Toward a universal extinction spectrum of self-affine silver colloid clusters: Experiment and simulation

B. Vlčková
Department of Physical and Macromolecular Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

C. Douketis and M. Moskovits[a)]
Department of Chemistry, University of Toronto, and Photonics Research Ontario, 80 St. George Street, Toronto, Ontario, M5S 1A1, Canada

V. M. Shalaev
Department of Physics, New Mexico State University, Las Cruces, New Mexico 88003

V. A. Markel
Department of Physics and Astronomy, University of Georgia, Georgia 30602

(Received 16 October 1998; accepted 12 January 1999)

Polarized extinction spectra of large fractal aggregates of colloidal silver deposited gravitationally onto a quartz substrate were measured by transmission as a function of angle of incidence. The spectral components tangential and normal to the average plane of the clusters compacted along the direction of deposition were extracted from these and compared with spectra calculated from simulated fractal aggregates that were projected onto a plane. The two sets agree acceptably, suggesting that the normal and tangential spectral components represent ''universal,'' i.e., size-independent extinction spectra characterizing all (compacted) cluster–cluster aggregates of colloidal silver. © *1999 American Institute of Physics.* [S0021-9606(99)71414-5]

I. INTRODUCTION

The optics of fractals has been the subject of a number of theoretical[1,2] and experimental[2–5] studies over the past decade. Those studies were motivated, in part, by the continuing fascination with surface-enhanced effects such as surface-enhanced Raman scattering (SERS) and surface-enhanced nonlinear optical phenomena; in particular, four-wave mixing by colloidal metal aggregates. Many SERS-active systems such as aggregated silver or gold colloid and cold-deposited films have been demonstrated to be fractals.[6,7]

A common approach to the treatment of such fractals is to consider them to be assemblies of many ''monomers,'' which for colloidal clusters can each be associated with a colloid particle, that mutually interact by dipole–dipole coupling. (Of course, higher-order coupling can also be included at the expense of added complexity and very much greater computational demands.[8,9]) The resulting coupled equations can be diagonalized to yield a multitude of normal modes, each associated with a normal-mode frequency. When the cluster is excited by light with wavelength in the neighborhood of the surface plasmon excitation of the colloidal particles the magnitudes of the individual dipole oscillators become large, and so do the amplitudes of the resulting normal modes. This sort of treatment is general and independent of the arrangement of the monomers in the fractal. With fractals, however, a number of robust, general optical properties have been shown to result[4–7] from the dilational symmetry characterizing the aggregate, and hence independent of the specific positions occupied by the monomers, so long as the overall geometry belongs to a given fractal class. These predicted properties have been discussed and reviewed[10] and need not, therefore, be expounded at length here. Pertinent to this study are the facts that (1) many optical properties such as the extinction spectrum of fractal clusters of a certain class[11] become independent of cluster size beyond a minimum size; hence, there will be a ''universal extinction spectrum'' characterizing fractal clusters of any given type, and (2) that the absorption spectrum will be broad compared with those characterizing compact (i.e., nonfractal) clusters, the width being the inhomogeneously broadened envelope of the normal modes characterizing the cluster. Some elements of these predictions have been tested experimentally and reported previously. For example, the extinction spectra calculated for 3-D Ag colloidal clusters formed by cluster–cluster aggregation were reported and compared with measured extinction spectra of silver hydrosols aggregated with fumaric acid.[2] Likewise, SERS excitation profiles of silver colloidal aggregates containing ~4000, 7000, and 15 000 particles were found to be virtually independent of the number of particles constituting the cluster.[5]

In this paper, we report polarized extinction spectra of silver colloidal clusters aggregated by the addition of phthalazine and deposited gravitationally onto a quartz substrate. The deposition was carried out at a sufficient dilution such that, on average, no colloid cluster fell on top of an already deposited aggregate. Extinction spectra were measured both for *s*- and *p*-polarized light as a function of the

a)Author to whom correspondence should be addressed.

angle of incidence. The *s*-polarized spectra correspond to excitation tangential to the average surface of the deposited clusters. The extinction cross section for radiation polarized normal to the average surface can be extracted from the *p*-polarized spectra at angles of incidence greater than 0 deg. The normal and tangential extinction spectra were compared with calculated spectra, numerically determined for clusters containing up to 10 000 particles, generated in 3-D, then allowed to project onto a surface, simulating the experimental situation.

