Molecular spectroscopy of a single aerosol particle

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The absorption spectrum of a single micrometer-sized aerosol particle is measured for the first reported time in the IR. Particle absorption is determined through the IR modulation of visible scattered light near a structure resonance. This technique, termed structure resonance modulation spectroscopy, is used to measure the IR absorption spectrum of an $(NH_4)_2SO_4$ aerosol droplet of 5.4-μm diameter in the region from 970 to 1280 cm^{-1}. The resulting spectrum, when fitted by Mie theory, enables one to determine the molecular composition of the droplet.

In this Letter we report the first measurement made to our knowledge of the IR absorption spectrum of a single aerosol particle. This achievement makes possible spectral investigations of interfacial chemistry on the surface and within the bulk of a particle. A topical example is the acidification of a water droplet in the presence of SO_2 and other environmental gases. In what follows we outline our measurement principle, describe our experimental setup, and present the first reported spectrum taken of a solution droplet of $(NH_4)_2SO_4$.

The experimental concept was described earlier by Arnold and Pluchino.[1] Although our experimental setup is different from the one suggested in Ref. 1, the concept remains intact, and a brief description is provided for completeness.

The method described in what follows, structure resonance modulation spectroscopy (SRMS), allows one to take broadband absorption spectra at low intensity by using the properties of structure resonances. Small spherical particles at particular wavelengths can exhibit extremely narrow resonances.[2] These resonances, which are the natural electromagnetic frequencies at which the dielectric sphere oscillates, may be observed in a particle's scattered-light excitation spectrum.[3] One can show that, for a particular resonant mode in a particle of constant refractive index, the resonant wavelength λ_r divided by the particle radius R remains constant as R changes.[1] Therefore, as a particle changes size by a fraction $\Delta R/R$, every resonance will shift in wavelength by precisely the same fraction; $\Delta(\lambda_r/R) = 0$; thus $\Delta R/R = \Delta\lambda_r/\lambda_r$. For example, as a particle shrinks in size by 1 part in 10^5, the resonant wavelength will shift to a shorter wavelength by 10 parts in 10^6. With a laser-excitation energy positioned on the short-wavelength side of a resonance, a shrinkage in particle size will cause an increase in scattered light as the resonance shifts toward the laser wavelength. The observed fractional change in scattered light S depends on the wavelength of the probe and the particular resonance chosen. A measure of this change in scattered light with particle size is the transfer function $\beta = (R/S)(\partial S/\partial R)$. Values of β can easily reach 5×10^3. Thus a -0.05-Å change in radius for a particle 2.5 μm in size (radius) would lead to a +1.0% change in scattered light. For a solution containing an involatile component and in equilibrium with external water vapor, IR heating will cause the drop to shrink to a new stable size. The mechanism for this phenomenon may be understood for an ideal solution in terms of Raoult's law. Simply stated, the vapor pressure of water at the surface of such a solution is the vapor pressure of pure water, P_0, times the mole fraction of water in the solution, X_w. When a drop is heated, P_0 increases, a flux of vapor is emitted into the external medium, and the drop shrinks. Since this shrinkage causes a decrease in the mole fraction of water within the particle, the vapor pressure at the surface of the drop begins to fall. Eventually the particle reaches a vapor pressure equal to the external environment and stabilizes in size. Such a droplet can demonstrate a large variation in visible scattered light as it is heated with IR radiation. Arnold and Pluchino have estimated that a 2.5-μm particle of 0.5 M K_2SO_4 heated with an IR intensity of 0.5 mW/cm^2 at 9.1 μm (principal IR vibrational line of SO_4^{-2}) when probed with a laser near the 34th transverse-magnetic (TM) mode should demonstrate a shift in particle size of -0.3 Å, accompanied by a change in backscattered light of +20%.[1] Near thermal equilibrium, the size change ΔR and the temperature change ΔT would be proportional, so the fractional change in scattered light to first order is given by

$$\frac{\Delta S}{S}(\lambda_2) = F(B, K_a, X_w, T)\beta(\lambda_2)Q_a(\lambda_1)I(\lambda_1), \quad (1)$$

where λ_1 and λ_2 are the IR (excitation) and visible (probe) wavelengths, K_a is the thermal conductivity of the ambient gas, X_w is the mole fraction of water, T is

