

Laser optogalvanic and emission spectrum of N₂ in the 5400–6150 Å region

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Abstract. Laser optogalvanic (LOG) and emission spectra of the N₂ molecule have been recorded at different discharge voltages and gas pressures in the spectral region 5400–6150 Å. It is observed that in the optogalvanic spectrum bands belonging to several systems develop extensively. Under the present discharge conditions bands of the first positive system are predominant. The variation of the signals with pressure and voltage in the two cases is discussed.

Keywords. Optogalvanic effect; two photon excitation; emission spectrum.

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1. Introduction

The molecular spectrum of nitrogen has been a subject of investigation for almost eight decades and a large number of valence and Rydberg electronic states have become known and are characterized to varying degrees of completion (see the compilation by Lofthus and Krupnie 1977; Huber and Herzberg 1979). The optogalvanic technique for the detection of spectral transitions developed during the last two decades proved effective in unravelling further details about molecular energy levels and mechanisms of excitation even in the case of molecules already well studied by other techniques (see the articles in *J. de Chim. Phys.* 1983; Rai *et al* 1987). It was therefore, natural that this technique was also used for the investigation of N₂ spectra (Suzuki and co-workers 1981, 1982, 1983; Miyazaki *et al* 1983; Feldman 1979; Pfaff *et al* 1984 and Seltzer and co-workers 1987, 1988). However no attempts were made to investigate the distribution of the molecules over the various electronic and vibrational energy levels under consideration. The present series of investigations were carried out to remove these shortcomings.

We have used a d.c. discharge in low pressure N₂ gas to create a distribution of N₂ molecules over its relatively low lying vibronic states. This distribution has been probed to a certain extent by recording the emission spectrum from the discharge. We have varied the gas pressure as well as the applied voltage to a certain extent and noted the changes that are caused by them on the spectrum. The discharge in each condition has been irradiated by light from a dye laser pumped either by an Ar ion laser or by the second harmonic of a Nd–YAG laser and the resulting optogalvanic signals have been recorded. We observe signals corresponding to several bands not observed in the emission spectrum which illustrates to the superior sensitivity of the

LOG technique. Variation in these signals with discharge voltage and pressure has been explained.

2. Experimental

The experimental set-up used for recording the optogalvanic and emission spectrum is shown in figure 1. A glass discharge tube with 1 cm internal diameter and 15 cm length is fitted with two hollow cylindrical nickel electrodes separated from each other by 1.5 cm. One of the electrodes was earthed while the other was connected to the high negative voltage terminal of a stabilised d.c. supply whose voltage could be varied. The gas used in the present work had a purity of 99% and a flow was maintained with a fine needle valve. A pirani gauge (Hind Hivac Model AGSTM) was used to measure the pressure in the discharge tube. Measurements were made only after the discharge had stabilised and the gas had attained a constant pressure. Measurements were made at three different gas pressures and three different discharge voltages. The discharge tube was aligned with the axis of a 0.5 m monochromator (Spex, USA) for recording of the emission spectrum.

The dye lasers used were (1) a cw dye laser (Spectra Physics Model 375B) with Rh6G dye pumped by a 4w all line Ar ion laser (Spectra Physics Model 164) with a tuning range limited from 5700 Å to 6300 Å and a spectral bandwidth of ~100 GHz and (2) a Quanta Ray PDL-2 pulsed dye laser pumped by the second harmonic radiation from a Nd-YAG laser (Model DCR-2 from Quanta Ray) with a tuning range 5400–5850 Å. The pulse repetition rate for the PDL-2 dye laser was 10 Hz. The cw laser beam was chopped at 25 Hz with a mechanical chopper (Precision Instrument Radiation Chopper CTX-534) and the signal was detected by a lock-in amplifier (Stanford Research Model SR-530). For the pulsed laser measurements a boxcar averager (EG and G Model 163) was used.

