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An Optical-optical Double Resonance Excitation of Bromine to a New D(0_u^+) Ion-pair State

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An optical-optical double resonance (OODR) technique utilizing a sequential three-photon absorption has been applied to study the electronic structure of Br_2. Two pulsed dye lasers were used to excite the molecules to appropriate rovibronic levels of the $B^3\Pi(0_u^+)$ state and subsequently into an ion-pair state by simultaneous two-photon transition. The OODR excitation spectra showed a number of transitions consisting of closely-spaced O, Q, and S branches which combine the $B^3\Pi(0_u^+)$ state with a new ion-pair state designated D(0_u^+). The following spectroscopic constants of the D(0_u^+) state were determined for the $^{79}Br_2$ isotope species: $T_e=49925.4(6)$, $\omega_e=135.7(3)$, $\omega_e x_e=0.27(3)$, $B_e=0.04190(14)$, and $\alpha_e=5.9(23)\times10^{-5}\,\mathrm{cm}^{-1}$.

It has been demonstrated that an optical-optical double resonance (OODR) method is very promising to study the spectroscopic details of high-lying electronic states in atoms and molecules.1) In particular, this technique is attractive in the spectroscopy of diatomic halogens to explore their excited states of the ion-pair type whose precious information is normally inaccessible by the conventional single-photon spectroscopy.2) Recently we have reported a series of ion-pair states observed in the two or three photon transitions through the $B^3\Pi_{0_u^+}$ state.3–5) In this report, we present the analysis of a new D(0_u^+) state of Br_2 which might belong to the lowest group of ion-pair states correlating with $Br^-(^1S)+Br^+(^3P_2)$.

In our experiments the output pulses from two synchronously pumped dye lasers are focused inside a fluorescence cell containing $^{79}Br_2$ vapor from opposite directions and are aligned to overlap with each other at the focusing point. One laser, refered as the pump laser, is operated at a fixed wavelength to pump the molecules to appropriate rovibronic levels of the $B^3\Pi_{0_u^+}$ state through a visible B-X transition at around 583 nm. The setting was performed by monitoring the near-infrared B-X fluorescence. The second dye laser, the probe laser, is scanned in the wavelength region of 600—660 nm to promote two-photon transitions from the pumped levels of the B state to an ion-pair state. The OODR signals are detected by the UV emission between 240 and 290 nm.

The outputs of the dye lasers are horizontally polarized in the normal experiments. Polarization studies to examine anisotropic characters of the two-photon transitions from the B state are carried out for several of the strong transitions by changing the polarization angles of the probe laser light.

Results and Discussion

Figure 1 presents a part of a typical OODR excitation spectrum observed in the experiments on the $^{79}Br_2$ molecule. The pump laser (ν_1) was adjusted to a photon energy of $17155.9\,\mathrm{cm}^{-1}$ which is in resonance with the three rotational lines of the $B^3\Pi_{0_u^+}-X^1\Sigma_g^+$ transition within our laser bandwidth; (9–0) P_{25} and R_{29}, and (10–0) P_{71}. The spectrum was recorded by scanning the probe laser (ν_2) using a sample pressure of 1.1 Torr (1 Torr$\approx$133.322 Pa). There is no time delay between the pump and probe laser pulses. Under the conditions, the relaxations in the intermediate B levels are negligible, so that the OODR spectrum is very simple and the assignment is straightforward.

First of all, we found that the probe laser induced three types of transitions to form an ion-pair state by overall three-photon processes.

Type (I) $\nu_1+(2\nu_2)$
Type (II) $\nu_1+(\nu_1+\nu_2)$
Type (III) $\nu_2+(2\nu_2)$

The type (I) transition denotes the (1+2) process, which corresponds to the excitation of the Br_2 molecules to the specific rovibronic levels of the B state by pump frequency (ν_1) and thence to an ion-pair state in the virtual two-photon transition by probe frequency ($2\nu_2$). On the other hand, the two-photon process in the type (II) transition proceeds by a combination of pump and probe lasers ($\nu_1+\nu_2$). The type (II) transitions appear because of temporal overlap of pump and probe laser pulses. They can be distinguished from the type (I) transitions by the dependence of the line intensities on the time delay of the two laser pulses and more easily by the polarization effects on their transition strengths. For example, when the polarization of the probe laser light is changed from horizontal to vertical, the anisotropic change of line intensities is predicted in the type (II) transitions. Because randomly oriented molecules cannot distinguish the vertically polarized photons from the horizontally polarized ones in the type (I) transitions. In the spectrum, typical results of the polarization effects for the type (II) transitions are shown in Fig. 1. These bands disappeared under the conditions of a 15 ns time delay between laser pulses, as being expected. The type (III) transitions produced by the probe laser alone appear only if the double resonance condition of two transition components is satisfied at a given frequency. They are obviously not suitable for a systematic analysis of an ion-pair state.

