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UNIVERSITY OF OKLAHOMA RESEARCH INSTITUTE CH INSTITUTE
Norman, Oklahoma

Submitted by

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CHARACTERIZATION OF THE ALUMINUM OXIDES AND DIATOMIC ALUMINUM

Excitations of electronic spectra in the systems $\text{Al-O}_2\text{-N}_2$, Al-Al , Al-N_2 and $\text{Al-Al}_2\text{O}_3\text{-He}$ have been investigated at the University of Oklahoma Naval Ordnance Laboratory and Vanderbilt University. These studies suggested fruitful lines of research for complete descriptions of the spectrothermochemistry of AlO , AlN and Al_2 .

A. Aluminum arc in air ($\text{Al-O}_2\text{-N}_2$)

Since the only previous full development of emission by any of the species was by means of a four to eight ampere aluminum arc¹ the first step was to extend the arc spectrum. This was most practical in the red where the bands are analogous to those already observed for molecules isoelectronic with AlO . At the low currents of eight to ten amperes, the very unsteady flame of the arc was photographed at a dispersion of $5 \text{ \AA}/\text{mm}$.² A complex band system was observed of intensity of about five per cent of that of the green bands of AlO , and extending from $7500 \text{ \AA}$ to the infrared limit of Kodak I-M plates. Analysis of the structure was not practical.

B. Aluminum-aluminum oxide arc in air ($\text{Al-Aluminum-N}_2\text{-O}_2$)

It was evident that higher dispersion photographs of the new "red" bands were necessary if analysis was to be effected. This would require long

1 Pearse and Gaydon, "Identification of Molecular Spectra" 2nd ed. p. 51 and Plate I, the well known "green bands" of AlO , $\lambda\lambda$ 4400-5400.

2 Three-meter grating spectrograph of the U. S. Naval Ordnance Laboratory, White Oak, Maryland.

CHARACTERIZATION OF THE ALUMINUM OXIDES AND OF DIATOMIC ALUMINUM

Excitations of electronic spectra in the systems $\text{Al-O}_2\text{-N}_2$, $\text{Al-alundum-O}_2\text{-N}_2$, Al-N_2 and $\text{Al-Al}_2\text{O}_3\text{-He}$ have been investigated at the University of Oklahoma, the Naval Ordnance Laboratory and Vanderbilt University. These studies have suggested fruitful lines of research for complete descriptions of the spectra and thermochemistry of AlO , AlN and Al_2 .

A. Aluminum arc in air ($\text{Al-O}_2\text{-N}_2$)

Since the only previous full development of emission by any of the desired species was by means of a four to eight ampere aluminum arc¹ the first attempt was to extend the arc spectrum. This was most practical in the red where a band system analogous to those already observed for molecules isoelectronic with AlO was expected, and where atomic lines of aluminum are not plentiful and strong. Using currents of eight to ten amperes, the very unsteady flame of the arc was photographed at a dispersion of $5 \text{ \AA}/\text{mm}$.² A complex band system was observed, with intensity of about five per cent of that of the green bands of AlO , and strongest from $7500 \text{ \AA}$ to the infrared limit of Kodak I-M plates. Analysis of the structure was not practical.

B. Aluminum-aluminum oxide arc in air ($\text{Al-alundum-N}_2\text{-O}_2$)

It was evident that higher dispersion photographs of the new "red bands" were necessary if analysis was to be effected. This would require longer exposures

1 Pearse and Gaydon, "Identification of Molecular Spectra" 2nd ed., p. 51 and Plate I, the well known "green bands" of AlO , $\lambda\lambda$ 4400-5400.

2 Three-meter grating spectrograph of the U. S. Naval Ordnance Laboratory, White Oak, Maryland.

(ca. 45 minutes) and, therefore, a steadier arc. The latter was achieved by packing the aluminum electrode tips in alundum cement and by carrying the heat of the arc away by water-cooling the aluminum rods. It was hoped that the TiO_2 and ZrO_2 in the alundum cement would not give enough TiO and ZrO to mask the desired "red bands." For example, Phillips¹ found that observation of red bands of TiO using a 21-foot grating required exposure of a high tension arc for 20 minutes at $6600 \text{ \AA}$, and 60 minutes at $8000 \text{ \AA}$.

