

Development of a spatial heterodyne Raman spectrometer with echelle-mirror structure

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Abstract: Spatial heterodyne Raman spectroscopy is a spectroscopic detection technique that is particularly suitable for Raman measurements. The spectral range of traditional spatial heterodyne Raman spectrometer (SHRS) is limited by its spectral resolution and the number of detector elements. We propose an SHRS with an echelle-mirror structure that employs multiple diffraction orders to achieve a broad spectral coverage and high spectral resolution simultaneously. This SHRS is used to obtain the Raman spectra of organic liquids, inorganic solid targets, and mixed targets. Observations of aqueous solutions, and minerals are presented. In addition, anti-Stokes Raman shifts are also presented. The proposed SHRS technique shows good performance for broadband, high-resolution Raman measurements.

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1. Introduction

Raman spectroscopy is popular in material identification and analysis applications because it is nondestructive, requires no sample preparation, and allows for both organic and inorganic substances to be measured in a variety of states. Given these advantages, Raman spectroscopy has already been applied in numerous fields, including physics [1,2], chemistry [3,4], biology [5,6], medicine [7,8], geology [9,10] and semiconductor technology [11]. The spatial heterodyne Raman spectrometer (SHRS) offers multiple advantages, including a large aperture, high light throughput, in a compact, rugged package without moving parts, and compatibility with both pulsed lasers and gated detectors [12]. The combination of these characteristics makes the SHRS highly suitable for Raman measurements.

The SHRS has been proven to be a very promising and useful technique for Raman experiments. Gomer et. al outlined the proof of concept for an SHRS to perform Raman measurements [13]; Foster et. al developed a standoff SHRS to make in situ observations of liquid samples to rapidly identify xylene, monoethylene glycol, triethylene glycol, methanol and compressor oil within a gas pipeline [14], while another SHRS was used to conduct transmission Raman measurements on paracetamol tablet samples [15]; Hu et. al showed that an SHRS has the ability to investigate the liquid and solid targets [16,] and to obtain two-dimensional (2-D) spectra of analytes in containers [17] and the standoff Raman spectra of chemical warfare agents and simulants [18]; Egan et. al proved that the SHRS can be used for Raman measurements to unambiguously identify minerals, organic compounds and biomarkers [19]. However, the SHRS systems mentioned above are hard to satisfy the requirements of broadband pass and high spectral resolution simultaneously. If a high spectral resolution of 2.47 cm⁻¹ is needed and the number of detector elements in the spectral dimension is 1024, a bandpass of only 1262.8 cm⁻¹ can be obtained [19]. If a broad bandpass of 4488 cm⁻¹ is

required and the number of pixels is 1360, the spectral resolution is only 7.3 cm⁻¹ [20]. In a traditional SHRS system, there is the inverse relationship between the bandpass and spectral resolution. However, in many fields, there is the need for instruments with high spectral resolution and broadband coverage to perform Raman measurements. As a related technique, a two echelle gratings structure [12] can be used in the absorbed spectrum technique. To remove the shadow ghosts caused by the different orders of the two echelle gratings, a rotating mask can be used and two CCD frames should be taken for a complete spectrum. However, the results showed that shadow ghosts were still observed [21].

In this paper, we describe the design and performance of a broadband, high-resolution Echelle grating-Mirror SHRS (EMSHRS). The proposed EMSHRS is based on a Michelson interferometer, which is modified by replacing the mirror in one arm with an echelle grating. This system takes advantage of the multiple diffraction orders and high diffraction efficiency of the echelle grating to obtain a broad spectral range without the need for a mixture of the different orders. In this study, the fundamental principles and the calibration results of the EMSHRS are given. Raman spectroscopy of organic liquids, inorganic solids and mixtures of targets using different diffraction orders are discussed in detail. The results from investigations of aqueous solutions, minerals and anti-Stokes Raman shifts are also presented.

