into account. According to Kitaĭgorodskiĭ the space group C_{2h}^{6} is possible for the molecules with symmetry $\bar{1}$ or 2, but it is less probable. The packing conditions in the b-axis direction are determinant since the packing here occurs at right angles to the $a\,c$ layer. In the case of mercury diethylene oxide the puckered form of the ring enables the close approach of the molecules also in the b-axis direction even when the molecules are occupying the twofold symmetry axis positions. The perfect cleavage already quoted is also well explained by the observed molecular arrangement, as may be seen easily from the above description.

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The Crystal Structure of Sulfur Dioxide*

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Oscillation diagrams have been obtained of single crystals of sulfur dioxide at −130±5° C. The unit cell is orthorhombic and contains four molecules. Cell dimensions are: a = 6·07, b = 5·94, c = 6·14 Å (all ±0·01 Å). The most probable space group is *Aba*.

The four sulfur atoms in the unit cell lie in face-centered positions. The parameters of the oxygen atom are: x = 0·140, y = 0·150, z = 0·118. The length of the S–O bond is 1·430±0·015 Å, the intramolecular O–O distance is 2·46±0·01 Å; the O–S–O angle is 119°±2°.

Introduction

Giauque & Jones (1948) have reported calorimetric evidence of disorder in solid sulfur dioxide close to the melting point. To account for the disorder they postulated a structure in which adjacent molecules are paired with their molecular planes 90° apart and with the O–O sides of the triangles together. A structure of this type, it was felt, offered a number of possibilities for orientational disorder.

Sulfur dioxide is one of a large number of substances of chemical importance whose crystal structures have not been studied because they happen to be liquids or gases at room temperature. Techniques and apparatus have been developed which make single-crystal X-ray investigations of such compounds feasible down to the temperature of liquid air (Kaufman & Fankuchen, 1949; Abrahams, Collin, Lipscomb & Reed, 1950; Post, Schwartz & Fankuchen, 1951). In this paper the determination of the crystal structure of sulfur dioxide, using these techniques, is described.

Experimental

The low-temperature X-ray camera used in the investigation has been described elsewhere (Post, Schwartz & Fankuchen, 1951). Specimens of sulfur dioxide suitable for X-ray diffraction studies were obtained by distilling 99·8% pure sulfur dioxide gas into thin-walled pyrex glass capillary tubes immersed in liquid nitrogen. When half to three-quarters full of solid sulfur dioxide the capillary tubes were sealed with a flame.

Powder diagrams and single-crystal oscillation diagrams were obtained using filtered copper and molybdenum radiation. To avoid possible difficulties in structure determination due to disorder near the melting point, all X-ray diagrams used in this investigation were obtained at −130±5° C., approximately 60° C. below the melting point.

Experimental difficulties were appreciable; single crystals suited for X-ray diffraction purposes were grown with great difficulty and generally began to break up into fragments soon after X-ray exposures were begun. The crystals, moreover, showed a marked

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Table 1. *Observed and calculated structure factors*

(*hkl*)	F_o	F_c
200	33	35
400	5	6
600	17	20
020	29	29
120	31	30
220	37	37
320	13	12
420	27	28
520	9	11
620	12	12
820	8	7
040	9	8
140	7	10
240	27	26
340	6	4
440	25	25
640	7	7
060	22	22
260	15	12
460	6	7
080	10	9
111	60	61
211	30	30
311	23	23
511	17	16
711	12	13
131	20	21
231	5	7
331	36	37
531	17	17
151	20	19
251	12	11
351	16	15
551	9	10
171	13	13
202	36	36
402	27	27
602	10	14
022	36	35
122	21	23
222	30	30
322	10	10
422	23	22
522	7	9
622	11	12
042	27	26
142	7	8
242	22	21
442	18	17
642	10	9
062	18	16
262	13	12
462	8	10
113	24	26
213	19	20
313	28	31
513	18	16
133	33	32
333	16	15
533	11	11
153	16	14
353	13	12
204	25	27
404	27	27
024	29	29
124	13	16
224	20	20
424	15	15
044	28	26
244	15	14
264	12	10
215	6	10
315	20	21
515	13	11
135	20	21
355	11	8
155	10	10
355	9	8
226	12	11
046	10	12

tendency to grow in one preferred orientation (with the *c* axis of the orthorhombic unit cell parallel to the capillary axis). Oscillation diagrams were obtained with the crystal aligned for oscillation only about this axis.

Unit cell and space group

The oscillation diagrams were indexed on the basis of an orthorhombic unit cell with

$$a_0 = 6{\cdot}07\pm0{\cdot}01,\ b_0 = 5{\cdot}94\pm0{\cdot}01,\ c_0 = 6{\cdot}14\pm0{\cdot}01\ \text{Å}\,.$$

The unit cell dimensions were computed from measurements of powder diagrams taken with a 71·6 mm. radius camera; corrections were made for film shrinkage and absorption.

The volume of the unit cell is 221 Å^3. The density of the solid at −196° C. has been reported as 1·928 g.cm.$^{-3}$ (Blitz & Hulsmann, 1932). The assumption of four molecules of sulfur dioxide per unit cell leads to an X-ray density of 1·92 g.cm.$^{-3}$ (at −130° C.).

Relative intensities of reflections were estimated visually using multiple films. Independent estimates of intensities were obtained from films using copper and molybdenum radiation; these showed satisfactory agreement. The usual Lorentz and polarization corrections were applied. No absorption corrections were considered necessary; the specimens were all cylindrical and less than 0·09 mm. in diameter. This is less than half the optimum specimen size for copper radiation.

