

Backscattering Raman spectroscopy using multi-grating spatial heterodyne Raman spectrometer

JIANLI LIU,^{1,2} BAYANHESHIG,^{1,3} XIANGDONG QI,¹ SHANWEN ZHANG,¹ CI SUN,¹ JIWEI ZHU,¹
JICHENG CUI,^{1,4} AND XIAOTIAN LI^{1,*}

¹Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin 130033, China

²University of Chinese Academy of Sciences, Beijing 100049, China

³e-mail: bayin888@sina.com

⁴e-mail: jicheng_cui@163.com

*Corresponding author: lixt_1981@163.com

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Spatial heterodyne Raman spectrometry (SHRS) is a spectral analysis technique used to study material structures and compositions. We propose a multi-grating SHRS system that uses a multi-grating module rather than the single grating used to terminate each arm in traditional spatial heterodyne spectrometry (SHS). The proposed system not only retains the advantages of traditional SHS but also resolves the mutual limitation between system spectral range and resolution. The increased spectral range and resolution that can be achieved in detection are dependent on the number of sub-gratings used in the module. A verification system was built using 130 gr/mm and 150 gr/mm sub-gratings and calibrated. Under different experimental conditions (including laser power, integration time, container material and thickness, pure and mixed samples, and standoff experiments), the backscattered Raman spectra of different types of targets (including organic solutions, inorganic powders, and minerals) were tested. The multi-grating SHRS shows good performance for broad spectral range and high-resolution Raman detection. © 2018 Optical Society of America

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1. INTRODUCTION

In 1928, the Indian physicist Raman [1] used the 435.83 nm blue light from a mercury arc lamp to irradiate a CCl₄ solution and discovered the existence of the inelastic scattering of light. This inelastic scattering behavior was named Raman scattering, and the spectrum produced is called a Raman spectrum. Raman spectroscopy is a nondestructive detection technique based on the interactions of light and materials with inelastic Raman scattering light. Depending on the chemical structure or the physical state of the material to be measured, the molecules of the material have corresponding vibrational bands, i.e., their characteristic Raman spectrum. After modulation by the material, Raman scattered light carries structural information. By measuring the relative intensities of specific spectral components and their frequency shifts relative to incident light frequency, the related molecular system information can then be obtained. Therefore, Raman spectroscopy has become an effective method for the study of molecular structures. Raman spectroscopy has been widely applied in various physical [2], chemical [3], astronomical [4], medical [5,6], biological [7,8], semiconductor [9], and industrial fields [10], because it enables rapid analysis of the compositions and structures of

various materials via a noncontact measurement process that causes no damage to the samples. The method is therefore becoming increasingly popular with researchers.

Spatial heterodyne Raman spectrometry (SHRS) is a new type of Fourier transform Raman spectrometry method that has proven to be a promising and useful technique for Raman detection systems. SHRS was first proposed by Gomer *et al.* [11], and the SHRS structure is consistent with the design of the spatial heterodyne spectrometry (SHS) system (as described by Harlander [12]), which is similar to a Michelson interferometer but uses tilted diffractive gratings rather than planar reflectors. SHRS offers the advantages of high spectral resolution equal to the resolving power of the combined diffraction gratings, high optical throughput, large field of view, and no moving parts; these advantages mean that SHRS can be applied to more complex environments for a wider range of applications. Egan *et al.* [13] presented time-resolved Raman spectra of carbonate, sulfate, and silicate minerals that were measured using standoff SHRS, which proved that SHRS has potential for use in planetary science applications. Hu *et al.* showed that SHRS has the ability to detect chemical warfare agents and simulants [14], and used two-dimensional SHRS to measure the Raman signals from organic liquid and

inorganic solid targets [15]. Ultraviolet Raman measurements of stones and Teflon that were performed using SHRS were reported by Lamsal and Angel [16]. In medicine, Strange *et al.* [17] presented the transmission Raman spectra detected by SHRS from ibuprofen and acetaminophen tablets. However, the principle of the technique indicates that, when the number of detector pixels is fixed, the spectral range and resolution of the SHRS system described above are mutually restricted. To achieve a high spectral range, the resolution of the instrument must be sacrificed, which thus limits development of the SHRS process to some extent.

To achieve both a broad spectral range and high resolution simultaneously for SHRS, we propose a multi-grating SHRS setup that uses multi-grating modules rather than the mirrors that are used to terminate each arm in Michelson interferometers. The number of sub-gratings in the module is the key factor that can be used to change the spectral range and resolution of the instrument. Multi-grating SHRS is equivalent to using multiple, conventional interferometers, stacked on top of each other, while the multiple mosaic sub-gratings result in a compact form of these stacked interferometers. To provide a clear understanding of the properties and detection capabilities of multi-grating SHRS, a breadboard version of the system has been built. In this paper, we describe the theory of multi-grating SHRS, and calibration results of the breadboard system are also provided. Using a variety of different experimental conditions (including laser power, integration time, container material and thickness, pure and mixed samples, and standoff experiments), the backscattered Raman spectra of different types of targets (including organic solutions, inorganic powders, and minerals) are presented and analyzed in detail.

2. PRINCIPLE

A. Basic Theory

Figure 1 shows a schematic diagram of the multi-grating SHRS configuration. The Michelson interferometer structure is used, but the plane reflectors used to terminate each arm are replaced with multi-grating modules composed of n ($n \geq 2$) sub-gratings mosaicked together. In each module, each of the

sub-gratings can have a different groove density, and this density is the same in both the direction of the groove line and the direction of dispersion. Each of the sub-gratings is arranged along the grating groove direction, and the sub-gratings used at the two terminated arms correspond to each other.

Backscattered Raman light generated by a laser beam focused on the target surface is collected using the convergent lens, and Rayleigh scattered light is filtered using Raman filters (either edge or notch filters). The collimated light arrives at a 50/50 beam splitter and is split into two beams. The separated light beams then irradiate each sub-grating at the same angle; diffraction of non-Littrow wavenumbers by the gratings means that there is a small angle ($\pm\gamma$) between the direction of propagation and the optical axis. γ is determined using the grating Eq. (1) below:

$$\sigma[\sin \theta_L + \sin(\theta_L - \gamma)] = mG, \quad (1)$$

where σ is the wavenumber of the incident light, θ_L is the Littrow angle, m is the diffraction order, and G is the grating groove density.

The difference angle between the two light wavefronts is 2γ ; therefore, the spatial frequency of the two-beam interference with wavenumber σ is given by Eq. (2):

$$f_x = 2\sigma \sin \gamma = 4(\sigma - \sigma_L) \tan(\theta_L). \quad (2)$$

To avoid spectral overlap, one of the multi-grating modules is rotated by an angle of $\alpha/2$ about the x axis to produce a 2D interferogram. This interferogram is imaged on the CCD detector, and when the Raman signal radiance from the target is $B(\sigma)$, the intensity is recorded as determined by Eq. (3):

$$I(x, y) = \int_0^\infty B(\sigma) [1 + \cos\{2\pi[4(\sigma - \sigma_L)x \tan \theta_L + \sigma y \alpha]\}] d\sigma, \quad (3)$$

where x is measured on the detector on the dispersion plane of the gratings. A Fourier transform is then used to recover the Raman spectrum.

