Chinese Science Bulletin

Micro-Raman investigations on the structures of the surface and the inner of $MgSO_4$ droplets

WANG Feng, SHOU JingJing & ZHANG YunHong†

The Institute of Chemical Physics, Beijing Institute of Technology, Beijing 100081, China

Spherical $MgSO_4$ droplets were deposited by a syringe on the hydrophobic Teflon substrate. Using micro-Raman technique, the laser beam was highly focused twice on the surface and in the center of spherical droplets. The Raman spectra for the surface and the inner of $MgSO_4$ droplets were accordingly obtained, suggesting formation of a thin layer of gels on $MgSO_4$ droplets at low relative humidity. The gel layer covered the surface and exhibited a significant delay in response to the change of ambient relative humidity, resulting in the structural difference between the surface and the inner of $MgSO_4$ droplets.

$MgSO_4$ droplet, micro-Raman, gel structure, mass transfer limitation

Hygroscopic property is one of the most fundamental physicochemical properties for atmospheric aerosols, affecting the air quality, visibility, and global climate and so on[1−4]. Atmospheric aerosols are generally expected to instantaneously achieve equilibrium with ambient environments in the process of gas-aerosol water transport[5]. However, a series of studies found that serious mass transfer limitation occurred in $MgSO_4$ aerosol droplets under low relative humidity (RH)[6,7]. Subsequent spectroscopic investigations and theoretical calculations suggested that the chain structures formed by contact ion pairs (CIPs) of Mg^{2+} and SO_4^{2-} should be responsible for the mass transfer limitations[8,9]. In our recent Raman spectroscopic investigations of $MgSO_4$ droplets deposited on the quartz substrate, the structures for gels were identified and the Raman bands at 1021 and 983 cm^{-1} were assigned to the chain structures and the free SO_4^{2-} ions. The intensity ratio of the two Raman bands, i.e., I_{1021}/I_{983}, was suggested to describe the extent of gel formation[10]. However, the $MgSO_4$ droplets were easily spread on the quartz substrate with thickness of few microns. It is difficult to get the structural difference between the surface and the inner of the droplets on the hydrophilic substrate with micro-Raman technique. Teflon is a kind of hydrophobic substrate, which can be used to prepare droplets with very large contact angle. Thus the $MgSO_4$ droplets on Teflon substrate would have a spherical shape allowing for the investigations of the structures of the surface and the inner under low RHs.

In the depth-scanning process, the laser beam can be focused twice on the top surface and in the centre of the spherical droplet as shown in Figure 1. In ideal cases, the laser beam through the confocal microscope is conical and the conical point is the focus of the laser beam, which is masked with O_1 in Figure 1. In the initial step of depth-scanning process (the scanning depth d = 0 μm), the laser beam is focused on the top surface of the droplet (Figure 1 (a)), and the collected spectral information should be entirely from the surface. When the laser beam penetrates the surface of the droplet, refraction should occur at the interface of the two media. After refraction, the “focus” becomes diffusive for the laser beams before and beyond the center of the droplet, ac-

Received March 25, 2008; accepted May 14, 2008
doi: 10.1007/s11434-008-0329-y
†Corresponding author (email: yhz@bit.edu.cn)
Supported by the National Natural Science Foundation of China (Grant Nos. 20673010 and 20640420450), the “111” Project (Grant No. B07012), and the Incubation and Reward Foundation for Excellent Doctoral Dissertation of Beijing Institute of Technology

