

High-Resolution Study of the Spectrum of the CBr Radical

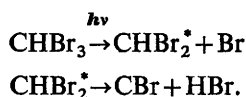
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The CBr radical absorption spectrum near 3000 Å has been photographed at high resolution and the transition is shown to be ${}^2\Delta(a) \leftarrow {}^2\Pi(a)$. A rotational analysis of one doublet component of the 0—0 band gives the following bond lengths; $r'_0 = 1.813$ Å, $r''_0 = 1.821$ Å. The second doublet component of the 0—0 band is diffuse, establishing an upper limit of 94.7 kcal/mole for the ground-state dissociation energy. An interpretation of the spin-orbit coupling in the ground states of the carbon halides CF, CCl and CBr is given in terms of the extent to which the partially filled molecular orbital is localized.

The absorption spectra of the carbon halides CBr and CCl have been reported by Simons and Yarwood.¹ This paper describes a high resolution study of the bands between 3000 and 3060 Å which they ascribed to the CBr radical. CBr was produced and studied in a similar manner, by flash photolysis of bromoform vapour. Simons and Yarwood report the evidence which indicates the following reaction mechanism.



EXPERIMENTAL

The flash photolysis apparatus used was similar to that described by Calloman and Ramsay.² The reaction vessel consisted of a quartz tube 60 cm in length and 5 cm diam. equipped with a multiple traversal mirror system.³ These mirrors were of quartz meniscus construction, back-surfaced with aluminium so as to overcome the corrosive effects of exposure to bromine vapour.⁴ The 4000 J photolysis flash has a half-peak duration of 25 μsec. CBr radicals were produced by photolyzing bromoform vapour at a pressure of 2–3 mm Hg. The absorption spectrum through a 2–6 m path length was photographed in the second order of a 21 ft concave grating spectrograph using a delay time of 5 μsec. Exposures of 50–100 flashes were required, and since one of the products of the photolysis is Br₂ vapour, which absorbs strongly in the ultra-violet, it was necessary to refill the reaction vessel after every flash.

Final plates were taken with a 25 μ slit ($\equiv 0.33$ cm⁻¹). A neon-filled iron hollow-cathode lamp was used for wavelength calibration. The wavelengths of the reference lines were taken from the M.I.T. tables² and used with the vacuum corrections of Edlen.² The plates were measured on a comparator equipped with a photoelectric scanning device,⁷ giving a relative accuracy of ± 0.05 cm⁻¹.

RESULTS

The bands first obtained by Simons and Yarwood were photographed under high resolution making a rotational analysis of the band at 3052 Å possible. The spectrum consists of two strong and two weaker absorption bands, assigned by Simons and Yarwood to the 0—0 and 1—1 doublet bands of the CBr radical. The long wavelength bands have sharp rotational structure and are violet degraded. The short wavelength pair are diffuse and apparently not strongly degraded (plate 1).