Secondly, the type (I) and (II) transitions clearly show the closely-spaced rotational lines, which should correspond to the O, Q, and S branches in the 0_u^+–0_u^+ transition from the following considerations. Molecular bromine belongs to the symmetry of $D_{\infty h}$ and its ion-pair states are known to be described in Hund's case c due to large multiplet splittings. From the dipole matrix elements of two-photon absorption, the symmetry species of the upper state which combine with the $B^3\Pi_{0_u^+}$ state by identical photons in the type (I)

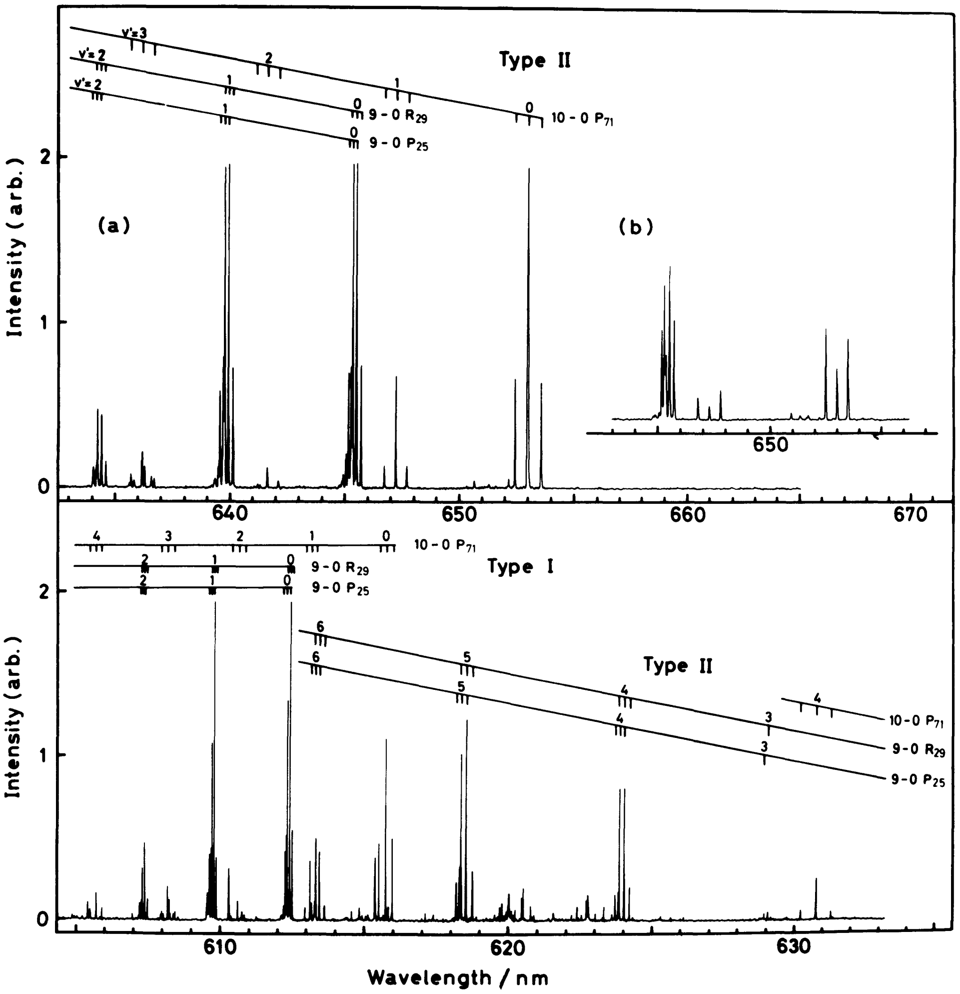

Fig. 1. A portion of the OODR excitation spectrum of $^{79}Br_2$. The pump frequency (ν_1) is in resonance with (9–0) P_{25} and R_{29}, and (10–0)P_{71} of the B–X transition within laser bandwidth. The probe laser (ν_2) was scanned in the wavelength region of 605—655 nm using dyes, Rh-610 and Rh-640. Two-photon transition from the B state proceeds according to the selection rule of $\Delta J=0, \pm 2$ by the probe laser alone (type I, $2\nu_2$) and by the probe and pump lasers (type II, $\nu_1+\nu_2$). The pump laser is polarized horizontally, while the probe laser is polarized (a) horizontally and (b) vertically. No correction is made for signal intensities with the variation of laser power.

