Broadband photophoretic spectroscopy

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Received February 11, 1980

A means for obtaining broadband photophoretic spectra is described. The sensitivity of the technique is found in accordance with radiometric theory to increase markedly with pressure reduction below 1 atm. Noise oscillation induced by radiometric torques is contained through the use of electronic damping. The first broadband spectrum on a single crystallite (~5 μm) of CdS is presented.

Photophoresis is a term that describes the force induced on a small particle suspended in a gas by light.[1] A great deal of previous work has established that this force is principally of radiometric origin.[2] Although more will be said in what follows about photophoresis, its radiometric nature suggests that a measure of the spectral dependence of this phenomenon could be used in investigating the character of picogram quantities of material. Recently Pope *et al.*[3] showed that the onset of the light-induced force on a small crystallite (~10 μm in radius) of perylene with increasing photon energy is correlated with the absorption of the same material in bulk. This experiment (carried out at a pressure of 120 mm Hg at three wavelengths from an Ar$^+$ laser) was used to infer the possibility of a new spectroscopy, photophoretic spectroscopy. We show that this inference is essentially correct and present the first reported broadband spectrum of CdS. In addition, application of electronic damping enables one to extend the same technique to lower pressures than those used previously.[3] This is an important modification since reduction in pressure from 240 to 10 mm Hg is found to increase the force on a 5-μm crystallite by more than a factor of 10, consistant with the radiometric model. Such an increase is significant from a practical standpoint, since the intensity from a conventional arc-lamp–monochromomator combination is now sufficient for obtaining spectra.

The origin of photophoresis is best understood in the free-molecule regime, in which the mean free path in the gas λ is considerably larger than the particle radius a; Knudsen number $K_n = \lambda/a \gg 1$. In this limit, each of the colliding molecules may be thought of as acting independently from a gas at infinity with constant temperature T_∞. The illuminated particle with its unevenly heated surface will reflect both specularly and diffusely. The diffusely reflected molecules on average will acquire an enhanced mean velocity characteristic of the surface temperature. The reaction on the surface to the impulses imparted to the molecules will be larger for higher surface temperatures. A particle that is warmer on the side facing the absorbed light will therefore be driven away from the source. So long as heat is conducted through the particle at a faster rate than it is carried away by the gas, the force is found to be proportional to the pressure P of the gas.[2] The force will also be proportional to the intensity I of the light at low intensities, at which nonlinear mechanisms such as reradiation can be neglected. As the pressure is raised further, so that the mean free path λ of the molecules becomes comparable with the radius $a(K_n \simeq 1)$, the force reaches a maximum. At still higher pressures, such that $K_n \ll 1$, the force, which is controlled by thermal creep,[4] should diminish as P^{-1} with increasing pressure. For light absorbed only on the surface, Reed[4] has estimated the force in the $\lambda \ll a$ limit to be

$$F_P = +2\pi K \frac{\mu^2 a R f I}{P M}\left(\frac{1}{K_S + 2K_F}\right), \tag{1}$$

where K is a constant associated with creep and having a magnitude between 0.75 and 1.50, μ is the gas molecular viscosity, a is the particle radius, R is the universal gas constant, f is the fraction of light absorbed, I is the intensity, P is the gas pressure, K_S is the thermal conductivity of the particle, and K_F is the thermal conductivity of the gas.

Few calculations exist concerning the effects of finite extinction on the photophoretic force. Most workers have assumed no internal heat sources. Akhtaruzza-

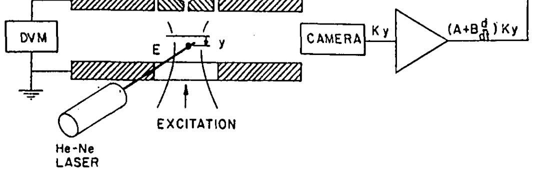

Fig. 1. Servomechanism used for levitating samples and measuring the photophoretic force. The excitation source is described in the text.