The dye laser beam coming out from the discharge tube is reflected in right angle direction by a 95% reflecting mirror. A small part of the laser beam transmitted through the mirror is permitted to fall on the slit of the monochromator to provide wavelength calibration. The signals from the PMT of the monochromator and from the lock-in amplifier (Boxcar averager) were recorded on a two pen recorder (Digital

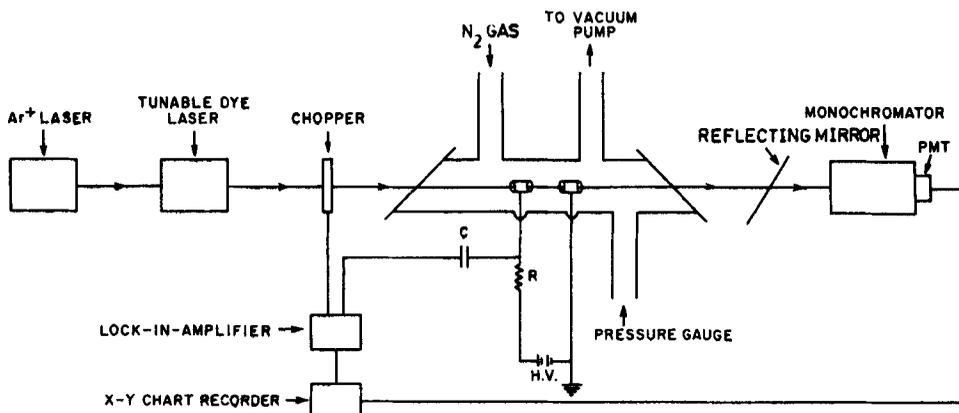


Figure 1. Schematic of the experimental set-up.

electronics). While changing the pressure or voltage of the discharge all the other experimental parameters were left unchanged.

To record the emission spectrum, the dye laser beam was blocked before it entered the discharge tube and the reflecting mirror was removed. The emission radiation of the discharge column was made incident on the slit of the monochromator. The spectrum was recorded both photographically as well as photometrically. For photographing the structure an exposure time of 10 h duration on a forte panchromatic 400 ASA film was used. The overlapping second order spectrum was avoided using optical filter.

3. Observation

(A) Emission spectrum

A part of the emission spectrum observed with an applied voltage of 500 V at 0.5 torr pressure is shown in figure 2. The majority of bands belong to the 4,0 and the 5,0 sequences of the first positive system (25310–4780 Å) though some bands of the Gaydon–Green system (6370–5040 Å) and the first negative system (5870–2860 Å) are also seen as is the 0,0 band of the Ledbetter system (5980–4360 Å). The first positive bands are recognized by their well-known four-headed structure though in many bands the Q_{33} head is too weak to be seen (see figure 2).

The intensity of the bands seems to increase gradually as one moves from the 4,0 band to the higher members of this sequence but starts to decrease after the 10,6 band reaching a minimum near $v' \sim 13, 14$ after which the intensity increases again before finally decreasing. The last band seen in this sequence has been assigned 21, 17. The 5,0 sequence of the bands also shows a similar behaviour and the 13,8 band is the least intense. These results are consistent with the reported predissociation in the $v = 13$ levels of the $B^3\pi_g$ state. The intensity of the individual bands and of the four heads in one band does vary with experimental conditions. The spectrum towards the shorter wavelength is quite complex due to superposition of the bands belonging to two different sequences.

