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EFFECT OF PARTICLE CLUSTERING ON DECAY RATES OF ADMOLECULES AT THE INTERFACE OF A COMPOSITE MATERIAL SUBSTRATE

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The decay rates of admolecules at the surface of a composite material are investigated theoretically in the limit of low volume fraction for the metallic particles in the composite. The optical properties of the substrate are described by both the Maxwell-Garnett and the fractal-cluster models, simulating situations where the metal particles distribute themselves randomly, and where they coalesce to form localized clusters within the host material, respectively. It is found that in the case of particles coalescing to form clusters, a very small fraction of particles could lead to very large surface-induced damping for the admolecule at low emission frequencies, together with a red-shifted resonance peak in the decay rate spectrum. Hence, studies on the damping of vibrational states of admolecules at such composite material surfaces could lead to information concerning the distribution of particles in the substrate.

THE OPTICAL properties of composite materials such as cermet have remained a topic of intensive interest and research due to their practical significance [1]. While most of the theoretical modeling of such properties is done using either some version of effective medium theory (EMT) [2–4] or via computer simulation [5], experimental study of these properties has been limited largely to light scattering experiments such as far-IR absorption spectroscopy [6]. It is therefore of interest to explore the possibility of alternative optical probes, such as fluorescence, which will lead to the characterization of the structure of the composite. The following work presents a theoretical study of possible novel phenomena for molecules fluorescing at the interface of a composite substrate. Our modeling will be phenomenological [7], and our main interest is to see how the distribution of particulates in the composite will affect the decay rates of the admolecules. Without loss of generality, we shall compare the effects between the two cases where the particulates are randomly distributed vs the case where these particles coalesce to form localized clusters within the host material. We shall limit ourselves to low concentrations of particulates and to the fractal-cluster model where particle coalescence does occur.

The geometry of our problem is as follows. We consider a fluorescing admolecule modeled as an oscillating point dipole and oriented normal (for simplicity) to the surface of a composite substrate which is characterized by a local dielectric function $\epsilon(\omega)$. For the molecule located in a medium of dielectric constant ϵ_1 and at a distance d from the substrate, the phenomenological theory gives the decay rate normalized to the free decay rate value

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$(d \to \infty)$ in the form [7]

$$\frac{\gamma}{\gamma_0} = 1 + \frac{3q}{2} \operatorname{Im} \int_0^\infty du \frac{\epsilon l_1 - \epsilon_1 l}{\epsilon l_1 + \epsilon_1 l} \frac{u^3}{l_1} e^{-2kl_1 d}, \quad (1)$$

where q is the quantum yield, $k = \sqrt{\epsilon_1}\omega/c$ is the emission wave number of the molecule, $l = -i\sqrt{\epsilon - u^2}$ and $l_1 = -i\sqrt{\epsilon_1 - u^2}$. This result is obtained by modeling the admolecule as a damped oscillating dipole with the surface-induced damping originating from the reflected field of the fluorescent emission acting on the dipole site. The integral essentially arises from the solution of the Sommerfeld problem for a dipole antenna above the surface of the Earth [7]. In two previous works [8, 9], the effects due to a composite substrate on equation (1) have been studied using both the Maxwell-Garnett (MG [2]) and Bruggeman (BR [3]) theories for the description of the substrate properties, i.e., $\epsilon(\omega)$. However, both of these two theories assume the particles in the composite to be distributed randomly throughout the host material, thus leaving the case with coalescence among these particles uninvestigated. To model coalescence we shall follow the formulation of Hui and Stroud, which adopts a differential effective medium approach for the calculation of $\epsilon(\omega)$, assuming particles to form localized fractal clusters. According to this fractal clustering (FC) description, one obtains [10]

$$\frac{\epsilon(R)}{\epsilon_p(a)} \left[\frac{\epsilon_m - \epsilon_p(a)}{\epsilon_m - \epsilon(R)}\right]^3 = f', \quad (2)$$

where $\epsilon(R)$ is the dielectric function of the cluster (radius R) which consists of (metallic) particles [radius a, dielectric function $\epsilon_p(a)$] distributed in an insulating medium of dielectric function ϵ_m. f' is the volume fraction of the particles in the cluster, given by

$$f' = \left[\frac{R}{a}\right]^{3(3-d_f)}, \quad (3)$$

with d_f being the fractal dimension of the cluster. The dielectric function of the composite which contains these clusters is ultimately obtained by the application of the MG theory treating the substrate as a composite of these clusters (of concentration f_c) and the insulating medium [10]. Note that for a given amount of total particle concentration of volume fraction f in the host material, we have $f = f' \cdot f_c$. Since this approach is limited to low particle concentrations ($f \ll 1$), we shall contrast our results with those obtained previously from the MG theory [2] for the case in which no clustering occurs. The $\epsilon(\omega)$ from the MG theory is well known and is given implicitly by the expression

$$\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} = f \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m}. \quad (4)$$

