

ROTATIONAL ANALYSIS OF SOME OF THE BANDS OF THE ORANGE SYSTEM OF FeO

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ABSTRACT

The orange bands of FeO are excited in a low pressure arc in oxygen and photographed at dispersions of 0.8 and 0.5 Å/mm. respectively. Rotational analysis of five of the bands shows that they involve a ${}^2\Sigma - {}^2\Sigma$ transition. The vibrational and rotational constants (in cm.⁻¹) of the upper and lower Σ states are found to be

	Lower state	Upper state
B_0	0.349 ₁	0.306 ₃
a_0	0.002 ₉	0.003 ₂
w_0	870.7	($\Delta G_{\frac{1}{2}} = 770.0$)
$w_0 x_0$	4.3 ₉	..

In the low-pressure arc it is found that highly excited atomic lines appear very much reduced in intensity in contrast to spectra excited in an arc at atmospheric pressure.

INTRODUCTION

EMISSION spectrum of iron arc in air or oxygen consists of strong bands in the orange and infra-red which are attributed to FeO molecule (Rosen, 1945). A weaker system in the blue is emitted from exploding wires (Malet and Rosen, 1945). The orange bands, in the region 5300–6600 Å, are arranged into two systems, A and B, both involving a common final level. The A

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system is found to consist of doublets though an electronic doublet could not arise from a neutral FeO molecule. Recently, Rosen in a compilation (Gatterer, Junkes and Salpeter, 1957) of molecular spectra of metallic oxides revised much of the earlier data on FeO bands and suggested further investigation of the bands be undertaken as the proposed analysis of the band systems was unsatisfactory and some of the bands were of doubtful origin. It is therefore thought worthwhile to investigate the conditions of excitation of the different band systems of FeO and study them under high resolution. The present paper deals with the A bands of the orange system and the results of their rotational analysis.

EXPERIMENTAL

The emission spectrum of the Fe arc in air or oxygen is always found to be overlapped heavily by the atomic lines of iron. Several methods of excitation like the hollow cathode discharge have been tried to see which source would favour molecular bands. Of all the sources tried, it is only a low-pressure (~ 5 cm.) arc that has been found to bring out the molecular bands almost to the exclusion of atomic lines (Dhumwad and Bass, 1963). Spectra resulting from such a low-pressure arc are photographed on the 9.15 m. concave grating spectrograph of the Argonne National Laboratory, U.S.A., in the second and third orders, at dispersions of 0.8 and 0.5 Å/mm. respectively. Eastman Kodak 103-0 plates are used to photograph the spectra. Atomic lines of thorium excited in a microwave discharge through thorium iodide, have been used as wavelength standards. The spectrograms have been measured on a photo-electric comparator and vacuum wave numbers of the spectral lines obtained using an IBM 7090 computer. Measurements of unblended and sharp lines are found to be accurate to ± 0.02 cm.⁻¹

RESULTS

(i) *Vibrational Structure*

The gross vibrational structure of the bands could be analysed into Deslandres scheme as shown in Table I. Delsemme and Rosen (1945) had earlier proposed a similar scheme. The band origins (found from the following rotational analysis) are given in italics below the band head data in Table I. As expected, the band origin data give a better fit in the vibrational scheme. It may be pointed out that v' , v'' numberings are not absolute and may have to be altered when more extensive data become available.