(B) Optogalvanic spectrum

The optogalvanic spectrum has been recorded in the spectral range 5400–6150 Å using the discharge under different conditions. A large number of bands have been recorded (see figure 3). As mentioned earlier we have recorded the spectrum using cw as well as pulsed dye laser. The two spectrum visually appear little different from each other in the overlapping region due to large power difference and the resolution. The assignments of these bands posed some problem because the relatively large bandwidth (100 GHz) of the dye laser caused a lot of overlapping. The possibility of the LOG signal being positive or negative caused further confusion and only a careful comparison of the band positions and nature of the peak resulted in the final assignment. It is found that in the LOG spectrum, bands due to $C'_5\ ^1\Sigma_u^+ - a''\ ^1\Sigma_g^+$ Rydberg system (5879 Å) also appear in addition to the bands seen in the emission spectrum. In the spectral range 5400–5830 Å, where the Nd–YAG laser pumped dye laser radiation was used, we could mark LOG signals due to some bands of the

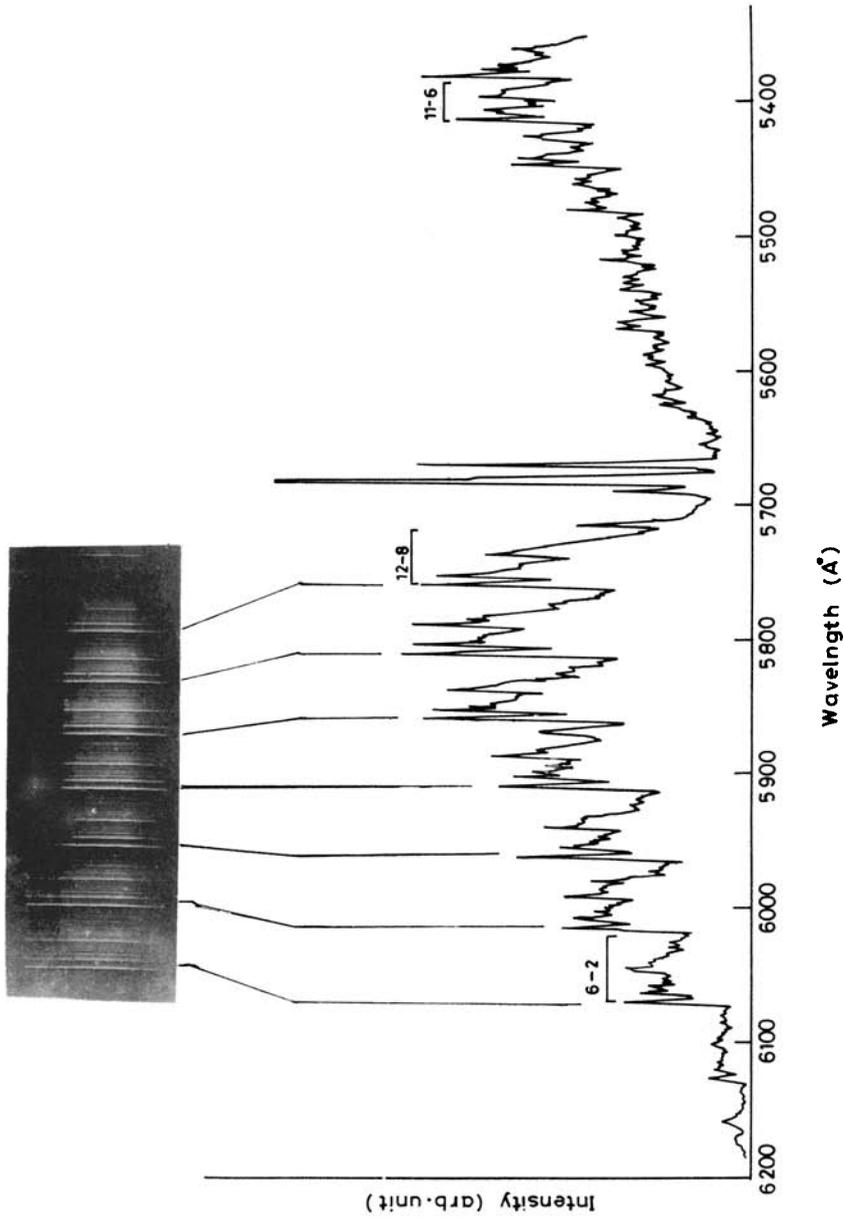


Figure 2. Part of the emission spectrum recorded using 0.5 m monochromator.