The maximum spectral resolution of the multi-grating SHRS system corresponds to the theoretical resolution of the grating, which is written as

$$\delta\sigma = \frac{1}{4W \sin \theta_L}, \quad (4)$$

where W is the width of the illuminated grating. The resolving power is given by

$$R = \frac{\sigma}{\delta\sigma} = 4W\sigma \sin \theta_L. \quad (5)$$

From the above, if the detector has N pixels in the spectral dimension, then the spectral range that can be detected by this detector is given by Eq. (6):

$$\Delta\sigma = N\delta\sigma = \frac{N}{4W \sin \theta_L}. \quad (6)$$

Equation (6) indicates that the spectral range is limited by the number of pixels N in the spectral dimension of the detector and by spectral resolution $\delta\sigma$. The contradiction between the requirements for the resolution for Raman spectrum measurements and the spectral range to be detected is effectively resolved using the multi-grating SHRS structure. Each

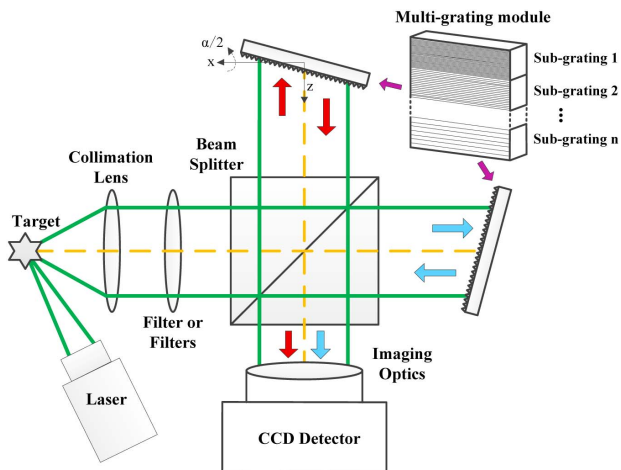


Fig. 1. Schematic diagram of multi-grating SHRS system.

sub-grating satisfies the analysis principle above, which means that if the number of sub-gratings contained in each multi-grating module is n (where $n \geq 2$), the total spectral range of the multi-grating SHRS system can then be given as

$$\Delta\sigma_n = n\Delta\sigma = nN\delta\sigma = \frac{nN}{4W \sin \theta_L}. \quad (7)$$

In the case of a fixed number of pixels N , if the resolution $\delta\sigma$ is given, then the extension of the total spectral range $\Delta\sigma_n$ can be realized easily by increasing the number n of sub-gratings in each multi-grating module; conversely, if the total spectral range $\Delta\sigma_n$ is predetermined, then the resolution $\delta\sigma$ can also be improved dramatically by increasing the number n of sub-gratings in each multi-grating module. Therefore, the ability of the system to detect the material's Raman signal is greatly improved when using multi-grating SHRS.

For a multi-grating SHRS, based on the theory of the conventional SHRS system with a shot-noise limit, the SNR can be predicted as [12]

$$\text{SNR} = \sqrt{\frac{\mu A \Omega}{2N}} I \delta\sigma T, \quad (8)$$

where μ is the optical efficiency, A is the effective area of the system, Ω is the etendue of the system, I is the intensity of the continuum in photons per second per unit area per steradian per unit wavenumber, which is proportional to the laser power for the measurements, and T is the total integration time.

The experiment uses 130 gr/mm and 150 gr/mm mosaicked gratings to build the multi-grating verification system. Raman spectra of different materials are detected and analyzed using this system.

B. Calibration Theory

The calibration procedure establishes the spectral response of the multi-grating SHRS system based on its spatial frequency response to a known input from a standard source, such as a mercury lamp. The sub-grating used for calibration is defined here as G_{norm} , while the calibration procedure follows the process outlined by Englert *et al.* [18] and is summarized here. The Littrow wavelength of sub-grating G_{norm} can be calculated using Eq. (9):

$$\lambda_L = \frac{f_2 - f_1}{(f_2/\lambda_1) - (f_1/\lambda_2)}, \quad (9)$$

where λ_1 and λ_2 are the known wavelengths from the calibration source, and f_1 and f_2 are the measured fringe cycles across the detector width that were obtained from the fast Fourier transform (FFT) of the interferogram:

$$\theta_L = \arcsin\left(\frac{\lambda_L \times G}{2}\right), \quad (10)$$

where θ_L is the Littrow angle, and G is the grating groove density of sub-grating G_{norm} .

When the Raman scattered light arrives at each sub-grating at this Littrow angle, the Littrow wavenumber of each sub-grating is given by Eq. (11):

$$\sigma_{L,n} = \frac{G_n}{2 \sin \theta_L}, \quad (11)$$

where G_n is the grating groove density of the sub-gratings, and n ($n \geq 2$) is the number of sub-gratings contained in the multi-grating module.

The resolution of the multi-grating SHRS system can be calculated using Eq. (12):

$$\delta\sigma = \frac{1/\lambda_1 - 1/\lambda_2}{f_1 - f_2}. \quad (12)$$

From Eqs. (6), (7), and (12), the spectral ranges of each sub-grating and the total spectral range of the multi-grating SHRS system can be obtained.

3. EXPERIMENT

A. Breadboard

The layout of the experimental devices is shown in Fig. 2, and the main parameters of these devices are listed in Table 1. The multi-grating SHRS consists of a 50.8 mm cube-shaped beam splitter (20BC17MB.1, Newport) and a multi-grating module composed of a 130 gr/mm grating and a 150 gr/mm grating (Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences) at each arm termination in the structure. The first diffraction order is used for each grating, and the active area of each grating is 10.4 mm (in the direction of the groove line) $\times$ 20.8 mm (in the direction of dispersion).

In the experiments, the power of the 532 nm laser (MSL-FN-532, Changchun New Industries Optoelectronics Tech. Co., Ltd.) is 400 mW, and a linear variable filter is used to realize linear adjustable incident laser power over the range from 0 mW to 400 mW. After it passes through the cleanup filter, the laser beam is divided into two beams by beam splitter 1. Coaxial detection of backscattered Raman light is realized using mirror 1, the dichroic beam splitter, and the collimation lens. After it is reflected by mirror 2, the laser beam is used to produce Raman light transmission. The samples were placed on an objective table in the focal plane of a 25 mm diameter converging lens (49662, Edmund Optics). A razor-edged long-pass

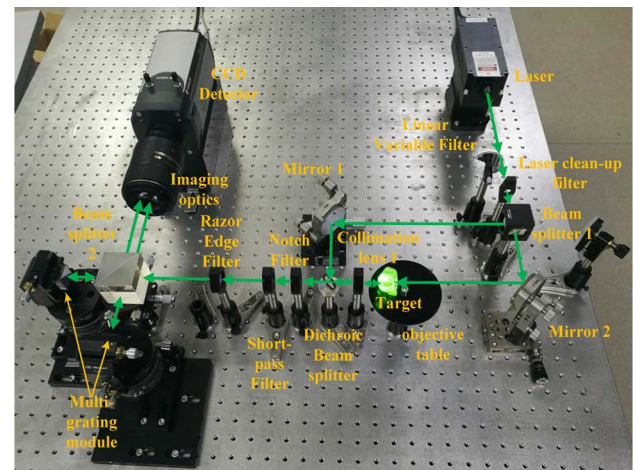


Fig. 2. Multi-grating SHRS system arrangement.