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the ambient temperature, β is proportional to the activation energy for evaporation [water-vapor pressure $\propto \exp(-B/T)$], Q_a is the particle-absorption efficiency, and I is the infrared intensity.[1] The most important aspect of Eq. (1) is that for small perturbations in size and temperature F is expected to be constant, and therefore the IR-wavelength dependence of $\Delta S/S$ is the wavelength dependence of Q_a, the absorption spectrum. In addition, although the description of scattering at the probe wavelength is complicated, the description of Q_a for the same particle in the IR need not be. A particle excited in the visible near 600 nm has 15 times the optical size ($2\pi R/\lambda$) of the same particle excited at 9 μm; consequently, the number of terms in the Mie expansion for Q_a can be relatively small. Indeed, in some cases the absorption by a 2.5-μm particle at a wavelength of 9 μm may be described with simple Rayleigh theory.[1]

The particle is electrically suspended in air within a sealed chamber by the use of a quadrupole trap.[4] This trap is optically servo controlled so that the particle is maintained at the center of the trap, and its mass is directly monitored.[5] The sample particle is prepared by injecting a dilute solution droplet of $(NH_4)_2SO_4$ from an impulse jet placed above the chamber. Water evaporates from this suspended drop until the resulting droplet reaches a vapor pressure at its surface, which is approximately the vapor pressure above a saturated KCl solution. This solution is placed within the chamber and provides a stable water-vapor background. At this point it is observed through light scattering excitation spectroscopy[3] that the positions of structure resonances remain stable to within 2 Å over several minutes. A typical sample is 5–6 μm in diameter. A dye laser with a bandwidth of 0.3 Å is used as the source for light scattering. The laser beam is introduced from below, as shown in Fig. 1. The IR excitation is provided by a SiC Glo-Bar operated at 1100 K. This source is imaged onto an optical wedge monochromator having an intrinsic band width that is ~1.5% of the center-band wavelength (16 cm^{-1} at $\lambda_1^{-1} = 1100\ cm^{-1}$). The power at this point was measured to be 50 μW at $\lambda_1 = 9.1$ μm. A lens just outside the chamber was used to collimate

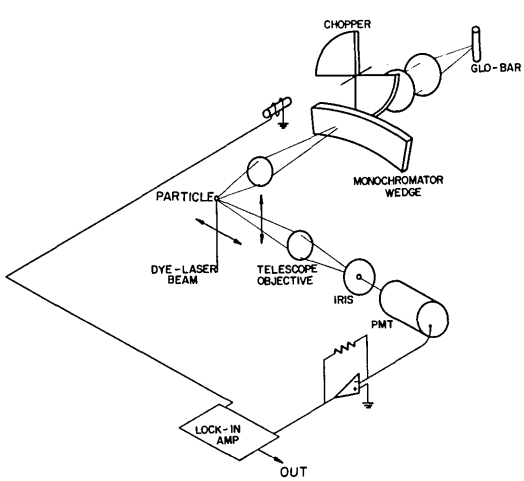

Fig. 1. Schematic diagram of the measurement system in SRMS.

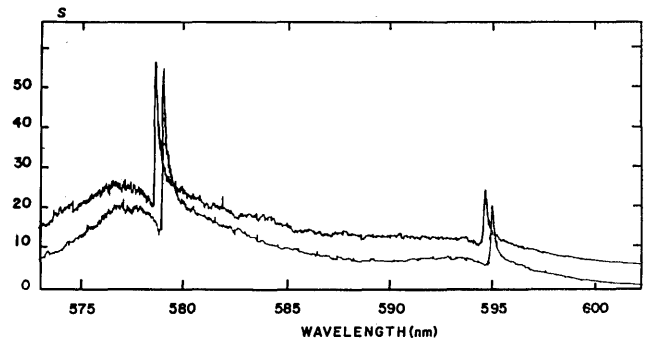

Fig. 2. The scattered-light excitation spectrum for a particle of $(NH_4)_2SO_4 \sim 2.7$ μm in radius. The detector is positioned as shown in Fig. 1. The upper excitation spectrum was taken for the same particle irradiated with broadband IR (1100 K) having an intensity of 240 mW/cm^2.