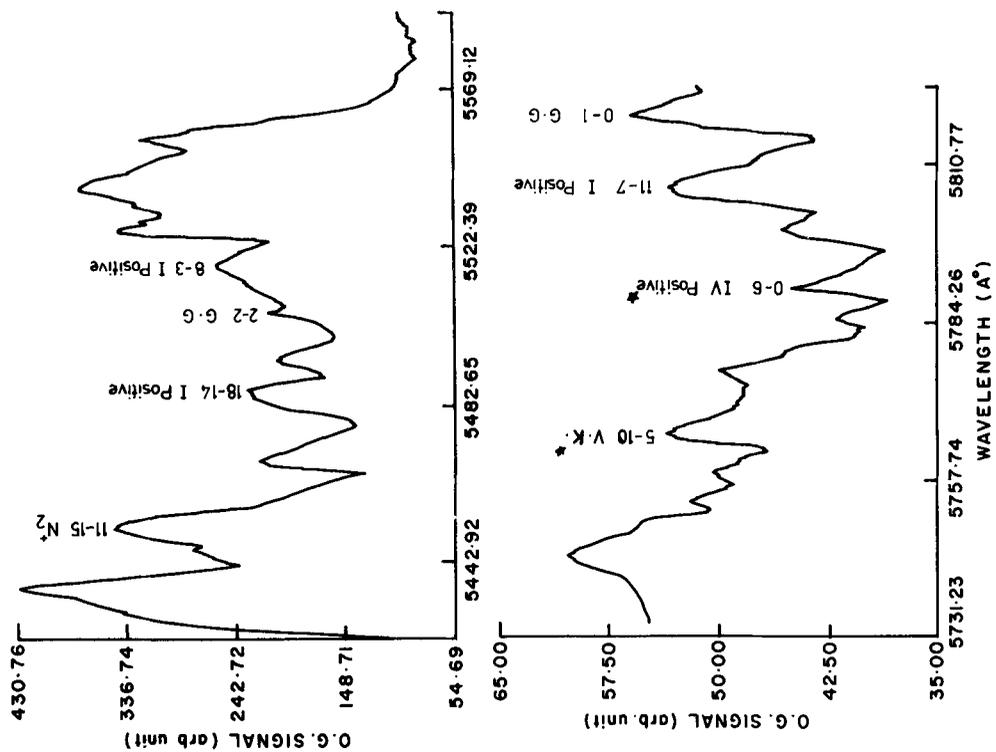


Figure 3b. Optogalvanic spectrum of N₂ using pulsed dye laser, * indicates two photon transition.

