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# An Analysis of the $E(0_g^+)$ Ion-pair State of Bromine through Stepwise Excitation Technique

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The pulses of the fundamental and its frequency doubled outputs from a tunable dye laser are used to promote a stepwise exciation of the $E(0_g^+)$-$X^1\Sigma_g^+$ transition through the $B^3\Pi(0_u^+)$ state in molecular bromine. The double resonance is detected by the associated UV emission which originates from the $E(0_g^+)$ state radiating back to the $B^3\Pi(0_u^+)$ state. The $E(0_g^+)$ state is analyzed in detail on the basis of the selection rules of two transition components and the E-B fluorescence spectrum. The molecular parameters are derived as $T_e$= 49778.5 $cm^{-1}$, $\omega_e$=150.8 $cm^{-1}$, $\omega_e x_e$=0.41 $cm^{-1}$, and $r_e$=3.197 Å for the $^{79}Br_2$ isotope species.

The electronic structure of diatomic halogens has been studied many times both theoretically and experimentally, and yet several important problems remain unsolved with regard to the existence and positions of certain electronic states.[1] In particular, the high-lying excited states of the ion-pair type are the subjects of recent interest and curiosity, because of their recent use in the development of the laser emissions in the ultraviolet and vacuum ultraviolet regions.[2-5] Designing a halogen laser system requires detailed spectroscopic and kinetic data on the emitting state itself as well as the surrounding electronic states.

It is well-known that the ion-pair states of $Br_2$ correlate with $Br^-(^1S)+Br^+(^3P, ^1D, ^1S)$ at the dissociation limit and the dominant attractive term in their potential function is simply $-e^2/r$. Therefore, all the ion-pair states are empirically taken to have relatively large internuclear distances (3.2 Å) and dissociation energies (35000 $cm^{-1}$) with small vibrational frequencies (150 $cm^{-1}$), and to group in accordance with the energies of the various $Br^+$ states.[6] Thus the 6 states ($0_u^+(D)$[7], $0_g^+(E)$[8], $1_u$, $1_g$, $2_u$, and $2_g(D')$)[9] from $Br^+(^3P_2)$ would belong to the lowest group lying at around 49000 $cm^{-1}$, the 2 states ($0_u^+(F)$[10] and $0_g^+(f)$[11]) from $Br^+(^3P_0)$ and the 4 ($0_u^-$, $0_g^-$, $1_u$, and $1_g$) from $Br^+(^3P_1)$ would locate near 53000 $cm^{-1}$. The 6 states ($0_u^+$, $0_g^+$, $1_u$, $1_g$, $2_u$, and $2_g$) from $Br^+(^1D)$ would be expected at around 60000 $cm^{-1}$, and 2($0_u^+$ and $0_g^+$) from $Br^+(^1S)$, very considerably higher.

This work is part of a series[7,10,11] where the spectroscopic properties of the ion-pair states are examined for the $Br_2$ molecule. Since its optical pumping from the ground state requires large Franck-Condon shifts due to the large internuclear separation of the ion-pair states, our method involves a stepwise excitation through the $B^3\Pi_{0_u^+}$ state as an intermediate. The g or u ion-pair states can be proved if one or virtual two-photon transitions originate from the B state. In the experiment described here, the $Br_2$ molecules are pumped to the B state by the output of a tunable dye laser operated in the visible region and subsequently excited into the $E(0_g^+)$ ion-pair state by its second harmonics in the ultraviolet. It is obvious that the excitation proceeds only if the double resonance condition is satisfied for the two transition components. We can detect the resonances by the E-B emission and the stepwise processes are analyzed.

## Experimental

The experimental apparatus is similar to that used in previous experiments.[11] Briefly, a nitrogen laser pumped dye laser provided 8 ns pulses with an energy of 1 mJ/pulse and 0.1 Å resolution, and a KDP crystal was installed for frequency doubling (conversion efficiency 5%). Both the fundamental laser light and its frequency doubled output passed through a UV fluorescence cell to excite the $Br_2$ molecules in a stepwise process. The fluorescence was dispersed by a 50 cm monochrometer in the second order and detected by a photomultiplier. The output signals were amplified ten times and averaged by a boxcar integrator.

