A STUDY OF PHASE TRANSFORMATION IN HYGROSCOPIC AEROSOLS BY RAMAN SPECTROSCOPY

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Aerosol particles composed of inorganic salts such as chlorides, sulfates, and nitrates are hygroscopic by nature and exhibit the properties of deliquescence and efflorescence in humid air. These aerosols play an important role in many atmospheric processes which affect local air quality, visibility degradation, and the global climate as well. The hydration behavior, the oxidation and catalytic capabilities for trace gases, and the optical and radiative properties of the ambient aerosol, all depend crucially upon the chemical and physical states in which these microparticles exist. Indeed, the existence of hygroscopic aerosol particles as metastable aqueous droplets at high supersaturation has routinely been observed in laboratories (Orr et al. 1958; Tang et al. 1977; Richardson and Spann, 1984) and recently been verified in the ambient atmosphere (Rood et al. 1989). Because of the high degree of supersaturation at which a solution droplet solidifies, a metastable crystalline or amorphous state often results. The formation of such state is not predicted from bulk-phase thermodynamics and, in some cases, the resulting metastable state is entirely unknown heretofore (Tang et al. 1995).

In this paper, preliminary results of the hydration and crystallization of inorganic-salt particles composed of $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2$, or $Mg(NO_3)_2$ are reported. Both laser Raman and Mie scattering techniques are used to probe the chemical and physical state of the microparticle before and after phase transformation. Our earlier work on $Sr(NO_3)_2$ particles has revealed new metastable solid states and hydration behaviors that are not observed in the bulk phase. A systematic study of the alkaline earth metal nitrates would be expected to yield further insights into the structure and stability of the metastable states formed only in microparticles. Experiments were carried out with electrostatically charged particles, 12-15 μm in diameter and individually levitated in an electrodynamic cell, in which the relative humidity (RH) can be precisely controlled. The apparatus and experimental procedure have been described elsewhere (Tang and Munkelwitz, 1989; Fung et al. 1994).

Figure 1 shows the hydration behavior of a $Sr(NO_3)_2$ particle, where the particle mass change resulting from water vapor condensation or evaporation is expressed in moles of H_2O per mole of solute (#H_2O/solute) and plotted as a function of %RH. A crystalline anhydrous particle, whose Raman spectrum shown in Figure 2(a) displays a narrow peak at 1058 cm^{-1} and a shoulder at 1055 cm^{-1}, was first subjected to increasing RH (filled circles). The solid particle was seen to deliquesce at 83 %RH when it spontaneously gained weight by water vapor condensation and transformed into a solution droplet containing about 13 #H_2O/solute. Further growth of the droplet, as RH was again increased, was in complete agreement with the curve computed from bulk solution data (Robinson and Stokes, 1970). As RH was reduced, the droplet started to lose weight by evaporation (open circles). It remained a supersaturated metastable solution droplet far below the deliquescence point until abruptly it

transformed into an amorphous solid particle at ~60 %RH. The particle retained some water even in vacuum. The Raman spectrum of such a particle is shown in Figure 2(b), displaying a broad band at 1053 cm^{-1}, in sharp contrast to the anhydrous particle. In most cases, an amorphous solid particle would slightly but continuously absorb water upon increasing RH until they deliquesced at 69 %RH. Once in solution, the particle would behave like a typical solution droplet. In the special case shown in Figure 1, however, the particle (crosses) was observed to have transformed first into an anhydrous particle during increasing RH and then deliquesced at 83 %RH, indicating that the amorphous solid particle was metastable with respect to the anhydrous state.

A Ba(NO$_3$)$_2$ particle was found to deliquesce at 98.5 %RH, and the resulting solution droplet solidified at ~91 %RH upon evaporation. The Raman spectra taken of the solid particle before and after hydration were both identical to that of the bulk anhydrous crystals as shown in Figure 3, displaying a narrow peak at 1046 cm^{-1}. Thus, Ba(NO$_3$)$_2$, like alkali metal nitrates, is a simple system having only anhydrous state both in microparticles and in the bulk phase.