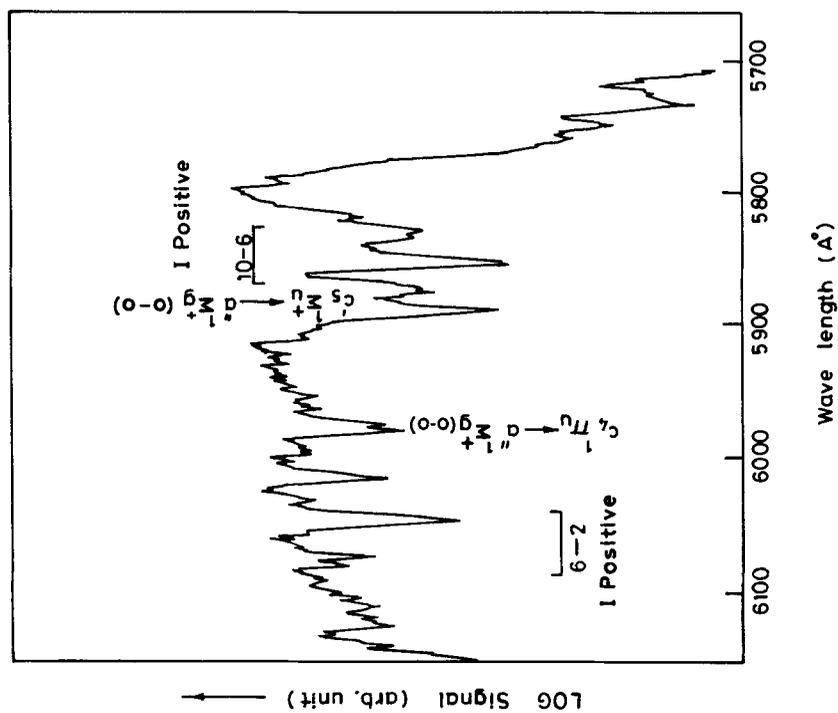


Figure 3a. Optogalvanic spectrum of N₂ using cw dye laser.

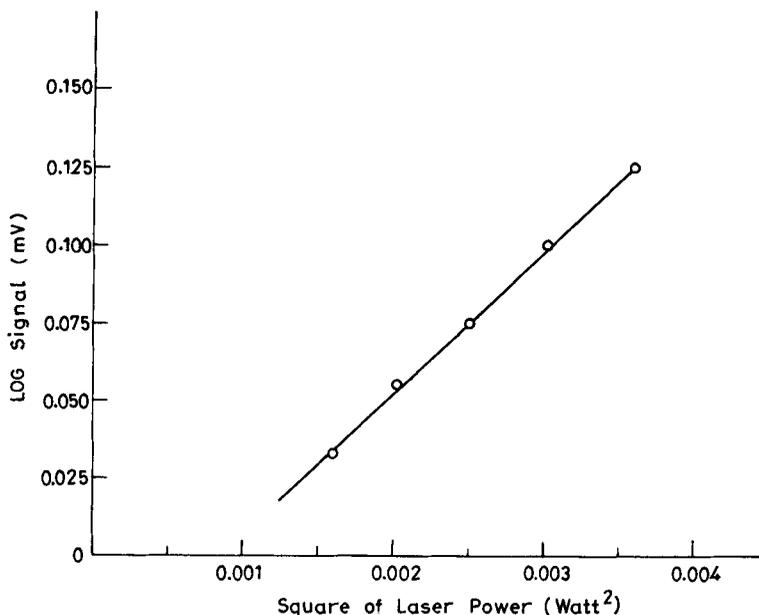


Figure 4. Dependence of LOG signal at $\lambda = 5673.26 \text{ \AA}$ on laser power.

second positive system (5460–2680 \AA), Gaydon–Herman system (3670–2220 \AA) and Vegard–Keplan system (3425–1250 \AA) involving the simultaneous absorption of two photons. The two-photon nature of these transitions was confirmed by the dependence of the signal on the dye laser intensity (see figure 4).

4. Discussion

A comparison of the emission spectrum obtained by us with the literature (Loftus and Krupnie 1977) shows that the d.c. discharge is a reasonably good source as most of the bands expected in this spectral region are actually observed. The small intensity and non-observation of some particular heads in the bands with $v = 13$ –16 of the $B^3\pi_g$ state is in agreement with the predissociation of this state by the $^5\Sigma_g^+$ state (Gaydon 1968; Verma 1984; Patridge *et al* 1988). This state is not well characterized as yet though it is implied from the observation of the infrared ($^5\pi_u^0 - ^5\Sigma_g^+$) transition (Patridge *et al* 1988).

