

# NATURE OF THE BOND IN THE OXYGEN COMPOUNDS OF SULFUR

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Calculations were carried out for  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  by the method of molecular orbitals with self-consistency. It was established that there is an effective positive charge on the sulfur atom, the magnitude of this depending on the number of ligands. An experimental relationship was obtained between the force constant  $f_{\text{SO}}$  of the bond and the interatomic distance  $R_{\text{SO}}$ . A relation was obtained for the total order  $p_{\text{SO}}$  of the bond as a function of the interatomic distance and the force constant of the bond.

Increased accuracy in the structural study of crystals, arising from the use of computers and the transition to "three-dimensional" experimental data, renders possible a systematic investigation of the correlation between various bond characteristics obtained by other physico-chemical methods and structural analysis data on interatomic distances. Such attempts were made earlier for inorganic compounds. These attempts, however, were either based on sparse and inexact experimental material [1], or else arose from theoretical considerations which by now have undergone change [2, 3].

TABLE 1. Calculated Self-Consistent LCAO-MO for  $\text{SO}_2$

Energy $\epsilon$ of MO eV	Representation	Coefficients $c_{ij}$									
		$3p_z$	$3p_x$	$3p_y$	$3d_{xy}$	$3d_z^2$	$3d_{x^2-y^2}$	$3d_{yz}$	$3d_{xz}$	$\sigma$	$\pi$
-19,81	$1b_2$		-0,73						0,032	-0,656	0,177
-16,38	$1a_1$	0,65				0,046	-0,06			0,615	0,43
-15,78	$1b_1$			0,75				0,1			0,647
-12,02	$2b_2$		0,009						0,226	0,255	0,94
-11,70	$2a_1$	-0,042				-0,115	0,125			0,61	-0,77
-10,82	$1a_2$				0,476						0,88
-8,33	$2b_1$			-0,646				0,29			0,71
-5,95	$3a_1$	-0,745				0,146	-0,188			0,494	0,380
-5,36	$3b_2$		0,656						0,29	-0,69	0,11
-3,46	$4b_2$		0,131						-0,93	-0,175	0,269
-2,91	$3b_1$			0,114				0,95			-0,286
-2,68	$2a_2$				0,88						-0,476
-1,99	$4a_1$	-0,007				0,756	0,654			0,012	0,003
-1,36	$5a_1$	0,127				0,625	-0,72			-0,063	-0,267

The latest experimental structural and spectral data for molecules and oxyanions of the  $\text{SO}_n^{m-}$  type, taken together with computed results, allow us to conduct an analysis, better-founded than before, of the relation linking the order  $p_{\text{SO}}$  and force constant  $f_{\text{SO}}$  of the bond with the interatomic distance.

As a basis for studying such correlations we take the following series of molecules and ions:  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{S}_2\text{O}_6^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ .\* In all the members of this series, only the molecular bonding orbitals are occupied by electrons.

\* We considered all the molecules and ions in the ground state only (all the compounds mentioned, except  $\text{S}_2\text{O}_6^{2-}$ , were calculated by Rutan's method).

TABLE 2. Calculated Self-Consistent LCAO-MO for SO<sub>3</sub>

Energy $\varepsilon$ of MO, eV	Repre- senta- tion	Coefficients $c_{ij}$							
		3s	3p <sub>x</sub>	3p <sub>y</sub>	3p <sub>z</sub>	3d <sub>yz</sub>	3d <sub>xz</sub>	$\sigma$	$\pi$
-24,8	1a' <sub>1</sub>	0,78						0,63	
-16,33	1e'		0,70	0,70				0,11	0,70
-12,3	1e''					0,32	0,32		0,94
-11,2	1a' <sub>2</sub>								1,0
-11,1	1a'' <sub>2</sub>				0,45				0,90
-8,91	2e'		0,706	0,706				0,244	0,665
-5,13	2a' <sub>1</sub>	0,63						-0,78	
-2,99	3e'		0,10	0,10				0,964	-0,248
-2,35	2a'' <sub>2</sub>								-0,45
-0,17	2e''				0,90	0,94	0,94		-0,32

Ions and radicals having antibonding electrons (SO, S<sub>2</sub>O<sub>4</sub><sup>2-</sup>) will be treated separately.