the IR radiation onto an internal ZnSe lens planted in the torus ring of the quadrupole.[4] This lens images the IR radiation onto the particle. A typical intensity at the particle at 9.1 μm was ~0.2 mW/cm^2. This IR radiation was chopped at 20 Hz. Light scattering from the particle was detected at 90° with a photomultiplier through a telemicroscope aimed in the direction of the incident polarization (this light scattering is defined in Ref. 3 as $90\perp$). The output from this phototube was conditioned by a current-to-voltage converter and fed along with the IR chopper signal into a lock-in amplifier. To construct an IR spectrum, we plotted the output of this amplifier versus the center-band wavelength transmitted by the IR wedge.

The lower curve in Fig. 2 shows the scattered-light excitation spectrum for a particle ~2.7 μm in radius without IR irradiation. The resonances at 579.1 and 595.0 nm correspond to two adjacent TM modes of the particle. The upper spectrum, which illustrates the effect of the full IR source (60 mW, as measured at the monochromator wedge), was taken within a minute of the lower curve. It is observed that each of the resonances in this curve shifts by ~−3.5 Å within 0.5 sec, after which its position remains almost constant. This −3.5-Å shift is due to direct IR absorption by the particle. This conclusion is apparent since the SRMS spectrum will be seen to reveal the signature of SO_4^{-2} and SO_4^{-2} is confined to the particle alone. In addition, the shift is found to be proportional to intensity, in agreement with Eq. (1).

Figure 3 shows the SRMS spectrum between 970 and 1280 cm^{-1} for an $(NH_4)_2SO_4$ particle whose scattered-light excitation spectrum is shown in Fig. 2. The probe laser was positioned halfway up on the low-wavelength side of the resonance at 579.1 nm. The value of β measured at this point is 4.3×10^3. The scattered-light modulation induced by IR absorption at 20 Hz is given in percent as a peak-to-peak value. Considering our measured value for β, the largest peak-to-peak modulation in size is 0.09 Å. Although lower frequencies were not available to us for the particular chopper used, larger signals are expected at low frequencies since the particle-response time is ~0.1 sec. The absorption band that is shown has almost the same position in

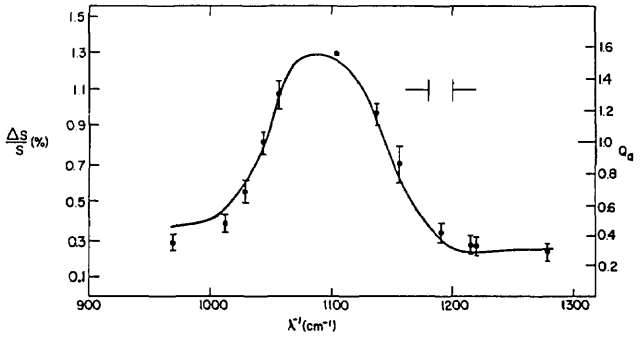

Fig. 3. The SRMS spectrum of the $(NH_4)_2SO_4$ solution droplet whose scattered-light excitation spectrum is shown in Fig. 2. This spectrum is compared in line shape to a calculation of Q_a for a 39% concentration.

