

The Crystal Structure of Thallium Trithionate, $\text{Ti}_2\text{S}_3\text{O}_6$

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absorption coefficient is correctly determined in the region of the discrete bands.³ It appears probable that this slight shoulder can be explained by the effects of excited lower vibrational states ($\nu'' > 0$), but this explanation ought to be tested by an analysis of absorption curves at several temperatures.

This I_2 absorption in the visible region is in all probability ${}^3\Pi_0+\leftarrow{}^1\Sigma^+$ almost entirely, overlain by a faint ${}^1\Pi\leftarrow{}^1\Sigma^+$ component.² That the latter must be faint is shown by the low intensity of the ${}^3\Pi_1\leftarrow{}^1\Sigma^+$ bands and continuum, taken together with the fact that the coupling in I_2 can hardly be very far away from α , i.e., intermediate between $\Omega-\Sigma$ and case c . With such coupling, ${}^1\Pi\leftarrow{}^1\Sigma^+$ should be of about the same intensity as ${}^3\Pi_1\leftarrow{}^1\Sigma^+$. [The ${}^3\Pi_1\leftarrow{}^1\Sigma^+$ continuum shows signs of a weak maximum, according to Brown, at $\lambda 7320$.]

As an alternative explanation analogous to (2) for Br_2 , A.A.B. suggest that one might attribute the weak $\lambda 7320$ peak to ${}^3\Pi_1\leftarrow{}^1\Sigma^+$, the shoulder on the main I_2 absorption to ${}^3\Pi_0+\leftarrow{}^1\Sigma^+$, and the main peak to ${}^1\Pi\leftarrow{}^1\Sigma^+$. This, however, can hardly be accepted, since it would make ${}^1\Pi\leftarrow{}^1\Sigma^+$ enormously stronger than ${}^3\Pi_1\leftarrow{}^1\Sigma^+$, which would be possible only for $\Lambda-\Sigma$ coupling. Aside from the general unreasonableness of such coupling for the ${}^3, {}^1\Pi$ of I_2 , it is to be noted that the empirical interval ${}^1\Pi-{}^3\Pi_0+$ given by this interpretation is too small, and the empirical interval ${}^3\Pi_0+-{}^3\Pi_1$ too large, to accord with $\Lambda-\Sigma$ coupling.² Moreover, the Franck-Condon principle argument in the case of I_2 (unlike that of Br_2), favors the attribution of the main peak to ${}^3\Pi_0+\leftarrow{}^1\Sigma^+$, especially in view of the fact that the recent work of Rabinowitch and Wood locates this peak at $\lambda 5200$ rather than at its previously accepted value $\lambda 5060$. Hence there can be no reasonable doubt that the A.A.B. interpretation (2) must be rejected for I_2 .

For Cl_2 either interpretation (1) or (2) appears to be consistent with existing data. According to (1), the continuum is mainly ${}^3\Pi_0+\leftarrow{}^1\Sigma^+$, while according to (2) it is mainly ${}^1\Pi\leftarrow{}^1\Sigma^+$. In any case, it seems clear that ${}^1\Pi\leftarrow{}^1\Sigma^+$ in Cl_2 is weaker than in Br_2 . In F_2 it is still weaker.

All in all, the work of A.A.B. appears to establish that ${}^1\Pi\leftarrow{}^1\Sigma^+$ is fairly strong in Br_2 , and stronger there than for any of the other halogens X_2 . This relieves us of the previously existing onus of finding a systematic explanation for the apparent surprising weakness of this transition in all X_2 . In the light of the work of A.A.B., it can be stated that the intensity of the transition ${}^3\Pi_0+\leftarrow{}^1\Sigma^+$ is a maximum for I_2 , is much weaker in Br_2 , and is probably still weaker, *perhaps* very much weaker, in Cl_2 and F_2 . This is explainable by diminution in case c tendency from I_2 toward F_2 , the occurrence of ${}^3\Pi_0+\leftarrow{}^1\Sigma^+$ at all being attributable (Van Vleck) to perturbation of the ${}^3\Pi_0+u$ wave function under case c influence by a ${}^1\Sigma^+u$ state lying above the ${}^3\Pi_0+u$.²

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University of Chicago,
April 14, 1936.

