Enhancement of Fluorescence Induced by Microstructure Resonances of a Dielectric Fiber

J. F. Owen, P. W. Barber,[a] P. B. Dorain,[b] and R. K. Chang
Department of Engineering and Applied Science, Yale University, New Haven, Connecticut 06520

(Received 8 May 1981)

Resonance-induced enhancement of fluorescence from a thin dye layer coated on a 9.8-μm-diam glass fiber has been observed. Enhancement occurs when the wavelengths of incident radiation and/or inelastic emission are resonant with natural modes of oscillation of a circular dielectric cylinder. These dielectric resonances are comparable to surface plasmon resonances in metallic microstructures, which are partially responsible for the surface-enhanced Raman effect.

PACS numbers: 78.40.Ha, 42.10.Fa, 77.90.+k

The inelastic scattering properties of molecules situated close to metal surfaces are of current interest. Experiments indicate a definite correlation between the existence of surface-enhanced Raman scattering (SERS) and/or enhanced fluorescence emission and the presence of metallic microstructures. For example, Raman enhancements on the order of 10^6 have been observed from molecules on metal colloids[1] and roughened surfaces of electrodes,[2-4] crystals,[5-7] and films.[8,9] Although the microstructure shapes and separations on roughened surfaces are uncertain and uncontrollable, models based on electromagnetic theory predict that the intensity of the incident field (with wavelength λ_i) at or near the surface is greatly enhanced when λ_i is resonant with the surface-plasmon modes of the metallic microstructure.[8,10-13] Theory also predicts that the inelastic reemission (wavelength λ_f) from molecules situated on or near the surface is greatly enhanced when λ_f is resonant with the surface-plasmon modes.[8,10-13] Thus, the metallic micro-objects act as efficient receiving and transmitting antennas for wavelengths in resonance with the plasmon modes.

We report the first experimental observation of enhanced fluorescence emission from molecules on the surface of a *dielectric* micro-object. Enhancement of fluorescence from a thin dye layer coated on a 9.8-μm-diam glass fiber has been observed when λ_i and/or λ_f are resonant with natural modes of oscillation for the dielectric cylinder. With the substitution of the appropriate dielectric constants, the electrodynamic formulation[14,15] for dielectric micro-objects is identical to that for a metallic system.[12] The results of these experiments and calculations for a single, cylindrical, dielectric fiber clearly demonstrate electromagnetic resonance enhancement of both the incident field and reemitted radiation. The study complements work performed on metallic microstructures with random sizes, shapes, and separations[16-18] and on metallic microstructures prepared by microlithography which have uniform quasispheroidal geometries.[19]

The glass fiber was coated by brief immersion in a solution of polystyrene and oxazine dissolved in chloroform. Analysis of elastic scattering spectra[15] taken before and after the fiber was coated indicated that the overcoating thickness was approximately 50 to 100 Å. The fluorescence was excited with an incident beam (from a rhodamine 6G dye laser) oriented at 90° to the fiber axis. The fluorescence emission was collected with a lens at 90° with respect to the incident beam, in the plane perpendicular to the fiber axis, and was imaged onto the entrance slit of a $\frac{3}{4}$-m double monochromator. To obtain elastic scattering spectra over a broad wavelength range, the fiber was illuminated perpendicular to its axis with a 200-W tungsten-iodide lamp and scattered radiation was collected at 120° from the forward direction.

