

slope of the derivative curves (Fig. 3) of the respective (10 and 18) electron systems. Our earlier calculated values were about 0.8 e.v. lower. Since the agreement was so close the present procedure seemed entirely justified.

The electron affinity of argon was estimated by assuming that the additional electron was added to the $3d$ or $4s$ shell. However the long extrapolation involved will only permit the statement that A^- is most likely unstable. Negative ions have been reported in argon¹⁷ but they may be due to an impurity or to excited atoms.

¹⁷ H. A. Barton, *Nature* **114**, 826 (1927).

The oxygen atom and the sulphur atom have large electron affinities as was to be expected. Of the other atoms dealt with, mercury has a large electron affinity of Hg^- ions have been reported in the mass-spectrograph by Nielsen.¹⁸

The general trend of these estimated electron affinities is entirely as expected.

I am indebted to the research grant committee of the Graduate School of the University of Minnesota for financial assistance which enabled me to have Dr. Donald L. Fuller assist me with the calculations.

¹⁸ W. M. Nielsen, *Phys. Rev.* **27**, 716 (1926); **31**, 1123 (1928); *Proc. Nat. Acad. Sci.* **16**, 721 (1930).

The Spectrum of Gallium Oxide

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(Received May 23, 1934)

The spectrum of gallium oxide has been photographed with a 21-foot grating. A band system lying in the region 3800–4200Å has been identified as a ${}^2\Sigma \rightarrow {}^2\Sigma$ transition and a vibrational quantum analysis is given. The band-heads are approximately located by the equation

$$\nu = \left. \begin{array}{l} 25,706.43 \\ 25,709.04 \end{array} \right\} + 763.63(v' + \frac{1}{2}) - 3.89(v' + \frac{1}{2})^2 - 767.69(v'' + \frac{1}{2}) + 6.34(v'' + \frac{1}{2})^2.$$

The spectrum of indium oxide is briefly discussed.

UNTIL recently there has been little study made of the band spectra of gallium and indium compounds. In 1916 Browning and Uhler,¹ while studying the atomic spectrum of gallium, discovered six new bands and eleven closely-spaced lines (believed also to be bands), and they suggested that these came from GaO or Ga_2 . Within the past year work has been reported on the spectra of the halides of gallium and indium.^{2, 3, 4} In a recent comprehensive

¹ P. E. Browning and H. S. Uhler, *Am. J. Sci.* **41**, 351 (1916).

² A. Petrikaln and J. Hochberg, *Zeits. f. Physik* **86**, 214 (1933).

³ E. Miescher and M. Wehrli, *Helv. Phys. Acta* **6**, 256, 457 (1933).

study of these halide spectra Miescher and Wehrli⁴ have discussed briefly the spectrum of GaO and have given vibrational quantum assignments to the bands observed. The analysis to be reported in this paper is based on spectrograms of this same system taken at higher dispersion. Measurements of the band-heads check those of Miescher and Wehrli and several additional bands have been noted. The more complete data now at hand indicate that the quantum assignments made by these workers are not entirely correct.

⁴ E. Miescher and M. Wehrli, *Helv. Phys. Acta* **7**, 357 (1934).

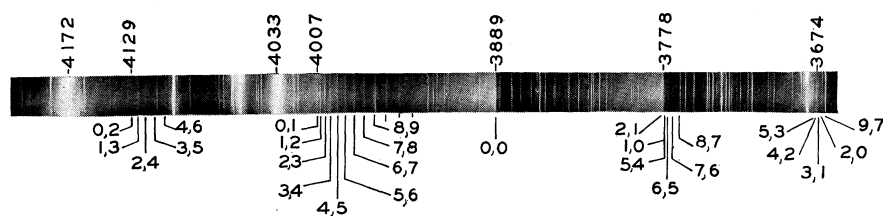


FIG. 1. Spectrogram of the GaO spectrum taken in the second order of a 21-foot grating.

