$v^\prime - v^{\prime\prime}$ 

length sides and are in the neighborhood of 24,980, 25,290, and 25,594 cm<sup>-1</sup>. If the three regions correspond to the -1, 0, and +1 sequences, respectively, the difference between the first two numbers should give an approximate value of  $\omega''$ , while the difference between the second and third numbers should correspond roughly to  $\omega'$ . Thus  $\omega''$  for this system may be expected to be about 310 cm<sup>-1</sup>, and  $\omega'$  about 304 cm<sup>-1</sup>. This value of  $\omega''$  is in good agreement with the value, 312 cm<sup>-1</sup>, for the other system.

The author wishes to express his appreciation

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#### PHYSICAL REVIEW

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### The Spectrum of Indium Oxide

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A rather complex spectrum of InO lying between the two In resonance lines at 4102A and 4511A is described. Most of the band heads are assigned to a  ${}^{2}\Pi \rightarrow {}^{2}\Sigma$  system with the frequencies of the main  $(R_{2}+Q_{2}?)$  heads given by the formula  $\nu = 23,595.10+626.66(v'+\frac{1}{2})-3.40(v'+\frac{1}{2})^{2}-703.09(v''+\frac{1}{2})+3.71(v''+\frac{1}{2})^{2}+0.285(v''+\frac{1}{2})^{3}$ .  $\nu_{e}$  for the other spin component is at 23,033.10. The large cubic term causes rapid convergence of the few band sequences, giving rise to prominent "tail" bands.

I N a report of the analysis of a band system due to the GaO molecule, Marjorie L. Guernsey<sup>1</sup> discussed briefly a complex spectrum of indium oxide lying largely between the two In resonance lines at 4102A and 4511A. Although the experimental conditions indicated the InO molecule to be the emitter, no obvious regularities in the distribution of bands were noted. And since among the band heads degrading predominantly to the red there occur a number of violet degrading heads, it was suggested that there are two InO band systems overlapping in this region. A reproduction of this spectrum is given in Fig. 1.

Spectra are known<sup>2</sup> for the diatomic oxides of all the other elements of Group III of the periodic table excepting Tl and Ac. These band systems are all transitions between  ${}^{2}\Pi$  and  ${}^{2}\Sigma$  electronic states, with a  ${}^{2}\Sigma$  state lying lowest in the level scheme for each molecule. Similarly we find that the vast majority of the InO band heads constitute either a  ${}^{2}\Pi \rightarrow {}^{2}\Sigma$  or a  ${}^{2}\Sigma \rightarrow {}^{2}\Pi$  system, with the former designation preferred because of the energy level arrangement of the related molecules. The complexity of the spectrum arises from the near equality of the doublet interval in the  ${}^{2}\Pi$  state with many of the  $\Delta G(v)$  values in both states, producing interlacing of the band sequences, as well as the rapid convergence of these sequences to cause "tail" bands. We give the details below.

TABLE VI. MgI bands.

to Professors Alpheus W. Smith and R. V. Zum-

stein for valuable discussions and suggestions

given during the course of this investigation.

-1

24010.6

16.4

19.2

26.2

28.9 36.0 0

24322.2

29.0

36.3

A Tl arc burning in air gives rise to no oxide band spectrum in the region of the resonance lines of Tl I. We conclude that one or both of the corresponding Tl O levels are unstable repulsion states, a situation harbingered by the fairly low stability of the lower state of the InO band system discussed in the present paper. This instability is to be contrasted with the apparently rather large dissociation energy of the ground state and the relative abundance of electronic levels in the intervening LaO molecule<sup>3</sup> in this group.

+1

24640.2

45.5

50.7

<sup>&</sup>lt;sup>1</sup> M. L. Guernsey, Phys. Rev. 46, 114 (1934).

<sup>&</sup>lt;sup>2</sup> Cf. W. Jevons, *Report on Band Spectra of Diatomic Molecules*, or H. Sponer, *Molekülspektren*, for constants of the known energy levels and references to original papers.

<sup>&</sup>lt;sup>3</sup> W. Jevons, Proc. Phys. Soc. 41, 520 (1929).

