Determination of the laser-induced damage threshold for graphite and coal with deep-UV micro-Raman spectroscopy

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A new type of compact deep-UV micro-Raman spectroscopy system was developed with a single monochromator, front-illuminated cooled charge-coupled device, and 266 nm nanosecond pulsed laser to overcome laser-induced fluorescence from surrounding minerals and organic material. Deep-UV micro-Raman spectroscopy is particularly useful in analyzing the fluorescence-free Raman spectra of dispersed low-maturity carbonaceous material and coal, although deep-UV excitation lasers may cause serious degradation and laser-induced heating of the sample surface, especially in microanalysis. The laser-induced damage threshold for fully ordered graphite and coal (VRr ≈ 0.5%) was assessed to facilitate the acquisition of accurate Raman spectra with a spot size of ~1 µm. For fully ordered graphite, there was no serious degradation of the sample surface with an energy fluence of 0.10–2.50 J cm⁻². Some sample surfaces became black at higher fluences of 1.96–2.50 J cm⁻², suggesting irreversible damage by deep-UV lasers. The Raman shift of the G band after measurement involves a downshift of 1.7–7.4 cm⁻¹ relative to other spectra obtained at low laser fluences of <0.34 J cm⁻². The G band full width at half maximum (FWHM) also increased with increasing laser fluence. Serious degradation of polished coal surfaces occurs at even lower laser fluences of 0.34–2.50 J cm⁻². The degree of change in Raman parameters such as the D and G band FWHM depends on the laser fluence during measurements. Heating and damage by a deep-UV laser is greater than that by visible lasers. Laser fluences of <0.16 and 0.34 J cm⁻² are required for accurate Raman analyses of dispersed carbonaceous material in sedimentary rocks and fully ordered graphite in metasediment, respectively.

Keywords: Deep-UV Raman spectroscopy, Graphite, Coal, Fluorescence, Laser fluence

INTRODUCTION

Micro-Raman spectroscopy is widely applied in the determination of peak metamorphic temperatures based on the crystallinity of carbonaceous material (CM) and dispersed organic matter in polished thin sections. The method is rapid and non-destructive, and it is particularly appropriate for analysis of small amounts of CM grains (<10 µm) along grain boundaries in sedimentary rocks. Wider application of micro-Raman spectroscopy has therefore been encouraged as a reliable geothermometer for elucidating the tectonic evolution of metamorphic terrains (Beyssac et al., 2004; Scharf et al., 2013; Groß et al., 2021; Nakamura et al., 2022). On the other hand, Raman intensities are 10⁻⁶ of the intensity required for laser excitation, and the Raman signal easily interferes with strong fluorescence induced by laser-excitation sources (Panczer et al., 2012). For low-maturity CM and coal, broad green to red fluorescence (520–650 nm) is excited by a mercury arc lamp and blue laser (e.g., Hackley and Kus, 2015). A strong fluorescence spectrum of organic compounds (e.g., PAH fluoranthene) excited by a 266 nm laser ranges over 420–650 nm, corresponding to the visible region (Eshelman et al., 2014). These previous studies indicate that it is impossible to avoid laser-induced fluorescence in organic samples when using a conventional micro-Raman spectroscopy system equipped with light blue (488 nm), green (532 nm), and red (633 nm) excitation lasers. Alleon et al. (2021) reported that quasi-periodic ripples derived from strong fluorescence may result in serious misinterpretation of Raman spectra of organic molecules, especially in fossil and biological samples. Fluorescence-free and novel Raman techniques such as time-gated and surface-enhanced Raman spectroscopy are therefore required for Earth and planetary sciences.
A new type of micro–Raman spectroscopy system using near-infrared (NIR; 1064 nm) and deep-UV (244–266 nm) lasers has recently become available, with the advantage that it avoids laser-induced fluorescence in biological and mineral samples (e.g., Tarcea et al., 2007; Eshelman et al., 2014). Raman intensity is proportional to the excitation wavelength to the inverse fourth power ($1/\lambda^4$), and micro–Raman spectroscopy using deep-UV lasers has advantages over Fourier Transform (FT) and visible Raman spectroscopy. It should be borne in mind that deep-UV lasers may cause serious degradation and heating on the sample surface, especially in microanalysis. Previous studies have often avoided sample degradation by using a broad laser spot of >75 µm diameter (Abbay et al., 2017; Sapers et al., 2019), sample rotation (Ferrari and Robertson, 2001; Tarcea et al., 2007), or accumulations at different spot areas (Kumamoto et al., 2011). However, such methods cannot achieve microanalysis of dispersed low-maturity CM of <10 µm diameter in sedimentary rocks when using previous deep-UV Raman spectroscopy. Therefore, a new type of compact deep-UV micro–Raman spectroscopy was developed here for dispersed CM and coal particles of <10 µm diameter, and an attempt made to assess the laser-induced-damage threshold for samples to enable the acquisition of accurate Raman spectra with a spot size of ~1 µm.