To exclude the spectral congestion problem, monoisotopic $^{79}Br_2$ was used in the experiments. A sample pressure was 3.1 Torr (1 Torr=133.3 Pa). The emission spectra were recorded with a spectral resolution of 0.2 Å and studied as a function of excitation wavelength.

## Results and Discussion

When the $^{79}Br_2$ molecules were excited both by the fundamental and its second harmonic outputs of the dye laser operated in the wavelength region between 595 and 621 nm, several series of fluorescent progressions were observed at around 310 nm. These closely resemble the $f(0_g^+)$—$B^3\Pi_{0_u^+}$ system of $Br_2$ (265—285 nm) which we have recently analyzed.[11] The emission bands consisted of the P and R doublets, and the vibrational spacing observed at the shortest wavelength was about 155 $cm^{-1}$, close to the vibrational frequency of the B state ($\omega_e$=167.6 $cm^{-1}$).[12] From its position in the spectrum, the emission under study appears to be the $E(0_g^+)$—$B^3\Pi_{0_u^+}$ system observed by Tellinghuisen and co-workers[8] in conventional discharge experiments. In our case, the pumping to the E state was obviously achieved by a stepwise excitation through the B state. As a matter of fact, the emission vanished by blocking either the visible or the ultraviolet laser light with a suitable glass filter.

Table 1 summarizes the strong double resonance signals observed in the experiment. The laser frequencies noted here correspond to the positions of the rotational lines of the B-X absorption involved in the excitation process. Under our experimental conditions, the relaxations in the intermediate B state are negligible, so that the assignments of the following E-B transitions were straightforward. The rotational quantum number ($J$)

Table 1. Observed transitions and term values of the double resonance experiments on $^{79}Br_2$

| $E(0_g^+)$ ←$h\nu_{UV}$[a)]— $B(^3\Pi_{0_u^+})$ ←$h\nu_{VIS}$— $X(^1\Sigma_g^+)$ | | | $h\nu_{VIS}/cm^{-1}$ | $T^E_{v,J}/cm^{-1}$ |
|---|---|---|---|---|
| $v=0$, $J=33$[b)] | (0—11)$P_{34}$[c)] | (11—4)$P_{35}$[d)] | 16118.8 | 49900.0[e)] |
| 0 33 | (0—11)$P_{34}$ | (11—4)$R_{33}$ | 16122.9 | 49900.9 |
| 1 57 | (1—10)$R_{56}$ | (10—3)$P_{57}$ | 16249.2 | 50140.3 |
| 1 101 | (1—9)$R_{100}$ | (9—2)$R_{99}$ | 16274.0 | 50431.5 |
| 1 101 | (1—9)$P_{102}$ | (9—2)$R_{101}$ | 16263.2 | 50431.5 |
| 2 11 | (2—10)$P_{12}$ | (10—3)$P_{13}$ | 16339.3 | 50158.1 |
| 2 37 | (2—7)$P_{38}$ | (7—1)$P_{39}$ | 16532.9 | 50208.6 |
| 2 46 | (2—7)$P_{47}$ | (7—1)$R_{46}$ | 16526.7 | 50242.1 |
| 3 46 | (3—9)$R_{45}$ | (9—2)$P_{46}$ | 16469.1 | 50389.6 |
| 3 87 | (3—8)$P_{88}$ | (8—1)$P_{89}$ | 16493.0 | 50617.0 |
| 3 95 | (3—8)$P_{96}$ | (8—1)$R_{95}$ | 16483.1 | 50677.4 |
| 4 43 | (4—11)$P_{44}$ | (11—3)$P_{45}$ | 16411.2 | 50526.6 |
| 4 86 | (4—10)$R_{85}$ | (10—2)$P_{86}$ | 16447.5 | 50756.1 |
| 5 65 | (5—10)$R_{64}$ | (10—2)$P_{65}$ | 16538.7 | 50771.0 |
| 7 58 | (7—9)$R_{57}$ | (9—1)$P_{58}$ | 16753.6 | 51025.4 |
| 9 19 | (9—11)$P_{20}$ | (11—2)$R_{19}$ | 16784.1 | 51189.8 |

a) Excitation was performed by the second harmonics of the laser light used for the B-X transition ($h\nu_{UV}=2h\nu_{VIS}$). b) Definition of the final level in the E state. c) Assignment to the E-B transition. d) Assignment to the B-X transition. e) Term values of the final ($v$, $J$) level in the E state relative to the potential minimum of the ground state.