The variation of the emission characteristics with the variation in the discharge voltage and the discharge pressure is shown in figures 5a and 5b. The increase in both parameters separately causes an initial increase in the intensity of the emission which gradually saturated. The initial intensity increase with the increase in pressure is essentially due to the increased population density while the later saturation is probably due to the competition of collisional de-excitation with radiative relaxation. The increase of the discharge voltage causes an increase in the electron temperature leading to an increased rate of molecular excitation. Again however, this will not continue indefinitely as the other process reducing the effective excitation of emission would come into play. There are four line-like feature near 5681 \AA which could not be assigned to any known transition. These lines are not present in optogalvanic

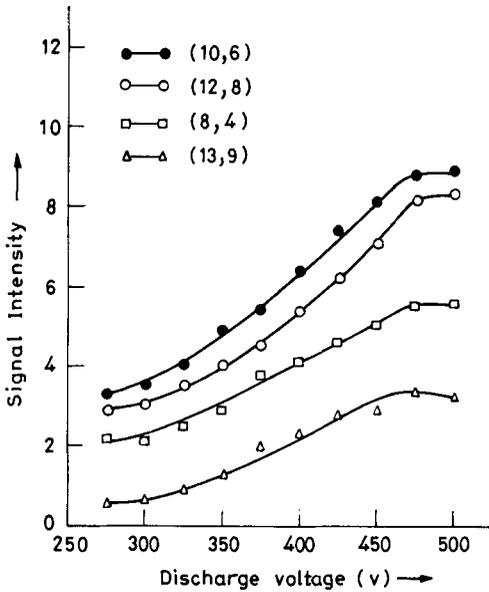


Figure 5a. Variation of emission signal with discharge voltage at a constant pressure.

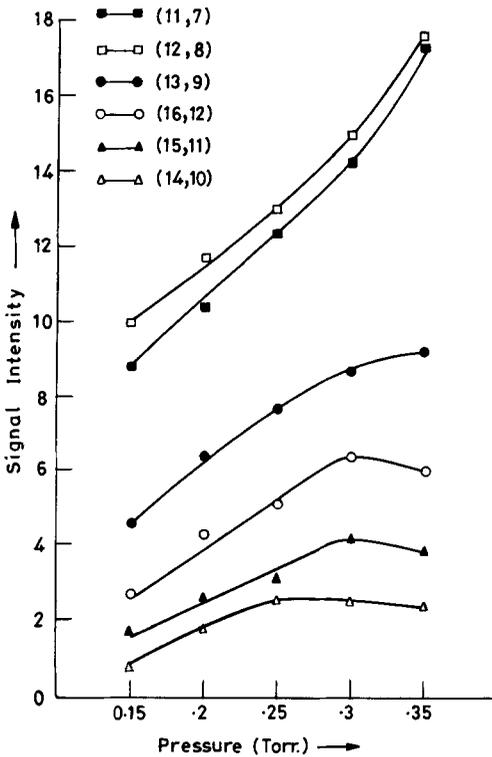


Figure 5b. Variation of emission signal with pressure at a constant discharge voltage.

spectrum or the emission spectrum photographed here or earlier and they are probably due to some artifact.

As mentioned earlier in the optogalvanic spectrum we could observe bands due to the first positive system, second positive system, first negative system, Ledbetter system,

Rydberg system $C'_5\ ^1\Sigma_u^+ - a''\ ^1\Sigma_g^+$, Gaydon–Herman system and Gaydon–Green appear quite extensively. The second positive, Vegard–Keplan and Gaydon–Herman systems have been observed due to simultaneous absorption of two photons for the first time using this technique. Seltzer *et al* (1987, 1988) have studied the second positive system of N_2 using LOG technique taking the frequency doubled radiation of a dye laser. Therefore their observation is actually due to one photon transitions.

In contrast to the work of Feldmann (1979) and Pfaff *et al* (1984) who obtained only the bands of the 4,0 sequence of the first positive system we have obtained many bands of the 5,0 sequence also in the LOG spectrum. It is interesting to note that the LOG signals for the 5, 1; 6, 2; 7, 3; and 8, 4 bands of this system (first positive) are negative but for the bands with higher (v', v'') they are positive. The 8, 4 and 9, 5 bands give a very weak LOG signal as already noted by Feldmann (1979).

