

Fourier transform infrared spectrometer for a single aerosol particle

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A spectrometer is reported here for obtaining the infrared spectrum of a single aqueous aerosol particle by a Fourier transform technique. The particle is held in an electrodynamic balance and irradiated simultaneously by the infrared output from a Michelson interferometer and the visible light from a dye laser. The size of the particle is modulated by chopping the IR beam, and the resulting visible scattered light fluctuation is detected at 90° with a photomultiplier tube. The amplitude of the scattered light fluctuation is measured with a lock-in amplifier at each interferometer mirror position. The electronic circuitry for stepping the interferometer mirror is presented and discussed. Inverting the lock-in signal by a discrete fast Fourier transform routine (FFT) yields the particle absorption spectrum. The resulting spectrum for an $(\text{NH}_4)_2\text{SO}_4$ droplet is presented.

INTRODUCTION

The ability to characterize and chemically analyze aerosol particles has been of great interest in aerosol research. This effort has been pursued along two main streams; in one direction attention is directed to a whole assembly of particles, and in the other a single particle is isolated and studied. The advantage of the first approach is that the number of particles under study can be made large, and thus various conventional analytical techniques can be used to characterize them. On the other hand, the single-particle technique has become a versatile tool for studying fundamental processes occurring within an aerosol particle. Among the various applications of the single-particle technique are evaporation and condensation phenomena,^{1,2} chemical reactions,³ photoemission from a single particle,⁴ photophoretic spectroscopy,⁵ material phase transitions,⁶ and energy transfer within a microparticle.⁷ The versatility of the single-particle approach arises from the ability to monitor continuously the charge-to-mass ratio as well as the scattered light from the particle. Hence, any changes in the particle size or its refractive index can be readily observed. In addition, nonlinear phenomena such as the optical resonances⁸ in the scattered light from a single particle can be employed to detect small changes in the size or refractive index of a microparticle.

Recently a method for obtaining the infrared spectrum of a single particle was conceived⁹ and demonstrated.^{10,11} In the method a single charged particle is levitated in an electrodynamic balance by the fields generated in quadrupolar geometry.¹²⁻¹⁴ The infrared spectrum was obtained by illuminating the particle with a dye laser, and simultaneously heating the particle periodically with an IR source. The excitation wavelength in the IR is selected with a wedge monochromator. Heating the particle periodically causes a modulation in its size, which induces a corresponding fluctuation in the scattered light from the particle. This scattered light fluctuation is measured at 90° (for geometrical simplicity),

using a photomultiplier tube (PMT). By phase sensitively detecting the amplitude of the scattered light fluctuation as a function of the IR wavelength, an absorption spectrum of the particle is obtained.

We have recently reported a variation of the above method, where the IR spectrum of an aqueous droplet is obtained by a Fourier transform technique,¹⁵ similar to that suggested earlier.⁹ In this method the particle is irradiated by the output from a Michelson interferometer. The amplitude of the scattered light fluctuation is measured as a function of the interferometer mirror position. The resulting scan (called an interferogram), is stored in a computer and the spectrum is obtained by inverting the scattered light data by a discrete fast Fourier transform (FFT) routine. The purpose of the present paper is to describe the Fourier transform spectrometer, show a spectrum for an $(\text{NH}_4)_2\text{SO}_4$ particle, discuss the performance of the instrument, and outline where simplifications can be made.

I. THE APPARATUS

In the technique described here a single aqueous solution microparticle is levitated in an electrodynamic balance (also called a quadrupole trap). The trap consists of top and bottom electrodes between which a dc potential is held, and a ring electrode to which an ac voltage is applied.^{2,16} Once trapped in this device, a charged particle can be held almost indefinitely. The trap is positioned inside a vacuum chamber which allows for accurate control of the pressure and vapor phase surrounding the particle.

A schematic diagram of the single-particle FTIR spectrometer is shown in Fig. 1, where the vacuum chamber is omitted for clarity. As indicated the particle is illuminated simultaneously by a dye laser and the IR output from a Michelson interferometer. The 90° scattered light from the particle falls on a photomultiplier tube, and the resulting PMT current is measured with a picoammeter. The laser is tuned