2. Theoretical

2.1 Basic theory

The design of the EMSHRS instrument produced is given in Fig. 1. The optical structure between beam splitter 1 and the dichroic beam splitter is convenient for the precise alignment of the Littrow angle of the grating, to produce backscatter and transmission Raman light at the same time, and to ensure that the intersection points of laser beam and the sample are always in the optical axis of the EMSHRS. Raman signal can always be detected even the sample is not at the focus of the collimation lens. The laser beam, after passing through the linear variable filter and the clean-up filter, is split into two beams using beam splitter 1. After being reflected by mirror 1, such that the angle between the laser and the 532 nm razor edge dichroic is 45° , the excitation light is then focused on the sample to produce backscatter Raman light. The laser beam which passes to mirror 2 can be used to produce transmission Raman light. The Raman scattered light is collimated using the collimation lens and the Rayleigh scattered light is filtered using a Raman edge filter or a notch filter. The filtered light then enters beam splitter 2 and is split into two beams. The separated light beams arrive at the echelle grating and the plane mirror, and the generation of the off-Littrow angle γ , which is related to the wavenumber, is determined using the grating equation:

$$\sigma(\sin\theta_L + \sin(\theta_L - \gamma)) = mG \tag{1}$$

where σ is the wavenumber of the incident light, *m* is the order of diffraction, θ_L is the Littrow angle, and *G* is the grating groove density. For a small γ , the generation of the spatial frequency of fringes is related to the wavenumber by the equation:

$$f_{x} = \sigma \sin \gamma = 2(\sigma - \sigma_{L}) \tan \theta_{L}$$
⁽²⁾

To separate the echelle grating orders and avoid spectral overlap, the echelle grating was rotated by an angle $\alpha/2$ about the *x*-axis to produce a 2-D interferogram. These fringes are recorded onto the charge-coupled device (CCD), and the intensity of the interferogram can be written as:

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



where $B(\sigma)$ is the input spectral intensity as a function of wavenumber, and *x* is measured on the detector in the dispersion plane of the echelle grating. The inverse Fourier transform of the interferogram yielded the Raman spectrum.



Fig. 1. Spatial heterodyne Raman spectrometer system layout for Raman measurements.

The maximum theoretical resolving power of the EMSHRS is equal to the theoretical resolving power of the echelle grating, which is given by:

$$R = \frac{\sigma}{\delta_{\sigma}} = 2W\sigma\sin\theta_L \tag{4}$$

where W is the width of the echelle grating, and δ_{σ} is the spectral resolution.

In the EMSHRS configuration, the spectral range of each individual order is limited by the number of horizontal axis pixels on the detector. If the detector has *N* pixels on the *x*-axis, the spectral range of one diffraction order is represented by the following equation:

$$\Delta \sigma = \frac{N}{2} \delta_{\sigma} \tag{5}$$

From Eq. (5), we can see that the spectral range of a given diffraction order is determined by the number of pixels N and the spectral resolution δ_{σ} . For Raman measurements which require a large band pass and high resolution, the EMSHRS can be chosen to work in multiple diffraction orders. If the total number of diffraction orders used in the EMSHRS is M ($M \ge 1$), the spectral range can be expressed as:

$$\Delta \sigma_{M} = \frac{MN}{2} \delta_{\sigma} = \frac{MN}{4W \sin \theta_{I}} \tag{6}$$

From Eq. (6), we can see that if the resolution limit δ_{σ} is given, the total spectral range $\Delta \sigma_M$ can be easily improved by increasing total diffraction orders number M; similarly, if the total spectral range $\Delta \sigma_M$ is given, the resolution limit δ_{σ} can also be largely improved by increasing total the total number of diffraction orders M.

2.2 Calibration theory

The echelle grating has a designed Littrow angle. During the alignment of the EMSHRS, the incident angle of the echelle grating needs to be adjusted to be very near to the designed Littrow angle. Then, the echelle grating is rotated by a small angle about the *x*-axis to produce a 2-D interferogram. After the 2-D Fourier transform, the different orders of the echelle grating are

separated in the f_y dimension. The real spectral positions of different orders in the f_y axis can be determined by the 2-D interferogram of the Raman laser. First, the sample, notch filter, and RazorEdge filter should be removed from the optical structure shown in Fig. 1. A beam expander should be added at the position of the sample, and then the interferogram of the laser can be obtained. Assuming the off-Littrow angle γ is zero, the diffraction order k of the laser wavelength can be acquired by Eq. (7), as follows:

$$m = 2\sigma_L \sin \theta_L / G \tag{7}$$

After the 2-D Fourier transform of the laser interferogram, the spectral positions of the k^{th} order can be determined. If we assume the number of pixels between the laser spectrum position and pattern center in the f_y dimension is n_y , then the number of pixels of the adjacent orders in the f_y dimension is also equal to n_y . Generally, n_y should be large enough to avoid cross contamination between adjacent orders.

