

OPTICAL PROPERTIES OF METALLIC COPPER IN RELATION TO THE PHOTOCHROMIC SYSTEM $\text{CuCl(s)}-\text{H}_2\text{O(l)}$

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Summary

An extended Mie theory has been used to interpret the green colour change observed in the photochemical disproportionation of CuCl . Comparison of calculated and experimental spectra leads to the following conclusions: (i) the green colour arises from colloidal metallic copper in CuCl present in low concentrations (<5 vol %); (ii) the colloid consists of particles with an average diameter of about 3 nm in diameter and probably oblate in shape with an axis ratio of about 0.6; (iii) under the conditions of the present experiment the spectrum of the green species stayed constant, *i.e.* continued exposure has primarily the effect of increasing the number of copper particles without affecting their size and shape.

Introduction

The absorption spectrum of a thin homogeneous film of metallic copper is characterized by a broad absorption band with λ_{max} around 450 nm giving rise to the well-known copper red colour. The absorption band arises from an interband transition. Colloidal metallic copper yields a quite different absorption spectrum. The fundamental difference between this spectrum and that of a metal film is the appearance of an additional absorption band at longer wavelengths. This band arises from transitions caused by the conduction electrons and involves excitation at the plasma frequency of the metal. In the case of a film this excitation is not possible as the incoming light is perpendicular to the plasma wave. Contrary to the transition previously mentioned the absorption band due to conduction electrons is of a collective nature. This makes the band quite sensitive to particle size, particle shape and concentration of metal as well as to the dielectric properties of the surrounding medium.

CuCl in contact with water is photosensitive and exhibits photochromism. The photochromic reaction is the disproportionation of CuCl

into metallic copper and Cu^{2+} . At heavy exposure small grains of metallic copper with the characteristic metallic lustre can be observed visually. At lighter exposure a green colour is observed and this colour has not been satisfactorily explained. However, comparison of observed spectra with calculated spectra for colloidal metal solutions clearly suggests that the green colour arises from absorption by metallic copper. This study reports a detailed analysis of such spectra for the elucidation of the photochromic process.

Theory

The theory for the calculations of the absorption spectra reported herein is primarily based on the classical Mie theory [1]. However, the theory neglects the size dependence of the dielectric constant of the metal, which is mainly explained as being caused by a limitation in the mean free path of the conduction electrons. A method used by Kreibig and Frangstein [2] makes it possible to correct for this effect and is used in the present study. The original Mie theory treats only spherical particles. Gans [3] extended the Mie theory to include small ellipsoids. This extended Mie theory is used here in a simplified version.

According to Mie theory the absorbance, *i.e.* attenuation, $A = c d K$ where c stands for concentration (vol/vol), d for the path length and K for the attenuation coefficient. The expression for K is:

$$K = \frac{3\pi}{\alpha^3 \lambda'} \cdot \text{Im} \left[\sum_{\nu=1}^{\infty} \nu (-1)^\nu \cdot (a_\nu - p_\nu) \right] \quad (1)$$

$\lambda' = \lambda/m_0$ where λ is the wavelength of the light in vacuum and m_0 is the refractive index of the surrounding medium; $\alpha = R\pi/\lambda'$ where R is the particle radius; a_ν and p_ν describe the contributions from the electric and the magnetic components, respectively, of the electromagnetic field.

The terms a_ν and p_ν are functions of α and of the relative refractive index of the metal $m' = (n - ik)/m_0$. In the present study calculations were carried out for particle sizes up to 100 nm in diameter and, in order to calculate K , only the terms a_1 , a_2 and p_1 had to be considered. For particles having a diameter of less than 40 nm the term a_1 dominates and thus the attenuation coefficient is solely determined by the electric dipole oscillation. The size dependence of the dielectric constant of the metal becomes important for particle sizes less than 40 nm in diameter and is accounted for by applying eqns. (2) - (4), [2]:

$$n^2 - k^2 = A_1 + B_1 = 1 - \frac{\omega_1^2}{[\omega^2 + \omega_0(R)^2]} + B_1 \quad (2)$$

$$2nk = A_2 + B_2 = \frac{\omega_1^2 \omega_0(R)}{\omega [\omega^2 + \omega_0(R)^2]} \quad (3)$$

$$\omega_0(R) = \omega_0(R \rightarrow \infty) + \frac{V_F}{R} \quad (4)$$

ω_1 = plasma frequency, ω_0 = collision frequency, ω = light frequency and V_F = Fermi velocity. B represents the contribution from the bond electrons and are considered to be independent of the particle size.

