

$F^2\Delta_r - A^2\Pi_i$ BAND SYSTEM OF CN*

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ABSTRACT

The spectrum of CN has been studied in condensed electrical discharge through flowing CH_3CN vapour. Ten new bands of $F^2\Delta_r - A^2\Pi_i$ system in the region 2100–2700 Å are obtained. The vibrational constants $\omega_0' = 1229.7 \text{ cm}^{-1}$ and $\omega_0'x_0' = 14.0 \text{ cm}^{-1}$ are obtained for the first time for the $^2\Delta$ state of CN.

1. INTRODUCTION

THE spectrum of CN molecule has been observed in arcs and discharge tubes with different parent compounds.¹ An extensive amount of work has been done by Douglas and Routly² in which they reported many new bands of the CN red system ($A^2\Pi - X^2\Sigma$) and violet system ($B^2\Sigma - X^2\Sigma$) and also bands arising out of a completely new set of electronic levels. The new transitions observed by them are $H^2\Pi - B^2\Sigma$, $F^2\Delta - A^2\Pi$, $D^2\Pi - A^2\Pi$, and $D^2\Pi - X^2\Sigma$. No transitions involving the vibrational quanta of $F^2\Delta$ and $H^2\Pi$ levels were observed by them and the vibrational frequencies of these states are not known till now.

While attempting to study the stability of the CN molecule for absorption experiments, preliminary experiments showed strong CN emission in electrical discharge through CH_3CN vapour. The spectra showed new emission bands of the $F^2\Delta_r - A^2\Pi_i$ transition resulting in the determination of vibrational frequency of the $^2\Delta$ state. The results observed in this band system along the corresponding analysis are discussed here.

2. EXPERIMENTAL

A condensed electrical discharge through flowing CH_3CN vapour, with 0.8 Kva transformer working at 15,000 volts using a condenser of $0.005 \mu\text{F}$

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capacity, is found to be the best to obtain the system. The spectra are recorded on a Littrow quartz spectrograph (dispersion of 2.1 Å/mm. at 2325 Å) and also in the second order of a Jarrell-Ash 3.4 metre plane grating spectrograph (dispersion 2.5 Å/mm.). Kodak 0 and Kodak B-10 plates are used to photograph the spectra. Exposures of the order of 45 minutes and 1½ hours are needed on the grating and prism spectrographs respectively. The heavy carbon deposit formed in the discharge tube during the excitation of the vapour had to be removed at frequent intervals. Iron spectrum is used as standard. Figure 1 shows the enlargement of some of the bands photographed.

3. RESULTS AND DISCUSSION

Douglas and Routly observed five bands of the system in the region 2040–2400 Å. They assigned the bands as arising from zero upper vibrational state to the lower 1, 2, 3, 4 and 5 vibrational states. The assignment of $^2\Pi$ as the lower state of this transition is in conformity with the vibrational quanta and rotational constants known from CN red system. They further assigned $^2\Delta$ as the upper state from the rotational analysis carried out on 0–2 and 0–3 bands. In our experimental investigation we have observed ten new bands of the above system together with four of the bands observed earlier. The bands lie in the region 2100 to 2700 Å. All the bands are double-headed, with double-head separation 110 cm.⁻¹, and are degraded to red. They form well-developed sequences suggesting that both lower and upper state frequencies are involved in the observed band system. Assuming the known values of ω_0 and $\omega_0 x_0$ of A $^2\Pi$ state all the band-heads can be represented by the formula :

$$\nu = \frac{50624.8}{50514.8} + 1229.7 v' - 14.0 v'^2 - 1799.7 v'' + 12.6 v''^2$$

suggesting for the upper electronic state the vibrational constants

$$\omega_0' = 1229.7 \text{ cm.}^{-1} \quad \text{and} \quad \omega_0' x_0' = 14.0 \text{ cm.}^{-1}$$

Table I shows the Deslandres' scheme of the bands with visual estimation of the intensity. It may be noted here that only one branch of Condon parabola has been observed. The other branch, as can be seen from the analysis, lies in the vacuum ultra-violet and hence is not observed in the present experiments.

Using the above formula for the band-heads one expects the (0, 1) band to lie at 48838 cm.⁻¹ However, Douglas and Routly have reported to have

TABLE I
Deslandres' scheme for the band-heads with visually estimated intensity

ν'' \ / \ ν'	2	3	4	5	6	7	8	9	$\Delta G(\nu'' + \frac{1}{2})_{\text{obs.}}$	$\Delta G(\nu' + \frac{1}{2})_{\text{cal.}}$
0	(2) 47077 1798 1740	(4) 45339 1713 45227 1711	(4) 43626 1682 43516 1681 1217 1217	(4) 41944 41835 1213 1213	(4) 41495 1662 41385 1663 1190 1190	(4) 39864 1631 39753 1632 1183 1185	(4) 38257 1607 38147 1606 1185 1186	(2) 37860 1582 37750 1583 1155 1155	1216	1215
1			(3) 44843 1686 44733 1685	(4) 43157 1662 43048 1663	(4) 41495 1631 41385 1632 1190 1190	(4) 39864 1607 39753 1606 1185 1186	(2) 38257 1607 38147 1606 1185 1186	(2) 37860 1582 37750 1583 1155 1155	1186	1188
2					(2) 42685 1638 42575 1637	(3) 41047 1605 40938 1605	(4) 39442 1582 39333 1583 1155 1155	(2) 37860 1582 37750 1583 1155 1155	1155	1160
3							(1) 40597 40488			
	$\Delta G(\nu'' + \frac{1}{2})_{\text{obs.}}$	1739	1712	1684	1663	1635	1606	1583		
	$\Delta G(\nu' + \frac{1}{2})_{\text{cal.}}$	1736	1711	1685	1660	1634	1608	1582		

observed this band at 48815 cm.^{-1} . We have not been able to locate this band on our plates.