EXPERIMENTAL PROCEDURE

Gallium metal was placed in the lower electrode of a copper arc which was run in air. The arc was operated at low currents (2 to 3 amperes) to reduce the continuous radiation to a minimum and prevent sputtering of the liquid metal. Photographs were taken in the first, second, and third orders of a 21-foot grating where the dispersion was approximately 5.2, 2.47, and 1.5 Å/mm, respectively. The exposure times ranged from $\frac{1}{2}$ to $2\frac{1}{2}$ hours although the difficulties in operating the arc, due to oxidation of the metal, made the actual running times a great deal longer.

RESULTS

This band system lies near the atomic resonance lines of gallium and covers the region 3890–4130 Å. All of the bands degrade to the red and most of the heads are double, the average separation being 2.61 cm^{-1} . Fig. 1, a spectrogram taken in the second order of the 21-foot grating, shows the main portion of the spectrum and indicates how the bands are grouped in sequences, each of which is well separated from the next. The wave numbers, quantum assignments, and estimated intensities are given in Table I, and a matrix diagram of intensities in Table II. The positions of all the band-heads in this system are given approximately by the equation:

$$\nu_{\text{head}} = \left. \begin{array}{l} 25,706.43 \\ 25,709.04 \end{array} \right\} + 763.63(v' + \frac{1}{2}) - 3.89(v' + \frac{1}{2})^2 - 767.69(v'' + \frac{1}{2}) + 6.34(v'' + \frac{1}{2})^2.$$

This is undoubtedly a ${}^2\Sigma \rightarrow {}^2\Sigma$ system in which the R_2 and R_1 branches form the close double

heads. The near equality of the ω_e values, which is characteristic of the other oxides in the third column of the periodic table, causes the bands to be grouped in long sequences which lie on a narrow Condon parabola. The $\Delta v = +1$ and $+2$ sequences have convergence points at low v'' values (1 and 3, respectively), and the bands of higher v'' values lie to the violet of this point, some of them coinciding with the first bands of the sequence. In each case the bands are crowded together giving the impression of a single band with several double heads. Because of low dispersion Browning and Uhler, and Miescher and Wehrli measured each of these sequences as a single band.

In the $\Delta v = 0$ sequence the convergence point occurs immediately so that the 1,1 band coincides with the 0,0 band. The intensity in this sequence drops off so rapidly that no bands beyond the 2,2 have been observed. The $\Delta v = -1$ and -2 sequences have a rather striking appearance because they begin immediately to diverge to the violet. This same phenomenon has been found in the spectra of CaF and SrF,⁵ which are also isoelectronic molecules and probably have a structure somewhat similar to that of GaO. Miescher and Wehrli did not observe the first band in this sequence but did observe the second. However, they assumed that several bands, crowded together at the beginning of the sequence, had not been measured, and therefore they gave too high a quantum assignment to the remaining bands.

The writer has found evidence for a second band system in this spectrum lying in the region 4300–4900 Å, but the bands are faint, many of them being entirely obscured by the continuous background which it was found impossible to

⁵ R. C. Johnson, Proc. Roy. Soc. A122, 189 (1929).

TABLE I. Wave numbers, quantum assignments and intensities of lines of GaO.

| v', v'' | ν (cm ⁻¹) | Int. | v', v'' | ν (cm ⁻¹) | Int. |
|-----------|---------------------------|------|--------------|---------------------------|------|
| 0,2 | 24,208.20 24,211.84 | 3 | 11,12 | 25,349.11 | 1 |
| 1,3 | 24,233.64 24,236.94 | 4 | 0,0 (1,1) | 25,704.51 | 10 |
| 2,4 | 24,262.95 24,266.38 | 4 | 2,2 | 25,709.20 25,711.48 | 0 |
| 3,5 | 24,299.18 24,301.62 | 4 | 2,1 (3,2) | 26,451.85 26,454.09 | 9 |
| 4,6 | 24,339.22 24,343.08 | 4 | 1,0 (4,3) | 26,457.94 26,460.10 | 9 |
| 5,7 | 24,384.16 24,387.31 | 4 | 5,4 | 26,465.12 26,467.43 | 4 |
| 6,8 | 24,436.97 | 2 | 6,5 | 26,480.05 26,482.01 | 3 |
| 0,1 | 24,949.99 24,950.95 | 7 | 7,6 | 26,498.72 26,501.18 | 2 |
| 1,2 | 24,963.00 24,965.10 | 8 | 8,7 | 26,524.24 | 1 |
| 2,3 | 24,981.41 24,983.09 | 8 | 5,3 (6,4) | 27,183.64 27,185.49 | 6 |
| 3,4 | 25,004.21 25,006.15 | 8 | 4,2 (7,5) | 27,187.85 27,189.92 | 5 |
| 4,5 | 25,033.01 25,034.64 | 8 | 3,1 (8,6) | 27,192.96 27,197.06 | 4 |
| 5,6 | 25,064.14 25,067.18 | 7 | 2,0 | 27,204.94 27,209.16 | 0 |
| 6,7 | 25,100.70 25,103.98 | 7 | 9,7 | 27,219.17 | 0 |
| 7,8 | 25,145.47 | 7 | 6,3 | 27,899.22 | 1 |
| 8,9 | 25,189.75 | 5 | 10,7 | 27,904.46 27,907.95 | 0 |
| 9,10 | 25,235.40 | 5 | 5,2 | 27,915.7 | 0 |
| 10,11 | 25,292.29 | 3 | 7,3 | 28,605.8 | 0 |

