Molecular Structure Investigation of Chlorotrifluoroethylene by Electron Diffraction

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The molecular structures of chlorine and fluorine derivatives of ethylene such as tetrachloroethylene[1-3] and tetrafluoroethylene[4,5] have been studied by electron diffraction using a sector-microphotometer or visual methods (Table I).

In order to see the carbon-halogen bond distances and the valence angles of ethylene derivative including two kinds of halogens, we investigated chlorotrifluoroethylene (Kel F monomer) by electron diffraction using the visual method and compared it with those of the related compounds.

Experimental

The sample was prepared by Osaka Kinzoku Industrial Co.

The apparatus of electron diffraction was the same as that in the previous report[6]. In order to reduce the vapor pressure of the sample the liquid-sample reservoir was cooled by a mixture of dry ice and alcohol during the diffraction experiment. The diffraction photographs were measured by the visual method (Fig. 1).

Analysis and Results

The radial distribution and theoretical intensity curves have been calculated by the usual method. The thermal factors were omitted for convenience in all the theoretical intensity curves except curves D′ and D″ in which the mean amplitudes listed in Table III were used. Some of the intensity curves are shown in Fig. 1 and the molecular parameters of the corresponding models are listed in Table II.

As can be seen from the first peak of the radial distribution curve (Fig. 2), it is difficult to distinguish the C=C and the three C–F bond distances separately. The mean value of them is 1.31 Å. The second peak shows that the C–Cl bond distance is 1.71 Å.

When the angles FCF and FCCl of the models are varied, the C=C and all the C–F bond distances being fixed at 1.31 Å and the C–Cl band distance at 1.71 Å, the features of the maxima or the shelves at about $q=28\sim41$ of the theoretical intensity curves change appreciably and the curves C and D, in which the two angles are equal to 115 and 114°, respectively, fit better with the observed curve

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TABLE I. MOLECULAR STRUCTURES OF TETRACHLOROETHYLENE AND TETRAFLUOROETHYLENE

Tetrachloroethylene

Reference	C–Cl, Å	C=C, Å	∠ClCCl	∠CCCl	Method
1	1.73±0.02	1.38		123.7±1°	visual
2	1.71±0.02	1.34±0.05	115.5±2°	122.1±1°	visual
3	1.72±0.01	1.30±0.03	113.5±1.5°		sector

Tetrafluoroethylene

Reference	C–F, Å	C=C, Å	∠FCF	Method
4	1.313±0.010	1.313±0.035	114±2°	sector
5	1.30 ±0.02	1.33 ±0.06	114±2°	visual

TABLE II. PARAMETERS OF MOLECULAR MODELS FOR THE THEORETICAL INTENSITY CURVES AND $q_{\text{calcd}}/q_{\text{obs}}$ VALUES

Model	C=C Å	C–F Å	C–Cl Å	∠FCF	∠FCCl	∠CCCl	$q_{\text{calcd}}/q_{\text{obs}}$	Average deviation
A	1.31	1.31	1.71	120°	120°	120°		
B	1.31	1.31	1.71	117°	117°	121.5°		
C	1.31	1.31	1.71	115°	115°	122.5°	1.000	0.017
D	1.31	1.31	1.71	114°	114°	123°	1.004	0.015
E	1.31	1.31	1.71	112°	112°	124°		
F	1.31	1.31	1.71	114°	117°	121.5°		
G	1.31	1.31	1.71	114°	120°	117°		
H	1.31	1.31	1.71	114°	114°	120°		
I	1.31	1.31	1.71	114°	114°	126°	0.993	0.012
J	1.31	1.31	1.71	114°	114°	128°		
K	1.31	1.27	1.73	114°	114°	123°		
L	1.31	1.29	1.71	114°	114°	123°	1.003	0.016
M	1.31	1.33	1.71	114°	114°	123°	0.993	0.014
N	1.31	1.35	1.73	114°	114°	123°		
O	1.31	{1.31(2) 1.29(1)	1.73	114°	114°	123°	0.995	0.016
P	1.31	1.31	1.67	114°	114°	123°		
Q	1.31	1.31	1.69	114°	114°	123°	1.003	0.017
R	1.31	1.31	1.73	114°	114°	123°	0.996	0.015
S	1.31	1.31	1.75	114°	114°	123°	0.995	0.017
T	1.29	1.31	1.73	114°	114°	123°		
U	1.35	1.31	1.73	114°	114°	123°		
V	1.37	1.30	1.70	116°	116°	122°	0.990	0.018
W	1.39	1.29	1.69	117°	117°	121.5°	0.987	0.022
X	1.25	1.32	1.73	112°	112°	124°	1.003	0.014
Y	1.23	1.33	1.73	111°	111°	124.5°		
D′	1.31	1.31	1.71	114°	114°	123°	0.998	0.015
D″	1.31	1.31	1.71	114°	114°	123°	0.994	0.017

than any other curves of different bond angles.