For ellipsoidal particles the resulting attenuation coefficient is dependent on the orientations of the particles. For randomly oriented small ellipsoids (diameter < 40 nm) the attenuation coefficient will be:

$$K = \frac{2\pi}{\lambda'} \text{Im} \left[\frac{1}{3} \cdot \frac{m'^2 - 1}{(m'^2 - 1)P/4\pi + 1} - \frac{2}{3} \cdot \frac{m'^2 - 1}{(m'^2 - 1)P'/4\pi + 1} \right] \quad (5)$$

P and P' being form factors related through $P + 2P' = 4\pi$. For a sphere $P = P' = 4\pi/3$. For an oblate ellipsoid $P > P'$ and for a prolate ellipsoid $P < P'$. The corresponding axis ratio can be found in the work by Gans [3]. In the present work with the photochromic system the particle shape and any preferred orientation is not known. The experimentally determined attenuation coefficient represents some kind of average and a useful approach to the theory may be to assume a single form factor for the particles using the expression:

$$K = \frac{2\pi}{\lambda'} \text{Im} \left[\frac{-(m'^2 - 1)}{(m'^2 - 1)P/4\pi + 1} \right] \quad (6)$$

Fitting to eqn. (6) will then give the resulting form factor of the system. Equation (6) can be interpreted as follows: the K value obtained refers to an average ellipsoid with its rotational axis parallel to the incoming light, *i.e.* perpendicular to the surface. This simplified treatment has been used by Flechsig in studying the light absorption of thin metal layers, in which the metal shows island structure [4].

Calculations

Spherical particles

Using eqn. (1) calculations of attenuation coefficients were made for copper spheres of various radii from 1 to 50 nm in three different media CuCl, Cu₂O and water. The complex indices of refraction for copper at wavelengths from 420 to 700 nm determined by Otter [5] were used.

Refractive indices for CuCl were taken from Landolt-Börnstein (6Aufl, band II/8) for 530 - 670 nm (2.00 - 1.93). For wavelengths less than 530 nm values had to be estimated by extrapolation [2.17 (430 nm), 2.13 (450 nm) and 2.50 (500 nm)]. For Cu₂O and water the values 2.50 and 1.33, respectively, were used for all wavelengths. Parameters required for eqns. (2) - (4) were obtained from Suffczynski, ($V_F = 1.32 \times 10^6$ m/s,

$\omega_1 = 1.43 \times 10^{16} \text{ s}^{-1}$; $\tau_s = [1/\omega_0(R \rightarrow \infty)] = 3.46 \times 10^{-14} \text{ s}$ (bulk) [6]. Attenuation coefficients for 13 wavelengths were calculated for the construction of the spectrum representative for a particular R and m_0 value.

Non-spherical particles

A set of calculations were based on eqn. (6), in which R was varied from 0.5 to 2.1 nm and $\bar{P}/4\pi$ from 0.2 to 0.7. The m_0 values of CuCl were used.

Experimental

Crystals of CuCl with an average diameter of 0.05 nm were used. The crystals were prepared by recrystallization of CuCl (Merck p.a.) from HCl. They were placed in a 0.1 mm thick cuvette containing 0.5 M H₂SO₄. The crystals were illuminated with the unfiltered light from a high pressure mercury lamp (500 W) and the colour change was followed spectrophotometrically using a Shimadzu MPS 50 L instrument with a microspectrophotometry accessory, using the non-illuminated crystal as a reference. This allowed the recording of spectra for very small areas, in the present case 20 μm in diameter. In 0.5 M H₂SO₄ the bleaching reaction is sufficiently slow to be neglected. Some experiments were also carried out at high pH.

Results

The spectrum observed for the photoinduced colour change is given in Fig. 1. In the system investigated here no changes in absorption spectrum were observed during continued exposure. Varying pH over the range 0 - 7 did not affect the photochromic spectrum.

Comparison of calculated and experimental spectra

Spheres

The attenuation coefficients for spheres are determined by the two parameters m_0 and R . Changing the particle radius (R) gives rise to two effects. One effect operating through the parameter $\alpha = R\pi/m_0$ is a red shift of the attenuation spectrum for R values > 20 nm (cf. Fig. 2). The other effect is a band broadening of the collective conduction electron band (A) for $R < 20$ nm [cf. Fig. 3(a)], where the reduction in mean free path becomes important. Higher refractive indices of the medium (m_0) shift the attenuation spectrum to longer wavelengths. This shift is accompanied by an increased size of the A-band.

