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# Integrated spectral and spatial information extraction in Raman spectroscopy

Qifeng Li[a], Huijie Wang[a], Xiangyun Ma[a], Yang Wang[a], Xinwei Zheng[b], and Da Chen[a]

[a]School of Precision Instrument and Opto-electronics Engineering, Tianjin University, Tianjin, China; [b]High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei, China

**ABSTRACT**

Raman spectroscopy has been widely used to analyze various substances quantitatively. Conventional studies are primarily focused on the spectral characteristics of Raman scattering. The spatial distribution is always ignored, which can be used to observe the physical properties, such as the particle size. In this article, the spatial information has been extracted from the Raman spectra of barium nitrate, demonstrating that the evident spatial width broadening varied with the particle size. The numerical result shows that the spatial width has a better linear correlation with the particle size, while the Raman intensity has a poor linear correlation. The integrated spectral and spatial information extracted in Raman spectroscopy has a potential application in the quantitative analysis of physical properties.

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**KEYWORDS**
Particle size; Raman spectroscopy; spatial distribution

## Introduction

Raman spectroscopy has been a very popular method for quantitative analysis of various substances.[1–4] In the conventional studies, the signal intensity and spectral pattern of Raman spectra are the focus, which can reflect the chemical compositions. To get one-dimensional Raman spectra (1D-RS), the original 2D-RS have to be binned spatially, which are collected by the traditional frequency-dispersive Raman spectrometers equipped with a CCD array detector. The spatial distribution of Raman scattering is always ignored, while it is closely related to the physical properties. Different from the conventional studies, the spatial information can be directly extracted from the original 2D-RS for the analysis of physical properties.

The spectral information is not sufficient for the measurement of particulate matter, which plays an important role in many fields, such as pharmaceuticals, material synthesis, and forensic analysis.[4–8] It has been known that the particle size can influence Raman scattering strongly.[7–16] Some studies have been conducted to investigate the particle-size effect, which were based on the spectral differences. There is a disagreement among the results, which is related to the measurement systems. Using the confocal systems, the Raman signal increases with the increasing particle size, even in the range of tens to hundreds of micrometers, which agrees with the general thesis of Kubelka–Munk model and its extensions.[10,17–20] Using the non-confocal systems, the results are opposite.[7–9] Diffuse reflectance is considered as the major factor.[7] However, it cannot be confirmed directly by the spectral information.

In this article, we extract the integrated spectral and spatial information from the Raman spectra of barium nitrate samples. The evident spatial width broadening related with particle size is observed, which has a better linear correlation with the particle size than the Raman intensity. The result implies that the particle size affects the spatial distribution of Raman scattering strongly, which results in the decrease of Raman intensity in the non-confocal systems.

## Experimental

### Sample preparation

Barium nitrate was purchased from Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China. The raw cubic crystalline powders were sieved to produce powders of a defined particle size. The aperture size ranges of eight sieve combinations (Dongzhen Machinery Co., Ltd., Xinxiang, China) were 35–65 $\mu$m, 65–85 $\mu$m, 85–115 $\mu$m, 115–135 $\mu$m, 135–165 $\mu$m, 165–185 $\mu$m, 200–300 $\mu$m, and 300–400 $\mu$m, respectively. The particle sizes were determined by the average values of the aperture size ranges, given as 50, 75, 100, 125, 150, 175, 250, and 350 $\mu$m, respectively.

### Spectral collection

The home-made non-confocal Raman system was used to collect the Raman spectra of barium nitrate with different particle sizes. The frequency-dispersive Raman system collected backscattered radiation, equipped with a 785 nm laser (B&W Tek, Inc., Newark, Delaware, USA), a grating-based spectrograph (Andor Technology Ltd., Belfast, UK), and a 1024 × 256 CCD detector (Andor Technology Ltd., Belfast, UK). The diameter of Raman laser beam was ~1 mm. Using a condenser lens of

CONTACT Da Chen dachen@tju.edu.cn School of Precision Instrument and Opto-electronics Engineering, Tianjin University, Tianjin, 300072, China.
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300 mm focal length, the focusing spot of excitation light was ~500 $\mu$m in diameter, which was larger than the maximum particle size. In this back-scattered Raman system, the condenser lens was primarily used to collect the Raman scattering. The barium nitrate powders were placed in 10 mm cubic quartz glass cuvettes thicker than the depth of field of the non-confocal Raman probe. The sample holder was movable along the direction of the incident laser for seeking the focusing position, with the step length of 400 $\mu$m.

