

## RESEARCH ARTICLE

# Raman spectroscopy of the photosensitive pigment Prussian blue

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**Abstract**

Prussian blue is a pigment highly sensitive to electromagnetic radiation, visible light included. This photosensitivity, associated with a complex redox behavior, causes a vulnerability even to Raman lasers, with the possibility of sample alteration or irreversible damage. In this study, we systematically explored the influence of the laser wavelength and laser power on different types of Prussian blue pigments, soluble and insoluble. The use of different laser wavelengths does not influence the position of the characteristic peak, though it affects the signal-to-noise ratio. The latter can be improved by increasing the number of accumulations and/or the acquisition time. Furthermore, we evaluated a safe level of Raman laser excitation or “safe zone” with laser power between 0.005 and 0.06 mW, where Raman analysis can be performed without laser-induced artifacts or damage for the sample. These artifacts may affect the characteristic spectral signature of the two different Prussian blue, leading to a wrong identification of the pigments. Moreover, artifacts can also hide features arisen from fading in objects presenting non-visible alterations of Prussian blue.

**KEYWORDS**

photosensitivity, pigment, Prussian blue, radiation damage, Raman Spectroscopy

## 1 | INTRODUCTION

Raman spectroscopy is now recognized as a standard spectroscopic technique for the characterization of cultural heritage materials, thanks in particular to the possibility to work at the micron-scale, no specific sample preparation and the non-destructiveness of the analysis. For the latter point, however, special care is needed when investigating compounds presenting a high sensitivity to electromagnetic radiation, such as iron oxides and hydroxides,<sup>[1]</sup> lead pigments,<sup>[2]</sup> or phthalocyanine pigments.<sup>[3,4]</sup> We show here that this is also the case for the pigment Prussian blue, known for its high photosensitivity associated with a complex redox behavior.<sup>[5]</sup>

Prussian blue is an iron(III) hexacyanoferrate(II) complex, whose color arises from an intervalent charge transfer via a cyano group between iron(II) and iron(III). Upon

strong light exposure, a photoreduction occurs and induces the fading of the pigment. This process depends on the substrate, the environment, impurities, as well as the structure and chemical composition of Prussian blue.<sup>[5,6]</sup> Raman spectroscopy has been used to characterize the pigment, especially by the presence of  $\nu(CN)$  bands between 2150 and 2160  $\text{cm}^{-1}$ .<sup>[7,8]</sup> Intrinsically, these bands contain useful information to further analyze the fading mechanisms of Prussian blue, because the wavenumber of the vibrational stretching mode depends upon the oxidation state of iron.<sup>[5,6,9,10]</sup>

It is thus principally possible to evaluate the redox state of Prussian blue by investigating the Raman spectral characteristics of the  $\nu(CN)$  peaks.<sup>[5,6]</sup> On the other hand, the high photosensitivity of Prussian blue translates into a sensitivity of the pigment towards radiation damage. This effect has been extensively studied in the X-ray

regime<sup>[11–13]</sup> but no study has been similarly performed in the UV-visible regime so far. This lack of knowledge prevents adequate analysis of the redox behavior of Prussian blue by Raman spectroscopy as radiation damage may strongly interfere within the process. Moreover, risks of damaging precious cultural heritage artifacts cannot be completely ruled out.

In this study, we systematically explore the influence of laser wavelength, laser power, and accumulated dose on the  $\nu(\text{CN})$  spectral signature of Prussian blue. A procedure for defining appropriate measurement conditions is proposed. In order to get rid of the eventual influence of the substrate, known to influence the photoredox behavior of the pigment,<sup>[12]</sup> this study focuses on powders only, investigating the spectral difference between two types of Prussian blue varying by their ratio Fe(II):Fe(III) and the presence of potassium cations. Raman-induced spectral variations for more complex Prussian blue-substrate systems found in cultural heritage will be investigated in a forthcoming paper.

