

## Infrared Absorption Spectra of Solid Metal Sulfites

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The IR spectra of metal sulfites with known structures have been examined. From the spectra it is possible to detect a predominant coordination of the sulfite ion. A general correlation between the average sulfur-oxygen distance and the average stretching frequency in compounds with the SO group has turned out to be valid also for the metal sulfites.

From IR studies Newman and Powell<sup>1</sup> have discussed structural features of some metal sulfites. The fact that the crystal structure of  $\text{NH}_4\text{CuSO}_3$ <sup>2</sup> does not fit into their assumptions initiated this investigation on the IR spectra of compounds with known structures.

### EXPECTED VIBRATIONS OF THE SULFITE GROUP IN THE CRYSTALLINE STATE AND CALCULATION OF $\nu_{\text{SO}}$

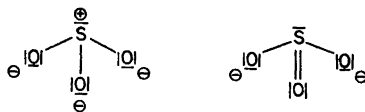
The free sulfite ion has  $C_{3v}$  symmetry, giving rise to four infrared and Raman active fundamental modes:  $\nu_1$  (symmetric stretch),  $\nu_2$  (symmetric bend),  $\nu_3$  (asymmetric stretch), and  $\nu_4$  (asymmetric bend). The two asymmetric modes are both doubly degenerate.

In the present paper the assignment of vibrational modes for the observed frequencies will follow the work of Evans and Bernstein.<sup>3</sup> From the polarisation effects in the Raman spectrum as well as from the relation between intensities of the Raman and IR spectra these authors concluded that the asymmetric mode  $\gamma_3$  in sodium sulfite solution occurred at lower frequency than the  $\gamma_1$  mode.

In the crystalline state there are several factors which affect the sulfite frequencies. The most dominant factors are the effect on the site symmetry of the ion in the structure and the effect of coordination of the ion.

The symmetry of the sulfite ion in a crystal must be  $C_{3v}$  or one of the subgroups  $C_3$ ,  $C_s$ , or  $C_1$ . Under the site symmetry  $C_3$ ,  $C_s$ , and  $C_1$  the degenerate modes  $\gamma_3$  and  $\gamma_4$  split and six vibrations would be expected.

Assuming that the  $3d$  orbitals of sulfur participate in bonding, the S—O bond in the sulfite group has at least partial double bond character. Two of the resonance structures of the sulfite ion can be written:



The attachment of oxygen to a positive atom (metal or hydrogen) should favour the former structure, and conversely the attachment of sulfur to a positive atom would support the latter one.

Consequently a decrease in the stretching frequency following the decrease of the bond order would be expected in a compound with oxygen coordination. Furthermore the symmetry of the group is changed to  $C_s$  and the number of infrared active fundamentals is increased to six because of the removal of the degeneracy from  $\nu_3$  and  $\nu_4$ .

If the sulfite group is coordinated to metal through sulfur the  $C_{3v}$  symmetry is essentially preserved, but the stretching modes should shift to higher frequency compared with the free ion because of the higher bond order.

Lehman<sup>4</sup> has derived an average rule for stretching frequencies of related molecules. The stretching frequency of an isolated AB group is approximately equal to the weighted average (more exactly the root-mean square value) of the symmetric and asymmetric stretching frequencies of a similar  $AB_x$  group provided that there is no mixing of the vibrations of the  $AB_x$  group and the rest of the molecule.

$$\nu_{AB} = (1/x) (\nu_{\text{sym}} + (x-1) \nu_{\text{asym}})_{AB_x}$$

This average rule has been applied to the  $SO_3$  group for the metal sulfites under investigation.

## EXPERIMENTAL

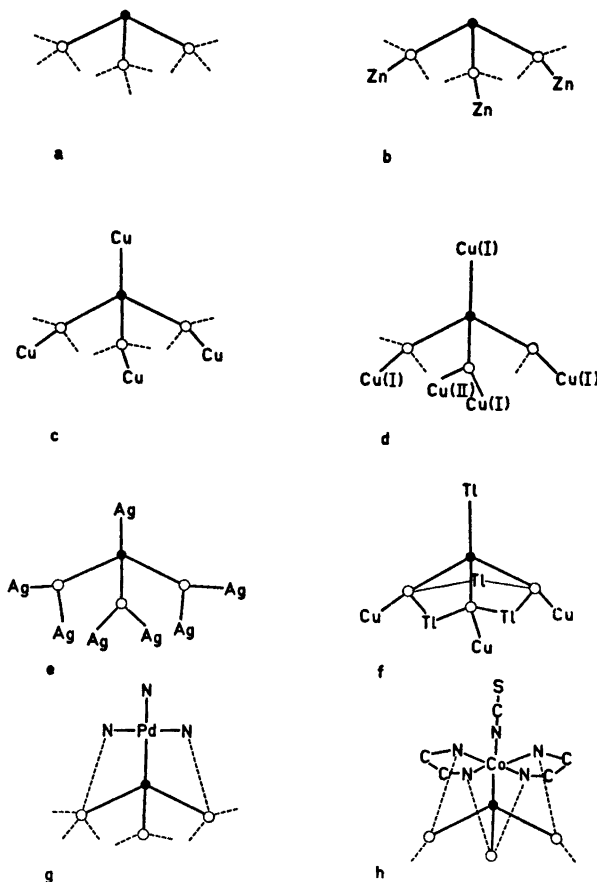
The IR samples were made by the KBr-pellet technique. The samples showed no reactions with KBr. The spectra were recorded with a Perkin-Elmer 180 spectrometer. X-Ray powder photograms of the compounds were recorded with a Hågg-Guinier camera with  $CuK\alpha_1$  radiation. The compounds were identified with the aid of the known cell-dimensions.