avoid. For this reason the present data are insufficient for a quantum analysis.

TABLE II. Matrix diagram of the GaO bands. Intensities in () represent bands that coincide with previous ones in the same sequence.

| v' | v'' | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|------|-------|----|------|-----|-----|-----|-----|-----|---|---|---|----|----|----|
| 0 | | 10 | 7 | 3 | | | | | | | | | | |
| 1 | | 9 | (10) | 8 | 4 | | | | | | | | | |
| 2 | | 0 | 9 | 0 | 8 | 4 | | | | | | | | |
| 3 | | | 4 | (9) | 8 | 4 | | | | | | | | |
| 4 | | | | 5 | (9) | 8 | 4 | | | | | | | |
| 5 | | | | 0 | 6 | 4 | 8 | 4 | | | | | | |
| 6 | | | | | 1 | (6) | 3 | 7 | 4 | 2 | | | | |
| 7 | | | | | 0 | | (5) | 2 | 7 | 7 | | | | |
| 8 | | | | | | | | (4) | 1 | | 5 | | | |
| 9 | | | | | | | | | 0 | | | 5 | | |
| 10 | | | | | | | | | 0 | | | | 3 | |
| 11 | | | | | | | | | | | | | | 1 |

Photographs have also been taken of the InO spectrum which consists mainly of a large group of bands lying between the two resonance lines of indium, 4102 and 4511A. The stronger bands degrade to the red but there are many which are shaded to the violet. This, together with the great irregularity in the distribution of the bands, suggests that there are two band systems overlapping in this region.

A prominent feature of this spectrum is the continuum which extends out from the resonance lines of indium to the high frequency side. Cases of such apparent broadening of resonance lines are known for the metals thallium, zinc, cadmium, mercury and magnesium,⁶ as well as for the gas helium.⁷ This continuum is undoubtedly due to semi-stable molecules of In₂. Further work is being done on this spectrum and it is hoped that a quantum analysis of InO may be possible in the near future.

The writer is indebted to Professor W. W. Watson for the suggestion of the problem, and the many discussions which have led to the quantum analysis presented here.

⁶ H. Hamada, *Phil. Mag.* **12**, 50 (1931).

⁷ J. J. Hopfield, *Astrophys. J.* **72**, 133 (1930).

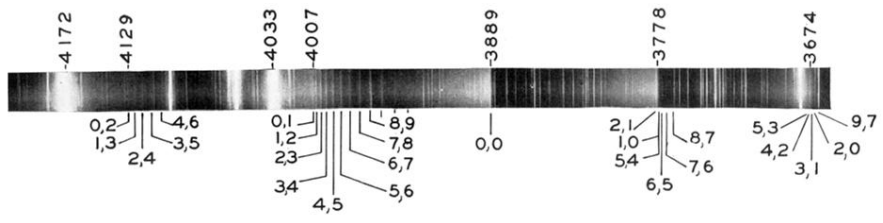


FIG. 1. Spectrogram of the GaO spectrum taken in the second order of a 21-foot grating.