wavelength as the major SO_4^{-2} band seen in absorption and reflection spectroscopy.[6] However, the breadth of the band in Fig. 3, ~140 cm^{-1}, is twice that measured in ordinary solution spectroscopy. This broadening is reminiscent of saturation effects, which occur in absorption spectroscopy. This implies a large concentration of SO_4^{-2}. For the particular equilibrium considered (equilibrium with the water vapor above saturated KCl), one expects the particle to have the same vapor pressure on its surface as the KCl solution when 38% of its mass is $(NH_4)_2SO_4$. This translates into an imaginary part for the refractive index at a wavelength of 9.1 μm of ~0.7. In a planar solution having this composition, 66% of the light at 9.1 μm would be absorbed in a depth of ~1 μm. Thus saturation effects are expected in our 5-μm particle. Fortunately refractive indices for a solution of 39% concentration have been measured by Remsberg.[7] Full Mie calculations have been performed based on these data and are plotted as the solid line in Fig. 3. The agreement is very good and shows that our spectroscopy produces a signal directly proportional to Q_a, consistent with Eq. (1). One can obtain compositional information by constructing a dielectric function for this region based on a single Lorentz oscillator for the SO_4^{-2} while considering the flat portion from 1200 to 1280 cm^{-1} to be due to H_2O. In this way the best fit to our data is obtained for 36 ± 2% $(NH_4)_2SO_4$, in good agreement with the concentration obtained assuming vapor-pressure equilibrium. Further compositional information may be obtained by considering other transitions for (NH_4^+) and H_2O near 3 μm. The composition determined from data taken near 3 μm is found to be self-consistent with the composition determined from the data in Fig. 3.

We have demonstrated, for the first time to our knowledge, a means for obtaining the IR absorption spectrum of a single particle. The SRMS signal is linear with intensity and directly proportional to the absorption efficiency of the particle. A missing link is the form of F in Eq. (1). If F were known, one would have a means for measuring Q_a quantitatively. In either case, the validity of a physical model of SRMS would be tested. Assuming Raoult's law, size equilibrium, the definition of β, and Eq. (1), F may be shown to be[1]

$$F = -\frac{1}{12(1-X_w)}\frac{B}{T^2}\frac{R}{K_a}, \tag{2}$$

and

$$Q_a = \left[\frac{12K_a(1-X_w)T^2}{IBR}\right]\frac{\Delta R}{R}. \tag{3}$$

One must understand in using Eq. (3) that $\Delta R/R$ represents the fractional change in radius to reach size equilibrium. For our particular case (the particle investigated in Figs. 2 and 3), ΔR is experimentally estimated to be 0.4 Å at 9.1 μm for an intensity of 0.2 ± 0.1 mW/cm^2. Using appropriate constants for B and K_a of 5300 K and 2.4×10^{-2} J/m-sec-K, respectively, and $X_w = 0.16$, we find that $Q_a = 2.1 \pm 1$, which compares favorably with the value of 1.56 determined from lineshape analysis.

It is interesting to note that the present sample represents the smallest solution mass (90 pg) for which an IR spectrum has reportedly been taken.

We have no doubt that SRMS will be used extensively in acid-rain research. The technique is not limited by the level of noise in our current measurements. Although a complete theory of SRMS including a detailed physical description of the evaporative relaxation process will be presented elsewhere, our preliminary theoretical results indicate that the intrinsic noise level resulting from stochastic motion in the phase boundary for an isothermal enclosure should be several orders of magnitude smaller than the error bars measured in Fig. 3. Consequently one can expect to measure much smaller concentrations of molecular species as temperature control is imposed on the levitation chamber.

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References

1. S. Arnold and A. B. Pluchino, Appl. Opt. **21,** 4194 (1982).
2. A. Ashkin and J. M. Dziedzic, Phys. Rev. Lett. **38,** 1351 (1977).
3. A. Ashkin and J. M. Dziedzic, Appl. Opt. **20,** 1803 (1981).
4. M. A. Philip, F. Gelbard, and S. Arnold, J. Colloid Interface Sci. **91,** 507 (1983).
5. S. Arnold, Y. Amani, and A. Orenstein, Rev. Sci. Instrum. **51,** 1202 (1980).
6. M. R. Querry, R. C. Waring, W. E. Holland, L. M. Earls, D. Herman, W. P. Nijm, and G. M. Hale, J. Opt. Soc. Am. **64,** 39 (1974).
7. E. E. Remsberg, Appl. Opt. **12,** 1389 (1973).