

[CONTRIBUTION NO. 1384 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

A Reinvestigation of the Structures of Chlorine Monoxide and Chlorine Dioxide by Electron Diffraction

BY J. D. DUNITZ AND KENNETH HEDBERG

Early electron diffraction investigations of the structures of chlorine monoxide¹ (Cl₂O) and chlorine dioxide² (ClO₂) by the correlation method led to the results Cl-O = 1.71 ± 0.02 Å. and ∠Cl-O-Cl = 111 ± 2° for the former and Cl-O = 1.53 ± 0.03 Å. for the latter, the ∠O-Cl-O not being determined. Later, Pauling and Brockway applied their radial distribution method³ to these molecules, among others, and obtained for chlorine monoxide Cl-O = 1.65 Å., ∠Cl-O-Cl = 120°; and for chlorine dioxide Cl-O = 1.53 Å., ∠O-Cl-O = 137°. These authors adopted the averages of the results of the two methods as the best available values.

In the case of chlorine monoxide, the corresponding internuclear distances obtained by the two methods differ significantly. A study of the radial distribution method by Schomaker⁴ has since shown that certain features of this early calculation cause the peaks of the radial distribution curve to be shifted somewhat from the correct positions and that, in general, the displacements are such as to increase the separation of well-resolved peaks. In particular, for chlorine monoxide these features appear to be (a) the omission of a term to represent the central part of the pattern (corresponding to the "zeroth" maximum of our curves), (b) the use of a wide-spaced summation without appropriate corrections, rather than an integration, and (c) the interpretation of the peaks of $D(l)$ rather than $lD(l)$ to obtain values of the internuclear distances. It is therefore to be presumed that the more nearly correct parameter values for chlorine monoxide are those which were obtained from the correlation treatment. It perhaps needs to be emphasized that the discrepancy between the results of the two methods found for chlorine monoxide is typical of the discrepancies found for numerous other compounds, and that Pauling and Brockway's³ averaged values are no doubt generally less reliable than the original values obtained by the correlation method.

The determination of the O-Cl distance in chlorine dioxide cannot be considered reliable, inasmuch as it is based upon very limited data (two maxima and three minima which extend to approximately $s = 12$). Further, the bond

angle must be regarded as undetermined, because the radial distribution peak which was ascribed to the O···O interaction is undoubtedly due mainly to inclusion in the calculation only of terms representing the maxima of the observed intensity curve.

We have recently found it convenient in connection with some other work to reinvestigate the structures of chlorine monoxide and chlorine dioxide. The results of our investigation of chlorine monoxide agree closely with those of the earlier correlation study. On the other hand, for chlorine dioxide we find the bond distance to be about 1.49 Å. instead of 1.53 Å. and have determined the bond angle to be about 116.5°. In both cases our data are much more comprehensive than the earlier data and permit us to place smaller limits of uncertainty on the structural parameters.

Experimental

Chlorine monoxide was prepared by the method of Secoy and Cady.⁵ About half of the preparation was distilled off by pumping at -80° in order to remove the greater part of any unreacted chlorine; the next fraction, comprising about half the remaining material, was used in the electron diffraction experiment. The chlorine dioxide was made by the method of Bray⁶ as described by Spinks and Taube.⁷ Similar purification techniques were employed to remove the contaminating carbon dioxide.

Electron diffraction photographs were made in the apparatus described by Brockway⁸ with a camera distance of about 11 cm. and an electron wave length of about 0.06 Å.⁹ The interpretation of the photographs of both substances was carried out by each of us independently of the other. Visual curves were drawn and radial distribution functions were calculated from the equation^{10,11}

$$rD(r) = \sum_{q=1,2,3,\dots}^{q_{max}} I(q) \exp(-aq^2) \sin \frac{\pi}{10} qr$$

by use of punched cards.^{11,12} The coefficients

(5) C. H. Secoy and G. H. Cady, *THIS JOURNAL*, **62**, 1036 (1940).

(6) W. Bray, *Z. physik. Chem.*, **54**, 463 (1906).

(7) J. W. T. Spinks and H. Taube, *Can. J. Research*, **B15**, 499 (1937).

(8) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(9) The electron wave length was determined by calibration against zinc oxide smoke. See C. S. Lu and E. W. Malmberg, *Rev. Sci. Instruments*, **14**, 271 (1943). Our results are, however, expressed in ångström units.