## 2 | METHODOLOGY

### 2.1 | Sample Preparation

Soluble Prussian blue (PBS) powder ( $K\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ , Fe:K ratio of 2:1) has been synthesized<sup>[5]</sup> by adding an equal volume of potassium hexacyanoferrate solution ( $K_4\text{Fe}^{\text{II}}(\text{CN})_6$ , 0.2 M) dropwise to a stirred solution of iron sulfate ( $\text{Fe}_2^{\text{III}}(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , 0.1 M). Insoluble Prussian blue (PBI) powder ( $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ ) was obtained from the same process, but the reagents have been mixed with a ratio of respectively 1:4 in volume. The precipitate of both solutions was filtered, washed with deionized water, dried at 60°C, and manually grounded.

### 2.2 | Raman spectroscopy

Raman analyses were performed on a Renishaw InVia dispersive Raman spectrometer, equipped with a Leica DM microscope to focus the laser on the sample with a 50× Standard objective (NA 0.75, WD 0.37 mm). Most experiments were performed using the 785 nm laser (diode-type, Renishaw HP NIR785 300 mW, 1200 l/mm grating). The size of light spot is about  $\approx 2$  mm using 50× objective, and the laser power on sample varied between 0.006 and 1.2 mW. All 785 nm measurements were performed with the pin-hole in to have better control on the spot size. Additional analyses were performed using 633 and 514 nm excitation. Every set of experiments was performed both on PBS and PBI. Raman spectra were recorded at a spectral resolution of 1  $\text{cm}^{-1}$  in the spectral

range between 120 and 3200  $\text{cm}^{-1}$  using the extended mode and focusing on the  $\text{C}\equiv\text{N}$  bands within 1900 and 2500  $\text{cm}^{-1}$  using the static measurement mode. Acquisition times varied between 40 and 120 s (to improve signal-to-noise [S/N] ratio), acquiring a single scan (unless specified otherwise). All Raman spectra were recorded after instrument calibration on the internal Si-reference standard ( $520.6 \pm 0.1 \text{ cm}^{-1}$ ). Powder samples were loosely pressed on an aluminum plate for the analysis.

### 2.3 | Data processing

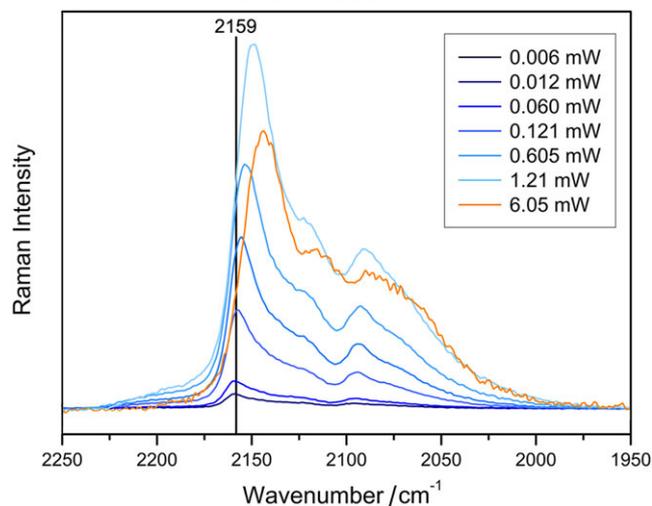
The raw data were processed using the Renishaw Software WiRE v.3.2. Saturated spectra were excluded, and spikes due to cosmic rays were removed using the “zap” function. Analysis of the  $\nu(\text{CN})$  band shift was performed by plotting the collected spectra (10 to 20 points per experiment), smoothing using Savitzky–Golay filter (window size = 11, polynomial = 6), and by determining the average and standard deviation of the  $\nu(\text{CN})$  peak position. Care was taken to ensure that smoothing did not influence the position of the peak. Comparison between Raman spectra and baseline corrections was performed on Peak-o-mat v.1.1.9 (<http://lorentz.sourceforge.net/>) open source software.