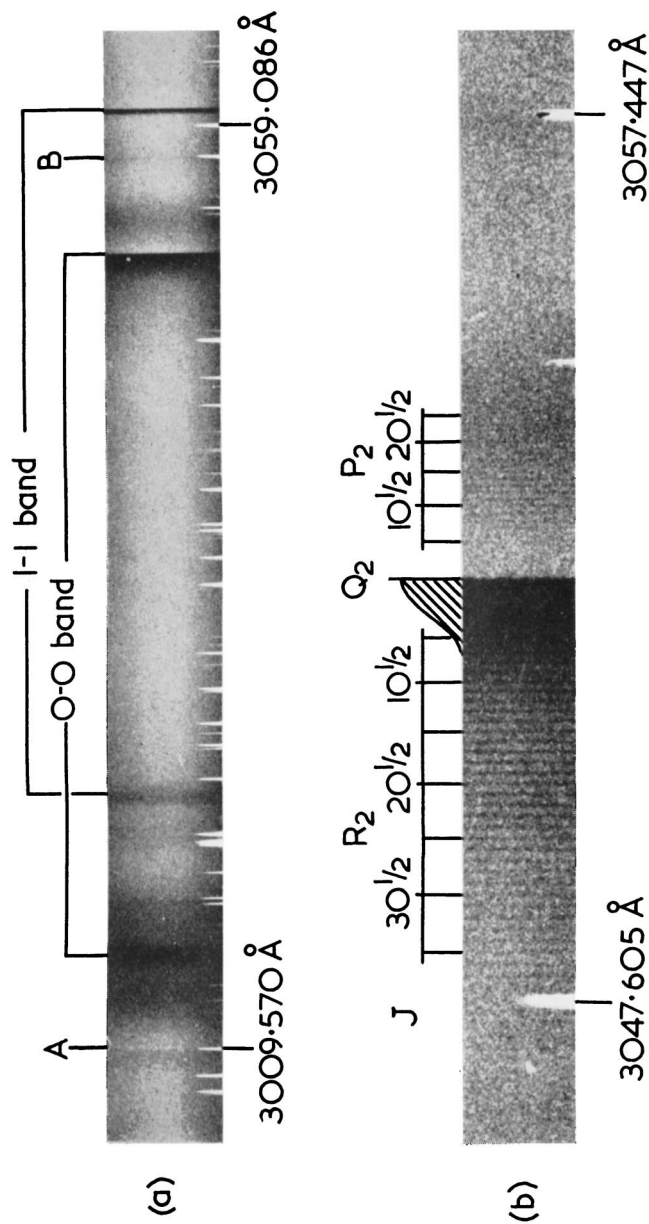


PLATE 1.—(a) The absorption spectrum of the CBr radical; (b) the assignment of the fine structure of the 3052 Å band.

[To face page 1484.]

TABLE 1.—BAND HEADS AND ABSORPTION MAXIMA FOR THE ${}^2\Delta(a)-{}^2\Pi(a)$ SYSTEM OF CBr

| feature | λ (air), Å | ν (vac), cm^{-1} | assignment |
|------------------------|--------------------|-------------------------------|----------------|
| weak head | 3059.999 | 32,670.34 | Q_2 1—1 band |
| very weak diffuse max. | 3057.30 | 32,699.1 | B see text |
| strong head | 3052.263 | 32,753.09 | Q_2 0—0 band |
| weak diffuse max. | 3023.03 | 33,069.8 | Q_1 1—1 band |
| strong diffuse max. | 3014.48 | 33,163.5 | Q_1 0—0 band |
| very weak head | 3009.50 | 33,218.4 | A see text |

ROTATIONAL ANALYSIS OF THE BAND AT 3052 Å

The 3052 Å band has a simple P , Q and R structure, the Q branch being strong though insufficiently degraded for resolution even at the highest J values. The strength of the Q branch is proof of a perpendicular transition. The wide separation of the doublet, 3052-3014 Å, indicates that at least one of the two states involved in the transition obeys Hund's case (a). By analogy with CCl and predictions based on the probable electron configuration of CBr the ground state is expected to be ${}^2\Pi_r$, and the excited state ${}^2\Sigma^+$ or ${}^2\Delta$ with a smaller spin-orbit coupling than in the ${}^2\Pi$ ground state. For case (a) the rotational levels may be represented by;

$$F_1(J) = -\frac{1}{2} |A - 2B| \Lambda + B_{1,\text{eff.}} J(J+1) - DJ^2(J+1)^2, \quad (1)$$

$$F_2(J) = +\frac{1}{2} |A - 2B| \Lambda + B_{2,\text{eff.}} J(J+1) - DJ^2(J+1)^2, \quad (2)$$

$$B_{1,\text{effective}} = B \left[1 - \frac{B}{|A - 2B| \Lambda} \right]; \quad B_{2,\text{effective}} = B \left[1 + \frac{B}{|A - 2B| \Lambda} \right] \quad (3)$$

and J has half-integral values. Thus,

$$\Delta_2 F''(J) = R(J-1) - P(J+1) = (4B''_{\text{eff.}} - 6D'')(J + \frac{1}{2}) - 8D''(J + \frac{1}{2})^3. \quad (4)$$

The J values of the lines were unambiguously assigned by fitting the experimental values of $\Delta_2 F''(J)$ to this equation and assuming that the Q head is a close approximation to the sub-band origin (table 2). The origin was more accurately determined by use of the equation,

$$R(J-1) + P(J) = 2\nu_0 + 2(B'_{\text{eff.}} - B''_{\text{eff.}})J^2 + \text{terms in } D. \quad (5)$$

If the upper state obeys case (a) then

$$\Delta_2 F'(J) = R(J) - P(J) - 4B'_{\text{eff.}}(J + \frac{1}{2}), \quad (6)$$

where J is half-integral: if it obeys case (b) then

$$\Delta_2 F'(J) \simeq 4B'_{\text{eff.}}(N + \frac{1}{2}), \quad (7)$$

where N is integral.