of the ion-pair state was derived from the emission spectrum depending on whether the P or R line was in resonance with the UV laser wavelength. The absolute $v'$ numbering was established by the characteristic intensity pattern of the fluorescent progression. The internuclear distance of the ion-pair states (typically $r_e$=3.2 Å) is much longer than that of the B state ($r_e$=2.68 Å). The low-$v$ level of the ion-pair state will display in emission a band system whose intensity distribution is modulated according to the probability distribution of the upper wavefunction. For example, the fluorescence spectra in Fig. 1 show (a) a double and (b) a single peak in emission envelope, and can be assigned to originate from the vibrational level of (a) $v'$=1 and (b) $v'$=0, respectively. The interpretation is confirmed by the energy level analyses and Franck-Condon calculations as described below.

The term energies $T^E_{v,J}$ of the ion-pair state in Table 1 were calculated relative to the potential minimum of the ground state. They were determined by adding the fundamental ($h\nu_{VIS}$) and its second harmonic ($h\nu_{UV}$) frequencies to the vibrational and rotational terms of the ground state levels ($G''_v$ and $F''_v(J)$) from which the stepwise transitions originate (Eq. 1).

$$T^E_{v,J} = h\nu_{VIS} + h\nu_{UV}(=2h\nu_{VIS}) + G''_v + F''_v(J) \quad (1)$$

Based on these derived term energies, we calculated the absolute wavelength positions of the expected P and R doublets in the emission spectra of the $E(0_g^+)$—$B^3\Pi_{0_u^+}$ transition using the known molecular constants of the B state.[12] The calculated values agreed with the experimentally derived ones within our experimental accuracy (±0.2 Å) and the transition from the E state terminates on the high vibrational levels of the B state as shown in Fig. 1.

The molecular constants of the $E(0_g^+)$ state were

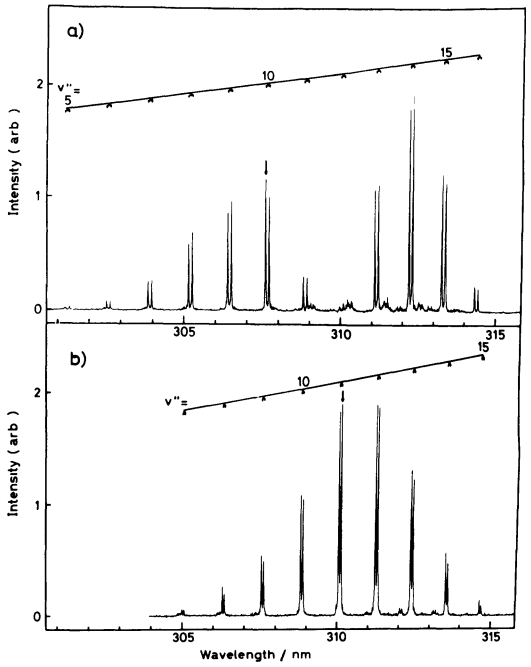


Fig. 1. Fluorescence spectrum of $Br_2$ corresponding to the $E(0_g^+) \rightarrow B^3\Pi_{0_u^+}$ transition.

$X^1\Sigma_g^+ \xrightarrow{h\nu_{VIS}} B^3\Pi_{0_u^+} \xrightarrow{h\nu_{UV}} E(0_g^+)$ $h\nu_{VIS}(cm^{-1})$

(a) (11-4) $R_{33}$ (0-11) $P_{34}$ 16122.9

(b) (10-3) $P_{57}$ (1-10) $R_{56}$ 16249.2

Spectral slitwidth, 0.2 Å. The UV laser wavelength is indicated by an arrow.

calculated to fit the term values to the form;

$$T^E_{v,J} = T_e + \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \left\{B_e - \alpha_e\left(v+\frac{1}{2}\right)\right\}J(J+1) - DJ^2(J+1)^2. \quad (2)$$

where the values of $\alpha_e$ and $D$ were estimated from the following relations[13] in order to reduce the parameter of the higher order.