The compound  $Na_2[Hg(SO_3)_2]$  was kindly delivered by Professor Bengt Aurivillius. References to earlier IR investigations are listed in Table 2.

## RESULTS AND DISCUSSION

For all the examined metal sulfites except sodium sulfite, a schematic drawing of the environment of S and O in the sulfite group is given in Fig. 1. In sodium sulfite the sodium oxygen bonds are weak and there is no hydrogen bonding; its spectrum can therefore be used as a standard for the comparison of the other sulfite spectra. For  $Na_2SO_3$  in the solid state Evans and Bernstein<sup>3</sup> have found the following values of the frequencies in  $cm^{-1}$ :

$\nu_1$	$\nu_3$	$\nu_2$	$\nu_4$
1010(m)	961(st)	633(st)	496(st)



*Fig. 1.* Schematic drawings showing the environment of the sulfur and the oxygen atoms in the sulfite group. (a)  $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$  and  $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$ ; (b)  $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ; (c)  $\text{NH}_4\text{CuSO}_3$ ; (d)  $\text{Cu}^{\text{II}}[\text{Cu}^{\text{I}}(\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$ ; (e)  $\text{Ag}_2\text{SO}_3$ ; (f)  $\text{Tl}_2[\text{Cu}(\text{SO}_3)_2]$ ; (g)  $\text{PdSO}_3(\text{NH}_3)_3$ ; (h)  $\text{Co}(\text{en})_2\text{SO}_3 \cdot \text{NCS} \cdot 2\text{H}_2\text{O}$ . Open large circles denote oxygen atoms linked to the sulfur atom (small filled circles). Dashed lines indicate possible hydrogen bonds.

*Table 1.* Vibrational frequencies of the free sulfite ion in  $\text{cm}^{-1}$ .

	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$
Solution (Raman)	967(st)	620(w)	933(m)	469(m)
Solution (IR)	1002(m)	632(w)	954(st)	—



Here the vibrational modes have frequencies similar to those of the free ion (*cf.* Table 1). In the present investigation  $\nu_1$  and  $\nu_3$  were not resolved. However, in the investigation of Evans and Bernstein, the average stretching frequency is  $\nu_{\text{SO}} 977 \text{ cm}^{-1}$  and in this study  $975 \text{ cm}^{-1}$  (*cf.* Table 3).

From the intensities of the vibrational modes it is difficult to make reliable assignments of the individual stretching frequencies. In Table 3 the symmetric ( $\nu_1$ ) and the asymmetric ( $\nu_3$ ) stretching frequencies are therefore listed together. Fortunately, only in the cases of  $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ <sup>9</sup> and  $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ <sup>10</sup> is an assignment necessary for the calculation of  $\nu_{\text{SO}}$ . For these compounds without sulfur coordination the symmetric stretching mode was assumed to have the highest frequency as in sodium sulfite.

The structure of the compounds can be divided into three groups after the sulfite ion coordination.

I. Compounds without sulfur coordination.

II. Compounds with both sulfur and oxygen coordination.

III. Compounds with dominant sulfur coordination.

To group I belong  $\text{Na}_2\text{SO}_3$ ,<sup>11</sup>  $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ ,<sup>9</sup>  $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$ <sup>12</sup> and  $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ .<sup>10</sup> The spectra for these compounds show resemblances with the sodium sulfite spectra, but there is at least one stretching mode at lower frequency in ammonium sulfite and in zinc sulfite. The expected splitting of  $\nu_3$  and  $\nu_4$  due to the lowering of the symmetry can only be seen in  $\nu_4$  for  $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$  and  $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ .

