

OPTOGALVANIC STUDY OF CARBON-NITROGEN RADICAL IN DISCHARGE

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Abstract:

Carbon-Nitrogen (CN) radical has been detected in arcs and containing carbon in discharge tubes, in shock tubes and in nitrogen gas after glows to which organic substances must have been added. The ground state CN radical is (Electronic State) $^2\Sigma^+$ with two (Vibrational State A-X) $A^2X-X^2\Sigma$ known as CN red or red band system of CN and (Vibrational State B-X) $B^2\Sigma^+ - X^2\Sigma^+$ known as CN violet, extends from near infrared to visible region (1500-4400 nm). The CN violet extends from near UV to visible region (460-300 nm). The bands of the A system are red degraded triple headed and B-X system peculiar behavior.

Keywords: Optogalvanic technique, triple headed conventional emission technique.

Introduction:

The Optogalvanic technique has been used for the last two to three decades for investigating the spectra of atoms and molecules. The spectrum of this radical was first recorded by Jevons (1926). The method of citation is not in conformity with this journal's method of citation, in an arc that observed three sequences in the B-X system.

The ground state of CN radical is $^2\Sigma^+$. Two band systems of this CN radical were developed strongly since 1926; viz the A-X known as CN red or red. Band system and B-X are known as CN violet system. Where as CN red extends from near infrared to visible region (1500-440 nm) the CN violet extends from near UV to visible region (450-300 nm). Beside large number of other band system involving lower excited to upper excited transition.

F.A. Jenkins, (1928) also recorded the bands involving higher vibrational number (v) of the X and B states. These bands involved different degradation and were named as tail bands' F.A. Jenkins, Y.K. Roots and

R.S. Mulliken, (1937) and A.E. Parker(1932) recorded the band in visible and near infrared region and analyzed them as due to $^2\Pi-^2\Sigma$ transition. Several other scientists studied the A-X system of this molecule since then (G. Herzberg et al (1948), A.E. Douglas et. al (1955), N.H. Kiess and H.P. Broida, (1961), J.M. Weinber e.t al. (1967) and F.J. Le Blanc. (1968)). A useful compilation of molecular data on the A-X system of CN has been given by Brocklehurst et al (ii), K. P. Huber and G. Herzberg, D. Von. Nostrand Reinhold Co. N.Y. (1979),Pearse and Gaydon et.al (1976) and S.N. Suchard et.al (1975).

J.U. White, (1940) recorded the B-X system radical with a better resolution and gave an improved analysis. Several other scientists (A.E. Douglas and P.M. Routly Astrophys., (1955), N.H. Kiess and H.P. Broida, (1961), J.U. White, (1940) and R. Engleman, Jr. (1974) studied the spectrum of this system and gave improved vibrational and rotational constants for the A and X state an extensive information and

about this system and about the state involved in this transition can be obtained from above mentioned compilations (K. P. Huber et.al. (1979), R.W. Pear et.al (1976) and S.N. Suchard et.al(1975).

All these clearly indicate that CN can be treated as a test molecule and can be utilized to test the sensitivity of any new technique. In the present work we recorded the emission and Optogalvanic spectrum of a discharge-containing vapor of organic compound in the same situation simultaneously. Our study clearly shows that Optogalvanic technique is much more sensitive than conventional emission techniques.

Experimental Method:-

The experimental set up in the present study is shown in fig (1) it consists of a rectangular tube with arms length 20cm and 30 cm and diameter 2.5 cm. The longer arm is fitted with two parallel nickel cylindrical electrodes (4 cm in diameter and 1 cm length) 8 cm apart. One end of the discharge tube is connected with a rotary pump to create low pressure in the discharge

tube. The other end tube is connected to the sample cell to introduce the gas form to be studied.

A Direct current (D.C.) potential from a variable 1.5 kV, power supply was used to get the stable discharge, several organic compounds (sample) viz: nitro benzene, aniline, C_2H_5CN and CH_3CN were used to get the stable discharge emitting strongly CN bands. The most stable discharge was obtained with CH_3CN . In the case of benzene derivatives the excess carbon liberated gets deposited on the wall making discharge unstable. Even in the case of CH_3CN the discharge starts becoming unstable after half an hour and we have to clean the tube.