The variation of the LOG signal with discharge voltage and discharge pressure for some bands of the 4,0 sequence of the $B^3\pi_g - A^3\Sigma_u^+$ system is shown in figures 6a and 6b respectively. It is seen that the signals for the bands 11, 7 and 12, 8 decrease rapidly with increase in discharge voltage (see figure 6a) and become negative. The

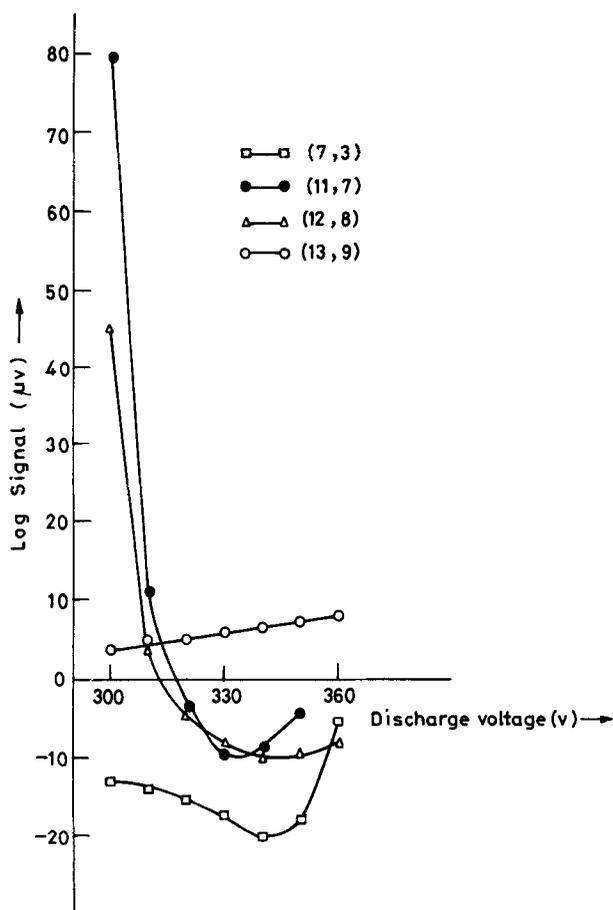


Figure 6a. Variation of LOG signal with discharge voltage at 0.5 torr pressure and 200 mW laser power at 5900 Å.

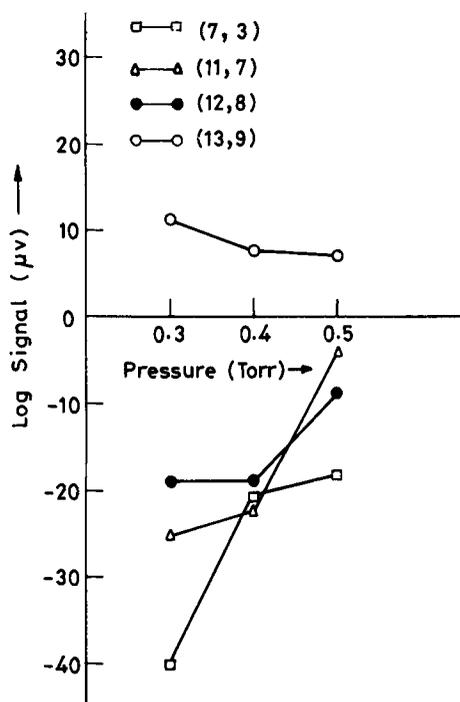


Figure 6b. Variation of LOG signal with pressure at 350 V and 200 mW laser power at 5900 Å.