An excitation spectrum for the oxazine-coated fiber is shown in Fig. 1(a) and experimental and calculated elastic scattering spectra over the same wavelength region are shown in Figs. 1(b) and 1(c), respectively. The incident beam was polarized perpendicular to the fiber axis (TE polarization) and the TE component of the fluorescence was monitored at 675.1 nm. The experimental and calculated elastic scattering curves are also for TE polarization. The refractive index m used in the calculation was deduced by matching theoretical and measured elastic angular scattering patterns for monochromatic radiation. The mode number n and order number l of individual natural modes of oscillation [14,15] are labeled as n,l in Fig. 1(c). Since the dye concentration was dilute, leading to small optical absorption, and the overcoating was relatively thin, the presence of the polystyrene/dye layer

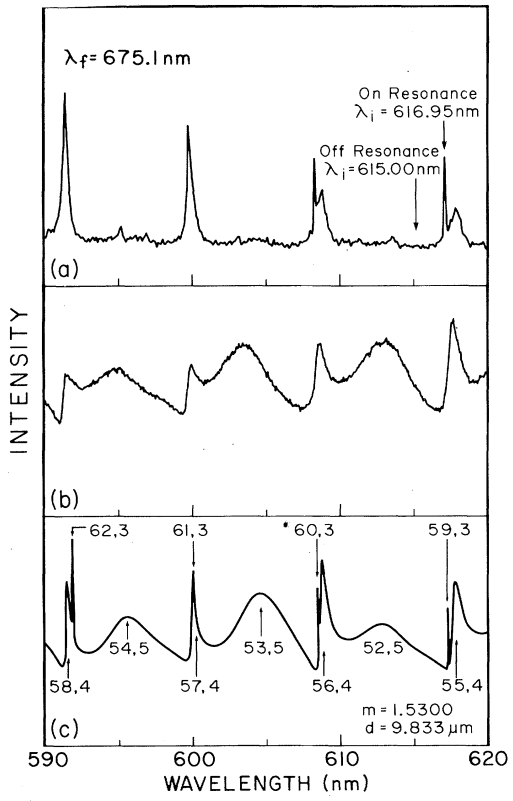

FIG. 1. (a) Fluorescence excitation, (b) experimental elastic scattering, and (c) calculated elastic scattering spectra from a 9.833-μm-diam glass fiber coated with approximately 50 to 100 Å of oxazine dye. Presence of the dye layer was neglected in the calculation. The mode number n and order number l of individual modes are denoted n,l. Arrows in (a) show excitation wavelengths for fluorescence spectra of Fig. 2(a).

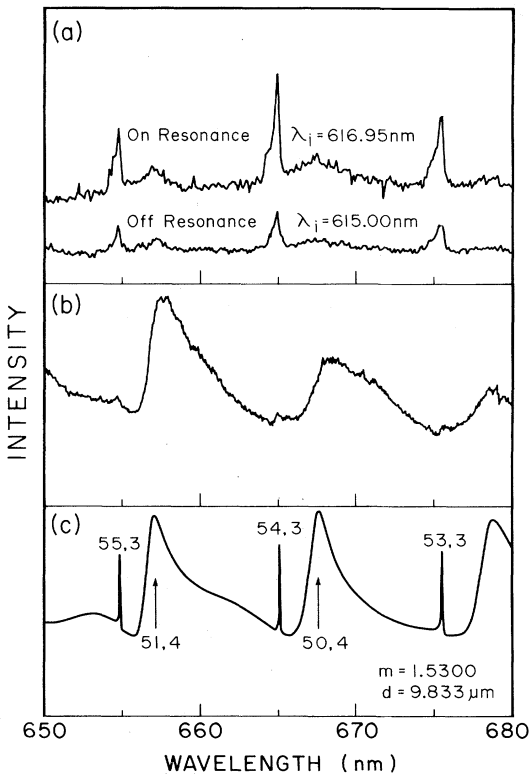

FIG. 2. (a) Fluorescence spectra, and corresponding (b) experimental and (c) calculated elastic scattering spectra from fiber of Fig. 1. The excitation wavelength for the upper fluorescence curve was resonant with mode 59,3 of the fiber; the excitation wavelength for the the lower curve was off resonance, as illustrated in Fig. 1(a).

was neglected in the calculations.