transition are 0_u^+, 1_u, and 2_u. According to the treatment of McClain and Harris,[6] their rotational selection rules are

$$\Delta J=0, \pm 2 \quad \text{for the } 0^+\text{-}0^+ \text{ transition,} \qquad \text{(I)}$$

$$\Delta J=0, \pm 1, \pm 2 \quad \text{for the } 1\text{-}0^+ \text{ and } 2\text{-}0^+ \text{ transitions,} \qquad \text{(II)}$$

and also the large anisotropic behavior of the Q branch as shown in Fig. 1(b) is only expected for that of the 0^+-0^+ transition as discussed in the previous publication.[3b)] The progression in the spectrum can be assigned from the splittings of the O and S branches ($\Delta\nu_{OS}$).

$$\Delta\nu_{OS}=(8J+4)B'_v \quad \text{for type (II).} \qquad \text{(III)}$$

B'_v denotes the rotational constant of a v' ion-pair state (typically $B'_v \simeq 0.04\,cm^{-1}$ for lower v' levels) and J is the rotational quantum number of the $B^3\Pi 0_u^+$ state from which the two-photon transition originates. The type (II) transitions show a series of the progressions with intervals of around 135 cm^{-1}. The rotational splittings and vibrational intervals in the type (I) transitions are equal to half of the corresponding values in the type (II) transitions.

Thirdly, the intensity distribution of each progression in Fig. 1(a) shows the characteristic profiles inherent to the pumped vibrational levels of the B state. The progressions increase their intensities at the longer wavelength ends and suddenly break off. As discussed later on the basis of their Franck-Condon factors, the first levels observed at the lowest energies are assigned to the transition terminating on a $v'=0$ level of the ion-pair state.

Finally, it should be pointed out that the strong perturbation was observed in the ion-pair state. For example, the O, Q, and S branches in the $v'=3$ levels in Fig. 1 (see (10–0) P_{71}) split into two with comparable intensities. They are excluded in the following analysis of the energy level. A high resolution study utilizing etalon tuning dye lasers is in progress from which the detailed information about the perturbation by the surrounding electronic states will be obtained.

The term energies of the ion-pair state, $T(v', J')$, relative to the potential minimum of the ground state are obtained by

$$T(v', J') = \nu_1 + 2\nu_2 + G''_v + F''_v(J) \quad \text{for type (I)}, \qquad \text{(IV)}$$

$$= 2\nu_1 + \nu_2 + G''_v + F''_v(J) \quad \text{for type (II)}, \qquad \text{(V)}$$

where G''_v and $F''_v(J)$ are the vibrational and rotational energies of the $X^1\Sigma_g^+$ level, respectively. The G''_v and $F''_v(J)$ values were determined from the constants of the Barrow, Clark, Coxon, and Yee.[7] The pump frequency (ν_1) corresponded to the position of either a P(J) or R(J) line in the B–X system. The probe frequency (ν_2) had three values in accord with the $\Delta J=0, \pm 2$ transitions from a pumped level.

We have measured 117 rovibronic levels of a 0_u^+ ion-pair state corresponding to $0 \leqq v' \leqq 8$ and $6 \leqq J' \leqq 78$ pumped through the B–X transitions of (9–0) P_{25}, R_{29}; (10–0) P_{71}, R_{75}; (12–1) P_{51}, R_{55}; (14–2) R_5; (15–2) P_{51}. They were fitted by a least-squares method to the limited expansions;

$$T(v', J') = T_e + \omega_e\left(v' + \frac{1}{2}\right) - \omega_e x_e\left(v' + \frac{1}{2}\right)^2 + \left\{B_e - \alpha_e\left(v' + \frac{1}{2}\right)\right\} J'(J'+1). \qquad \text{(VI)}$$

The derived molecular constants are summarized in Table I.

TABLE 1. MOLECULAR PARAMETERS OF THE D(0_u^+) STATE FOR $^{79}Br_2$

Parameter	Value
T_e/cm^{-1}	49925.4(6)[a]
ω_e/cm^{-1}	135.7(3)
$\omega_e x_e$/cm^{-1}	0.27(3)
B_e/cm^{-1}	0.04190(14)
α_e/cm^{-1}	5.9(23)×10^{-5}

a) Values in parentheses denote twice the standard deviation (2σ) and apply to the last digits of the constants.