(10) R. Spurr and V. Schomaker, *THIS JOURNAL*, **64**, 2693 (1942).

(11) P. A. Shaffer, V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

(12) P. A. Shaffer, V. Schomaker and L. Pauling, *ibid.*, **14**, 648 (1946).

(1) L. E. Sutton and L. O. Brockway, *THIS JOURNAL*, **57**, 473 (1935).

(2) (a) L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 868 (1933);

(b) L. O. Brockway, *ibid.*, **19**, 303 (1933).

(3) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **57**, 2684 (1935).

(4) V. Schomaker, Ph.D. Thesis, California Institute of Technology 1938.

TABLE I
 ELECTRON DIFFRACTION DATA FOR CHLORINE MONOXIDE

Max.	Min.	$q_{\text{obs.}}$		$q_{\text{calcd.}}/q_{\text{obs.}}$			
		J. D. D.	K. H.	110.3°	K. H.	J. D. D.	111.3°
	1	6.2	5.4	[1.081]	[1.241]	[1.064]	[1.222]
1		9.3	8.8	[0.978]	[1.034]	[0.978]	[1.034]
	2	12.3	11.8	[0.911]	[0.949]	[0.902]	[0.941]
2		16.0	15.8	0.981*	0.994*	0.975*	0.987*
	3	19.7	19.9	1.015*	1.005*	1.015*	1.005*
3		23.2	24.0	1.034	1.017	1.034	1.017
	4	26.8	26.5	1.026	1.038	1.019	1.030
4		30.0	29.6	0.973	0.986	0.973	0.986
	5	33.6	33.5	0.997*	1.000*	1.000*	1.003*
5		37.7	37.3	1.003*	1.013*	1.005*	1.016*
	6	41.7	41.8	1.010*	1.007*	1.012*	1.010*
6		45.0	45.7	1.018	1.002	1.002	0.986
	7	48.0	48.6	0.975	0.963	0.979	0.967
7		51.6	51.3	0.994	1.000	0.996	1.002
	8	55.4	55.6	1.004*	1.000*	1.007*	1.004*
8		59.6	59.3	1.010	1.015	1.008	1.013
	9	62.7	62.4	1.025	1.027	1.006	1.011
9		66.0	65.0	0.989	1.005	0.985	1.000
	10	69.6	69.1	0.993*	1.000*	0.994*	1.001*
10		73.4	73.3	1.001*	1.003*	1.004*	1.005*
	11	78.1	77.3	0.999*	1.009*	0.999*	1.009*
11			80.9		1.014		1.006
	12		84.0		0.988		0.988
12			86.2		1.009		1.010
	13	91.7	89.7	0.996	1.018	0.998	1.020
13			93.6		1.024		1.024
	14		96.7		1.029		1.031
Average, excluding parenthesized values				1.002(1)	1.006(8)	1.000(5)	1.005(4)
Av. deviation				0.013	0.012	0.011	0.011
Average, 9 starred values				1.000(3)	1.002(3)	1.001(2)	1.004(4)
Av. deviation				0.007	0.004	0.008	0.005

$$\text{Cl} \cdots \text{Cl}: 2.79 [1.003(1.000 + 1.002) + 1.001 + 1.004]/4 = 2.797^{13}$$

$I(q)$ were taken from the visual curves and the constant a was chosen to make $\exp(-aq^2)$ equal to 0.1 at q_{max} . The theoretical intensity curves employed in the correlation treatment were calculated^{11,12} from the equation¹⁰

$$I(q) = \sum_{i,j}' \frac{Z_i Z_j}{r_{ij}} \sin \frac{\pi}{10} q r_{ij}$$

Corrections were made for film expansion by both of us for chlorine dioxide and by K. H. for chlorine monoxide.¹³

Chlorine Monoxide.—The visual curves and radial distribution curves for chlorine monoxide are reproduced in Fig. 1. The radial distribution curves show two principal peaks, which give the following results.

	$r_{\text{Cl-O}}, \text{Å}$	$r_{\text{Cl} \cdots \text{Cl}}, \text{Å}$	$\angle \text{Cl-O-Cl}, \text{deg.}$
K. H.	1.71	2.81	110.5
J. D. D.	1.70	2.79	110.3

(13) The correction for K. H.'s chlorine monoxide measurements amounted to 0.27%, and, although no correction factor was determined by J. D. D. for his measurements, it is certain that approximately the same value would have been found. At the conclusion of the analysis J. D. D.'s distance results were multiplied by the factor 1.003. This adjustment brings the two sets of distances into complete agreement (see Table I).