¹ A. P. Acton, R. G. Aickin and N. S. Bayliss, *J. Chem. Phys.* **4**, 474 (1936).

² R. S. Mulliken, *Phys. Rev.* **46**, 549 (1934).

³ E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.* **32**, 547 (1936).

The Crystal Structure of Thallium Trithionate, $Tl_2S_3O_6$

The crystal structure of thallium trithionate has been investigated. Contrary to the statement in literature¹ it has been found not to be isomorphous with that of the corresponding potassium salt.^{2,3} The salt was prepared from equivalent portions of barium trithionate and thallous sulfate; it crystallizes in elongated rectangular tables or flat prisms.

By means of rotation- and oscillation-diagrams the symmetry was found to be monoclinic with the following dimensions of the elementary cell:

$$a = 13.20 \pm 0.05 \text{ \AA}, \quad b = 7.45 \pm 0.02 \text{ \AA}, \quad c = 7.58 \pm 0.02 \text{ \AA}, \\ \beta = 91^\circ 0'.$$

The number of molecules $Tl_2S_3O_6$ in this cell, calculated with the pycnometric density $d = 5.08$, was found to be $Z = 3.83 \pm 4$. The roentgenographic density and molar volume were calculated as $d_{ro} = 5.31$, $MV = 113.0$. The b axis, at right angles with the symmetry plane, lies in the direction of the longest dimension of the crystals, the faces of which are formed predominating by 100 and secondary by 101.

The space group was found to be $C_{2h}(C2/c)$, the eight thallium atoms occupying the general position $8(f)$: $x y z$, $\bar{x} \bar{y} \bar{z}$, $\bar{x} y \frac{1}{2} - z$, $x \bar{y} \frac{1}{2} + z$ and the same $+\frac{1}{2} \frac{1}{2} 0$, with the parameter values: $x = 0.14 \pm 0.005$, $y = 0.16 \pm 0.01$ and $z = 0.36 \pm 0.005$.

On account of their low scattering power the positions of sulfur and oxygen atoms could not be determined with accuracy. Of the 12 sulfur atoms four will be occupying the four equivalent position $4(e)$ with the point-symmetry C_2 , the other positions having the point-symmetry C_1 , resulting in linear S_3 groups. The other sulfur and oxygen atoms will probably be all in general positions. The symmetry of the S_3O_6 group is in this way found to be C_2 , the groups situated at right angles with the twofold axis, on which the middle sulfur atom of each group will be lying. This symmetry is in accordance with the results obtained by Zachariasen from the analysis of $K_2S_3O_6$. The molar volume of the thallium trithionate, 113.0, is low in comparison with those of the potassium and rubidium salts 116.3 and 125.2. The molar volumes of thallium salts are generally⁴ 2.5 cm^3 for one metal atom higher, resp. 1.5 cm^3 lower, than those of the corresponding potassium and rubidium salts. These values indicate a rather important difference between the crystal structures of thallium and of potassium trithionate.

Data concerning ammonium trithionate, which is also monoclinic, will be given later.

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July 27, 1936.

¹ E. J. Bevan, *Chem. News* **36**, 203 (1877).

² W. H. Zachariasen, *J. Chem. Phys.* **2**, 109 (1934); *Zeits. f. Krist.* **A89**, 529 (1934).

³ The rubidium salt was found to be wholly isomorphous with the potassium salt. The dimensions of the elementary cell are: $a = 9.93 \pm 0.02 \text{ \AA}$, $b = 14.20 \pm 0.05 \text{ \AA}$, $c = 5.86 \pm 0.02 \text{ \AA}$, $MV = 125.2$.

⁴ W. Biltz, *Raumchemie der festen Stoffe* (Leipzig, 1934).