The calibration procedure is based on the two known spectral wavelengths from standard source, such as the mercury lamp, and the two wavelengths should belong to the spectral range of the same diffraction order. Then, the Littrow wavelength of EMSHRS can be expressed as [22]:

$$\lambda_{L,k} = \frac{f_2 - f_1}{(f_2 / \lambda_1) - (f_1 / \lambda_2)}, k = m, m - 1, m - 2..., k \ge 1$$
(8)

where λ_1 and λ_2 are the known wavelengths of the calibration source, and f_1 and f_2 are the measured fringe frequencies of the two known emission lines. The spectral region belonging to higher orders k (k > m) is not needed and can be blocked by the RazorEdge filter. When the grating groove density G is assumed, the Littrow angle of the echelle grating is given by Eq. (9), as follows:

$$\theta_{L} = \arcsin(\frac{k\lambda_{L,k}G}{2}), k = m, m-1, m-2..., k \ge 1$$
(9)

After the Littrow angle is calibrated, the Littrow wavenumber of the k^{th} diffraction order can be expressed as:

$$\sigma_{L,k} = \frac{kG}{2\sin\theta_L}, k = m, m-1, m-2..., k \ge 1$$
(10)

The spectral resolution of the EMSHRS after calibration can be written as:

$$\delta_{\sigma} = \frac{(1/\lambda_1 - 1/\lambda_2)}{f_1 - f_2} \tag{11}$$

According to Eqs. (4), (9) and (11), the width of the grating can be calculated by:

$$W = \frac{1}{2\delta_{\sigma}\sin\theta_{L}} \tag{12}$$

After the grating width is acquired from Eq. (12), the spectral range of each order and total used orders can be separately computed using Eqs. (5) and (6).

3. Experimental

3.1 Breadboard

Figure 2 shows the layout of the experimental breadboard. The main components used for our experimental breadboard were all commercial off-the-shelf products, and their main parameters are listed in Table 1. The EMSHRS was constructed using a 50.8 mm cube beam splitter (model no. 20BC17MB.1, Newport), one 79 grooves/mm echelle grating and an aluminized plane mirror (Changchun Institute of Optics, Fine Mechanics and Physics, Chinese

Academy of Sciences). The optical flat of plane mirror was better than $\lambda/10$ (peak-to-valley) at a wavelength of 632.8nm. The power of the solid state 532 nm green laser (Changchun New Industries Optoelectronics Tech. Co., Ltd.) was linearly variable from 0 to 400 mW. A circular aperture was included in the imaging optics to block the unwanted light.



Fig. 2. Layout of EMSHRS breadboard instrumentation.

Components	Parameters	Performance index
Laser	Wavelength	532 nm, CW
	Beam diameter (1/e, mm)	~2.0
	Beam divergence	<1.5(full angle, mrad)
	Groove density	79 gr/mm
Echelle grating	Ruled area	$13.1 \times 25 \text{ mm}^2$
	Littrow angle	20.93°
Plane mirror	Size	$25 \times 25 \text{ mm}^2$
Beam splitter 2	Size	$50.8 \times 50.8 \times 50.8 \text{ mm}^3$
	Pixel numbers	1024×1024
CCD	Sensor size	$13.3 \times 13.3 \text{ nm}^2$
	Pixel size	$13 \times 13 \ \mu m^2$
Laser clean-up filter	Center wavelength	532 nm
	FWHM Banwidth	2.0 nm
532 nm Razor Edge	Edge wavelength	536.4 nm
long-pass edge Filter	Transition width	186 cm^{-1}
	Blocking band	OD _{abs} >6@532 nm
532 nm Razor Edge	Edge wavelength	537.2 nm
Dichroic laser-flat	Transition width	186 cm^{-1}
Beamsplitter		
532 nm single- notch	Notch band	17 nm
Filter	Blocking band	OD _{abs} >6@532 nm
700 nm Short pass	Cut-off wavelength	700 nm
Filter	Optical density	≥4
Imaging optics	Diameter	62 mm
	Focal length	105 mm