The other side of the discharge tube was fitted with 0.5m-Spex monochromatic to record the emission spectrum of CN. The laser radiation from a tunable dye laser filled with Coumarin 540A dye and pumped by Exile chloride (XeCl) laser was used to get Optogalvanic signal. A part of dye laser radiation splinted by a glass plate was used to get Optogalvanic signal of Ne for calibration.

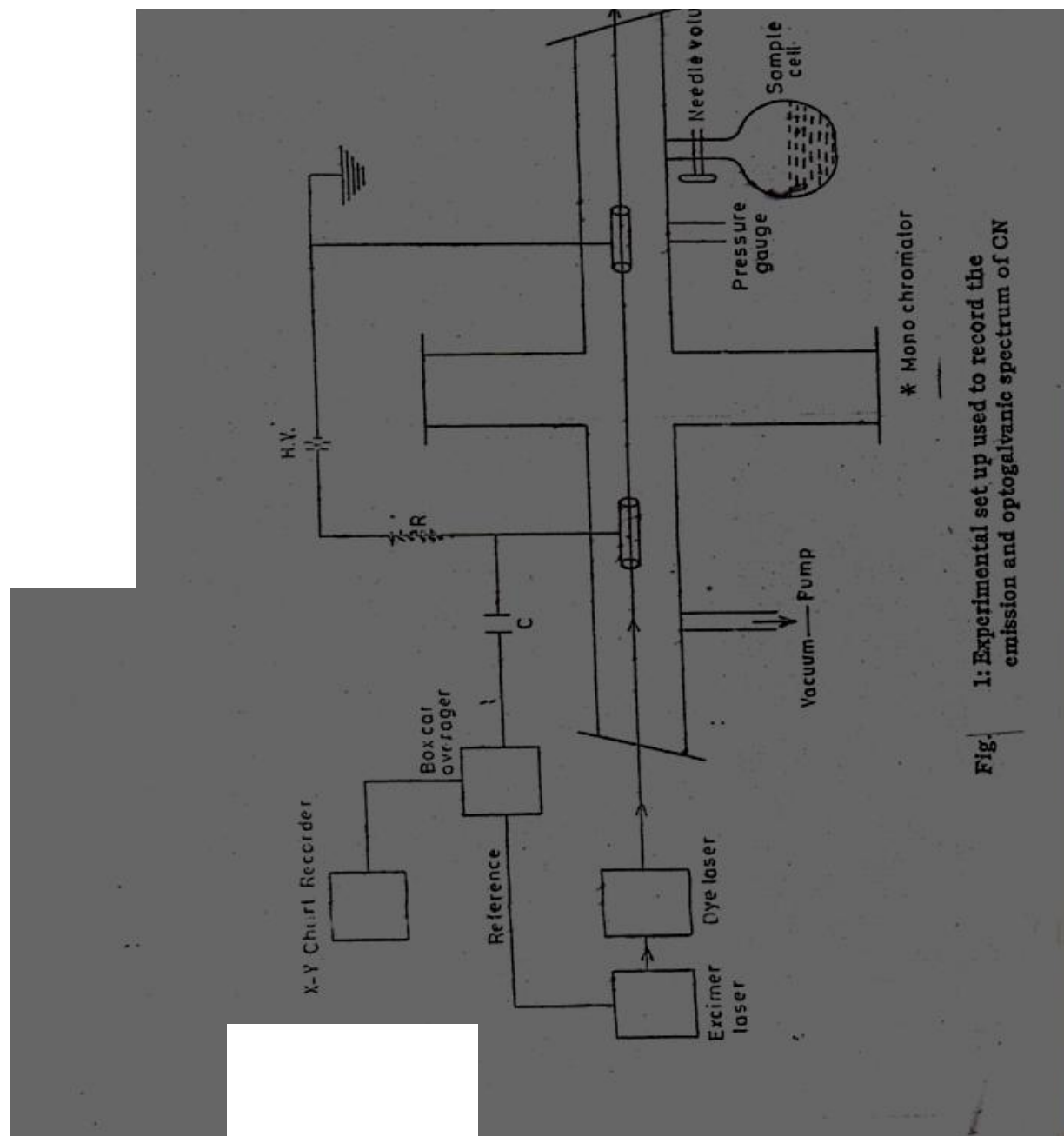


Fig. 1: Experimental set up used to record the emission and optogalvanic spectrum of CN