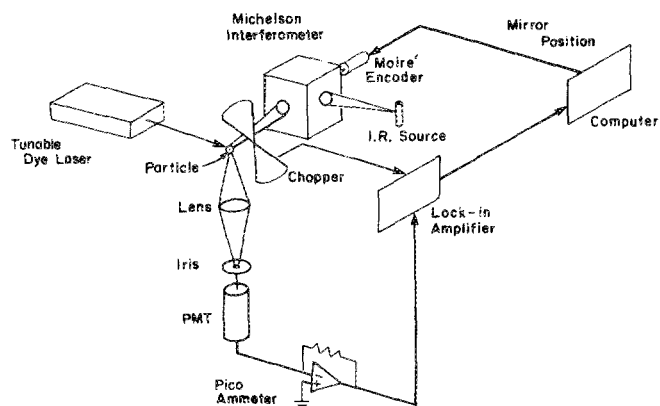


FIG. 1. Experimental system for single-particle Fourier transform infrared spectroscopy.

to an edge of an optical resonance⁸ where the scattered light from the particle is sensitive to changes in the particle size.⁹ From Fig. 1 it is also noted that the IR output of the interferometer is chopped prior to falling on the particle. When the IR radiation falls on the particle, its effect is to heat the particle slightly, causing evaporation of a small amount of water from the drop. Continued evaporation upon heating is restrained by the increase in the water activity of the droplet accompanying water loss. When the chopper shields the particle from the IR, water vapor recondenses on the particle and the droplet returns to its original size. Since the scattered light from the particle is highly sensitive to size changes, the size modulation caused by the periodic IR heating induces a corresponding fluctuation in the scattered light from the particle. This fluctuation is measured with a lock-in amplifier.

In conventional near IR interferometry, the interferometer mirror is moved continuously because the detector used has a fast response time compared with the modulation rate

of the IR intensity. However, in our experiment the detector is a single droplet whose response time is governed by the rate of water evaporation and condensation on the surface of the droplet. As earlier work showed,^{2,11} this rate is, in general, slow because of the large heat of vaporization of water. In addition, we have found that the signal-to-noise ratio of the scattered light signal from the particle was poor near the optical resonances. In order to increase the S/N ratio, we move the interferometer mirror in steps. This approach allows us to chop the IR beam and detect the scattered light modulation signal with a lock-in amplifier. By increasing the lock-in time constant, the S/N ratio of the scattered light signal can be improved. Thus a key to this experiment is the ability to accurately move the interferometer mirror in equal steps (down to $\approx 0.5 \mu\text{m}$ per step), over a distance ranging from a few hundred microns to a few millimeters. The steps must be of equal length because the discrete FFT inversion routine relies on this factor. The existing piezoelectric drivers capable of this step resolution usually have a range that is smaller than $100 \mu\text{m}$. A possible solution would have been to use an inchworm type of driver; however, to make use of available equipment, we decided to modify a conventional interferometer in which the moving mirror is mounted on air bearings and is driven by a geared down dc motor. The stepping of the mirror is achieved by applying a train of pulses to the motor and disabling the motion when the desired distance has been covered. The travel of the mirror is tracked with a moire' encoder that outputs a pulse every time the mirror travels $\approx 0.5 \mu\text{m}$.

A schematic diagram of the circuit used to control the mirror motion is presented in Fig. 2. To achieve equal repetitive steps, it is critical to disable the mirror motion immediately when the encoder signal arrives. For flexibility, the pulse rate and length were computer controlled; however, to achieve quick switch-off times the computer pulse was disabled by hardware. As shown in Fig. 2, an enable pulse from the computer triggers a $1\text{-}\mu\text{s}$ pulse (from a monostable) that

