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On the nature of first positive band of molecular nitrogen in LIF of polymer and comparison with Emission spectra in Discharge

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Abstract

The present work reports the first positive band system due to molecular nitrogen in the region 5692.9Å -6545.0 Å which is severely quenched where polymer of poly (p-phenylvinylene) is excited with the help of Argon ion laser (5145 Å). We report here similar band system in the region of 5692.9Å -6545.0 Å where a sample of m-nitrobenzaldehyde is excited is uncondensed transformer discharge. A comparison with the spectra is expected to throw sufficient light on the phenomenon of quenching.

Keywords: Quenching, LIF

INTRODUCTION

Polymers are usually long chain-like molecules with a regular repeat unit. Semi conducting properties arise from using conjugated repeat units, e.g. a repeat unit in which there is a linear pattern of alternating single and double bonds. The alternating single and double bonds lead to one electron in a p orbital on each carbon. The p orbital's overlap, leading to electron delocalization and semiconducting behavior. Many conjugated polymers are capable of light emission. This can be generated either optically, by shining light onto a sample to give fluorescence, or electrically, by applying a voltage to a polymer light emitting diode. The vigorous worldwide activity relating to the development of light emitting polymers has lead remarkable advances in materials over the past decade, facilitating the development of other application areas such as electronics, solar cells and lasers. There are several reasons why semiconducting polymers could be attractive laser materials [1-4]. The first is that there exist a range of polymers that can emit light across the visible spectrum. The polymers have broad spectra providing scope for making tunable lasers. They have very strong absorption coefficients ($\sim 10^5$ cm^{-1}) which imply that there is the potential for extremely strong amplification of light. The absorption and fluorescence spectra are well separated so that absorption of emitted light is weak. In many fluorescent organic molecules (including laser dye) light emission is severely quenched at high concentration-such as typically found in solid film [5]. During recent years we have carried out extensive studies on laser induced fluorescence of various polymers containing nitrogen with respect to their quenching behavior The salient feature observed is the first positive band of molecular nitrogen in the region 6068.5 Å-6545 Å while the entire region belonging to the first positive is quenched or suppressed [6-9]. The phenomenon usually occurs in a neat film. Similar situation is also observed in the emission of m-nitrobenzaldehide vapour when excited in transformer discharge. In this case also only the fluorescence system in the region 5692.9Å - 6545.0 Å belonging to the first positive system is observed. In the present work we make a comparative study between the two systems of spectra excited under different circumstances and a possible explanation is reported

MATERIALS AND METHODS

Experimental

In the present experiment a sample of neat polymer film of PPV [poly (1, 4 phenylene vinylene)] dropped with m-nitrobenzaldehide has been used. We have used a 500mW Argon ion laser with exciting radiation 5145 Å. The sample thickness was 1mm. The fluorescence spectrum was recorded on a two prism glass spectrograph and intensity of the bands are measured with the help of computer software available for this purpose. Fig-1 exhibits the spectrum along with its intensity measurement. For observing the discharge emission of the of the sample (melting point-56 to 58°c), the substance in the powder form kept inside the Π type discharge tube of length 20 cm with constriction in the middle. Nickel sheets are used as materials for electrodes. Spectroscopic ally pure liquid benzene kept in separate bulbs is connected to the rear side of the discharge tube through a needle valve. Bulb containing liquid benzene is kept in a freezing mixture consisting of ice and common salt. This procedure keeps the benzene in the solid form and helps to maintain a constant flow of vapor. A rotary pump capable of producing vacuum up to 10^{-3} torr is used to evacuate the tube continuously. A 10kv transformer is used to supply the necessary electric field through an auto transformer. The substance whose emission is to be observed through excitation is kept in the constricted part in powdered form and there is also provision for the sample tube to be heated from beneath with the help of a heating coil whose temperature can also be regulated.

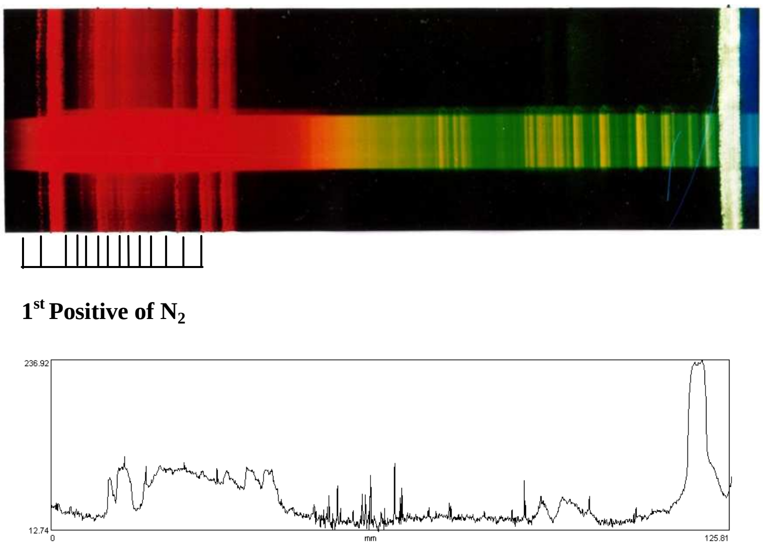

Fig-1: The LIF spectrum of PPV along with its intensity measurement

.A two prism glass spectrograph is used as a dispersing instrument. The role of benzene vapor is to suppress the CO angstrom band giving rise to white colour in discharge. In this way an emission in the visible region excited can be observed and photographed on a commercially available colour film. The intensity of the emission band was also measured with the help of the computer software for this purpose. The photographic film is kept on a scanner which in turn is connected to the computer for measurement of intensity. Fig-2 shows the spectrum along with the intensity measurement.

