may be taken as constants. When a normal time-independent projection operator acts on a current the expansion is

$$P\vec{k}J\vec{k} \simeq A\vec{k}[C_0+D_1k^2+D_2k^4+\ldots].$$

Although in the limit $k \rightarrow 0$ these two expressions become identical, for $k \neq 0$ they differ and this difference ultimately leads to terms that are the same order of magnitude as those given by Eq. (6) of this Letter.

(7) For a dilute gas the present authors[13] previously computed the structure factor, for the case of a steady thermal gradient, using a fluctuating kinetic equation. Although the formalism presented there is correct and equivalent to the one presented here, the value of the coefficient y is incorrect. The correct value, valid for all densities is given in Eq. (6) here. The bilinear term mentioned in that Letter defines, in kinectic theory, the new eigenvalue problem discussed in this paper in a hydrodynamic context.

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Observation of Structure Resonances in the Fluorescence Spectra from Microspheres

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Sharp intensity peaks are observed in the fluorescence spectra from dye-impregnated single polystyrene microspheres which are not seen in the spectra from bulk material. The resonant peaks are shown to correspond to the natural modes of oscillation of a dielectric sphere, and excellent correlation is found between experimental and theoretically predicted spectra. The results can be applied to the interpretation of inelastic emission (fluorescence and Raman) spectra obtained for the chemical speciation of aerosols and particulates.

A dielectric sphere possesses natural modes of oscillation at characteristic frequencies corresponding to specific size-to-wavelength ratios. These structure resonances have been studied both theoretically and experimentally in the microwave range[1, 2] and more recently in the optical range.[3-6] In all of these studies, the emphases have been on structure-resonance effects resulting from external excitation, usually by plane waves. The elastic absorption and scattering efficiencies and the optical levitation force are all known to be enhanced when the incident wavelength is commensurate with the natural modes of oscillation of the sphere.[3-6] Recent theoretical work[7-9] has predicted the existence of structure resonances in the inelastic emission.

We report the first experimental observation of structure resonances resulting from the internal emission of inelastic radiation by fluorescing molecules embedded in a microsphere. Sharp intensity peaks are measured in the fluorescence spectra from a single dye-impregnated polystyrene sphere which are not seen in the spectra from bulk material. Knowledge of structure resonances excited by internal sources has application to chemical speciation of molecules embedded in particulates by inelastic light-scattering spectroscopy[7-9] (fluorescence or Raman).

The eigenvalue equations for the natural resonant frequencies of dielectric spheres in homogeneous surroundings are well known.[10] For the transverse electric (TE) modes, continuity of the tangential electric and magnetic fields at the interface for a certain natural mode number n requires that

$$\frac{[mxj_n(mx)]'}{j_n(mx)}=\frac{[xh_n^{(1)}(x)]'}{h_n^{(1)}(x)}, \tag{1}$$

where m is the ratio of the refractive index of the sphere to that of the surrounding medium. The size parameter x is ka ($k=2\pi/\lambda$, where λ is the wavelength in the surrounding medium and a is the radius of the sphere) and $j_n(x)$ and $h_n^{(1)}(x)$ are the spherical Bessel function and spherical Hankel function of the first kind, respectively. The prime denotes differentiation with respect to the argument. The transcendental equation [Eq. (1)] is satisfied only by a discrete set of characteristic values of the size parameter, $x_{n,s}$, corresponding to the sth root for each n.

For the transverse magnetic (TM) modes, the continuity of the tangential fields requires that

$$\frac{[mj_n(mx)]'}{m^2j_n(mx)}=\frac{[xh_n^{(1)}(x)]'}{h_n^{(1)}(x)}. \tag{2}$$

Again, a discrete set of $x_{n,s}$ values satisfies this transcendental equation [Eq. (2)].

The natural resonant frequencies associated with the $\mathrm{TE}_{n,s}$ and $\mathrm{TM}_{n,s}$ modes are

$$\omega_{n,s}=x_{n,s}/a(\mu\epsilon)^{1/2}, \tag{3}$$

where μ is the permeability and ϵ the permittivity of the surrounding lossless medium. Thus, Eqs. (1) and (2) define the complex frequencies at which a dielectric sphere will resonate in one of its natural modes.

For a plane wave incident on a dielectric sphere, the elastically scattered field can be written as an expansion of vector spherical wave functions with coefficients a_n and b_n.[10] The scattered field becomes infinite at complex frequencies $\omega_{n,s}$ corresponding to the complex size parameters $x_{n,s}$ at which a_n and b_n become infinite. Resonances caused by the a_n coefficient occur at the precise frequencies corresponding to the $\mathrm{TE}_{n,s}$ natural modes specified by Eq. (1). Similarly, resonances of the b_n coefficient are associated with the $\mathrm{TM}_{n,s}$ natural modes as specified by Eq. (2).