Calculations were made within the framework of the molecular orbit method by Rutaan's method in a single approximation for the ground state of the molecules or ions. The details of the method are set out in [4].

The SO<sub>2</sub> molecule has an angular configuration ( $\angle$ OSO $\approx$ 120°) and is characterized by the electronic formula [4]: \*

$$(1b_2)^2(1a_1)^2(1b_1)^2(2b_2)^2(2a_1)^2(1a_2)^2.$$

The form of the self-consistent molecular orbits (MO) and their energy are shown in Table 1. It is seen from this that all the bonding orbits are filled with electrons, while the antibonding orbits stay free. The molecular shells are closed, so that in the ground state the molecule is diamagnetic.

Molecular orbits (2a<sub>1</sub>)<sup>2</sup>(2b<sub>2</sub>)<sup>2</sup> may be regarded as nonbonding, since the electronic density is in the main concentrated at the oxygen atoms. The lowest energy orbit (1b<sub>2</sub>)<sup>2</sup>  $\sigma$ -bonding, the orbit (1a<sub>1</sub>)<sup>2</sup> is mixed ( $\sigma > \pi$ ), and the orbits (1b<sub>1</sub>)<sup>2</sup>(1a<sub>2</sub>)<sup>2</sup> are pure  $\pi$ -orbits. It is significant that, in forming  $\pi$ -bonds, a considerable part is taken by the 3d-orbits of the sulfur atom. A particularly important part is played by orbit 3d<sub>xy</sub>, since its contribution to the molecular orbits is the greatest.

All the molecular orbits except (2a<sub>1</sub>)<sup>2</sup>(2b<sub>2</sub>)<sup>2</sup> and (1a<sub>2</sub>)<sup>2</sup> may be considered homopolar. Since the (2a<sub>1</sub>)<sup>2</sup>(2b<sub>2</sub>)<sup>2</sup>-electrons are localized at the oxygen atoms and are nonbonding, responsibility for the polarity of the SO bond rests on orbit (1a<sub>2</sub>)<sup>2</sup>. The charge on the sulfur atom is q<sub>S</sub> = +0.35. The total order of the bond without separation into the  $\sigma$ - and  $\pi$ -types equals 2.66. The bond order calculated in this way has only relative significance, i.e., in comparisons with analogously calculated parameters for other molecules of a homologous series. The coefficients  $c_{ij}$  offer

TABLE 3. Calculated Self-Consistent LCAO-MO for SO<sub>3</sub><sup>2-</sup>

Energy $\varepsilon$ of MO in eV	Repre- senta- tion	Coefficients $c_{ij}$								
		3s	3p <sub>A1</sub>	3p <sub>E</sub>	3d <sub>z2</sub>	3d <sub>A1</sub>	3d <sub>E</sub>	$\sigma$	$\pi^1$	$\pi^2$
-22,53	1a <sub>1</sub>	0,74	0,275			0,006		0,604	0,1	
-20,22	1e			0,615	0,10		0,297	0,42	0,437	0,437
-16,32	2a <sub>1</sub>	0,56	-0,595			-0,044		-0,345	-0,458	
-15,56	2e			0,222	-0,224		-0,373	0,699	-0,37	-0,37
-11,61	3a <sub>1</sub>	-0,342	-0,094			-0,105		0,58	-0,725	
-11,16	3e			0,0	0,0		0,0	0,0	0,71	0,71
-9,65	1a <sub>2</sub>								1,0	
-5,0	4a <sub>1</sub>	0,13	0,73			-0,22		0,42	-0,46	
-4,08	4e			0,70	0,037		-0,399	-0,559	-0,126	-0,126
-2,16	5e			0,15	-0,88			-0,142	-0,04	-0,04
-1,88	5a <sub>1</sub>	-0,014	-0,13			-0,968	0,41	0,053	0,205	
+3,18	6e			0,234	0,406		0,69	0,005	-0,39	-0,39

\* Group theoretical consideration of all the molecules calculated may be found in [1, 4, 17].