**ANALYTICAL METHODS AND SAMPLE SELECTION**

**Deep-UV micro–Raman Spectroscopy**

Previous studies have employed gas lasers (e.g., 244 nm frequency-doubled Ar$^+$ ion and 248.6 nm NeCu lasers) and large monochromators (focal length >80 cm) with nitrogen-cooled charged-coupled devices (CCDs) for deep-UV Raman spectroscopy (e.g., Tarcea et al., 2007; Kumamoto et al., 2011; Abbey et al., 2017; Quirico et al., 2020). However, such systems are large and expensive compared with conventional micro–Raman systems. In addition, the lifetime of gas lasers is only 2000–3000 h (Dubessy et al., 2012), and annual maintenance is required. Therefore, a compact deep-UV Raman system was developed with a single monochromator, a Peltier-cooled CCD detector, and a 266 nm microchip laser (SB1–266–1–5, Bright Solutions Srl, Prado, Italy) operated at the fourth harmonic of a nanosecond pulsed Nd:YAG (neodymium–doped yttrium aluminum garnet) laser. There are already reports of clear suppression of laser-induced fluorescence from organic compounds in 266 nm Raman spectroscopy (Eshelman et al., 2014). Our excitation source is a compact (<10 cm x 10 cm x 3 cm) maintenance-free nanosecond pulsed laser. Such a compact deep-UV Raman system can be assembled using commercial Raman edge filters and dichroic beam splitters for 266 nm Raman spectroscopy.

Details of the Raman optics system are shown in Figure 1. The deep-UV micro–Raman spectroscopy was customized from a Nikon LV100ND-based STR–Raman spectrometer installed at the Geological Survey of Japan, AIST. CW laser, continuous wave laser; UV, ultraviolet (200–350 nm); ND, neutral density; VIS, visible (350–700 nm); NA, numerical aperture; PFL, parfocal.

![Figure 1. Schematic optical diagram of the customized deep-UV micro–Raman instrument assembled at the Geological Survey of Japan, AIST. CW laser, continuous wave laser; UV, ultraviolet (200–350 nm); ND, neutral density; VIS, visible (350–700 nm); NA, numerical aperture; PFL, parfocal.](image-url)
Laser-induced damage threshold for graphite and coal

Excited by a 266 nm deep-UV laser. The 365 nm dichroic beam splitter in upright microscopy allows observation of a fluorescence spot instead of an invisible laser on the sample surface during Raman analysis. The deep-UV laser was focused with a spot size of ~1 µm diameter using a UV focusing objective with a numerical aperture of 0.49 (LMU-40X-UVB, Thorlabs, Newton, USA; Kumamoto et al., 2011). Raman signals from the sample surface were separated from Rayleigh scattering by the 270 nm dichroic beam splitter and a 266 nm RazorEdge® ultra-steeep pass edge filter (LP02–266RU–25, Semrock, IDEX Health & Science, Lake Forest, USA), and focused into a UV-enhanced φ100 µm quartz fiber cable through a UV-focusing lens. The quartz fiber was connected to a single monochromator (Shamrock 300i, Andor Technology, Belfast, Northern Ireland) with a front-illuminated cooled CCD detector (Newton 920P-0E, Andor Technology, Belfast, Northern Ireland). Raman scattering light was dispersed by a 2400 gr/mm with 300 nm blazes, allowing coverage of a bandwidth of 2500 cm⁻¹ (100–2600 cm⁻¹) with a center wavelength of 1400 cm⁻¹ (276.29 nm), respectively. The wavelengths (nm) and Raman shift (cm⁻¹) with deep-UV micro-Raman spectroscopy were calibrated using a low-pressure mercury lamp (bright lines) and a chemical vapor deposition (CVD) diamond wafer (~1332 cm⁻¹), respectively. Raman spectra of graphite and coal comprise three prominent bands of the G, D, and T, depending on the crystallinity (Ferrari and Robertson, 2001). Three bands were fitted with a pseudo-Voight function (Gaussian-Lorentzian Sum) using PeakFit 4.12 software (Kouketsu et al., 2014). All Raman spectra were corrected for background noise by subtracting a linear baseline in the spectral range of 500–2000 cm⁻¹. The following parameters were estimated: G band full width at half maximum (FWHM), D band FWHM, \( P_{\text{avg}}/f_{\text{rep}} \), D band separation (RBS; Wavenumber\(_G\) band − Wavenumber\(_D\) band).