Reflections of the following types were not observed: (*hkl*) with $k+l$ odd; (0*kl*) with *k* odd; and (*h*0*l*) with *h* odd. The most probable space groups are therefore *Aba* and *Abam*. The latter is compatible only with a linear molecule; electron-diffraction, dipole-moment and spectroscopic measurements indicate that sulfur dioxide is non-linear (Cross & Brockway, 1935; Schomaker & Stevenson, 1940; Crable & Smith, 1951). The non-linearity of the molecule can also be readily demonstrated from X-ray diffraction data.

In both *Aba* and *Abam*, the origin can be chosen so that the fourfold positions are at the corner and face centers of the unit cell. A Patterson (*hk*0) projection showed a peak interpretable as an S–O peak close to the face diagonal and about 1·2 Å from the origin. In *Abam* the molecules would have to be linear and either parallel or perpendicular to the *c* axis. These possibilities can be ruled out quickly by consideration of the intensities of the successive orders of *h*00, 0*k*0 and 00*l*.

Determination of oxygen parameters

For the [001] zone the structure factors are real and the signs of all F_{hk0}'s with *h* even are positive and are determined by the face-centered sulfur atoms. Only the oxygen atoms contribute to the signs of the F_{hk0}'s with *h* odd; the five observed reflections of this type undergo no changes in sign between the limits 0·125 and 0·167 for both *x* and *y*. The Patterson (*hk*0) projection had indicated that the oxygen atom was close to $x = y = 0{\cdot}145$. The signs of all observed F_{hk0}'s were therefore fixed and a projection of the electron density onto the (001) plane was computed. This is shown in Fig. 1.

The maximum of the oxygen peak was located graphically at $x = 0{\cdot}140$ and $y = 0{\cdot}150$. The function

$$r = \Sigma(|F_c|-|F_o|)\div\Sigma(|F_o|)$$

possesses a minimum at this point and rises rapidly as the oxygen atom is moved away from it.

A temperature factor of 2·5 Å^2 was computed in the usual way from the slope of a plot of $\ln|F_o|-\ln|F_c|$ against $(\sin\theta)^2/\lambda^2$. After multiplying the F_c's by the appropriate temperature corrections, the value of r for the ($hk0$) reflections was 7%. This low value of r reflects in part the fact that the sulfur atoms, in special positions, contribute the bulk of the X-ray scattering. For the five ($hk0$) reflections with h odd, the value of r is 14%.

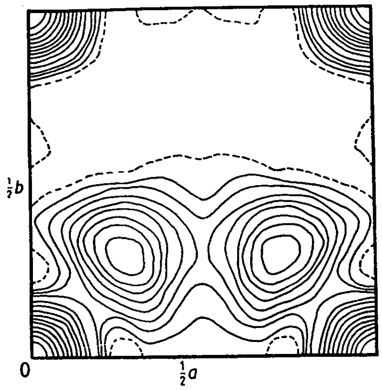

Fig. 1. Electron-density projection on (001).

The absence of the (004) reflection from powder diagrams indicated an approximate z parameter of 0·125. Values of $|F_{hkl}|$ were calculated over a range of values of z from 0·090 to 0·150. These were compared graphically with values of $|F_o|$. In space group Aba the values of F_{hkl} with $(h+k)$ odd are independent of the z parameter and these structure factors were not included in this comparison. The best value of z was found to be 0·118±0·003.

Values of $|F_o|$ and $|F_c|$ are listed in Table 1. The value of r for all observed (hkl) reflections is 7%; for those reflections to which only the oxygen atoms contribute it is 12%.

Discussion of the structure[*]

The sulfur dioxide molecules are all aligned in the crystal with the molecular planes parallel to the c axis. There is no evidence in the crystal structure of the type of molecular pairing postulated by Giauque & Jones (1948). The arrangement of molecules in one unit cell is shown in Fig. 2.

The shortest intermolecular distances are: O–O, 3·32 Å; S–O, 3·10 Å; S–S, 4·24 Å. Intramolecular distances and the O–S–O angle are listed in Table 2 together with recent results obtained by electron diffraction and microwave spectroscopy.

Table 2. *Structure of sulfur dioxide molecule*

	This paper	Electron diffraction[*]	Microwave spectra[†]
S–O	1·43±0·015 Å	1·43±0·01 Å	1·4321 Å
O–O	2·46±0·01 Å	—	—
O–S–O	119·5±1·5°	120±5°	119° 2·1′

[*] Schomaker & Stevenson (1940).

[†] Crable & Smitt (1951).

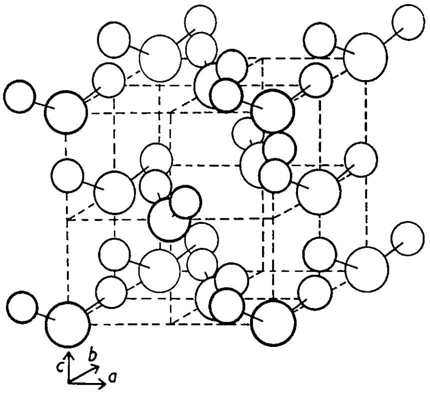

Fig. 2. Arrangement of molecules in one unit cell.

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[*] While this paper was being prepared for publication, a paper on 'The Crystal Structure of Sulfur Dioxide' (Sugawara & Kanda, 1950) was brought to the authors' attention. Sugawara & Kanda had very ingeniously indexed powder diagrams of sulfur dioxide. They assumed that the S–O bond length is 1·43 Å and the O–S–O angle is 120±5°. From this they deduced the crystal structure, correctly in its main outlines, and reported extremely good agreement between observed and computed intensities. They report $x = 0{\cdot}151$, $y = 0{\cdot}141$, $z = 0{\cdot}117$ compared with values of 0·140,, 0·150 and 0·118 reported in this paper.