| v', v'' | ν(cm <sup>-1</sup> )  | Int.                                  | v', v'' | ν(cm <sup>−1</sup> )  | Int.                                     | v', v'' | ν(cm⁻1)   | Int.             | v', v'' | ν(cm <sup>-1</sup> )  | Int.             |
|---------|---|---------------------------------------|---------|---|--|---------|---|------------------|---------|---|------------------|
| 0,0     | 22994.1<br>23057.2<br>23557.0<br>23619.2                                | 1<br>2<br>9<br>7                      | 2,3     | at.<br>at.<br>22735.0   | 3  | 5,5     | $\begin{array}{c} 22668.4\\ 22728.2\\ 23231.5\\ 23284.3\end{array}$ | 2<br>0<br>4<br>4 | 7,6     | $\begin{array}{c} 23215.5\\ 23254.9\\ 23771.9\\ 23817.5\end{array}$ | 5<br>4<br>1<br>1 |
| 0,1     | $22340 \\ \\ 22864.2 \\ 22940.5$  | 2<br>2<br>0                           | 3,1     | 24150.0<br>24178.8<br>24703.9   | 1<br>6<br>1                              | 5,6     | at.<br>at.<br>22604<br>22668.4                                      | 1<br>2           | 7,7     | $22604.0 \\ 22666.3 \\ \\ 23215.5$                                  | 5                |
| .1,0    | $23616.4 \\ 23666.7 \\ 24178.8 \\ 24227.2$                              | 9<br>9<br>6<br>6                      | 3,2     | 23463.5<br>24016.2<br>24061.0   | 2<br>7<br>10                             | 6,3     | at.<br>at.<br>25121.2   | 1                | 7,8     | $\frac{at.}{at.}$   | 1                |
| 1,1     | $\begin{array}{c} 22922.4\\ 22983.0\\ 23481.7\\ 23542.8\end{array}$     | 3<br>2<br>7<br>0                      | 3,3     | $\begin{array}{c} 22784.1 \\ 22840.4 \\ 23344.7 \\ 23399.6 \end{array}$ | $\begin{array}{c}1\\2\\10\\2\end{array}$ | 6,4     | 23905<br>   | 1                | 8,5     | at.<br>at.<br>24968.8   | 0                |
| 1,2     | <i>at.</i><br><i>at.</i><br>22784.1<br>22866.4                          | 0<br>2                                | 3,4     | at.<br>at.<br>22682.4<br>22750.5  | 1<br>5                                   | 8,6     | <i>at.</i><br><i>at.</i>  |                  | 10,7    | at.<br>at.<br>24860.9<br>24887.8                                    | 1<br>1           |
| 2,0     | $24227.2 \\ 24258.0 \\ \\ 24825.3$                                      | 6<br>5<br>3                           | 4,2     | $\begin{array}{c} 24053.6\\ 24083.5\\ 24609\\ 24647.6\end{array}$       | 0<br>2<br>1<br>0                         | 8,7     | 23732.7   | 5                | 10,8    | $\frac{23711.3}{at.}$   | 3                |
| 2,1     | 23542.8   | 0<br>3<br>1                           | 4,3     | 23386.2   | 6<br>4<br>4                              | 8,8     | 22591.6   | 2                | 10,9    | 23151.0   | 1                |
| 2,2     | $\begin{array}{c} 22850.2 \\ 22910.1 \\ 23410.9 \\ 23476.6 \end{array}$ | 2<br>0<br>10<br>1                     | 4,4     | $\begin{array}{c} 22724.5\\ 22781.7\\ 23283.3\\ 23342.6\end{array}$     | 1<br>1<br>4<br>10                        | 9,6     | at.<br>at.<br>24904.9<br>24928.9                                    | 2<br>0           | 10,10   | 22604.0<br>22666.3<br>23157.3                                       | 2<br>5<br>6      |
| 4,5     | at.<br>at.<br>22635<br>22709.0  | 2<br>0                                | 6,5     | $\begin{array}{c} 23261.8\\ 23306.2\\ 23817.5\\ 23865.3\end{array}$     | 1<br>4<br>0<br>3                         | 9,7     | 23743.6<br>23771.9<br><i>at.</i><br><i>at.</i>                      | 4<br>1           | 11,10   | 23709.6   | 1                |
| 5,2     | $\begin{array}{c} 24647.6\\ 24663.6\\ 25203.1\\ 25217.1\end{array}$     | 0<br>1<br>0<br>0                      | 6,6     | $\begin{array}{c} 22626\\ 22682.4\\ 23189.3\\ 23241.2 \end{array}$      | 1<br>1<br>1<br>7                         | 9,8     | 23157.3<br>23204.6<br>23708.3<br>23751.6                            | 6<br>1<br>2<br>1 | 12,11   | 23735.1   | 3                |
| 5,3     | 23971.8<br>24001<br><i>at.</i><br><i>at.</i>                            | $\begin{array}{c} 0 \\ 4 \end{array}$ | 6,7     | $\frac{at.}{at.}$ 22635   | 2  | 9,9     | 22591.6<br>   | 2                |         | н н.  |                  |
| 5,4     | 23311.7<br>23353.3<br>23875.8   | 4<br>0<br>3                           | 7,5     | 23843.1<br>23865.3<br><i>at.</i><br><i>at.</i>                          | 2<br>3                                   | 9,10    | $\frac{at.}{at.}$   | 5                |         |   |                  |

 TABLE I. Wave numbers, quantum assignments and intensities of band heads in the InO spectrum. at. denotes obliteration by the strong continuum associated with the In resonance lines.

