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LETTERS TO THE EDITOR

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Note on Absorption Processes in the Halogen Spectra

The interesting work of Acton, Aickin and Bayliss on the continuous absorption of bromine, which the writer has had the privilege of reading in manuscript, makes it easier than before to understand the electronic transitions involved in the halogen spectra. A.A.B. find the visible absorption continuum of Br_2 for $v''=0$ to be composite, with a stronger component *A* having its maximum near $\lambda 4150$, and a second component *B* of about a third or a fourth as large an integrated intensity as *A*, and with maximum near $\lambda 4950$ (cf. their Fig. 2). They offer two possible explanations, of which they favor the second: (1), *B* and *A*, respectively, represent $^3\Pi_1 \leftarrow ^1\Sigma^+$ and $^3\Pi_0+ \leftarrow ^1\Sigma^+$; (2), *B* and *A* represent $^3\Pi_0+ \leftarrow ^1\Sigma^+$ and $^1\Pi \leftarrow ^1\Sigma^+$, respectively. A.A.B. also suggest that interpretation (2) may be extended to I_2 and Cl_2 .

In the present note it will be shown that while explanation (2), somewhat modified, may (or may not) be applicable to Br_2 and Cl_2 , it is inapplicable to I_2 ; but that in any case the results of A.A.B., taken in connection with theoretical considerations, show that the transition $^1\Pi \leftarrow ^1\Sigma^+$ in the halogens is not so anomalously and universally weak as earlier data had indicated.

Let us first consider A.A.B.'s explanation (1) for Br_2 . If this is correct, then the transition $^3\Pi_1 \leftarrow ^1\Sigma^+$ (region *B*) is fairly strong. If this is true, the corresponding transition $^1\Pi \leftarrow ^1\Sigma^+$ must, according to theory, be as strong or stronger. For $\Omega-s$ or case *c* or an intermediate type of coupling (let us call these cases α), $^3\Pi_1 \leftarrow ^1\Sigma^+$ and $^1\Pi \leftarrow ^1\Sigma^+$ would be about equal in intensity, while for ideal $\Lambda-\Sigma$ coupling (call this β), $^3\Pi_1 \leftarrow ^1\Sigma^+$ should be vanishingly weak compared with $^1\Pi \leftarrow ^1\Sigma^+$.² It is reasonable in Br_2 to expect a case roughly half-way between β and α , perhaps most likely nearer α .² It is then clear that A.A.B.'s explanation (1) must be modified by attributing a considerable part, probably about half, of the strong component *A* of the continuum to $^1\Pi \leftarrow ^1\Sigma^+$, the remainder being $^3\Pi_0+ \leftarrow ^1\Sigma^+$. This requirement that component *A* must itself be composite is not necessarily in contradiction to the apparent singleness of *A*, since with $\Omega-s$ coupling one expects the potential energy curves of $^3\Pi_0+$ and $^1\Pi$ to run close together.

As a matter of fact, however, although A.A.B.'s absorption coefficient curve for $v''=0$ (their Fig. 2) does not show compositeness in *A*, their curve for $v''=1$ (their Fig. 3) does give decided evidence that three upper electronic

states are involved in *A* and *B*. Although only three maxima are shown in their Fig. 3 curve, their data indicate that the highest frequency maximum of these is really double (see experimental points in Fig. 3); they consider, to be sure, that this doubling is not incapable of being explained by experimental error. If this double maximum is real, its higher frequency component may be attributed to $^1\Pi \leftarrow ^1\Sigma^+$, the lower frequency component to $^3\Pi_0+ \leftarrow ^1\Sigma^+$. The two remaining maxima in Fig. 3 are then readily explained, the middle one involving contributions from all three electronic transitions. On the whole we see that A.A.B.'s explanation (1), modified by the admission of $^1\Pi \rightarrow ^1\Sigma^+$ as a strong transition, has strong support.

As A.A.B. point out, explanation (1) meets a serious difficulty in connection with the application of the Franck-Condon principle.¹ This can be slightly ameliorated, but not overcome, when the modification just given is introduced, according to which *A* is double. This difficulty is overcome, however, if explanation (2) is adopted. The strong maximum *A* must then be attributed to $^1\Pi \leftarrow ^1\Sigma^+$ alone. The apparent doubling of the high frequency maximum in Fig. 3 has to be attributed now to experimental error. In their explanation (2), A.A.B. attribute *B* to $^3\Pi_0+ \leftarrow ^1\Sigma^+$ and consider that $^3\Pi_1 \leftarrow ^1\Sigma^+$ is weak and lies at longer wave-lengths. It should, however, be noted that if $^3\Pi_1 \leftarrow ^1\Sigma^+$ is weak compared with $^1\Pi \leftarrow ^1\Sigma^+$, then we have nearly β type ($\Lambda-\Sigma$) coupling; but for $\Lambda-\Sigma$ coupling, levels $^3\Pi_1$ and $^3\Pi_0+$ in Br_2 should be rather close together (about 0.14 ev apart).² Thus if explanation (2) is essentially correct, we must probably suppose that the weak component *B* is really an unresolved composite of $^3\Pi_0+ \leftarrow ^1\Sigma^+$ and $^3\Pi_1 \leftarrow ^1\Sigma^+$. While all this is not untenable, it appears somewhat unlikely that the coupling departs so far from α , and approaches β so nearly, as seems to be required by explanation (2). On the whole, explanation (2) seems less probable than (1), but the Franck-Condon argument in favor of (2) is strong. A more accurate knowledge of the potential energy curve of the $^3\Pi_0+$ state, based on an analysis of data from the discrete Br_2 bands by the Rydberg-Klein method, should help to resolve this difficulty.

In the case of I_2 , the intense part of the absorption curve (partly continuum, partly bands) shows a shoulder on its long wave-length side, similar to that in the Br_2 continuum, and suggests that, again, the absorption involves two upper electronic states. Recent work of Rabinowitch and Wood, however, shows that this shoulder is only slight when the

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 $\Omega - s$ 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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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:

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

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 $C_{2h}^2(C2/c)$, 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).