The two visual curves in general agree well and constitute a good basis¹⁴ for comparison with curves calculated for various models of the molecule; a number of these curves are also reproduced in Fig. 1. Since the weights of the two sine components in the summation are about equal, the appearance of the curves changes rapidly as the bond angle is varied. Thus, although the curve for the 110.3° model is in good agreement with every feature of our visual curves, the 108.4 and 112.3° curves exhibit features which cannot be reconciled with our observations. Curves for models of 109.3 and 111.3° (which are not shown here) serve to define the limits of the bond angle determination even more closely. The 109.3° curve represents incorrectly the two unsymmetrically doubled fea-

(14) In the region of the weak ring or shoulder at $q \sim 45$, curve K. H. disagrees significantly with curve J. D. D. and the best theoretical curve. We have both carefully re-examined the photographs, however, and are convinced that this feature of the K. H. curve, which would suggest a smaller bond angle, is in error. The higher frequency component of the intensity function has been generally over-emphasized in curve J. D. D., as may be seen from the ratio of areas of the radial distribution peaks, but this, in this case at least, is an entirely innocuous kind of error.

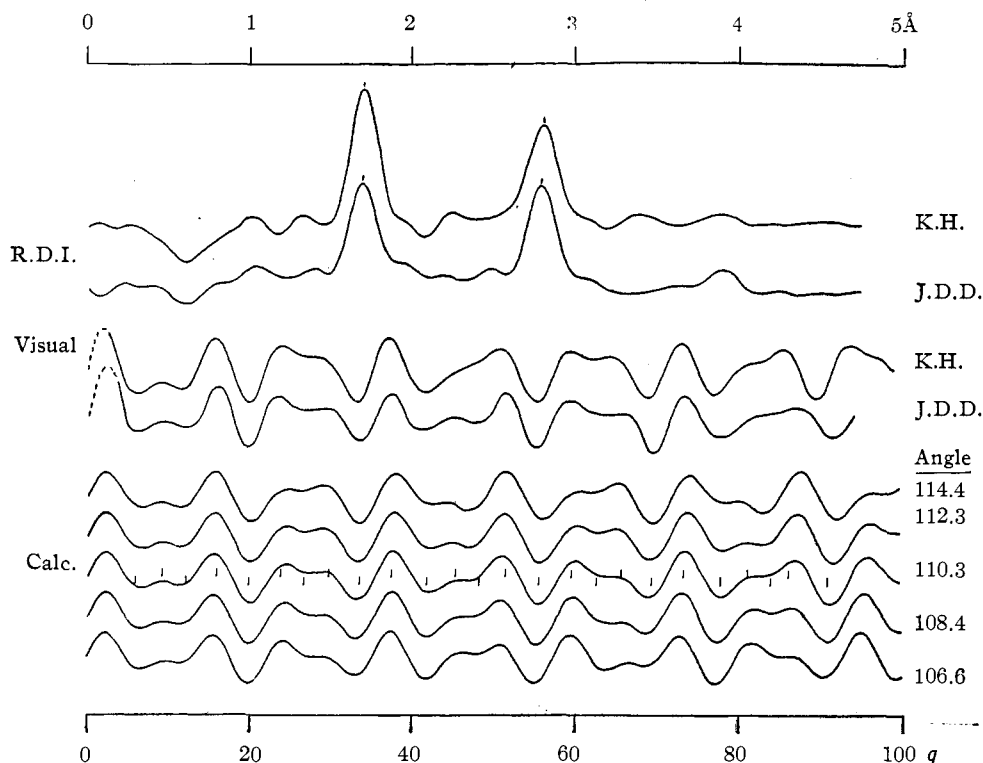


Fig. 1.—Chlorine monoxide: the vertical lines on the 110.3° curve represent the average of K. H.'s measurements multiplied by the factor 1.003^{12} and J. D. D.'s measurements. J. D. D. made no measurements of the positions of the 11th and 12th maxima and the 12th minimum.

tures adjacent to the minimum at $q = 54$ and hence is unacceptable. The 111.3° curve is an only slightly poorer representation of the observed scattering pattern than is the 110.3° curve, which suggests that the best model has a bond angle of about 110.8° , midway between these two values.

