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Band Spectra of AgO and CuO

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Band spectra of AgO and CuO, obtained by arcing between metal electrodes in oxygen at reduced pressure, have been photographed in the first order of a 21-foot grating. An ultraviolet and a blue system of AgO are subjected to vibrational analysis and are attributed respectively to ${}^2\Sigma \rightarrow {}^2\Sigma$ and ${}^2\Pi \rightarrow {}^2\Sigma$ transitions, with a common lower state. A third system in the far red was too faint for measurement. It is found that the red system of CuO is due to something more complicated than the ${}^2\Sigma \rightarrow {}^2\Sigma$ transition attributed to it by Mahanti.

THE arc source previously used¹ for the study of the spectrum of SnO has here been applied to AgO and CuO. It is simply an arc between metal electrodes operating in a stream of oxygen at some 5 cm pressure and has proved to be a rather intense and stable source for oxide spectra.

SILVER OXIDE BANDS

Hulthén and Zumstein,² while studying the spectrum of AgH observed a group of bands near 2600A which they attributed to the AgO molecule. These bands were not found in the present investigation, although three other systems were observed. One of these is in the ultraviolet between 3400 and 3700A and degrades to higher frequencies, a second is in the blue and degrades toward the red, and the third is in the red and degrades in the direction of decreasing frequencies. The bands in the red are of very low intensity and have not been photographed with sufficient dispersion to permit a vibrational

assignment. The other two systems have been photographed in the first order of a 21-foot grating with an average dispersion of 1.3A/mm. A vibrational analysis of these two systems has been made and it is found that the frequencies of their heads can be represented by the following expressions:

$$\nu = 28,074.6 + \left\{ 534.7(v' + \frac{1}{2}) - 6.10(v' + \frac{1}{2})^2 \right\} - \left\{ 493.2(v'' + \frac{1}{2}) - 4.10(v'' + \frac{1}{2})^2 \right\}, \quad (1)$$

$$\nu = \left. \begin{array}{l} 24,139.9 \\ 24,310.9 \end{array} \right\} + 233.0(v' + \frac{1}{2}) - \left\{ 493.2(v'' + \frac{1}{2}) - 4.10(v'' + \frac{1}{2})^2 \right\}. \quad (2)$$

These indicate, of course, that the two systems have a common lower state.

The frequencies and roughly estimated intensities of these bands, together with vibrational quantum assignments and deviations of observed frequencies from those calculated from Eqs. (1) and (2) are given in Tables I and II.

Since the vibrational spacings in the upper and lower states of the ultraviolet system are nearly equal, the bands are grouped into non-overlapping sequences and are comparatively easy to assign.

¹ Loomis and Watson, *Phys. Rev.* **45**, 805 (1934).

² Hulthén and Zumstein, *Phys. Rev.* **28**, 13 (1926).

TABLE I. *Ultraviolet system of AgO.*

INTENSITY	v'	v''	FREQUENCY	FREQUENCY OBS.-COMP.
0	3	1	29140.1	-0.7
1			28716.2	
1	5	4	28693.3	-1.1
1	4	3	28680.0	-1.2
3	3	2	28662.7	-1.2
3	2	1	28643.5	0.9
2	1	0	28615.7	-1.6
5	1	1	28133.2 (28130.0)*	0.9
4	0	0	28093.9	-0.9
2	2	3	27698.0	0.8
2	1	2	27655.4 (27652.4)*	-0.1
2	0	1	27610.7 (27607.3)*	0.9
0			27229.0	
0	1	3	27185.3	-1.6

* Some of the bands show a double-headed structure. The frequency of the second head is given in parentheses.

The estimated intensities of these bands are entered as functions of v' and v'' in Table III and, as is to be expected, lie along a narrow Franck-Condon curve.

The bands of the blue system occur in pairs, the bands of each pair being of apparently equal intensity and separated by a constant interval of 171 cm^{-1} . This must be the doublet interval of the upper state, since the lower state is common to both systems and no doubling is observed in the ultraviolet system.

The intensity distribution of the bands of the blue system is shown in Table IV. The system terminates abruptly after two v'' progressions, presumably indicating predissociation of the upper state for $v' > 1$.

