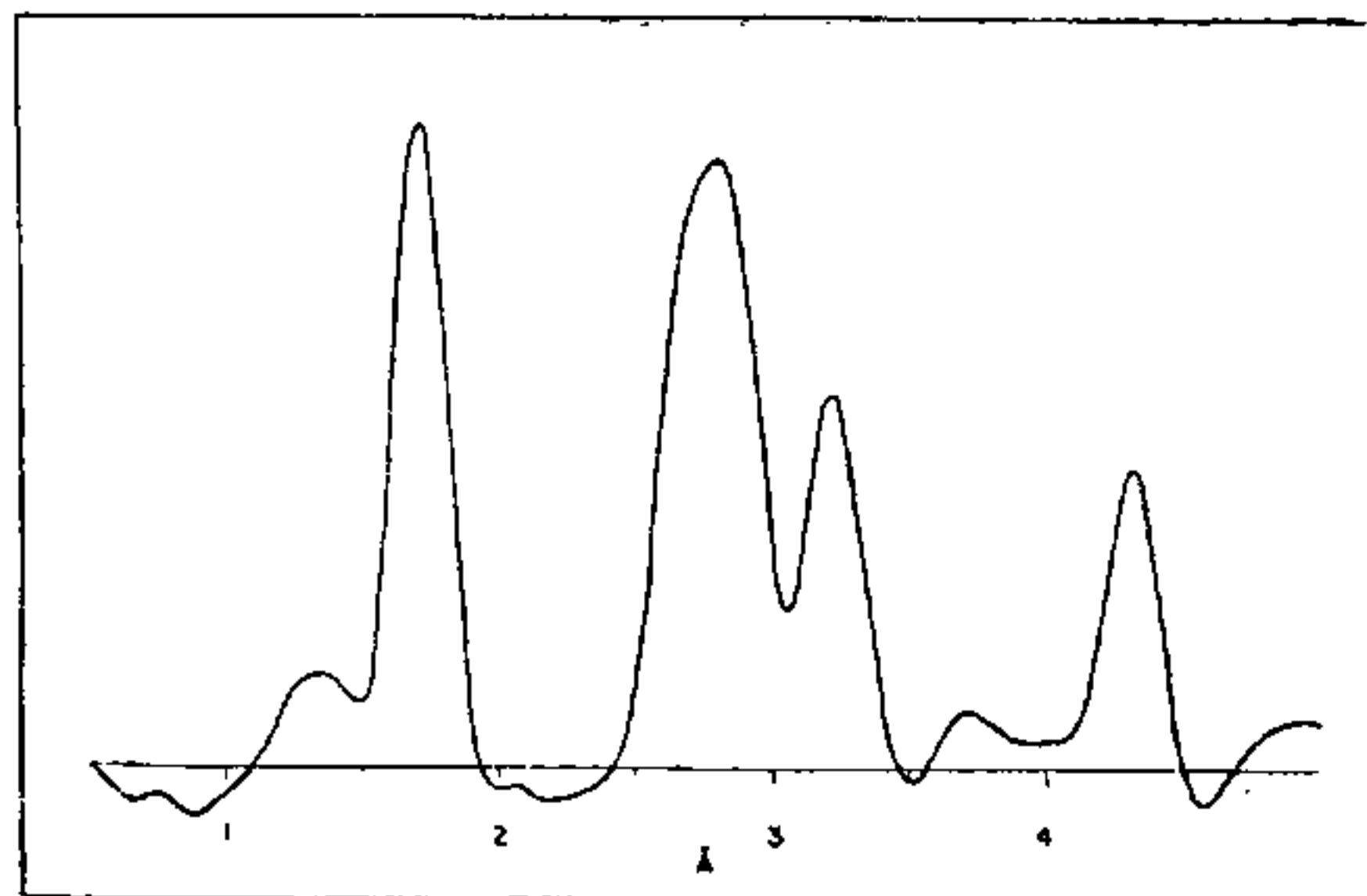


FIG. 1. Radial Distribution Curve for Tetrachloroethene.