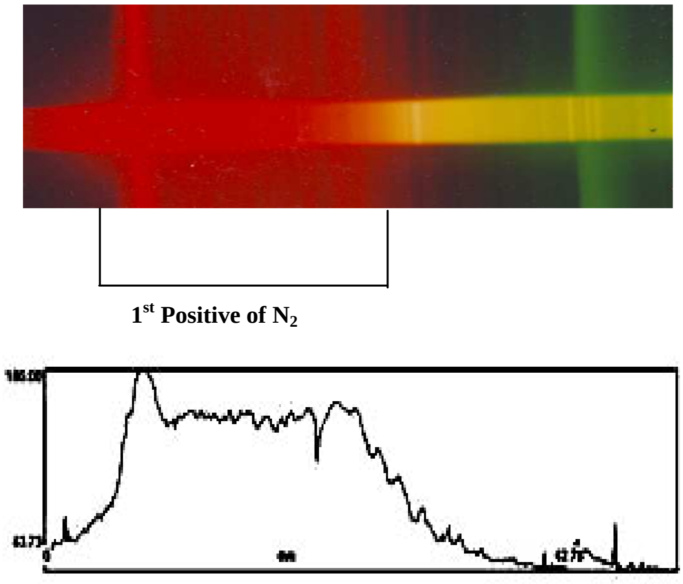

Fig-2: The emission spectrum along with the intensity measurement

RESULTS AND DISCUSSION

We have observed the Laser induced fluorescence spectra of heat polymer film of PPV in region 5692.9Å -6545.0 Å. In this case we have observed the first positive band of nitrogen molecule after substantial part of the spectrum being suppressed.   .

Table – 1

LIF band of wavelength (Å)	First Positive of Nitrogen	
	Å	υ’ – υ’’
5692.9	5692.9	6-1
5632.7	5632.7	5-0
5755.2	5755.2	12-8
5854.4	5854.4	6-10
5959.0	5959.0	8-4
6013.6	6013.6	7-3
6068.5	6069.7	6-2
6129.4	6127.4	5-1
6185.0	6185.2	12-9
6323.2	6252.8	11-8
6351.9	6322.9	10-7
6395.0	6394.7	9-6
6467.5	6468.5	8-5
6545.0	6544.8	17-4

From the measurement and also from the appearance it is identified as belonging to the first positive band of nitrogen molecule [10]. Only fourteen bands are measured in the region 5692.9Å -6545.0 Å, while the other bands below 5692.9Å and above 6545.0 Å are completely suppressed. Table 1 shows the position of the bands observed in the LIF of PPV with corresponding first positive band of nitrogen. It is due to the suppression of the bands in the higher and lower wavelength sector of the spectrum. It is phenomenon which is similar to Spectral narrowing that has been observed in a spontaneous emission in optically pumped luminescence polymer film. The emission spectra of discharge lie in the region 5692.9Å -6545.0 Å .The emission spectra shows the fourteen discrete bands in that region. Each band shows the triple headed structure which is characteristics of first positive band of spectrum of nitrogen molecules. the remaining parts of the first positive band system of nitrogen are completely quenched. The first positive system corresponding to $B^3\pi – A^3\pi$ transition. Table 2 indicates the measurement of emission spectra. The discharge occurred at 1- 100mm Hg. Pressure reduced the intensity of the first positive system This may be due to quenching of the $B^3\pi$ state. From what has been described above it appears certain that the LIF of first positive band of N_2 molecules observed in a polymer film is quite identical to discharge emission of N_2 molecules particularly first positive band. In both the cases only the spectrum lying in the region 5692.9Å - 6545.0 Å appears. It may be noted that the suppression of first positive band in a region was reported by Kokhanenko and Prelezhaeve [11] in discharge in pure and true five decades ago. The suppression of the band belonging to the first positive system of nitrogen molecules may bear considerable significance. Pending further work in this lines it is reasonable to believe that similar condition may exist in interstater space and observation of this system will validate our works

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Table -2

Emission band	First Positive of Nitrogen	
	Å	υ' – υ''
5692.9	5692.9	6-1
5632.7	5632.7	5-0
5755.2	5755.2	12-8
5854.4	5854.4	6-10
5959.0	5959.0	8-4
6013.6	6013.6	7-3
6068.5	6069.7	6-2
6129.4	6127.4	5-1
6185.0	6185.2	12-9
6323.2	6252.8	11-8
6351.9	6322.9	10-7
6395.0	6394.7	9-6
6467.5	6468.5	8-5
6545.0	6544.8	17-4

CONCLUSION

The present work reports a comparison between the emission spectra belonging to the first positive system of N_2 molecule which appear in different environments. The salient features observed quenching of bands which is strikingly similar in both the cases.

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