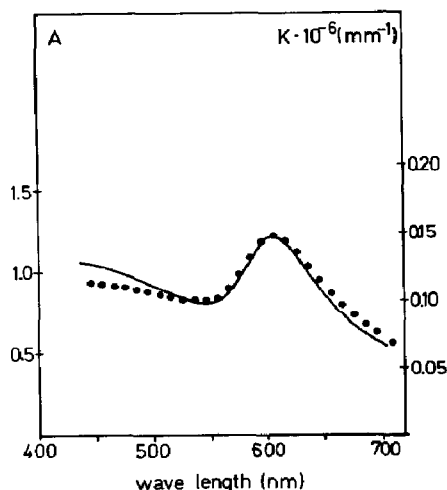


Fig. 1. Fitting of calculated and experimental spectra. ●, Experimentally obtained absorption spectrum for illuminated CuCl crystals (left scale); —, calculated spectrum for metallic copper ellipsoids in CuCl using eqns. (2) - (4) and (6) and assuming an average particle radius of 1.3 nm and a form factor $\bar{P}/4\pi = 0.267$ (right scale).

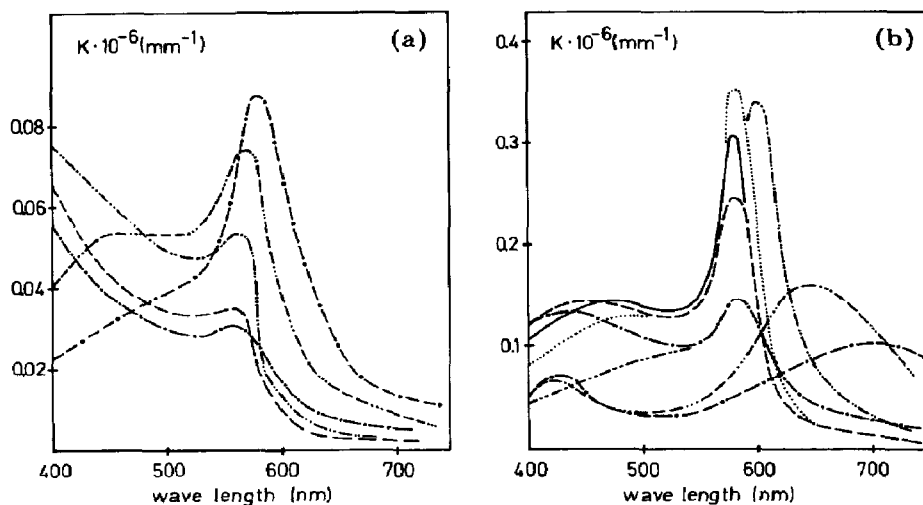


Fig. 2. Attenuation spectra for metallic copper spheres of various radii from 2 to 50 nm using eqns. (1), (2) - (4). (a): in H_2O ($m_0 = 1.33$); (b): in CuCl ($1.93 < m_0 < 2.17$); $R = 2.1$ nm (· · · · ·), $R = 6.1$ nm (- - -), $R = 10.1$ nm (—), $R = 16.1$ nm (. . .), $R = 26.1$ nm (· - - · -), $R = 40.1$ nm (· · · - - -), $R = 50.1$ nm (· - - ·).

As a consequence of the above described effects it ought to be possible to determine the size as well as the localization, *i.e.* the environment of the copper particles formed in the photochemical disproportionation of CuCl (Fig. 1).

In order to explain the observed widths of the A-band it is necessary to assume a particle radius around 1.0 - 1.5 nm. The position of the A-band is more difficult to explain satisfactorily. Straightforward application of eqn. (1) implies an environment with a refraction index of about 2.30, *i.e.*

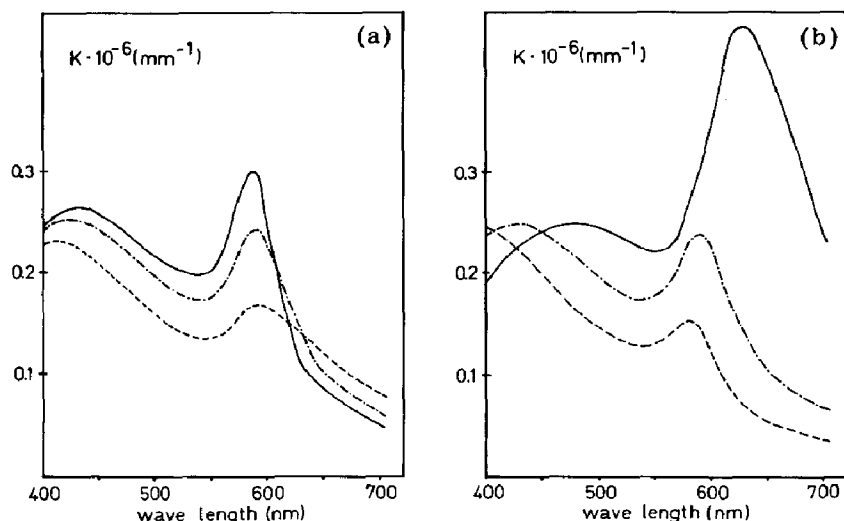


Fig. 3. (a) Attenuation spectra for small metallic copper spheres in CuCl applying eqns. (1), (2) - (4). $R = 0.9$ nm (---), $R = 1.5$ nm (- · - · -), $R = 2.1$ nm (—). (b) Attenuation spectra for small metallic copper ellipsoids in CuCl with an average radius of 1.5 nm. Rotational axis (b) parallel to the incoming light [eqns. (2) - (4), (6)]. —, Oblate ellipsoids with $\bar{P}/4\pi = 0.222$ ($b/a = 0.47$), - · - · -, spheres with $\bar{P}/4\pi = 1/3$ ($b/a = 1$); ---, prolate ellipsoids with $\bar{P}/4\pi = 0.400$ ($b/a = 2.50$).