II. EXPERIMENT

Ag colloid was prepared by reducing $AgNO_3$ (Aldrich) with $NaBH_4$ (Merck) as in Ref. 12. Briefly, 7.5 mL of 4.4×10^{-3} M solution of $AgNO_3$ cooled to approximately 10 °C were added dropwise, with constant stirring, to a solution containing 3.5 mg of $NaBH_4$ in 75 mL of water precooled to 2 °C. Stirring was continued for ~45 min. Distilled deionized water was used throughout. The colloids were aggregated by adding 10 μL of a 10^{-2} M solution of phthalazine (Aldrich) to 2 mL of Ag colloid. The resulting suspension was diluted in the ratio 1:4 colloid/water prior to deposition. Ag colloidal aggregates were gravitationally deposited out of this solution onto a quartz plate placed on a bottom of a covered beaker. The quartz plate was previously cleaned by immersion in 1:1 nitric acid for 20 min, and the clusters were allowed to settle for 8 h. The cluster-bearing quartz plates were dried in air and immediately transferred to the spectrometer for polarized extinction measurements. Samples for TEM imaging were prepared by placing one drop of diluted, aggregated colloid on a Formvar-coated Cu grid, allowing the system to dry before imaging. The grids were pretreated in a glow discharge.

A Zeiss optical microscope equipped with a 40× objective and a video camera in lieu of eyepiece was used to image the deposited aggregates. Images were photographed directly off the video monitor. TEM imaging was carried out on a Hitachi H 600 microscope operating at 75 kV.

Polarized UV-visible spectra were obtained using a Hewlett–Packard HP 8952 UV/vis spectrometer. The incident radiation was polarized either *s*- or *p*- with a Glan–Thompson polarizer placed in the sample compartment of the spectrometer. The quartz plate bearing the deposited aggregates was mounted on a calibrated rotational stage enabling the angle of incidence to be varied.

An optical micrograph of the sample of silver colloid aggregates gravitationally deposited onto a quartz plate used in the absorption experiments is shown in Fig. 1. A typical TEM image of deposited silver colloid clusters is given in Fig. 2, indicating the clusters to be fractal aggregates, as previously reported by Weitz *et al.*[6]

III. CALCULATIONS

Calculations were performed on a cluster–cluster aggregate built out of 10 000 monomers. The 2-D cluster was first constructed as a 3-D fractal on a square lattice using the method of Meakin,[13] then collapsed onto a plane such that no empty spaces existed underneath any monomer, but with no other rearrangement of the monomers. The clusters were constructed assuming 5 nm radius silver monomers arranged on an 8 nm square lattice. The optical constants for silver were taken from Ref. 14. The fractal dimension of the 3-D cluster generated was ≅1.8. When collapsed, the quasi-2-D aggregate becomes self-affine, with a fractal dimension ≅2.6, determined from the height–height correlation measured as a function of x and y (z being the direction of the collapse).

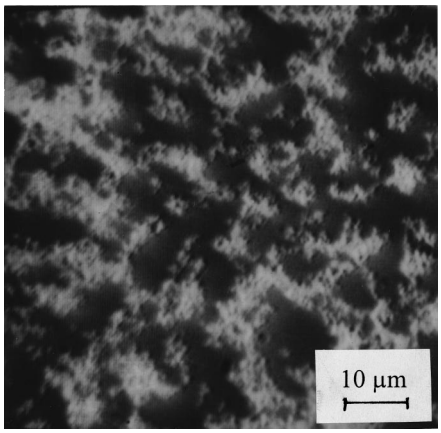

FIG. 1. Optical micrograph of the deposited colloidal silver clusters aggregates used for the polarized extinction measurements.

