Aerosol particle microphotography and glare-spot absorption spectroscopy

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The relative intensities of glare spots in the image of an electrodynamically trapped aerosol droplet are measured experimentally with an aerosol particle microscope and calculated theoretically. The theoretical calculations are in good agreement with these experiments and indicate that the intensities of these spots are extremely sensitive to the imaginary part of the refractive index. Experimentally, we obtain the molecular absorption spectrum of an impurity within a droplet by recording the spectrum of an individual glare spot produced by broadband illumination.

There are many applications for which it would be desirable to measure the absorption spectrum of the contents of an individual aerosol particle. However, such spectra have been obtained only indirectly, i.e., by measurement of the action spectra of various photothermal phenomena. A reason for the difficulty in measuring the absorption spectra of molecular constituents of aerosols is that the individual aerosol microparticles illuminated in the visible or the near infrared scatter light in all directions. Although the angular scattering by a particle depends on the absorption of its molecular species, and in theory the absorption of a species might be obtained by a complex inversion procedure, such methods are fraught with experimental and computational difficulties. Spectral measurements of molecular species in droplets have not been obtained from angular-scattering measurements, as far as we are aware.

We present here a more direct method for obtaining absorption spectra, one that is based on the spectroscopy of glare spots (glare-spot spectroscopy). This approach relies on recent theories of particle imaging. This work provides confirmation for the first application of this theory to spectroscopy. We show, both experimentally and theoretically, that glare spots in the image of a particle are very sensitive to the absorption coefficient of the material of the droplet.

In what follows we review the theory of imaging for spherical particles, compare this theory with experiments using the aerosol particle microscope, and demonstrate a means for obtaining absorption spectra.

In an attempt to describe the image of high-order rainbows, Lock considered the nature of glare-spot images from a single water droplet. He stated that the electromagnetic field at the retinal plane $E_r(x_r)$ of an eye positioned at scattering angle $\theta_0$ and range $R$ may be obtained from the field at the lens plane $E_{\text{Mie}}(\theta)$ by use of the equation

$$E_r(x_r) = \int_{-\theta_0/2}^{\theta_0/2} d\xi E_{\text{Mie}}(\theta_0 + \xi) \exp(-iR R x_r / d), \quad (1)$$

where $d$ is the distance of the lens to the retina (i.e., the image distance), $k$ is the propagation constant of the scattered light, $x_r$ is the position coordinate in the image plane, and $\theta_0$ is the angular width that the lens subtends from the center of the particle. Van de Hulst and Wang derived Eq. (1) formally, noting that for it to be accurate (a) rays must enter and leave the lens at small angles relative to its axis and (b) the variation in $E_{\text{Mie}}$ with the azimuthal angle $\phi$ must be negligible in comparison to the variation with the scattering angle $\theta$. Although Eq. (1) does not apply to scattering near the forward direction, Schaub et al. treated this imaging case by considering both azimuthal and polar variations in the scattered field.

If Eq. (1) is to apply to microscopy, for which the distance from the objective lens to the imaging detector is much greater than the distance from the lens to the particle, the criterion of small angles is equivalent to saying that the numerical aperture of the objective lens (N.A.) must be considerably less than 1.

Experiments were carried out in air at atmospheric pressure in the aerosol particle microscope, with a N.A. of 0.17 and a primary magnification of 30×, shown in Fig. 1. The particle is confined in a Paul trap having a static levitation field. In addition, small electrodes have been implanted in the midplane of the torus and electrified to cancel in-plane stray static fields at the trap center. With this addition, systematic fluctuations are eliminated and the rms displacement of the particle from the center of the trap $Y_{\text{rms}}$ is limited only by stochastic fluctuations associated with molecular collisions; for the present experiments $Y_{\text{rms}}$ is less than the optical wavelength. The particle was irradiated from the side or from...
Fig. 1. Aerosol particle microscope. Note the fiber optic used for extracting the light from a single glare spot for spectral analysis. OMA, optical multichannel analyzer.

below with laser (semiconductor at 635 nm) or collimated incandescent illumination (from a lamp bulb).

In addition to recording images with the integrating CCD camera under both laser and incandescent illumination, we made provisions for measuring the spectrum of an individual portion of the image (e.g., glare spots) under incandescent illumination. We obtained this spectrum by imaging the particle on a translucent screen (e.g., magic tape from 3M), as shown in Fig. 1, with a naked quartz optical fiber positioned at its center (core diameter 100 \(\mu m\)). This composite screen was then attached to an \(x-y\) stage that was positioned in such a way that the fiber could be moved over a region of interest in the image cast on the translucent screen. The fiber was led to a 0.25-m monochromator equipped with an optical multichannel analyzer in its exit plane. In this manner one could obtain a spectrum of any portion of the image.