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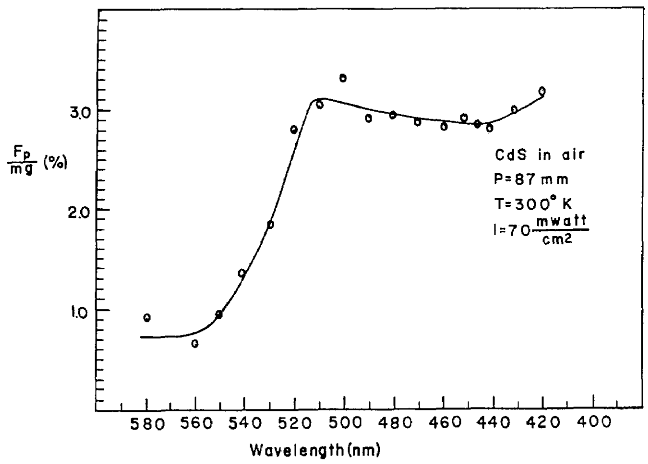

Fig. 2. Photophoretic spectrum of a crystallite of CdS. The crystallite was estimated to be between 5 and 10 μm in size. Resolution of the discharge-lamp–monochromator excitation source was 96 Å.

man and Lin[5] have made the first formal attempt to include extinction for $K_n \gg 1$. Our own calculations at wavelengths much smaller than the particle radius indicate a linear dependence with extinction for light-absorption depths in bulk K^{-1} greater than the particle radius. For $K^{-1} \leq a$, saturation is expected to set in, and the force will vary in a sublinear way with K.

The device used for recording photophoretic spectra will be described in more detail elsewhere.[6] A short summary is presented here for completeness. Excitation is provided by a 1000-W Xe lamp followed by a 0.125-m monochromator. Light from this combination is focused into a vacuum chamber using $f/1$ optics. This excitation enters a Millikan capacitor through a transparent conducting electrode E in the bottom plate and illuminates a suspended negative particle (see Fig. 1). A horizontal potential well is created for this particle by the use of an insulated electrode F in the top plate.[7] This electrode also acts as a reservoir for particles that are injected through it. Vertical stability is maintained by the use of an electro-optic servo loop. A camera detects laser light scattered from the particle at 6328 Å and provides a signal proportional to the vertical offset y from the center of the chamber. The camera signal, ky, is conditioned by the operator $A + B$ (d/dt) (Ref. 8) and fed back to the top plate of the capacitor, as shown in Fig. 1. The use of the voltage divider R and DVM (the resistance of our digital voltmeter) assures that the reading on the digital voltmeter is proportional to the electric field at the particle as long as the particle remains in the same position. In practice, the particle never strays vertically by more than a few micrometers, in comparison with a plate separation of 1 cm. In this way, the change in measured voltage ΔV corresponding to the light-introduced force divided by the voltage V in the absence of light is just equal to the photophoretic force F_p divided by the particle weight (mg).

Derivative feedback is of great importance in obtaining low-noise photophoretic spectra of individual crystallites at low pressure (<10 Torr). Under the influence of highly absorbed light, irregular particles undergo complicated oscillations.[2] Since the photophoretic force is measured in a vacuum, fluid damping must be replaced by electronic damping in order to reduce these oscillations. However, the situation is far from ideal. Electronic damping only operates on vertical motion, whereas fluid damping can also reduce horizontal oscillations. Under photophoretic excitation, some particles are seen to oscillate horizontally (at a few hertz) by as much as 150 μm from the center of the chamber. Derivative feedback has also been used in stabilizing optically levitated glass spheres (at pressures below 1 mm Hg) against photophoretic influences in the past.[8] Although a vertical laser beam is used for levitation and the particles are of extremely high symmetry, off-axis components of the photophoretic force may still be produced through Brownian rotation.

Figure 2 shows a typical photophoretic spectrum of a crystallite of CdS having an estimated size between 5 and 10 μm. The spectrum is surprisingly similar to that obtained by photoacoustic spectroscopy[9] and reveals a plateau at 2.1 ± 0.03 eV (515 ± 8 nm), in agreement with optical absorption measurements.[10] The cause of the residual effect below 560 nm is unknown but is most probably thermophoresis from heating of the bottom plate. A comparison between the photophoretic spectrum and the crystal-absorption spectrum is difficult to make because of the anisotropic nature of CdS; however, at any given polarization, the absorption edge is considerably steeper than its photophoretic counterpart. The difference between the photophoretic spectrum and the optical-absorption spectrum is too large to be due to limited optical resolution (96 Å). The key factors producing this disparity are most likely *saturation* effects for absorption depths considerably smaller than the particle size and *diffraction* effects that complicate the simple geometrical optics picture.[11] Saturation effects should be important in Fig. 2 since the absorption depth in bulk at 5000 Å is ~0.2 μm ($K \simeq 5 \times 10^4$ cm^{-1}) (Ref. 10), which is small in comparison with the particle size. Diffraction effects are expected to be of less importance since the particle size is considerably larger than the wavelength.