TABLE 4.\* Parameters of  $S_2O_4^{2-}$ ,  $S_2O_5^{2-}$ , and  $S_2O_6^{2-}$

	$S_2O_4^{2-}$	$S_2O_5^{2-}$	$S_2O_6^{2-}$
$R_{S-O}, \text{Å}$	2,389	2,209	2,15÷2,16
Group $SO_2^-$	1,496; 1,515	1,499	
$R_{SO}, \text{Å}$			
$\angle SSO$	98,02°; 99,38°	100,50°	
Group $SO_3^-$	—	1,431; 1,472	1,45
$R_{SO}, \text{Å}$			
$\angle SSO$	—	106,34°	103°÷105°

\* Table borrowed from [10].

bits, taking account of 16 electrons (all the sulfur electrons with quantum number  $n=3$ , and the 2p electrons of the oxygen atom); this is shown in Table 2.

Earlier, Moffitt [1] suggested a scheme for forming the molecular orbits, the ground state being described by the formula:

$$(1a_1')^2(1e')^4(1a_2'')^2(1e'')^4(2e')^4(2a_2')^2.$$

The first six electrons  $(1a_1')^2(1e')^4$  and the electrons  $(1a_2'')^2(1e'')^4$  form bonding molecular orbits; Moffitt assigned the  $(2e')^4(2a_2')^2$  electrons to nonbonding ones. Actually, our calculation shows that the  $(2e')^4$  electron also takes a considerable part in the formation of the bond. In  $SO_3$ , a large part in the formation of the  $\pi$ -bonds is played by the 3d-orbits of sulfur. The largest contribution is made by the  $3d_{yz}$ - and  $3d_{xz}$ -orbits. On the other hand,  $3d_{z^2}$  and  $3d_{x^2-y^2}$  and  $3d_{xy}$  take no part at all.

Moffitt indicated a strengthening of the double character of the SO bond in  $SO_3$  as compared with  $SO_2$  (due to the strengthening of the  $\pi$ -bond by the sulfur d-orbit). The charge on the sulfur atom  $q_S=0.0$ . Experimental data also confirm an insignificant strengthening of the bond. Thus,  $j_{SO}^{SO_3}=10.77 \cdot 10 \text{ dyn/cm}$ , and  $R_{SO}=1.430 \text{ Å}$ . However, our calculated order of the bond does not indicate this ( $p_{SO}^{SO_3}=2.63$ ), probably owing to the fact that the effect lies within the limits of computing error.

Now let us pass on to the analysis of the oxyanions (anions of oxy acids). We considered  $SO_3^{2-}$ ,  $S_2O_3^{2-}$  and (one of us, S. P. Ionov, together with M. E. Dyatkina and G. V. Ionova)  $SO_4^{2-}$ .

In 1932, Zachariasen [7] established by x-ray methods that the ion  $SO_3^{2-}$  in  $Na_2SO_3$  had a pyramidal structure with  $C_{3v}$  symmetry, the OSO angle being, within the limits of experimental error, tetrahedral.\*