$\Delta_2 F'(J)$ was found to be proportional to $(J + \frac{1}{2})$, apart from the small effect of centrifugal stretching, and therefore the excited state can only be ${}^2\Delta(a)$. No marked effects of spin uncoupling are present even at $J = 30$.

It remains to determine whether the spin-orbit coupling of the upper state is of the same or the opposite sign to that of the ground state (i.e., ${}^2\Delta_r$ or ${}^2\Delta_t$, assuming a ${}^2\Pi_r$ ground state). For the 3052 Å sub-band the value of $(B'_{2,\text{eff.}} - B''_{2,\text{eff.}}) = +0.0078 \text{ cm}^{-1}$ and the band is violet degraded. However, the diffuse band at 3014 Å is symmetrical as far as can be judged, and therefore $(B'_{1,\text{eff.}} - B''_{1,\text{eff.}}) \simeq 0$. The 3014 Å band is considerably more intense than the 3052 Å band and therefore involves the lower doublet component in the ground state. Combination of these observations and eqn. (3) proves that the spin-orbit splitting in the excited state is less than in the

ground state, and is of the same sign. The band with sharp structure is thus interpreted as ${}^2\Delta_{\frac{3}{2}r} \leftarrow {}^2\Pi_{\frac{3}{2}r}$.

The difference in the spin-orbit splitting in the two electronic states is given by the separation of the two sub-band origins. Since the 3014 Å sub-band is diffuse but symmetrical, its origin was taken to be at the centre of the Q branch. It was further

TABLE 2.—VACUUM WAVE NUMBERS AND ASSIGNMENTS OF THE LINES OF THE 3052 Å BAND OF CBr

| J | $R(J)$ | $P(J)$ | $\frac{\Delta_2 F''(J) = R(J-1) - P(J+1)}{R(J-1) - P(J+1)}$ | $\frac{\Delta_2 F'(J) = R(J) - P(J)}{R(J) - P(J)}$ | $R(J-1) + P(J)$ |
|-----------------|-----------|-----------|---|--|-----------------|
| $\frac{1}{2}$ | | | | | |
| $1\frac{1}{2}$ | | | | | |
| $2\frac{1}{2}$ | 32,756.55 | | | 6.08 | |
| $3\frac{1}{2}$ | 57.69 | 32,749.57 | 7.81 | 8.12 | 65,506.12 |
| $4\frac{1}{2}$ | 58.77 | 48.74 | 9.74 | 10.03 | .43 |
| $5\frac{1}{2}$ | 59.83 | 47.95 | 11.70 | 11.88 | .72 |
| $6\frac{1}{2}$ | 60.89 | 47.07 | 13.64 | 13.82 | .90 |
| $7\frac{1}{2}$ | 61.96 | 46.19 | 15.61 | 15.77 | 507.08 |
| $8\frac{1}{2}$ | 63.19 | 45.28 | 17.49 | 17.91 | .24 |
| $9\frac{1}{2}$ | 64.23 | 44.47 | 19.59 | 19.76 | .66 |
| $10\frac{1}{2}$ | 65.43 | 43.60 | 21.40 | 21.83 | .83 |
| $11\frac{1}{2}$ | 66.50 | 42.83 | 23.39 | 23.67 | 508.26 |
| $12\frac{1}{2}$ | 67.72 | 42.04 | 25.21 | 25.68 | .54 |
| $13\frac{1}{2}$ | 68.92 | 41.29 | 27.34 | 27.63 | 509.01 |
| $14\frac{1}{2}$ | 70.11 | 40.38 | 29.28 | 29.73 | .30 |
| $15\frac{1}{2}$ | 71.33 | 39.64 | 31.24 | 31.69 | .75 |
| $16\frac{1}{2}$ | 72.58 | 38.87 | 33.12 | 33.61 | 510.20 |
| $17\frac{1}{2}$ | 73.75 | 38.21 | 35.17 | 35.54 | .79 |
| $18\frac{1}{2}$ | 75.01 | 37.41 | 37.02 | 37.67 | 511.16 |
| $19\frac{1}{2}$ | 76.24 | 36.73 | 38.99 | 39.56 | .74 |
| $20\frac{1}{2}$ | 77.58 | 36.02 | 40.98 | 41.56 | 512.31 |
| $21\frac{1}{2}$ | 78.82 | 35.31 | 42.93 | 43.51 | .89 |
| $22\frac{1}{2}$ | 80.14 | 34.65 | 44.82 | 45.49 | 513.47 |
| $23\frac{1}{2}$ | 81.42 | 34.00 | 46.73 | 47.42 | 514.14 |
| $24\frac{1}{2}$ | 82.76 | 33.41 | 48.68 | 49.35 | .83 |
| $25\frac{1}{2}$ | 84.12 | 32.74 | 50.51 | 51.38 | 515.50 |
| $26\frac{1}{2}$ | 85.41 | 32.25 | | 53.16 | 516.37 |
| $27\frac{1}{2}$ | 86.76 | | | | |
| $28\frac{1}{2}$ | | | | | |
| $29\frac{1}{2}$ | 89.62 | | | | |
| $30\frac{1}{2}$ | 90.81 | | | | |
| $31\frac{1}{2}$ | 92.17 | | | | |
| $32\frac{1}{2}$ | 93.56 | | | | |
| $33\frac{1}{2}$ | 94.99 | | | | |
| $34\frac{1}{2}$ | 96.33 | | | | |
| $35\frac{1}{2}$ | 97.58 | | | | |

