Quantitative diffuse reflectance and transmittance spectroscopy of loosely packed powders

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(Received 10 August 1990; in final form and accepted 29 January 1991)

Abstract—A self-consistent discontinuum theory describing the dependence of the diffuse reflectance and diffuse transmittance of powders on their optical absorption coefficient is presented. The theory is valid for particle sizes large compared to the exciting wavelength. It constitutes generalization and evolution of the statistical theory of absolute diffuse reflectance of powders put forth by N. T. MELAMED [J. Appl. Phys. 34, 560 (1963)]. Experimental evidence of the spectroscopic utility of the theory in determining absolute optical absorption coefficients self-consistently from both the reflectance and transmittance measurement channels sequentially is provided for two powders, and the new photothermal technique of Diffuse Transmittance Infrared Fourier Transform Spectroscopy (DTIFTS) is introduced. It is shown that the transmittance channel can be used advantageously to measure small changes in optical absorption spectra, as it is more sensitive to such changes than the diffuse reflectance. Practical experimental limits of the validity of the discontinuum theory are also established.

1. INTRODUCTION

IN ATTEMPTS to provide realistic descriptions of the optical properties of large powders (i.e. powders of size in the order, or greater than, ca ten times that of the probing wavelength), several workers abandoned the classical continuum theories of absorption and scattering of powder layers [1]. Many of those attempts treated discrete particles as plane parallel layers [2-4]. MELAMED [5] replaced the plane parallel layers with a statistical summation of reflected light intensity fractions over one layer of discrete particles reflecting light diffusely according to the laws of geometrical optics. The subsequent popularity [6-8] of Melamed's model is due to his quasi-realistic treatment of the discrete nature of absorbing powders, which includes geometrical factors dependent on packing density (or void fraction) and particle shape. Unfortunately, the model was found to contain conceptual inconsistencies, such as the use of a continuous substrate layer underneath the surface particle layer, having the same diffuse reflectance R. Therefore, the Melamed model must be considered a hybrid of discrete and continuum theories and, as such, physically artificial. Furthermore, it is too restrictive in that it treats a semi-infinite layer of nondescript continuum lying underneath a single layer of powder. For the work described below, our development of a photopyroelectric (P^2E) transmission detector has allowed us, for the first time, to obtain photothermally mid-IR diffuse transmission spectra from loose powders of low absorptance. Thus, we required a model to treat both diffuse reflectance and transmittance from finite thickness particle layers.

In this work, a self-consistent non-hybrid theory is given in agreement with the fundamental physical principle of optical energy conservation. Expressions are developed for the diffuse reflectance and trasmittance of layers of discrete particles of arbitrary thickness (i.e. arbitrary number of layers in a multi-stack system). The theory is then applied to calculations of optical absorption spectra of Na₂CO₃ and surface derivatized powders using photopyroelectric Fourier transform infrared (FTIR- P^2E) detection and self-consistent manipulation of the diffuse reflectance (DRIFTS) and the new diffuse transmittance (DTIFTS) data channels.

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2. DIFFUSE REFLECTANCE AND TRANSMITTANCE THEORY OF MULTI-LAYERED POWDER STACKS

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The multi-layer geometry considered in this work is shown in Fig. 1(a). The assumed regularity of the powder stack is idealized, as depicted in Fig. 1(a), however, any deviations of real powders from the ideal stack geometry impact on the value of the packing density only [5]. This value is derived by a fit of experimental data to the theory (see Section 3 below), and as such it does not represent a limitation on the applicability of this treatment to specific stack geometries. The building blocks of the theory consist of: (a) single particle diffuse reflectance and transmittance functions; (b) optical transfer functions for interfacial incidence in the two-layer stack; (c) optical transfer functions of two-layer stack for incident intensity from below (due to back-scattered bulk radiation); (d) multiple-layer treatment via single-particle equivalent (SPE) transfer functions.

2.1. Single particle diffuse functions

In the entirety of this theoretical treatment, spherical particle geometries of large diameter compared to the wavelength of the exciting radiation will be assumed throughout. Although sphericity is a convenient oversimplification of actual powder stacks, it is by no means restrictive of the scope of the theory: besides a small effect due to powder packing density variations (to be dealt with in Section 3 below), particle geometry is mostly important at the single particle level, and specifically in calculating the fraction of radiation reaching the particle surface after absorption throughout its bulk. Therefore, different shapes will result in integrating Lambert's cosine law over a different volume, thus changing the functional dependence of the non-absorbed fraction M on particle geometry. Application of Lambert's cosine law to an idealized spherical particle yields [5]:

$$M(k) = \frac{2}{(kd)^2} [1 - (kd + 1) \exp(-kd)]$$
(1)

where $k = k(\lambda)$ is the particle optical absorption coefficient at wavelength λ , and d is the particle diameter. For optically thin particles, Eqn (1) gives upon expansion of the exponential:

$$M(kd \leq 1) \approx 1 - \frac{2}{3}(kd) + \frac{1}{4}(kd)^2 - \dots,$$
 (2)

so that

$$M(0) = 1 \tag{3}$$

for absolutely transparent particles. Assuming unit incident intensity of radiation on a single spherical particle, and following Melamed, the initial contribution to the diffuse reflectance due to the surface particle $R^{(s)}$ is taken to be [5] $2x\bar{m}_e$, where x is the fraction of radiation scattered in the upward direction, expressed as a fraction of 4π steradians, and $\bar{m}_e(n)$ is the average external reflection coefficient, a function of the refractive index n. The factor 2 appears due to the fact that the reflected component of the incident ray is scattered through approximately 2π steradians by the surface particle. No such factor is required for reflections from underlying particles. Such particles are assumed to scatter the reflected component of the incident radiation through a 4π sterad solid angle, due to the symmetric presence of nearest neighbors in all directions. In the geometry of Fig.

(a)





Fig. 1. (a) Idealized geometry of a uniform, multilayered powder as ordered stacks of single, identical particles of diameter d. The thickness of the powder, corresponding to N layers, is L = Nd. Incident monochromatic radiation at wavelength λ of unit intensity $I_i = 1$ is assumed to result in diffuse reflectance $R_{IM}^{T}(k)$ and diffuse transmittance $T_{IM}^{T}(k)$; $k(\lambda)$ is the powder optical absorption coefficient at excitation wavelength λ ; (b) geometry for the calculation of single particle diffuse reflectance and transmittance. All symbols are defined in Eqn (4).

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$$I_1 = 2x\bar{m}_e \tag{4a}$$

$$I_2 = 1 - 2x\bar{m}_e \tag{4b}$$

$$I_3 = I_2 M \tag{4c}$$

$$I_4 = \bar{m}_i I_3 = \bar{m}_i M I_2 \tag{4d}$$

$$I'_3 = I_3 - I_4 = (1 - \bar{m}_i)MI_2$$
 (4e)

$$I_5 = I_4 M = \tilde{m}_i M^2 I_2 \tag{4f}$$

$$I_6 = \bar{m}_i I_5 = \bar{m}_i^2 M^2 I_2 \tag{4g}$$

$$I_7 = I_5 - I_6 = (1 - \bar{m}_i)\bar{m}_i M^2 I_2$$
(4h)

$$I_8 = I_6 M = \bar{m}_i^2 M^3 I_2 \tag{4i}$$

$$I_9 = x\bar{m}_i I_8 = \bar{m}_i^3 M^3 I_2 \tag{4j}$$

$$I'_8 = I_8 - I_9 = (1 - \bar{m}_i)\bar{m}_i^2 M^3 I_2.$$
(4k)

In Eqns (4), the symbol $\bar{m}_i = \bar{m}_i(n)$ stands for the average internal reflection coefficient, a function of the refractive index n.

Upon addition of all the optical intensity fractions contributing to upward transmission (i.e. to diffuse reflectance) one obtains:

$$R^{(s)} = I_1 + I_7 + I_{12} + \dots = 2x\bar{m}_e + (1 - \bar{m}_i)\bar{m}_i M^2 I_2 + (1 - \bar{m}_i)\bar{m}_i^3 M^4 I_2 + \dots$$
$$= 2x\bar{m}_e + (1 - \bar{m}_i)\bar{m}_i M^2 I_2 [1 + (\bar{m}_i M)^2 + (\bar{m}_i M)^4 + \dots]$$

or, for infinite internal interreflections:

$$R^{(s)}(k) = 2x\bar{m}_{e} + (1 - 2x\bar{m}_{e}) \left[\frac{(1 - \bar{m}_{i})\bar{m}_{i}M^{2}}{1 - (\bar{m}_{i}M)^{2}} \right].$$
 (5)

Furthermore, summing up the infinite number of fractions contributing to downward transmission (i.e. to diffuse transmittance) yields:

$$T^{(s)} = I'_{3} + I'_{8} + \cdots = (1 - \bar{m}_{i})MI_{2} + (1 - \bar{m}_{i})\bar{m}_{i}^{2}M^{3}I_{2} + \cdots$$
$$= (1 - \bar{m}_{i})MI_{2}[1 + (\bar{m}_{i}M)^{2} + (\bar{m}_{i}M)^{4} + \cdots]$$

or

$$T^{(s)}(k) = (1 - 2x\bar{m}_e) \left[\frac{(1 - \bar{m}_i)M}{1 - (\bar{m}_iM)^2} \right].$$
 (6)

It will be noticed that Eqn (6) is the result of unidimensional geometric considerations (upward and/or downward light diffusion). Taking into account lateral diffusion properly would yield a three-dimensional solution to the problem for the price of essentially analytically intractable geometric complications. Instead, lateral contributions have been resolved into their upwards and downwards components [5] via the assumption of isotropic scattering from a particle, with the sole effect of defining x in terms of the probability for diffuse scattering in the upward direction only (Section 3 below). Equations (5) and (6) can be easily shown to give for absolutely transparent particles

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$$R^{(s)}(0) + T^{(s)}(0) = 1 \tag{7}$$

as expected from conservation of optical energy in the case of no absorptive losses.