## EXPERIMENTAL PROCEDURE

The light source was a 220-volt d.c. arc in air carrying 3 amperes between an anode of indium metal packed into a shallow copper cup and a water-cooled copper cathode. The indium metal was kindly supplied to us by Professor H. S. Uhler.<sup>4</sup> Gallium was present to such a slight extent as to make the GaO bands of negligible intensity. By using  $In_2O_3$  in the anode of this  $^{4}$  H. S. Uhler and P. E. Browning, Am. J. Sci. 42, 389 (1916).



FIG. 1. Spectrum of InO. Corresponding bands in the bracketed groups have the constant spacing of 560 cm<sup>-1</sup> interpreted as the interval between the two spin components of a <sup>2</sup>II state.

arc the same InO spectrum could be produced but with considerably lowered intensity. Spectrograms were taken in the second and third orders of the 21-foot grating in a stigmatic mounting, the dispersion being 2.45 and 1.43A/mm.

#### INO SPECTRUM

Band heads in this system are observed from 3847A to 4763A, the strong bands being confined to the region between the In resonance lines as exhibited in Fig. 1. Although the majority of the heads degrade to the red, some are diffuse and a number degrade definitely to the violet. Quantum analysis is rendered difficult because of the considerable interlacing of band structure and the lack of evident regularity of spacing of the heads. Also the continuum extending out from each of the In resonance lines on its high frequency side (evidence probably of the existence of quasi-stable In<sub>2</sub> molecules) obliterates a considerable portion of two of the band sequences. However, it is evident that the principal band heads fall roughly into three main groups, with a similar arrangement of successive strong heads (those bracketed in Fig. 1) on the high frequency sides of the two more intense groups.

Between band heads in these two brackets a constant frequency difference of 560  $\rm cm^{-1}$  was found to exist. Both the magnitude and the constancy of this interval suggested that it represented the multiplet spacing in a  $^{2}\Pi$  state of InO. With this and the lower state vibrational frequency which could be approximately predicted for InO as guides, vibrational quantum assignments of most of the heads of appreciable intensity were made. These assignments are presented in Table I. The four heads assigned to each pair of vibrational quantum numbers are probably the heads formed by the  $Q_1$ ,  $R_1$ ,  $R_2 + Q_2$ , and  ${}^{s}R_{21}$  branches of a  ${}^{2}\Pi \rightarrow {}^{2}\Sigma$  transition. For many of the bands, structure representing the remaining branches of this type of band is present, but due to incomplete resolution and

overlapping the analysis of this structure cannot be made. This frequent overlapping and fusion of band heads also considerably perturbs the intensity distribution in some of the bands.

The following formula gives quite accurately the frequency of the third  $(R_2+Q_2?)$  head of each of the bands listed in Table I.  $\nu = 23,595.10$  $+ \left[ 626.66(v' + \frac{1}{2}) - 3.40(v' + \frac{1}{2})^2 \right] - \left[ 703.09(v'' + \frac{1}{2}) \right]$  $-3.71(v''+\frac{1}{2})^2-0.285(v''+\frac{1}{2})^3$ ]. The  $\nu_e$  for the first (Q?) heads is at 23,033.10.  $\omega_e''$  is just about that predicted by comparison with the values for other third group diatomic oxide molecules. Of most interest is the large negative cubic term in the lower state. This reduces the successive  $\Delta G(v'' + \frac{1}{2})$  values at an accelerated rate, causing the sequences to converge at fairly low vibrational quantum numbers with consequent production of "tail" bands degrading to the violet. The  $\Delta v = -1$ , 0 and +1 sequences have convergence points at v''=6, 8 and 10, respectively, and the two most markedly violet degrading heads 23,157.3 and 23,735.1 fit very well according to the formula into the (10, 10) and (12, 11) bands, respectively. Early in this investigation we tried without success to place the violet degrading heads into a separate band system. The assignment of most if not all of these heads as "tail" bands in this  ${}^{2}II \rightarrow {}^{2}\Sigma$  system is indicated by our analysis, but we cannot positively exclude the existence of another fragmentary band system interlaced with the one here described.

Because of the more rapid decrease in  $\Delta G(v'' + \frac{1}{2})$  values with increasing v, there is near equality throughout most of the v', v''matrix scheme of the  $\Delta G(v' + \frac{1}{2})$ , the  $\Delta G(v'' + \frac{1}{2})$ and the electronic multiplet interval at every point. This produces a considerable amount of overlapping of band sequences and partial fusions of various band heads. Together with the presence of "tail" bands, this coincidence in intervals makes for the general irregularity in band distribution which proved so puzzling in the earlier investigation.<sup>1</sup>



FIG. 1. Spectrum of InO. Corresponding bands in the bracketed groups have the constant spacing of 560 cm<sup>-1</sup> interpreted as the interval between the two spin components of a <sup>2</sup>II state.