assumed that the difference between the effective rotational constants in the upper and lower levels of this band is zero. Eqn. (3) was then used to give the values of $(A - 2B)\Lambda$. The observed rotational constants B'_2 , $err.$ and B''_2 , $err.$ may now be corrected for the slight effect of spin uncoupling to give B'_0 and B''_0 (tables 3 and 4).

Bromine has two isotopes of approximately equal abundance. Calculation indicates that the vibrational and rotational isotope splittings should not be resolved in the bands observed. Thus, the rotational constants determined above are weighted

means of those for the two isotopic species $C^{79}Br$ and $C^{81}Br$, and the bond lengths for CBr were calculated using a mean reduced mass (table 4).

The very weak features indicated at A and B in plate 1 have the expected appearance and frequency of the forbidden components of the 0—0 band, ${}^2\Delta_{\frac{3}{2}} \leftarrow {}^2\Pi_{\frac{3}{2}}$ and ${}^2\Delta_{\frac{3}{2}} \leftarrow {}^2\Pi_{\frac{1}{2}}$ respectively, and confirm the values of $(A-2B)\Lambda$ to within 1 cm^{-1} . However, it is not clear why such transitions should occur.

TABLE 3.—CONSTANTS OBTAINED FROM THE ANALYSIS OF THE SPECTRUM

| | | |
|--|--|---|
| 3052 Å BAND | $B'_{2,\text{eff.}} = 0.4956 \pm 0.0003\text{ cm}^{-1}$, $B''_{2,\text{eff.}} = 0.4877 \pm 0.0003\text{ cm}^{-1}$; | |
| | $D' = (1.2 \pm 0.4) \times 10^{-6}\text{ cm}^{-1}$, $D'' = (0.6 \pm 0.4) \times 10^{-6}\text{ cm}^{-1}$; | |
| | $v_0 = 32,753.10 \pm 0.05\text{ cm}^{-1}$. | |
| 3014 Å BAND | $B'_{1,\text{eff.}} - B''_{1,\text{eff.}} \approx 0$; | $v_0 = 33,163.5 \pm 0.5\text{ cm}^{-1}$; |
| | $(A'' - 2B'')\Lambda'' - (A' - 2B')\Lambda'$ | $= 410.4 \pm 0.5\text{ cm}^{-1}$. |
| 1—1 AND 0—0 BANDS (MEAN OF BOTH SUB-BANDS) | | |
| | $\Delta G''(\frac{1}{2}) - \Delta G'(\frac{1}{2})$ | $= 88.2 \pm 1\text{ cm}^{-1}$. |

TABLE 4.—DERIVED MOLECULAR CONSTANTS

| | |
|--|---|
| $B''_0 = 0.4872 \pm 0.0003\text{ cm}^{-1}$, | $B'_0 = 0.4912 \pm 0.0008\text{ cm}^{-1}$; |
| $(A-2B)'' = 465 \pm 10\text{ cm}^{-1}$, | $2(A-2B)' = 54 \pm 10\text{ cm}^{-1}$; |
| $r''_0 = 1.8209 \pm 0.0005\text{ Å}$, | $r'_0 = 1.8134 \pm 0.0015\text{ Å}$. |

ELECTRONIC STRUCTURE

The electron configuration and term type of the ground states of the carbon halides is expected to be

$$(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2(v\pi); \quad {}^2\Pi_r$$