While in the bulk phase a Ca(NO$_3$)$_2$ solution is saturated at 8.4M at 25°C, it readily supersaturates. These supersaturated solutions, on further concentration, pass into semi-solid gels. At about 21M the clear homogeneous gel breaks down into a striated form (Stokes and Robinson, 1948). Ca(NO$_3$)$_2$ particles were also found to remain in a liquid or glassy state even in vacuum. Like Sr(NO$_3$)$_2$, there was always residual water left in the particle in an amount varying between 1 and 2 #H$_2$O/solute. The Raman spectrum of the particle, shown in Figure 4(b), displays a broad band centered at 1055 cm^{-1}, which is in contrast to the narrow peak at 1050 cm^{-1} obtained for the stable bulk tetrahydrate crystals, Ca(NO$_3$)$_2$•4H$_2$O, as shown in Figure 4(a). The crystalline tetrahydrate form, which would have a deliquescence point at 50 %RH according to solution thermodynamics (Robinson and Stokes, 1970), was never observed to exist in microparticles. Instead, the glassy particles always formed, which were observed to transform into a solution droplet between 10 and 15 %RH during growth. Once in solution, the droplet grew and evaporated following the same hydration curve computed from bulk solution data (Robinson and Stokes, 1970). However, if the solution droplet was left in the water vapor for an extended period of time, the droplet started to lose its mass, and at the same time the Mie scattering curve of the droplet also became less and less defined, indicating the formation of some crusty substance on the droplet surfaces. A plausible explanation is that gaseous HNO$_3$ was volatilizing from the droplet, leaving behind Ca(OH)$_2$, which precipitated out because of its low solubility in water.

The same material loss during droplet growth/evaporation was observed in the case of Mg(NO$_3$)$_2$. As Mg(OH)$_2$ is only sparingly soluble in water, it is more likely to precipitate out once it is formed as a result of HNO$_3$ volatilization. The stable crystalline form in the bulk phase is the hexahydrate, Mg(OH)$_2$•6H$_2$O, whose Raman spectrum is identical to the particle spectrum shown in Figure 5(a), displaying a narrow peak at 1060 cm^{-1}. Crystalline hexahydrate particles, however, gradually lost water content in vacuum and finally became an amorphous solid containing ~2 #H$_2$O/solute. As shown in Figure 5(b), the Raman spectrum of these amorphous solid particles displays a broad peak at 1066 cm^{-1} and a shoulder at ~1048 cm^{-1}. During growth, the amorphous solid particle first transformed into a solution droplet at ~0.8 %RH and then solidified into a hexahydrate particle at ~3.5 %RH, which again deliquesced at 52 %RH to form a solution droplet. Because of the excessive material loss, the hydration behavior was not always reproducible for Mg(NO$_3$)$_2$ particles. More work is in progress to elucidate the origin of material loss in microparticles, which until now has been observed to occur only in particles containing volatile solutes such as NH$_4$NO$_3$ (Richardson and Hightower, 1986) and NH$_4$Cl (Tang and Munkelwitz, 1989).

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References.

Fung, K. H.; Imre, D. G.; Tang, I. N. *J. Aerosol Sci.* **25**, 479 (1994)

Orr, C.; Hurd, F. K.; Corbett, W. J. *J. Colloid Sci.* **13**, 472 (1958)

Richardson, C. B.; Hightower, R. L. *Atm. Environ.* **21**, 971 (1987)

Richardson, C. B.; Spann, J. F. *J. Aerosol Sci.* **15**, 563 (1984)

Robinson, R. A.; Stokes, R. H. Electrolyte Solutions, 2nd Ed., Butterworth, London, 1970

Rood, M. J.; Shaw, M. A.; Larson, T. V.; Covert, D. S. *Nature* **337**, 537 (1989)

Stokes, R. H.; Robinson, R. A. *J. Am. Chem. Soc.* **70**, 1870 (1948)

Tang, I. N.; Munkelwitz, H. R. *J. Colloid Interface Sci.* **128**, 289 (1989)

