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J. S. TOOMS
M. RUGHEIM

Applied Geochemistry Research Group,
Imperial College,
London SW7.

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Ground State of Gaseous FeO

THE electronic states of the gaseous diatomic oxides of the transition metals are not yet well understood. In the first transition series, the ground state of ScO is known¹ to be . . . $\sigma^2 \Sigma^+$, that of VO is² . . . $\delta^2 \sigma^4 \Sigma^-$, and the ground state of TiO appears³ to be . . . $\delta \sigma^3 \Delta$. The lowest known state of CrO seems⁴ to be . . . $\sigma \delta^2 \pi^5 \Pi$, but . . . $\delta^3 \sigma^3 \Delta$ has also been suggested⁵. There is some evidence of a vertical variation in the relative stabilities of the outer σ and δ orbitals, so that, for example, the ground state of TaO is⁶ . . . $\delta \sigma^2 \Delta$, and that of ZrO is not . . . $\delta \sigma^3 \Delta$, but⁷ . . . $\sigma^2 \Sigma^+$, although for NbO⁺ the ground state may⁸ again be Δ .

The orange bands of FeO at $\lambda \sim 6000 \text{ \AA}$ have been known for many years⁹. More recently they have been observed in absorption in flash photolysis¹⁰ and in flash heating¹¹. Low pressure arcs provide a better source of the bands in emission, and some of the lines of bands of a $v' = 0$ progression have been analysed as a ${}^1\Sigma - {}^1\Sigma$ transition¹². It is difficult to accept this analysis, for (a) ground state Fe (5D) + O (3P) cannot give singlet molecular states; (b) the internuclear distance derived for the lower state seems to be much too large in comparison with other molecules of the series.

VALUES OF r_e'' (Å)				
ScO	TiO	VO	CrO	FeO
1.668	1.620	1.589	(1.627)	— ? 1.97

We have recently taken new spectrograms of the four bands of FeO discussed by Dhumwad and Narasimham¹² in similar experimental conditions. Wavelengths of the R heads are given in Table 2. The shorter wavelength part of each band consists chiefly of two branches, R and P , but there are obvious perturbations, and at longer wavelengths the density of lines increases markedly. About 270 lines have been assigned to R and P branches of the 0-0, 0-1, 0-2 and 0-3 bands. Our assignment differs from that of the previous analysis. Some values of the common upper state differences, $\Delta_2 F''(J)$, which provide the key to the analysis, are given in Table 1. The values of $\Delta_2 F''(J)$ are within errors of measurement represented by the simple expressions

$$\Delta_2 F''_v = 4 B''_v (J + \frac{1}{2}) - 8 D''_v (J + \frac{1}{2})^3$$

and the values of D''_v fit well with that subsequently obtained from Kratzer's relation, $D \sim 4B^3/\omega^2$. The upper state is too perturbed (by states of smaller B value) for any useful value of D' to be obtained, but it seems certain that the branches are R and P and not, for example, 3R and R ; in other words, that they are main and not satellite branches.

The most likely interpretation is that the lines analysed arise from the $\Omega' = 0 - \Omega'' = 0$ part of a multiplet $\Sigma - \Sigma$ transition. The isoelectronic molecule MnF is thought¹³ to have a ${}^7\Sigma$ ground state: the most likely ground state

Table 1. VALUES OF $\Delta_2 F''(J)$

J	0-0	0-1	0-2	0-3
20	38.51	38.55	38.48	38.47
21	40.06	40.10	40.14	40.06
22	42.08	42.08	42.12	42.18
23	43.96	43.93	44.02	43.96
24	45.95	45.82	45.91	45.89
25	47.75	47.74	47.75	47.79
26	49.75	49.67	49.73	49.74
27	51.67	51.65	51.69	51.69
28	53.53	53.50	53.50	53.46
29	55.35	55.36	55.34	55.37
30	57.31	57.30	57.29	57.22
31	59.15	59.14	59.19	59.07
32	61.10	61.05	61.10	61.03
33	62.90	62.98	62.94	62.94
34	64.82	64.84	64.80	64.83
35	66.63	66.66	66.64	66.64
36	67.39	67.47	67.45	67.39
37	70.21	70.25	70.23	70.24
38	72.27	72.15	72.18	72.16
39	74.16	74.14	74.16	74.16
40	75.94	75.99	—	75.93

for FeO is ${}^5\Sigma$ or ${}^7\Sigma$. In either case, the $\Omega = 0-0$ transition may, by spin-orbit coupling, be somewhat separated from $\Omega = 1-1, 2-2, \dots$ sub-bands. From the apparent value of B''_v , a value of the internuclear distance in gaseous FeO may be derived, $r_e = 1.626 \text{ \AA}$: this value is close to those observed in ScO, TiO, VO and CrO, as might be expected, but it is subject to unknown errors arising from spin-orbit, spin-spin and spin-rotation interactions. It may be noted here that no expressions for the energy levels of Σ states of multiplicity greater than quartet have yet been given, except for the limiting case where λ/B is small¹⁴.

Table 2. SUMMARY OF CONSTANTS

$v' - v''$	R head (Å)	B''_v (cm ⁻¹)	$10^7 D''_v$ (cm ⁻¹)
0-0	5582.65	0.51083 ± 45	6.6 ± 1.5
0-1	5868.00	0.50707 ± 33	6.45 ± 1.23
0-2	6180.53	0.50330 ± 21	6.25 ± 0.72
0-3	6524.15	0.49969 ± 48	7.9 ± 2.1

The limits given are three times the standard errors and, for example, 0.51083 ± 45 is written for 0.51083 ± 0.00045.

Lower state constants:

$$G_v = 880.53 (v + \frac{1}{2}) - 4.63 (v + \frac{1}{2})^2$$

$$B_v = 0.51271 - 0.00376 (v + \frac{1}{2})$$

$$r_e = 1.625 \text{ \AA}; \alpha(\text{Pekeris}) = 0.00359$$

$$10^7 D (\text{Kratzer}) = 6.95$$

Upper state constants:

$$v_{00} \sim 19,700; B_0 = 0.471 \text{ cm}^{-1}; r_0 = 1.69 \text{ \AA}$$

Values of the constants obtained in the present work are summarized in Table 2. Further progress with this spectrum, as with those of similar molecules, demands a source of lower rotational temperature; the final answer may lie in flash-photolysis combined with high resolution.

R. F. BARROW
M. SENIOR

Physical Chemistry Laboratory,
University of Oxford.

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