The Raman scattering is recorded by the CCD array detector, as shown in Figs. 1a and 2a. Due to the internal digitization processing of the CCD array detector, the minimum value interval of recorded Raman intensities is $10^{-4}$. In the 2D-RS, the rows represent the spatial positions and the columns represent the spectral positions. By spatially binning, the 1D-RS are generated, as shown in Fig. 2b. For facilitating the discussion, the 2D spectral-spatial Raman spectra are labeled as 2D-SSRS.

### *Spatial width extraction*

The spatial widths are determined by two-term 2D Gaussian fitting. In the 2D-RS, the spectral widths are similar, which are limited by the line shape function inherent to the Raman systems. The spectral widths are fixed to 1.4 for Raman peaks at ~1065 $cm^{-1}$. In the spatial dimension, the wider widths are chosen to characterize the spatial widths, which represent the spatial broadening of Raman scattering. The narrower widths are fixed to 1.4, which are closely related to the laser beam intensity distribution at the focusing position. The correlation coefficients of Gaussian fitting are all more than 0.9. The values of spatial widths are accurate to four decimal places.

## Results and discussion

Figure 1a shows the 2D-SSRS of barium nitrate samples at different sampling positions. To clearly show the differences in spatial distribution, the intensity is normalized. The spatial distributions of Raman peaks at ~750 and ~1065 $cm^{-1}$ both get narrower from Position 1 to Position 9 and get wider from Position 9 to Position 15, when the sample holder is moved along the direction of the incident laser. Figure 1b shows the extracted spatial widths at different sampling positions. There is a minimum spatial width, whose corresponding position is considered as the focusing position. This trend is consistent for different particle sizes. The barium nitrate samples with different particle sizes were all measured 10 times at the focusing position.

Figure 2a shows the 2D-SSRS of barium nitrate samples with the particle sizes of 50, 150, and 350 $\mu$m, respectively. The spatial distributions of Raman peaks at ~750 and ~1065 $cm^{-1}$ both get wider as the particle size increases, while the spectral widths are similar. The linear fitting result of the spatial width at ~1065 $cm^{-1}$ versus the particle size is shown in Fig. 3a. There is a positive linear correlation between the spatial width and particle size. The absolute correlation coefficient is 0.9924.

Figure 2b shows the 1D-RS of barium nitrate samples. The Raman intensities at ~750 and ~1065 $cm^{-1}$ both decrease as the particle size increases. The Raman intensities refer to the peak heights. The linear fitting result of the Raman intensity at ~1065 $cm^{-1}$ versus the particle size is shown in Fig. 3b. There is a negative linear correlation between the Raman intensity and particle size. The absolute correlation coefficient is 0.8912. The relationship between the Raman intensity and particle size is in agreement with the previous studies using the non-confocal systems.[7–9]