**Evaluation of laser fluence on sample surface**

Laser power was measured on ten scales (setup 1–10) beneath the UV focusing objective using two different power sensors (S120VC and S401C with PM100USB, Thorlabs, Newton, USA). The sensitivity of the thermal sensor was constant from the UV to NIR regions, and it is widely used in measurements of laser fluence. However, laser powers of 3–20 µW are below the detection limit of the thermal sensor, so an UV–extended Si photodiode sensor was used here for measurement of laser fluence on sample surfaces (Table 1). The sensitivity of this sensor is strongly dependent on the incident wavelength, and measurement uncertainty increases with decreasing wavelength, with the measured laser power being 10–15% higher than that measured by a thermal sensor. The observed Si photodiode sensor values may include other incident wavelengths derived from the excitation laser and stray light in the Raman optics box. Therefore, a higher laser power of 20–100 µW was used for thermal sensor measurements. For the lower power region of <20 µW, laser powers measured by the Si photodiode sensor were calibrated by a linear relationship between two sensors (\( LP_{\text{corrected}} = 0.8592 \times LP_{\text{Si photodiode}} \), \( R^2 = 0.9996 \)). Mean laser powers were converted to laser fluences (J cm⁻²). Two parameters; 1) Energy per pulse (E) and 2) peak pulse powers (\( P_{\text{peak}} \)) were calculated using following equations.

\[
E (J) = P_{\text{avg}}/f_{\text{rep}} \tag{1}
\]

and

\[
P_{\text{peak}} (W) = P_{\text{avg}}/(f_{\text{rep}} \times \tau) \tag{2}
\]

where \( P_{\text{avg}} \) is the measured laser powers (W), \( f_{\text{rep}} \), the repetition rate (5 kHz), and \( \tau \) the pulse width (1 ns). The calculated values are listed in Table 1.

**Experimental samples**

It is difficult to analyze dispersed organic material and low-maturity CM in sedimentary rocks directly because the small grains (<10 µm) have large variations in microstructure. Fully ordered graphite and coal samples, which are suitable as analog materials for amorphous and graphitic carbon, were prepared to evaluate laser-induced heating and sample degradation by a deep-UV laser.

| Laser Setup | Laser Power \( \sigma \) (µW) | Laser Power \( \sigma \) (µW) | Energy per pulse (nJ) | Peak pulse power (W) | Energy density (J cm⁻²) |
|-------------|------------------|------------------|------------------|------------------|------------------|
| 1           | 112.56 ± 0.31    | 97.96 ± 3.49     | 19.59            | 19.59            | 2.50             |
| 2           | 92.10 ± 0.41     | 76.95 ± 1.96     | 15.39            | 15.39            | 1.96             |
| 3           | 44.32 ± 0.39     | 38.51 ± 3.16     | 7.70             | 7.70             | 0.98             |
| 4           | 30.90 ± 0.16     | 27.09 ± 1.85     | 5.42             | 5.42             | 0.69             |
| 5           | 24.62 ± 0.16     | 22.12 ± 2.81     | 4.42             | 4.42             | 0.56             |
| 6           | 19.73 ± 0.48     | 16.95 ± –        | 3.39             | 3.39             | 0.43             |
| 7           | 15.36 ± 0.29     | 13.19 ± –        | 2.64             | 2.64             | 0.34             |
| 8           | 7.49 ± 0.13      | 6.44 ± –         | 1.29             | 1.29             | 0.16             |
| 9           | 5.26 ± 0.01      | 4.52 ± –         | 0.90             | 0.90             | 0.12             |
| 10          | 4.35 ± 0.04      | 3.74 ± –         | 0.75             | 0.75             | 0.10             |

Two laser powers \( \sigma \) were measured by UV–extended Si photodiode and thermal power sensors using the same UV focusing objective (40×). Setups 6–10 for laser power \( \sigma \) were calibrated by the linear relationship between the two sensors.