Calculation by the MO method with self-consistency showed that in the main the  $SO_3^{2-}$  ion had the configuration:

$$(1a_1)^2(1e)^4(2a_1)^2(2e)^4(3a_1)^2(3e)^4(1a_2)^2.$$

The form of the molecular orbits and LCAO coefficients is shown in Table 3. The  $1a_1$ -orbit is strongly bonding and very low in energy. To the  $A_1$  representation belong linear combinations of atomic orbits both of the  $\pi$ - and the  $\sigma$ -type, but the  $c_{ij}$  coefficients allow us at once to say that the  $1a_1$ -orbit is essentially of the  $\sigma$ -type. The orbit next in energy, the  $1e_1$ , is doubly degenerate, and in it lie four electrons. This orbit has already a less clearly expressed  $\sigma$ -character. Approximately the same  $\sigma$ -character appertains to the  $2a_1$ -orbit. We must, however, take account of the fact that the role of the  $p_\pi$ -orbits of the oxygen atoms increases in the order  $1a_1$ ,  $1e_1$ ,  $2a_1$ . The 3d-orbits of the sulfur atom take no part in the  $\sigma$ -bonds.

Orbits  $1a_2$  and  $3e$ , in which six electrons are disposed, are essentially nonbonding and localized in the oxygen atoms. All the remaining occupied molecular orbits must belong to the  $\pi$ -type. Here it is interesting to consider the role of the 3d-orbit. In general, the 3d-orbits take a smaller part in the formation of bonds than the 3p-orbits but out of the five 3d-orbits  $d_{x^2-y^2}$  and  $d_{z^2}$  give the greatest contribution.

\* Horsfield and others [8] showed on the basis of optical and EPR-spectra that the radical  $SO_3^-$  had symmetry  $C_{3v}$ .

the possibility of characterizing the SO bond in  $SO_2$  as essentially double. Further, the "nonbonding" electrons  $(2a_1)^2(2b_2)^2$  play a small but real part in forming the bond.

With the calculated data we must now compare some experimental characteristics of the  $SO_2$  gas molecule. The interatomic distance is  $1.432 \text{ Å}$  (from spectral data [5]), while Simon and Krigsman [6] showed that, for the SO bonds in various compounds, the force constants could to a satisfactory degree of accuracy be calculated on the valence-force model. The force constant of the SO bond in  $SO_2$  so found is  $f_{SO}=10.23 \cdot 10^5 \text{ dyn/cm}$ .

Another example in which the SO bond bears an essentially double nature is that of  $SO_3$  gas. The  $SO_3$  molecule has  $D_{3h}$  symmetry. We derived the self-consistent molecular or-

TABLE 5. Calculated Self-Consistent LCAO-MO for  $S_2O_3^{2-}$ 

MO energy in eV	Representation	Coefficients $c_{ij}$										
		3s	3p <sub>A1</sub>	3p <sub>E</sub>	3d <sub>22</sub>	3d <sub>A1</sub>	3d <sub>E</sub>	$\sigma$	$\pi^1$	$\pi^2$	$\sigma^S$	$\pi^S$
-23.9	1a <sub>1</sub>	0.788	0.335			0.0		0.41	0.06		0.32	
-21.2	1e			0.72	0.09		0.09	0.46	0.26			0.34
-17.1	2a <sub>1</sub>	-0.583	0.656			0.056		0.261	0.40	0.28	0.08	
-12.6	2e			0.038	0.18		0.16	-0.77	0.31	0.40		0.31
-11.9	3a <sub>1</sub>	-0.174	-0.01			-0.11		0.73	-0.54		-0.38	
-10.8	3e			0.064	0.13		0.056	0.136	0.164	0.62		-0.74
-10.6	4e			0.0	-0.06		-0.032	0.0	-0.82	0.51		0.24
-10.4	1a <sub>2</sub>							1.0				
-10.2	4a <sub>1</sub>	-0.18	0.248			-0.15		-0.21	-0.65		0.64	
-5.58	5e			-0.588	0.53		0.28	0.33	0.11	0.10		0.34
-3.30	5a <sub>1</sub>	-0.21	-0.60			0.287		0.40	0.19		0.55	
-3.12	6e			0.19	0.73		-0.61	-0.10	-0.137	-0.126		-0.10
-1.46	6a <sub>1</sub>	0.05	0.18			0.93		-0.10	-0.25		-0.12	
+0.3	7e			0.31	0.35		0.71	-0.137	-0.31	-0.30		-0.26