Table 1. Main Parameters of Devices Used in the Experimental Breadboard

Device	Specification	Index
Laser	Power	400 mW
	Wavelength	532 nm
	Beam diameter	~2.0 mm
	Beam divergence	<1.5 (full angle, mrad)
Laser cleanup filter	Center wavelength	532 nm
	FWHM bandwidth	2.0 nm
	Edge wavelength	537.2 nm
Dichroic beam splitter	Transition width	186 cm^{-1}
	Edge wavelength	536.4 nm
Razor edge long-pass edge filter	Transition width	186 cm^{-1}
	Blocking band	$\text{OD}_{\text{abs}} > 6$ at 532 nm
Short-pass filter	Cutoff wavelength	700 nm
	Optical density	≥ 4
532 nm single notch filter	Notch band	17 nm
	Blocking band	$\text{OD}_{\text{abs}} > 6$ at 532 nm
Sub-grating 1	Groove density	130 gr/mm
	Ruled area	10.4 mm $\times$ 22 mm
Sub-grating 2	Groove density	150 gr/mm
	Ruled area	10.4 mm $\times$ 22 mm
Beam splitter 2	Size	50.8 $\times$ 50.8 $\times$ 50.8 mm^3
Imaging optics	Diameter	62 mm
	Focal length	105 mm
CCD detector	Pixel numbers	1024 $\times$ 1024
	Pixel size	13 $\mu\text{m} \times$ 13 μm

filter (LP03-532RU-25, Semrock) was used to filter out the Rayleigh-scattered light and any other stray light at wavelengths lower than 532 nm. A 700 nm short-pass edge filter (84-714, Edmund) was used to eliminate ambient stray light and fluorescence at wavelengths higher than 700 nm. Another 532 nm notch filter (NF01-532U-25, Semrock) was used to provide selective reflection of the laser wavelength in some cases. A CCD detector (iKon-M 934, Andor) with 1024 $\times$ 1024 pixels was used to collect the interference images. The experiments were carried out at room temperature (25°C). All light sources were closed off to minimize interference from ambient stray light.

B. Calibration

A mercury lamp was used as the calibration light source in the experiments; the lines of interest from the mercury lamp are those above 532 nm, so the characteristic lines at 546.075 nm, 576.961 nm, and 579.067 nm in the bandpass were used to calibrate the spectrum. The raw interferogram (a) and recovered mercury lamp spectrum (b) are shown in Fig. 3.

In the multi-grating module, the 130 gr/mm and 150 gr/mm sub-gratings cause heterodyne interference, respectively. The main characteristic line of the mercury lamp is near 546 nm; therefore, according to the principles of spatial heterodyne interferometry, the spectrum belongs within the measurement range of the 150 gr/mm grating, and thus the interference signal intensity in the lower half of Fig. 4(a) is higher than that in the upper half.

From Eqs. (9)–(12), the Littrow wavelength is estimated to 533.29 nm; the Littrow angle is calculated to be 2.29°; and the Littrow wavenumbers corresponding to 130 gr/mm and 150 gr/mm are 16251.3 cm^{-1} and 18751.5 cm^{-1} , respectively. The spectral coverage ranges of the 150 gr/mm and 130 gr/mm gratings are $[-1491 \text{ cm}^{-1}, 1582 \text{ cm}^{-1}]$ and $[1009 \text{ cm}^{-1}, 4082 \text{ cm}^{-1}]$, respectively, and these are delta-wavenumbers relative to the laser wavenumber. Therefore, the verification system can realize Raman spectroscopy detection over the $[-1500 \text{ cm}^{-1}, 4000 \text{ cm}^{-1}]$ range approximately. The width of the grating that was imaged on the detector was estimated to be 20.79 mm, and spectral resolution was 3.01 cm^{-1} . Calibration results nearly matched the theoretical values of the multi-grating SHRS system. The full width at half maximum (FWHM) of 546.075 nm is about 5.6 cm^{-1} (1.86 times 3.01 cm^{-1}), which can be regarded as the actual spectral resolution. There are two main reasons for spectral line broadening [15]: finite sampling of the interferogram, which can broaden the FWHM of a spectral band to about 1.21 times the ideal FWHM; and nonuniform illumination produces an envelope function multiplied to the interferogram, which causing broadening of spectral lines.

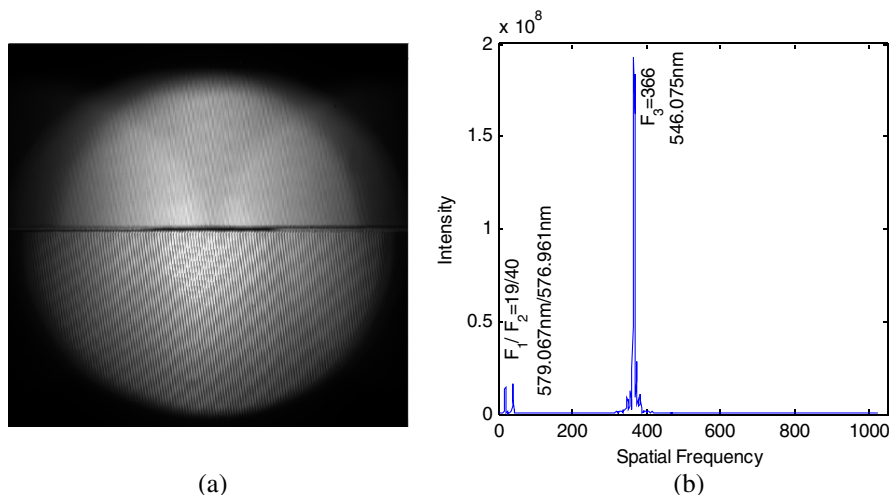


Fig. 3. (a) Raw interferogram and (b) recovered mercury lamp spectrum.