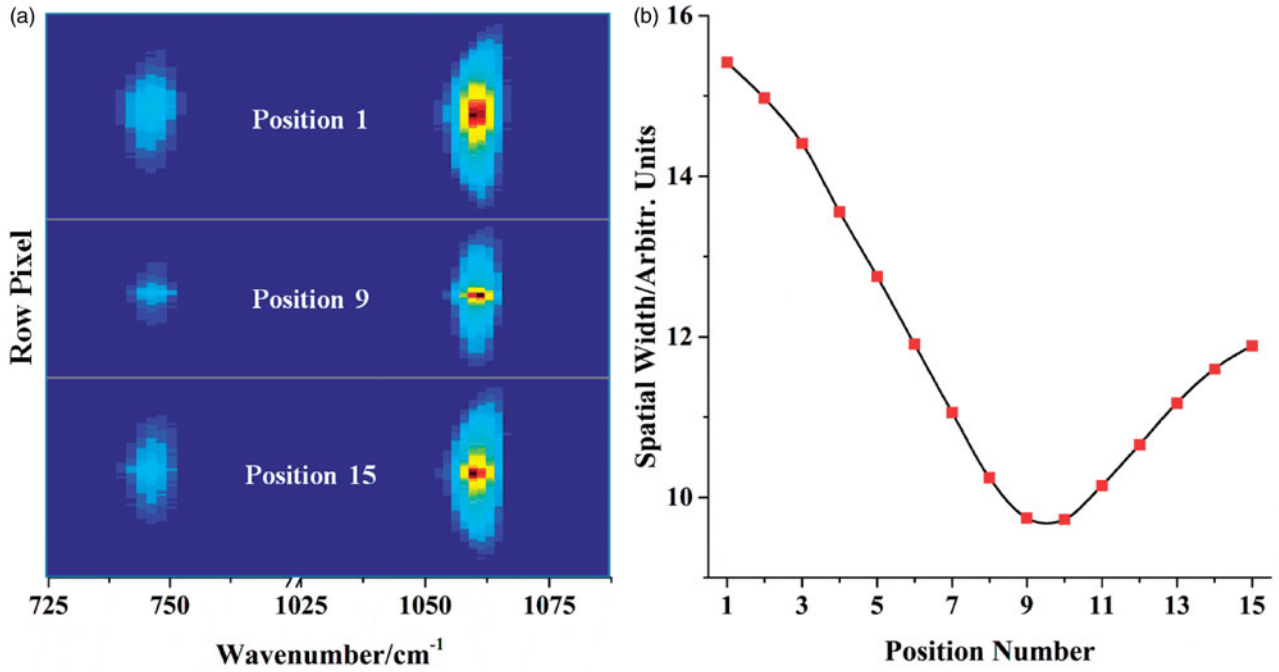


Figure 1. Extraction of spatial information from Raman scattering of barium nitrate samples at different sampling positions. (a) Two-dimensional spectral-spatial Raman spectra (2D-SSRS) of barium nitrate samples at different sampling positions. (b) The extracted spatial widths of Raman scattering which vary with the sampling positions.

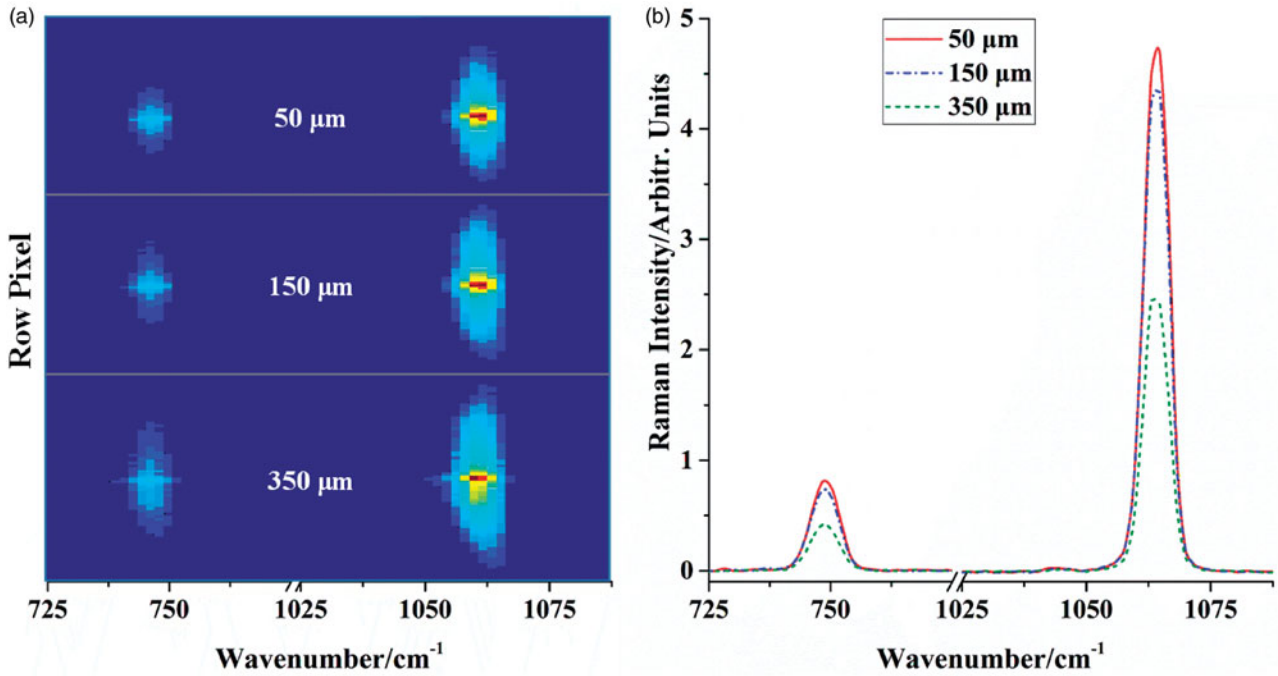


**Figure 2.** Extraction of spatial information from Raman scattering of barium nitrate samples with different particle sizes. (a) 2D-SSRS of barium nitrate samples with different particle sizes. (b) 1D-RS of barium nitrate samples with different particle sizes.