TABLE I

Deslandres scheme for the band heads of the orange system of FeO
 Band origin data are given in italics

$\frac{v'}{v''}$	0	1	2	3
0	17907.6 (870.8)	17036.8 (861.4)	16175.4 (852.0)	15323.4
	<i>17903.20 (870.70)</i>	<i>17032.50 (861.90)</i>	<i>16170.60 (853.12)</i>	<i>15317.48</i>
		(770.8)		
		(770.0)		
1		17807.6		
		<i>17802.50</i>		

(ii) Rotational Structure

Though the bands, in general, show rather complicated rotational structure, five of them at 5582.7, 5614.0, 5868.1, 6180.5 and 6524.2 Å are relatively free from overlap and hence are chosen for detailed rotational analysis. Figure 1 shows a representative spectrogram of the 0-0, 0-2 and 0-3 bands. Each of the bands consists of single series of *P* and *R* branches which do not show any Λ -doubling even at high *N* values of 40. Vacuum wave numbers of the *P* and *R* lines of the five bands are given in Table II. Such a structure is characteristic of a $^1\Sigma - ^1\Sigma$ transition. Combination differences of the initial states, Δ_2F' (*N*), of the bands at 5582.7, 5868.1, 6180.5 and 6524.2 Å are given in Table III and are found to be in good agreement indicating that the bands form a v'' -progression with a common v' value. They are tentatively designated as the 0-0, 0-1, 0-2 and 0-3 bands. The lower state combination differences, Δ_2F'' (*N*), of the band at 5614.0 Å agree with the corresponding values of the band at 5868.1 Å (Table III). This observation is thus in conformity with the vibrational assignment of the 5614.0 Å band as the 1-1 band in the Deslandres Scheme (Table I). The vibrational and rotational constants of the initial and final Σ states are obtained graphically (Herzberg, 1950) and given in Table IV.

The proposed analysis shows that the bands of the orange system A arise out of a singlet transition. In this connection it is interesting to note

TABLE II

Vacuum wave numbers and assignments of P and R lines of the bands of FeO

N	0-0 band at 5582.7 Å		1-1 band at 5614.0 Å	
	R (N)	P (N)	R (N)	P (N)
15	17902.88	17883.96
16	17901.99	17882.06
17	17900.98	17879.86
18	17899.94	17877.54
19	17898.76	17875.12
20	17897.16	17873.04
21	17896.38	17870.41
22	17895.04	17867.89	17794.48	17767.43
23	17893.64	17865.23	17792.98	17764.69
24	17892.15	17862.46	17791.60	17762.18
25	17890.64	17859.83	17790.22	17759.42
26	17889.01	17856.96	17788.28	17756.62
27	17887.32	17853.98	17786.46	17753.43
28	17885.59	17850.93	17784.85	17750.71
29	17883.68	17847.88	17783.14	17747.41
30	17881.69	17844.68	17780.73	17744.27
31	17879.59	17841.47	17778.62	17740.88
32	17877.54	17838.19	17776.61	17737.44
33	17875.35	17834.80	17774.84	17733.85
34	17873.04	17831.32	17771.89	17730.62
35	17870.85	17827.84	17769.42	17727.15
36	17868.65	16824.27	17766.95	17723.29
37	17866.01	17820.62	17764.19	17719.26
38	17863.39	17816.95	17761.60	17715.51
39	17860.86	17813.14	17759.02	17711.51
40	17858.14	17809.29
41	17855.41	17805.30
42	..	17801.62

TABLE II (Contd.)