4. RESULTS AND DISCUSSION

A. Raman Spectra of Carbon Tetrachloride and Methyl Salicylate with Various Laser Powers

Figure 4(a) shows the Raman spectra of carbon tetrachloride (CCl_4) that were measured at different laser powers with the same integration time of 1 s. The laser power is increased from 54 mW to 180 mW, and the adjustment step size is 18 mW. When the CCl_4 solution is irradiated using a laser power of more than 180 mW, the detector may become oversaturated or even damaged. Multiple Raman characteristic signals of the CCl_4 are obviously detected within the spectral range. The symmetric deformation (ν_2) and asymmetric deformation (ν_4) modes are assigned to the 218 cm^{-1} and 314 cm^{-1} bands, respectively. The third band at 459 cm^{-1} is assigned to the symmetric C-Cl stretching (ν_1) mode. The fourth band at 762 cm^{-1} is assigned to the combination mode ($\nu_1 + \nu_4$). The asymmetric stretching (ν_3) mode is detected at 790 cm^{-1} [19,20]. To provide a better illustration of the effects of the detection spectrum, the [650 cm^{-1} , 900 cm^{-1}] range is locally magnified and shown in the inset graph. The graph shows that when the laser power is 54 mW, the weak peaks at 760 cm^{-1} and 790 cm^{-1} are still visible. The enhancement of the laser power means that the 762 cm^{-1} and 790 cm^{-1} characteristic peaks can also be distinguished more clearly.

Figure 4(b) shows the measured signal-to-noise ratio (SNR) of the characteristic Raman peak at 459 cm^{-1} versus various laser powers. The noise is estimated by calculating the root-mean-square (RMS) value in the spectrum beyond 1000 cm^{-1} in the recovered 2D FFT spectrum for CCl_4 . Then the intensity of the 459 cm^{-1} Raman peak divided by this noise value gives the measured SNR. Figure 4(b) shows that the SNR grows almost linearly with increasing laser power at the integration time of 1 s when the laser power is lower than 126 mW; when the laser power is greater than 126 mW, the SNR growth rate slows down and nearly stops increasing. At 180 mW, the SNR is slightly lower than the corresponding

SNR at 162 mW. The SNR plot in Fig. 4(b) is similar to a square-root function, which coincides with Eq. (8).

Figure 5(a) shows the Raman spectrum of methyl salicylate (MS) when measured at various laser powers with the same integration time of 1 s. The out-of-plane substituent sensitive ($\gamma_{\text{CX}(X)}$) mode appears at 360 cm^{-1} . The bands at 566 cm^{-1} and 680 cm^{-1} are attributed to the in-plane phenyl deformation (δ_{Ph}) and $\delta_{\text{Ph}(X)}$ modes, respectively. The out-of-plane CH deformation bands (γ_{CH}) are expected to occur in the 720–995 cm^{-1} region, and the band at 814 cm^{-1} is assigned to this mode [21]. The in-plane CH deformation (δ_{CH}) mode is clearly observed at 1037 cm^{-1} . The C(=O)–O stretching vibration ($\nu_{\text{C(=O)-O}}$), which is often considered the C–O asymmetric stretch, appears at 1256 cm^{-1} . Experimental results give 1471 cm^{-1} as the (δ_{aCH_3}) asymmetric in-plane deformation mode. The bands observed at 1589 cm^{-1} and 1620 cm^{-1} are both assigned to the phenyl stretching (ν_{Ph}) modes. The C=O stretching vibration ($\nu_{\text{C=O}}$) mode also occurs at 1681 cm^{-1} in these spectra. The experimentally observed bands at 2850 cm^{-1} and 2963 cm^{-1} are assigned to the (ν_{sCH_3}) symmetric stretching and (ν_{aCH_3}) asymmetric stretching modes, respectively. The CH stretching (ν_{CH}) mode of the benzene ring is observed at 3090 cm^{-1} [22]. The vibrational spectrum of MS was also clearly detected, and only part of the spectral peak is marked in the figure.

When the laser power was gradually increased from 90 mW to 198 mW, the intensity of the vibration spectrum was also enhanced and exceeded 198 mW, meaning that the detector was oversaturated. Figure 5(b) shows the calculated SNR for the vibrational wavenumber at 814 cm^{-1} for various laser powers in the same integration time of 1 s. We can see that when the laser power is smaller than 140 mW, the SNR grows rapidly with the increase in laser power; when the laser power is larger than 140 mW, the SNR stops increasing and fluctuation occurs. The SNR plot in Fig. 5(b) is also consistent with Eq. (8). The Raman spectrum and SNR analysis of CCl_4 and MS show that multi-grating SHRS has the capability to detect organic solutions.

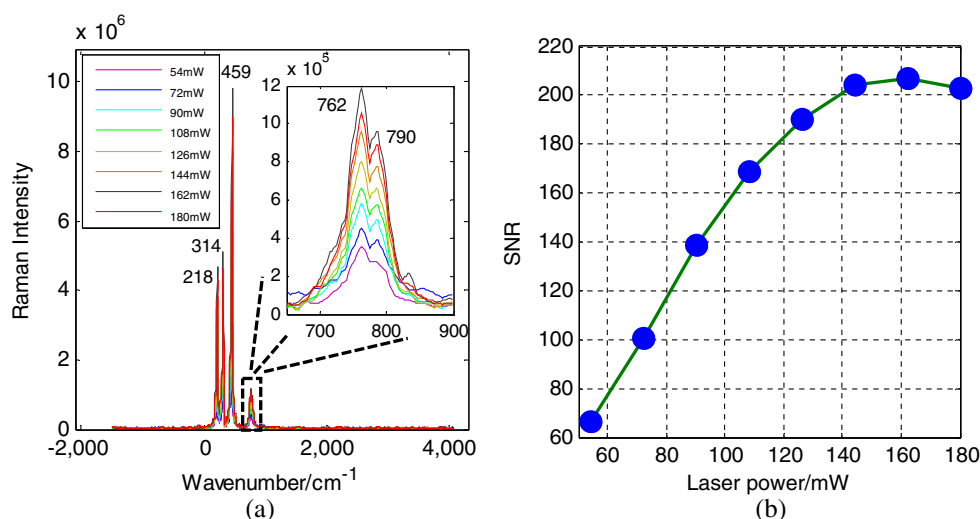


Fig. 4. (a) Raman spectrum of CCl_4 when measured at multiple laser powers with the same integration time of 1 s. (b) Measured signal-to-noise ratio of the 459 cm^{-1} vibration band versus different laser powers.

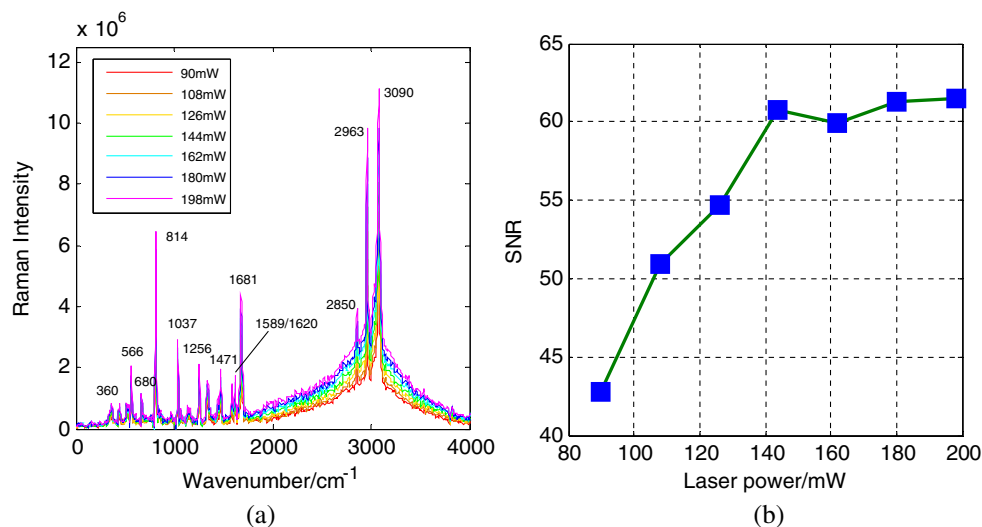


Fig. 5. (a) Raman spectrum of methyl salicylate when measured at various laser powers with the same integration time of 1 s. (b) Measured SNR of the 459 cm⁻¹ Raman peak versus different laser powers.