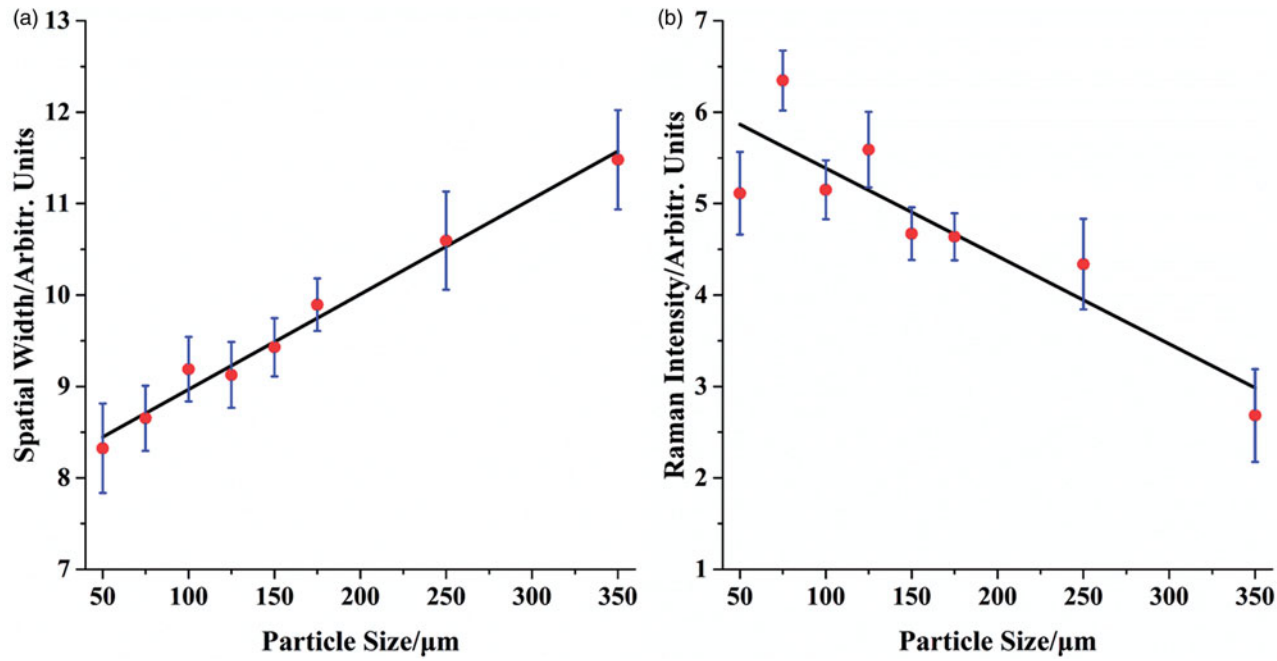


**Figure 3.** The particle-size effect on the extracted spectral and spatial information from Raman scattering of barium nitrate samples. (a) The relationship between the extracted spatial widths of the 2D-SSRS and the particle sizes. (b) The relationship between the Raman intensities of the 1D-RS and the particle sizes.

As the spatial width and Raman intensity have the same resolutions of $10^{-4}$, we can determine that the spatial width of 2D-SSRS has a better linear correlation with the particle size than the Raman intensity of 1D-RS, which implies that the particle size has a strong effect on the spatial distribution of Raman scattering. We think that the spatial width broadening comes from the long effective excitation path when the Raman laser goes through the sample. The particle size affects the length of the effective excitation path strongly. The smaller particles with stronger diffusion effect will shorten the effective excitation path, which provides the narrower spatial width broadening, while the larger particles provide the wider spatial width broadening.

Due to the definite effective excitation path of the Raman laser, the overall Raman scattering from a definite volume of barium nitrate samples has been recorded by the CCD array detector in fact. We think that the overall Raman scattering consists of two parts: one is from the laser excitation spot at the focusing position and the other is the broadening part which comes from the long effective excitation path closely

related with the particle size. Thus, we extract the spatial widths by the two-term 2D Gaussian fitting method mentioned above.

The spatial width broadening effect is obviously dominant in the non-confocal Raman systems, which can collect all the Raman signals along the effective excitation path. Due to the finite entrance slit of the grating-based spectrograph in the non-confocal Raman system, the incident throughput decreases with the increasing spatial width. Meanwhile, the spatial width increases with the increasing particle size. As a result, a negative linear correlation between the Raman intensity and particle size is generated. The Kubelka–Munk model can be extended to describe the particle-size effect on the spot-excited Raman scattering with some limitations in three dimensions.[21] The positive particle-size effect in Kubelka–Munk model also modifies the Raman intensity, which suggests that the Raman intensity should increase with the increasing particle size.[17–20] Both of the opposite particle-size effects should be considered in the non-confocal Raman systems, which can explain the Raman intensity fluctuation in Fig. 3b.

## Conclusions

In this article, the spatial information as well as spectral information is extracted from the Raman spectra, demonstrating the particle-size effect of barium nitrate samples. The spatial width has a better linear correlation with the particle size, which can explain the decrease of Raman intensity in the non-confocal systems. The result implies that the integrated spectral and spatial information is essential for the quantitative analysis of physical properties.

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## ORCID

Huijie Wang http://orcid.org/0000-0001-8954-9857

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