Table 1. Key Parameters of Components Used in the Experimental Breadboard

In the experiments, the sample was placed on the focal plane of a 25-mm-diameter collimation lens at a distance of approximately 30 mm from the 532 nm razor edge dichroic laser-flat beam splitter. The angle between the dichroic beam splitter and the optical axis was 135°, which meant that the dichroic beam splitter reflected the laser line while efficiently transmitting the Raman-shifted wavelengths. A 532 nm razor-edge, long-pass filter (LP03-532RU-25, Semrock) was used to filter out the stray laser light and the Rayleigh-scattered light. The ambient light and fluorescent light at wavelengths higher than 700 nm were filtered out using a 700 nm short-pass filter (84-714, Edmund). In some cases, another 532 nm notch filter (NF01-532U-25, Semrock) was used for laser line rejection. A

CCD detector with $1024 \times 1024 13 \ \mu\text{m}$ pixels (iKon-M 934, Andor) was used to record the fringe image. The CCD was cooled to -60° C to reduce the thermal noise within the sensor chip. The echelle grating and the mirror were blocked separately to correct the background of the fringe image. The spectra were collected and then the Fourier transforms of the fringe images were performed using a 2-D fast Fourier transform (FFT) function. The wavelet threshold de-noising function was then used to effectively separate the signal from the noise [23].

3.2 Calibration

We used a mercury lamp to perform the calibration. The two known emission lines of mercury lamps are 576.961 nm and 579.067 nm. A 578 nm narrow band-pass filter was used to filter out any other emission lines. The raw interferogram of the mercury lamp (a), the raw spatial frequency profile of the mercury lamp (b), and the mercury lamp spectrum acquired using EMSHRS (c) are shown in Fig. 3.



Fig. 3. (a) Raw interferogram of the mercury lamp. (b) Spatial frequency profile obtained from the FFT. (c) Mercury lamp spectrum as measured after calibration; the absolute line positions are 576.961 nm and 579.067 nm.

From Figs. 3(b) and 3(c), we see that the 577.083 nm line produced 113 fringes and the 579.161 nm line produced 173 fringes. Based on Eqs. (5) and (9), the Littrow wavelength was calculated to be 565.344 nm, which corresponds to an echelle grating angle of 20.934° . The spectral range was from 648.8 cm⁻¹ to 1720.5 cm⁻¹ only using the 16th diffraction order. The width of the grating that was imaged on the detector was estimated to be 12.45 mm, and the spectral resolution was 1.051 cm^{-1} . The breadboard experimental results proved that the calibration results were close to the designed EMSHRS performance. The full width at half maximum (FWHM) at 576.083 nm was about 2.61 cm⁻¹. This result was in almost exact agreement with the theoretical spectral resolution.

4. Results and discussions

4.1 Raman spectra of carbon tetrachloride (CCl₄), sulfur and other artificial targets contained in bottles

Figure 4 shows the raw interferograms for carbon tetrachloride (a) and sulfur (b) acquired at a laser power of 108 mW with an integration time of 15 s and at a laser power of 90 mW with an integration time of 5 s, respectively; the recovered Raman spectra of carbon tetrachloride are shown (c) for two different laser powers of 108 mW and 36 mW at the same integration time of 10 s, and the recovered Raman spectra are also shown for sublimed sulfur and powder sulfur contained in glass or plastic bottles (d) at a laser power of 108 mW with an integration time of 5 s.



Fig. 4. (a) Raw interferogram of CCl_4 at a laser power of 108 mW with an integration time of 15s. (b) Raw interferogram of sulfur at a laser power of 90 mW with an integration time of 5 s. (c) Recovered Raman spectra of CCl_4 at a laser powers of 108 mW and 36 mW with the same integration time of 15 s. (d) Recovered Raman spectra of sublimed sulfur and powder sulfur in a glass or plastic bottle at a laser power of 90 mW with an integration time of 5 s.