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**Table 1. Summary of laser fluences on the sample surface**
graphite was sampled from the Kahatagaha–Kolongaha mine, Sri Lanka (Hewathilake et al., 2018). A polished thin section was prepared from a carefully selected graphite crystal, avoiding structural defects by polishing. A polished coal sample from Miocene sedimentary rocks, Daigo, Ibaraki, Japan (e.g., Hosoi et al., 2020), was also prepared. Crushed samples (<20 mesh) were mounted in resin and polished with a 0.5 µm alumina suspension. The mean random vitrinite reflectance (VRr) was measured with a spot diameter of ~10 µm at a wavelength of 546 nm using a Zeiss upright microscope equipped with a J&M Microsystem TIDAS S MSP 200 photomultiplier and 50× oil–immersion objective coupled to a 10× ocular. All measured values were calibrated with reference standard values of glass (0%), sapphire (0.587%), and yttrium–aluminum–garnet (0.900%). Further details of the method are provided by Asahina et al. (2021). The average VRr value (± standard deviation, SD) of the coal sample is 0.51 ± 0.03% (N = 53).

RESULTS AND DISCUSSION

Optimization of analysis settings

Optimum analysis conditions at low laser fluence of 0.16 J cm⁻² were established based on exposure time and number of accumulations using the deep-UV micro-Raman system (Table 2). Raman intensity (G and D bands) was determined from peak deconvolution and background noise (defined as the SD of background between 2000 and 2500 cm⁻¹). Signal-to-noise ratios (SNR-G = S_G band/C²[2000-2500 cm⁻¹]) were estimated from the ratio of

Table 2. Analytical conditions and Signal-to-noise ratio of each band at low laser fluence of 0.16 J cm⁻²

| Time (sec) | Number of accumulation | Total time (sec) | SNR-G | SNR-D |
|-----------|------------------------|------------------|-------|-------|
| 5         | 5                      | 25               | 7.5   | 1.7   |
| 10        | 5                      | 50               | 10.6  | 3.8   |
| 20        | 5                      | 100              | 18.4  | 5.7   |
| 40        | 5                      | 200              | 28.9  | 9.7   |
| 80        | 5                      | 400              | 47.7  | 16.1  |
| 160       | 5                      | 800              | 65.5  | 21.2  |
| 320       | 5                      | 1600             | 86.7  | 29.1  |
| 10        | 1                      | 10               | 4.2   | 1.0   |
| 10        | 5                      | 50               | 7.8   | 2.4   |
| 10        | 10                     | 100              | 10.7  | 3.1   |
| 10        | 20                     | 200              | 14.8  | 4.1   |
| 10        | 40                     | 400              | 16.4  | 5.3   |
| 10        | 80                     | 800              | 24.3  | 8.0   |
| 10        | 160                    | 1600             | 33.2  | 11.0  |

Figure 2. (a) Deep-UV Raman spectra of coal at different SNR-G values of 7.5–87. (b) Variations in G and D band FWHM with increasing signal-to-noise ratio (SNR). Red lines indicate mean values of G and D band FWHM estimated from 30 Raman spectra with high SNR-G (92.1 ± 4.87). (c) Relationship between total time and SNR. Total time is the exposure time multiplied by the number of accumulations. (d) Relationship between total time and background noise (σ²[2000-2500 cm⁻¹]).
Raman signal ($S_{G \text{ band}}$) to the SD of background noise ($\sigma_{\text{SD}}$) (McCreery, 2000). The SNR-G increased with increasing exposure time and number of accumulations (Fig. 2a and Table 2). Although Raman spectra of the G band become clear with an SNR-G of at least 7.5, fitting Raman parameters such as G and D band FWHMs indicates a wide variation exceeding 2σ values of mean values of G and D band FWHM estimated from 30 Raman spectra with high SNR-G (92.1 ± 4.87; Fig. 2b). Previous studies have suggested that the limit of detection in quantitative Raman analysis involves an SNR of >3 (McCreery, 2000). Here, we found that parameters obtained from peak deconvolution of coal had errors larger than those with detection of Raman signals only, indicating that robust Raman spectra obtained with SNR-G >66 and SNR-D >8 should be utilized (Fig. 2b).