The method used to calculate the components of the extinction efficiency of the cluster along the xyz directions is described elsewhere.[2] The extinction coefficient $Q_{\alpha\beta}$, where α indicates the direction of propagation of the incident light and β the direction of polarization of its electric vector, is given by $Q_{\alpha\beta}=\sigma_e/(N\pi R_m^2)$, where σ_e is the extinction cross section and R_m the radius of a monomer.

IV. RESULTS AND DISCUSSION

Figure 3 shows the calculated components of the extinction coefficients for a 10 000-monomer cluster. The ambient medium was assumed to be vacuum. The extinction coefficient calculated for an incident wave propagating along the average surface of the collapsed cluster and polarized normal

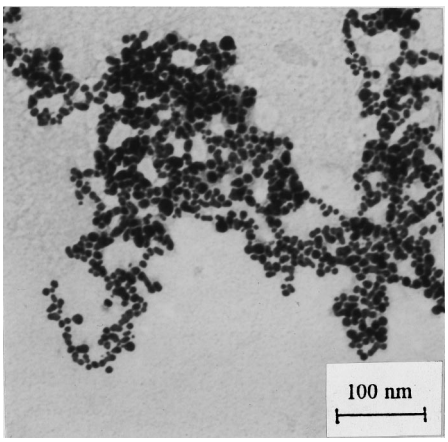

FIG. 2. TEM image of a drop of Ag colloid aggregated by phthalazine, diluted, deposited, and allowed to dry on a Formvar-coated copper grid.

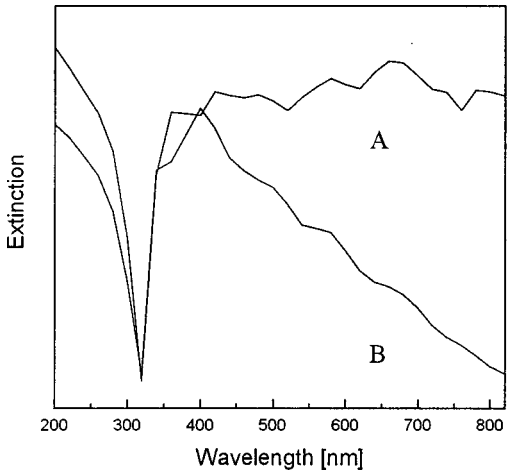

FIG. 3. Calculated extinction coefficients ($Q_{\alpha\beta}$), for a silver aggregate comprised of 10 000 monomers and collapsed onto a plane along the *z*-direction (α, β indicate, respectively, the propagation direction of the incident light and its polarization): curve A: a tangential extinction coefficient, Q_{zx}; curve B: a normal extinction coefficient, Q_{xz}.

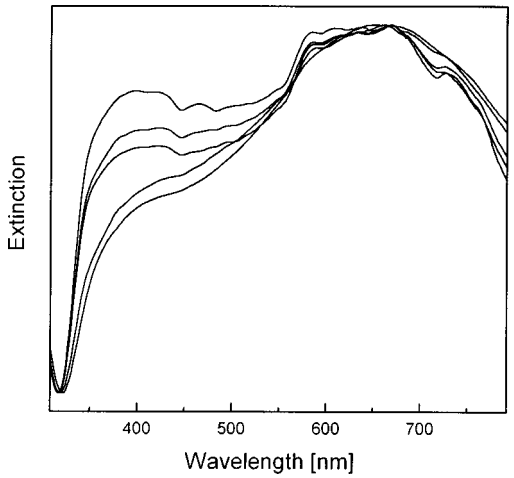

FIG. 5. Extinction spectra of deposited colloidal aggregates measured with *p*-polarized radiation as a function of the angle of incidence (0, 40, 60, 70, and 80 deg).