We have performed some numerical calculations by varying the relevant parameters which include the molecular emission frequency, the molecule-substrate distance, the size and fractal dimension of the particulate clusters in the substrate, etc. To make comparisons with previous work, we have used the same values as in [9] for the characterization of the optical properties of both the host and the particulates in the substrate. We have hence assumed the molecule to be located in a medium of dielectric constant $\epsilon_1 = 1.5$ and the substrate to be an insulator host of constant $\epsilon_m = 25$ with embedding metallic particles whose optical properties are described by the Drude function $\epsilon_p = 1 - [\omega_p^2/\omega(\omega + i\Gamma)]$. Employing units such that the plasmon frequency $\omega_p = 1$, we have set the damping constant as $\Gamma = 0.01$. For this model calculation, we have also used most of the quantities in their normalized form.

Figure 1 displays the results of the normalized decay rate vs the emission frequency of the molecule normalized to the plasmon frequency of the metal particles at a fixed normalized molecule-substrate distance $\bar{d} = k_1 d = 0.5$. The fractal dimension for the

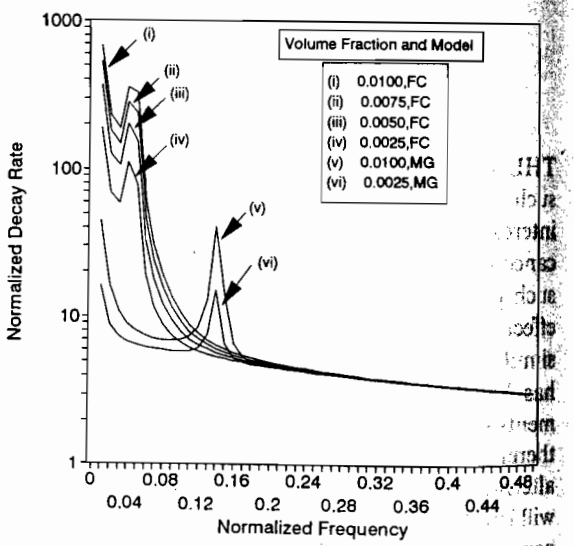

Fig. 1. Normalized decay rate vs normalized emission frequency for fixed molecule-surface distance for various volume fractions of metal particles in the composite substrate. Comparison of the results is shown for both the fractal-cluster modeling and the Maxwell-Garnett theory. The following parameters are held constant at the indicated values: fractal dimension $d_f = 2.5$, normalized fractal radius = 10, normalized distance = 0.5. Other relevant parameters are either shown in the figure or are found in the text.

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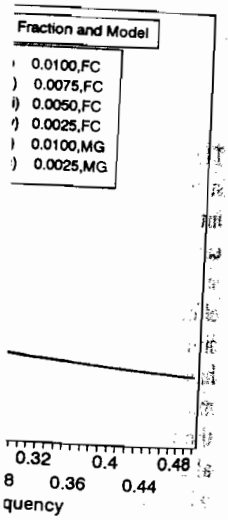

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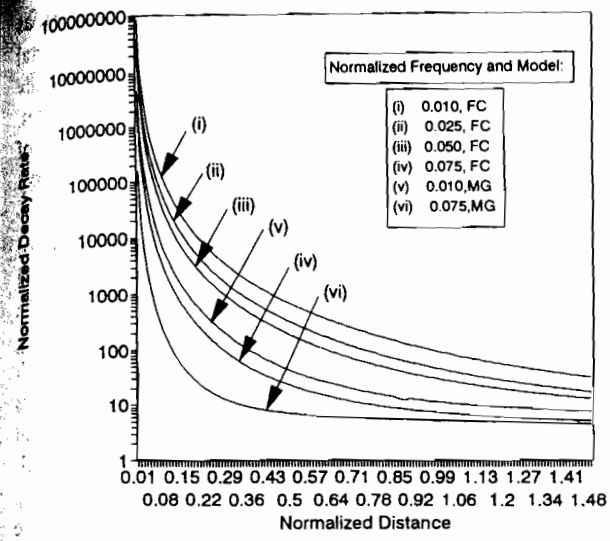

