The Infrared Absorption Spectrum of Cuprous Oxide

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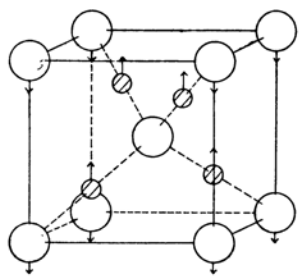
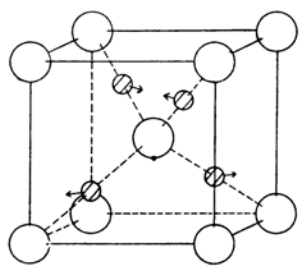
Cuprous oxide Cu_2O is a well-known crystal whose bond character is considerably covalent. It has a crystal structure belonging to the space group O_h^4. The unit cell contains four copper atoms and two oxygen atoms. A group theoretical consideration shows that this crystal has two F_{1u} optically-active lattice vibrations. Their vibrational modes are shown in Fig. 1. The a mode in Fig. 1 is considered to cause the relatively higher frequency band, and the b mode, the lower one.



Mode a



Mode b

Fig. 1. Infrared active vibrational modes of Cu_2O.

Copper ○ Oxygen

In order to examine the bond character of cuprous oxide, the present writer made an infrared absorption measurement of cuprous oxide in the KBr pellet and in a polyethylene film.[1] The spectrum obtained is shown in Fig. 2. Absorption measurements in the rock-salt, potassium bromide and cesium bromide regions were made by the use of a Perkin-Elmer model-221 spectrometer, and those in the far infrared region, by the use of a grating spectrometer built by Yoshinaga et al.[2]

In the spectral region examined, two strong absorption bands, were found at 617 cm^{-1} and 147.5 cm^{-1}. These are evidently attributable, respectively, to the optically-active lattice

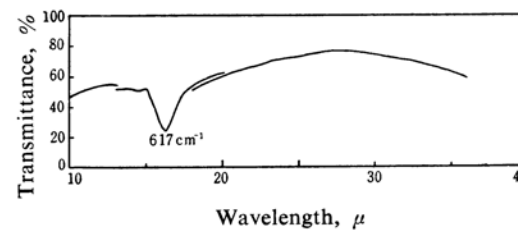


Fig. 2a. Infrared absorption spectrum of Cu_2O in KBr disc.

1) H. Yoshinaga and R. A. Oetjen, *J. Opt. Soc. Am.*, **45**, 1085 (1955).
2) H. Yoshinaga, S. Hujita, S. Minami, A. Mitsuishi, R. A. Oetjen and Y. Yamada, ibid., **28**, 315 (1958).

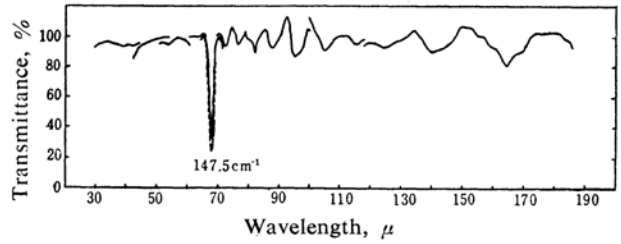


Fig. 2b. Infrared absorption spectrum of Cu_2O in polyethylene film.
(——) 50 mg./2 g. polyethylene
(------) 100 mg./2 g. polyethylene

vibrations a and b mentioned above. Of these two strong bands, the one at 617 cm^{-1} had already been found by O'Keeffe[3] and had been assigned by him to one (a) of the two expected infrared active vibrations. However, it has been a question where the other band (b) is situated. O'Keeffe assigned a band at 1122 cm^{-1} to one (b) of the two infrared-active lattice vibrations. On the other hand, Huang[4] predicted that it would be at 120 μ (83.3 cm^{-1}) on the basis of his calculation of the lattice frequencies of this crystal.

The problem is now settled by the present experiment. It has been found that the b band is situated at 147.5 cm^{-1}, at much lower frequency than that assigned by O'Keeffe but at a cosiderably higher frequency than that predicted by Huang. Huang assumed in his calculation an ionic character of the Cu-O bond in cuprous oxide. The fact that the actually obserwed frequency (147.5 cm^{-1}) is somewhat higher than that predicted (83.3 cm^{-1}) is considered to indicate that the bond is more covalent than he assumed.

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3) M. O'Keeffe, *J. Chem. Phys.*, **39**, 1789 (1963).
4) K. Huang, *Z. Physik*, **171**, 213 (1963).