Sharp peaks occur in the excitation spectrum for the oxazine-coated fiber at wavelengths which correspond to resonances in the elastic scattering spectra. The largest peaks in the excitation spectrum correspond to the narrow $l = 3$ modes (60,3 and 59,3), smaller peaks occur for the $l = 4$ modes (56,4 and 55,4), and little or no increase in intensity is evident for the broad $l = 5$ modes (54,5, 53,5, and 52,5). Although the elastic scattering data [Fig. 1(b)] were obtained with spectrometer resolution sufficiently high to resolve the $l = 3$ modes, peaks corresponding to these resonances do not appear. Also, the widths of the $l = 3$ peaks in the excitation spectrum [3 Å full width at half maximum (FWHM)] are considerably greater than the widths in the calculated elastic spectrum (0.2 Å FWHM). Deviations as small as 40 Å in the fiber diameter along the illuminated length (~ 3 mm) would give rise to this degree of linewidth broadening.

Figure 2(a) shows fluorescence spectra from the oxazine-coated fiber for two incident wavelengths. For the upper fluorescence spectrum, λ_i is resonant with the 59,3 mode while λ_i for the lower curve is off resonance [see Fig. 1(a)]. The intensity of the "on-resonance" spectrum is approximately three times that of the "off-resonance" curve. Corresponding experimental and calculated elastic scattering spectra are shown in Figs. 2(b) and 2(c). As is the case in the excitation spectrum, the largest enhancement in fluorescence occurs at wavelengths corresponding to $l = 3$ modes, even though these peaks are barely observable in the experimental elastic scattering curve [Fig. 2(b)]. Much smaller fluorescence enhancement is associated with the $l = 4$ modes. Again, the linewidths of the fluorescence peaks are large compared to the calculated values for $l = 3$ modes.

To investigate the relationship between the elastic scattering spectra and the fluorescence excitation and emission spectra, we have performed calculations of the internal electric field intensity for infinite circular dielectric cylinders illuminated by a plane wave. Figure 3 shows the average field intensity integrated around a circle centered at the fiber axis as a function of the radius, r, of the circle. Results are shown for values of size parameter x ($x = 2\pi a/\lambda$, where a is the fiber radius) which correspond to resonance frequencies of modes with $n = 53$ and $l = 1$–5, as well as for an off-resonance case. Note that the resonant modes make large contributions to the electric field near the edge of cylinder but make no contribution in the center. In addition, the intensity at the fiber perimeter increases dramatically as l decreases. The calculations do not include optical loss which would damp the structure modes, particularly for low l, and thereby decrease the internal field intensities.