2.2. Optical transfer functions for interfacial incidence in a two-layer stack

A transfer function corresponds to the optical response (output) of a particle (reflection, transmission and absorption) to unit intensity of incident radiation (input). In this context $R^{(s)}(k)$ and $T^{s}(k)$ are single particle reflectance and transmittance transfer functions, respectively, for light incidence from above. At the interface between two identical particles, members of a two-layer powder stack, a finite incident intensity in the downward direction results from transmission through the surface particle layer. Figure 2(a) shows that contributions to diffuse reflectance from the lower particle arise from (i) direct external reflection at its upper surface, of magnitude:

$$R_1^{(b)} = x\bar{m}_c; \tag{8}$$

and (ii) penetration into the lower particle, multiple internal reflection, and reemergence from the upper surface, of magnitude:

$$R_2^{(b)} = (1 - x\bar{m}_e)R^{(b)}(k)$$
(9)

where $R^{(b)}(k)$ is the upward reflected fraction of unit intensity incident on a bulk (i.e. below the surface layer) particle. An approach similar to the calculation of $R^{(s)}(k)$ yields:

$$R^{(b)}(k) = \frac{(1 - \bar{m}_i)\bar{m}_i M^2}{1 - (\bar{m}_i M)^2}$$
(10)

so that the total amount of reflected energy from the lower particle is:

$$q \equiv R_1^{(b)} + R_2^{(b)} = x\bar{m}_e + (1 - x\bar{m}_e)R^{(b)}(k).$$
(11)

It should be noticed that q differs from $R^{(s)}(k)$ only to the extent that the fraction of radiation x scattered upward is assumed to suffer symmetric scattering through 4π , rather than 2π , steradians by the bulk particle. Furthermore, it is convenient to define in Fig. 2(a) the fraction $T^{(b)}(k)$ of t_i intensity (penetrating the lower particle) which exits from the bottom surface as T_1 , so that:

$$T_1 = t_i T^{(b)}(k) = (1 - x\bar{m}_e) T^{(b)}(k).$$
(12)

An approach similar to the calculation of $T^{(s)}(k)$ gives:

$$T^{(b)}(k) = \frac{(1 - \bar{m}_i)M}{1 - (\bar{m}_i M)^2}.$$
(13)

In order to account for the infinite reflections between the surface and bulk particles at the interface, one may assume single particle reflectance and transmittance transfer functions, $F_{(1)}^{(R)}$ and $F_{(1)}^{(T)}$, respectively, for light incidence from below, Fig. 2(b), and then treat the two-particle system as two planar material layers, between which light interferes in the classical geometric optics limit consistent with the large size of the particles. The geometry is shown in Fig. 2(c), with each particle represented by a thin layer of infinite lateral dimensions accounting for infinite interreflections. Using the symbols shown in

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Fig. 2. Geometry for the calculation of two-particle stack optical transfer functions. (a) Calculation of total amount of reflected energy from bulk particle, assuming unit input intensity from above, $I_i = 1$. $R_1^{(b)}$, $R_2^{(b)}$ and t_i were defined in the text. T_1 corresponds to transmission after infinite interreflections. $R_1^{(b,i)} = (1-x)m_e R_1^{(b)}$; and $r_i = R_1^{(b)} - R_1^{(b,i)} = [1-(1-x)m_e]xm_e$ is the fraction of returning light coupled into the surface particle. The two particles were artificially separated from contact to illustrate interfacial optical processes; (b) schematic for the calculation of single particle optical transfer functions for incidence at lower surface. If the depicted particle is not a surface layer member, $F^{(R)}$ and $F^{(T)}$ must be replaced by $F_{(N-1)}^{(R)}$ and $F_{(N-1)}^{(T)}$, respectively [see Eqns (17)]; (c) calculation of optical transfer functions R_{IF} and T_{IF} for interfacial contributions to diffuse reflectance and transmittance.

Figs 2(b) and (c) we write:

$$F_{1}^{(R)} = qF_{(1)}^{(R)}$$
(14a)

$$F_{1}^{(T)} = qF_{1}^{(T)}$$
 (14b)

$$T_1 = (1 - x\bar{m}_e)T^{(b)}$$
 (14c)

$$T_2 = (1 - x\bar{m}_c)T^{(b)}F_1^{(T)} = q(1 - x\bar{m}_c)T^{(b)}F_{(1)}^{(T)}$$
(14d)

$$F_{2}^{(R)} = qF_{1}^{(T)}F_{(1)}^{(R)} = q^{2}F_{(1)}^{(T)}F_{(1)}^{(R)}$$
(14e)

$$F_2^{(T)} = q F_{(1)}^{(T)} F_1^{(T)} = q^2 [F_{(1)}^{(T)}]^2$$
(14f)

$$T_3 = (1 - x\bar{m}_e)T^{(b)}F_2^{(T)} = q^2(1 - x\bar{m}_e)T^{(b)}[F_{(1)}^{(T)}]^2$$
(14g)

$$F_3^{(\mathbf{R})} = q F_2^{(\mathbf{T})} F_{(1)}^{(\mathbf{R})} = q^3 [F_{(1)}^{(\mathbf{T})}]^2 F_{(1)}^{(\mathbf{R})}.$$
 (14h)

Summing up all the upward reflected fractions gives the contribution of the two-particle stack to the reflectance for unit input interfacial intensity T=1, i.e. the interfacial reflectance transfer function:

$$R_{\rm IF} = \sum_{j=1}^{\infty} F_j^{\rm (R)} = q F_{(1)}^{\rm (R)} + q^2 F_{(1)}^{\rm (R)} F_{(1)}^{\rm (T)} + q^3 [F_{(1)}^{\rm (T)}]^2 F_{(1)}^{\rm (R)} + \dots = \frac{q F_{(1)}^{\rm (R)}}{1 - q F_{(1)}^{\rm (T)}}.$$
 (15)

Similarly, one obtains the two-particle stack interfacial transmittance transfer function:

$$T_{\rm IF} = \sum_{j=1}^{\infty} T_j = (1 - x\bar{m}_e) T^{\rm (b)} (1 + qF_{\{1\}}^{\rm (T)} + q^2 [F_{\{1\}}^{\rm (T)}]^2 + \cdots)$$
$$= (1 - x\bar{m}_e) \left[\frac{T^{\rm (b)}}{1 - qF_{\{1\}}^{\rm (T)}} \right].$$
(16)

Equations (15) and (16), valid for a two-particle stack with an interface, where the upper layer of particles is the surface layer with transfer functions $F_{(1)}^{(R)}$ and $F_{(1)}^{(T)}$, may be easily generalized to represent the transfer functions of the interface between the (N-1)th and Nth layers. The only change required for this extension is the replacement of $F_{(1)}^{(R)}$ and $F_{(1)}^{(T)}$ with appropriate transfer functions for the (N-1)th layer:

$$F_{(1)}^{(R)} \to F_{(N-1)}^{(R)}$$
 (17a)

$$F_{(1)}^{(\mathrm{T})} \rightarrow F_{(N-1)}^{(\mathrm{T})}.$$
(17b)

Under these conditions we may write:

$$R_{\rm IF}^{(N)} = \frac{qF_{(N-1)}^{(R)}}{1 - qF_{(N-1)}^{(T)}}$$
(18)

and

$$T_{\rm IF}^{(N)} = (1 - x\bar{m}_e) \left[\frac{T^{(b)}}{1 - qF_{(N-1)}^{\rm (T)}} \right].$$
 (19)

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In order for the total diffuse reflectance of the N-layer particle stack $R_{(N)}^{T}$ to be calculated, $R_{1F}^{(N)}$ must be multiplied by the optical transmission output $T_{(N-1)}^{T}$ of the SA(A) 47:7-I

(N-1)-layer stack, resulting from unit intensity incidence on the surface (N=1) layer, and the product should then be added to the total diffuse reflectance $R_{(N-1)}^{T}$ of the (N-1)-layer stack. The total diffuse transmittance of the N-layer particle stack, $T_{(N)}^{T}$, can be found upon multiplying $T_{1F}^{(N)}$ by the optical transmission output $T_{(N-1)}^{T}$ of the (N-1)-layer stack, resulting from unit intensity incidence on the surface layer. Conservation of optical energy for the Nth layer transfer functions may be proven in the limit k=0 as follows: Given conservation of the (N-1)th layer functions

$$F_{(N-1)}^{(T)}(0) + F_{(N-1)}^{(R)}(0) = 1,$$
(20)

then Eqns (18) and (19) give:

$$R_{1F}^{(N)}(0) + T_{1F}^{(N)}(0) = \frac{qF_{(N-1)}^{(R)}(0) + (1 - x\bar{m}_{e})T^{(b)}(0)}{1 - qF_{(N-1)}^{(T)}(0)}$$