In a simple l.c.a.o. m.o. model the $(w\pi)$ and $(v\pi)$ orbitals are linear combinations of atomic p orbitals on the carbon and halogen atoms. The spin-orbit coupling in the ground states of the carbon halides CF , CCl and CBr may be used to give an indication of the localization of the $(v\pi)$ orbital. The major contribution to the spin-orbit coupling comes from those parts of the wave-function close to the nuclei.⁸ Thus, the spin-orbit coupling constant A_{CX} of the ground state of the CX molecule is closely approximated by,

$$A_{CX} = c_1^2 |A_C| + c_2^2 |A_X|; \quad c_1^2 + c_2^2 = 1, \quad (8)$$

where A_C and A_X are the spin-orbit coupling constants of the carbon and halogen atoms respectively in their ground states. Since $|A_X| \gg |A_C|$ for all three halogen atoms A_{CX} can be used to give the values of c_1^2 and c_2^2 . If the overlap between the carbon and halogen p orbitals is neglected ($S \approx 0.2$), c_1 and c_2 may be identified with the coefficients of the expanded $(v\pi)$ orbital,

$$(v\pi) = c_1(p\pi_C) - c_2(p\pi_X).$$

TABLE 5.—A COMPARISON OF SPIN-ORBIT COUPLING CONSTANTS

| molecule | | CF | CCl | CBr |
|------------------------------|---------------------------|-------|-------|-------|
| carbon atom | $A_C, \text{ cm}^{-1}$ | 28 | 28 | 28 |
| halogen atom X | $A_X, \text{ cm}^{-1}$ | -269 | -587 | -2457 |
| CX molecule ($X, {}^2\Pi$) | $A_{CX}, \text{ cm}^{-1}$ | 77 | 135 | 466 |
| | c_2^2 | 0.203 | 0.185 | 0.180 |

The data in table 5 show that in all three cases the ($v\pi$) orbital is not completely localized on either the carbon or the halogen atom. It must therefore be considerably antibonding in character. Since the ($v\pi$) orbital must be orthogonal to the ($w\pi$) orbital, the ($w\pi$) orbital also will not be entirely localized on the more electronegative halogen atom and will therefore be considerably bonding. The five π electrons have the effect of increasing the bond strengths of the CX radical ground states compared with CX single bonds. This is borne out by the data in table 6. There is a parallel change in the ratio $r_{\text{MeX}}/r_{\text{CX}}$ and c_2^2 . In each case, the CX radical bond length is close to that of $\equiv\text{CX}$.

TABLE 6.—C—X BOND LENGTHS IN VARIOUS MOLECULES

| X | F | Cl | Br |
|--------------------------------|-------|-------|-------|
| CX(X, 2Π), Å | 1.275 | 1.651 | 1.820 |
| CH ₃ X, Å | 1.385 | 1.781 | 1.939 |
| CH ₂ =CHX, Å | 1.348 | 1.736 | 1.89 |
| CH \equiv CX, Å | 1.28 | 1.63 | 1.80 |
| $r_{\text{MeX}}/r_{\text{CX}}$ | 1.086 | 1.079 | 1.065 |

The 2Δ excited states of CCl and CBr probably arise from the electron configuration,

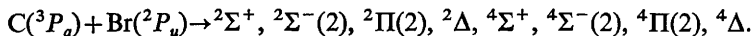
$$(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)(v\pi)^2; \quad 2\Sigma^+, 2\Sigma^-, 2\Delta, 4\Sigma^-.$$

Since in both cases the excitation results in a slight shortening of the bonds the ($x\sigma$) orbital must be rather more antibonding than the ($v\pi$) orbital. The ($v\pi$) orbital is half-filled and will give no direct contribution to the spin-orbit coupling of the 2Δ states. The observed slight spin doubling of the 2Δ states must therefore arise from spin-other orbit coupling or by mixing with higher 2Δ states.

PREDISSOCIATION

The band at 3014 Å arising from the $2\Delta_{3/2} \leftarrow 2\Pi_{3/2}$ component of the 0—0 transition is diffuse, as is also the corresponding component of the 1—1 band. Thus the $v' = 0$ $2\Delta_{3/2}$ level must lie above the lowest dissociation limit of CBr, giving a value of $D_0^0(\text{CBr}) < 94.7$ kcal/mole (= 4.11 eV). Combination of the kinetic data of Simons and Yarwood on the production of CBr¹ with the heat of formation of bromoform and the dissociation energy of HBr⁹ leads to an approximate value of $D_0^0(\text{CBr}) = 97 \pm 5$ kcal/mole. Thus, it would appear that the true value is not much below the spectroscopic upper limit.

