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# Laser optogalvanic spectrum of pure bromine discharge

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**Abstract.** Doppler limited laser optogalvanic (LOG) spectra are obtained by irradiating a bromine discharge with a cw dye laser. The discrete bands of the $Br_2$ $B$-$X$ system appear superimposed on a strong continuum. The LOG spectrum is closely identical with the absorption/emission spectrum of $Br_2$. Some extra bands and assigned in the $B$-$X$ system are also observed and their vibrational quantum number assignment is given.

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## 1. Introduction

Laser optogalvanic (LOG) spectrum of $I_2$ has been studied extensively by several workers [Rettner *et al* (1981), Demuynck and Destombes (1981), Beterov and Fateyev (1982), Haner *et al* (1983), Webster *et al* (1983) and Rai *et al* (1987)]. Large variation in the magnitude of the discrete bands of the $B$-$X$ system as well as in the background continuum of $I_2$ molecule with discharge voltage has been observed (Rai *et al* 1987). When the excitation is transverse to the discharge optogalvanic signals in $I_2$ can be detected even outside the discharge region Rettner *et al* (1981).

It is known that the electronic structure (potential energy curve, repulsive states etc.) of the $Br_2$ molecule is very similar to that of the $I_2$ molecule (Capelle *et al* 1971). It is therefore natural to expect similar effects in the LOG spectrum of $Br_2$ molecule also. We report here the first observation of the LOG signals from a discharge in pure bromine vapour.

## 2. Experimental

The experimental set up used in the present study is very similar to that employed by Rettner *et al* (1981) and by Rai *et al* (1987) and is shown in figure 1. Dimension of the hollow cathode discharge tube are of the same nature as used in the case of $I_2$ molecule. Pure natural bromine in liquid form (E. Merck, India) is kept in a reservoir placed in a liquid nitrogen bath and the whole system was evacuated with a rotary vacuum pump. When the pressure inside the tube becomes sufficiently low ($\simeq$0·03 torr) the liquid nitrogen bath is removed and the reservoir is placed in an ice bath. The flow of $Br_2$ through the discharge tube was controlled with the help of a needle valve. It was found that the discharge in $Br_2$ vapour is not as stable as in the case of $I_2$. It was found that a voltage of 500 to 525 V was needed to produce a quiet discharge at a pressure 0·04 torr.

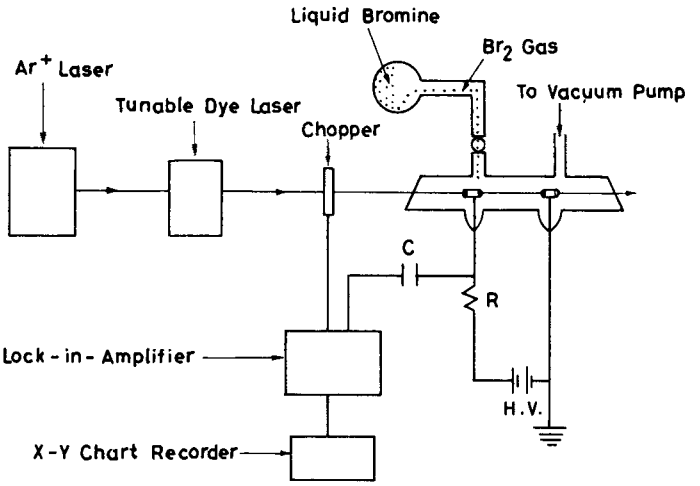


**Figure 1.** Laser optogalvanic spectroscopy of $Br_2$.

Spectra physics linear dye laser (Model 375B) pumped with a 4 watt all lines $Ar^+$ laser was used for excitation. The dye laser beam was chopped with a mechanical chopper (EG & G Model 125A) at 27 Hz and the laser beam after the chopper was split into two parts (10:90%). The 10% beam is directed on to the slit of a 1 meter monochromator (Minuteman) for wavelength calibration and the 90% laser beam is passed through the discharge region of the hallow cathode discharge tube containing $Br_2$ vapour. The LOG signal has been detected through a capacitor with the help of lock-in amplifier (EG & G Model 186-A) and finally recorded on a x-y recorder as shown in figure 1.

## 3. Results and discussion

The laser optogalvanic spectrum of $Br_2$ in the region 570–635 nm is shown in figure 2. As is clear from the figure the nature of the spectrum is very similar to that of $I_2$ [Demuynck and Destombes (1981), Rai *et al* (1987)]. There are well defined discrete bands due to the *B-X* system of $Br_2$ superposed on a background continuum extending throughout the region.

