

***In situ* Quantification of Ammonium Sulfate in Single Aerosol Droplets by Means of Laser Trapping and Raman Spectroscopy**

Shoji ISHIZAKA,^{*,**†} Kunihiro YAMAUCHI,^{***} and Noboru KITAMURA^{***}

^{*}*Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-hiroshima 739-8526, Japan*

^{**}*PRESTO-JST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

^{***}*Department of Chemistry, Faculty of Science and Department of Chemical Sciences and Engineering, Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-0810, Japan*

Noncontact levitation in air of single micrometer-sized water droplets containing ammonium sulfate was successful by a laser trapping technique. The trapping laser beam was also used simultaneously as an excitation light source for the Raman spectroscopy of trapped droplets. Raman scattering of the symmetric stretching vibration of the SO_4^{2-} anion and the OH stretching vibrations of H_2O were observed at 980 and 3420 cm^{-1} , respectively. The intensity ratio of these two Raman peaks was linearly proportional to the ammonium sulfate concentration in water. Therefore, the *in situ* quantification of ammonium sulfate in single aerosol droplets was achieved by means of laser trapping and Raman spectroscopy. To the best of our knowledge, this study is the first experimental observation of the independence of ammonium sulfate concentrations of aerosol water droplets to those of the mother solutions under constant relative humidity conditions.

Keywords Laser trapping, Raman spectroscopy, aerosol

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Introduction

Micrometer-sized aerosol droplets play key roles in both fundamental and applied research fields, represented by atmospheric chemistry, chemical vapor deposition, nanoparticle synthesis, and so on. The physical and chemical properties of aerosol droplets are often governed by the surface curvature and the solute concentration, and thus it is necessary to investigate individually its properties as a function of the droplet diameter. An optical trapping-microspectroscopy (absorption/emission/Raman) technique is the fundamental basis for studying aerosol droplets, since the technique can manipulate and interrogate an arbitrary sized single droplet in the gas phase.¹⁻⁸ However, since micrometer-sized aerosol droplets easily evaporate and quickly disappear in air, the number of reports on the optical trapping of aerosol microparticles is still limited compared with that of colloidal particles (*i.e.*, microparticles in a liquid phase).⁹ As we showed in a previous publication, the noncontact levitation of a single micrometer-sized water droplet in air can be achieved by a laser trapping technique.¹⁰⁻¹²

In order to achieve stable trapping of single micrometer-sized water droplets in air, aqueous droplets containing a solute (ammonium sulfate, sodium chloride, *etc.*), which reduces the vapor pressure of the droplet, are generated by using an ultrasonic nebuliser.¹⁰⁻¹² In the aerosol stream from the nebulizer, the size of a droplet varies by collision/coalescence between

droplets as well as by the evaporation/condensation of the droplet in accordance with the relative humidity (RH) of the surrounding gas phase. These situations indicate that the solute concentration in an aerosol droplet is not necessarily equal to that of the mother solution set in the nebulizer. Therefore, an experimental approach to *in situ* determination of the solute concentrations of individual droplets is absolutely required.

A laser beam used as a trapping light source can be used simultaneously as an excitation light source for Raman spectroscopy, which provides information on a fingerprint of chemical composition of an aerosol water droplet. Therefore, *in situ* characterization of the chemical composition of a trapped droplet can be achieved by means of laser trapping and Raman spectroscopy.¹² It is well known that ammonium sulfate is one of the common chemical species present in the atmosphere.¹³ Therefore, knowledge about $(\text{NH}_4)_2\text{SO}_4$ concentration effects on various phase transitions of aerosol water droplets is of primary importance for the modeling of cloud droplets (5 – 20 μm in diameter).¹⁴⁻¹⁷ Therefore, we focused our attention on quantitative measurements of ammonium sulfate included in a micrometer-sized water droplet in air. In the present study, *in situ* quantification of $(\text{NH}_4)_2\text{SO}_4$ in single aerosol droplets was conducted by means of laser trapping and Raman spectroscopy. By using this experimental approach, we demonstrated that the $(\text{NH}_4)_2\text{SO}_4$ concentration of aerosol droplets is independent to that of the mother solution under constant RH conditions.