= $[q\{1 - F_{(N-1)}^{(T)}(0)\} + \{(1 - x\bar{m}_{e})/(1 + \bar{m}_{i})\}]/[1 - qF_{(N-1)}^{(T)}(0)]$
= $\frac{1 - qF_{(N-1)}^{(T)}(0)}{1 - qF_{(N-1)}^{(T)}(0)} = 1.$ (21)

2.3. Optical transfer functions for two-layer stack; incidence from below

The calculation of these functions is necessary because back-scattered radiation from low lying particle layers acts as an optical source for overlying particles. Therefore, the effects of a new underlying Nth layer on the diffuse functions of the (N-1)-layer stack amount to: (i) an additive contribution to reflectance due to light, transmitted through the (N-1)-layers, being partially reflected upwards by the Nth layer; and (ii) a multiplicative attenuation of the transmittance, as the light transmitted through the (N-1)-layers must pass, and be partially absorbed, through the body of the Nth layer. In the single particle geometry of Fig. 2(b) incidence from below is equivalent to incidence from above, Fig. 1(b), provided that x is replaced by (1-x), indicating the fraction of radiation scattered back in the *downward* direction, expressed as a fraction of $4^{\text{T}}_{(1)}$, viewed as a 'downward reflectance', which contributes, of course, to the overall transmittance:

$$F_{(1)}^{(\mathrm{T})} \equiv p = (1-x)\bar{m}_e + [1-(1-x)\bar{m}_e]R^{(\mathrm{b})}$$
(22)

where the first term on the right-hand side is due to direct reflection of the incident energy at the lower surface of the particle, and the second term is the sum of fractions of radiation penetrating the particle material, which, upon internal reflection and absorption, exit the lower surface after successive, infinite round trips. Similarly, one finds that, since the direct reflected fraction at the lower surface is $(1-x)\bar{m}_e$, the fraction penetrating the particle material is $[1-(1-x)\bar{m}_e]$ and, reasoning as in the derivation of Eqn (6),

$$F_{(1)}^{(R)} \equiv J = [1 - (1 - x)\bar{m}_e]T^{(b)}.$$
(23)

It ought to be noticed that the functions $R^{(b)}$ and $T^{(b)}$ have been employed in Eqns (22) and (23) instead of $R^{(s)}$ and $T^{(s)}$, consistent with the bulk nature of all lower-side particle surfaces, including that of surface layer particles.

Once the single particle transfer functions $F_{(1)}^{(R)}$ and $F_{(1)}^{(T)}$ have been determined, the two-layer stack diffuse functions can be readily determined from Eqns (18) and (19) and the operations described in the paragraph following those equations. Setting N=2,



Fig. 3. Schematic representation of total diffuse reflectance and transmittance for a two-layer stack as a combination of simple algebraic operations between the upper and lower layer subsystems. The ∞ symbols indicate summations of infinite partial rays contributing to the operation shown.

 $T_{(N-1)}^{T} = T^{(s)}, R_{(N-1)}^{T} = R^{(s)}$ one obtains:

$$R_{(2)}^{\mathsf{T}} = \left[\frac{qF_{(1)}^{(\mathsf{R})}}{1 - qF_{(1)}^{(\mathsf{T})}}\right] T^{(\mathsf{s})} + R^{(\mathsf{s})} = R^{(\mathsf{s})} + q\left(\frac{J}{1 - qp}\right) T^{(\mathsf{s})}$$
(24)

and

$$T_{(2)}^{\mathrm{T}} = (1 - x\bar{m}_{e}) \left[\frac{T^{(b)}}{1 - q\bar{F}_{(1)}^{(\mathrm{T})}} \right] T^{(s)} = \left(\frac{K}{1 - qp} \right) T^{(s)}$$
(25)

where

$$K \equiv (1 - x\bar{m}_{\rm e})T^{\rm (b)}$$
. (26)

In a laborious, but straightforward manner, it can be shown algebraically that Eqns (24) and (25) are consistent with the requirement for conservation of optical energy in the two-layer stack:

$$R_{(2)}^{\mathrm{T}}(k=0) + T_{(2)}^{\mathrm{T}}(k=0) = 1.$$
(27)

Figure 3 shows schematically the combination of operations required to produce the diffuse functions for N=2. It is important to note that the optical transfer functions for

two particles can be described by considering the upper particle as a 'black-box' characterized by its own forward and back-scattering transfer functions $F^{(R)}$ and $F^{(T)}$, which multiply the inputs from the lower particle plus the interface, according to Eqns (15) and (16). This description is extremely useful for building up multi-layer diffuse functions, with the (N-1) upper layers being considered as a single-particle-equivalent (SPE) black box with known transfer functions.

2.4. SPE treatment of multiple-layered stacks

In view of Part 2.3 above, multi-layer stacks can be easily treated by considering the effects of the presence of (N-1)-layers over the Nth layer. For a three-layer stack, this entails calculating the outputs of a two single-particle equivalent (2-SPE) structure for an arbitrary interfacial optical input T_a from below, as is the case with the additive reflectance contribution from a new (3rd) underlayer: the geometry is entirely similar to Fig. 2(c) with $F_j^{(R)} \rightarrow F_{(2)j}^{(R)}$; $F_j^{(T)} \rightarrow F_{(2)j}^{(T)}$; $T_j \rightarrow T_{(2)j}$; and with the T=1 downward input having been replaced by $T = T_a$, an upward input as shown in Fig. 4. Then infinite series of contributions to $F_{(2)}^{(R)}$ and $F_{(2)}^{(T)}$, similar to the fractions of Part 2.2 above, may be written and summed up to yield:

$$F_{(2)}^{(R)} = T_{a} \left[\frac{F_{(1)}^{(R)}}{1 - q F_{(1)}^{(T)}} \right]$$
(28)

and

$$F_{(2)}^{(\mathrm{T})} = p + (1 - x\bar{m}_{e}) \left[\frac{T^{(b)} F_{(1)}^{(\mathrm{T})}}{1 - qF_{(1)}^{(\mathrm{T})}} \right] T_{a}.$$
 (29)

When unit intensity, $I_i = 1$, is incident from below the 2-SPE, T_a becomes the single particle reflection transfer function $F_{(1)}^{(R)} = J$, Fig. 2(b); in addition, the term $F_{(1)}^{(T)} = p$ appears in Eqn (29) as the lower particle's individual contribution to the transmittance.



Fig. 4. Schematic illustration of transfer functions from two-single-particle equivalent (2-SPE) layer; the equivalence of the two-particle stack with, and replacement by, a single 2-SPE is also shown.

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Equations (28) and (29) become the 2-SPE transfer functions and may thus be re-written as:

$$F_{(2)}^{(R)} = \frac{J^2}{1 - qp} \tag{30}$$

and

$$F_{(2)}^{(\mathrm{T})} = p \left[1 + \left(\frac{KJ}{1 - qp} \right) \right]. \tag{31}$$

Since the interface between the N=1 and N=2 layers may also be taken to be the (N-1)th and Nth layer interface, Eqns (28) and (29) may also be written generally as the following optical transfer functions:

$$F_{(N)}^{(\mathbf{R})} = J\left(\frac{F_{(N-1)}^{(\mathbf{R})}}{1 - qF_{(N-1)}^{(\mathbf{T})}}\right)$$
(32)

and

$$F_{(N)}^{(T)} = p + J\left(\frac{KF_{(N-1)}^{(T)}}{1 - qF_{(N-1)}^{(T)}}\right)$$
(33)

where p appears in Eqn (33) as the contribution of the Nth particle layer alone to diffuse transmittance.

Equations (30) and (31), along with Eqns (18) and (19), and the operations described in the paragraph following those equations, can readily give the diffuse functions for the three-layer stack: Setting N=3, $T_{(N-1)}^{T}=T_{(2)}^{T}$, $R_{(N-1)}^{T}=R_{(2)}^{T}$ one obtains:

$$R_{(3)}^{\mathsf{T}} = \left[\frac{qF_{(2)}^{(\mathsf{R})}}{1 - qF_{(2)}^{(\mathsf{T})}}\right]T_{(2)}^{\mathsf{T}} + R_{(2)}^{(\mathsf{T})}.$$
(34)

Use of Eqns (22), (24), (25) and (30) gives:

$$R_{(3)}^{\mathrm{T}} = R^{(s)} + \frac{qJT^{(s)}}{1 - qp} \left(1 + \frac{KJ}{(1 - qp)[1 - qF_{(2)}^{\mathrm{T}}]} \right).$$
(35)

Similarly, for the diffuse transmittance:

$$T_{(3)}^{\mathrm{T}} = (1 - x\tilde{m}_{e}) \left[\frac{T^{(b)}}{1 - qF_{(2)}^{\mathrm{T}}} \right] T_{(2)}^{\mathrm{T}},$$
(36)

so that use of Eqns (22) and (25) gives:

$$T_{(3)}^{\mathrm{T}} = \left(\frac{K^2}{(1-qp)[1-qF_{(2)}^{(\mathrm{T})}]}\right)T^{(\mathbf{s})}.$$
(37)

The diffuse functions for the four-layer stack can be easily found considering a three-single-particle-equivalent (3-SPE) overlayer 'black box' with a single particle layer below the 3-SPE: (a) Since the transfer functions for the 2-SPE are known, Eqns (30)

and (31), those of the 3-SPE may be found from Eqns (32) and (33) with N=3:

$$F_{(3)}^{(\mathbf{R})} = J\left(\frac{F_{(2)}^{(\mathbf{R})}}{1 - qF_{(2)}^{(\mathbf{T})}}\right),\tag{38}$$

and

$$F_{(3)}^{(\mathrm{T})} = p + J\left(\frac{KF_{(2)}^{(\mathrm{T})}}{1 - qF_{(2)}^{(\mathrm{T})}}\right);$$
(39)

