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Note: The $^3\Pi_{1u}$ State and the Absorption Continuum of the Bromine Molecule

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AS is well known the discrete band absorption spectrum of Br_2 consists of two systems, one of which, the main system, occurs between 5110A and 6590A and the other, the extreme red system, between 6450A and 7600A.[1] These systems are attributed, respectively, to the electronic transitions $^3\Pi_{0+u}\leftarrow{}^1\Sigma_g^+$ and $^3\Pi_{1u}\leftarrow{}^1\Sigma_g^+$. The vibrational and rotational constants and the numerations of the common lower state and the upper state of the main system are known fairly accurately but as no measurements of the vibrational isotope effect and no rotational analysis in the case of the extreme red system has been recorded as yet the existing data for the upper state of this system are very incomplete. The data tabulated by Jevons[2] and by Sponer[3] are based on Brown's provisional numeration and are not corrected for Brown's suggested possible increase of 4 ± 2 units in v'.

As a preliminary to the interpretation of a number of diffuse ultraviolet bands in the Br_2 emission spectrum which I have photographed I have attempted, by raising the absorbing vapor to higher temperatures than was done by Brown, to photograph and measure bands of the extreme red system due to transitions from higher v'' levels to lower v' levels than those already recorded. It was hoped thereby to observe measurable isotope head separations and thence to determine the true quantum numeration. As a more complete knowledge of the $^3\Pi_{1u}$ state is necessary for the interpretation of the continuous absorption spectrum recently examined by Acton, Aickin and Bayliss[4] and discussed by Mulliken[5] a brief account of my results and a few comments insofar as they are related to the continuous spectrum may be of interest.

In spite of the very considerable increase in vapor temperature (450°C, cf. 100°C (Brown)) only two new $\Delta G'(v+\frac{1}{2})$ values and three new $\Delta G''(v+\frac{1}{2})$ values were obtained. The region in which it had been hoped that an extension would appear is occupied by seven new short v' progressions ($v''=8$ to $v''=14$) of the main system which after being unobservable in the region occupied by the extreme red system between 6600A and 7100A reappears, coexists with and then above 8180A extends beyond the observed extreme red system. A precise determination of the true numeration has not been effected as only three isotope heads have been measured with reasonable certainty. From them a most probable numeration increase n of 7 units with a possible error of ±2 is predicted. This proposed increase is supported by other considerations relating to (1) the position which the upper P. E. curve must occupy with respect to the lower to account for the nonappearance of the $v''=0$ progression or, if this is not due to dissociation, to account for the close proximity of the predicted intensity maximum in this progression to the system convergence, (2) observation of the sharpest head in a progression it being assumed that for the corresponding band the isotopic separation is least. If Brown's provisional numeration is increased by 7 units the vibrational constants of the bromine molecule in the excited state of the extreme red system are as follows: $\omega_e'=170.7$ cm^{-1}, $x_e'\omega_e'=3.694$, $\nu_e=13{,}814$ cm^{-1}, $\nu^{00}_{\text{head}}=13{,}737$ cm^{-1}, $\nu^{0}_{\text{con.}}=15{,}920$ cm^{-1}, $D_0'=2180$ cm$^{-1}=0.269$ ev. This value of D_0' is almost twice as great as that quoted by Jevons and by Sponer, *viz.* 0.144 ev. From the empirical law $\omega_e''r_e''^p=\omega_e'r_e'^pr_e'$ is found to be 2.64A.