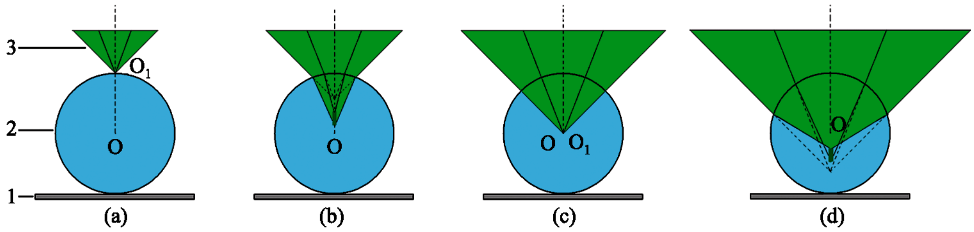

Figure 1 Schematic diagram of the focus of the laser beam with different depths in the spherical droplet. (a) The focus on the top surface; (b) the focus between the surface and the center; (c) the focus at the center; (d) the focus beyond the center of the droplet. 1, hydrophobic substrate; 2, spherical droplet; 3, beam of laser. The dark green regions in (b) and (d) denote the diffusive focus of the laser beam after refraction.

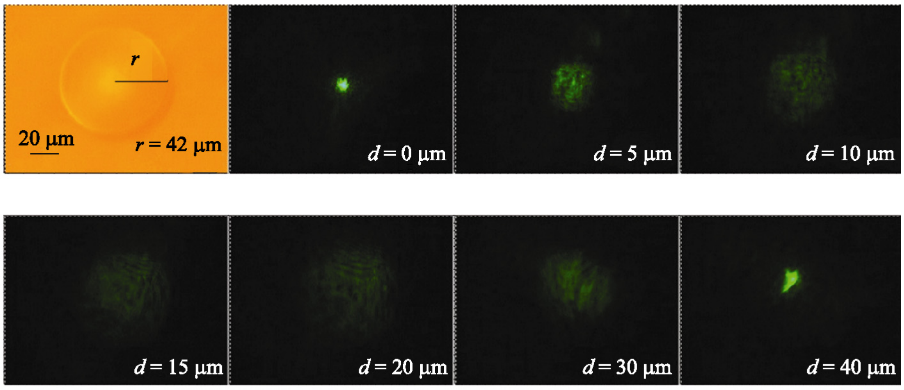

Figure 2 Changes of the focus of the laser beam versus the scanning depth (masked with "*d*") for the spherical droplet with a radius of 42 μm. Highly focused points are observed at $d = 0$ μm (on the surface) and $d = 40$ μm (at the center of the droplet).

cording to the dark green regions in Figure 1(b) and (d). In both cases, the "focus" of laser beam diffuses in the small region along the axes of laser rather than concentrates on a certain point. As a result, a highly focused point cannot be obtained. However, when the laser beam focus coincides with the center (marked with O in Figure 1 with the scanning depth d equalling the radius r of the droplet) of the spherical droplet, the laser beam penetrates perpendicularly the surface of the droplet without refraction (Figure 1(c)), when a highly focused point can be obtained again.

The above conclusions can be supported by the following Raman measurements. Figure 2 displays the changes of laser beam focus with the scanning depth for the spherical droplet with a radius of 42 μm. It is apparent from Figure 2 that highly focused points can only be observed on the top surface (d = 0 μm) and nearly at the center of the droplet (d = 40 μm). At other scanning depths, only diffusive laser focuses are obtained. For the droplets with different sizes, the radius (r) can be evaluated by the scanning depth d when the laser beam focuses again in the centre of the droplets. Figure 3 shows a good linear relationship between the radius evaluated by the scanning depth d and that evaluated by the microscope. Thus, the laser beam can always focus again at the center of droplets for the spherical droplets in the range of r = 10~65 μm. Highly focused point can be obtained twice on the top surface and at the center of one spherical droplet in the depth-scanning process. Accordingly, the collected Raman spectra should be exclusively from the surface and the center of droplets, respectively, which

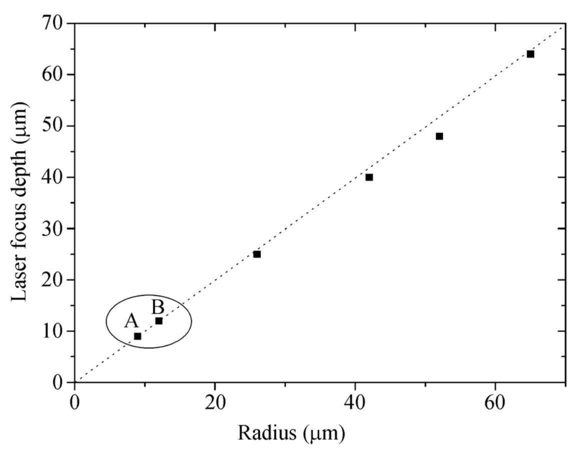

Figure 3 Changes of the scanning depth versus the radiuses of droplets when the laser beam gets highly focused on droplets with different radiuses. Points A and B are from the same droplet at different RHs.