(b) Equations (38) and (39) when combined with Eqns (30) and (31) give the 3-SPE transfer functions for incidence from below (an optical source due to the presence of the fourth layer):

$$F_{(3)}^{(\mathbf{R})} = \frac{J^3}{(1-qp)[1-qF_{(2)}^{(\mathbf{T})}]} = \frac{J^3}{(1-qp)^2 - qpKJ}$$
(40)

and

$$F_{(3)}^{(\mathrm{T})} = p \left[1 + \left(1 + \frac{KJ}{1 - qp} \right) \left(1 + \frac{KJ}{1 - qp \left[1 + \left(\frac{KJ}{1 - qp} \right) \right]} \right) \right]; \quad (41)$$

(c) Upon calculation of the 3-SPE transfer functions, the effects of the presence of layer four can be found by replacing the 'surface particle' in Fig. 2(c) with the 3-SPE. Computationally, the recipe outlined in Part 2.2 above must be followed, so as to yield:

$$R_{(4)}^{\mathrm{T}} = \left[\frac{qF_{(3)}^{(\mathrm{R})}}{1 - qF_{(3)}^{(\mathrm{T})}}\right]T_{(3)}^{\mathrm{T}} + R_{(3)}^{\mathrm{T}}$$
(42)

and

$$T_{(4)}^{\mathrm{T}} = (1 - x\tilde{m}_{e}) \left[\frac{T^{(b)}}{1 - qF_{(3)}^{(\mathrm{T})}} \right] T_{(3)}^{\mathrm{T}};$$
(43)

(d) Substituting Eqns (22), (35), (37), (40) and (41) into Eqns (42) and (43) gives for the four-layer stack diffuse functions the following expressions:

$$R_{(4)}^{\mathrm{T}} = R^{(5)} + qJ \left\{ \frac{1}{1 - qp} + \frac{KJ}{(1 - qp)^{2} [1 - qF_{(2)}^{(\mathrm{T})}]} + \frac{(KJ)^{2}}{(1 - qp)^{2} [1 - qF_{(2)}^{(\mathrm{T})}]^{2} [1 - qF_{(3)}^{(\mathrm{T})}]} \right\} T^{(5)}(44)$$

and

$$T_{(4)}^{\mathrm{T}} = \left(\frac{K^{3}}{(1-qp)\left[1-qF_{(2)}^{\mathrm{(T)}}\right]\left[1-qF_{(3)}^{\mathrm{(T)}}\right]}\right)T^{(s)}$$
(45)

The proofs of optical energy conservation for the three- or four-layer stacks of particles are too cumbersome to perform algebraically; however, it can be easily shown with computer simulations that

$$R_{(N)}^{T}(k=0) + T_{(N)}^{T}(k=0) = 1; N \ge 3.$$
(46)

The procedure followed in steps (a)-(d) above for the calculation of $R_{(4)}^{T}$ and $T_{(4)}^{T}$ may be repeated for N>4 stacks of powders, and general expressions result, which can be

written in a compact form as follows:

$$R_{(N)}^{\mathrm{T}} = R^{(\mathrm{s})} + qJT^{(\mathrm{s})} \sum_{m=1}^{N-1} \frac{1}{1 - qF_{(m)}^{(\mathrm{T})}} \left[\frac{(JK)^{m-1}}{\left(\prod_{i=0}^{m-1} \left[1 - qF_{(i)}^{(\mathrm{T})} \right] \right)^2} \right]$$
(47)

and

$$T_{(N)}^{\mathrm{T}} = \left(\begin{array}{c} \frac{K^{N-1}}{\prod_{i=0}^{N-1} \left[1 - qF_{(i)}^{(\mathrm{T})}\right]} \end{array} \right) T^{(s)}$$
(48)

where

$$\prod_{i=0}^{J} [1 - qF_{(i)}^{(T)}] = [1 - qF_{(0)}^{(T)}][1 - qF_{(1)}^{(T)}] \dots [1 - qF_{(j)}^{(T)}]$$
(49)

with the convention

$$\prod_{i=0}^{0} \left[1 - q F_{(i)}^{(T)} \right] = 1 - q F_{(0)}^{(T)} = 1 \text{ (i.e. } F_{(0)}^{(T)} = 0 \text{).}$$
(50)

The range of validity of the number of layers N in the powder, which appears in Eqns (47) and (48) is

$$1 \leq N < \infty$$
 (51)

always subject to condition (46).

Equation (33) provides a recursion relation for the numerical calculation of $F_{(j)}^{(T)}$ from the value of $F_{(j-1)}^{(T)}$ in Eqns (47) and (48):

$$F_{(j)}^{(\mathrm{T})} = p + KJ\left(\frac{F_{(j-1)}^{(\mathrm{T})}}{1 - qF_{(j-1)}^{(\mathrm{T})}}\right); j \ge 1.$$
(52)

According to our convention (50), seed value for j=0 in Eqn (52) is

$$F_{(0)}^{(\mathrm{T})} = 0, \tag{53}$$

with Eqns (22), (31) and (41) giving the expressions for j=1, 2 and 3, respectively. Expressions for higher (j) values are best obtained numerically, although analytic expressions are always possible.

3. Computer Simulations of Diffuse Functions and Parameter Dependence Studies

The multi-layer powder theory has been used in computer simulations to study the large-size powder spectroscopic behavior from the viewpoint of diffuse reflectance and transmittance dependences on the optical absorption coefficient k via the absorptance, kd. In this work the product (kd) is used in lieu of the more conventional spectroscopic notation $1 - T^{T}(k) - R^{T}(k)$. The calculations require evaluation of the external and internal reflection coefficients, $\bar{m}_{e}(n)$ and $\bar{m}_{i}(n)$, respectively, at the single-particle level.

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Recent calculations of these coefficients [9] for absorbing particles producing uniformly diffuse radiation gave the following functional dependences on refractive index:

$$\bar{m}_{e}(n) = \frac{n^{4} - \frac{8}{3}n^{3} + 2n^{2} - \frac{1}{3}}{2(n^{2} - 1)^{2}} + \frac{n^{8} - 8n^{6} + 6n^{4} + 1}{2(n^{2} + 1)^{2}(n^{2} - 1)^{2}} - \frac{2n^{3}}{(n^{2} + 1)^{2}} + \left[\frac{8n^{4}(n^{4} + 1)}{(n^{2} + 1)(n^{2} - 1)^{4}}\right] \ln(n) - \left[\frac{n^{2}(n^{2} - 1)^{2}}{(n^{2} + 1)^{3}}\right] \ln\left(\frac{n + 1}{n - 1}\right); n \ge 1$$
(54)

and

$$\bar{m}_{i}(n) = 1 - \frac{1}{n^{2}} + \frac{1}{2(n^{2} - 1)^{2}} \left(n^{2} - \frac{8}{3}n + 2 - \frac{1}{3n^{2}} \right) - \frac{2n}{(n^{2} + 1)^{2}} + \frac{n^{6} - 8n^{4} + 6n^{2} + n^{-2}}{2(n^{2} + 1)^{2}(n^{2} - 1)^{2}} \\ + \left[\frac{8n^{2}(n^{4} + 1)}{(n^{2} + 1)(n^{2} - 1)^{4}} \right] \ln(n) - \left[\frac{(n^{2} - 1)^{2}}{(n^{2} + 1)^{3}} \right] \ln\left(\frac{n + 1}{n - 1}\right); n \ge 1.$$
(55)

The above expressions can, in principle, be modified appropriately to include effects of the extinction coefficient of strongly absorbing particles, without further changes in the theoretical framework presented above. In that case, one needs to replace $\bar{m}_e(n)$ with $\bar{m}_e(n, k)$ and $\bar{m}_i(n)$ with $\bar{m}_i(n, k)$. Another parameter which appears in the theory is the fraction x of radiation scattered in the upward direction [and the fraction (1-x)scattered in the downward direction]. This parameter has been given by MELAMED [5] as a function of the average single particle transmission $\langle T \rangle$ throughout its entire surface:

$$x = \frac{x_u}{1 - (1 - 2x_u)\langle T \rangle}$$
(56)

where in the present theoretical framework we can show [see Eqns (10) and (13)]:

$$\langle T \rangle = \frac{(1 - \bar{m}_{\rm i})\bar{m}_{\rm i}M^2}{1 - (\bar{m}_{\rm i}M)^2} + \frac{(1 - \bar{m}_{\rm i})M}{1 - (\bar{m}_{\rm i}M)^2} = \frac{(1 - \bar{m}_{\rm i})M}{1 - \bar{m}_{\rm i}M}$$
(57)

and x_u is a constant representing the probability for diffuse scattering in the upward direction, thus contributing to diffuse reflectance. MONAHAN and NOLLE [8] took into account the anisotropic emission from particles due to simultaneously occurring absorption, and presented a more complete expression for x:

$$x = \frac{x_{u}}{1 - (1 - x_{u}[1 + \exp(-kd)])\langle T \rangle}.$$
 (58)

