AEROSOL PARTICLE ANALYSIS BY RAMAN SCATTERING TECHNIQUE

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October 1992

For presentation at the
Advanced Laser Technology for
Chemical Measurements Conference
Santa Fe, NM
October 19-21, 1992

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This research was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

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Aerosol Particle Analysis by Raman Scattering Technique

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ABSTRACT

Laser Raman spectroscopy is a very versatile tool for chemical characterization of micron-sized particles. Such particles are abundant in nature, and in numerous energy-related processes. In order to elucidate the formation mechanisms and understand the subsequent chemical transformation under a variety of reaction conditions, it is imperative to develop analytical measurement techniques for in situ monitoring of these suspended particles. In this report, we outline our recent work on spontaneous Raman, resonance Raman and non-linear Raman scattering as a novel technique for chemical analysis of aerosol particles as well as supersaturated solution droplets.

INTRODUCTION

The chemical characterization of airborne particles has always been a formidable challenge. Both fluorescence and infrared techniques have been applied to the analyses of these minute particles. Fluorescence in principle is an excellent spectroscopic technique for gaseous molecules. However, in solids and liquids, spectral lines can be significantly broadened by the formation of crystalline complexes and the molecular motions, respectively. Meanwhile, atmospheric samples do not always fluoresce, and often do so only in the ultraviolet region. Even when fluorescence spectra are obtained, they often consist of overly congested broad bands and can seldom provide definitive species identification. In essence, fluorescence is a good technique for molecules with a narrow absorption bandwidth, such as some gaseous molecules and radicals.

On the other hand, infrared spectroscopy generally gives a great deal of finger print type molecular information. Ingenious adaptation of infrared absorption with Mie scattering and thermal lensing techniques has shown such approaches are feasible for particle analyses. In these experiments, only ammonium sulfate solution droplets were used. The detection limit was about 100g/m³. However, the influence from water vapor absorption masked any lower signals. In addition, Mie scattering limits the optical path length, hence infrared absorption spectroscopy has not yet been applied to microparticles successfully.

Despite the low scattering cross-sections, Raman spectroscopy has been used rather successfully in particle analyses. Unlike fluorescence or infrared absorption techniques, Raman scattering can

* This work was conducted under Contract No.DE-AC02-76CH00016 with the U.S. Department of Energy under the Division of Chemical Sciences within the Office of Energy Research.
be applied to optically opaque, irregular shaped samples. It is also ideally suited for microscopic samples as well. Moreover, it delivers rich vibrational molecular information that is comparable to infrared spectroscopy for identification purpose. Raman microprobe is a well-established method for analyzing samples on a substrate. Early work in this area of research was led by Etz et al.\(^5\) Raman scattering from single suspended particle has shown considerable progress in recent years.\(^6\) These particles are usually optically levitated or by means of electrodynamic forces. Particle sizes varying from 10 \(\mu\)m to 25 \(\mu\)m in diameter are often used in these experiments. The samples are mostly in the form of pure solid or liquid samples. In the case of solution droplets, the concentration is usually high in order to provide adequate scattering signals. Although stimulated Raman shows some promises of being more sensitive than spontaneous Raman, the interaction between the resonators due to the boundary conditions and the Mie resonance conditions are not well characterized yet.\(^6\) Their relative signal intensity is strongly dependent on the Raman scattering signal and the particle size. Meanwhile, both the Raman scattering from water and the Mie scattering interfere with the Raman signal from the solute in dilute solution droplets. Thus the detection sensitivity for the solutes is still quite unsatisfactory. To complicate the matter further, these results from non-linear scattering process are much harder to be quantified for analytical purposes.

The objective of this study is to develop a better understanding of the sensitivity and limitations in applying Raman scattering techniques for chemical analysis of solution droplets of low concentrations. It is important to establish the intramolecular and extramolecular processes which may enhance the Raman scattering efficiency. These processes include Mie resonance, resonance Raman scattering, stimulated Raman scattering and coherent Raman scattering.

RESULTS AND DISCUSSIONS

Ambient aerosols typically contain large proportions of hygroscopic inorganic salts such as sulfates and nitrates, which are in the form of solution droplets or crystalline particles depending upon the relative humidity in the air. The deliquescence properties and phase transformation of the salt particles have been the subject of many investigations concerned with the environmental and health effects of the ambient aerosols.\(^7\) It is, therefore, desirable to develop a technique capable of not only chemical characterization of an aerosol particle but identifying its physical state as well. Since molecular vibrations are influenced by the medium surrounding the molecule and by its own motions in the liquid phase, Raman effects are clearly suited for the desired chemical and physical characterization.

Thus, inorganic salt particles in the crystalline state usually exhibit characteristic Raman shifts with a very narrow bandwidth, whereas in solution the corresponding Raman shifts are slightly displaced but the peaks are considerably broadened. An example of the physical transformation is shown in Fig.1. The Raman spectra were recorded with an intensified diode array detector, therefore accumulative rather instantaneous spectra are presented here. The Raman spectra show clearly those of a NaNO\(_3\) particle (a) as a solution droplet, (b) during phase transition from liquid solution to solid state, and (c) as a crystalline particle. The observed Raman shifts at 1051 cm\(^{-1}\) for NO\(_3\)\(^-\) in the aqueous solution droplets and at 1067 cm\(^{-1}\) for the NaNO\(_3\) crystal particles are in good agreement with the literature data obtained for bulk samples. The measured linewidth for the
Figure 1. Raman spectrum of (a) aqueous solution droplet of NaNO₃ at 1051 cm⁻¹; (b) same particle during phase transition showing the appearance of the crystalline state; and (c) crystalline NaNO₃ particle at 1067 cm⁻¹.

A droplet is typically 6 cm⁻¹, compared with only 2 cm⁻¹ for the solid particle. Thus, the Raman shifts combined with the large difference in linewidth between solid and liquid states provide a viable means for particle characterization.

Raman spectra have been obtained for levitated single particles composed of many common inorganic salts such as sulfates, nitrates, phosphates, chromates and permanganates. In addition, the extent of resonance absorption to enhance Raman scattering was also investigated. Using the available laser lines from an argon ion laser, the largest enhancement factor measured, when compared to a non-resonance species such as nitrate, was about 5.5x10⁴ for p-nitrosodimethylaniline⁹. The corresponding detection limit for a 45 µm diameter droplet was 3.2x10⁻⁶ molar, which represents a new detection limit for micron-sized solution droplets. These results have now opened new possibilities of higher sensitivity for detecting ambient nitrates and sulfates by means of resonance Raman scattering.

In solution chemistry, the degree of ion-ion interactions can be enhanced by concentration effects. Careful examination reveals that the nitrate ion in Fig. 1(b) has a peak position at 1053 cm⁻¹ rather
than the 1051 cm$^{-1}$ of nitrate ion as in Fig. 1(a). Moreover, both peak positions are shifted when compared to dilute solution of nitrate which has a vibrational band center at 1048 cm$^{-1}$. These spectral shifts are indications of the ion behavior in the solution. Conventionally, heating is used to obtain supersaturation. Subsequently, the Raman bands measured are broadened due to heating. However, because of the high purity and the absence of nucleation centers in suspended solution droplets, supersaturated conditions can be readily achieved without heating. A variety of bisulfate and nitrate aqueous solutions which exhibit such interactions were studied in the suspended droplet conditions. In addition, polarization Raman spectroscopy has also been applied to assist the identification of the transition species in the supersaturated solution droplets. The results from the droplet experiments provide new insight into the chemical properties of supersaturated solutions.

REFERENCES

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