A voltage range $\sim 600-800V$ was applied on the discharge tube and a stable discharge was achieved by controlling the flow of CH_3CN kept in cell with the help of a needle valve. The Optogalvanic signal was received through a resistance inductance coupled circuit and fed to the boxcar average which is reference to the repetition rate (i.e. 10 Hz) of the

excimer laser. The signal from the boxcar is connected to one pen of a double recorder. The other pen of the recorder monitors the Optogalvanic signal of Ne for calibration. The gate with and delay in the boxcar was adjusted to get optimum signal from the sample combination of the resistance and capacitance and were varied to further optimized the signal.

The Optogalvanic and emission signals were monitored simultaneously in the wavelength region 540-580 nm. In order to see whether laser beam affects the emission signal or not we monitored the emission spectrum again in the absence of the laser beam (the laser beam was blocked by a card board). It was observed that difference was noticed in the both cases. Finally, the tubes were reversed i.e. the tube filled with electrodes was used to monitor the emission and other for Optogalvanic measurements. Again difference as seen in the tow cases of course there was a small change in the intensity but over all bands appear in both the situations.

Results and Discussion

The emission spectrum of CN radical (see fig 2) well sequenced bands since the spin orbit-coupling constant in the A^2X state is very small. The sub bands $^2\Pi_{1/2}-^2\Sigma$ and $^2\Pi_{2/3}-^2\Sigma$ lie close to each other. The bands R_1 and R_2 could be seen very clearly. Even rotational (S_{r21}) head which is very weak could be marked. Since there is very weak structure in between the sequence bands it posed no problem in identification. It is very similar to the observation made easily on the basis of the previous workers. The bands thus observed one given in the table (1) these bands are (9,3), (10,4) and 11,5) belonging to (6,0) sequence. All the four heads corresponding to these could be observed.

The Optogalvanic spectrum recorded in the 570 nm region does not show (see fig.3) only these sequence bands but large number of other bands. The assignment of these bands could be

made on the basis of the molecular constants given the references (K. P. Huber et.al (1979), R.W. Pear et.al (1976) and S.N. Suchal et.al (1975). These bands are given in table (2). As is clear from the spectrum and also from the table (2) that along with (9,3), (10,4) and (11,5), and other series of bands there appear bands (14,7), (15,8) (18,10), (19,11) (12,12) belonging to (7,0), (8,0) and (9,0) sequences. The (5, 0) band also appears here with appreciable intensity. The non appearance of these bands in emission spectroscopy (in the present case) is due to their small Franck Condon factor and small intensity of discharge. This clearly establishes that Optogalvanic technique is much more sensitive compared to conventional emission technique. The band of (7.0), (8,0), and (9.0) sequences appear nearly with the same intensity as the bands of (6.0) sequence; though their Franck Condon factor is small, this supports the fact that the Optogalvanic signal does not follow the Franck Condon principle.

Conclusion: We have studied the emission and optogalvanic spectrum of CN radical. CN radical in spectroscopy is used as a test molecule to test the sensitivity of newly developed spectroscopic/ laser techniques. In this section we have tested the sensitivity of optogalvanic technique with respect to conventional emission technique. The discharge through different organic vapours were used as source of CN. It was marked that CH_3CN gives a stable discharge of CN with appreciable CN yield. Large of new bands not appearing in emission could be observed with good intensity in laser optogalvanic technique.