N	0-1 band at 5868.1 Å		0-2 band at 6180.5 Å		0-3 band at 6524.2 Å	
	R(N)	P(N)	R(N)	P(N)	R(N)	P(N)
15	16172.56	16153.86
16	16171.91	16151.84	15320.15	..
17	16171.21	16150.00	15319.60	..
18	16170.42	16147.92	15318.95	..
19	16169.68	16146.14	15318.28	..
20	16168.84	16144.21	15317.48	..
21	16167.91	16142.00	15316.68	..
22	17026.29	16999.03	16166.94	16139.82	15315.82	..
23	17025.10	16996.74	16165.93	16137.55	15314.97	..
24	17023.74	16994.12	16164.85	16135.20	15314.02	15284.40
25	17022.28	16991.51	16163.73	16132.99	15312.93	15282.16
26	17020.59	16988.88	16162.53	16130.43	15311.83	15279.72
27	17019.20	16985.70	16161.29	16127.90	15310.71	15277.29
28	17017.66	16983.10	16159.92	16125.32	15309.45	15274.84
29	17016.21	16980.26	16158.50	16122.67	15308.28	15272.36
30	17014.13	16977.02	16156.91	16119.97	15306.97	15269.90
31	17012.33	16973.98	16155.47	16117.20	15305.60	15267.32
32	17010.40	16970.95	16153.86	16114.41	15304.33	15264.97
33	17008.40	16967.64	16152.19	16111.56	15302.76	15262.14
34	17006.16	16964.40	16150.60	16108.70	15301.32	15259.48
35	17003.79	16960.97	16148.73	16105.68	15299.76	15256.68
36	17002.12	16957.84	16147.00	16102.66	15298.16	15253.79
37	16145.05	16099.62	15296.36	15251.05
38	16143.02	16096.48	15294.61	15248.25
39	16141.15	16093.32	15292.16	15245.25
40	16139.15	16090.10	15291.18	15242.25
41	16136.92	16086.68	15289.38	15239.21
42	16083.27	..	15236.10

TABLE III

Combination differences of the observed bands of FeO

N	$\Delta_2 F''(N) = R(N-1) - P(N+1)$			$\Delta_2 F'(N) = R(N) - P(N)$		
	(1-1)	(0-1)	(0-0)	(0-1)	(0-2)	(0-3)
15	18.92	..	18.82	..
16	19.99	..	20.07	..
17	21.08	..	21.21	..
18	22.39	..	22.49	..
19	23.64	..	23.54	..
20	24.62	..	24.63	..
21	25.97	..	25.87	..
22	27.15	27.26	27.12	..
23	32.30	32.17	28.41	28.36	28.38	..
24	33.69	33.59	29.70	29.62	29.65	29.62
25	34.98	34.86	30.80	30.77	30.74	30.77
26	36.50	36.64	32.04	31.71	32.10	32.11
27	37.57	37.49	33.35	33.50	33.39	33.42
28	39.05	38.94	34.66	34.56	34.60	34.61
29	40.58	40.64	35.81	35.95	35.83	35.92
30	42.26	42.23	37.02	37.11	36.95	37.07
31	43.29	43.18	38.21	38.35	38.27	38.28
32	44.77	44.69	39.36	39.45	39.45	39.36
33	45.99	46.00	40.56	40.76	40.63	40.62
34	47.43	47.43	41.82	41.76	41.90	41.84
35	48.60	48.75	43.02	42.82	43.05	43.08
36	50.16	49.96	44.38	44.26	44.34	44.37
37	51.44	51.56	45.39	..	45.43	45.31
38	52.68	52.67	46.48	..	46.54	46.41
39	47.76	..	47.83	47.71
40	48.91	..	49.05	48.93
41	50.24	50.17
42	51.25	..

TABLE IV

Rotational and vibrational constants (in cm^{-1}) of the lower and upper electronic states of the orange system of FeO

	Lower state	Upper state
B_3	0.339 ₀	..
B_2	0.341 ₉	..
B_1	0.344 ₈	0.301 ₅
B_0	0.347 ₇	0.304 ₇
B_e	0.349 ₁	0.306 ₃
α_e	0.002 ₉	0.003 ₂
w_e	870.7	(770.0)
$w_e x_e$	4.3 ₉	..

Value in bracket refers to $\Delta G_1'$.

that the band at 5582.7 Å, designated as the 0-0 band, was observed in absorption by 'flash heating' by Bass *et al.* (1964). They had, in addition, observed the band at 5614.0 Å which is the 1-1 band, according to the present studies. Detailed investigation of the rest of the bands of the orange system will enable the identification of electronic states involved in their transition.

