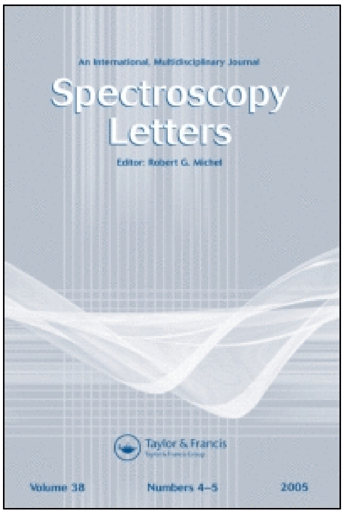

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Quantitative UV-Visible Diffuse Reflectance Spectroscopy of Solid Powders

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QUANTITATIVE UV-VISIBLE
DIFFUSE REFLECTANCE SPECTROSCOPY
OF SOLID POWDERS

Key Words: Diffuse reflectance spectroscopy; Quantitative UV-Visible Spectra of Solid Powders

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INTRODUCTION

In spite of difficulties in attaining high resolution, the determination of UV-VIS-NIR spectra via diffuse reflectance spectroscopic measurements on solid powders; provides several advantages. Compounds which are difficult to obtain as suitable single crystals, or are found to be unstable or insoluble in liquid solution, can only be studied by diffuse reflectance spectroscopy. Also, since no solvents are required, any effects due to solvation are eliminated. However, it is not possible to resolve the observed spectrum into its anisotropic components, as in the case of single crystal spectra.

In this paper we report a quantitative spectroscopic study of K_2PtCl_4, K_3 $Fe(CN)_6$ and $NiSO_4$-$7H_2O$ as solid powders, in the ultra violet-visible ranges.

THEORETICAL DEVELOPMENT

Of the various theories that have been proposed to account for the electronic spectroscopic properties of solids; the following two approaches are most significant:

1) Differential and integral equation methods which group the fundamental absorbing and scattering properties of a solid sample into arbitrary constants[1,2] 2) The statistical model approach based on the scattering properties for individual particles. The latter is basically more sound but is not as conveniently applied.[3] Melamed[4] achieved better correlations between absorption derived from a statistical model and that obtained from transmission spectra, by summing over individual particles rather than plane-parallel layers. The general solution for the absolute diffuse reflectance of an infinitely thick powder, R_∞, is given by

$$R = 2x\bar{m}_e + \frac{x(1-2x\bar{m}_e)\ T\ (1-\bar{m}_e R_\infty)}{(1-\bar{m}_e R_\infty) - (1-x)\ (1-\bar{m}_e)\ T\ R_\infty} \qquad (1)$$

where x is the fraction of the radiation which emerges from the interior of a particle and is scattered in the direction of the surface, $\bar{m}_e$ is the average value of the reflection coefficient of the surface of an individual particle for externally incident radiation, and T is the transmission of an individual particle. This equation is quadratic in R_∞, and since R_∞ must lie between 0 and 1, only positive roots are used for evaluating R_∞.

Melamed assumed that the irregular particles of the sample could be approximated by uniform spheres of an average diameter, and he assumed that spheres scatter according to the Lambert cosine law. The radiation which reaches the surface of the particle within an angle dθ in the direction θ, for unit incident flux is

$$dm(\theta) = [\exp\ (-kd\cos\theta) \quad (1/\pi)\cos\ \theta \quad (2\pi)\ \sin\theta]d\theta \qquad (2)$$

where k is the absorption coefficient and d is the diameter of the particle. The total radiation reaching the surface of a particle is therefore,

$$M = 2\int_0^{\pi/2} \exp(-kd\cos\theta)\sin\theta\cos\theta d\theta$$
$$= 2/(kd)^2[1-(kd+1)\exp(-kd)] \qquad (3)$$

If $\bar{m}_i$ is the average reflection coefficient of the surface of a particle for internally incident radiation, the portion of the initial ray which emerges is $\bar{m}_i M$. The surface of the spheres is assumed to have identical scattering properties at each point, so that the radiation which emerges after an infinite number of internal reflections is the sum of a geometric series in $\bar{m}_i M$. Thus, the fraction of the radiation transmitted is

$$T = \frac{(1-\bar{m}_i)M}{(1-\bar{m}_i M)} \qquad (4)$$

while the average refractive index, $\bar{n}$, is

$$\bar{n}^2 = \frac{(1-\bar{m}_e)}{(1-\bar{m}_i)} \qquad (5)$$

Assuming that in addition to obeying the Lambert cosine law, the Fresnel relation for specular reflection for unpolarized radiation is valid, then the average value of the external reflection coefficient, $\bar{m}_e$, for light incident from a rarer to a denser medium is

$$\bar{m}_e = 2\int_0^{\pi/2} m(\theta)\sin\theta\, d\theta$$

where $m(\theta)$ is the reflection coefficient determined from Fresnel's equation. For radiation incident from the denser to the rarer medium,

$$\bar{m}_i = (1-\sin^2\theta_c) = 2\int_0^{\theta_c} m(\theta)\sin\theta\cos\theta\, d\theta$$

where θ_c is the critical angle.