From these qualitative comparisons and from the data of Table I, assuming the starred value averages to be the most reliable, we obtain the following values and probable limits of uncertainty for the structural parameters: $\text{Cl-O} = 1.701 \pm 0.020 \text{ \AA.}$, $\text{Cl}\cdots\text{Cl} = 2.797 \pm 0.020 \text{ \AA.}$, $\angle \text{Cl-O-Cl} = 110.8 \pm 1.0^\circ$.

Chlorine Dioxide.—The two visual curves and the corresponding radial distribution curves for chlorine dioxide are shown in Fig. 2. The radial distribution curves show small peaks at 2.55 and 2.51 \AA. , respectively, in addition to the principal peak at 1.50 \AA. , indicating an O-Cl-O bond angle of about 116° . Theoretical intensity curves were calculated for models in which the bond angle was varied between 110 and 122.5° . Because the Cl-O term is very much more important than the $\text{O}\cdots\text{O}$ term, the appearance of calculated curves changes only slightly from model to model. We are, however, in complete agreement with regard to the appearance of details of the pattern which serve to exclude all models outside the range of $\angle \text{O-Cl-O} =$

$114-119^\circ$. Among these are the broad symmetrical shape of the second maximum, the relative depths of the third, fourth, fifth and sixth minima, and the shapes of the third and fifth maxima.¹⁵ The determination of the bond angle in chlorine dioxide was checked by comparing the photographs with the rather closely similar photographs of sulfur dioxide,¹⁶ which are especially significant for this purpose now that a highly precise value for its bond angle, confirming the electron diffraction result, has been afforded by a microwave investigation.¹⁷

From the considerations mentioned above and from the data presented in Table II we obtain the following values and limits of uncertainty for the structural parameters: $\text{O-Cl} = 1.491 \pm 0.014 \text{ \AA.}$, $\angle \text{O-Cl-O} = 116.5 \pm 2.5^\circ$.

(15) The disagreement between the shapes of the third and fifth maxima in the respective visual curves needs to be mentioned. It may be described in terms of the positions of the points of inflection: for curve J. D. D. the point of inflection is considerably lower down on the outside of the third maximum and also on the inside of the fifth maximum than for curve K. H. Upon consultation we have decided that curve K. H. is actually a better representation of these features than curve J. D. D.

(16) V. Schomaker and D. P. Stevenson, *THIS JOURNAL*, **62**, 1270 (1940). Most of the pertinent differences in appearance of the two patterns can be described in terms of the greater width, for chlorine dioxide, of the second ring, the shallower fourth minimum, and the more marked asymmetry of the fifth ring. These differences can be easily seen on the photographs.

(17) B. P. Dailey, S. Golden and E. Bright Wilson, Jr., *Phys. Rev.*, **72**, 871 (1947).

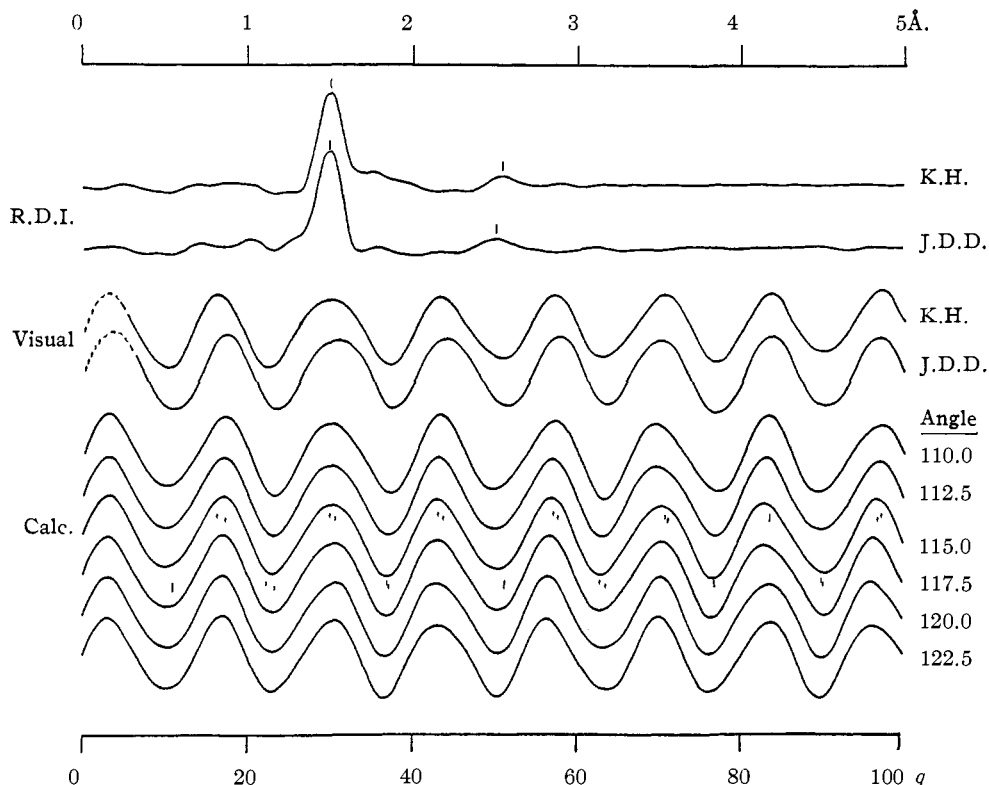
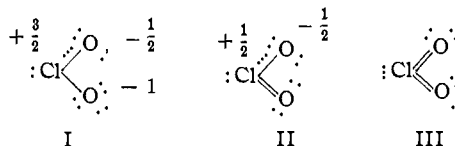