(iii) Intensity Features Characteristic of Low Pressure Arc

The observed spectrum further shows the following intensity features which are characteristic of the low-pressure arc. In general, highly excited atomic lines appear very much reduced in intensity in contrast to spectra excited in an arc at atmospheric pressure. This is particularly seen in Fig. 2 which shows a portion of the line spectrum of iron excited in an arc (a) at atmospheric pressure and (c) at a low pressure of 5 cm. Wavelengths (Harrison, 1939) are marked alongside the iron atomic lines. Electronic transitions (Crosswhite, 1958) of the lines and their excitation energy values, E' in cm^{-1} , are also given in Fig. 2 for ready reference. It is readily seen that all those lines that arise out of $E' \approx 50,000 \text{ cm}^{-1}$ are practically absent in the spectrum of the low-pressure arc (c) while only those corresponding to low

$E' \approx 27,000 \text{ cm.}^{-1}$ can be seen. The energy obtained in a low-pressure arc is presumed to be below the dissociation energy of the FeO molecule. This observation is further substantiated by the fact that in the low-pressure arc, the band spectrum of FeO is preferentially excited and the atomic spectrum of iron is practically absent.

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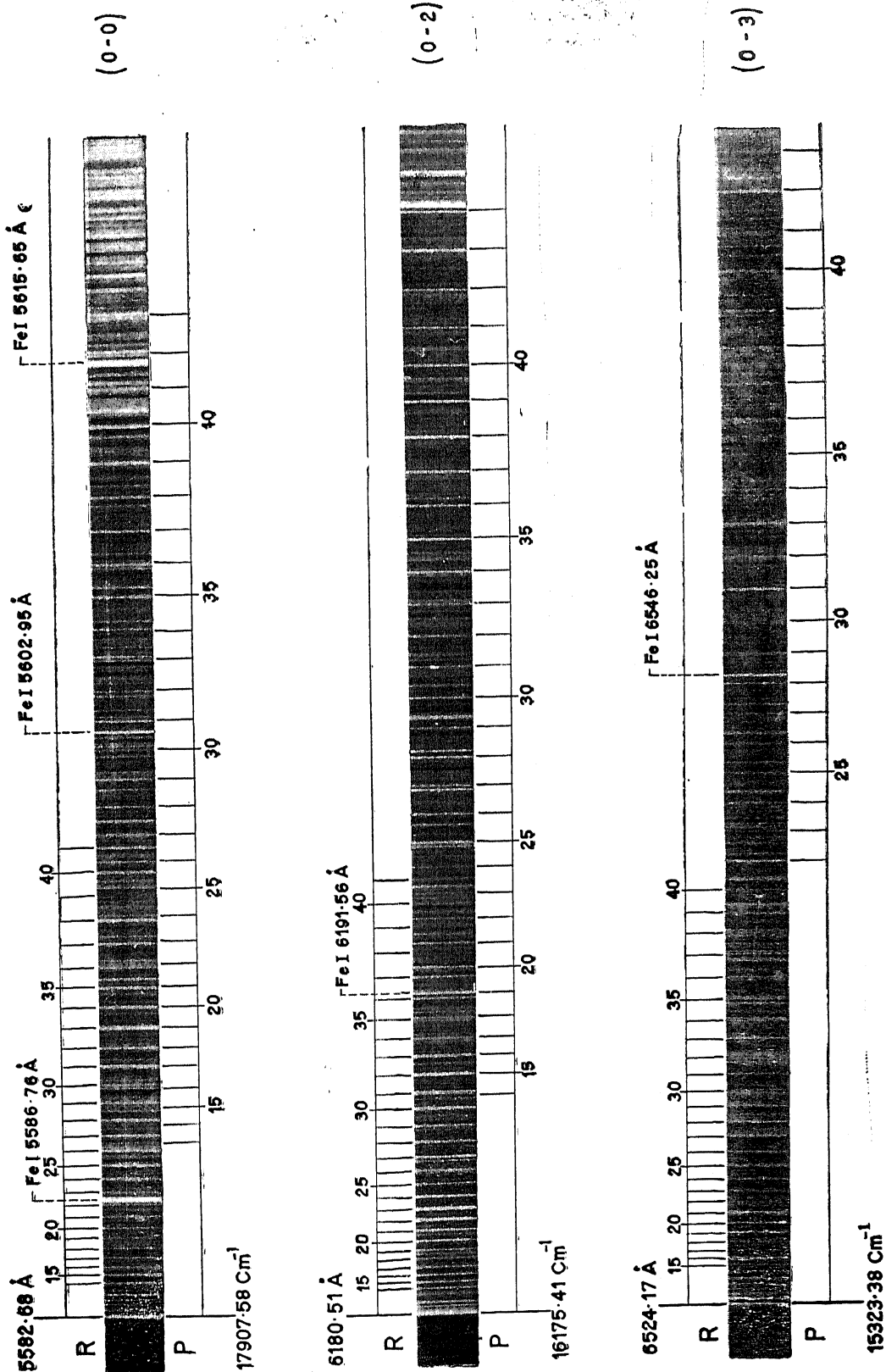