(i.e., along the *z*-axis) to that surface (Q_{xz}) drops off rather rapidly in the visible region of the spectrum (400–700 nm), whereas the extinction coefficients for waves polarized tangentially (Q_{xz} and Q_{yz}) (only one of which is shown in the figure for clarity) are predicted to fall off much more gently, actually remaining more or less constant over the visible region. The two tangential components, one corresponding to a wave propagating along the surface normal, the other propagating along the surface, although qualitatively similar, differ quantitatively indicating that, in general, the spectra also depend on the direction of propagation of the light as well as on its polarization.

The analogous experimental results are shown in Figs. 4–6. Figures 4 and 5 show the *s*-polarized and *p*-polarized extinction spectra obtained for the deposited silver clusters as a function of angle of incidence. The angles used were: 0, 40, 60, 70, and 80 deg. Because the sample had rather low absorption, the baseline shifted significantly from measurement to measurement. Accordingly, the measured spectra were normalized such that the extinction minimum at ~320 nm and the extinction maxima at ~700 nm were brought into coincidence for all of the spectra. When this is done, one obtains an extinction spectrum more-or-less independent of angle of incidence for the *s*-component, as expected. For the *p*-component, the normalized spectra are also approximately independent of angle of incidence in the region to the red of ~550 nm. However, in the region from ~320–550 nm, an extinction feature appears which increases with increasing angle of incidence, implying that this feature derives from the component of extinction normal to plane of the substrate. A normal component of extinction was extracted from these spectra using the expression $Q_{\text{normal}} \cong (Q_\theta - Q_0)/\tan\theta$, where Q_θ and Q_0 are the normalized *p*-polarized spectra at angle of incidence θ, and 0 deg, respectively. The $\tan\theta$ term arises as a result of the angle-of-incidence contribution of the normal component to the *p*-polarized component of extinction, and also as a result of the normalization of the spectra. A spectrum of Q_{normal} as a function of wavelength is shown in Fig.

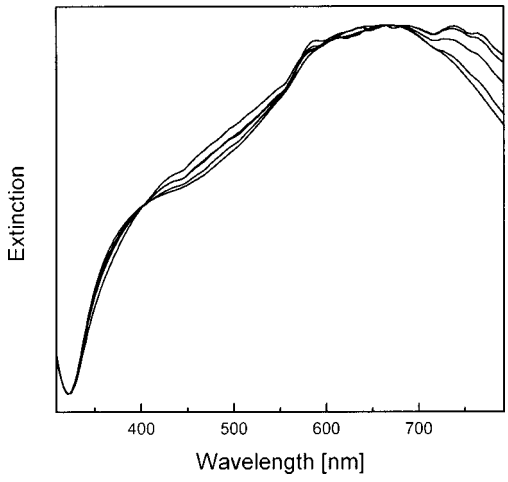

FIG. 4. Extinction spectra of deposited colloidal aggregates measured with *s*-polarized radiation as a function of the angle of incidence (0, 40, 60, 70, and 80 deg).

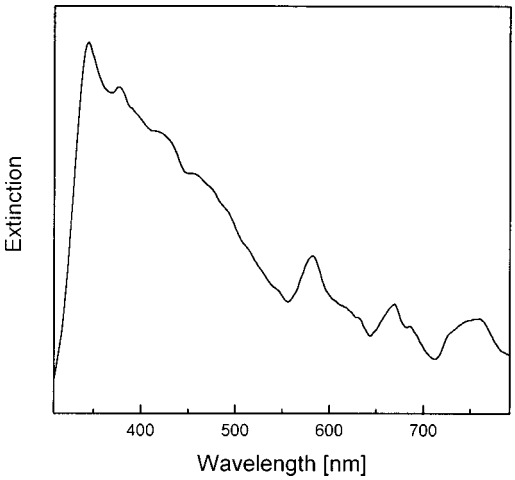

FIG. 6. Spectrum of the normal component of extinction extracted from the spectra shown in Fig. 5.