The spectrum of  $\text{NH}_4\text{CuSO}_3$ <sup>2</sup> is almost identical with the sodium sulfite spectrum, but the structure has strong copper-sulfur bonds and in addition copper-oxygen bonds and hydrogen bonding. The effect is a sulfite group like the sulfite group in sodium sulfite.

Besides ammonium copper(I) sulfite  $\text{Ag}_2\text{SO}_3$ ,<sup>13</sup>  $\text{Cu}^{\text{II}}[\text{Cu}^{\text{I}}\text{SO}_3]_2 \cdot \text{H}_2\text{O}$ <sup>14</sup> and  $\text{Ti}_2[\text{Cu}(\text{SO}_3)_2]$ <sup>15</sup> belong to the second group with both metal-sulfur bonds and metal-oxygen bonds. The spectra of these compounds show stretching frequencies of high intensity above and below  $975 \text{ cm}^{-1}$ . Analogous shifts have been observed for thiosulfate complexes.<sup>16</sup>

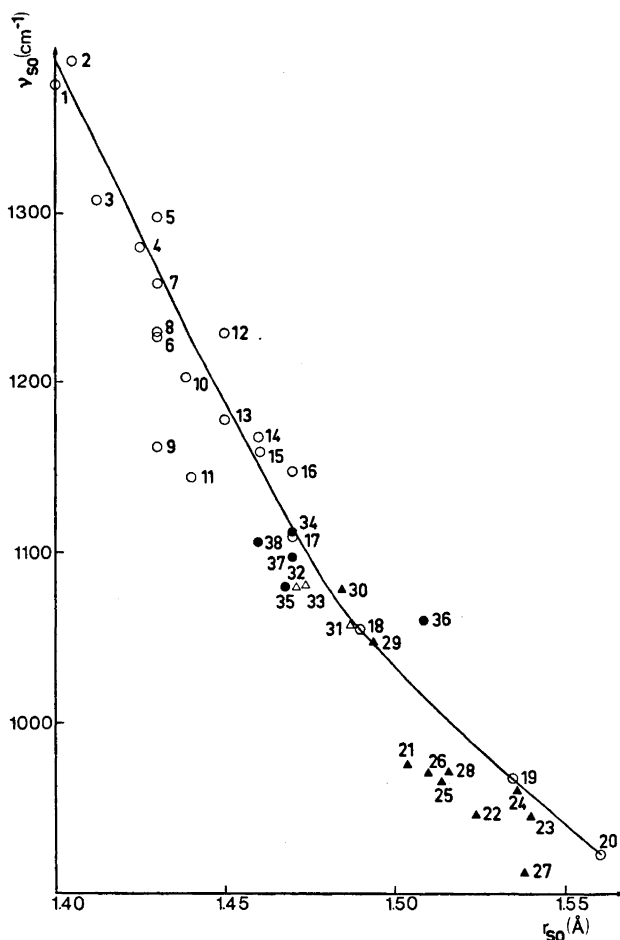
Table 4.  $r_{\text{SO}}$ , the asymmetric ( $\nu_{\text{as}}$ ) and the symmetric ( $\nu_{\text{s}}$ ) stretching frequencies and the calculated  $\nu_{\text{SO}}$  for some metal thiosulfates and sulfates.

Compound	$r_{\text{SO}}^a$ (Å)	$\nu_{\text{as}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{s}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{SO}}$ ( $\text{cm}^{-1}$ )	No. in Fig. 2
$\text{SnSO}_4$	1.487 <sup>19</sup>	1183,1064,1031	975 <sup>20</sup>	1063	31
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1.471 <sup>21</sup>	1136,1087	981, <sup>20</sup>	1079	32
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	1.474 <sup>22</sup>	1143,1087	976 <sup>20</sup>	1080	33
$\text{Na}_{2n}[\text{Cu}(\text{NH}_3)_4]_n[\text{Cu}(\text{S}_2\text{O}_3)_{2n}]_n$	1.470 <sup>23</sup>	1177,1137	1012 <sup>16</sup>	1109	34
$\text{Mg S}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	1.468 <sup>24</sup>	1120	998 <sup>16</sup>	1079	35
$\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$	1.509 <sup>25</sup>	1120,1105,1075	1007,988 <sup>16</sup>	1066	36
$\text{Na}_2\text{S}_2\text{O}_3$	1.47 <sup>26</sup>	1160,1130	1002	1097	37
$\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$	1.46 <sup>27</sup>	1150	1018	1106	38

<sup>a</sup> All values without corrections for vibrational motion.