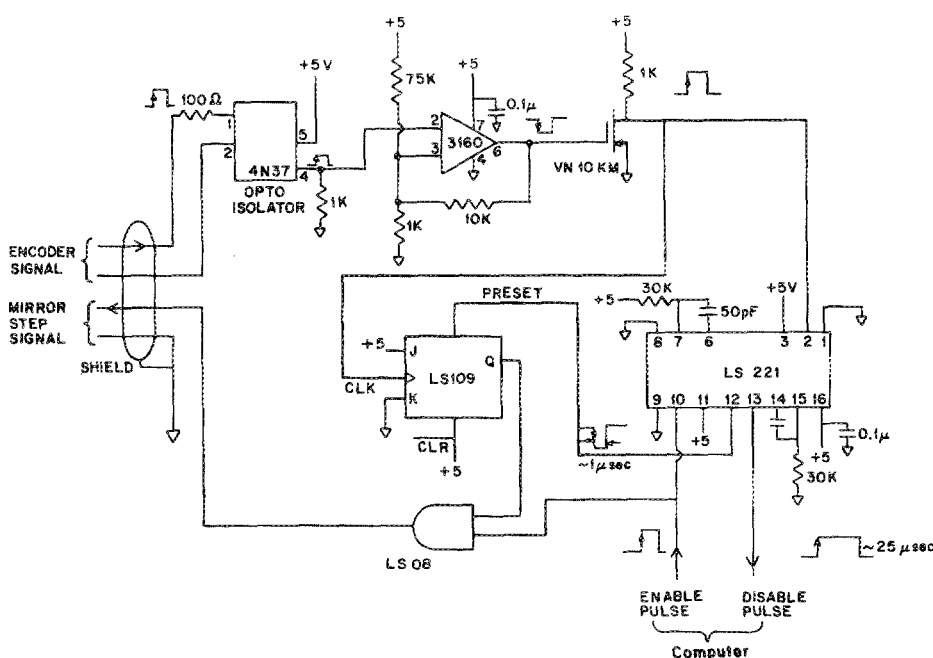


FIG. 2. Electronic circuitry for stepping the interferometer mirror.

presets a J - K flip-flop. The Q output of the flip-flop and the computer enable pulse are sent to the inputs of an AND gate, the output of which forms the mirror step signal. The encoder signal is optically isolated from the driving electronics to avoid grounding problems. To shorten the rise and fall times of the optical isolator output pulse, the signal was sent to a Schmitt trigger followed by a FET transistor. The main purpose of the FET output is to stop the mirror enable signal by clocking the flip-flop that turns the Q output low. In addition the rising edge of the FET signal triggers a monostable, the output of which is sent to the computer and tells the program to stop the current enable pulse.

After the mirror was stepped to a new position, enough time must be allowed for the lock-in signal to stabilize before a new data point is taken. This can be done either manually or automatically. The delay time between moving the mirror and taking a new A/D reading depends on the lock-in time constant. In most cases the lock-in time constant was 10–30 s, and 140 data points were taken. Thus it usually took 1–2 h to record a complete scan.

II. THEORY

The measured signal in this experiment is the lock-in output (which is proportional to the amplitude of the scattered light fluctuation), as a function of the interferometer mirror position, 1. For a particle with an initial radius a_0 , and an initial scattered light intensity S_0 , the signal measured at the output of the lock-in amplifier is given by¹⁵

$$\frac{\langle \delta S(l) \rangle}{S_0} = - \int_{-\infty}^{\infty} B(k) e^{i(kl + \theta)} dk, \quad (1)$$

where $\delta S(l)$ is the scattered light fluctuation, k is the infrared wavenumber, $2\pi/\lambda$, and $B(k)$ is given by¹¹

$$B(k) = \frac{\beta}{a_0} \frac{\alpha(k) I_s(k) T(k)}{(\omega^2 + \gamma^2)^{1/2}}, \quad (2)$$

where $T(k)$ is the transmission of the optical elements in the IR pathway, $I_s(k)$ is the IR source intensity, ω is the IR chop rate, and γ is the relaxation rate of a heated particle to its unheated original size. In Eq. (1) θ is given by $\theta = -(\omega/\gamma)$. β is the amplification factor that allows one to relate the changes in the particle size to the measured fluctuations in the scattered light and is given by⁹

$$\frac{\delta S}{S_0} = \beta \frac{\delta a}{a_0}. \quad (3)$$

Finally, $\alpha(k)$ is proportional to the particle absorption coefficient Q_a and therefore contains the desired chemical information about the particle.

III. RESULTS

An example of a scattered light interferogram taken on an aqueous $(\text{NH}_4)_2\text{SO}_4$ particle is shown in Fig. 3. The chopping frequency during this scan was 4 Hz, and the mirror was stepped 140 times with a separation of $\approx 1 \mu\text{m}$ between successive steps. The zero point of the mirror position in Fig. 3 is at the equal arm point of the Michelson interferometer. Recall that the interferometer consists of a beam splitter and two mirrors that reflect the split beam

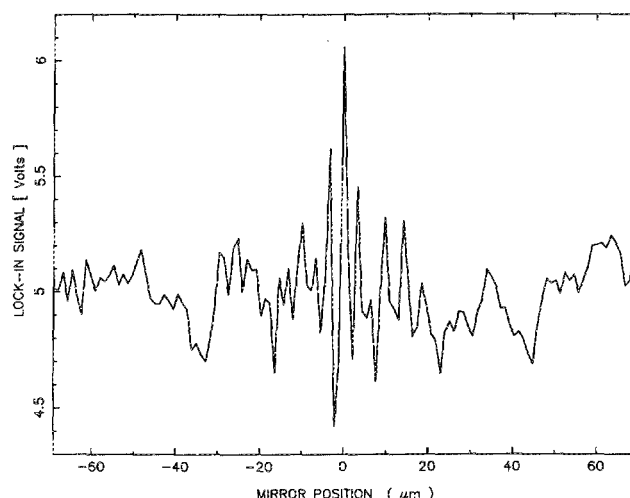


FIG. 3. The amplitude of the scattered light modulation, obtained with a lock-in amplifier, as a function of the interferometer mirror position for a 35% (by mass) $(\text{NH}_4)_2\text{SO}_4$ - H_2O solution particle, $3.0\text{-}\mu\text{m}$ radius.