FIG. 1. Some bands of FeO.

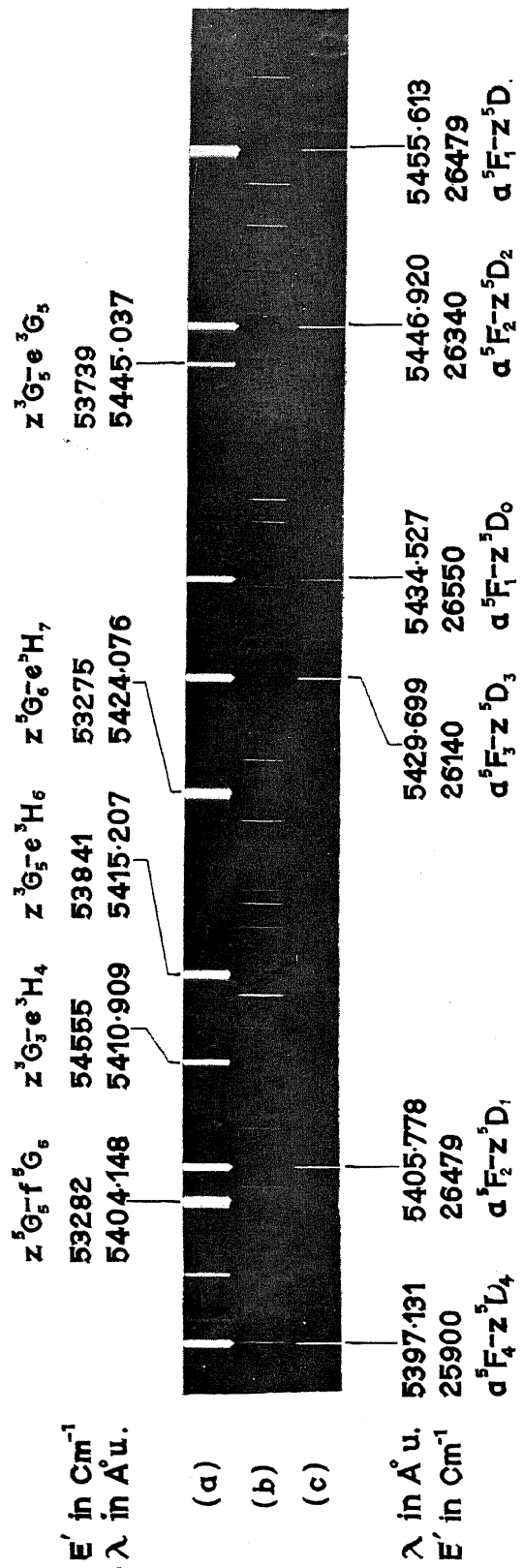


FIG. 2. Fe arc spectrum (a) in air and (c) in flowing oxygen at a pressure of 5 cm. Hg. (b) is of thorium.