The total order of the bond, according to Mulliken, is evidently 2.2. The reduced order of the bond corresponds to the significant fall in its force constant  $f_{SO} = 5.5 - 5.9 \cdot 10^5$  dyn/cm and  $R_{SO} = 1.45 \pm 0.02$  Å [15]. The calculated charge on the sulfur atom  $q_S = +0.45$  i.e., on each oxygen atom is concentrated 0.82 of an electron. The addition of two electrons to the neutral molecule  $SO_3$  leads to an intense disintegration of the SO bond and a change in symmetry (the bond becomes strongly heteropolar). In ions of the  $(RSO_3)^{2-}$  type, just as in  $SO_3^{2-}$ , the  $SO_3$  group has pyramidal structure. To ions of this type belong, as particular cases,  $S_2O_3^{2-}$  and  $S_2O_6^{2-}$ , which may be considered as the combinations  $S^{\delta+} - SO_3^{\delta-}$  and  $^{\delta-}O_3S - SO_3^{\delta-}$ . The structure of the latter ion was established with special care in papers by Stanley [9] and Dunitz [10]. The  $S_2O_6^{2-}$  ion has  $D_{3d}$  symmetry. The basic experimental data on the geometry of the  $S_2O_6^{2-}$  ion (in comparison with other neighboring ions) is shown in Table 4.

As shown by calculation (Table 5), the electron density distribution in  $RSO_3^-$  changes insignificantly in comparison with  $SO_3^{2-}$ . This change may qualitatively be represented as a certain displacement of the electron density from the oxygen atoms to the sulfur atom, which shows up in the lowering of the positive effective charge on the sulfur atom to  $q_S = +0.38$  and in the slight strengthening of the SO bond. The results of the calculation are in good accord with the force constants of the bond  $f_{SO} = 7.84 \cdot 10^5$  dyn/cm for  $S_2O_6^{2-}$  and  $f_{SO} = 8.5 \cdot 10^5$  dyn/cm for  $S_2O_3^{2-}$ .

In complex inorganic compounds of the sulfite group, there must evidently be an electron distribution intermediate between those characterizing  $SO_3^{2-}$  and  $S_2O_3^{2-}$  ( $RSO_3^{\delta-}$ ). According to data of Kharitonov [11], the force constants of the bond for the intraspherical sulfite group in complex compounds lie in the region of  $f_{SO} = 6.09 - 6.36 \cdot 10^5$  dyn/cm, which confirms the proposition mentioned.

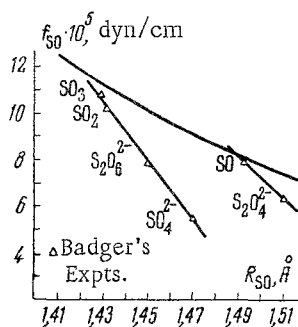


Fig. 1. Force constant  $f_{SO}$  of the bond as a function of interatomic distance  $R_{SO}$ .

The last of the oxyanions in our series of oxygen compounds with closed and completely filled bonding molecular orbits is the  $SO_4^{2-}$  ion, having symmetry  $T_d$ . The electron density distribution is given in Table 6. The disposition of the 24 electrons in the molecular orbits with least energy gives the ground state

$$(1a_1)^2(1t_2)^6(2t_2)^6(1e)^4(1t_1)^6.$$

The  $1a_1$  orbit is strongly bonding and belongs to the  $\sigma$ -type: it is formed from the 3s-orbit of the sulfur atom and a  $\sigma$ -combination of orbits of the oxygen atoms. The bonding orbit  $1t_2$  may be assigned to the mixed  $\sigma, \pi$ -type. The remaining molecular orbits, except the nonbonding  $1t_1$ , approximate to the  $\pi$ -type. Just as in ions  $SO_3^{2-}$  and  $S_2O_3^{2-}$ , the main part in forming the  $\pi$ -bonds is played by the  $3d_{x^2-y^2}$  and  $3d_{z^2}$  orbits of the sulfur atom. These give an essentially bonding, twice degenerate  $1e$ -orbit. All the bonds in  $SO_4^{2-}$  are essentially heteropolar. This fact is well expressed both by the charge  $q_S = +0.7$  and the order of the bond  $p_{SO} = 1.7$ .