From the Raman spectra of CCl₄ shown in Fig. 4(c) at 196 mW, the degenerate deformation (T_2) and the symmetric stretching vibrational modes (A_1) were clearly visible at 314 cm⁻¹ and 459 cm⁻¹, respectively. The third band at 762 cm⁻¹ was assigned to the combination mode $T_2 + A_1$. The fourth band at 790 cm⁻¹ was assigned to the mode T_1 [24]. Observation was also made at 36 mW, where all peaks were still visible including the weak 762 cm⁻¹ band and the 790 cm⁻¹ band. Thus all features could be identified. We thus see that the EMSHRS has excellent sensitivity. To quantify the performance of the EMSHRS here, the signal-to-noise ratio (SNR) for the measurement of the Raman spectrum is defined as follows:

$$SNR = \frac{I_{peak_signal}}{RMS_{Noise}}$$
(13)

where $I_{\text{peak}_\text{signal}}$ is the amplitude at the Raman peak, and *RMS* _{Noise} is the root-mean-square (RMS) value of the noise in the spectrum. The CCl₄ spectra after 2-D FFT processing are shown in Fig. 4(c), and the measured SNRs at the two different laser powers of 108 mW and 36 mW with the same integration time of 10 s were 623 and 105 after denoising. The SNR of the raw data at 108 mW with an integration time of 15 s was 589.

In Fig. 4(d), clearly identifiable Raman peaks were observed for both sublimed sulfur and powder sulfur when contained in a glass bottle or a plastic bottle at the same laser power of 90 mW with an integration time of 5 s. The thickness of the glass bottle is approximately 1.5 mm, while the thickness of the plastic bottle was approximately 2 mm. There were nearly no differences in the spectral resolution among the three spectra shown in Fig. 4(d). However, the SNR decreased as a result of the reflection of the laser light or the fluorescence of the plastic

bottle. The measured SNRs of sublimed sulfur and powder sulfur when contained in a glass bottle or a plastic bottle were 171,161 and 138. The Raman peaks observed at 154 cm⁻¹ and 219 cm⁻¹ were assigned to the antisymmetric and symmetric bond-bending modes of the S_8 molecule, respectively. The symmetric bond-stretching mode of sulfur appears at 473 cm⁻¹ and thus the peak at 85 cm⁻¹ was attributed to the other vibration mode [25].



Fig. 5. (a) Recovered Raman spectra of $NaSO_4$ at a laser power of 135 mW with an integration time of 2 s in a glass bottle. (b) Recovered Raman spectra of p-xylene in a plastic bottle at a laser power of 54 mW with an integration time of 8 s.

Figure 5(a) shows the Raman spectrum of solid sodium sulfate (Na₂SO₄) contained in a glass bottle at a laser power of 135 mW with an integration time of 2 s. The main peak corresponded to the $v_1(A_1)$ mode centered at 1105 cm⁻¹. The v_2 (449 cm⁻¹), v_4 (647 cm⁻¹), and v_3 (1151 cm⁻¹) modes were also detected on the low-wavenumber and in the high-wavenumber sides, respectively [26]. The measured SNR of Na₂SO₄ was 394 after denoising. The Raman spectrum of p-xylene in a bottle at the laser power of 54 mW with an integration time of 8 s is shown in Fig. 5(b), we can see the 1463 cm⁻¹ peak was produced by the vibration of atoms H₁₃, H₁₄, H₁₆, H₁₇ and H₁₈ and the stretching vibration of H₁₂, H₁₃, H₁₆, H₁₈ together with the wagging of H₁₄ and H₁₇ at 1532cm⁻¹ [27]. The measured SNR of p-xylene was 103.

This investigation of CCl₄, sulfur, Na₂SO₄, and p-xylene when contained in plastic or glass bottles showed that the EMSHRS has the ability to determine the Raman spectra of targets when contained in glass or plastic containers. This is very useful for measuring dangerous explosives or toxic chemicals that must be contained in transparent containers.