B. Raman Spectra of Titanium Dioxide and Potassium Sulfate with Different Integration Times

Figure 6(a) shows the Raman spectrum of titanium dioxide (TiO₂) within the [100 cm⁻¹, 800 cm⁻¹] range at various integration times. The spectrum shows remarkable detected intensities for the E_g modes peaking at 144 cm⁻¹ [$E_g(\nu_6)$] and 639 cm⁻¹ [$E_g(\nu_1)$], although these modes have quite different relative intensities. The scattering intensity is particularly strong for the $E_g(\nu_6)$ mode peak at 144 cm⁻¹. The other Raman peaks at 397 cm⁻¹ and 515 cm⁻¹ correspond to the $B_{1g}(\nu_4)$ and $B_{1g}(\nu_2)$ modes, respectively. The $E_g(\nu_1)$ and $B_{1g}(\nu_2)$ modes are attributed to Ti-O bond stretching type vibrations, while the $E_g(\nu_6)$ and $B_{1g}(\nu_4)$ modes are attributed to O-Ti-O bending type vibrations [23,24].

A relatively low laser power of 54 mW was used to study the changes that occurred in the vibrational spectrum at multiple

integration times. The integration time was increased from 1 s to 16 s, and results show that the intensities of the spectral lines increase with increasing integration time, but the noise that was introduced by the experimental conditions also changes. Figure 6(b) shows the measured SNR of TiO₂ at 144 cm⁻¹ at various integration times for the same laser power of 54 mW. Figure 6(b) shows that the SNR grows dramatically in the [1 s, 2 s] range. However, when the integration time is longer than 2 s, the increase of SNR slows down, even decreases at some integration times. Then, when the integration time exceeds 16 s, the detector is saturated. The SNR plot is in accordance with Eq. (8) roughly.

Several components of the lattice modes of potassium sulfate (K₂SO₄) powder in the low-frequency region are shown in Fig. 7(a). The free sulfate ion has T_d symmetry and the internal vibrations of the SO_4^{2-} are responsible for peaks that occur

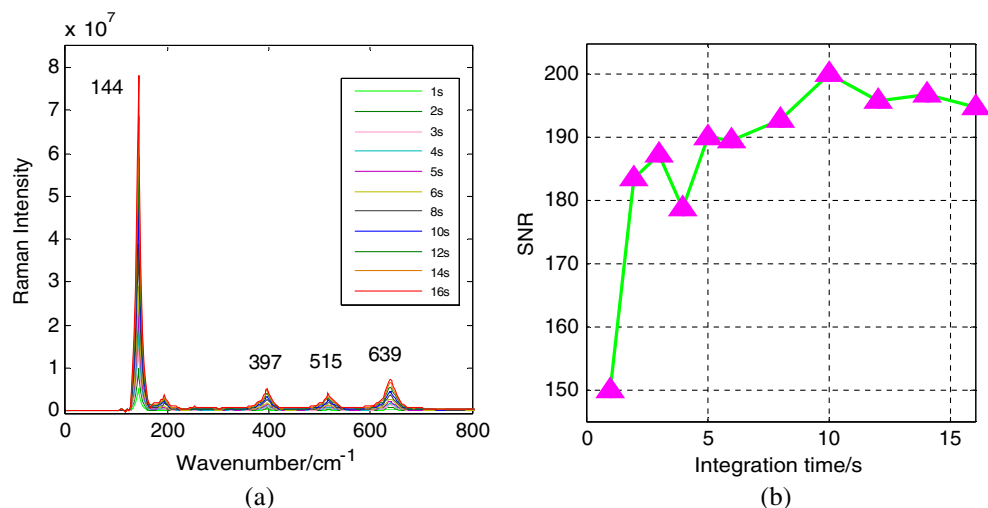


Fig. 6. (a) Raman spectra of TiO₂ at various integration times at a laser power of 54 mW. (b) Measured SNR of 144 cm⁻¹ Raman peak versus integration time.

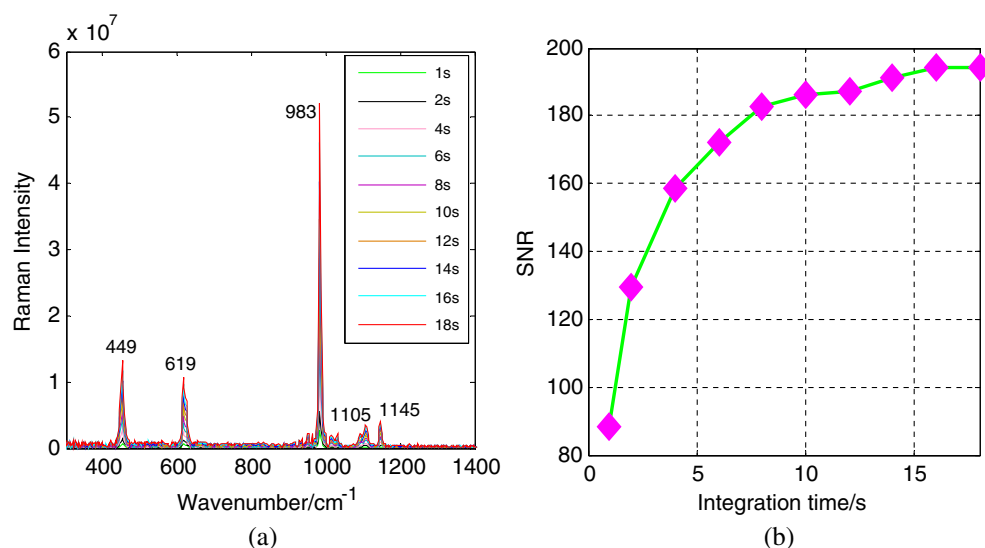


Fig. 7. (a) Spectra of K_2SO_4 at various integration times for a laser power of 126 mW. (b) SNR of 983 cm^{-1} vibration band versus integration time.

above 400 cm^{-1} . The band at 449 cm^{-1} is assigned to the doubly degenerate $E(\nu_2)$ mode; the Raman peak at 619 cm^{-1} corresponds to the triply degenerate $F_2(\nu_4)$ mode. A totally symmetrical mode is centered at 983 cm^{-1} and is an $A_1(\nu_1)$ mode. The two weak bands at 1105 cm^{-1} and 1145 cm^{-1} are attributed to the ν_3 mode, and the triply degenerate ν_3 (1105 cm^{-1}) mode belongs to the F_2 symmetry species [25,26].