## 3 | RESULTS

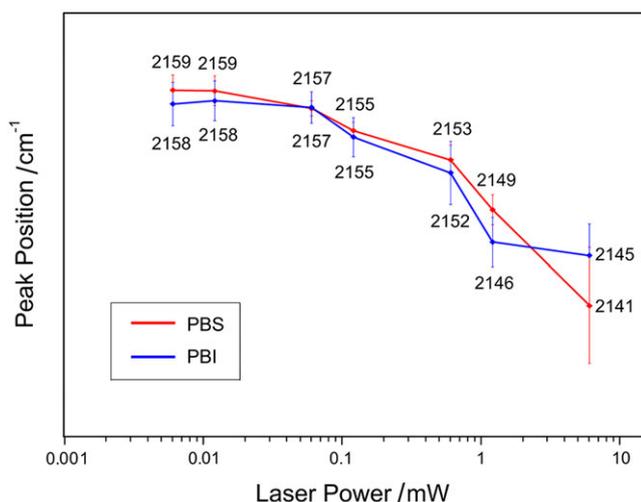
### 3.1 | Influence of the laser power on the characteristic $\nu(\text{CN})$ band of Prussian blue

The influence of the Raman laser energy on the  $\nu(\text{CN})$  band shift has been evaluated by performing experiments at increasing excitation levels and exposure times of 40 and 120 s on PB powders. Raman spectroscopy shows a shift of the characteristic CN band towards lower values of wavenumber proportional to the increase of the laser power intensity (Figure 1). This shift has been observed both on PBS and PBI powders (Figure 2). The relative Raman signal intensity variation of the two peaks is inversely proportional to the increase of the laser power. However, at low intensities, the signal is weak and the respective ratio between the two main peaks cannot be estimated with sufficient reliability.

The  $\nu(\text{CN})$  band shifts towards lower wavenumbers by up to 8  $\text{cm}^{-1}$  due to overexcitation, although the band shift was observed to be reversible. Non-reversible damages show up at high excitation (incident laser beam of 6.05 mW on sample) and level up to complete destruction of the pigment for higher laser power (Figure 3).



**FIGURE 1** Raman spectra of soluble Prussian blue (PBS) powder collected by using different laser intensities ( $\lambda_{\text{ex}}=785$  nm,  $t=40$  s, 1 accumulation). As the power of the laser increases, the position of the  $\nu(\text{CN})$  peak shifts towards lower wavenumbers [Colour figure can be viewed at [wileyonlinelibrary.com](#)]



**FIGURE 2** Position of the  $\nu(\text{CN})$  peak as a function of laser power ( $\lambda_{\text{ex}}=785$  nm). Each point is an average of 20 measurements [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

The behavior of the shift measured at 40 and 120 s of exposure times is comparable, suggesting that the shift does not depend on total accumulated energy but on the critical excitation level.

### 3.2 | Reversibility of the shift

In order to prove the shift of the  $\nu(\text{CN})$  band being a function of laser power, sequential spectra were collected on the same spot, starting below 0.012 mW to beyond the safe zone up to 1.21 mW to purposely foster the shift without inducing permanent damage. The reverse path was then

analysed by continuously decreasing the excitation levels again to below 0.012 mW.

The  $\nu(\text{CN})$  band shift provoked is in the order of  $\approx 4$   $\text{cm}^{-1}$  (from 2160 to 2156  $\text{cm}^{-1}$ ) when the analysis is performed outside the safe zone prior to permanent damage but fully recovers to the initial value of the first acquisition (2160  $\text{cm}^{-1}$ ) on the reducing leg (Figure 4). The recovery of the shift from excitation levels of 1.21 mW is immediate.