4.2 Raman spectra of potassium sulfate in solid state and in aqueous solution

From the Raman spectra obtained for powder potassium sulfate (K_2SO_4) that are shown in Fig. 6, the main Raman peak at 983 cm⁻¹ was assigned to the $v_1(A_1)$ mode. The first and second Raman peaks at 449 cm⁻¹ and 619 cm⁻¹ corresponded to the $v_2(E)$ and $v_4(F_2)$ modes, respectively. The $v_3(F_2)$ mode is centered at 1105 cm⁻¹ [26]. We compared the Raman spectra that were recorded for powder K_2SO_4 and for an aqueous solution of K_2SO_4 . The symmetric stretching v_1 , doubly degenerate v_3 , and triply degenerate v_4 vibration modes were clearly discernible in the Raman spectra of both dry K_2SO_4 and K_2SO_4 in aqueous solution. However, the degenerate v_2 mode at 449 cm⁻¹ was not observed in the aqueous solution of K_2SO_4 because this v_2 mode is resolved in water and cannot be detected using the EMSHRS. The measured SNRs of powder potassium sulfate and potassium sulfate in aqueous solution were 158 and 54. The detection capabilities of the EMSHRS demonstrated in this work are very promising for applications in geochemistry and environmental measurements.



Fig. 6. Recovered Raman spectra of potassium sulfate in the solid state and in aqueous solution at a laser power of 72 mW with the same integration time of 2 s.

4.3 Raman spectra of mixture of organic liquids and inorganic solids

Figure 7(a) shows the Raman spectra of cyclohexane, carbon tetrachloride, acetone, and a mixture of these three organic liquids. In the spectra of cyclohexane, carbon tetrachloride and acetone, the main Raman peaks were well detected. Because of the difference intensities of the three organic liquids, the 1267 cm⁻¹, 1446 cm⁻¹, 2853 cm⁻¹, and 2923 cm⁻¹ peak of cyclohexane, the 459cm⁻¹ peak of carbon tetrachloride, and the 786cm⁻¹, 1707cm⁻¹, and 2918 cm⁻¹ peak of acetone, could be distinguished in the Raman spectral of the mixture of the three organic liquids. The SNRs were between 130 and 473.

Figure 7(b) shows the Raman spectra of sulfur, titanium dioxide and potassium sulfate. In the Raman spectra of the pure solids, the Raman peaks were clearly visible. The main Raman peaks of the pure solids can also visible in the Raman spectrum of the mixture of three solids. The SNRs were between 87 and 238.

Figure 7(c) shows the distribution of the spatial frequency of cyclohexane, Using the point in the center of Fig. 7(c) as the relative intensity of $(f_x, f_y) = (0,0)$, from the left to right in the pink textbox, we could clearly recognize the Raman peaks at 803 cm⁻¹, 1029 cm⁻¹,1267 cm⁻¹,1446 cm⁻¹, 2853 cm⁻¹, 2918 cm⁻¹ and 2923 cm⁻¹. The bands at 803 cm⁻¹, 1029 cm⁻¹, 1267 cm⁻¹ and 1446cm⁻¹ were in the spectral range of the 16th diffraction order, while the bands of 2853 cm⁻¹, 2918 cm⁻¹ and 2923 cm⁻¹ were in the spectral range of the 14th diffraction order.

Figure 7(d) shows the spatial frequency distributions of a mixture of the three inorganic solids: sulfur, titanium dioxide, and potassium sulfate. Using the relative intensity of the point in the center (f_x , f_y) = (0,0), from the left to right in the red textbook, we could distinguish the Raman peaks at 153 cm⁻¹, 218 cm⁻¹, 397 cm⁻¹, 449 cm⁻¹, 472 cm⁻¹, 516 cm⁻¹, 639 cm⁻¹, 983 cm⁻¹, and 1105 cm⁻¹. The bands at 472 cm⁻¹, 516 cm⁻¹, 639 cm⁻¹, and 1105 cm⁻¹ were in the spectral range of the 16th diffraction order. The bands at 153 cm⁻¹, 218 cm⁻¹, 397 cm⁻¹, and 449 cm⁻¹ were in the spectral range of the 17th diffraction order.