The peak positions and the areas of each peak are listed in Table I. Also listed are the approxi-

TABLE I
Radial distribution results

Distance	Peak Position, \AA	$\overline{\Delta r_{ij}}$	Area	$nZ_i Z_j / r_{ij}$
C—C	1.33 ₉	..	17.4	11.4
C—Cl	1.72 ₄	0.05	100	100
C—Cl	2.82	..	159.9	148.9
Cl—Cl (short)		..		
Cl—Cl (inter-mediate)	3.22 ₃	0.10	64.7	75.9
Cl—Cl (long)	4.32	0.06 ₅	47	56.5

mate mean amplitudes of vibration, $\overline{\Delta r_{ij}}$, for some of the peaks; these were obtained using the Karles' method.^{8,9} The radial distribution curve shows some negative areas and other extraneous features. No attempt was made to improve the radial distribution curve by performing Fourier inversions on the extraneous features.² Experience has indicated that such an improvement would have no appreciable effect on the interatomic distances, but would improve the general appearance of the radial distribution curve.^{1,2} There is, however, reasonable agreement of the peak areas with calculated values of $nZ_i Z_j / r_{ij}$. No attempt was made to decompose the third peak in the radial

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distribution curve which is due to a combination of the C-Cl and Cl-Cl (short) distances. The ClCCl angle and the C-C distance calculated from the C-Cl, the Cl-Cl (intermediate) and the Cl-Cl (long) distances are $113^{\circ}18'$ and 1.327 \AA respectively. This calculated value for the C-C distance does not agree with the position of the C-C peak in the radial distribution curve, because of the small contribution of the carbon atoms to the scattering. The final parameters by the sector-visual radial distribution curve are compared with the results of Lipscomb³ and Karle and Karle⁴ in Table II. The

TABLE II
Final parameters of tetrachloroethene
by the different methods

Parameter	Visual*	Sector-Visual†	Sector-Micro- photometer‡
C—C ..	$1.34 \pm 0.05 \text{ \AA}$	1.327 \AA	$1.30 \pm 0.03 \text{ \AA}$
C—Cl ..	$1.71 \pm 0.02 \text{ \AA}$	1.724 \AA	$1.72 \pm 0.01 \text{ \AA}$
$\angle \text{ClCCl}$..	$115^{\circ}36'$	$113^{\circ}18'$	$113^{\circ} \pm 1.5^{\circ}$

* Lipscomb, W. N.³

† This research.

‡ Karle, I. L. and Karle, J.⁴

C-Cl distance and the ClCCl angle from this investigation agree closely with Karle's results by the sector-microphotometer method and the C-C distance is within the limits of error reported by them.

From Table I it is seen that the mean amplitude of vibration of the *cis* Cl-Cl atom pair is much larger than that of the *trans*-Cl-Cl atom pair. This is probably because the contribution from the modes associated with bending of the

$\angle \text{ClCCl}$ is quite appreciable. This is consistent with the spectroscopic information and the earlier observations.⁴

The results of this investigation together with the other results on the chloroethenes^{3,10,11} indicate no regular trend in the C-Cl and C-C distances and dispute Pauling's proposal that there is an increase in the C-Cl distances in the chloroethenes as the number of chlorine atoms adjacent to the double-bond is increased.

Work on this and similar compounds indicates that the visual interpretation of sector diffraction patterns gives results which are considerably more reliable than those obtained by the visual interpretation of non-sectored plates and only slightly less accurate than can be obtained by the sector-microphotometer method.

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ANOMALOUS TRANSMISSION OF X-RAYS BY SINGLE CRYSTAL GERMANIUM

THE anomalous transmission of X-rays through nearly perfect crystals was first observed by Borrmann and Campbell and has been discussed theoretically by Zachariasen, Hirsch and Von Laue. The effect has been measured in calcite by Schwartz and Rogosa and found to agree reasonably well with theory.

Since the anomalous transmission arises because the lattice planes of the crystal coincide with the nodal planes, of the X-ray standing wave field in the crystal, it is clear that any gross lattice imperfections will destroy the effect and even subtle crystal defects will seriously reduce the transmitted intensity. This suggests that the intensity of the anomalously transmitted beam should furnish a sensitive tool for the investigation of crystal perfection. In recent times it has been possible to grow

single crystals of germanium which exhibit a high degree of crystal perfection as indicated by ordinary standards. It was accordingly decided to investigate the anomalous transmission of X-rays by good single crystal germanium, both from the point of view of the effect itself and from the point of view of its use as a tool in the investigation of crystal perfection. In this paper results are given which show how details of the imaginary part of the atomic structure factor of germanium can be measured using essentially perfect germanium crystals and also how sensitive the anomalous transmission is to such crystal defects as dislocations and elastic strain.

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