Table II shows the observed and calculated values of band-head frequencies along with the corresponding estimated values of intensity.

TABLE II
Band-head data with assignments

Intensity	Wavelength of heads in Å	Assignments v', v''	ν in vac. cm.^{-1}	ν calculated in vac. cm.^{-1}
2	2123.5	0, 2	47077	47076
4	2204.9	0, 3	45339	45339
3	2229.3	1, 4	44843	44843
4	2291.5	0, 4	43626	43628
4	2316.4	1, 5	43157	43157
2	2342.0	2, 6	42685	42684
4	2383.4	0, 5	41944	41941
4	2409.2	1, 6	41945	41496
4	2435.5	2, 7	41047	41048
1	2462.5	3, 8	40597	40597
4	2507.8	1, 7	39864	39860
4	2534.6	2, 8	39442	39437
2	2613.1	1, 8	38257	38249
2	2640.5	2, 9	37860	37851

4. TAIL BANDS

A fairly large number of tail bands of the CN violet system are known and have been the subject of investigation by many workers. Recently, a large number of additional tail bands are reported by Pannetier and Marsigny³ in an electrical discharge through CH_3CN vapour. In our present experiment four new tail bands are observed along with most of the known tail bands. The wavelengths and the analysis are as follows:

Wavelength in Å	$v' \quad v''$
3078.34	12, 8
3089.72	22, 14
3231.23	11, 8
3262.39	12, 9

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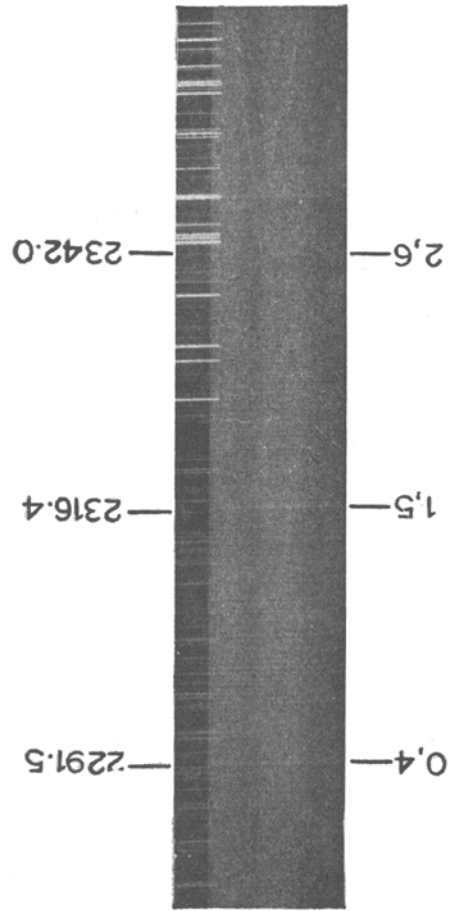
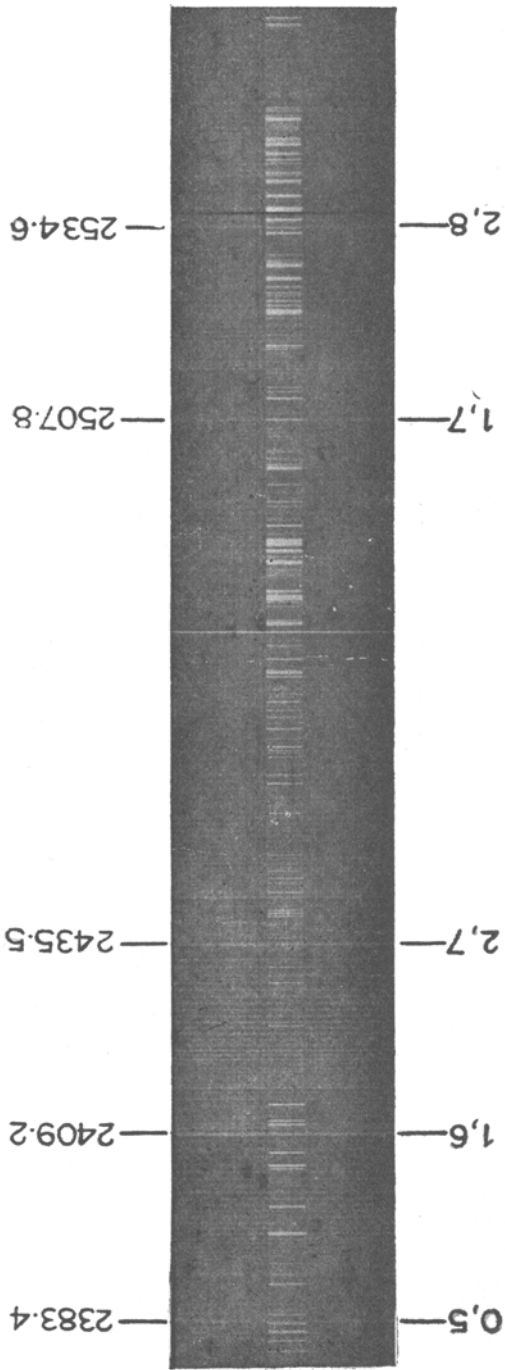


FIG. 1