The Raman vibration bands of K_2SO_4 are obvious, and the intensities of these bands increase with increasing integration time from 1 s to 18 s, but this does not mean that a longer integration time leads to a better detection effect. Figure 7(b) shows the SNR of K_2SO_4 at 983 cm^{-1} for various integration times at the same laser power of 126 mW. In Fig. 7(b), we see that the SNR grows rapidly in the [1 s, 4 s] range; within the range of [6 s, 18 s], the SNR growth is not obvious, or even stops growing at some integration times. Slight fluctuations occur during the period; this is attributed to increases in the integral time, and the noise conditions in the experiment will also vary under the influence of ambient light, fluorescence, or other stray light. The SNR plot is similar to a square-root function, which coincides with Eq. (8).

The Raman spectrum and SNR analysis of TiO_2 and K_2SO_4 described above show that multi-grating SHRS has the detection capability for inorganic powders, which is promising for environmental monitoring applications.

C. Raman Spectra of Ethanol and Methanol in Different Containers

Figure 8(a) shows the Raman spectra of ethanol samples that were contained in plastic bags or a plastic bottle with different thicknesses. Both the plastic bags and the bottle were made from polyethylene (PE). All spectra were measured at a laser power of 180 mW using an integration time of 4 s. While the samples were in different containers, the Raman peaks of the ethanol were detected well, and the ethanol spectrum in the 0.02 mm thick plastic bag was specially magnified to

show that multi-grating SHRS clearly detected the five weak vibration modes in the lower-frequency region. The bands at 884 cm^{-1} and 1051 cm^{-1} were assigned to the stretching of the $-CCO$ and $-CO$ groups, respectively. The deformation vibration of $-CCO$ appears at 1094 cm^{-1} . The two bands appearing at 1282 cm^{-1} and 1453 cm^{-1} were assigned to the deformation modes of the $-CH_2$ and $-CH_3$ groups, respectively. The band at 2880 cm^{-1} contains both the symmetric stretching contributions of the $-CH_2$ and $-CH_3$ groups [27]. The bands at 2931 cm^{-1} and 2978 cm^{-1} were attributed to the antisymmetric stretching modes of $-CH_2$ and $-CH_3$, respectively. The last three bands are very obvious, which is why researchers commonly use them to analyze the characteristics of ethanol [28,29]. The intensity of the signal from the ethanol that was stored in plastic bags with a thickness of 0.1 mm was slightly lower than that from the ethanol in the plastic bags with a thickness of 0.02 mm, and the spectrum of ethanol when stored in a 0.2 mm thick glass bottle showed greater fluorescence interference than that in the plastic bags. There is almost no spectral resolution difference among these three spectra.

The yellow and cyan curves in Fig. 8(b) show the Raman spectra of methanol in plastic and glass bottles under condition of a laser power of 270 mW and an integration time of 3 s. The purple curve represents the spectrum of methanol in a glass bottle at a laser power of 90 mW and an integration time of 5 s. The plastic bottle is 0.6 mm thick, while the transparent glass bottle is 1 mm thick. The inset shows an enlarged view of the [800 cm^{-1} , 1600 cm^{-1}] range and shows two weak bands at 1037 cm^{-1} and 1453 cm^{-1} that belong to the $-CO$ stretching vibration mode and the $-CH_3$ deformation vibration mode, respectively. The two main methanol peaks at 2835 cm^{-1} and 2945 cm^{-1} were assigned to the symmetric and antisymmetric stretching vibration modes of the $-CH_3$ group, respectively [30]. Comparison of the yellow and cyan spectra of methanol shows that there are no significant differences between the two spectra under the same laser power and integration time conditions. An obvious broadband fluorescence

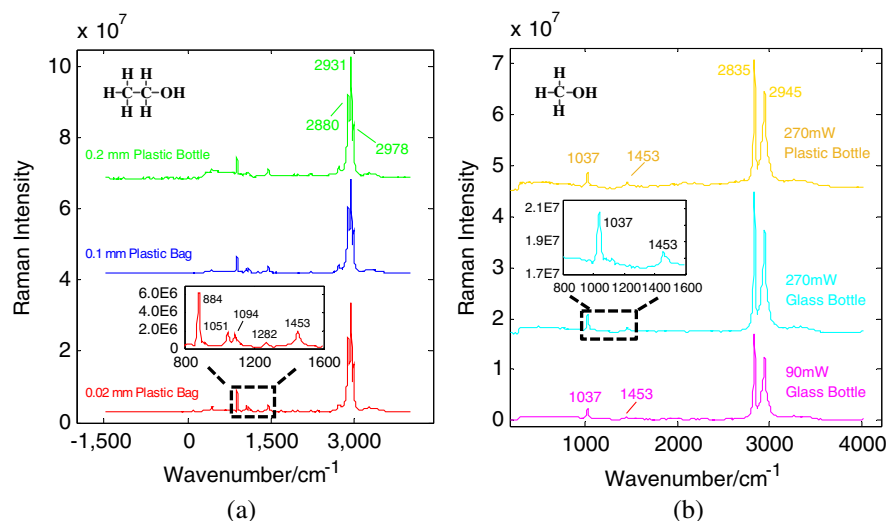


Fig. 8. (a) Spectra of ethanol stored in plastic containers of various thicknesses at a laser power of 180 mW and an integration time of 4 s. (b) Raman spectra of methanol in different types of bottles at a laser power of 270 mW and an integration time of 3 s and the spectrum of methanol in a glass bottle at a laser power of 90 mW and an integration time of 5 s.

background that was added to the spectrum is detected for the methanol that was contained in the plastic bottle, but the Raman peaks remain strong enough to be recognized. When the laser power is reduced to 90 mW, the weak bands occurring at 1037 cm^{-1} and 1453 cm^{-1} can still be detected, even though the spectral intensity decreases.

The results of these methanol and ethanol detection experiments indicate that multi-grating SHRS is capable of detecting Raman spectra of targets stored in plastic bags, plastic bottles, and glass bottles, and that it is also suitable for target Raman detection in transparent vessels of various thicknesses. This is very helpful for use in the detection of hazardous chemicals that have been sealed in transparent containers.