In order to confirm the absolute v' numbering of the ion-pair state, we have compared the intensity distribution of the OODR spectra with the calculated Franck-Condon factors. In the FCF calculations we used the version from Hougen of the RKR and FCF programs which were originally written by Zare, Schmeltekopf, Harrop, and Albritton for use.[8] The potential curve of the B state was constructed by using the constants of Barrow *et al.*,[7] while that of the ion-pair state was approximated by a Morse function defined by three parameters (ω_e, $\omega_e x_e$, and B_e) in Table 1. The patterns of observed vibrational progressions are reproduced in the FCF calculations as shown in Fig. 2. The calculated intensities using the different v' numbering have never fitted the observed intensities, since our spectrum includes the transition to a $v'=0$ level of the ion-pair state. For example, the calculations by shifting the v' numbering upward have always predicted significantly strong bands at longer wavelengths which were not observed.

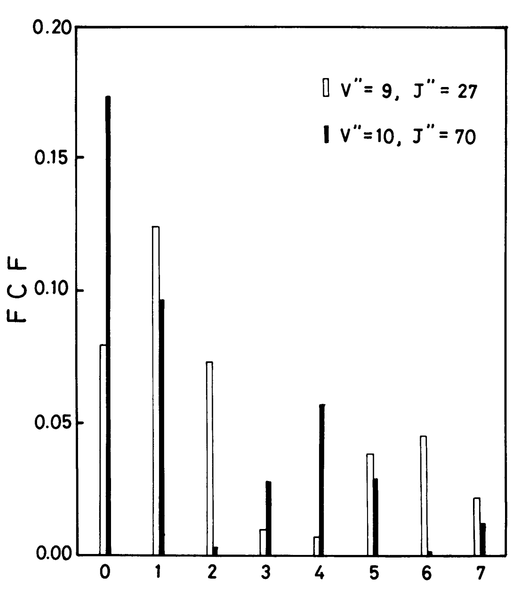

Fig. 2. Calculated Franck-Condon factors for the transitions shown in Fig. 1.

According to our preliminary results, the UV fluorescence spectrum of Br_2 observed in the experiment closely resembles that of the F(0_u^+)–$X^1\Sigma_g^+$ system analyzed recently.[5] The strong parallel bands were observed at around 269 nm. The emission system showed the vibrational structure which we could assign to a transition originating from a $v'=0$ level of the ion-pair state and terminating on the $X^1\Sigma_g^+$ ground state at the high vibrational levels around $v''=48$. Other fluorescence terminating on the low valence states was present at the longer wavelengths (≈310 nm) in the spectra.

To summarize the results, a new 0_u^+ ion-pair state of Br_2 has been observed by the OODR excitation technique utilizing a sequential three-photon absorption through the B state. The new state is the third ion-pair state spectroscopically characterized in any detail among the 6 states (0_u^+, 0_g^+(E), 1_u, 1_g, 2_u, 2_g (D')) arising from $Br^-(^1S)+Br^+(^3P_2)$, and could be labelled as D(0_u^+) in the analogy of I_2. The D state lies about 1000 and 150 cm^{-1} higher than the D' and E states, respectively, with a similar equilibrium internuclear distance of 3.19 Å but with a smaller vibrational frequency of 135.7 cm^{-1}; $T_e=48930 \pm 100$ cm^{-1}[12], $\omega_e=150.86$ cm^{-1}, and $r_e=3.170$ Å for D' (2_g),[9] and $T_e=49777.96$ cm^{-1}, $\omega_e=150.83$ cm^{-1}, and $r_e=3.194$ Å for E(0_g^+).[11]

We plan further investigations on the D(0_u^+) ion-pair state of Br_2. Macdonald, Donovan, and Gower[13] have recently studied the fluorescence spectrum of Br_2 directly excited at 158 nm (F_2 laser) and reported three bound-free transitions originating from the D(0_u^+) state in the region of 210—440 nm. It is obvious that they excite the molecules to the high vibrational levels of ion-pair state more than $v'=100$. By extending the probe frequency to analyze these high levels, we can provide the accurate potential curve of the D state which might not only answer the correct numbering of D levels in the VUV absorption but also explain the spectrum observed by Macdonald *et al.*[13]

Experimental

Experimental details were described previously.[3b)] Briefly, a nitrogen laser pumped dye lasers (Molectron UV-24 and DL-14) provided 10 ns pulses with an energy of around 0.5 mJ/pulse and 0.4 cm^{-1} linewidth. The experiments were performed at 10 Hz. The signals from a solar blind photomultiplier (Hamamatsu TV R-166) were processed by a boxcar integrator (PAR 162/164) through a preamplifier (PAR 115).

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