Although the resolution available was inadequate for a rotational analysis of either system, it is possible to ascertain the nature of the states involved by the following argument. A rough approximate calculation, assuming that ω/B is of the order of 1000 in both states, as is the case with monoxides which have been studied, leads to some 6 cm^{-1} for the order of magnitude of the

TABLE II. *Blue system of AgO.*

INTEN- SITY	v'	v''	FRE- QUENCY	FRE- QUENCY OBS.- COMP.	INTEN- SITY	v'	v''	FRE- QUENCY	FRE- QUENCY OBS.- COMP.
5			24415.6	0.8	0			22982.5	-1.8
5	1	0	24243.9	0.1	2	1	3	22812.0	-1.0
4			23930.7 (23930.2)*	0.9	3	0	3	22753.2	1.9
4	1	1	23760.3 (23759.6)*	0.3	1	0	3	22580.0	0.0
2			23518.2		1			22741.5	
3			23451.9 (23450.7)*	-1.4	2	0	4	22292.0	1.0
2	1	2	23281.7	-0.6	1	0	4	22119.5	-0.4
2			23223.8	3.8	1			22134.8	
2	0	2	23049.5	0.5	1			22107.3	
					1	0	5	21838.5	0.0
					1			21664.0	-2.0

* In bands where double heads were observed due to the isotope effect, the second head has been included in parentheses.

TABLE III. *Intensities of bands of ultraviolet system of AgO as functions of v' and v'' .*

$v' \backslash v''$	0	1	2	3	4
0	4	2			
1	2	5		0	
2		3	2	1	
3		1	3	—	
4				1	—
5					1

TABLE IV. *Intensities of the bands of the blue system of AgO as functions of v' and v'' .*

$v' \backslash v''$	0	1	2	3	4	5
0	—	—	2	1	1	1
	—	—	2	3	2	1
1	5	4	2	2		
	5	4	3	0		

separation between heads and origins of the bands of the ultraviolet system. If Q heads were present at anything like this separation from the P heads, they should be clearly visible, but they are not. Moreover, in two favorably situated bands, the dip in intensity corresponding to the origin can actually be seen at about the expected location. It may be concluded that the ultraviolet system is a $\Sigma - \Sigma$ transition. A similar calculation shows that one would not expect to be able to resolve the R and Q heads of the blue system.

Hence the fact that Q heads are not observed in that system either is not in contradiction with the conclusion, drawn from the occurrence of pairs of bands of equal intensity, that the upper state of that system is a doublet with $\Lambda > 0$. Hence from the rule that $\Delta\Lambda = \pm 1$ or 0 and the assumption that these strong systems are not likely to be transitions between states of different multiplicity one may deduce that the blue system is ${}^2\Pi \rightarrow {}^2\Sigma$ and the ultraviolet system ${}^2\Sigma \rightarrow {}^2\Sigma$.

According to Aston,³ silver has two isotopes of masses 107 and 109 in nearly equal abundance. The bands of the ultraviolet system are all so near the system origin that the calculated isotope effect is small, and the effect was in fact not observed. In the blue system, however, certain favorably situated bands were observed to have a double-headed structure, with separations which agree, within the accuracy of measurement, with those calculated from the usual expressions for the vibrational isotope effect. This observation serves to confirm the vibrational assignment and the identification of the emitting molecule.

COPPER OXIDE BANDS

Incidentally to the above, we have taken occasion to photograph the red bands of CuO in

³Aston, *Mass Spectra and Isotopes* (1933).

the oxygen arc. These bands have often been observed⁴ in various flame and arc sources. In 1930 Mahanti⁵ published a note on them, attributing them to a ${}^2\Sigma \rightarrow {}^2\Sigma$ transition, with vibrational intervals of 620 and 345 cm^{-1} . Our 21-foot grating measurements of the frequencies of the heads, and sub-heads, of these bands can indeed be fitted into Mahanti's scheme, with only slightly different constants, but when this is done it appears that the two halves of the so-called doublet have obviously very different intensities. The bands are degraded to the red and the fainter heads are 40 cm^{-1} to the violet of the stronger ones. It seems to us more likely that these fainter heads belong to satellite branches and hence that the transition is something more complicated than ${}^2\Sigma \rightarrow {}^2\Sigma$. Other vibrational arrangements than Mahanti's also appear to be possible, including one with a doublet interval about 275 cm^{-1} , if one is willing to assume slight variation from band to band of the separation between heads and origins. It seems unlikely that the matter can be cleared up without a rotational analysis, which promises to be difficult.

⁴Hertenstein, *Zeits. Wiss. Phot.* **11**, 69, 119 (1912); Eder and Valenta, *Atlas Typischer Spectren* (1924); Mulliken, *Phys. Rev.* **26**, 1 (1925).

⁵Mahanti, *Nature* **125**, 819 (1930).