Finally the compounds  $\text{PdSO}_3(\text{NH}_3)_3$ <sup>17</sup> and  $\text{Co(en)}_2\text{SO}_3 \cdot \text{NCS} \cdot 2\text{H}_2\text{O}$ <sup>8</sup> (en = ethylenediamine) have metal-sulfur bonds and the crystals are composed of discrete molecules held together by hydrogen bonds. The spectra have stretching frequencies above  $975 \text{ cm}^{-1}$ . The spectra are all consistent with the site symmetry of the anion.

Gillespie and Robinson<sup>18</sup> have applied Lehman's average rule to the  $\text{SO}_x$  group in various compounds. From the value of  $\nu_{\text{SO}}$  they calculated a force



*Fig. 2.* Plots of  $\nu_{\text{SO}}$  versus  $r_{\text{SO}}$ . The curve is from Gillespie and Robinson and is based on the values (O) 1–20. (1)  $\text{S}_3\text{O}_8$ ; (2)  $\text{SO}_3\text{F}_3$ ; (3)  $\text{SOF}_3$ ; (4)  $\text{SO}_2(\text{OH})_2$ ; (5)  $\text{SO}_2\text{Cl}_2$ ; (6)  $(\text{CH}_3)_2\text{SO}_2$ ; (7)  $\text{SO}_2$ ; (8)  $\text{SO}_3$ ; (9)  $\text{S}_2\text{O}_6^{2-}$ ; (10)  $\text{S}_2\text{O}_7^{2-}$ ; (11)  $\text{NH}_2\text{SO}_3^-$ ; (12)  $\text{SOCl}_2$ ; (13)  $\text{NH}(\text{SO}_3)^{2-}$ ; (14)  $\text{EtO} \cdot \text{SO}_3^-$ ; (15)  $\text{CH}_2(\text{SO}_3)^{2-}$ ; (16)  $\text{HO} \cdot \text{SO}_3^-$ ; (17)  $(\text{CH}_3)_2\text{SO}$ ; (18)  $\text{SO}_4^{2-}$ ; (19)  $\text{SO}_2(\text{OH})_2$ ; (20)  $\text{HO} \cdot \text{SO}_3^-$  ( $\nu_{\text{SO}}$  calculated for S–O(H)). The following numbers (21–38) are explained in Tables 3 and 4.  $\blacktriangle$ , sulfites.  $\triangle$ , sulfates.  $\bullet$ , thiosulfates.

constant of the SO bond and found a linear relationship between  $\log k_{\text{SO}}$  and  $\log r_{\text{SO}}$ , where  $k_{\text{SO}}$  is the stretching force constant and  $r_{\text{SO}}$  is the bond length.

Table 3 shows  $\nu_{\text{SO}}$  and  $r_{\text{SO}}$  for the compounds described in this investigation. Table 4 presents  $\nu_{\text{SO}}$  and  $r_{\text{SO}}$  for some thiosulfates and sulfates with known structures. In Fig. 2 the values are plotted together with the calculated curve from Gillespie and Robinson.<sup>18</sup> The metal sulfites fit to the curve fairly well, but there is a tendency finding a shorter sulfur-oxygen distance than would be expected from the vibrational frequency using this curve. Nevertheless an average S—O bond length compared to the bond length in sodium sulfite can be suggested from the value of  $\nu_{\text{SO}}$ . However, in the assignments of  $\nu_1$  and  $\nu_3$  and in the calculation of  $\nu_{\text{SO}}$  and  $k_{\text{SO}}$  there are several sources of error, so that a proposed bond length from the infrared absorption spectrum has no great accuracy. Robinson<sup>28</sup> has suggested a theoretical value of 1.54 Å for the free sulfite ion in solution on the basis of a proposed relationship between  $\nu_{\text{SO}}$  and bond order. A discussion of bond length in various metal sulfites is given by Kierkegaard et al.<sup>29</sup>

The conclusion of this study is that in most metal sulfites the coordination of the sulfite ion can be derived from the infrared absorption spectra. A stretching mode of high intensity above 975  $\text{cm}^{-1}$  is an indication of coordination through sulfur. Conversely a mode with high intensity below 960  $\text{cm}^{-1}$  is a sign of coordination through oxygen. A spectrum with stretching frequencies around 975–960  $\text{cm}^{-1}$  can only indicate that the compound is either ionic, e.g. sodium sulfite, or has the sulfite group engaged in covalent bonding with bonds to sulfur as well as to oxygen (cf.  $\text{NH}_4\text{CuSO}_3$ ).

A spectrum of a compound,  $\text{Na}_2[\text{Hg}(\text{SO}_3)_2]$ , with unknown structure, was also recorded. The observed frequencies in  $\text{cm}^{-1}$  are 1125(st), 1020(vw), 975(st), 640(st), 520(vw), 510(vw), and 495(st). From the criteria above we propose a structure with a Hg—S bond.

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