The Band Spectrum of Copper Oxide

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Many bands in the red, green, blue and violet region of the spectrum have been attributed to copper oxide. They occur in different sources of light; an arc between copper electrodes in air or oxygen, copper salts in flame or in active nitrogen containing trace of oxygen, exploded copper wires, an electrodeless discharge through a bulb containing copper, neon and trace of oxygen. Many measurements have been made of the band heads among others by HERTENSTEIN 1 and LEJEUNE and ROSEN 2. Attempts have been made to give vibrational and rotational analyses. However, none of these seems to be quite convincing. The red bands above 6000 Å characteristic of CuO have been treated by GUNTSCH 3, who performed vibrational and rotational analyses of this system. His $\omega$ values ($\omega' = 286$, $\omega'' = 319$) seem to be too small, his $B$ values ($B' = 0.59$, $B'' = 0.63$) too high.

In this institute many exposures have been taken of the CuO spectrum. The light sources used have been arcs and an electrodeless discharge. The spectrum has been photographed from 4000 Å up to 7000 Å. The spectrographs employed have been concave gratings (21 feet, first and second orders and 10.7 m, first and second orders) and a plane grating (dispersion 3 mm/Å), the last instrument used only for the red bands.

In the violet part of the spectrum rotational analysis has been carried out on a rather isolated band with its head at 4182 Å. The band consists of one strong and one strong P branch. A number of perturbations in the upper state confirm the analysis. The following constants (in $\rm{cm}^{-1}$) have been derived for the main isotopic molecule Cu$^{64}$O$^{16}$:

$$B' = 0.4429, \quad B = 0.419, \quad D'' = 0.94 \times 10^{-4}$$

The branches of the isotopic molecule Cu$^{68}$O$^{16}$ have also been found. From these we get

$$B'' = 0.4400.$$  

The ratio between $B''$ and $B'$ is 0.9935 in good accordance with the expected value which should be approximately 0.9938.

From Kratzer's relation, $\omega^2 = \frac{4B^2}{D}$, the $\omega$ value of the lower state is

$$\omega' \sim 610 \text{ cm}^{-1}.$$  

The character of the transition is of great interest. In a way it resembles that of a $\Sigma - \Sigma$ transition where the double split is negligible. The expected ground state of CuO is a $^2\Pi$ state. Thus it is more likely that the 4182 band forms the sub-band $^2\Pi_{12} - ^2\Pi_{11}$ of a $^2\Pi - ^2\Pi$ transition. This assumption is also confirmed by the following observation. Towards longer wavelengths in the blue region there are many bands. Some of them seem to have the same rotational constants for the lower level as the 4182 band. Some bands have two R and two P branches ($^2\Pi_{12} - ^2\Pi_{11}$ sub-bands), some only single R and P-branches ($^2\Pi_{12} - ^2\Pi_{13}$ sub-bands). It seems as though many electronic transitions are involved and that they have the same lower electronic level. As the B value 0.4429 is the same for several bands it seems reasonable that this B value is that of the lowest vibrational level of the ground state. It has not yet been possible to definitely arrange the bands into different systems. Thus the presence of several systems, which have different multiplet splittings make the vibrational analysis very difficult.

The red system round and above 6000 Å is most probably a transitional with $|\Delta \lambda| = 1$. The difference 275 cm$^{-1}$ between the main bands forms surely the difference of the mean between the multiplet splittings of the upper and lower states. The value $\omega''$, which is round 600 cm$^{-1}$ (MAHANTI 4, LOOMIS and WATSON 5 and LEJEUNE and ROSEN 3) agrees very well with the one crudely derived from K r a t z e r 's formula for the 4182 band. The red bands have most likely the same lower state as the 4182 band. The structure of the red bands is, however, extremely complicated. It is possible to find branches which have second combination differences agreeing for several $J$ values very well with those of the lower level of the 4182 band. The large number of overlapping branches makes, however, the analysis somewhat doubtful. The structure of the red main bands became not very much simpler when we used pure Cu$^{68}$ isotope and an electrodeless discharge. The explanation of the complicated structure may be that the $\omega'$ and $\omega''$ values are very similar, and thus the 0,0, 1,1 and 2,2 bands very heavily coincide and overlap.

The nuclear distance $r_0$ derived for the lower state of CuO is 1.726 Å. Taking the mean of the nuclear distances of O$_2$ (HERZBERG 6) and Cu$_2$ (ÅSLUND et al. 7) one obtains 1.712 Å in close agreement with the value observed. The rotational analysis of the 4182 band may turn out to be the key for the interpretation of the CuO spectrum. Thus we hope to be able to return to the spectrum of CuO in future papers.

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