a value between $m_0 = 1.97$ (600 nm) for CuCl and $m_0 = 2.50$ for Cu_2O . The assumption of $m_0 = 2.30$ and $R = 1.3$ nm gives a spectrum which closely agrees with that experimentally obtained.

A chemical interpretation of this result could be that the copper particles partly become surrounded by Cu_2O , due to oxidative processes. However, in order to explain an m_0 value of 2.30 it is necessary to assume very high concentrations of Cu_2O close to the copper particles. This means that the main product of the photochromic reaction should be Cu_2O which does not seem very likely. The experimental spectra show no pH dependence. Even when the pH is so high that CuCl is partly converted to Cu_2O no shift in the A-band is observed. The conclusion is therefore reached that a m_0 value 2.30 is unrealistic. A broad size distribution ($R \approx 25$ nm) of copper particles in CuCl may possibly yield spectra of the type experimentally obtained. However, such a distribution ought to vary with the concentration of the photochemically produced copper, thus affecting the spectrum and causing a change in λ_{max} of the A-band. Experimentally this is not observed.

Non-spheres

According to eqn. (10) the attenuation coefficient of small non-spherical particles treated as ellipsoids depends on three parameters m_0 , R and the form factor \bar{P} . As the calculations reported above show better agreement for spheres in CuCl than in water, it was concluded that for reasonable assumptions of \bar{P} the m_0 values of CuCl are the most relevant.

Changes in \bar{P} has almost the same effect on the attenuation spectrum as changing the m_0 value, but the direction of the effect is reversed, *i.e.* a decrease in \bar{P} corresponds to an increase in m_0 [cf. Fig. 3(b)].

Varying the parameters R and \bar{P} it was possible to obtain calculated spectra which closely agree to that experimentally obtained. This is illustrated in Fig. 1. It is thus concluded: (1) the green colour observed in the photochemical disproportionation of CuCl is due to colloidal metallic copper formed in the CuCl matrix; (2) the size of the copper particles corresponds to an average radius of about 1.3 nm; (3) the shape of the particles is characterized by a value of 0.27 for $\bar{P}/4\pi$. This corresponds to an average oblate with an axis ratio of 0.62 (oriented with the rotational axis perpendicular to the surface).

Assuming the ellipsoids to be oblates and preferentially oriented with their rotational axes perpendicular to the surface may form the starting point for further discussions. The first assumption is reasonable on ground that prolate ellipsoids must have the shape of needles oriented with the long axis along the surface to yield a spectrum represented by $\bar{P} = 0.27$. The second assumption is not so critical since the second term in expression (5) dominates even in the case of a random distribution of orientations.

The expression used for an estimate of the dependence on particle size of the dielectric constant is strictly only valid for spheres. The average radius introduced when applying eqn. (6) may be interpreted as the mean value of the axes' lengths, $R = 1.3$ nm and $\bar{P}/4\pi = 0.27$, therefore, implying oblates with axes 1.8 and 3.0 nm in length. This corresponds to particles consisting of about 800 atoms.

The theory used in the present study is based on classical physics. As the copper particles were found to be extremely small the question arises whether quantum effects become important. This is, however, not likely as Kreibig and Fragstein found that a quantum mechanical treatment leads to almost the same results as the classical theory when applied to small silver particles in a photosensitive glass [2, 7]. It should, however, be stressed that a systematic error in the absolute value of R may be present due to a possible effect of impurities in the metal particles studied. It is known that the mean free path of the conduction electrons is reduced due to impurities and this will affect the values of n and k . The error is believed not to be too large since particle sizes measured with electron microscopy agreed well with those calculated in the study on silver particles by Kreibig and Fragstein [2].

The concentration dependence

Mie theory is only valid for dilute colloidal metal solutions. For such solutions there exists a direct proportionality between the measured attenuation and the concentration of metal particles. For more concentrated solutions there is a deviation from linearity, which is accompanied by spectral changes [8, 9]. The experimental results show no spectral changes during continued exposure. It is thus concluded that the shape and the

size of the metal particles stay essentially constant and that the concentration of metal particles is low. A maximum concentration of 5 vol % is estimated [8].

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