MELAMED [5] used the value $x_u = 0.284$ corresponding to a solid angle of $(4 - \sqrt{3}/2)\pi$ steradians, which represents close-packed spheres. In our experience [9] and that of others [6], the actual value of x_u required for best fits of theoretical diffuse reflectance curves to experimental data has little physical significance and may be fixed empirically so as to give the best fit for a given powdered specimen. Equation (58), in comparison with Eqn (56), is a further manifestation of the fact that solid angle considerations alone may not be adequate to calculate a physically meaningful value of x, or the effective x_u value, for an ideal powder stack. Besides, it is very difficult to calculate x_u analytically for non-spherical (i.e. real) powders stacked in non-ideal geometries, unlike Fig. 1(a). In our view, the main experimental significance which may be attributed to x_u is that best-fit reproducibilities of its value in each case are important as characteristic indicators of the reproducibility of average packing conditions in powered samples. For applications of the present theory, Eqn (56) was chosen to represent x, as it was previously found [9]



Fig. 5. Computer simulations of $R_{(N)}^{T}$ and $T_{(N)}^{T}$, Eqns (47) and (48), respectively, for N=5; n=1.46 (an average for Na₂CO₃ powders); $0.1 \le x_u \le 0.4$ in steps of 0.05: (a) absolute diffuse reflectance; and (b) absolute diffuse transmittance.

that the actual functional form of x = x(kd) has little effect on powders of loose packing, such as those in our experiments. Figure 5 shows computer simulations of $R_{(N)}^{T}$ and $T_{(N)}^{T}$ for N = 5, as functions of the particle absorptance kd, with x_u as a parameter. Figure 5(a) indicates that the actual value of x_{u} has less than 10% effect in the value of the diffuse reflectance at high values of $kd \ge 1$, with negligible effect at $kd \le 0.1$. As the particle size increases, the reflectance decreases due to enhanced absorptance by the larger particles, in agreement with well-known experimental observations in this and extensive earlier work [10], regarding non-strongly absorbing powders. At the same time, an increased packing density is expected to incur a decreased scattering probability in the upward (back-scattered) direction, due to the enhanced probability for multiple scattering of primary rays off the sides of neighboring particles. This would decrease the x_{u} value. The overall effect is one of an increase in the diffuse reflectance with increasing x_{u} , as shown in Fig. 5(a). On the other hand, the increased sideways and downward scattering is expected to enhance the value of overall transmittance. Therefore, the diffuse transmittance is increased with decreasing x_u , as observed in Fig. 5(b). The effect is less pronounced than that on the diffuse reflectance, since a substantial component of the contributed intensity due to scattering is absorbed by underlying particles, especially at high values of kd [extreme right of Fig. 5(b)]. The essential low sensitivity of $T_{(5)}^{t}(kd)$ to the only quasiarbitrary parameter in the present theory renders the use of this channel advantageous over that of $R_{(5)}^{(t)}(kd)$ for purposes of accurate spectroscopic measurements

of large-size powders. Overall, however, it should be kept in mind that the values of both diffuse functions are affected by ca 10% or less by the actual value assigned to x_u .

Figure 6 shows the effects of changing refractive index (n) on the diffuse reflectance: the only parameters affected by such changes are the coefficients $\bar{m}_e(n)$ and $\bar{m}_i(n)$, Eqns (54) and (55). The diffuse reflectance, Fig. 6(a), is quite sensitive to the value of n in the range $1 \le n \le 1.2$, however, it exhibits less than 10% sensitivity to n for $1.2 \le n \le 2$ in the experimentally important range of $0 \le kd \le 1$. An increased refractive index results in an enhancement on $R_{(5)}^T(kd)$, as expected due to increased optical mismatch at the powder-air interface. Figure 6(b) indicates that the reflectivity enhancement is substantial for kd > 1, the opaque limit for most powdered specimens. Cross-overs among curves of different n in the kd < 1 region, Figs 6(a) and (b), have been previously observed in the original Melamed treatment (Ref. [5], Fig. 4) and in a corrected version (Ref. [9], Fig. 4). The flattening of the curves toward the high end of kd values in Fig. 6(b) is due to the fact that in the very opaque limit the only contribution to diffuse reflectance is from direct reflection at the upper surface of the uppermost powder particle layer, i.e.

$$R_{(N)}^{\mathrm{T}} \approx R^{(\mathrm{s})} \approx 2x\bar{m}_{e}(n) \tag{59}$$

from Eqns (47) and (5). In this limit $M \approx 0$, and $R_{(N)}^T$ scales with $\bar{m}_e(n)$, independent of N. Figure 7 shows the dependence of $T_{(5)}^T(kd)$ on n under conditions identical to those of Fig. 6(a). Unlike the $R_{(5)}^T(kd)$ behavior, the diffuse transmittance appears to be very



Fig. 6. Diffuse reflectance dependence on refractive index (n) of the powder. N=5, $x_u=0.284$; (a) $1.01 \le n \le 2.01$ in steps of 0.2. The range $kd \le 1$ is experimentally important for many powdered samples; (b) $1.1 \le n \le 5.1$ in steps of 1.0.



Fig. 7. Diffuse transmittance dependence on refractive index (n) of the powder. N=5, $x_u = 0.284$; $1.01 \le n \le 2.01$ in steps of 0.2.

sensitive to the actual value of *n* in the entire $1.01 \le n \le 2.01$ range; it exhibits no cross-overs and decreases monotonically, essentially to zero level for n > 1.8 and kd > 0.2. In an extended kd range, transmittance becomes zero (i.e. non-measurable on a linear scale) for $kd \ge 2$ at n = 1.01. It is very important to note that, upon comparison of Figs 6(a) and 7, the decrease of diffuse transmittance with kd is steeper than the equivalent decrease of diffuse reflectance in the experimentally important range kd < 1. Thus, it appears that the transmittance channel can be used advantageously to measure small changes in $k(\lambda)$ spectra, since it is more sensitive to such changes than the reflectance, especially toward the high-kd end, where the $R_{(M)}^{T}$ curves saturate, Fig. 6(b). MELAMED [5] was the first to recognize this essential limitation of diffuse reflectance measurements, while the present work indicates an alternative operation as a solution, namely diffuse transmittance spectroscopy from thin layers of non-transparent powders.

Figure 8 shows the dependence of the diffuse functions on the number of layers N in the powder stack. A comparison between Figs 8(a) and 8(b) indicates that transmittance is much more sensitive to N for all values of N in the entire kd range under consideration. Generally, zero-transmittance semi-infinite powder conditions set in for kd values of ca 0.8 (5 layers), 0.4 (7 layers) and 0.3 (9 layers). This observation is important in that the availability of blackbody transmission P^2E detectors described below may help determine when a powdered specimen is thick enough to be considered semi-infinite, a condition supplying a powerful criterion for quantitative spectroscopic analysis. Figure 8(a) further shows that the relative lower sensitivity of $R_{(N)}^T(kd)$ to N cannot form a good criterion for ascertaining semi-infinite behavior. This characteristic may, in turn, be thought of as an advantage of the diffuse reflectance channel, as absolute quantitative determination of k does not depend crucially on the total effective number of layers N, except at very low $kd (\leq 0.2)$.

Figure 9 is the diffuse reflectance from a 35 layer stack assumed to approximate a truly semi-infinite sample. At k = 0 the reflectance is 0.963, with a concomitant value of 3.7% for transmittance. The values chosen for the parameters n and x_u are the same as those used by MELAMED [5] for fitting didymium glass data to his semi-infinite theory. Although Melamed did not disclose the thicknesses of his $34 \,\mu\text{m}$ and $128 \,\mu\text{m}$ particle diameter powders, he attributed deviations in the low range of experimental values (kd < 0.02) in part to the failure of the sample geometries to conform to a semi-infinite thickness. Figure 9 substantiates this early hypothesis and any fits to experimental data would result in $R_{(N)}^{T}(kd \rightarrow 0) < 1$, as observed by Melamed, in disagreement with his model. As $R_{(N)}^{T}(kd)$ is quite sensitive to the value of N at kd < 0.1, the Melamed approach can be severely limited in that transparent regime. A physically consistent version [9] of Melamed's hybrid theory, which is consistent with optical energy conservation between

the upper (discrete) particle layer and the energy transmitted in the continuum substrate yields absolute diffuse reflectance values $R_{\infty}^{T}(kd=0) \approx 0.58$, much below experimental data values which tend to agree very well with the present theory. Thus, Fig. 9, curve #2represents the internally consistent normalized expression for diffuse reflectance [9]. This discrepancy between the two curves must be sought in the inconsistent assumption of the original Melamed theory [5] that the diffuse reflectance of a discrete single layer of particles be the same as that of a semi-infinite substrate continuum, which neglects the effects of transmitted optical energy through the very important first layer. $R_{(M)}^{T}(kd)$ simulations of Eqn (47) with N=1, i.e. Eqn (5), yield $R_{(1)}^{T}(0)$ values close to the value 0.58 stated above, a further clue that the hybrid nature of the earlier discrete theories [5, 9] was primarily dominated by their single particle layer character, at least at low kd with an inconsistent correction made through the assumption that reflectances with and without the upper particle layer are identical [5]. Better fits to the data with large kd in Fig. 9 than the one shown (curve #1) are possible to obtain with the present theory by altering the value for x_u . In Fig. 9, curve #1, $x_u = 0.284$ was chosen for direct comparison with Melamed's theory. Convergence of both curves in the high kd region is expected, as the dominant contribution to diffuse reflectance is made by the surface discrete particle layer in both theories. This is indeed the case with Melamed's original theory [5] for values of $kd \ge 0.07$.