The data of Figs. 7(c) and 7(d) demonstrated the broad spectral coverage from the mixed inorganic solid and cyclohexane using only four diffraction orders (14,15,16,17). The presented orders could be separated, which was approximately three vertical pixels wide. If a wider spectral coverage and high resolution of SHS are needed for the Raman detection, the echelle grating will work at more diffraction orders.



Fig. 7. (a) Recovered Raman spectra of organic liquids at a laser power of 90 mW with the same integration time of 5 s. (b) Recovered Raman spectra of inorganic solids at the laser power of 108 mW with the same integration time of 10 s. (c) Spatial frequency distribution of the mixture of organic liquids. (d) Spatial frequency distribution of the mixture of inorganic solids.

4.4 Raman spectra of minerals



Fig. 8. Recovered Raman spectra of three rocks: Calcite, at a laser power of 126 mW with an integration time of 4 s. Celestine, at a laser power of 54 mW with an integration time of 20 s. and rose Quartz at a laser power of 216 mW with an integration time of 5 s.

Figure 8 shows the Raman spectra of calcite, celestine, and rose quartz. In calcite, the intense sharp Raman band at 1085 cm⁻¹ was assigned to the $v_1(CO_3)^{2-}$ symmetric stretching mode. The $v_5(CO_3)$ vibration mode and the $v_4(CO_3)$ bending mode were clearly visible at 282 cm⁻¹ and 711 cm⁻¹, respectively. The lattice mode of calcite at 155 cm⁻¹ can also be distinguished [28]. The main Raman peaks of celestine and rose quartz are also distinguished easily. The measured SNRs of calcite, celestine, and rose quartz were 146, 166, and 375. The results from these three



rocks clearly showed that the EMSHRS is capable of capturing the weak Raman signals from these minerals.

4.5 Stokes and anti-Stokes Raman detection of sulfur and carbon tetrachloride

Figure 9 shows the Stokes and anti-Stokes Raman spectra of sulfur and carbon tetrachloride that were recorded at room temperature. To test the anti-Stokes band, the edge filter was replaced with a 532 nm notch filter to limit the pass band and minimize noise. In the Stokes region, the Stokes Raman shifts at 473 cm⁻¹ for the sulfur and at 459 cm⁻¹ and 314 cm⁻¹ for CCl₄ could be seen, but the anti-Stokes band at 314 cm⁻¹ was blocked by the notch filter. However, because of the strong laser power, strong Rayleigh scattering light was detected in the Raman spectra of both sulfur and CCl₄. There is a simple way to solve this problem, where one or more additional notch filters can be used in the EMSHRS instrument.



Fig. 9. (a) Stokes and anti –Stokes Raman spectra of sulfur at a laser power of 90 mW with an integration time of 10 s. (b) Stokes and anti –Stokes Raman spectra of carbon tetrachloride at a laser power of 108 mW with an integration time of 5 s.

5. Conclusions

In this paper, a broadband, high-resolution EMSHRS breadboard has been designed and built. This instrument provides the proof of concept of a new method for broadband, high-resolution EMSHRS. The EMSHRS takes advantage of the multiple orders of the echelle grating to obtain a broad spectral range that meets the requirements of Raman detection. It is therefore more convenient to adjust the optical system of the proposed instrument.

In the experiments, the spectra of sulfur when contained in a glass bottle or a plastic bag were detected, thus proving that the EMSHRS has the capability to detect targets in containers; this may be useful where toxic targets (e.g., CCl₄, acetone) in containers should not be opened. We also demonstrated the ability of the EMSHRS to measure the Raman spectra of sulfates in two states: solid salts and aqueous solutions. The spectra of mixed targets composed of organic liquids or inorganic solids were also detected, which demonstrated that the EMSHRS not only exhibits a sufficiently broad spectral coverage to satisfy the requirement of Raman detection of targets but also has the ability to detect mixed targets with high resolution. We have also demonstrated that it is possible to measure the Raman spectra of rocks with the EMSHRS. The spectra of sulfur and CCl₄ were also detected to show that the EMSHRS has the ability to detect anti-Stokes Raman shifts and Stokes Raman shifts simultaneously. The experimental results indicate that this EMSHRS design is very promising for broadband, high-resolution Raman measurements in a wide range of applications.

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