The coefficient x occurring in equation (1) can be calculated by assuming a set of parameters x_u, x_s, and x_d which represent the average values for the fractions of the radiation emerging from the interior of a particle respectively in the upward (x_u), sideways (x_s), and downwards (x_d) directions relative to the surface of the sample. The probability that radiation emerging from a particle is scattered upward, including that which is laterally diffused initially is given by

$$x = x_u / (1 - x_s T) \qquad (6)$$

For small absorption coefficients, the radiation can be assumed to leave a particle isotropically, so the $x_d = x_u$. Since $x_u + x_d \pm x_s = 1$,

$$x = x_u / [1 - (1 - 2x_u)T] \qquad (7)$$

For close packed spheres, x can be taken to be 0.284 which corresponds to a solid angle of $(4-\sqrt{3/2})$ steradians. Companion[5] had to use the factor 0.1 for x_u in diffuse reflectance measurements on V_2O_5 powders. This infers that small crystals, because of their flat faces, can lie closer together than spheres of the same effective diameter used in the model for deriving the theory. Melamed's theory is superior to the previous ones, due to the fact that it comes closer to providing an _a priori_ theory of reflectance, in which the fundamental properties of the absorbing and scattering are included.

EXPERIMENTAL

The particle size dependence of the diffuse reflectance spectrum has been investigated by several authors[6,7] who attribute the increase in absorbance when the particle size is reduced to the reduction of the specular component of the reflection. This inverse dependence of absorbance on particle size for both large or small absorption coefficients shows that even in the case of fine powders the influence of specular reflection cannot be neglected. In addition to the particle size dependence of the absorption coefficient, the fraction of regular surface reflection which exists causes the diffuse reflection spectra of powders to have greatly flattened maxima compared to an analogous transmission spectrum. For very small particles, the apparent absorbance increases and resolution of the spectrum is increased due to the more complete elimination of the fraction of specular reflection[8].

Sample Preparation

After a number of trial measurements with varying particle sizes, a mean particle diameter of 10 ± 1 microns was adopted. Below this particle size, small changes in the mean particle diameter (10 microns) are reflected by extreme (nonlinear) changes in the diffuse reflection curves and the absorption coefficient. In the 10 micron range, small deviations in particle size (± 1 micron) produce errors within the error range of the method and yet small changes in the absorption coefficient are detected with sufficient resolution in the diffuse reflectance spectra.

Samples of K_2PtCl_4, $K_3Fe(CN)_6$ and $NiSO_4 \cdot 7H_2O$ powders, prepared from Reagent Grade chemicals and recrystallized from solution, were ground in a high speed pulverizer equipped with agate jars and agate grinding balls. Sample mixtures with reference standards (MgO, KCl, etc.) were carefully weighed out and dispursed in a mixer-mill. Subsequent to the grinding phase and prior to mixing, the samples were examined under a microscope fitted with a micrometer eyepiece. If the mean diameter (30 minimum particle count) per particle was not 10 ≠ 1 microns, the grinding process was continued.

Equipment

Samples were mounted in a specially constructed double-beam cell, which consisted of a black bakelite block with cylindrical cavities of 1 cm diam. x 1 cm depth. Accurately determined masses of powders were introduced into the cell cavities by applying uniform pressure to successive layers of 2 mm, until the cavities were filled. The cells were fitted to a Beckman DK-1 spectrophotometer with recording reflectance attachment, and the diffuse reflectance spectra measured from 200-700 mμ against MgO as the standard.

The raw spectral data were processed by programming Melamed's equations for the DEC System PDP-10 computer.

Data Processing

All observed reflectances (R_0) were converted to absolute values (R_∞), as derived from independent measurements on MgO. Values of the $\bar{m}_e$ and $\bar{m}_i$ coefficients were derived from tabulations[4,9] using average refractive indices obtained from standard handbooks.

Equations (3) and (4) were programmed for the PDP-10 computer, and the absorption coefficient, k, calculated by the Newton-Raphson successive approximation method.