Tang, I. N.; Munkelwitz, H. R.; Davis, J. G. *J. Aerosol Sci.* **8**, 149 (1977)

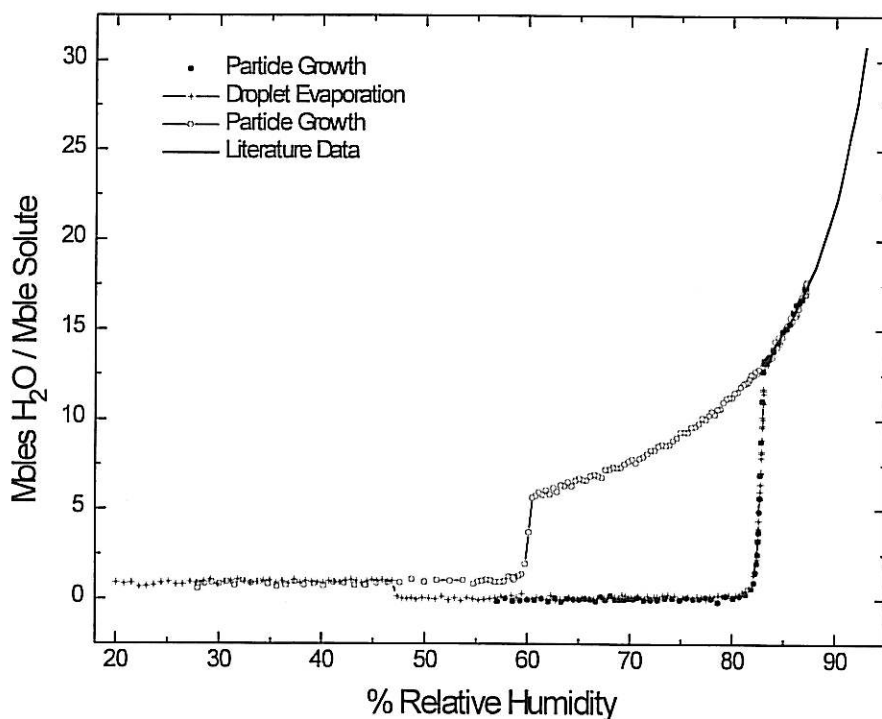Tang, I. N.; Fung, K. H.; Imre, D. G.; Munkelwitz, H. R. *Aerosol Sci. Technol.* (1995), in press

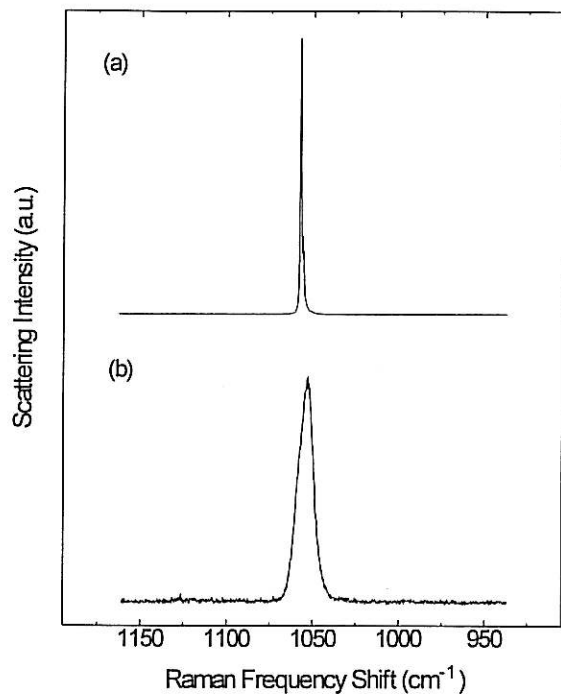Figure 1. Growth and evaporation of a strontium nitrate particle.