By comparing the features and $q_{\text{calcd}}/q_{\text{obs}}$ values of the intensity curves of the models which have bond angles different from those of models C and D, the acceptable regions of the two bond angles FCF and FCCl were determined as 114±2° and the bond angle CCCl as 123±2°.

And then by comparing the intensity curves of the models in which C–Cl bond distance was varied from 1.67 Å to 1.75 Å, the C–Cl bond distance was determined as 1.72±0.02 Å.

If either one of the C=C or the C–F bond distance is longer and the other is shorter than 1.31 Å, a considerably good intensity curve is obtained by altering both the bond angles and C–Cl distance in the acceptable regions which have been described previously. But as the contribution of the C–F atomic pairs to the total intensity curve is much greater than that of C=C atomic pair, the acceptable region of C=C distance is much larger than these of C–F distances. They were 1.31±0.06 Å for C=C and 1.31±0.02 Å for C–F, respectively.

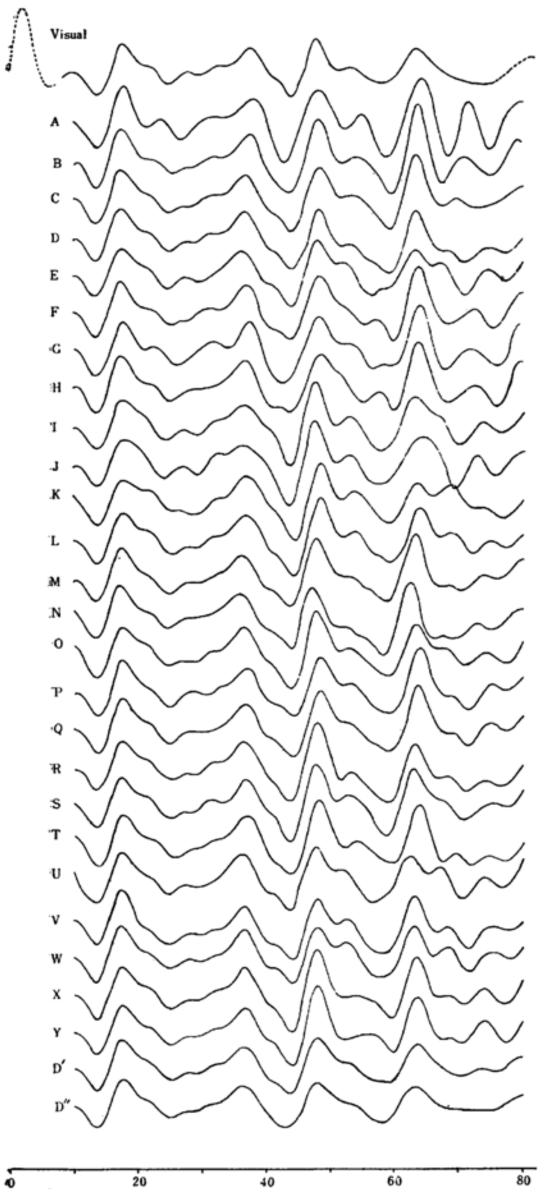
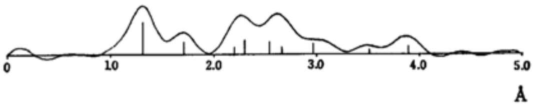


Fig. 1. Intensity curves.



Vartical lines show the interatomic distances of model D.

Fig. 2. Radial distribution curve.

TABLE III. MEAN AMPLITUDES USED FOR THE CALCULATIONS OF INTENSITY CURVES D′ AND D″

Atomic pair	Mean amplitude, Å	
	Model D′	Model D″
C=C	0.04	0.04
C–F	0.04	0.05
C–Cl	0.05	0.05
C···F	0.06	0.06
C···Cl	0.06	0.06
F···F	0.06	0.09
cis F···F	0.09	0.09
trans F···F	0.06	0.11
Cl···F	0.06	0.09
cis Cl···F	0.09	0.09
trans Cl···F	0.06	0.11

Finally the theoretical intensity curves of model D including thermal factors listed in Table III are compared. They are not greatly different from that of the rigid model, but curve D′ seems a little better than curve D″.

When the above results are compared with those in Table I, all the parameters of the molecule are practically identical with those of Refs. 3 and 4, although the present results by visual method have broader limits of uncertainty than those of the sector-microphotometer method.

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