The foregoing treatment in the limit of geometric optics did not take explicitly into consideration any effects due to the partial polarization of the scattered light. Since the tacit assumption of incident natural light was used, it can be shown [11] that the



Fig. 8. Variation of diffuse functions with the number of layers N in the powder stack; n = 1.41and $x_u = 0.284$. (a) Diffuse reflectance $R_{(N)}^T$; (b) diffuse transmittance $T_{(N)}^T$.



Fig. 9. Diffuse reflectance response of an approximately semi-infinite sample: N=35, n=1.55, $x_u=0.284$ (curve #1); internally consistent and normalized curve (#2), from Ref. [9]; data points for didymium glass powder, from Ref. [5].

unpolarized fraction of the scattered light from a single spherical particle in the forward direction is $ca \ 10^3$ times higher than the polarized fraction (with a maximum in the transverse plane). The above calculation involves a dielectric sphere of large size compared to the probe wavelength. Therefore, polarization considerations appear to have little effect on the quantitative validity of our treatment and were ignored in this work. This simplification is further in agreement with instrumental tests (see below) and the experimental fact that quantitative optical absorption coefficient results presented below varied minimally (within 10%) whether or not cross-polarizers were utilized in the paths of incident and scattered radiation.

4. INSTRUMENTATION AND MATERIALS

The Bomem DA3 Fourier Transform Infrared (FTIR) spectrometer was used to obtain data throughout this work. This particular instrument, in addition to its availability of selectable mirror velocities, provides access to the interferogram phase, an important information channel in FTIR photopyroelectric spectroscopy (FTIR-P²ES) [12]. A Globar source and a Ge-coated KBr beam splitter provided optical interferograms of powder spectra. For our purposes the wavenumber range 2000-4000 cm⁻¹ was found to be adequate. A single photopyroelectric detector assembly was used as the sample holder for diffuse reflectance (DR) infrared Fourier transform spectroscopy (DRIFTS) as well as the detector for the new diffuse transmittance infrared Fourier transform spectroscopy (henceforth referred to as DTIFTS). The details of the conventional photopyroelectric detector have been presented elsewhere [12, 13]. The sample holder/detector used in this work consisted of thin (28 µm) Kynar polyvinylidene fluoride (PVDF) films from Pennwalt [14] inserted in an Inficon microbalance housing [12]. The surfaces of the PVDF film were sputter-coated with ca 250 nm of Ni-Al layers serving as electrodes for carrying P^2E voltages to amplification and detection electronics. In PVDF and other pyroelectric materials, a change in the temperature causes a molecular rearrangement, thus changing the charge density and surface potential. When the temperature change is due to photon absorption, and subsequent thermal conversion of optical energy, the resulting voltage across the material is the photopyroelectric effect [15]. The PVDF P^2E element used for these experiments has an active area of circular cross-section and diameter equal to 9 mm. In order to eliminate contributions to the reflectance from light reflected directly from the metallized sample holder (PVDF) surface, great care was taken to blacken that surface by depositing a thick layer of carbon soot ($\approx 100 \,\mu$ m), so as to generate zero-level signals in the DA3 InSb semiconductor

diffuse reflectance detector. This sensor is known to exhibit non-linear response under conditions of high photon fluxes. In order to check for such undesirable effects, the energy in the single-beam spectrum was checked below the cutoff at 1800 cm⁻¹ by examining the phase spectra, and was found to be zero, thus eliminating the possibility of non-linearities. The sample holder was mechanically adapted and fitted to the "Praving Mantis" diffuse reflectance accessory (Harrick Scientific Corp., Model IMG 2700 L) of the FTIR spectrometer, as shown schematically in Fig. 10. Although the Harrick "Praying Mantis" DR accessory does not collect all the diffusely reflected radiation and ideally only an integrating sphere will allow the true DR spectrum to be measured, collecting the DR spectra between 0° and 90° with our instrument was expected to be representative of the true diffuse reflectance within reasonable error due to the recently demonstrated angular dependence of DR spectra [16-18]. This expectation was substantiated by the very good agreement between DRIFT and DTIFT spectra of thin Probimide 408 films [12], where the latter spectrum is not subject to the instrumental limitations of the "Praying Mantis" accessory. The positioning of the sample holder/ detector cell was optimized so as to be able to monitor the reflectance and the transmittance either simultaneously or sequentially. The cell was mounted at approximately the focal plane of the Globar beam, the spot size of which was ca 4-5 mm when focused using the largest DA3 throughput aperture (#1). Care was taken for the sample powder surface plane to coincide with the beam focal plane. Output P^2E transmission voltages were carried outside the FTIR spectrometer sample chamber by a coax cable via a Microdot-to-BNC connector. An Ithaco Model 1201 low noise, wide bandwidth preamplifier was used to amplify the P^2E signals to levels compatible with the analog-todigital converter (ADC) of the DA3 (~0.1-10 V). The output of the pre-amp was connected directly to the input board of the spectrometer, thus completing the FTIR- P^2ES circuit. Signal processing of the diffuse reflectance InSb detector was carried out using standard DA3 amplification and detection circuitry. Data acquisition and spectroscopic manipulations were performed using standard Bomem software for both reflectance and transmittance channels.

The samples chosen for the spectroscopic experiments consisted of powdered Na_2CO_3 . This material was able to satisfy the majority of requirements for testing our theory: it possessed a well-defined bulk absorption band in the 2115 cm⁻¹ region (identified during preliminary FTIR spectral scans); the absorption was not saturated even for thick specimens; the powders exhibited well-defined particle sizes easy to separate after sieving; samples of small thickness could be easily prepared to monitor the transmittance



Fig. 10. Schematic view of combined DRIFTS and DTIFTS measurement geometry in the Bomem DA3 FTIR spectrometer sample chamber.



Fig. 11. (a) Normalized DRIFT and (b) normalized DTIFT spectrum of Na₂CO₃ powders. Nominal particle size: 80–100 μm; Resolution: 4 cm⁻¹; Number of co-added scans: 25 (DRIFT) and 45 (DTIFT); interferometer scanning speed: 0.5 cm/s (DRIFT) and 0.03 cm/s (DTIFT). The arrows point at the peak used in the quantitative analysis. Insert in (b): P²E phase spectrum of the 2115 cm⁻¹ peak region. (See text for details.)

signal; and the important requirement of depth homogeneity throughout the bulk of the loose powder could be easily and reproducibly satisfied largely free from clustering or agglomeration. The powder Na₂CO₃ was obtained after thermal treatment of NaHCO₃ at 250°C for 1.5 h. It is believed that the absorption feature is a combination band of fundamentals at lower wavenumber, although its exact origin is not clear. An absorption feature was previously observed [19] in the 2300 cm⁻¹ range of a Na₂CO₃ · 10H₂O mull. Spectral feature shifts are expected between suspensions and loose powders, however, direct comparisons are hard to make, due to the nominal absence of H₂O from our samples, and the fact that there was no indication of water in the sample spectra in the region around 3500 cm⁻¹ (Fig. 11). The powders were ground and sieved, and several average diameter ranges of randomly-shaped particles were obtained satisfying the principal requirement of the theory that particle size be large compared to the maximum optical wavelength (5 μ m at 2000 cm⁻¹). In addition, smaller size particle powders of silica were used to test practical validity limits of the foregoing theory due to the commercial unavailability of small diameter/size Na₂CO₃ powders. These samples were LiChroprep Si 100 silica powders from E. Merck AG, Lausanne, Switzerland, $25-40 \,\mu$ m nominal diameter range. Subsequently, they were treated chemically with two aminosilane reagents: one containing a cyano group recently synthesized in our laboratory: dimethyl-(5-cyano-3, 3-dimethyl pentyl)-(dimethyl amino silane) with chemical formula [20] (CH₃)NSi(CH₃)₂C₇H₁₄CN, abbreviated as DMP.CN; and a reference reagent: (3,3-dimethyl butyl)-dimethyl-(dimethyl amino) silane with chemical formula [21] (CH₃)₂NSi(CH₃)₂C₆H₁₃, abbreviated as DMB. The silylation reaction

$Si-OH + (CH_3)_2NSi(CH_3)_2R \rightarrow Si-O-Si(CH_3)_2R + (CH_3)_2NH \uparrow$

using the two above-mentioned aminosilanes yields two sets of product powders: one exhibiting an absorption band centered at 2250 cm^{-1} due to $-C \equiv N$ groups, and another (reference) powder with nearly the same structure, but without the cyano group or the absorption band around 2250 cm^{-1} . Thus, small-size powders exhibiting surface, rather than bulk, absorption were prepared, with stack inhomogeneities in the bulk due to electrostatic clustering.

KBr powders from E. Merck AG, Lausanne, Switzerland, were used as a reference for absolute diffuse reflectance measurements. They were finely ground in a Wig-L-Bug mill capsule (Crescent Manufacturing Co., Chicago, IL) to sizes less than $20 \,\mu$ m.

5. EXPERIMENTAL, RESULTS AND DISCUSSION

The Globar source and beam splitter compartments of the spectrometer were evacuated during the experiments ($\sim 10^{-5}$ torr). The sample chamber was purged with dry nitrogen for 5 min before all spectra acquisitions in order to eliminate residual absorptions due to atmospheric water and CO₂. DRIFT and DTIFT spectra were obtained sequentially. The former were normalized by the (assumed) 100% reflecting semiinfinite thickness KBr spectrum. The latter were normalized by the blackbody spectrum of the empty, soot-coated PVDF sample holder/detector.