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FIG. 2

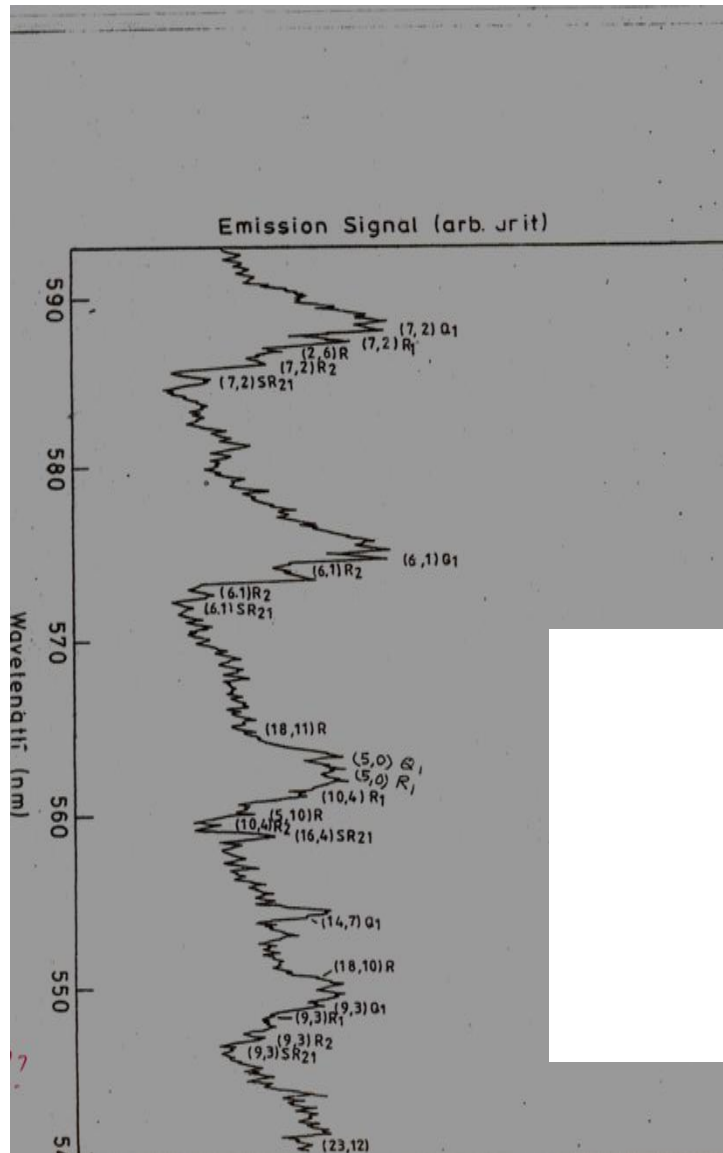


Table 1) Bands observed in the emission spectrum of CN in the 545.0 nm region.

Bands	Branches	Wave length (nm)	Wave number (cm ⁻¹)
(7,2)	Q ₁	587.77	17008.74
	R ₁	587.14	17026.99
	R ₂	585.82	17065.45
	S _{R21}	584.93	17091.33
(6,1)	Q ₁	574.82	17391.96
	R ₁	574.32	17407.07
	R ₂	572.99	17447.47
	S _{R21}	571.90	17480.63
(5,0)	Q ₁	562.53	17771.89
	R ₁	562.05	17787.23
(10,4)	Q ₁	561.53	17803.55
	R ₁	561.04	17819.10
	R ₂	559.79	19858.88
	S _{R21}	558.94	17886.17
(9,3)	Q ₁	574.82	18206.89
	R ₁	574.32	18225.08
	R ₂	572.99	18264.80
	S _{R21}	571.90	18282.67