Figure 2(a) shows the topograph of a typical image of a glycerol particle 25.5 \(\mu m\) in diameter illuminated from the side with a vertically polarized \((z\text{-polarized})\) laser beam. Figure 2(b) shows an intensity trace along the symmetry axis of the image. As one can readily see the peak at the far side of the particle is the most intense and the peak in the interior is the least intense.

To compare the theory of Lock\(^6\) with the results in Fig. 2(b), we evaluated Eq. (1) by using a numerical algorithm for \(E\text{_{Mie}}\) (Ref. 11) and included the effect of the finite size of the CCD pixels. Figure 2(c) shows the calculation from Eq. (1) for a particle with a diameter of 25.5 \(\mu m\) and a refractive index \(m = 1.4746\) in which we have averaged over each pixel width. As one can see, three peaks were produced, just as in the experiment. In fact, the relative heights of the peaks as calculated from theory agree well with the relative heights in the experiment [Fig. 2(b)].

The theoretical effect of absorption on various glare spots is very telling, as can be seen from Fig. 2(c). With an imaginary part of the refractive index of \(\delta = 10^{-3}\), the peak on the far side (i.e., the left side) falls to 67% of its original height, the peak on the right falls to 35%, and the smallest peak in the interior is apparently unchanged. The explanation for this effect can be understood in terms of ray trajectories.\(^{12}\) The interior peak is due to a direct reflection at 45° and is controlled by the associated Fresnel coefficient. As a consequence, this peak is substantially diminished by being near the Brewster angle and is not expected to change significantly for our small \(\delta\). However, for the peak on the far side a light ray typically traverses one chord (i.e., \(p = 1\) in the notation of van de Hulst\(^{12}\)) within the particle. It is expected to be attenuated in accordance with Beer's law. The peak on the near side requires at least three chords \((p = 3)\) within the particle and consequently is attenuated even more than the peak on the far side.

It is apparent from Fig. 2(c) that a ratio of the peak on the far side to the interior peak, \(r\), can provide information concerning absorption. A problem is that light emanating from a given edge may result from ray orbits corresponding to a number of different \(p\)'s, each of which can have a considerably different path length. For example, for weak absorption, resonant modes (morphology-dependent resonances) also contribute to the light coming from the edge at particular frequencies, and these modes correspond to many in-
ternal chords.\textsuperscript{13} As a consequence, if the ratio $r$ is used in constructing an absorption spectrum it will contain an undesirable wavelength dependence. Because resonances are excited by the part of the plane wave that impacts near the edge of the sphere, the localization principle\textsuperscript{14} implies that one can best avoid the problem of multiple paths by lowering the impact parameter. The impact parameter is minimized for the $p = 1$ ray viewed with back illumination.

Figure 3(a) shows a topograph of an image of a back-illuminated glycerol sphere 44 $\mu$m in diameter. The particle’s image, which is surrounded by a ring of light, is dark in its interior except for a particle’s image, which is surrounded by a ring of light, is dark in its interior except for a back-illuminated glycerol sphere 44 $\mu$m in diameter.

For a particle of the same size but containing Rhodamine 6G dye (7.5 $\times$ 10$^{-4}$ M), we obtain the spectrum of curve (ii) in Fig. 3(b). If one assumes that the particle is acting as a cuvette, the intensity with dye to that without dye is $I_{\text{dye}}/I_{\text{no dye}} = 10^{-\varepsilon_m d}$, where $\varepsilon$ is the molar extinction coefficient, $m$ is the molarity, and $d$ is the path length through the cuvette. Figure 3(b), curve (iii), shows the log($I_{\text{dye}}/I_{\text{no dye}}$) spectrum. This spectrum reveals the usual spectral features of Rhodamine 6G in a polyalcohol: a principal maximum at 530 nm and the prominent shoulder at 500 nm. Using the peak value of the log ratio of 0.38, we compute the path length to be 46 $\mu$m, in good agreement with the particle diameter. It appears that $p = 1$ rays are responsible for the central peak, consistent with the geometrical ray tracing in Fig. 3(a). Although ripples corresponding to Fabry–Perot modes should occur in a planar cuvette of the same length, in a droplet the rays propagate over different paths at different angles, causing such modes to be muted.

Although microscopy, as it is used in biology, seldom allows one to calculate an image from an analytical description of the electromagnetic field, the isolated particle is a prime candidate for such an approach. By imaging a homogeneous particle, we have only begun the potential investigations. Electromagnetic fields from particles having layers and other structure have been derived,\textsuperscript{15} and the relationship between images obtained from such particles and theory should be of great interest. In addition, the electromagnetic field associated with a small point dipole within a particle has been calculated. We can now ask: Does the dipole show up in the image, and, if so, is it located in the same place in the image and in the particle? Clearly such imaging relates to molecular optics and would have to be done while one is viewing spontaneous fluorescence or Raman scattering. This surely will require long-term imaging. The stability within the aerosol particle microscope aids is this adventure.

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References