Typical spectra recorded from Na₂CO₃ powders of sizes between $80-100 \mu m$ (ca 16-20) times higher than the maximum wavelength) and thickness $ca 300 \,\mu\text{m}$ are shown in Fig. 11. The spectra were obtained using crossed polarizers in the optical paths of the incoming and reflected optical beams, so as to minimize contributions to the diffuse reflectance from specularly reflected radiation [22]. BRIMMER and GRIFFITHS [17] have effectively shown that crossed polarizers actually pass more front surface reflection that is collected off-axis than aligned polarizers. Experiments with the BOMEM instrument in this laboratory using crossed and aligned polarizers showed that the polarization is conserved with the Harrick DR accessory and thus most of the specular reflectance is eliminated with crossed polarizers. With large-size powders it was found necessary to use small thicknesses in order to have a measurably large, reproducible DTIFT spectrum; 7 and 14 mg of powder were used to obtain ca 150 and 300 μ m thicknesses, respectively. The powders were placed on the sample holder/ P^2E detector and were agitated (vibrated) mechanically until a homogeneous layer was obtained. The degree of homogeneity was deemed satisfactory if FTIR spectra obtained with the exciting beam focused on different locations on the powder surface were roughly identical in intensity. No baseline corrections in the spectra of Fig. 11 have been made, in agreement with the absolute kd absorptance nature of the theory in Section 2.

The absorption band centered at 2115 cm^{-1} was further digitized from DRIFT and DTIFT spectra and the absolute reflectance and transmittance signals were converted to values of kd using theoretical plots similar to those shown in Fig. 5. Optical absorption coefficient spectra were determined by varying the x_u value and adjusting the number of layers N for optimal overlap between DRIFT and DTIFT originating spectra. Then, the effective value of d was calculated from L/N, Fig. 1(a), and was checked for self-consistency with the range of d values resulting from sieving. This procedure amounts to a unique identification of two unknown (adjustable) parameters, x_u and N, from two

equations (one for reflectance and one for transmittance) at each wavenumber throughout the entire spectral region of interest, with the minimization of the difference in the two values for $k(\lambda)$ between the $R_{(N)}^{T}$ and $T_{(N)}^{T}$ -derived spectra as the guiding criterion at each λ . Out of these two parameters, the value of N could subsequently be verified independently through comparison with actual powder geometries. This comparison yielded, in all cases, very good agreements between the (initially guessed and subsequently "fine tuned") integral value of N from the theory, and the (generally noninteger) value of N calculated independently from knowledge of the container volume and the average sieved particle size of the powder. Thus the value x_u remains as the only quasi-arbitrary (i.e. not independently verifiable) parameter subject, however, to stringent requirements for optimization of the overlap between DRIFT and DTIFT spectra.

Figures 12 and 13 show results from these operations. The effective particle diameters were

$$\langle d \rangle = \frac{L}{N} \cong \frac{1}{4} \times (300 \pm 30 \,\mu\text{m}) = 75 \pm 7 \,\mu\text{m}$$
 (60)

from Fig. 12, and

$$\langle d \rangle = \frac{L}{N} \approx \frac{1}{2} \times (150 \pm 20 \,\mu\text{m}) = 75 \pm 10 \,\mu\text{m}$$
 (61)

from Fig. 13. Clearly, these values are consistent with the $80-100 \mu m$ range of the sieve mesh. Due to the uncertainties in the actual particle size, the absolute $k(\lambda)$ scales are believed to be accurate to within 10% of the actual k values. The n value chosen (1.46) for Na₂CO₃ is the average of published values [23] of sodium carbonate and its decahydrate, strictly valid for excitation at the sodium light visible line (589.3 nm). These values are 1.535 and 1.405, respectively. Within this range, the sensitivity of either the R(k) or the T(k) curves on the absolute value of the refractive index is not high (less than 5%) (1.4 < n < 1.55), as shown in Figs 6(a) and 7. On the contrary, the theoretical sensitivity of these curves, and especially the T(k) curve, on the actual N-value is very high, as observed in Fig. 8(b). Finally, in the range of diffuse reflectance values obtained experimentally from the samples in Figs 12 and 13, $0.30 \le R_N^T \le 0.39$, the actual value of



Fig. 12. Absolute optical absorption coefficient spectra of the band indicated by arrows in Fig. 11. •: DRIFT-derived spectrum; \bigcirc : DTIFT-derived spectrum. Parameters used in Eqns (47) and (48) for the best possible overlaps: N=4, $x_u=0.5$, n=1.46. The error bars indicate deviations of two sets of FTIR spectra taken several days apart with different samples of $300 \pm 30 \,\mu$ m thick, 14 mg powders.



Fig. 13. Absolute optical absorption coefficient spectra similar to those in Fig. 12, from $150 \pm 20 \,\mu\text{m}$ thick, 7 mg samples. The error bars indicate deviations of two sets of spectra taken several days apart with different specimens. $\textcircled{\}$: DRIFT-derived spectrum; \bigcirc : DTIFT-derived spectrum. Parameters used in Eqns (47) and (48): N=2, $x_u=0.5$, n=1.46.

 x_u producing acceptable overlap with the transmittance spectrum had a tolerance $0.4 \le x_u \le 0.7$, with optimum overlap for $x_u = 0.5$. This range was primarily determined from the diffuse reflectance signal and its x_u -dependence in Fig. 5(a). As shown in Fig. 5(b), the diffuse transmittance is little sensitive to the x_u value. The agreement between the absorption curves derived from DRIFTS and DTIFTS in Fig. 12 is quite good, with the worst differences less than 10% on the low energy side (2090–2115 cm⁻¹) where the photon throughput is relatively low. The *ca* 10% variation in $k(\lambda)$ is within the general uncertainty of the $\langle d \rangle$ value for the experiment.

Figure 13 shows a blue shift of the P^2E transmittance peak with respect to the DRIFT spectrum by ca 11 cm⁻¹. The origin of this shift is not entirely clear, however, it is believed to be due to the thermal wave nature of the P^2E signal generating the DTIFT spectrum. At the wavenumber \bar{v} position of the peak, 2115 cm⁻¹, the interferogram intensity modulation frequency for the P^2E data of Fig. 13 at v = 0.03 cm/s is [24]

$$f = 2v\bar{v} = 127 \text{ Hz.}$$
 (62)

The thermal diffusion length in the powder at the given modulation frequency is given by the expression [25]

$$\mu_{\rm s}(f) = (\alpha_{\rm s}/\pi f)^{1/2} \tag{63}$$

where α_s is the powder thermal diffusivity. Although no readily available value for Na₂CO₃ could be obtained from the literature, the order of magnitude was assumed to be $\sim 10^{-3}$ cm²/s, in view of the measured values for K₂Cr₂O₇ powders [26], $\alpha_s = 1.4 \times 10^{-3}$ cm²/s, and for CaCO₃ powders [27], $\alpha_s = 1.56 \times 10^{-3}$ cm²/s. Using $\alpha_{Na_2CO_3} \cong 1.5 \times 10^{-3}$ cm²/s gives the value

$$\mu_{\text{Na}_2\text{CO}_3}(127 \text{ Hz}) = 19 \,\mu\text{m}.$$
(64)

For a powder thickness of $150 \pm 20 \,\mu$ m, i.e. 6.8–8.9 thermal diffusion lengths, there is evidence [12] that corrections to slightly distorted FTIR spectra are required, due to thermal diffusion contributions to the P^2E signal. No such corrections would be necessary for the $300 \pm 30 \,\mu$ m powder, the thermal behavior of which is expected to be fully decoupled from the PVDF response to directly transmitted radiation [15]. Very small ripples in the FTIR- P^2E phase spectrum ($\Delta \phi < 4^\circ$) corresponding to Fig. 13 in the immediate vicinity of the DTIFT peak at $2126 \,\mathrm{cm}^{-1}$ were found to exist in anticorrelation with the peak structures, thus giving further strong support to a photothermal origin of the shift [28]. It should be mentioned that no such correlations were found between the 300 μ m sample absorption peak, Fig. 11(b), and its phase ripple (insert, Fig. 11(b)]. Figures 12 and 13 show that the spectral position of the DRIFT-originating band remains unshifted for both powder thicknesses. The fact that both best overlaps occurred with $x_u = 0.5$ is particularly significant, since it indicates similar geometric configurations in the body of both powders, i.e. we were able to essentially reproduce the same approximately homogeneous depth profile of the particles with mechanical means.

Figure 14 shows $k(\lambda)$ spectra of sieved Na₂CO₃ powders of nominal sizes 30–60 μ m and thickness ca $150 \pm 30 \,\mu$ m. The agreement of the absolute values of $k(\lambda)$ with those of Figs 12 and 13 is within 15%, a very good quantitative result, in view of the widely different powder geometries. Due to the lower reflectance signals of this size powder, compared to the larger sizes of Figs 12 and 13, the theoretical diffuse reflectance sensitivity to the value of x_u increased significantly, as observed for low R_{λ}^{T} -range values in Fig. 5(a). As a result, the range of x_{u} values producing acceptable overlaps between reflectance and transmittance spectra was, in this case, $0.05 < x_u < 0.15$. Figure 14 exhibits the same blue shift of the DTIFT peak as that observed in Fig. 13. Best overlap was achieved with N=4and $x_u = 0.1$ in Eqns (47) and (48). The N value gives $\langle d \rangle = 37.5 \pm 7.5 \,\mu \text{m}$ consistent with the nominal dimensions. The lower x_{u} value is indicative of the smaller size particles (higher packing density), and according to its definition [5] represents a lower probability for diffuse scattering in the upward direction than the larger particles. This is reasonable, as the smaller sized particles are expected to be more spatially uniform, scattering centers through a 4π steradian solid angle, than larger particles. In the limit of very large particles, it is intuitively expected that the upward scattering fraction will be greatly enhanced, at the expense of sideways and downward scattering. These hypotheses are further consistent with the theoretical x_u -dependence trends of Figs 4(a) and (b) and with the discussion of those trends.