Acton, Aickin and Bayliss have found that the absorption continuum of Br_2 in the visible due to transitions from $v''=0$ may be supposed to consist of two unresolved maxima, a strong one A at 24,100 cm^{-1} and a weaker one B at 20,400 cm^{-1}. For transitions from $v''=1$ there are three maxima at 27,000 cm^{-1}, 22,000 cm^{-1} and 19,000 cm^{-1}. They have offered two alternative explanations *viz.* that A and B are due, respectively, to (1) $^3\Pi_{0+u}\leftarrow{}^1\Sigma_g^+$ (main), $^3\Pi_{1u}\leftarrow{}^1\Sigma_g^+$ (ext. red) or (2) $^1\Pi\leftarrow{}^1\Sigma_g^+$ (unobserved, $^1\Pi$ being a theoretically

[1] W. G. Brown, Phys. Rev. **38**, 1179 (1931); **39**, 777 (1932).
[2] W. Jevons, *Report on Band Spectra* (1932).
[3] H. Sponer, *Molekülspektren*, vol. 1 (1935).
[4] A. P. Acton, R. G. Aickin and N. S. Bayliss, J. Chem. Phys. **4**, 474 (1936).
[5] R. S. Mulliken, J. Chem. Phys. **4**, 620 (1936).

predicted repulsive state), $^3\Pi_{0+u}\leftarrow{}^1\Sigma_g^+$ (main). Their discussion is based on predictions from Morse P. E. curves and in both cases they find it necessary to shift the $^3\Pi_{1u}$ curve (plotted evidently on the basis of the provisional numeration) so that r_e' becomes 2.6A "which is considerably less than would be predicted by the usual empirical rules" (2.9A). This difficulty is not removed by the proposed numeration amendment leading to a value of $r_e'=2.64$A for the necessary deepening of the curve has not been taken into account in their calculations. Explanation (1) receives little or no support from the wave mechanics formulation of the Franck-Condon principle when the more correct Morse $^3\Pi_{1u}$ curve is drawn. The assignment in explanation (2) of the B maximum, 20,400 cm^{-1} to $^3\Pi_{0+u}\leftarrow{}^1\Sigma_g^+$ is well supported for the predicted maximum is at 20,500 cm^{-1}. The $^3\Pi_{1u}$ curve corresponding to a numeration increase of $n=8$ crosses the $^3\Pi_{0+u}$ curve very near $r'=2.28\text{A}=r_e''$. On this basis B is composite, the main and extreme red maxima coinciding very near 20,500 cm^{-1}. This is in harmony with Mulliken's suggested modification of explanation (2) and it becomes unnecessary to suppose as do A. A. and B. that the $^3\Pi_{1u}\leftarrow{}^1\Sigma_g^+$ continuum lies farther to the red in a region they were unable to examine.

There is one other possible explanation suggested by the application of the Franck-Condon principle. For $n=6$ the extreme red maximum should occur at 23,400 cm^{-1} and for $n=5$ at 24,700 cm^{-1} and so maximum A might be due to $^3\Pi_{1u}\leftarrow{}^1\Sigma_g^+$. The transition assignments of explanation (1) would then be interchanged. The greater intensity of maximum A is not in this case as readily understood as in explanation (2) and one must suppose that the maximum due to $^1\Pi\leftarrow{}^1\Sigma_g^+$ is outside the range of A. A. and B.'s measurements.

A. A. and B. do not correlate the three $v''=1$ maxima with Franck-Condon predictions. One of them at 27,000 cm^{-1} may be identified with $^3\Pi_{0+u}\leftarrow{}^1\Sigma_g^+$ for which the predicted position is 26,500 cm^{-1}. One of the others 19,000 cm^{-1} and 22,000 cm^{-1} may be due to $^1\Pi\leftarrow{}^1\Sigma_g^+$ but not both since the repulsive state curve would cross the $^3\Pi_{0+u}$ and $^3\Pi_{1u}$ ($n=8$) curves near their intersection and maximum B would be composed of contributions from all three transitions leaving A entirely unaccounted for.

It appears that none of the explanations accounts completely for all five observed maxima. More accurate knowledge of the $^3\Pi_{1u}$ state as regards numeration and the value of r_e' is essential for the unambiguous prediction of maxima. To this end preparations are now being made in this department for the high resolution photography and rotational analysis of the extreme red system.