Figure 3 shows the enhancement in the photophoretic force as the pressure is reduced below 240 mm Hg. The results are similar to pressure effects on optically levitated spheres discussed by Ashkin and Dziedzic.[12] The crystallite used in the present measurements had a mass equivalent spherical radius of 2.7 μm. This size was estimated from measurements of the voltage change corresponding to the emission of a single electron.[13] The results in Fig. 3 were carried out at an intensity of 70 mW/cm^2 and with a wavelength w of 5000 Å. The force-to-weight ratio is found to vary approximately as the inverse pressure between 240 and 30 mm Hg, in agreement with radiometric theory [Eq. (1)]. The maximum force should occur at a Knudsen number near but less than 1 for spherical particles.[4] Our maximum at 1.1 is likely to be due to the irregular shape of the particles.

It is interesting to compare the magnitude of our measured effect with the predicted force on a *surface-absorbing sphere*. Dividing the force from Eq. (1) by the weight, we find that

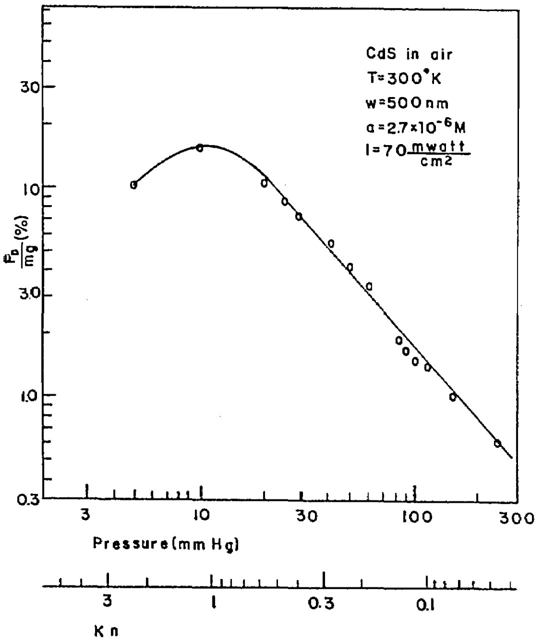

Fig. 3. Pressure dependence of the photophoretic force-to-weight ratio F_p/mg for a CdS crystallite having an equivalent spherical radius of 2.7 μm. The excitation source was tuned to 500 nm with 96-Å resolution. Kn is the Knudsen number of the particle–gas system.

$$\frac{F_p}{mg} = \frac{9}{8}\frac{\mu^2 I(Kf)}{\rho_g \rho_s T g a^2 (K_S + 2K_F)}, \qquad (2)$$

where ρ_g and ρ_s are mass densities of the gas and the solid, respectively, T is the temperature of the gas far from the particle, and g is the gravitational acceleration. For the conditions given in Fig. 3, the force estimated from Eq. (2) at 60 mm Hg is approximately twice the measured force. Considering the fact that our sample is irregular in shape, the estimate given by Eq. (2) is surprisingly close to the experimental value and lends added support to the importance of saturation at 5000 Å. Experiments are being constructed to test the validity of Eq. (2) for smaller spherical particles.

Broadband photophoretic spectroscopy (PPS) provides a new optical method for investigating the composition of micrometer-sized particles. Although studies in visible excitation will reveal a good deal about the electronic nature of these particles, work in the infrared should give "fingerprint" information from which chemical composition can be derived. For model atmospheric aerosols, the PPS method provides a nearly *in situ* opportunity for investigating important processes, such as the conversion of sulfur dioxide to sulfuric acid. However, the richest application of PPS may well be in the area of imaging. The photophoretic force has a different wavelength dependence for different materials, and therefore particular components in a heterogeneous suspension may be driven selectively to a surface. Such photophoretic imaging[3] will rely heavily on PPS for identifying materials that can be imaged photophoretically.

We thank M. Pope of New York University, M. Kerker of Clarkson College, and L. Newmann of the Brookhaven National Laboratory (BNL) for useful discussions of this research. Our gratitude is also extended to the Department of Atmospheric Chemistry at BNL for Department of Energy support for Y. Amani and to the Institute for Imaging Sciences of the Polytechnic Institute of New York for partial summer support for S. Arnold.

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