D. Raman Detection of Mixture of Organic Solutions and Inorganic Powders

Figure 9(a) shows Raman spectra of three organic solutions (CCl_4 , cyclohexane and acetone) that were measured under the same experimental conditions (laser power: 108 mW; integration time: 2 s). The vibrational bands of the three organic solutions overlap individually, but they are mostly distinct from each other, so they represent an ideal selection of experimental organic samples. In the Raman spectrum (red curve) of acetone, eight characteristic peaks can be measured. A few of the lines, such as those at 1066 cm^{-1} , 1220 cm^{-1} , 1428 cm^{-1} , and 1707 cm^{-1} , are weaker than the other spectral lines, but can still be distinguished clearly. The cyan spectrum shows that seven vibrational bands of cyclohexane were detected; each of these bands is very obvious, and the entire distribution of the spectrum is similar to that of acetone. Five CCl_4 peaks are detected in the lower frequency range. The first three Raman bands of the spectrum of the mixture (blue curve) are consistent with CCl_4 , while the 762 cm^{-1} and 790 cm^{-1} spectral lines of CCl_4 overlap with the 803 cm^{-1} line of cyclohexane and the 786 cm^{-1} line of acetone. The detection of characteristic peaks at 1029 cm^{-1} , 1267 cm^{-1} , 2853 cm^{-1} ,

and 2938 cm^{-1} indicates that cyclohexane is present in the mixture solution, in which the 1446 cm^{-1} and 2923 cm^{-1} peaks of cyclohexane overlap with the 1428 cm^{-1} and 2918 cm^{-1} peaks of acetone. The 1066 cm^{-1} , 1707 cm^{-1} , and 3001 cm^{-1} spectral lines in the Raman spectrum of the mixture are relatively weak, but they are all independently detected to reveal the existence of acetone in the mixture.

Figure 9(b) shows Raman spectra of three inorganic solid powders (CaCO_3 , Na_2SO_4 and K_2SO_4) detected at a laser power of 90 mW with an integration time of 15 s. The spectrum of the mixture of these powders is detected at a laser power of 270 mW and an integration time of 10 s. The red spectrum shows that the five Raman peaks of K_2SO_4 can be isolated with high intensity. The Na_2SO_4 Raman spectrum (cyan curve) contains nine characteristic peaks, where the spectral lines are close together and the distribution is relatively dense. The three vibrational bands of CaCO_3 are spaced farther apart from each other, and the peak position of the spectrum (green curve) differs significantly from those of the other two samples. With increasing laser energy and integration time, the noise interference in the Raman spectrum of the mixture is enhanced, which means that some of the weak spectral lines are not above the noise, but the main Raman peaks of each inorganic solid powder can also be distinguished well in the spectrum of the mixture.

Taking CCl_4 and acetone as suitable examples from the measurements above, their raw Raman interferograms corresponding to the results in Fig. 9(a) are shown in Fig. 10. The dominant Raman peaks of CCl_4 and acetone belong to the 150 gr/mm and 130 gr/mm grating measurement ranges, respectively, so the interference fringes of these substances appear in different half-zones. The experiments demonstrated that multi-grating SHRS not only has wide spectral range to meet the requirements of detection, but also has the ability to detect mixtures with high resolution. If the instrument requires a wider spectral range and higher resolution, the multi-grating module can be operated with additional sub-gratings.

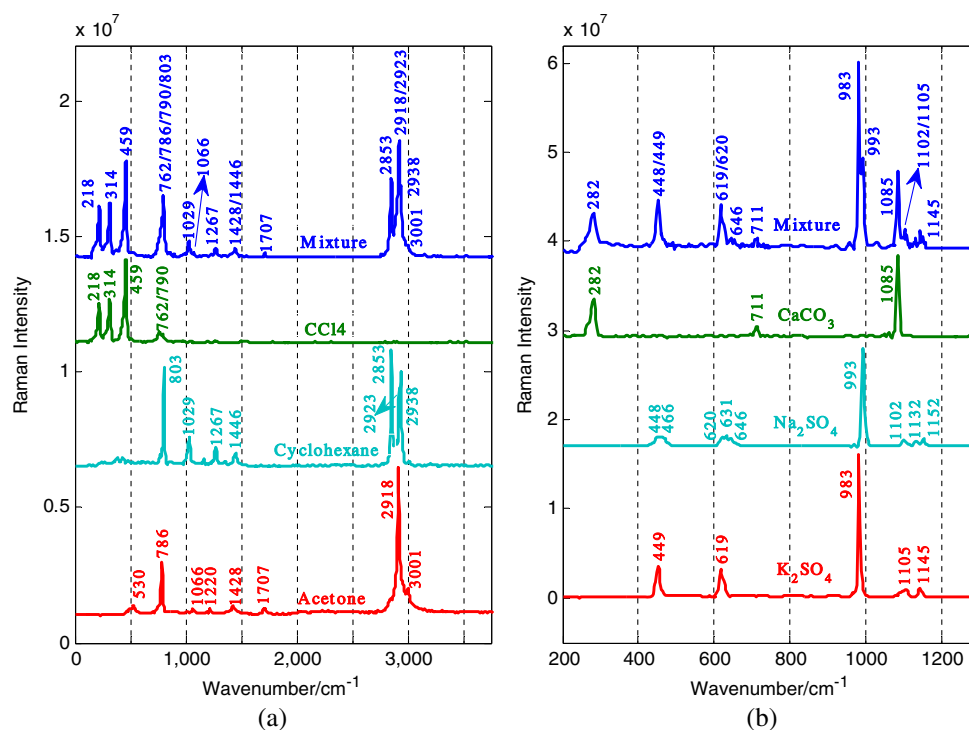


Fig. 9. (a) Raman spectra of organic solutions at a laser power of 108 mW and an integration time of 2 s. (b) Raman spectra of pure inorganic solid powders at a laser power of 90 mW and an integration time of 15 s; and the spectrum of the mixture at a laser power of 270 mW and an integration time of 10 s.

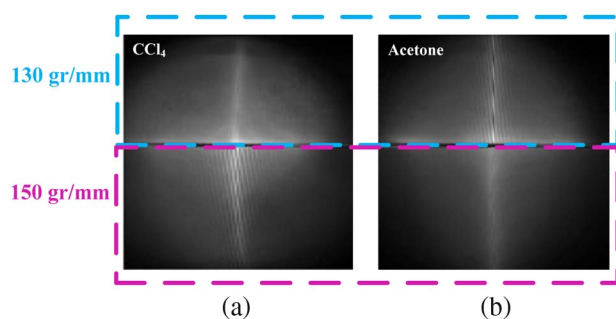


Fig. 10. Raw interferograms of (a) CCl₄ and (b) acetone, corresponding to Fig. 9(a).