† To whom correspondence should be addressed.
E-mail: ishizaka@hiroshima-u.ac.jp

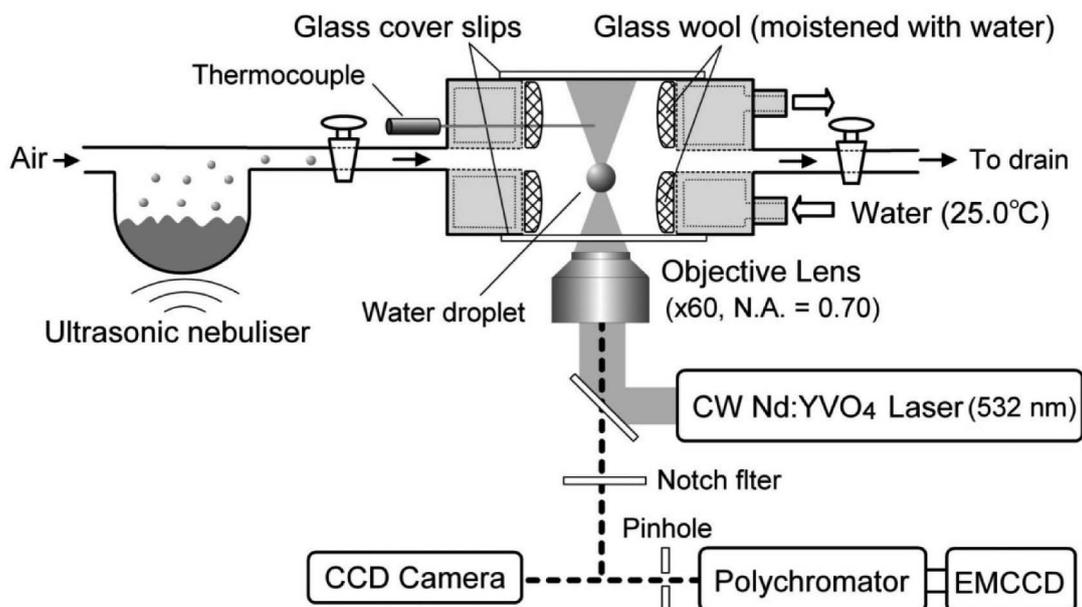


Fig. 1 Schematic illustration of a laser trapping and spectroscopic system.

Experimental

Laser trapping and spectroscopy of single aerosol droplets have been discussed in previous publications, and will be described only briefly here.¹⁰⁻¹² A particular focus of this study is to examine ammonium sulfate concentration of aerosol droplets under constant RH conditions. Therefore, the sample chamber was modified as shown in Fig. 1. In order to maintain constant relative humidity (RH ~100%) within the chamber (internal diameter of 4 cm and height of 4 cm) set on the stage of an inverted optical microscope (Olympus, IX71), the inner wall of the chamber was covered with glass wool moistened with pure water. Temperature inside the chamber was kept constant at $(25.0 \pm 0.4^\circ\text{C})$ by flowing thermostat water (Fine, FR-007N), and was monitored by a thermocouple (IWATU, SC-0107) set ~2 cm above the trapped droplets. Single droplets were trapped by a focused laser beam from a CW-Nd:YVO₄ laser (532 nm, Coherent, Verdi) through an objective lens ($\times 60$, N.A. = 0.7). Stable trapping of single droplets with the diameters of 5 – 12 μm was achieved with a laser trapping power of 3 – 20 mW. The laser beam was simultaneously used as an excitation light source for the Raman spectroscopy of single trapped droplets. Raman scattering light from the trapped droplet was collected by the same objective lens. After passing through a single-notch filter (Semrock, NF03-532E-25) to remove Rayleigh scattering by the droplet, Raman scattering light was focused onto the entrance slit of a polychromator (SOLAR TII, MS3504i, 300 grooves/mm), and analyzed by a cooled EMCCD detector (ANDOR, Newton DU970N-BV). Water was purified by reverse osmosis, and deionization prior to use (Merck Millipore, Milli-Q Integral 3). Ammonium sulfate (Wako Pure Chemical Co., Ltd.) was used without further purification.

Results and Discussion

Laser trapping and Raman spectroscopy of single aerosol droplets containing ammonium sulfate