For real frequency excitation, neither the amplitudes of the a_n and b_n coefficients nor the natural modes of the sphere associated with Eqs. (1) and (2) can have infinite amplitude. However, sharp finite-amplitude resonances do occur. These resonances are of current theoretical interest[4-6] and have been experimentally verified at optical wavelengths[3] with micrometer-sized spheres. While previous experiments probe the structure resonances with external excitation, internal sources emitting at a discrete frequency or over a range of optical frequencies different from the incident radiation frequency can also excite the natural modes of the sphere defined by Eqs. (1) and (2). Specifically, the spectrally broad inelastic reemission from fluorescent molecules within a sphere can induce natural-mode resonances. The fluorescent wavelengths which induce the natural modes shouls be predictable from the well-known solutions for external excitation by plane waves, i.e., the resonances of the a_n and b_n coefficients with the size parameter x set equal to that for the fluorescence wavelength in the surrounding medium.

To obtain experimental data on the wavelength dependence of fluorescence from microspheres, nominally monodispersed polystyrene spheres having diameters of 9.92 μm (2% standard deviation) and containing a volume-distributed fluorescing dye were suspended in water and illuminated by an Ar laser operating at 457.9 nm. As indicated in Fig. 1, the fluorescence from the suspension was collected perpendicular to the excitation beam by a lens of $f/1.2$ and imaged onto the entrance slit of an optical multichannel analyzer (OMA) consisting of a self-induced-transparency vidicon camera (OMA II from PAR) positioned at the focal plane of a 1-m, single, concave, holographic grating spectrograph. A wavelength-dispersed range of approximately 20 nm of the fluorescence spectrum was recorded simultaneously on one axis of the 512 × 512-element vidicon detector array. The other axis provided spatial resolution of the laser track within the sample cell. Consequently, using the OMA approach, it was possible to isolate the fluorescence from a single microparticle by scanning only a selected portion of the vidicon array corresponding to the particle's position within

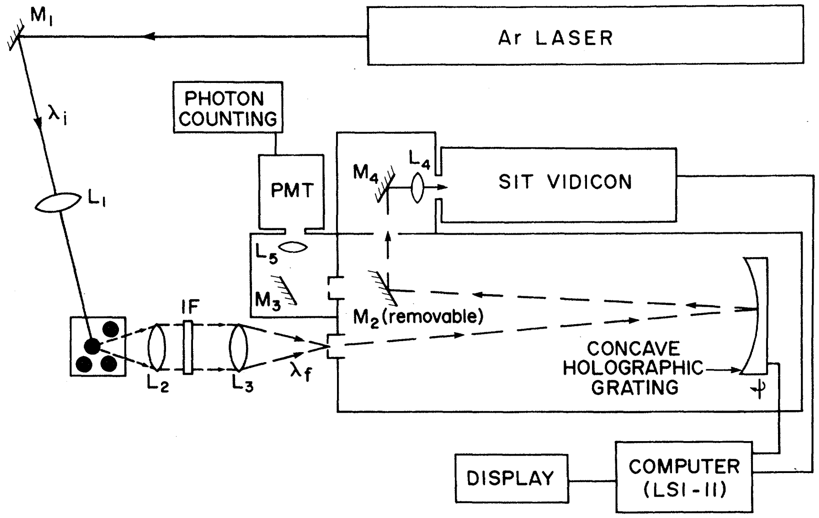

FIG. 1. Schematic representation of the multichannel spectrograph system used to monitor simultaneously a 20-nm wavelength range of the fluorescence emission from a single microsphere suspended in a fluid.

the laser track, and simultaneously to monitor the particle's wavelength-dispersed fluorescence profile as it floated into and out of the excitation beam. In contrast to the featureless, broadband fluorescence intensity profile expected from a bulk solution of dye molecules, Fig. 2 shows fluorescence data for three different microspheres contained within a suspension of 9.92-μm-diam particles ($m = 1.195$) in water. Although a resonance pattern with similar structure is observed in each of the spectra, slight variations in particle size cause the fluorescence peaks for individual spheres to be shifted in wavelength. Consequently, fluorescende spectra must be collected from single particles since those from a distribution of even nominally monodispersed spheres will contain a wide variation in the positions of structure resonances in the fluorescence emission and approach the featureless spectra of the bulk dye solution with increasing number of particles.

The observation of structure resonances in the fluorescence is not restricted to isolated spheres in homogeneous surroundings. We have observed similar effects in the fluorescence emission of spherical particles deposited on a hemicylindrical Al_2O_3 prism using both plane and evanescent wave excitation.[11]

The principal advantage of collecting data from suspended particles is that comparison with theoretical results is possible. Elastic scattering calculations have been made for $d = 2a = 9.92$ μm and $m = 1.195$, corresponding to the experimental data shown in Fig. 2. Specifically, the extinction efficiency[12] has been calculated over the range of the experimentally obtained fluorescence spectra. The calculated extinction efficiency is shown in Fig. 3, curve a, along with the observed fluorescence spectrum, Fig. 3, curve b, [same as Fig. 2, curve a]. Although the correspondence