Raman intensities of each band are similar if the total times (exposure time multiplied by number of accumulations) are equal. However, SNR-G values for long exposure times (e.g., 80 s × 5 times) are 2–3 times those for large numbers of accumulations (10s × 40 times; Fig. 2c), due to the difference in background noise (Fig. 2d) even with equal total times (400 s; Table 2). This phenomenon is derived from the difference between readout noise and dark current from a cooled CCD detector (McCreery, 2000; Dubessy et al., 2012). Our data also indicate a similar relationship between exposure time and number of accumulations. However, the rate of increase of SNR decreases with increasing exposure time (>80 s), but not linearly (Fig. 2c), even over long exposure times. A combination of long exposure time (80–320 s) and small numbers of accumulations (2–10) is an effective method for increasing the SNR and denoising the cosmic ray. Such a relationship between exposure time and number of accumulations may also be valid for visible (488, 514, and 532 nm) micro-Raman microscopy.

### Laser-induced damage threshold

Laser damage and spectral changes with laser fluences of

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**Table 3. Summary of each Raman parameter of graphite at laser fluences from 0.10 to 2.50 J cm$^{-2}$**

| Laser fluence (J cm$^{-2}$) | G band (cm$^{-1}$) | 1σ | G band FWHM | 1σ | SNR-G | 1σ |
|-----------------------------|------------------|----|-------------|----|-------|----|
| 2.50                        | 1574.6           | 0.52| 31.9        | 0.99| 620.5 | 36.31|
| 1.96                        | 1575.4           | 0.30| 30.4        | 0.60| 735.6 | 9.90 |
| 0.98                        | 1580.0           | 0.27| 25.7        | 0.06| 696.8 | 76.53|
| 0.69                        | 1579.4           | 0.70| 26.0        | 0.99| 553.5 | 189.71|
| 0.56                        | 1579.9           | 0.51| 25.4        | 0.36| 497.3 | 71.89 |
| 0.43                        | 1580.3           | 0.39| 24.5        | 0.28| 403.9 | 65.24|
| 0.34                        | 1580.7           | 0.35| 24.6        | 0.42| 301.1 | 59.76 |
| 0.16                        | 1581.4           | 0.22| 24.6        | 1.65| 108.9 | 16.30|
| 0.12                        | 1581.5           | 0.28| 24.4        | 0.64| 103.0 | 14.98|
| 0.10                        | 1581.7           | 0.28| 24.2        | 0.37| 75.1  | 20.42|

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**Table 4. Summary of each Raman parameter of coal at laser fluences from 0.10 to 2.50 J cm$^{-2}$**

| Laser fluence (J cm$^{-2}$) | G band (cm$^{-1}$) | 1σ | G band FWHM | 1σ | D band (cm$^{-1}$) | 1σ | D band FWHM | 1σ | SNR-G | 1σ | SNR-D |
|-----------------------------|------------------|----|-------------|----|--------------------|----|--------------|----|-------|----|-------|
| 2.50                        | 1607.9           | 0.19| 70.2        | 0.88| 1361.5             | 2.34| 327.8        | 4.86| 111.0 | 9.16| 38.0  |
| 1.96                        | 1608.1           | 0.17| 69.4        | 0.93| 1360.8             | 1.85| 328.9        | 4.81| 110.5 | 9.87| 38.6  |
| 0.98                        | 1607.5           | 0.09| 69.9        | 1.03| 1362.4             | 0.70| 334.0        | 7.07| 112.4 | 6.78| 44.0  |
| 0.69                        | 1608.2           | 0.31| 68.8        | 1.03| 1359.7             | 1.89| 339.2        | 7.37| 112.4 | 6.78| 44.0  |
| 0.56                        | 1608.0           | 0.69| 69.9        | 0.62| 1360.2             | 1.28| 332.7        | 13.39| 99.3  | 7.86| 36.9  |
| 0.43                        | 1608.5           | 0.33| 68.2        | 0.97| 1360.7             | 2.38| 330.2        | 4.88| 96.9  | 3.34| 35.9  |
| 0.34                        | 1608.1           | 1.02| 69.4        | 1.42| 1363.5             | 0.47| 323.4        | 10.68| 83.1  | 4.34| 32.3  |
| 0.16                        | 1609.4           | 0.33| 68.2        | 1.33| 1362.6             | 2.26| 289.9        | 6.19| 92.1  | 4.87| 32.8  |
| 0.12                        | 1609.5           | 0.66| 67.5        | 0.75| 1363.1             | 3.07| 293.5        | 8.96| 78.4  | 2.12| 25.3  |
| 0.10                        | 1609.7           | 0.12| 66.9        | 1.71| 1365.9             | 1.92| 287.1        | 7.85| 62.5  | 7.84| 19.4  |