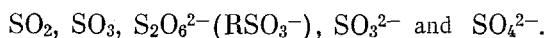
Experimental data agree completely with the calculations: the interatomic distance  $R_{SO} = 1.47$  Å the force constant  $f_{SO} = 5.52 \cdot 10^5$  dyn/cm.\*

\* All the force constants of the bond are taken from the papers by Krigsmann [6] and Moffitt [1].

TABLE 6. Calculated Self-Consistent LCAO-MO for  $\text{SO}_4^{2-}$ 

MO energy in eV	Representation	Coefficients $c_{ij}$										
		3s	3p <sub>x</sub>	3p <sub>y</sub>	3p <sub>z</sub>	3d <sub>z<sup>2</sup></sub>	3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	3d <sub>xy</sub>	3d <sub>xz</sub>	3d <sub>yz</sub>	$\sigma$	$\pi$
-24,79	1a <sub>1</sub>	0,78									0,63	
-19,05	1t <sub>2</sub>		-0,663	-0,663	-0,663			0,152	0,152	0,152	-0,603	0,417
-12,74	2t <sub>2</sub>		0,126	0,126	0,126			0,37	0,37	0,37	0,49	0,78
-12,33	1e					0,319	0,319					0,945
-9,1	1t <sub>1</sub>											1,0
-5,13	2a <sub>1</sub>	0,63									-0,78	
-3,10	3t <sub>2</sub>		0,708	0,708	0,708			0,328	0,328	0,328	-0,615	-0,615
-1,065	4t <sub>2</sub>		0,208	0,208	0,208			-0,855	-0,855	-0,855	-0,125	0,455
-0,067	2e					0,945	0,945					-0,319

It is interesting to analyze the form of the correlation between the three characteristics of the bond: the two experimental aspects (interatomic distance  $R_{\text{SO}}$  and force constant  $f_{\text{SO}}$ ) and the calculated order of the bond  $p_{\text{SO}}$ . All the numerical values of the characteristics in question are shown in Table 7. Let us start with the relation between the first two of these. Figure 1 shows  $f_{\text{SO}}$  as a function of  $R_{\text{SO}}$  for the series.



The results fall very well on a common curve, which, on the one hand, indicates high accuracy in the experimental determination of  $R_{\text{SO}}$  and  $f_{\text{SO}}$ , and, on the other, confirms the existence of a clear correlation between the parameters  $R_{\text{SO}}$  and  $f_{\text{SO}}$  for compounds which have, as a common trait of their electronic structure, occupied bonding molecular orbits. The relation between  $f_{\text{SO}}$  and  $R_{\text{SO}}$  has a linear form within the limits 1.43 to 1.47 Å. On the same figure appear two points corresponding to the  $f_{\text{SO}}$  and  $R_{\text{SO}}$  of the SO and  $\text{S}_2\text{O}_4^{2-}$  groups, substantially differing in their electronic structure: in each of these groups, two electrons find themselves in antibonding levels.