A seven to eight ampere arc between the modified electrodes was exposed for 40 minutes at a dispersion of $1.25 \text{ \AA/mm}$.² The band structure was very complex over the region $6500\text{-}9000 \text{ \AA}$. Lines were so close together that branches could be picked out only after the wave number measurement of the more than 20000 lines. Even then the lines were so badly superimposed that it was difficult to find branches with reasonable intensity distributions. Thus the only outstanding features were regularly spaced lines at 7340 and $7160 \text{ \AA}$ on an otherwise clean background. These features indicate a B-value of about 0.2 cm^{-1} , as would be expected for Al_2 . However, no intensity alternation was observed and, in the absence of Q-branches, the analysis could not be carried further. It is likely that other tentative bands (of quite different spacing) could be confirmed if the spectrum could be simplified and/or photographed at still higher resolution. The higher resolution could be obtained only in "cooler" sources which would give narrower spectral lines, as discussed in D and E. Lower effective temperatures will also

1 J. G. Phillips, *Astrophys. J.* 114, 152 (1951).

2 Twenty-one foot grating spectrograph at Johns Hopkins University.

simplify the spectrum by involving fewer vibrational states. But it is evident from analysis to date that several emitters are responsible for the spectrum, and the greatest simplification should be achieved by viewing them one at a time, as discussed particularly in C.

C. Aluminum arc in nitrogen (Al-N_2)

To test our impression that more than one emitter contribute to the new red bands of the aluminum arc, a closed arc was designed wherein pure Al tips fit into water-cooled Al holders, which, in turn, slide through O-ring seals into a closed cylinder of brass. This arc was burned at about eight amperes in air and in N_2 , each at one atmosphere, and the emission was photographed at a dispersion of 5 Å/mm. Atomic aluminum lines are observed much more strongly in the flame in a nitrogen atmosphere--where the band structure is selectively weaker--than from the flame in air. Particularly at lower wavelengths, bands which clearly persist in nitrogen can presumably be assigned to AlN . For the desirable study of the AlN bands at higher dispersion, the arc holder needs to be redesigned so that longer burnings are possible. This is also desirable for the study of the arc burning in He-O_2 mixtures, where heat dissipation is a much greater problem. Modified designs for closed arcs are being considered.

D. Stainless steel hollow cathode containing $\text{Al-Al}_2\text{O}_3$ ($\text{Al-Al}_2\text{O}_3\text{-He}$)

We operated a hollow-cathode discharge tube of conventional design (pyrex envelope) at currents of 25-500 ma. in an attempt to observe, for the first time in a discharge tube, the green bands of AlO . The green bands developed at 450-500 ma. and were very intense. Extensive study of the green bands at the higher resolution

made possible by this "low" temperature source, and investigation of accompanying emission in other regions (red bands?) at correspondingly high resolution, seems very desirable; in fact, may be termed the most promising hope for further study of AlO. The major defect in the discharge tubes first used was that the thin-walled cathodes employed could not withstand attack by hot aluminum for an appreciable length of time. It is felt that a heavier cathode, or perhaps one made of tungsten, will contain the aluminum for, say, thirty minutes. Such a cathode will be tried.

E. King furnace

A second method of reducing the temperature of observation is being explored during summers at the Naval Ordnance Laboratory. A high temperature electric furnace, suitable for absorption or emission spectroscopy,¹ has now been completed by the shop there. The green bands of AlO have already been observed in emission as an impurity in such a furnace¹ and it is hoped that with charges of Al-Al₂O₃ in an inert atmosphere the spectrum of AlO may be explored rather completely.

1 P. B. Zeeman, Can. J. Phys. 32, 9 (1954).

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