Fig. 2. Normalized decay rate vs normalized molecule-surface distances for various fixed normalized emission frequencies. Parameters held constant: particle fraction = 0.1, fractal dimension = 2.5, normalized fractal radius = 10.

metal cluster in the composite is taken as 2.5 and the normalized cluster radius (R/a) as 10 [10]. It is clear that the fluorescent decay rate of the admolecule is red-shifted and enhanced appreciably due to the clustering of the metal particles in the substrate, even for a very small fraction of the particles in the host insulator! This is totally consistent with previous experimental [6] and theoretical [10] results which studied the far-infrared absorption of these substrates with possibly clustering structures. Furthermore, it is observed that the increase in the amount of metal particles simply enhances further the induced decay of the molecule without appreciably shifting the resonance position in the decay rate spectrum. This is true in both the cases whether the particles coalesce to form clusters (the FC results) or they distribute themselves randomly throughout the host (the MG results).

Figure 2 shows the effect vs the variation of the molecule-surface distance for different fixed emission frequencies. The volume fraction of the metal particles is fixed at 0.01, and the other parameters are the same as in Fig. 1. At very close distances, the substrate-induced damping is extremely large for both the FC and MG modeling; such huge damping enhancement is sometimes unrealistic due mainly to the use of local dielectric functions [11] in the above equations (1)–(4). For a given frequency, the surface-induced effect in general drops less rapidly in the case of FC modeling as the molecule is moved away from the substrate. In both the FC and MG cases, the rate goes down much faster with the increase of distance when the emission is at a higher frequency.

Figures 3–5 explore the effects on the induced molecular decay rate in terms of the properties of the embedded metal particles in the substrate. Figure 3 shows the variation in terms of the volume fraction with the distance fixed at $\bar{d} = 0.5$ for different emission frequencies. For low emission frequencies, the FC results show roughly a linear increase of the surface-induced damping vs an increase in particle occupancy; however, for high frequencies and for all

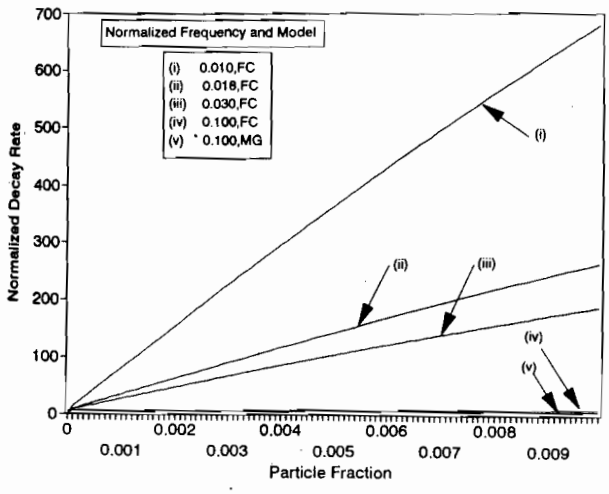

Fig. 3. Normalized decay rate vs particle volume fraction for different fixed emission frequencies. Parameters held constant: fractal dimension = 2.5, normalized fractal radius = 10, normalized distance = 0.5.

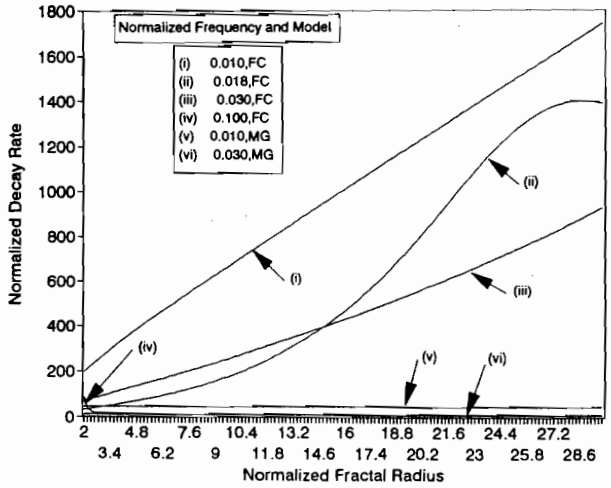

Fig. 4. Dependence of the decay rate on the size of the metal cluster via a plot vs the normalized fractal radius of the cluster for different fixed emission frequencies. Parameters held constant: particle fraction = 0.01, fractal dimension = 2.5, normalized distance = 0.5.