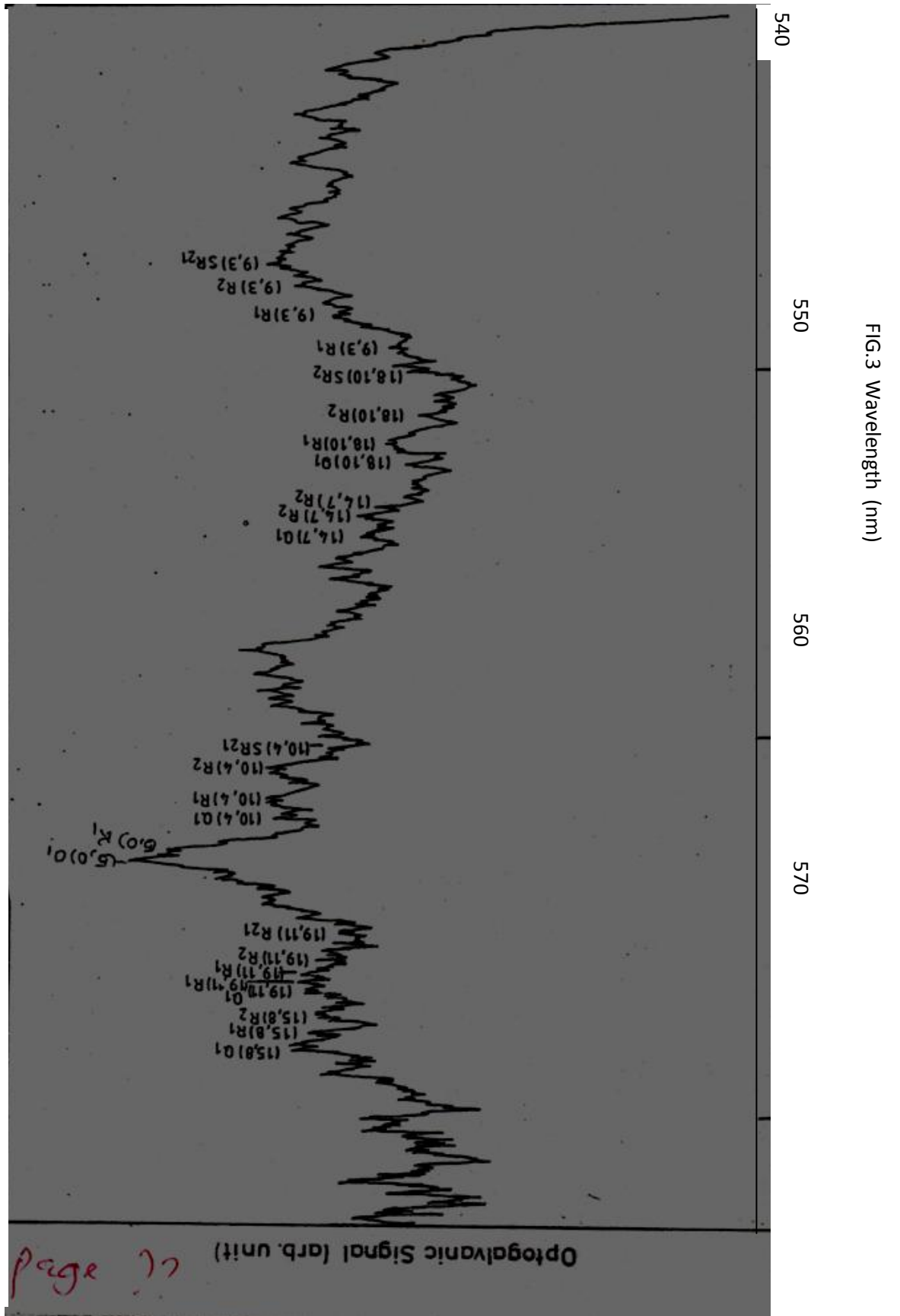


Table 2 Bands observed in the Optogalvanic spectrum of CN in the 540.0 to 570.0 nm region.

Bands	Branches	Wave length (nm)	Wave number (cm ⁻¹)
(15.8)	Q ₁	568.12	17597.06
	R ₁	567.57	17613.96
	R ₂	567.07	17629.46
	S _{R21}	566.04	17661.70
(19,11)	Q ₁	566.54	17646.26
	R ₁	566.04	17661.70
	R ₂	565.45	17680.25
	S _{R21}	564.02	17725.58
(5.0)	Q ₁	562.53	17771.89
	Q ₁	562.05	17789.23
(10.4)	Q ₁	561.53	17803.55
	R ₁	561.04	17819.10
	R ₂	559.79	19858.88
	E _{R21}	558.94	17886.17
(14.7)	Q ₁	554.17	18042.05
	R ₁	553.64	18056.58
	R ₂	553.13	18074.47
	E _{R21}	552.20	18104.35
(18.10)	Q ₁	552.42	18097.14
	R ₁	551.98	18111.57
	R ₂	551.24	18135.98
	S _{R21}	550.00	18176.77
(9.3)	Q ₁	574.82	18206.89
	R ₁	574.32	18225.08
	R ₂	572.99	18264.80
	S _{R21}	571.90	18282.67
(21.12)	Q ₁	541.92	18447.75