An aqueous ammonium sulfate solution ($[(\text{NH}_4)_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$) was nebulized and introduced into the chamber, and a single micrometer-sized water droplet was trapped among the dense flow of aerosol water droplets (averaged diameter ~2 μm). Upon trapping, the droplet underwent further collisions with other non-trapped aerosol droplets in the nebulized stream, leading to growth of the droplet size. When the diameter (d) of the trapped droplet became approximately 10 μm , the flow of aerosol droplets from the nebulizer was stopped. The inlet and outlet valves of the aerosol flow of the chamber were closed, and the droplet was kept trapped for over 30 min in order to make all of the non-trapped water droplets fall down onto the bottom glass cover slip in the chamber. This enabled us to levitate only one droplet in the chamber. As a typical example, the Raman spectrum of the trapped droplet ($d = 10.6 \mu\text{m}$) in air is shown in Fig. 2(a), together with that of the mother solution ($[(\text{NH}_4)_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$) used to generate the droplets (Fig. 2(b)). A sharp peak observed at 980 cm^{-1} and a broad peak at around 3420 cm^{-1} were assigned to the symmetric stretching vibration of the SO_4^{2-} anion and the OH stretching vibrations of water, respectively.¹⁸ It is worth noting that the Raman scattering intensity ratio (I_{980}/I_{3420}) of the droplet (Fig. 2(a)) was smaller than that of the mother solution (Fig. 2(b)). As described in a previous publication, the I_{980}/I_{3420} value was linearly proportional to the ammonium sulfate concentration in water, the slope and intercept values of the calibration curve were determined to be $1.18 \pm 0.01 \text{ dm}^3 \text{ mol}^{-1}$ and 0.05 ± 0.02 , respectively.¹² On the basis of the Raman intensity ratio ($I_{980}/I_{3420} = 0.172$), the ammonium sulfate concentration in the droplet was determined to be 0.10 mol dm^{-3} , which was much lower than that of the mother solution ($[(\text{NH}_4)_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$). The results clearly indicate that the water vapor in the chamber was condensed to the trapped droplet under the present RH conditions, demonstrating

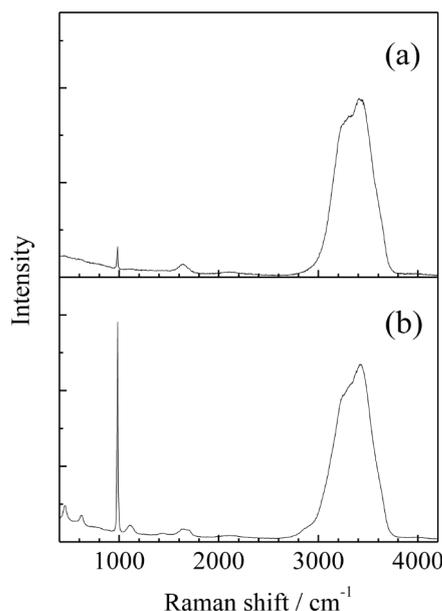


Fig. 2 Raman spectra of a water droplet containing ammonium sulfate (a) and the mother solution ($[(\text{NH}_4)_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$) in the nebulizer (b).

the vapor pressure of the trapped droplet containing ammonium sulfate is lower than that of the surrounding gas phase.

The thermodynamically equilibrium state of a micrometer-sized droplet in air is known to be described by the Köhler theory, which accounts for the influence of the Kelvin effect and the solute effect on the vapor pressure of a droplet.¹⁹ The water droplet size with the radius of r in equilibrium with the surrounding gas phase at a given RH is given by

$$\text{RH} = \left[1 + \frac{a}{r} - \frac{b}{r^3} \right] \times 100, \quad (1)$$

where a and b are given by the following equations:

$$a = \frac{2\sigma m_v}{\rho_w RT}, \quad (2)$$

$$b = \frac{3im_v M}{4\pi\rho_w m_s}. \quad (3)$$

In Eq. (2), σ is the surface tension of a water droplet, ρ_w is the density of the solution, m_v and m_s are the molecular weight of water and a solute, respectively. R and T have their usual meanings. In Eq. (3), M is the solute mass and i is the van't Hoff factor. The (a/r) and (b/r^3) terms in Eq. (1) represent the Kelvin and the solute effects on the vapor pressure of the droplet, respectively. The vapor pressure of a spherical water droplet is larger than that of flat and bulk water due to the difference in the Laplace pressure between the two systems. The Kelvin effect demonstrates an increase in the vapor pressure of a droplet with a decrease in the droplet size. On the other hand, the presence of an inorganic solute leads to a lowering of the vapor pressure of a droplet. These discussions indicate that the vapor pressure of a droplet decreases with a decrease in the droplet size and an increase in the concentration of a nonvolatile solute in the droplet. When the vapor pressure of a droplet resulting from the interplay of these two effects is equal to that