Experiments were also performed with semi-infinite Na₂CO₃ powder thickness. The DRIFT spectrum is shown in Fig. 15, corresponding to conventional practice in diffuse reflectance spectra acquisition [24]. In this case, however, there exists an independent criterion of quasi-infinite thickness in the mid-IR range, for the first time to the authors' best knowledge: the complete absence of transmittance as measured by the P^2E blackbody detector in direct and intimate contact with the sample. The conventional spectrum shown in Fig. 15 is in good quantitative agreement with those of Figs 12–14 with a reproducibility from powder to powder to within 10–15%. This degree of agreement between spectra was achieved by setting $x_u = 0.5$ for the 80–100 μ m powders,



Fig. 14. Absolute optical absorption coefficient spectra of $30-60 \,\mu\text{m}$ diameter Na₂CO₃ powders, $150 \pm 30 \,\mu\text{m}$ thick, 7 mg samples. Parameters used in Eqns (47) and (48): N = 4, $x_u = 0.1$, n = 1.46. $\textcircled{\bullet}$: DRIFT-derived spectrum; \bigcirc : DTIFT-derived spectrum.



Fig. 15. Absolute optical absorption coefficient, DRIFT-derived spectrum of Na₂CO₃ powders, 80-100 μ m in diameter, and semi-infinite thickness (3 mm, 140 mg). Parameters used in Eqn (47): N=37, x_u=0.5, n=1.46, d=80 μ m.

an excellent indication that the depth profiles and packing densities of the 'semi-infinite', 3 mm thick stack, and those of the thinner stacks $(300 \,\mu\text{m} \text{ and } 150 \,\mu\text{m})$ of $80-100 \,\mu\text{m}$ -size particles were similar. The fact that the chosen Na₂CO₃ absorption peak at 2115 cm⁻¹ is not very strong, Fig. 11(a), led to a non-saturated spectrum in Fig. 15 without the need of powder dilution in KBr.

Finally, some important issues of practical limits of validity for the foregoing quantitative spectroscopic analysis were investigated in terms of the sensitivity of the theory to relative values between optical wavelength and particle size and uniformity. The theory presented in Part 2 is rigorously valid in the theoretical limit $d \ge \lambda$. Experimentally, the theory was found to yield reasonable quantitative $k(\lambda)$ spectra for $\langle d \rangle \cong 37.5 \pm 7.5 \,\mu$ m, Fig. 14, i.e. for $\langle d \rangle \cong 8\lambda_{\text{peak}} (\lambda_{\text{peak}} = 4.73 \,\mu\text{m} \leftrightarrow 2115 \,\text{cm}^{-1})$. For the purpose of finding some experimental limitations of the theory, the absorption band of -CN in the surface absorbed $C_{10}H_{20}NSi$ on silica centered at 2250 cm⁻¹ was recorded by the DRIFTS and DTIFTS methods and the FTIR spectra were normalized by the KBr reference spectrum and the blackbody spectrum, respectively, as outlined earlier.

The powders had nominal diameters in the $25-40\,\mu$ m range. In order to obtain reproducible surfaces (and presumably particle depth profiles), a pressure was applied with a precision mechanical lever on the surface for 30 s and the powder was allowed to relax during that period. This treatment assured very good reproducibility of the measured spectra in both channels, however not entirely uniform powder stacks were obtainable due to interparticle electrostatic interactions leading to some clustering. In order to obtain good quality transmission spectra an optimal thickness of $300 \pm 30\,\mu$ m was chosen. The powders exhibited no measurable transmission for $L \ge 400\,\mu$ m. Such thicknesses were assumed to yield the semi-infinite response, a fact which was confirmed from the invariance of the diffuse reflectance with increasing powder thickness in the 0.4-2.0 mm range.

Figure 16 shows the best overlap of $k(\lambda)$ spectra obtained using Eqns (47) and (48). For these calculations the value n = 1.46 for silica was used [29]. The optimal value N = 10 gave

$$\langle d \rangle = \frac{L}{N} \approx \frac{1}{10} \times (300 \pm 30 \,\mu\text{m}) = 30 \pm 3 \,\mu\text{m}$$
 (65)

consistent with the nominal value range. It can be seen from the figure that no quantitative consistency is possible between the DRIFTS-derived and DTIFTS-derived $k(\lambda)$ values, even for unrealistically low values of x_u , a result of the breakdown of the validity of our model. Independent measurements of $k(2250 \text{ cm}^{-1})$ have been performed

using the transmittance from liquid solution of $C_{12}H_{26}N_2Si$, which exhibits the same (CN)-group spectroscopic behavior as the $C_{10}H_{20}NSi$ compound. These measurements yielded

$$k(2250 \text{ cm}^{-1}) = 32 \pm 4 \text{ cm}^{-1}$$
 (66)

i.e. a value close to the DTIFTS data peak values. Clearly, the stack uniformity, the bulk absorption coefficient, and/or the $d \ge \lambda$ assumptions were not valid in the range

$$\langle d \rangle \!\leq\! (6.75 \pm 0.7) \lambda \tag{67}$$

for the surface-treated silica powders.

As an immediate consequence, it is expected that, if the violation of the last assumption is important, particle sizes in this range should exhibit continuum behavior, in view of the breakdown of the present discrete behavior approach. In order to test this hypothesis, the degree of agreement of the behavior of 'semi-infinite' powder layers with the simple semi-infinite layer Kubelka–Munk function [1]

$$\frac{k}{s} = F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$
(68)

was examined. In Eqn (68), R_{∞} is the value of the diffuse reflectance from a semi-infinite layer $(L \rightarrow \infty)$ and $F(R_{\infty})$ is the Kubelka-Munk function, defined as the ratio of the powder optical absorption coefficient k and the scattering coefficient s. 400 μ m thick powders identical to those of Fig. 16 were used as mixtures of the cyano-modified silica and the alkyl-modified silica. The cyano-modified silica concentration was varied between 2.5 and 100%. Subsequently, the DRIFT values of the peak at 2250 cm⁻¹ were plotted as a function of the cyano-modified silica percentage (c) in the Kubelka-Munk plot of Fig. 17. The straight line behavior of $F[R_{\infty}(c)]$ vs c = [CN] indicates that the assumption of a concentration-independent scattering coefficient s is valid and thus

$$k = k(c) \propto [CN]. \tag{69}$$

The straight line fit of Fig. 17 demonstrates that Eqn (68) is valid for the silica powder samples. This observation carries the important interpretation that powders of particle sizes smaller than $ca 7\lambda$, Rel. (67), behave optically like a completely continuous material



Fig. 16. Absolute optical absorption coefficient spectra of 100% $C_{10}H_{20}NSi$ powders, $300 \pm 30 \,\mu m$ thick, 25-40 μm nominal d. Parameters used in Eqns (47) and (48): N = 10, $x_u = 0.01$, n = 1.46. $\textcircled{\ }$: DRIFT-derived spectrum; \bigcirc : DTIFT-derived spectrum.



Fig. 17. Kubelka–Munk function vs [CN] concentration of mixtures of silica powders with $C_{10}H_{20}NSi$ and $C_8H_{19}Si$ surface groups. Powder size: 400 μ m.

layer, for it is only in this limit that the Kubelka–Munk formalism [30] is strictly valid. Furthermore, it appears that depth inhomogeneity is not particularly serious in these stacks, as witnessed by the goodness of fit of the data to the simple Kubelka–Munk expression for homogeneous particle layers throughout the entire concentration range. In Fig. 17 the intercept of the straight line is not at c = 0, as expected, due to the residual absorption in the silica reference powder.

Very recently two papers from GRIFFITHS' group [31, 32] have dealt with diffuse reflectance and diffuse transmittance spectroscopy of self-supported samples in the small-size particle (continuum) limit. Although the treatments therein are not in the large particle-geometric optic regime, with which the present work deals exclusively, nevertheless, the set of those papers and the present treatment constitute three of the only investigations in which diffuse transmittance has been reported in any detail.

6. CONCLUSIONS

In this work an exact, self-consistent discrete theory of diffuse reflectance and transmittance for large particle-size powders was developed and applied to experimental data from FTIR spectroscopic measurements using the conventional DRIFTS technique and a new photopyroelectric DTIFTS method for monitoring reflectance and transmittance sequentially. Good quantitative measurements of mid-IR optical absorption coefficient spectra of loose powders were thus made possible under a wide variety of optical, geometric and packing density conditions. It was further shown that the theory breaks down when the bulk absorption, stack homogeneity, and $d \ge \lambda$ assumptions of the model do not hold, for particle sizes smaller than $ca 7 \times$ the wavelength of the exciting radiation, in which case the conventional continuum interpretation holds.

Acknowledgement—The partial financial support of the Swiss Fonds National and the Ontario Laser and Lightwave Research Center (OLLRC) is gratefully acknowledged. One of us (A.M.) wishes to thank Professor E. sz. Kóvats for his hospitality at EPFL during his sabbatical research leave and for valuable assistance with the powder surface derivatization method. Several useful suggestions by the referee are also thankfully acknowledged.

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