TABLE 7. Order of Bond, Force Constant, and Interatomic Distances

Compound	$f_{\text{SO}} \cdot 10^5$ , dyn/cm	$R_{\text{SO}}$ , Å	$p_{\text{SO}}$
SO <sub>3</sub>	10,77	1,430 ± 0,001	2,63
SO <sub>2</sub>	10,23	1,432 ± 0,001	2,66
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	8,50	1,450 ± 0,005	2,42
SO <sub>3</sub> <sup>2-</sup>	5,5 ÷ 5,9	—	2,2
SO <sub>4</sub> <sup>2-</sup>	5,52	1,470 ± 0,005	1,7

In the electronic structure, the SO molecule is analogous to O<sub>2</sub> molecule. The  $\text{S}_2\text{O}_4^{2-}$  ion may be regarded as a compound consisting of two  $\cdot\text{SO}_2^-$  fragments, in which the electron representing the difference from the neutral SO<sub>2</sub> molecule must find itself in an antibonding 3b<sub>2</sub>-orbit. As seen from Fig. 1 the presence of the antibonding electrons leads to a change in the characteristics of the bond; in  $\text{S}_2\text{O}_4^{2-}$  the SO distance is increased with respect to neutral SO<sub>2</sub>, and the force constant  $f_{\text{SO}}$  is lowered. However, the  $R_{\text{SO}}$  increase appears much sharper than the fall in  $f_{\text{SO}}$ , as a result of which both points (SO as well as  $\text{S}_2\text{O}_4^{2-}$ ) lie to the side of the curve. Thus, correlation between  $f_{\text{SO}}$  and  $R_{\text{SO}}$  may evidently only be established between groups having identical characters in their molecular orbits (viz., bonding or antibonding).

Figure 1 also gives Badger's [12] curve in the representation of Simon and Krigsman [6]:

$$f_{\text{SO}} = 1,86 \cdot 10^5 / (R_{\text{SO}} - 0,88)^3,$$

not taking account of the character of the SO bond. As seen from Fig. 1, this curve does not reflect the true characteristics of the molecules, and leads to increased values of the force constants for the majority of the groups. The increase in interatomic distance on calculating with Badger's formula has already been mentioned by Kharitonov [11].

The correlation between  $f_{\text{SO}}$  and  $R_{\text{SO}}$  for groups not having antibonding electrons, in this part has a linear character. The disposition of the points on the curve shows that the SO bond slowly weakens in the sequence (SO<sub>2</sub>, SO<sub>3</sub>), RSO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>. For the ion SO<sub>3</sub><sup>2-</sup>, there exists in the literature only one more or less reliable experimental value for the length of the bond, 1.45 Å, for which a probable error of ± 0.03 Å is given [15] (structure solved by one projection).

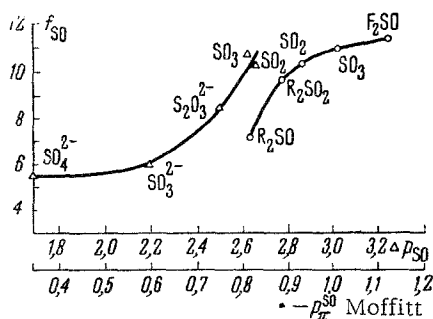


Fig. 2. Order of bond  $p_{SO}$  as a function of force constant  $f_{SO}$

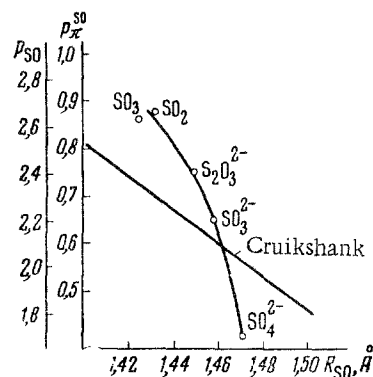


Fig. 3. Order of the bond  $p_{SO}$  as a function of interatomic distance  $R_{SO}$ .

The force constant of the bond, according to various data, lies within the limits  $5.5$  to  $5.9 \cdot 10^5$  dyn/cm, which defines a region in Fig. 2 disposed entirely to one side of the curve. Taking into consideration, however, a certain subjectivity in evaluating the error in structural treatments (usually on the low side), and the higher accuracy of spectral data, and taking the mean result from the latter, we may assume that the  $R_{SO}$  distance in the  $SO_3^{2-}$  ion must have the value  $1.467$  Å.