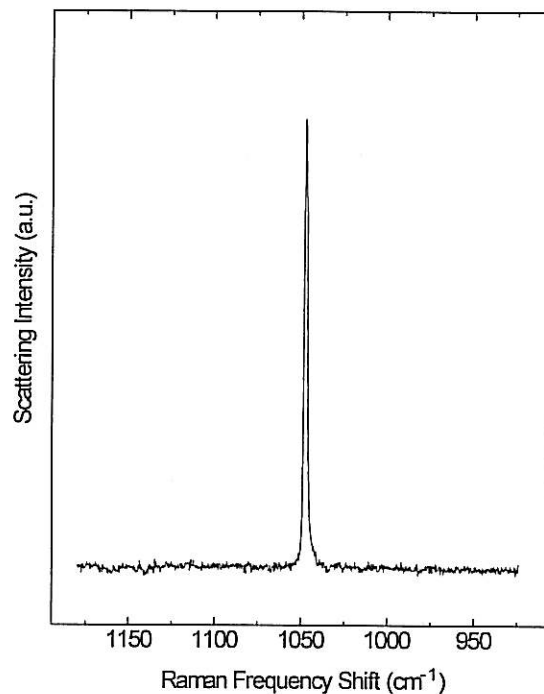Figure 2. Raman scattering spectra of (a) bulk strontium nitrate $Sr(NO_3)_2$ and (b) strontium nitrate particle.
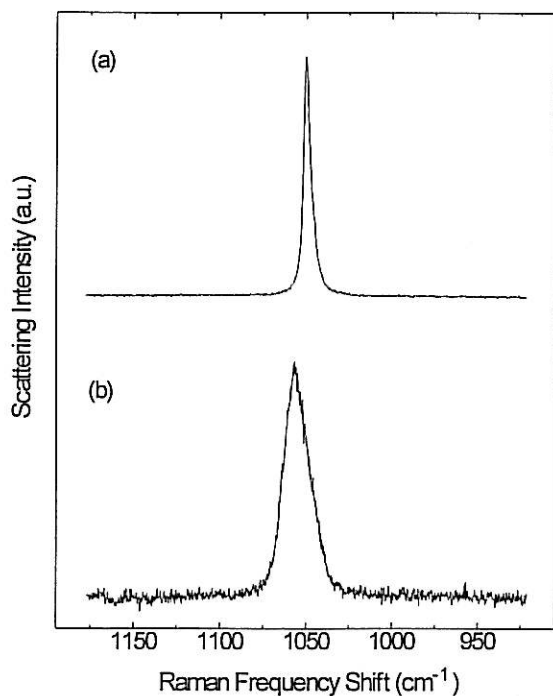

Figure 3. Raman scattering spectrum of barium nitrate $Ba(NO_3)_2$.

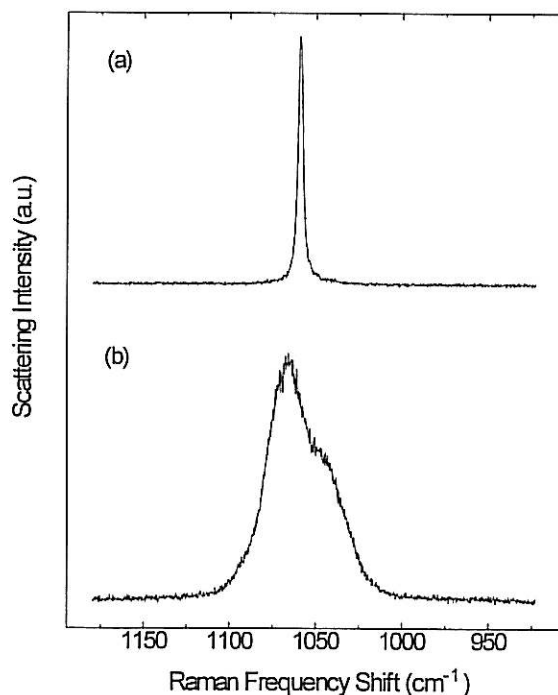Figure 4. Raman scattering spectra of (a) bulk calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$ and (b) calcium nitrate particle.

Figure 5. Raman scattering spectra of (a) bulk magnesium nitrate $Mg(NO_3)_2 \cdot 6H_2O$ and (b) magnesium nitrate particle.