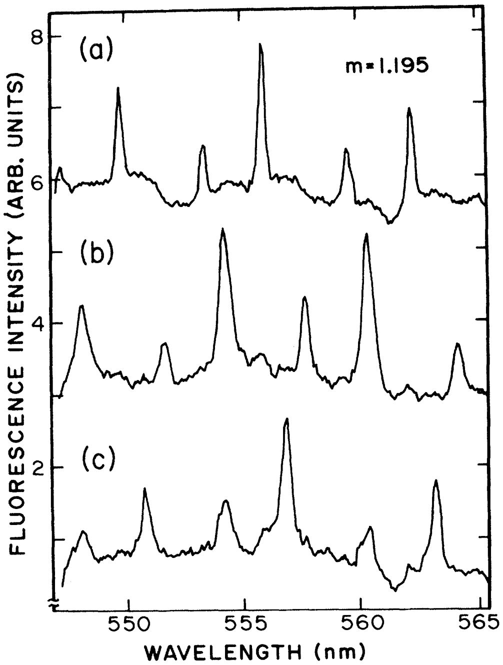

FIG. 2. Fluorescence spectra for three particles from a nominal monodispersion of 9.92-μm polystyrene spheres.

between Fig. 3, curves *a* and *b*, appears to be poor, shifting the calculated curve approximately 4 nm to the right [Fig. 3, curve *c*] results in a much improved fit between the experimental and theoretical results. Shifting the theoretical curve along the wavelength scale by 4 nm corresponds to a change in d of 0.07 μm, i.e., Fig. 3, curve *c*, is the theoretical result for a 9.99-μm sphere, implying that the sphere from which the fluorescence spectrum [Fig. 3, curve *b*] was obtained had $d = 9.99$ μm, rather than $d = 9.92$ μm. The fractional variation from the nominal size is well within the 2% standard deviation quoted by the particle manufacturer.[13] We note that the theoretical curve could also be shifted by varying the refractive index in the calculation. However, a change in the refractive index from that of pure polystyrene, resulting from anomalous dispersion associated with the absorption of the dye molecules, is unlikely when we consider the low dye concentrations in the spheres.

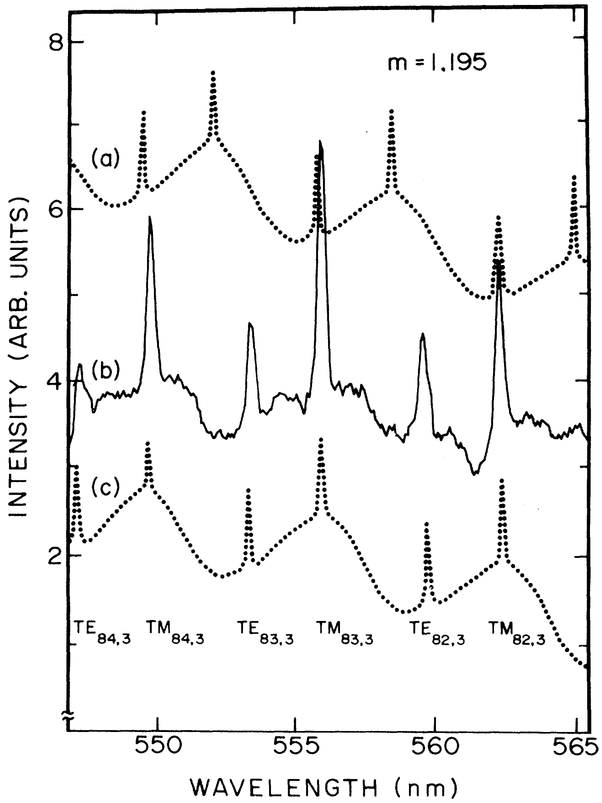

FIG. 3. Fluorescence spectra from a single polystyrene sphere in water. Curve *a*, theoretical result for a 9.92-μm sphere; curve *b*, the experimental result; and curve *c*, the theoretical result for a 9.99-μm sphere. The resonant peaks in curves *b* and *c* are identified by their mode numbers.

Extensive numerical studies[5,8] have shown that for a given n, the $s = 1$ root results in the narrowest resonances, with the width of the resonances increasing as s increases. The resolution of the calculated curves in Fig. 3 suppresses the narrow first- and second-order resonances ($s = 1$ and 2) and shows only the third-order resonances[5] ($s = 3$). The higher-order resonances are so broad that they are lost in the background. The resonances alternate with increasing wavelength between $\mathrm{TE}_{n,s}$ and $\mathrm{TM}_{n,s}$ modes. For $x \gg 1$, the incremental spacing between successive TE or TM peaks has been shown[5,6] to be constant when plotted as a function of x. This implies that when plotted as a function of wavelength, as in Fig. 3, the resonance spacing increases with increasing wavelength. In fact, the spacing varies continuously and this feature greatly facilitates the unambiguous fitting of theoretical to experimental results. We conclude that the natural modes of a sphere can be excited by internal sources and the structure resonances in the fluorescence are the same as when the sphere is excited by an incident plane wave at the fluorescence wavelength.

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