6. The spectra of Q_{normal}, extracted from the *p*-polarized spectra at all angles of incidence, coincide within experimental error, as required. The spectrum shown in Fig. 6 is an average of the four Q_{normal} spectra extracted from the *p*-polarization spectra measured at 40, 60, 70, and 80 deg.

The measured and predicted spectra of the normal component of extinction are rather similar (cf. Figs. 3 and 6). However, those of the tangential components, although similar qualitatively, do show some differences. For example, the experimental tangential extinction spectrum drops off more rapidly in the 400–600 nm region than the analogous computed spectrum does. Otherwise, the spectra are quite similar especially regarding their high intensity in the red region and its prodigious breadth.

We conclude that the optical theory of fractal aggregates accounts acceptably well for the observed normal and tangential components of the extinction spectra of fractal assemblies of colloidal silver particles, and that the spectra shown (Figs. 4 and 5) correspond to the size-independent extinction spectra of cluster–cluster aggregates of silver (apart from an intensity scaling factor).

ACKNOWLEDGMENTS

The authors thank Mr. B. Calvieri, Dept. of Medicine, Univ. of Toronto for TEM imaging of deposited clusters. M.M. thanks NSERC for financial support. B.V. thanks the Grant Agency of Charles University (Grant No. 219/1996/B/CH) and Grant Agency of Czech Republic (Grant No. 203/97/0259) for partial financial support.

[1] V. M. Shalaev and M. I. Stockman, Zh. Eksp. Teor. Fiz. **92**, 509 (1987) [Sov. Phys. JETP **65**, 287 (1987)]; Z. Phys. D **10**, 71 (1988); V. A. Markel, L. S. Muratov, M. I. Stockman, and T. F. George, Phys. Rev. B **43**, 8183 (1991); M. I. Stockman, T. F. George, and V. M. Shalaev, *ibid.* **44**, 115 (1991); M. I. Stockman, V. M. Shalaev, M. Moskovits, R. Botet, and T. F. George, *ibid.* **46**, 2821 (1992).
[2] V. N. Markel, V. M. Shalaev, E. B. Stechel, W. Kim, and R. Armstrong, Phys. Rev. B **53**, 2425 (1996).
[3] D. P. Tsai, J. Kovacs, Z. Wang, M. Moskovits, V. M. Shalaev, J. S. Suh, and R. Botet, Phys. Rev. Lett. **72**, 4149 (1994).
[4] P. Zhang, T. L. Haslett, C. Douketis, and M. Moskovits, Phys. Rev. B **57**, 15 513 (1998).
[5] B. Vlčková, X. Gu, and M. Moskovits, J. Phys. Chem. **101**, 1588 (1997).
[6] D. A. Weitz and M. Oliveria, Phys. Rev. Lett. **52**, 1433 (1984).
[7] C. Douketis, Z. Wang, T. L. Haslett, and M. Moskovits, Phys. Rev. B **51**, 11022 (1995).
[8] Y-L. Xu, Appl. Opt. **34**, 4573 (1995).
[9] K. A. Fuller, J. Opt. Soc. Am. A **11**, 3251 (1994).
[10] V. M. Shalaev, Phys. Rep. **272**, 61 (1996).
[11] In general, this is true of clusters of fractal dimensions less than than 3 for 3D aggregates [M. V. Berry and I. C. Percival, Opt. Acta **33**, 577 (1986)]. The appropriate conditions for size independence to be valid in the case of compacted quasi-2D aggregates have not been established, generally, but the results presented in Ref. 5 suggest that the clusters used in this study belong to this class.
[12] K. Solecká-Čermáková, B. Vlčková, and F. Lednický, J. Phys. Chem. **100**, 4954 (1996).
[13] P. Meakin, Phys. Rev. Lett. **51**, 1119 (1983).
[14] P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).