| 1σ | RBS | 1σ | $I_D/I_G$ | 1σ |
|----|-----|----|-----------|----|
| 1.35| 246.5 | 2.21| 0.34        | 0.020|
| 2.71| 247.3 | 1.69| 0.35        | 0.009|
| 1.60| 245.1 | 0.62| 0.39        | 0.015|
| 1.60| 248.4 | 1.76| 0.37        | 0.010|
| 2.03| 247.8 | 1.95| 0.37        | 0.010|
| 0.97| 247.9 | 2.58| 0.39        | 0.010|
| 0.83| 244.6 | 1.13| 0.36        | 0.022|
| 1.31| 246.8 | 2.54| 0.34        | 0.012|
| 0.59| 246.4 | 2.41| 0.32        | 0.001|
| 2.38| 243.8 | 1.81| 0.31        | 0.004|

$I_D/I_G$: IntensityD band/IntensityG band; RBS, WavenumberG band - WavenumberD band.
sufficient SNR values for low-maturity CM. All Raman measurements were repeated three times for calculating mean values with standard deviations. Detailed changes in each Raman parameter are listed in Tables 3 and 4.

**Fully ordered graphite**

There was no serious degradation on the sample surface with laser fluences of 0.10–2.50 J cm$^{-2}$ (Fig. 3a), although some sample surfaces became black with fluences of 1.96–2.50 J cm$^{-2}$, suggesting irreversible damage by a deep-UV laser. The G band positions converged to 1582 cm$^{-1}$, corresponding to an ideal $E_{2g}$ vibration mode of graphite (Wang et al., 1990). Assuming that maximum 2σ value (~ 1.4 cm$^{-1}$) of analysis data was an analytical error, the Raman shift of the G band obtained at laser fluences of 0.43–2.50 J cm$^{-2}$ clearly displayed a down-shift of 1.7–7.4 cm$^{-1}$ relative to reference Raman spectra (1582 cm$^{-1}$; Figs. 4a and 5a). The G band FWHM also increased with increasing laser fluence (Fig. 5b). On the other hand, the SNR–G and laser fluences did not have a linear relationship (Fig. 5c). This implies that the focus shift due to sample degradation may occur with fluences of 1.96–2.50 J cm$^{-2}$.

Crystal structures of opaque minerals are generally easily altered by laser heating during micro-Raman spectroscopy (Shebanova and Lazor, 2003), with changes in Raman spectra possibly leading to a misinterpretation of crystal structure. Laser-induced thermal effects can be evaluated using (1) the anti-Stokes to Stokes Raman intensity ratio (Shebanova and Lazor, 2003; Tsuji et al., 2008; Sun et al., 2017), (2) the positions of Raman bands (Kagi et al., 1994), and (3) Raman bandwidths (Iwasaki et al., 2013). Here, spectral changes inferred from the positions of Raman bands and bandwidths were consistent with previous results obtained with visible lasers (2, Kagi et al., 1994; 3, Iwasaki et al., 2013). Some studies have suggested that robust Raman spectra of fully ordered graphite and low-maturity CM should be obtained with
laser powers of <1 mW, to avoid heat–induced downshifts of the G and D bands (Kagi et al., 1994; Nakamura et al., 2019). We found more sensitivity to laser heating by a deep–UV laser, with more serious effects than previously reported with visible lasers. Laser fluences of <0.34 J cm\(^{-2}\) (measured mean laser power ~ 13 µW) should be used to avoid laser heating of fully ordered graphite during deep–UV micro–Raman spectroscopy.

Coal

Significant degradation of the polished coal surface was observed with laser fluences of 0.34–2.50 J cm\(^{-2}\) (Fig. 3b), with the fluence with ~1 µm spot size preferably being maintained at <0.16 J cm\(^{-2}\) for deep–UV micro–Raman spectroscopy. Three samples irradiated by a deep–UV laser of 0.10–0.16 J cm\(^{-2}\) were altered with white halos, suggesting photo–bleaching (Fig. 3b).