$$\alpha_e = 6B_e(\sqrt{\omega_e x_e \cdot B_e} - B_e)/\omega_e, \quad (3)$$

$$D = 4B_e^3/\omega_e^2. \quad (4)$$

The $B_e$ values were calculated based on $r_e$ values at around 3.2 Å at intervals of 0.001 Å and the equations fitted by the least squares method iteratively. Using sets of the derived constants, we have calculated the Franck-Condon factors for the E–B system.[14] The potential curve of the B state was constructed by the RKR method, while we approximated the potential curve of the E state by a Morse function using a set $r_e$ value, and $\omega_e$ and $\omega_e x_e$ values determined from Eqs. 2, 3, and 4. Since the fluorescence intensity distribution shows a strong $J$ dependence, the effective potential curve, $U_J(r)$, for the corresponding $J$ level was used in the Franck-Condon calculations,

$$U_J(r) = V_0(r) + J(J+1)\hbar^2/2\mu r, \quad (5)$$

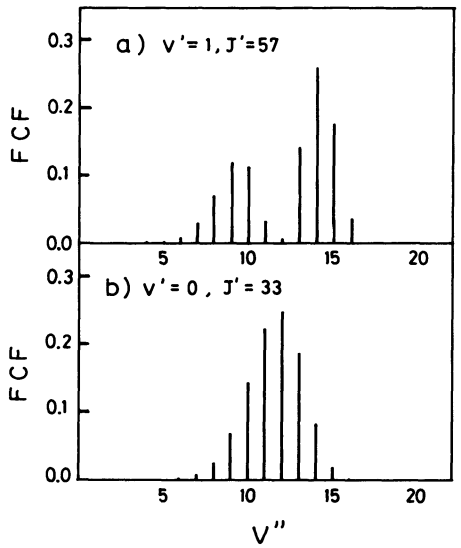


Fig. 2. Calculated Franck-Condon factors of the E $(0_g^+) \rightarrow B^3\Pi_{0_u^+}$ transition.

Table 2. Molecular parameters of the $E(0_g^+)$ state for $^{79}Br_2$

| Parameter | Value |
|---|---|
| $T_e/cm^{-1}$ | 49778.53(52)[a] |
| $\omega_e/cm^{-1}$ | 150.78(27) |
| $\omega_e x_e/cm^{-1}$ | 0.41(3) |
| $B_e/cm^{-1}$ | 0.04180[c] |
| $\alpha_e/cm^{-1}$ | $1.47\times10^{-4}$ |
| $D/cm^{-1}$ | $1.28\times10^{-7}$ |
| $r_e$/Å | 3.197 |

a) Values in parentheses denote twice the standard deviation ($2\sigma$) and apply to the last digits of the constants. b) Calculated value corresponding to $r_e=3.197$ Å. c) From the Franck-Condon factor analysis. The accuracy is estimated to be $\pm0.003$ Å assuming that the emission intensities fluctuate by 10%.

where $V_0(r)$ denotes the potential curve for $J=0$.

We found that the intensity distributions were fairly consistent with the results of the FCF calculations with setting $r_e=3.197$ Å. Typical examples of the agreements are shown in Fig. 2 for the fluorescence series from (a) $v'=1$, $J'=57$ and (b) $v'=0$, $J'=33$, corresponding to the results in Fig. 1 (a) and (b). Measured intensities are not corrected for instrumental sensitivity because this was essentially constant in the wavelength region under experiment. The derived spectroscopic parameters of the $E(0_g^+)$ ion-pair state are listed in Table 2.

With the completion of this work, the $E(0_g^+)$ ion-pair state of $Br_2$ correlating with $Br^-(^1S)+Br^+(^3P_2)$ has been spectroscopically characterizd in detail. The 310 nm emission system observed in the spectrum of discharge experiments can be definitely attributed to the $E(0_g^+)$—$B^3\Pi_{0_u^+}$ transition. This system was first studied by Venkateswarlu and Verma,[15] who deduced that the lower state was the $B^3\Pi_{0_u^+}$ state. Berwanger, Viswanathan, and Tellinghuisen[8] recently re-analyzed the spectrum based on a completely different vibrational numbering, but still using the B state as the terminating state. The set of molecular constants of the E state given here are in very good agreement with the values reported by Tellinghuisen and coworkers and obviously support their analyses.[8]

Finally, it should be pointed out that the selective excitation technique for ion-pair states of diatomic halogens is now available through stepwise processes. Efforts are being made in this laboratory to elucidate the relaxation processes involving these high-lying electronic states, especially for the inert gas–halide excimer formation mechanism in the reaction between inert gases and halogen molecules.

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