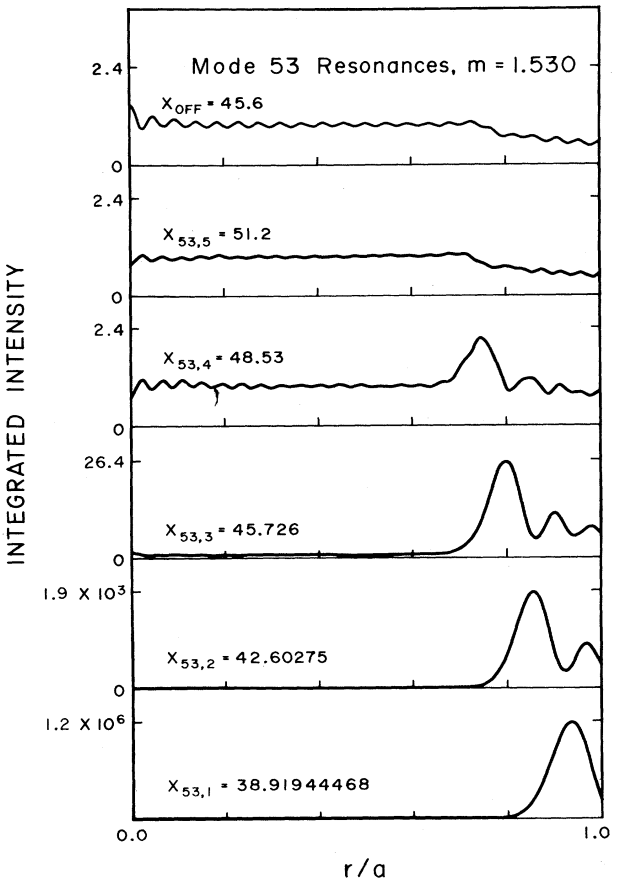

FIG. 3. Calculated average field intensity integrated around a circle of constant radius r within a lossless dielectric cylinder of radius a, as a function of r. Calculations are shown for m and x satisfying resonance conditions for various modes, as well as for an off-resonance condition.

The origins of the peaks in the excitation and fluorescence spectra from the dye-coated fiber are evident from the internal field calculations. When λ_i is resonant with a mode of the fiber, the fluorescent molecules experience an enhanced incident field. For example, the electric field intensity at the perimeter of a fiber ($r/a = 1$ in Fig. 3) for λ_i resonant with mode 53,3 is about an order of magnitude larger than the intensity for an off-resonance condition. In this sense the dielectric microstructure acts as a receiving antenna. For a perfect fiber, with a dye layer sufficiently thin that absorption in the layer and difference in index from the bulk can be ignored, a peak with a magnitude approximately 10 times that of the background is expected in the excitation spectrum at the resonant wavelength. This is in contrast to the twofold increase in elastic scattering intensity which is expected when λ_i is resonant with $l = 3$ modes [see Figs. 1(c) and 2(c)]. The fact that the $l = 3$ peaks observed in the excitation spectrum [Fig. 1(a)] are significantly smaller and broader than predicted for a perfect fiber, as well as the lack of $l = 3$ resonances in the elastic scattering spectra [Figs. 1(b) and 2(b)], indicates that these resonances are damped, probably as a result of losses and irregularities in the fiber. However, the height and width of the $l = 4$ peaks in the excitation and elastic scattering spectra are in agreement with predicted values, consistent with the observation that the broader, higher-l modes are less sensitive to imperfections than lower-l resonances.[12]

Peaks in the fluorescence spectra occur at wavelengths which correspond to resonance frequencies since, at these wavelengths, the near-field components (terms $\propto r^{-1}$, r^{-2}, and r^{-3}) of the fluorescing dipoles couple efficiently to the resonant modes. The detected electric field intensity of the fluorescence at these wavelengths has contributions from the far-field components (term $\propto r^{-1}$) of the resonant modes of the fiber, as well as from the far-field terms of the individual molecules. Thus, the dielectric microstructure acts as a transmitting antenna for the inelastic emission.

In summary, enhancement of inelastic scattering from molecules situated on or near a dielectric fiber is observed when the incident and/or reemitted radiation wavelengths are resonant

with natural modes of oscillation of the fiber. The enhancement mechanism is identical to proposed local field enhancement mechanisms for SERS from metallic microstructures, where the analogous resonant modes are surface plasmon modes and the n,l values correspond to various multipolar plasmon resonances.

We thank Dr. Prabhat Gupta of Owens-Corning Fiberglas for supplying us with the glass fiber. We also gratefully acknowledge the partial support of this work by the National Science Foundation (Grant No. ESC79-20113) and the Gas Research Institute (Basic Research Grant No. 5080-363-0319).

[a]Present address: Department of Bioengineering, University of Utah, Salt Lake City, Utah 84112.

[b]Present address: Chemistry Department, Brandeis University, Waltham, Mass. 02254.

[1]J. A. Creighton, C. G. Blatchford, and M. G. Albrecht, J. Chem. Soc. Faraday Trans. 2 75, 790 (1979).

[2]M. Fleischmann, P. J. Hendra, and A. J. McQuillan, Chem. Phys. Lett. 26, 163 (1974).

[3]T. E. Furtak and J. Kester, Phys. Rev. Lett. 45, 1652 (1980).