Special interest for ourselves lies in the sulfite groups, which come into the inner sphere of the complex ions of transitional metals. The values of  $f_{SO}$  for such groups in the compounds of  $Co^{III}$ ,  $Rh^{III}$ ,  $Ir^{III}$ ,  $Pt^{IV}$  were obtained from spectral data by Kharitonov. These data lie on the correlation curve in the region  $R_{SO} = 1.465 - 1.462$  Å. Attempts to establish theoretical or semiempirical links between the constants  $f$  or distances  $R$  and the order of the bond were made by Moffitt [1], Pauling [13], Cruikshank [2], Wagner [3], and Gillespie [16].

An essential characteristic of the degree of multiplicity of the bond is the concept of the bond order. We have used the total bond order (not separating the bonds into the  $\sigma$ - and  $\pi$ -types), since for interpolymer molecules it is not a priori clear what order the  $\sigma$ -bond has, and which bond ( $\sigma$  or  $\pi$ ) is the more sensitive to displacement of the charge. Further, separation of the bonds into  $\sigma$  and  $\pi$ -types requires considerable coarsening of the calculations (Moffitt and Cruikshank took the order of the  $\sigma$ -bond as unity).

Hence, the total bond order was calculated from Mulliken's formula

$$p(r, s) = N(i) c_r c_s \frac{1 + S_R}{2 c_r c_s S_R + 1},$$

where  $S_R$  is the exchange integral.

Table 7 collects all our correlated data for the main series  $SO_2$ ,  $SO_3$ ,  $SO_3^{2-}$ ,  $S_2O_3^{2-}$ ,  $SO_4^{2-}$ .

The variation of the force constant  $f_{SO}$  with the total bond order (our calculations) and with the order of the  $\pi$ -bond (Moffitt's data) is shown in Fig. 2. Although the curves define different theoretical parameters, it would be natural to expect that these forms would be analogous. As seen from the graph, the forms of the curves are substantially different. The main cause appears to be the insufficient account taken of the dynamics of electron density redistribution on using the Moffitt  $\pi$ -bond concept, as well as the fact that Moffitt analyzed only compounds with  $f_{SO}$  values lying in a fairly narrow range.

Figure 3 presents another relation touching on the two former: the bond order as a function of distance  $R_{SO}$ . Two curves are shown: one for the total bond order (our data), and the other for the order of the  $\pi$ -bond (Cruikshank's data). Here, there is no similarity between the run of the curves.

From the curve  $p_{tot} = f(R_{SO})$ , we may obtain an independent estimate of the distances  $R_{SO}$  in the  $SO_3^{2-}$  ion and in the intrasphere sulfite group. The calculated value of  $p_{SO}$  for  $SO_3^{2-}$  is  $2.2$ , so that  $R_{SO}$  must be  $1.46$  Å. The intrasphere sulfite group must have the same or a somewhat lower bond length.

The scatter of the points obtained on theoretical calculation of the charge  $q_s$  is quite considerable (Fig. 4). However, taking into consideration the approximate nature of the calculations, we may say that the general picture

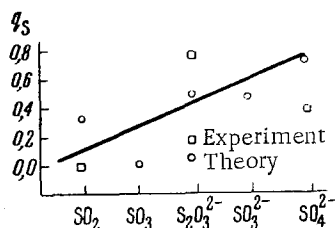


Fig. 4. Variation of charge on the sulfur atom.

is fairly satisfactory. The mean deviation of points from the general curve equals 0.1 el., and the maximum deviation for  $SO_2$  and  $SO_3$  is 0.2 el. each, on opposite sides. The experimental values of the charge obtained from x-ray data [14] are also quite close.

It is significant that the charge on the sulfur atom is in all cases positive, and rises with increasing number of ligands, agreeing with the chemical representations of the distribution of charges. The charge on the sulfur atom is also positive in those cases in which the system as a whole has an excess negative charge; the latter is concentrated on the oxygen atoms.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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