Although Raman spectra at the different fluence levels are similar (Fig. 4b), Raman parameters calculated by peak deconvolution display significant changes with increasing laser fluence from 0.10 to 2.50 J cm\(^{-2}\). The Raman shift in the G and D bands systematically decreased with increasing laser fluence, suggesting downshifting by laser heating and/or amorphization of the sample surface (Fig. 5d). The change in G and D band FWHM values also became more prominent (Fig. 5e). The observed degrees of change in Raman parameters were consistent with the laser fluence and depression sizes. SNR–G and SNR–D values decreased significantly with fluences of <0.16 J cm\(^{-2}\) (Fig. 5f), so a fluence of ~ 0.16 J cm\(^{-2}\) should be maintained for acquisition of accurate Raman spectra without laser damage of sample surfaces.

It is difficult to evaluate the influence of photo–bleaching by deep UV laser based on our experiments because all spots were bleached or damaged. However, Raman parameters of the bleached spots between 0.10 and 0.16 J cm\(^{-2}\) are roughly the same within one sigma uncertainty (Figs. 5d–5e). Lopnow et al. (2004) argued that the Raman spectra of hydrocarbon at photo-bleached spots by deep UV laser did not change with increasing exposure to the UV exciting light, and such Raman spectra still contain primary information about the chemical structure of hydrocarbon. Our observations also suppose the previous conclusion.

Here, all Raman measurements involved a single maceral grain, with the crystallinity of coal appearing constant. However, \(I_D/I_G\) ratios, and RBS and D band FWHMs, which are efficient thermal indicators (Ferrari and Robertson, 2000; Kouketsu et al., 2014; Henry et al., 2019), display wide variations with laser fluence (Fig. 6). In particular, the D band FWHM fluctuated by
10–15% within a single coal grain during changes in laser fluence. Reliable thermal indicators for low-maturity CM are sensitive to laser-induced thermal effects and/or sample degradation. A typical Raman spectrum of coal (VR_r = ~ 0.51%) with no fluorescence background at low laser fluence of 0.16 J cm$^{-2}$ is shown in Figure 7, with the difference in fluorescence backgrounds of 532 and 266 nm Diode Pumped Solid State (DPSS) lasers being obvious.

Mean laser powers in this study were in the range of 4–98 µW (Table 1), with almost all analysis spots at >10 µW being damaged through laser-induced heating or sample degradation. The laser-damage threshold for coal (VR_r = ~ 0.51%) is much lower than measured laser powers (300–500 µW) reported previously (Quirico et al., 2020). Other studies have also reported a wide range of laser-damage thresholds, including ~ 1000 J cm$^{-2}$ (Skuilnova et al., 2014), ~ 59 J cm$^{-2}$ (Abbey et al., 2017), and 0.075 J cm$^{-2}$ (Hollis et al., 2021). The laser-damage threshold for organic material and coal is thus strongly dependent on the crystallinity of amorphous carbon, laser spot size, and laser properties (continuous wave or pulsed lasers) used in deep-UV Raman spectroscopy. It is particularly important to determine the laser-damage threshold for each sample to ensure an accurate Raman spectrum, especially when analyzing amorphous materials. Analysis spots without sample degradation and heating provide information about crystal structures even with deep-UV micro–Raman spectroscopy.

**CONCLUSIONS**

A compact deep-UV micro–Raman spectroscopy system was developed with a single monochromator, a front-illuminated cooled CCD detector, and a 266 nm nanosecond pulsed laser. This system makes it possible to detect very weak Raman signals from sample spots of ~1 µm diameter with a laser fluence of <0.16 J cm$^{-2}$ and with no sample degradation. Laser powers for coal (VR_r = ~ 0.51%) and graphite analyses should be maintained at <0.16 and 0.34 J cm$^{-2}$, respectively, to avoid damage to sample surfaces. Laser-induced thermal effects from deep-UV lasers are more serious than those of visible lasers.

The analyzed spot size for deep-UV micro–Raman spectroscopy is much smaller than that for vitrinite reflectance. The system is particularly suitable for analysis of dispersed low-maturity CM in terrestrial rocks and extraterrestrial materials, using polished thin sections or slabs without special treatment. Furthermore, the deep-UV Raman spectroscopy system is more robust and user-friendly than earlier 244 and 248.6 nm deep-UV Raman systems. We expect there to be wider applications for assessing the crystallinity of low-maturity CM and coal using 266 nm deep-UV micro–Raman spectroscopy.

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