To convert the absorption coefficient into a molar extinction coefficient, use is made of the Bouguer-Lambert[10] relation and the Lambert law for attenuation of radiation in an absorbing medium which is

$$I/I_0 = \exp\,(-4\pi/\lambda o)K_1 d \qquad (8)$$

where K_1 is the absorption index, λo is the wavelength of incident radiation in a vacuum, and d is equal to layer thickness of the absorbing medium. The absorption coefficient usually employed in spectroscopy, k, is related to K_1 through

$$k = (4\pi/\lambda o)K_1 \qquad (9)$$

therefore,

$$I/I_0 = \exp(-kd) \qquad (10)$$

from the Beer-Lamber law

$$I/I_0 = 10^{-\varepsilon dc} \qquad (11)$$

where ε is the molar extinction coefficient and c is the molar concentration. Equating (10) and (11) gives

$$k = 2.3\varepsilon c \qquad (12)$$

$$\frac{k_{(\text{reflectance})}}{2.3} = k_{(\text{transmission})} \qquad (13)$$

Equation (12), corresponds to the Beer-Lambert Law, $I/I_0 = 10^{-\varepsilon cd}$, for both transmission measurements and diffuse reflectance. Thus, equations (12) and (13) are the relationships for relating absorption coefficients derived from transmission spectra and those derived from diffuse reflectance spectra. An experimental comparison between the two coefficients was carried out from values derived from transmission and diffuse spectra of colored glass.[11] At all wavelengths considered, the ratio of $k_{(\text{reflectance})}/k_{(\text{transmission})}$ is greater than 2.0. Although there are other factors to be considered, in any case, the fact is that the absorption coefficients measured in transmission are proportional but not identical to absorption coefficients measured in diffuse reflectance. The proportionality factor as determined experimentally appears to vary in the range 2.3 - 2.9, due to surface scattering effects.[11] Of course the true constant should be 2.3.

The fact that the extinction coefficient derived from diffuse reflectance studies should be proportional to the concentration in the same manner as the Beer-Lambert Law is valid for dilute solutions, was substantiated by testing the Kubelka-Munk function $F(R_\infty)$ by G. Schwuttke.[12] The Kubelka-Munk function can be written as follows

$$F(R_\infty) = \frac{c}{s}\text{, or } \log F(R_\infty) = \log C + B \qquad (14)$$

where s is the scattering coefficient, c the concentration and B a constant. Thus $F(R_\infty)$ is dependent upon the extinction coefficient and the concentration as long as the scattering remains constant. These conditions are essentially met in a sample diluted in a relatively large quantity of inert standard of high R_∞.

Conditions were such in these investigations that mole fraction concentrations were equivalent to molar concentrations. As an example: 0.0035 grams of K_2PtCl_4 and 0.0600 grams of KCl are used for one of the initial samples. The mole fraction is

$$\text{Mole fraction}(K_2PtCl_4) = \frac{\text{Moles}(K_2PtCl_4)}{\text{Moles }(K_2PtCl_4) + \text{Moles (KCL)}}$$

$$= \frac{0.0035\text{ g}/415\text{ g/mole}}{(0.0035\text{g}/\ 415\text{ g/mole} + (0.0600\text{ g}/74.6\text{ g/moles})}$$

Since the concentration of K_2PtCl_4 is small compared to KCl

$$\text{Mole fraction}(K_2PtCl_4) = \frac{\text{Moles}(K_2PtCl_4)}{\text{Moles (KCl)}}$$

$$= \frac{8.43 \times 10^{-6}\text{moles }(K_2PtCl_4)}{8.00 \times 10^{-4}\text{ moles (KCl)}}$$

$$= 1.05 \times 10^{-2}$$

If the sample is diluted with enough diluent KCl to fill the sample cell (1 cm x 1 cm), the molar concentration of the final sample is

$$C_{(K_2PtCl_4)} = \text{Moles }(K_2PtCl_4)\ /\ \text{volume of the cylinder}$$

$$C_{(K_2PtCl_4)} = 8.43 \times 10^{-6}\text{ moles}\ /\ \pi\ r^2h$$

$$C_{(K_2PtCl_4)} = [8.43 \times 10^{-6}\text{ moles}/\ 3.14(0.5)^2(1\text{ cm})](1\text{x}10^3\text{ cm}^3/\text{liter})$$

TABLE I.