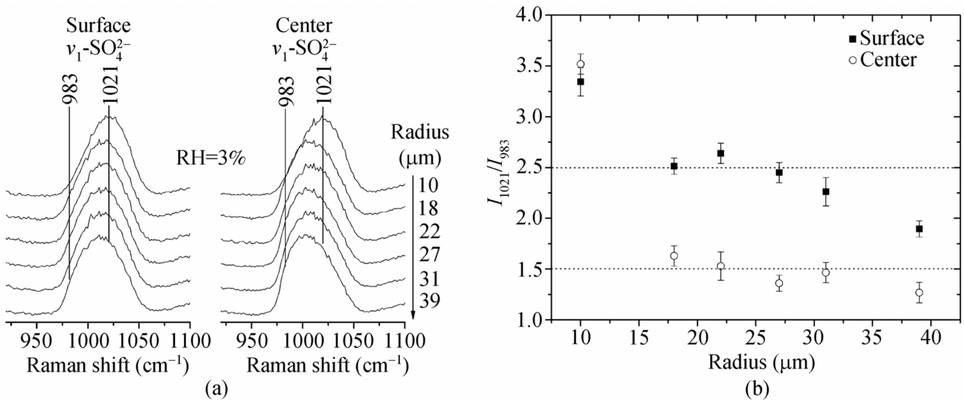

Figure 4 (a) Raman spectra of v_1-SO_4^{2-} and (b) I_{1021}/I_{983} on the surface and at the center of $MgSO_4$ droplets with different radiuses at 3% RH.

makes it possible to get the different structural information between the surface and the inner of $MgSO_4$ droplets by comparing the Raman spectra of the two focuses.

Figure 4(a) shows the evolution of v_1-SO_4^{2-} band on the surface and at the center of spherical $MgSO_4$ droplets with different radius at 3% RH. The v_1-SO_4^{2-} band was very sensitive to mass transfer limitation[10]. The intensity ratio of I_{1021}/I_{983} can be used to indicate the extent of the gel formation in Figure 4(b). For the droplet with a radius of 10 μm, the ratios are nearly the same between the surface and the inner, indicating an almost uniform droplet. For the droplets with larger radiuses, the value of I_{1021}/I_{983} on the surface (~2.5) of the droplet is obviously much higher than that at the center (~1.5), due to the formation of gels causing structural differences between the surface and the inner. Increasing the radius of the droplet by more than 10 μm, values of I_{1021}/I_{983} for both the surface and the center remain almost constant, suggesting that the gels in $MgSO_4$ droplets should be of certain thickness. However, as the radius increases by more than 39 μm, the values of I_{1021}/I_{983} always change with time even for the equilibrium time of more than 6 h at the ambient RH=3%. As a result, the values of I_{1021}/I_{983} for both the surface and the center of the droplet are obviously lower than the small droplets.

According to the above investigations, it can be concluded that the gels exist as a film with certain thickness in $MgSO_4$ droplets. The film covers the surface to cause significant mass transfer limitations with changing the ambient RH, resulting in structural differences between the surface and the inner. Further spatially-resolved investigations and dynamical studies can be predicted to elucidate the mechanisms of mass transfer limitations. In summary, for spherical droplets deposited on the hydrophobic substrate, two highly focused points can be achieved by micro-Raman technique, i.e., on the surface and at the center, facilitating the investigation of the surface and the inner of droplets. This method should be effective and practical in atmospheric aerosols and solution chemistry.

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