Fig. 2.—Chlorine dioxide: the vertical lines on the 115.0° curve show the measured positions of the maxima and minima.

Discussion

Our results for chlorine monoxide, $\text{Cl-O} = 1.701 \text{ \AA.}$ and $\angle \text{Cl-O-Cl} = 110.8^\circ$, agree closely with those of the earlier study by the correlation method. The bond distance, which is in fair agreement with the sum of the Schomaker-Stevenson covalent single bond radii corrected for electronegativity difference of the atoms¹⁸ (1.685 \AA.), and the bond angle are in accord with expectation based upon the representation $\text{:}\ddot{\text{Cl}}\text{-O-}\ddot{\text{Cl}}\text{:}$ for the electronic structure of the molecule.

Our results for chlorine dioxide are $\text{Cl-O} = 1.49 \text{ \AA.}$ and $\angle \text{O-Cl-O} = 116.5^\circ$, the bond distance being 0.04 \AA. shorter than that reported in the earlier investigation. It is interesting to consider these results in relation to the electronic structure of the molecule, and for this purpose it is convenient to compare them, together with the dipole moment, with the corresponding results for sulfur dioxide. From general considerations we may suppose that the principal types of resonance structures for these molecules are those represented by the formulas



in which structures I, II, III require the use of four, five and six orbitals, respectively, by the apical atom.

If the Cl-O bond in chlorine monoxide is regarded as a pure single bond, the Cl-O bond in chlorine dioxide, being 0.21 \AA. shorter, must be regarded as essentially a double bond, as far as Pauling's distance criterion¹⁹ is concerned. As far as we are aware, no very reliable distance for the S-O single bond has been published, although the value $1.64 \pm 0.05 \text{ \AA.}$ has been reported for ethyleneglycol sulfite ester.²⁰ The Pauling-Huggins radii give 1.70 \AA. for the S-O single bond and 1.49 \AA. for the S-O double bond. The Schomaker-Stevenson value for the S-O single bond distance is 1.69 \AA. The observed value of the S-O bond in sulfur dioxide, 1.43 \AA. , is thus at least as short as the value expected for the S-O double bond.

It is not possible to estimate the relative importance of the resonance structures from the bond

(19) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940, Chap. V.

(20) B. Keilin, Ph.D. Thesis, California Institute of Technology, 1950.

(18) V. Schomaker and D. P. Stevenson, *THIS JOURNAL*, **63**, 37 (1941).