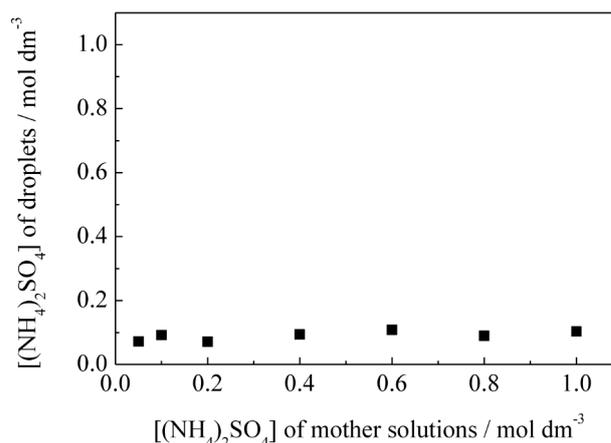


Fig. 3 Relationship between the ammonium sulfate concentration of the droplets in air and those of the mother solutions.

in the surrounding gas phase at a given RH, the droplet should be in the thermodynamically equilibrium state, and maintains a constant size. In the present experiments, the I_{980}/I_{3420} value in Fig. 2(a) demonstrates that the amount of ammonium sulfate (M/m_s) solubilized in the trapped droplet is evaluated to be $6.4 \times 10^{-14} \text{ mol}$. Thus, the a and b values in Eq. (1) were calculated to be $1.1 \times 10^{-9} \text{ m}$ and $6.2 \times 10^{-19} \text{ m}^3$, respectively: $T = 297.8 \text{ K}$, $\sigma = 0.0725 \text{ N m}^{-1}$, $m_v = 18.016 \text{ g mol}^{-1}$, $\rho_w = 1.005 \times 10^6 \text{ g m}^{-3}$, $i = 2.301$, $m_s = 132.14 \text{ g mol}^{-1}$. Substituting these values into Eq. (1), the RH value in the chamber is estimated to be 99.6%: $r = 5.3 \text{ }\mu\text{m}$. Since a sufficient amount of pure water was presented in the chamber at constant temperature (see also Fig. 1), the water vapor pressure was saturated in the chamber under the present experimental conditions. Therefore, we conclude that the theoretical prediction of RH = 99.6% based on Eqs. (1) - (3) is a reasonable consequence.

The Köhler theory also predicts that the ammonium sulfate concentration in the trapped aerosol water droplet should be independent of that of the mother solutions under a given RH condition. In order to confirm such a theoretical prediction, we studied the relationship between the ammonium sulfate concentration in a trapped aerosol water droplet and that in the relevant mother solution by laser trapping and Raman spectroscopy. Similar experiments with those in Fig. 2 were conducted at several concentrations ($[(\text{NH}_4)_2\text{SO}_4] = 0.05 - 1.00 \text{ mol dm}^{-3}$), and the ammonium sulfate concentrations in aerosol water droplets were plotted against those in the relevant mother solutions (Fig. 3). It is worth emphasizing that the ammonium sulfate concentrations in the individual trapped droplets were almost constant at $0.07 - 0.11 \text{ mol dm}^{-3}$, while those in the mother solutions were varied in the range of $0.050 - 1.00 \text{ mol dm}^{-3}$. As summarized in Table 1, furthermore, the RH value in each experiment was calculated to be 99.6 - 99.7% on the basis of the ammonium sulfate concentration in each droplet with r and Eq. (1). These results clearly demonstrate that the ammonium sulfate concentration in a micrometer-sized droplet in air is governed by the RH value of the surrounding gas phase. Consequently, the ammonium sulfate concentration in an individual aerosol water droplet is essentially independent of that of the mother solution for generation of aerosol droplets.

Table 1 Ammonium sulfate concentration in aerosol droplets determined by the Raman spectra, and those of mother solutions used for the generation of the droplets

[(NH ₄) ₂ SO ₄]/mol dm ⁻³		<i>r</i> /μm	RH, ^a %
Mother solution	Droplet		
0.05	0.07	5.1	99.7
0.10	0.09	5.3	99.6
0.20	0.07	5.1	99.7
0.40	0.09	5.6	99.6
0.60	0.11	4.8	99.6
0.80	0.09	4.9	99.6
1.00	0.10	5.3	99.6

a. RHs were calculated from the ammonium sulfate concentration and radius (*r*) of each droplet by using Eq. (1).

Conclusions

Since the equilibrium sizes of and the solute concentrations in micrometer-sized droplets in air are governed by the RH of the surrounding gas phase, the solute concentration of the droplet is independent of that of the nebulized solution. Therefore, the experimental approach to investigate the chemical compositions in individual water droplets in air is of primary importance. *In situ* characterization of single droplets in air can be achieved by means of laser trapping-Raman spectroscopy. In this study, we succeeded in the experimental observation that the (NH₄)₂SO₄ concentration of aerosol droplets is independent to that of the mother solution under constant RH conditions. Therefore, we are convinced that the laser trapping-Raman spectroscopic technique is a powerful means to study aerosol chemistry.

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