[4]D. A. Weitz, T. J. Gramila, A. Z. Genack, and J. I. Gersten, Phys. Rev. Lett. 45, 355 (1980).

[5]J. E. Rowe, C. V. Shank, D. A. Zwemer, and C. A. Murray, Phys. Rev. Lett. 44, 1770 (1980).

[6]P. N. Sanda, J. M. Warlaumont, J. E. Demuth, J. C. Tsang, K. Christmann, and J. A. Bradley, Phys. Rev. Lett. 45, 1519 (1980).

[7]S. G. Schultz, M. Janik-Czachor, and R. P. Van Duyne, Surf. Sci. 104, 419 (1981).

[8]C. Y. Chen and E. Burstein, Phys. Rev. Lett. 45, 1287 (1980).

[9]J. G. Bergman, D. S. Chemla, P. F. Liao, A. M. Glass, A. Pinczuk, R. M. Hart, and D. H. Olson, Opt. Lett. 6, 33 (1981).

[10]S. L. McCall, P. M. Platzman, and P. A. Wolff, Phys. Lett. 77A, 381 (1980).

[11]W. H. Weber and G. W. Ford, Phys. Rev. Lett. 44, 1774 (1980).

[12]M. Kerker, D.-S. Wang, and H. Chew, Appl. Opt. 19, 4159 (1980).

[13]J. Gersten and A. Nitzan, J. Chem. Phys. 73, 3023 (1980).

[14]M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation* (Academic, New York, 1969), p. 255.

[15]J. F. Owen, P. W. Barber, B. J. Messinger, and R. K. Chang, Opt. Lett. 6, 272 (1981).

[16]G. Ritchie, E. Burstein, and R. B. Stephens, Bull. Am. Phys. Soc. 26, 359 (1981); C. Y. Chen, I. Davoli, G. Ritchie, and E. Burstein, Surf. Sci. 101, 363 (1980).

[17]T. J. Gramila, D. A. Weitz, and S. Garoff, Bull. Am. Phys. Soc. 26, 339 (1981); S. Garoff, D. A. Weitz, T. J. Gramila, and C. D. Hanson, Opt. Lett. 6, 245 (1981).

[18]H. G. Craighead and A. M. Glass, Opt. Lett. 6, 248 (1981); A. M. Glass, P. F. Liao, J. G. Bergman, and D. H. Olson, Opt. Lett. 5, 368 (1980).

[19]P. F. Liao, J. G. Bergman, D. S. Chemla, A. Wokaun, J. Melngailis, A. M. Hawryluk, and N. P. Economou, to be published.

Surface Relaxation of ^{3}He on Small Fluorocarbon Particles

L. J. Friedman, P. J. Millet,[a] and R. C. Richardson
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853

(Received 7 August 1981)

The nuclear magnetic polarization of ^{3}He on the surface of a fluorocarbon substrate is controlled by the polarization of the ^{19}F in the substrate. The apparent relaxation rates of the ^{3}He measure the coupling between the spin baths of the ^{3}He and the ^{19}F nuclei within the substrate.

PACS numbers: 76.60.Es, 67.70.+n

We have observed unusual nuclear relaxation and polarization phenomena in a fluorocarbon polymer in contact with films of ^{3}He. Our measurements show that the spin temperatures of the ^{3}He and the ^{19}F are held in close contact, most likely through the nuclear magnetic dipolar coupling at the interface.

In our experiments we packed a powder of fluorocarbon beads in a cylindrical coil form 4.8 mm in diameter and 9.5 mm high. We then measured the relaxation properties of the ^{19}F with various coverages of ^{3}He on the surface of the beads. The beads were approximately 0.2 μm in diameter and had a rather narrow size distribution. The polymer is quite similar to polytetrafluoroethylene (or Teflon) and is sold by Dupont under the trade name DLX-6000. Our measurements were conducted in the temperature range