DIFFUSE REFLECTANCE SPECTRA OF

K_2PtCl_4 IN KCl

Concentration = 2.6×10^{-3}M

λMaxima (mu) /	341	351	385	490	495	579
R	0.80	0.84	0.86	0.97	0.96	1.00
T	0.88	0.90	0.90	0.93	0.93	0.93
k	0.6	0.5	0.5	0.3	---	0.3
ε	100.3	83.6	83.6	50.2	----	55.8

Concentration = 5.9×10^{-2} M

λMaxima (mu) /	341	351	385	490	495	579
R	0.28	0.32	0.36	0.51	0.54	0.89
T	0.20	0.31	0.40	0.65	0.69	0.91
k	----	----	6.0	2.4	2.1	0.4
ε	----	----	44.1	17.7	15.4	2.9

R Absolute Diffuse Reflectance

T Transmission

k Absorption Coefficient

ε Extinction Coefficient

$$C_{(K_2PtCl_4)} = 1.07 \times 10^{-2} \text{ moles / liter}$$

Therefore, $C_{(\text{initial})}(\text{mole fraction}) = C_{(\text{final})}(\text{moles/liter})$

RESULTS AND DISCUSSION

Powder samples ranging in concentration from about 2×10^{-3} – 6×10^{-2} and 1×10^{-4}–1×10^{-3} molar, for K_2PtCl_4 and KCl and K_2SO_4 as the respective diluents. The $NiSO_4$-$7H_2O$ was measured in pure form, as dilution was found to be unneccessary.

TABLE II

COMPARATIVE ELECTRONIC SPECTRA OF K_2PtCl_4

Solution Spectrum[a]	Crystal Spectrum[b]		Diffuse Reflectance[c]
(mu)	(mu)	(Polarization)	(mu)
565	578	(xy)	579
476	495	(z)	490
	490	(xy)	495
392	385	(xy)	385
264	351	(xy)	351
217	341	(z)	341
	274 (?)		264
			215 (?)

(?) questionable values

a. See reference 13.

b. See reference 14.

c. This work.

Comparisons with single crystal and aqueous solution spectra are provided in Tables II and III.

Near UV-visible diffuse reflectance spectra of the $PtCl_4^{2-}$ chromophore are presented in part (because of space limitations) in Table I and Figure 1 a, b.

Similar data are also presented (in part) for $K_3Fe(CN)_6$ and for $NiSO_4$-$7H_2O$, in Figure 2 a, b and Table IV respectively.

It can be readily seen that good agreement between powder, crystal and liquid solution spectra has been obtained for anisotropic (D_{4h}symmetry) $PtCl_4^{2-}$, and isotropic (O_h symmetry) $Fe(CN)_6^{3-}$ and $Ni(OH_2)_6^{2+}$ optical chromophores. Of course, this is due in part to

TABLE III

K_2PtCl_4 EXTINCTION COEFFICIENTS

(mu)	Crystal[a]	Powder[b]	Error
	(ε)	(ε)	
351	57	62	9%
385	45	45	0%
490	17	18	6%
495	20	20	0%
579	(5)	6	--
341	70	67	4%

Error = ±4%

a. See reference 14.

b. This work.

( ) Uncertain values.

TABLE IV

COMPARATIVE ABSORPTION COEFFICIENTS
FOR $NiSO_4$-$7H_2O$

Maxima	k^a_{soln}	$k^a_{crystal}$	$k_{(this\ work)}$	$k_{(Englert-Boudreaux)}{}^b$
380	2.8	4.0	2.3	1.9
650	1.5	---	1.6	1.4
680	1.8	1.8	1.7	1.4
1170	2.0	2.5	2.1	1.8

a. See references 15 a-c.

b. There are corrections to those given in reference 16.