E. Raman Spectra of Minerals

To examine the natural target detection capability of multi-grating SHRS, three natural stones (rose quartz, celestine, and calcite) were tested. The laser energies and integration times used to detect the clear Raman spectrum of each stone were different. Figure 11 shows Raman spectra of the three stones; the compositions of the stone samples differ from each other, so their characteristic Raman lines are dramatically different. For example, calcite is an important polymorph of CaCO₃. The two low-frequency E_g modes at 155 cm⁻¹ and 282 cm⁻¹ correspond to the out-of-phase and in-phase vibrations of the carbonate ions, respectively. Vibrations with frequencies in the 700–900 cm⁻¹ range correspond mainly to the bending I modes of the carbonate ions; the E_g mode (711 cm⁻¹)

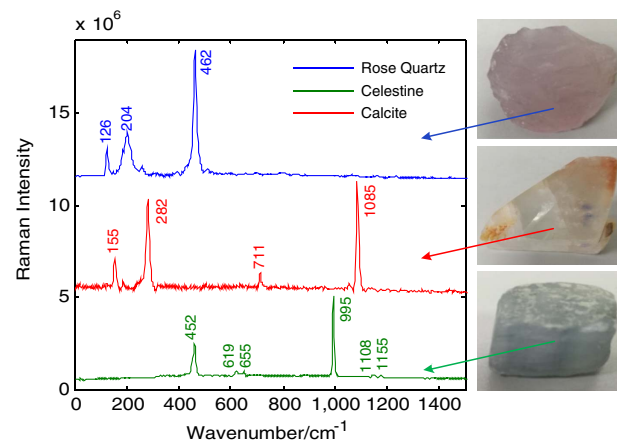


Fig. 11. Raman spectra of three minerals: rose quartz, at a laser power of 126 mW with an integration time of 20 s; calcite, at a laser power of 72 mW with an integration time of 6 s; and celestine, at a laser power of 54 mW with an integration time of 15 s.

represents the in-plane deformation of the planar CO₃ units. The band at 1085 cm⁻¹ was attributed to the symmetrical (A_{1g}) stretching I mode of the carbonate [31].

Because the surfaces of the stones are irregular and contain crevices, despite multiple cleaning cycles, small amounts of composition-unknown pollutants are still attached to the stones. Therefore, the Raman spectrum will also contain fluorescence noise. Under these conditions, the Raman spectra of

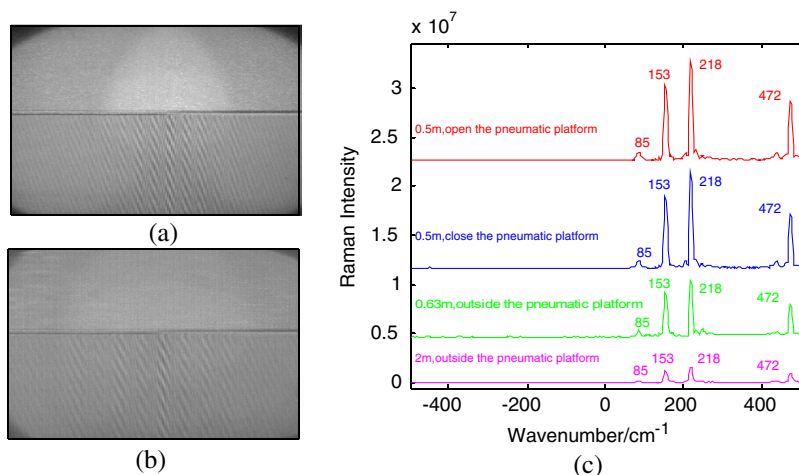


Fig. 12. Standoff Raman detection of sulfur: (a) raw interferogram from a distance of 0.5 m; (b) raw interferogram from a distance of 2 m; and (c) recovered spectra of sulfur on the platform (with open or closed pneumatic platform) and outside the platform.

rose quartz, celestine, and calcite are detected well, which indicates that multi-grating SHRS is promising for geological exploration applications.

F. Standoff Raman Detection of Sulfur

Figure 12 shows the detected interferograms for sulfur obtained from distances of approximately (a) 0.5 m or (b) 2 m, along with (c) the recovered standoff spectra of sulfur on the platform (with an open or closed pneumatic platform) and outside the platform. The pneumatic platform has an excellent vibration isolation function to avoid the influence of external vibration interference on the system. The experiments on standoff Raman detection of sulfur were all carried out under identical conditions of a laser power of 180 mW and an integration time of 1 s. The characteristic Raman peaks of sulfur are within the measurement range of the 150 gr/mm grating, so the corresponding interference fringes appear in the lower halves of Figs. 12(a) and 12(b). Obviously, the interference fringe in Fig. 12(a) is clearer than that in (b). This is because the collimation lens shown in Fig. 2 is removed, and no telescope or converging optics was used during the experiments. Only part of the backscattered light can enter the system, so a longer measurement distance corresponds to a smaller angle from which the backscattered light can be collected, and thus the intensity of the resulting interferogram becomes weaker.

In Fig. 12(c), the dominant vibrational lines present in the spectrum of sulfur are characteristic of the S_8 molecule and are assigned to the ν_9 symmetry [32,33] mode (85 cm⁻¹), the anti-symmetric bond-bending mode (153 cm⁻¹), the symmetric bond-bending mode (218 cm⁻¹), and the symmetric bond-stretching mode (472 cm⁻¹) [34]. The sample is fixed at a distance of 0.5 m. There is almost no difference between the intensities of the sulfur Raman spectra measured when the pneumatic platform is open (red spectrum) and when the pneumatic platform is closed (blue spectrum) when the sample is fixed at 0.5 m; then, when the sample is placed on a simple wooden table outside the pneumatic platform (distance: 0.65 m), the spectral intensity (green spectrum) is reduced, but the characteristic peaks are still obvious. These

results thus indicate that the multi-grating SHRS has good resistance to environmental interference. Finally, even when the detection distance is adjusted to 2 m, the characteristic peaks could still be recognized from the spectrum (purple spectrum). There are almost no spectral resolution differences among the four recovered spectra. The results of the sulfur experiments show that multi-grating SHRS not only has the ability to resist small vibrations within the environment, but it also provides a standoff detection capability, which is helpful for long-distance examination of explosives and in industrial applications.

5. CONCLUSION

In this paper, we proposed a multi-grating SHRS technique with a broad spectral range and high resolution, which is equivalent to using multiple, conventional interferometers, stacked on top of each other, while the multiple mosaic sub-gratings result in a compact form of these stacked interferometers. In multi-grating SHRS, the multi-grating module is used to replace the single grating used to terminate each arm in traditional SHS, and the mutual limitation between the spectral range and the resolution can be broken only by increasing the number of mosaicked sub-gratings used in the module to satisfy the Raman detection requirements.

Using 130 gr/mm and 150 gr/mm sub-gratings, which were mosaicked into a multi-grating module, a verification system was built to prove the principle and detection capability of multi-grating SHRS. From the experimental results (based on detection of CCl₄, MS, TiO₂, and K₂SO₄), we see that the system has the ability to detect the Raman spectrum of organic solutions and inorganic powders. Then, multi-grating SHRS was used to detect and compare the Raman spectra of methanol and ethanol in containers with different thicknesses (including PE plastic bags, a PE plastic bottle, and a glass bottle); the results indicate that the technique will be very helpful in the detection of hazardous chemicals sealed in transparent containers that cannot be opened. Additionally, mixtures of organic solutions and inorganic powders were tested and proved that multi-grating SHRS not only meets the broad Raman

spectral range detection requirements but also that the method is able to measure mixtures with high resolution. The Raman spectra of rocks (rose quartz, celestine, and calcite) were also detected, thus indicating that multi-grating SHRS is suitable for measurement of minerals. Sulfur detection experiments showed that multi-grating SHRS is suitable for standoff Raman detection of samples. Overall, multi-grating SHRS can achieve broad spectral coverage and high-resolution Raman detection simultaneously, which makes it suitable for a wide range of application fields.

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