back towards the beam splitter where they recombine. Therefore, at the equal arm point all the wavelengths recombine constructively. Hence, only at this point are all the absorbing species in the droplet excited simultaneously. Thus the energy absorbed by the droplet is higher, and the resulting scattered light fluctuation is larger than at any other point in the interferogram. As the mirror is stepped away from the zero point, the amplitude of the fluctuation drops since some of the wavelengths at which the droplet absorbs undergo destructive interference.

The spectrum of the particle is obtained from the interferogram by a discrete fast Fourier transform (FFT) routine. The resulting relative absorption spectrum, $B(k)/I_s(k)T(k)$, is shown in Fig. 4. This particular spectrum was obtained from a $3.0\text{-}\mu\text{m}$ solution droplet of 35% (by weight) ammonium sulfate. The absorption peaks of the sulfate, am-

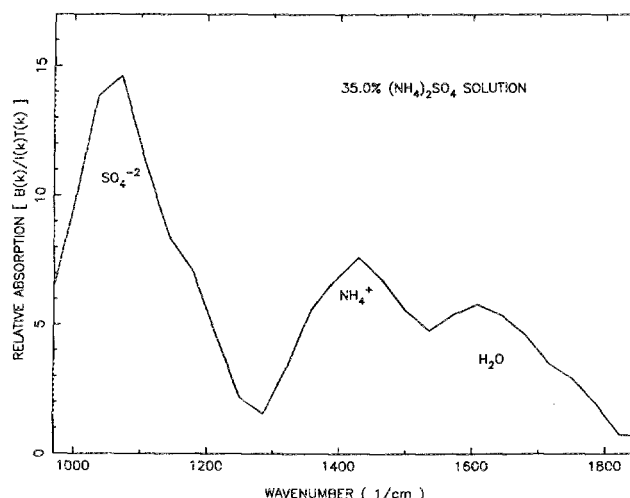


FIG. 4. The relative absorption spectrum $B(k)/I_s(k)T(k)$ of the $(\text{NH}_4)_2\text{SO}_4$ particle in Fig. 3.

monium, and water are indicated. The position of the peaks agrees with previous results for a single particle,¹¹ as well as with spectra obtained from bulk solutions.^{17,18}

IV. DISCUSSION

The spectrum shown in Fig. 4 was obtained by moving the mirror about 140 μm , giving rise to a theoretical resolution of $\approx 70\text{ cm}^{-1}$ in the displayed spectrum. It took roughly 2 h to obtain the scan displayed in Fig. 3 which means that at present the technique is suitable only for the study of static chemical systems. In order to facilitate the study of systems where chemical reactions might be occurring, the time necessary for a single scan must be shortened. One approach towards this goal is reducing the particle size, thereby reducing the particle relaxation time.^{2,11} The shorter relaxation time allows a faster chop rate of the IR, which in turn can reduce the required lock-in time constant and yield a shorter scan time.

Another approach to shortening the scan time, first proposed by Arnold and Pluchino,⁹ is to move the mirror continuously as in conventional IR interferometers. By moving the mirror continuously the use of the chopper and the lock-in amplifier is eliminated (thus simplifying the experiment). The modulation in the IR intensity at the droplet is now governed by the velocity v of the mirror. The resulting inverse transform $B(k)$ is given by

$$B(k) = \frac{\beta}{a_0} \frac{\alpha(k) I_s(k) T(k)}{\alpha_0 [(2kv)^2 + \gamma^2]^{1/2}} \quad (4)$$

As mentioned earlier the main difficulty in this approach is overcoming small signal-to-noise ratio in the scattered light from a particle near the optical resonance. The signal can be increased by using smaller particles and by increasing temperature of the IR source. For example, a Nurnst glower may be operated at temperatures above 2000 $^{\circ}\text{C}$, whereas the glow bar used here was operated at 1250 $^{\circ}\text{C}$. Among the possible sources of this noise are a small amount of dirt in the particle (or on its surface), which alters the amount of light scattered towards the photomultiplier

tube as the particle rotates; another source of noise is the fluctuations in intensity associated with the dye laser. However, if the signal-to-noise ratio can be improved, a continuous scan could be implemented which will both simplify the experiment as well as shorten the time required to obtain the spectrum of a single particle.

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