The $2\Delta_{3/2} \leftarrow 2\Pi_{3/2}$ components of both the 0—0 and the 1—1 bands are sharp, with a line width ~ 0.3 cm⁻¹. Hence the state which predissociates the $2\Delta_{3/2}$ levels does not greatly affect the $2\Delta_{3/2}$ levels. The selection rules for predissociation appropriate to Hund's case (a) are $\Delta\Lambda = 0, \pm 1$; $\Delta S = 0$; $\Delta\Sigma = 0$. The Wigner-Witmer rules predict the following possible molecular states of CBr from the combination of C and Br atoms in their ground states;



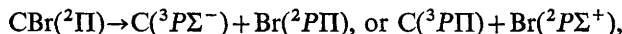
One of the 2Π states will correlate with the ground state of CBr (see below). An allowed predissociation of the excited 2Δ state by a state arising from ground state products is therefore possible by either a 2Π or a 2Δ state. The spin-orbit splitting in the ground state of the bromine atom is 10.4 kcal/mole, and the predissociating state may therefore have a spin-orbit splitting at the inter-nuclear distance of the crossing-point of the potential curves that is greater than one vibrational quantum of the bound 2Δ state (probably ~ 500 cm⁻¹ or 1.4 kcal/mole). Since the selection rules

above allow predissociation of ${}^2\Delta_{\frac{3}{2}}$ by ${}^2\Delta_{\frac{3}{2}}$ and ${}^2\Pi_{\frac{3}{2}}$ only, and ${}^2\Delta_{\frac{5}{2}}$ by ${}^2\Delta_{\frac{3}{2}}$ and ${}^2\Pi_{\frac{3}{2}}$ only, spin-orbit splitting could account for the observed predissociation of only one component of the excited ${}^2\Delta$ state.

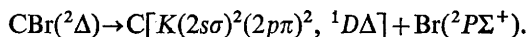
Mulliken has outlined a theoretical method of determining the dissociation products of a diatomic molecule by consideration of the Stark effect of atoms.⁸ When an atom with orbital angular momentum $L^*\hbar/2\pi$ is placed in a strong electric field the orbital motion becomes oriented so that the component of angular momentum in the field direction is $\pm\Lambda\hbar/2\pi$, where $\Lambda \leq L$, and the electronic energy depends on Λ . Thus, the degeneracy of the ground states of the C and Br atoms is lowered in an electric field to give

$$\begin{aligned} \text{C}({}^3P) &\rightarrow \begin{cases} K(2s\sigma)^2(2p\pi)^2; {}^3P\Sigma^- \\ K(2s\sigma)^2(2p\sigma)(2p\pi); {}^3P\Pi \end{cases} \\ \text{Br}({}^2P) &\rightarrow \begin{cases} KLM(4s\sigma)^2(4p\sigma)(4p\pi)^4; {}^2P\Sigma^+ \\ KLM(4s\sigma)^2(4p\sigma)^2(4p\pi)^3; {}^2P\Pi \end{cases} \end{aligned}$$

Mulliken further considers a "detailed $\sigma\mathcal{L}_r$ correlation rule", whereby it is assumed that as a diatomic molecule is dissociated the mutual effect of the electric fields of the atoms acts such that each σ electron in the molecule becomes an $s\sigma$ or a $p\sigma$ electron in one of the dissociation products, and each molecular π electron becomes an atomic $p\pi$ electron. Application of this rule to CBr shows that the ${}^2\Pi$ ground state will dissociate into ground state atoms;



but the excited ${}^2\Delta$ state will not. The lowest energy products possible for dissociation of the ${}^2\Delta$ state without violating this rule are



This is in agreement with the observation that the ${}^2\Delta$ excited state is a bound state above the lowest dissociation limit even though a ${}^2\Delta$ state can be formed from the ground state products, $\text{C}({}^3P) + \text{Br}({}^2P)$.

We are indebted to the D.S.I.R. for the award of a maintenance grant to one of us (H. W. K.) and to Mr. L. Faine for the construction of the spectrograph.

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⁶ Edlen, *J. Opt. Soc. Amer.*, 1953, **43**, 339.

⁷ Bennett and Koehler, *J. Opt. Soc. Amer.*, 1959, **49**, 466.

⁸ Mulliken, *Rev. Mod. Physics*, 1930, **2**, 60.

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