The existence of predissociative states e.g. $^1\pi_{1u}$ and other states of ungerade symmetry which cross or come close to the *B* state near $v' = 14$ and $v' = 1$ respectively has already been reported by Capelle *et al*. This explains the rapid variation of the effective lifetime of the *B* state with $v'$. We conclude therefore that in the present experiment also (as in $I_2$), the continuum is a real one and is caused by the predissociation of the *B* state. It is also known [McAfee and Hozack (1976), Kronig (1928), Chock *et al* (1968)] that the predissociation rat : is proportional to the inverse square of the molecular mass. Capelle *et al* (1971) reported that the lifetime for $Br_2$ is less than that of $I_2$ at equivalent wavelength and this is consistent with a larger predissociation contribution in $Br_2$ than in $I_2$ [Kronig (1928), Chock *et al* (1968)]. If we compare the intensity of the background continuum with that of the discrete bands in the case of $Br_2$ and $I_2$ (Rai *et al* 1987), we find that the background continuum has a

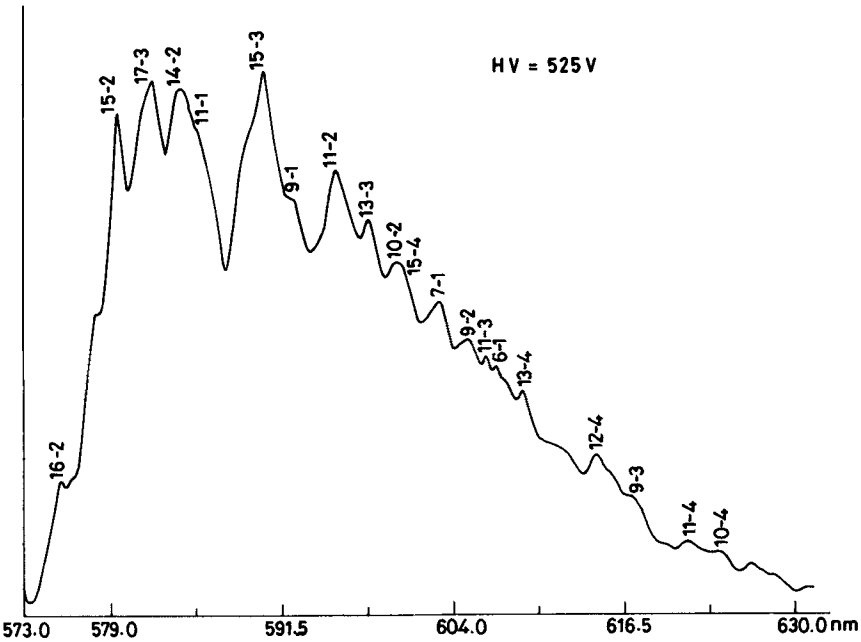


**Figure 2.** Laser optogalvanic spectrum of bromine molecule.

**Table 1.** Assignment of additional bands* observed in the *B-X* system of $Br_2$ molecule.

| Observed wavenumbers ($cm^{-1}$) | Assignment |
|---|---|
| 17178 | 17-3 |
| 17083 | 11-1 |
| 16930 | 15-3 |
| 16875 | 9-1 |
| 16649 | 15-4 |
| 16585 | 7-1 |
| 16457 | 6-1 |
| 16400 | 13-4 |
| 16269 | 12-4 |
| 16139 | 11-4 |

* Many of these bands have been attributed to an unknown system in the compilation of Kopp.

larger relative contribution in $Br_2$ than in $I_2$. This is in agreement with the earlier reported results [Capelle *et al* (1971), McAfee and Hozack (1976)].

The discrete bands observed in this spectral region (570–630 nm) are assigned easily with the help of the analysis proposed by Clyne *et al* (1980) and using the tabulation due to Rosen (1970). Most of the bands belong to the *B-X* system of $Br_2$. We are getting in addition several bands which were not assigned to the *B-X* system by these authors. In

his compilation Kopp *et al* (1974) has also reported several $Br_2$ bands in this region, which he tentatively ascribed to a transition between two unknown states. The wavelengths of the extra bands observed by us (see table 1) agree closely with the values reported by Kopp. The tentative vibrational assignment made by Kopp seems to be in error because the $\Delta G$ values obtained from these assignments are very erratic e.g. 345 $cm^{-1}$ to 1039 $cm^{-1}$. We have succeeded in assigning all these extra bands (table 1) into the same Deslandres scheme (*B-X* system) to within our experimental error.

A more detailed study (effect of discharge voltage, transverse excitation, etc.) of the LOG spectrum of $Br_2$ is under way, and will be reported in due course.

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