TABLE II
 ELECTRON DIFFRACTION DATA FOR CHLORINE DIOXIDE

Max.	Min.	$q_{\text{obs.}}$		$q_{\text{calcd.}}/q_{\text{obs.}}$			
		J. D. D.	K. H.	115.0°	K. H.	J. D. D.	117.5°
1	1	10.8	10.9	[0.924]	[0.917]	[0.924]	[0.924]
		17.2	16.2	[0.987]	[1.049]	[0.975]	[1.037]
2	2	23.2	22.2	[0.994]	[1.036]	[0.989]	[1.032]
		30.5	29.8	[0.986]	[1.010]	[0.992]	[1.017]
3	3	37.1	36.9	0.997	1.003	0.992	0.997
		43.6	43.0	0.981	0.995	0.983	0.998
4	4	51.1	51.2	0.984	0.982	0.988	0.986
		57.7	57.2	0.985	0.993	0.985	0.993
5	5	63.5	62.9	0.992	1.002	0.992	1.002
		71.1	70.8	0.990	0.994	0.992	0.996
6	6	76.9	76.9	0.998	0.999	0.994	0.995
		83.7	83.7	0.990	0.990	0.992	0.992
7	7	90.3	90.0	1.002	1.006	1.001	1.004
		96.9	97.3	0.999	0.995	0.994	0.990
Average, 10 features				0.991(8)	0.995(9)	0.992(3)	0.995(3)
Av. deviation				0.006	0.005	0.003	0.004
Cl-O: $1.50[0.992 + 0.996 + 0.992 + 0.995]/4 = 1.491$							

distances alone, because the shortening effect of the formal charges is not accurately known. The dipole moments, however, provide strong evidence that the structures I (in which the apical atom maintains its octet) are of comparatively small importance. If the molecules were completely represented by structures of the type (I) we should expect the molecules to have dipole moment contributions from the formal charges of the order of $4.8 \times 1.43 \times \cos 60^\circ = 3.4 D$ for sulfur dioxide and $3/2 \times 4.8 \times 1.49 \times \cos 58^\circ = 5.7 D$ for chlorine dioxide in addition to the resultants of the ordinary bond moments. On the basis of structure I, therefore, we expect large dipole moments for both molecules and possibly even a larger dipole moment for chlorine dioxide than for sulfur dioxide. The observed dipole moments are $0.78 D$ for chlorine dioxide^{21a} and $1.61 D$ for sulfur dioxide^{21b} and these are more in accord with expectation based upon the double bonded structures, II for sulfur dioxide and III for chlorine dioxide, taking the electronegativity differences into account. We conclude, therefore, that sulfur dioxide and chlorine dioxide may be represented mainly by double bonded structures in which the apical atom makes use of *d* orbitals for bond formation. This conclusion is in accord with the views of Phillips, Hunter and Sutton,²² who have argued, largely from dipole moment evidence, that the very short bonds formed between oxygen atoms and the central atom in the higher oxides and oxyacids of phosphorus, sulfur and

chlorine, are better represented by double bonds than by coordinate links.

The bond angle in chlorine dioxide is 116.5° , and that found in sulfur dioxide is 119.5° , the difference being small but significant. One possible explanation of this difference is based upon the fact that the separation of the *s* and *p* energy levels is greater for chlorine than for sulfur. The S-O bonds in sulfur dioxide will thus have more *s* character and hence greater strength, shorter bond distance and larger bond angle than the Cl-O bonds in chlorine dioxide. We consider, however, that at present it is more important to emphasize the close similarity between the bond angles rather than the small difference, since it is the similarity which suggests, in the first place, that the electronic structures of the molecules cannot be very different.

Acknowledgment.—We wish to thank Professor Verner Schomaker for many helpful discussions and suggestions.

Summary

The structures of chlorine monoxide and chlorine dioxide have been determined in the gas phase by the method of electron diffraction. The results for chlorine monoxide are Cl-O = $1.701 \pm 0.020 \text{ \AA}$, $\angle \text{Cl-O-Cl} = 110.8 \pm 1^\circ$, and $\text{Cl} \cdots \text{Cl} = 2.791 \pm 0.020$ and for chlorine dioxide they are Cl-O = $1.491 \pm 0.14 \text{ \AA}$ and $\angle \text{O-Cl-O} = 116.5 \pm 2.5^\circ$. These results are discussed in relation to the probable electronic structures of the molecules. From a comparison between the bond distances, bond angles and dipole moments of chlorine dioxide and sulfur dioxide, it is concluded that these molecules are best represented by double bonded structures.

(21) (a) C. T. Zahn, *Phys. Rev.*, **27**, 455 (1926). (b) D. Sundhoff and H-J. Schumaker, *Z. physik. Chem.*, **B28**, 17 (1935). For a convenient compilation of dipole moments see "Tables of Electric Dipole Moments," Technical Report No. 2, Laboratory for Insulation Research, Massachusetts Institute of Technology, 1947, compiled by L. G. Wessou.

(22) G. M. Phillips, J. S. Hunter and I. E. Sutton, *J. Chem. Soc.*, 146 (1945).