negative signal decrease on increasing the discharge voltage further. The same holds for the 7,3 band also though in this latter case even at the smallest voltage used in our studies the signal was negative. The behaviour of the signal for the 13,9 band however shows a monotonic increase. The mean lifetime of the upper electronic state $B^3\pi_g$ of these bands is much shorter (a few μs) as compared to that of the lower state $A^3\Sigma_u^+$ (~ 1 ms) (Huber and Herzberg 1979). Therefore the absorption of the laser light results in a decreased rate of ionization causing the impedance of the discharge to increase. At a given voltage the LOG signal for the bands 7,3; 11,7 and 12,8 is positive which decreases with the increase of gas pressure. For the 13,9 band the LOG signal is positive. Though it also decreases with the increase of gas pressure, it remains positive even at higher values of pressure (figure 6b).

We offer the following tentative explanation for these observations. As stated above the lifetime of the excited state reached after laser light absorption is much less than that of the lower state so the ionization rate should decrease. The variation of the lifetime with vibrational quantum numbers is not large enough to have any effect on this feature, except in the case of the vibrational level $v = 13$ of the upper state. It is known from our emission studies that the $B^3\pi_g$ curve is intersected by another potential curve causing some of the heads (P_{22} , P_{33} and Q_{33} heads) to disappear from the structure. Now if this other state is a relatively long-lived state then an energy exchange between the two states may cause a transfer of the molecules from the $B^3\pi_g$ state to this long-lived state. If the lifetime of the later is greater than for the A state then the LOG signal would correspond to an increased ionization rate after laser light absorption. It has been suggested that this second state is a $^5\Sigma_g^+$ state (Patridge 1988)

whose radiative decay to the $X^1\Sigma_g^+$ and $A^3\Sigma_u^+$ states is forbidden. Under our experimental conditions, this $^5\Sigma_g^+$ state may have a longer lifetime > 1 s which may be the cause of the abnormal behaviour of the 13,9 band. The $v = 11$ and 12 levels of the $B^3\Pi_g$ state are only weakly predissociated at higher J values by the same $^5\Sigma_g^+$ state (Gaydon 1968; Verma 1984; Patridge *et al* 1988) and at lower discharge voltage the signal involving these levels are also positive. It seems that with the increase of discharge voltage the mixing of $^5\Sigma_g^+$ state with $B^3\Pi_g$ is reduced causing a negative signal.

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References

- Feldmann D 1979 *Opt. Commun.* **29** 67
Gaydon A G 1968 *Dissociation energy and spectra of diatomic molecules* (London: Chapman and Hall)
Huber K P and Herzberg G 1979 *Spectra and structure of diatomic molecules* (von Nostrand Co.)
Lofthus A and Krupnie P H 1977 *J. Phys. Chem. Ref. Data* **6** 113
Miyazaki K, Scheingraber H and Vidal C R 1983 *J. de Phys. Colloque* **C7 44**, 411
Miyazaki K, Scheingraber H and Vidal C R 1983 *Phys. Rev. Lett.* **50** 1046
Patridge H, Langhoff S R, Bauschlicher Jr C W and Schwenke D W 1988 *J. Chem. Phys.* **88** 3174
Papers of the Colloque on Laser Optogalvanic Spectroscopy, 1983 *J. de Chim Phys.* **C7 44**
Pfaff J, Bergman M H and Saykally R J 1984 *Mol. Phys.* **S27** 541
Rai A K, Rai S B, Thakur S N and Rai D K 1987 *Chem. Phys. Lett.* **138** 215
Seltzer M D and Green R B 1987 *Spectrosc. Lett.* **20** 601
Seltzer M D, Piepmeier E H and Green R B 1988 *Appl. Spectrosc.* **42** 1039
Suzuki T 1981 *Opt. Commun.* **38** 364
Suzuki T and Kakimoto M 1982 *J. Mol. Spectrosc.* **93** 423
Suzuki T, Sekiguchi H and Kasuya T 1983 *J. de Chim. Phys. Colloq.* **C7 44**, 419
Verma R D 1984 *Can. J. Phys.* **62** 414, 569