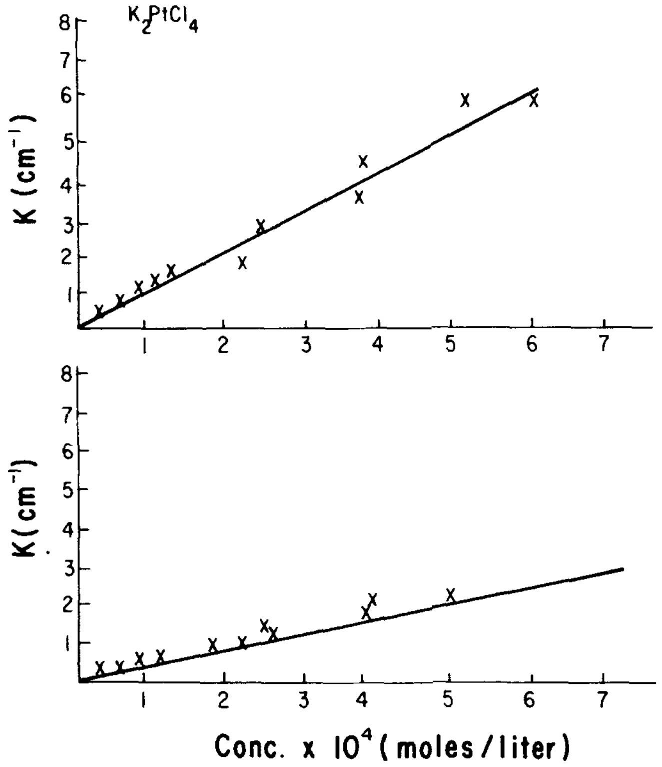

FIG. 1. a) Upper Curve: K_2PtCl_4/KCl powder (x) vs. K_2PtCl_4 crystal (solid line) 3 51 mμ. b) Lower Curve: K_2PtCl_4/KCl powder (x) vs. K_2PtCl_4 crystal (solid line) 490 mμ.

the fact that the optical integrity of these molecular units is preserved in each of these media.

The diffuse reflectance spectrum of $PtCl_4^{2-}$ closely matches that of the crystal and not the solution spectrum. Another interesting feature is that the polarized 490-495 mμ bands are 5 mμ out of phase.

The excellent results were obtained by carefully controlling the particle size, shape, and reducing the specular component of

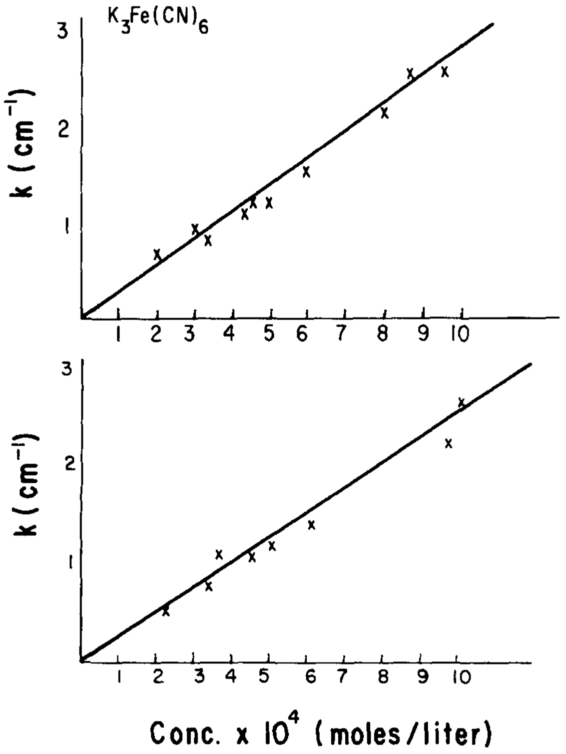

FIG. 2. a) Upper Curve: $K_3Fe(CN)_6/K_2SO_4$ powder (x) vs. $K_3Fe(CN)_6$ (aq) (solid line) at 254 mμ. b) Lower Curve: $K_3Fe(CN)_6/K_2SO_4$ powder (x) vs. $K_3Fe(CN)_6$ (aq) (solid line) at 417 mμ.

the sample. Control of the particle size is probably the most severe limitation of this statistical method. Large deviations in particle size resulted in erroneous results being obtained. The sieving and microscopic examination employed in this study minimized this error.

The ideal spherical geometry of the particle which was assumed in the derivation of the model, was maintained in essence by grinding the samples to a diameter of only 10 microns. Much smaller particles tend to fracture and would have necessitated a modification of the x_u factor.

Reduction of the specular component resulted in diffuse reflectance spectra which were well defined. Although the expected broadening of the maxima was observed, the spectra still compared very well with single crystal data and with solution, provided the crystal and solution spectra are equivalent. Reduction of the specular component was achieved by choice of diluent since the scattering coefficient was as high as that of the sample. Therefore, compounds with lower refractive indices were used as diluents and resulted in better resolved spectra.

Minimum error was also achieved by maintaining the diffuse reflectance values in the range of $0.3 \leq R \leq 0.7$, which was attained by diluting the samples. However, dilution also has the practical limitation that the sample size becomes small and hence major errors are introduced via contamination by handling. When this limit is reached, particle size reduction will also reduce the diffuse reflectance. Low diffuse reflectance values can also be increased by increasing the particle size. In this study, only dilution was used.

In conclusion, it appears that Melamed's statistical model in which the fundamental properties of the absorbing and scattering particles are directly related to measurable quantities, provides a reliable method for obtaining absorption coefficients for powders if the critical variables and proper conditions are maintained.

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