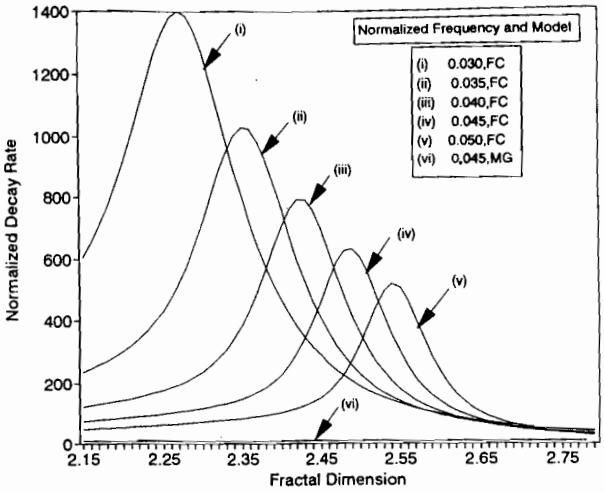

Fig. 5. Dependence of the decay rate on the "degree" of clustering via a plot vs the fractal dimension of the metal cluster for different fixed emission frequencies. Parameters held constant: particle fraction = 0.01, normalized fractal radius = 10, normalized distance = 0.5.

frequencies in the MG case, the surface effect is relatively insensitive to the variation of the amount of particles in the substrate. In terms of the variation of the configuration structure of the clustered particles for a fixed volume fraction ($f = 0.01$), Fig. 4 shows the effect of the variation of the fractal radius, and Fig. 5 the variation of the fractal dimension. It is interesting to note that the FC modeling yields results with the induced molecular decay rate increasing almost linearly with the fractal radius for low emission frequencies and nonlinearly for frequencies close to the resonant energy transfer peak (see Fig. 1). The rate of increase generally goes down as the emission frequency first increases before it comes close to the resonant value. Some of the MG results are also shown (which remain constant) for comparison purposes. In terms of the variation of the fractal dimension, Fig. 5 shows the results for various emission frequencies. The results exhibit a kind of resonant phenomenon in terms of the fractal dimension for each fixed emission frequency. While the resonance-induced effect decreases with an increase in frequency, the positions are shifted towards higher fractal dimensions for higher emission frequencies. We believe that all these phenomena could provide interesting correlations between the behavior of fluorescent admolecules and the geometry of the distribution of the embedded substrate particles.

In summary, we have studied by means of a phenomenological approach the fluorescent decay rates of admolecules at an interface of a composite material for different particulate structures in the host material. Among other results we have found that, in previous photoabsorption studies [6, 10], fractal clustering of particles could lead to dramatically enhanced surface effects at low emission frequencies. Hence, studies of the damping of vibrational states of admolecules at such composite material surfaces could lead to information concerning the distribution of particles in the substrate. To our knowledge, such a composite substrate could be achieved experimentally at least in two ways as reported in the literature. In the approach of Devaty and Sievers [12], a silver-polymer composite was fabricated with controllable coalescence among the silver particles in the host. Still a more interesting system is colloidal gold solution which is known to possess a fractal clustering structure among the gold particles [13]. One can imagine "floating" a layer of fluorescent dye on such a solution and performing a time-resolution spectroscopic study for the analysis of the decay lifetimes of these admolecules. It is possible that such an investigation may then open up the possibility of using a fluorescence probe to determine the particulate structure of a composite system. Indeed, a recent experiment [14] has reported time-resolved measurements of fluorescent lifetimes for dye molecules *embedded* in the bulk of a colloidal suspension of polystyrene spheres. It is thus possible and of interest to extend such a study to composites with metallic particles and to have the fluorescent molecules located at the interface of such a material.

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