### 3.3 | Recommendation for reliable measurements

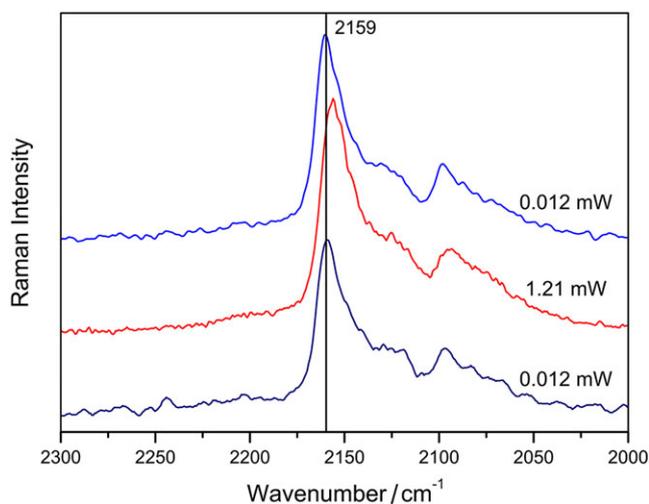
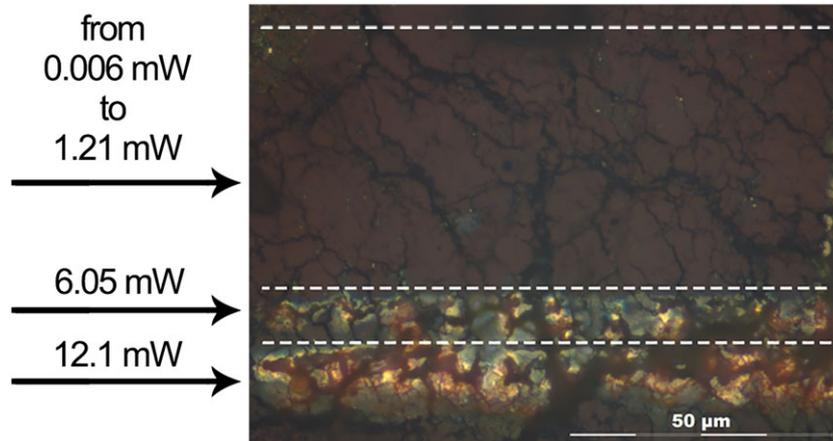
The S/N ratio at low laser power can assume sometimes low values, affecting the resolution of the spectrum. To improve the S/N ratio quality without increasing the laser power is possible to act on two variables of acquisition: exposure time and accumulations. A series of spectra were collected on PBS powder with an exposure time of 40 and 120 s (one accumulation). Another series of spectra on the same powder was collected with an increasing number of accumulations (one, five, and 10 a) at 40 s of exposure time (Figure 5).

The spectrum is clearly more readable and with better defined peaks when the time exposure and the accumulation increase. In the first case, the position of the  $\nu(\text{CN})$  peak has not varied, in the second case, there is no change either between one accumulation and five accumulations, whereas in the spectrum collected at 10 accumulations, there is a subtle shift of 1–2 wavenumbers, still inside the resolution of the instrument and in the range of the error (0.1 std. dev.). For this reason, we recommend to keep the number of accumulations in the range from one to five, in order to ensure that eventual oscillations in the value of the peak are related to the sample and not to the analytical conditions.

### 3.4 | Influence of laser wavelength

To understand the influence of the laser wavelength on the shift, the same series of measurements was performed with different laser wavelengths available, 514 and 633 nm (Figure 6). The shift observed upon increasing the power of the 514 nm laser evolved similarly to the 785 nm one, whereas the effect was less prominent using the 633 nm laser. This may suggest that the phenomenon may also depend on the excitation wavelength. Although the spectra collected with the 785 nm laser delivered a high S/N ratio at 40 and 120 s scans at an increased risk of inducing a shift on the  $\nu(\text{CN})$  band, the 514 nm laser required higher power levels to induce a spectral shift, yet delivered less signal intensity for identical acquisition parameters.

**FIGURE 3** Light microscopy image in bright field of soluble Prussian blue powder showing horizontal lines of 10 spot measurements with visible alteration immediately after Raman analysis at excitation levels  $>6$  mW ( $\lambda_{ex}=785$  nm) [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

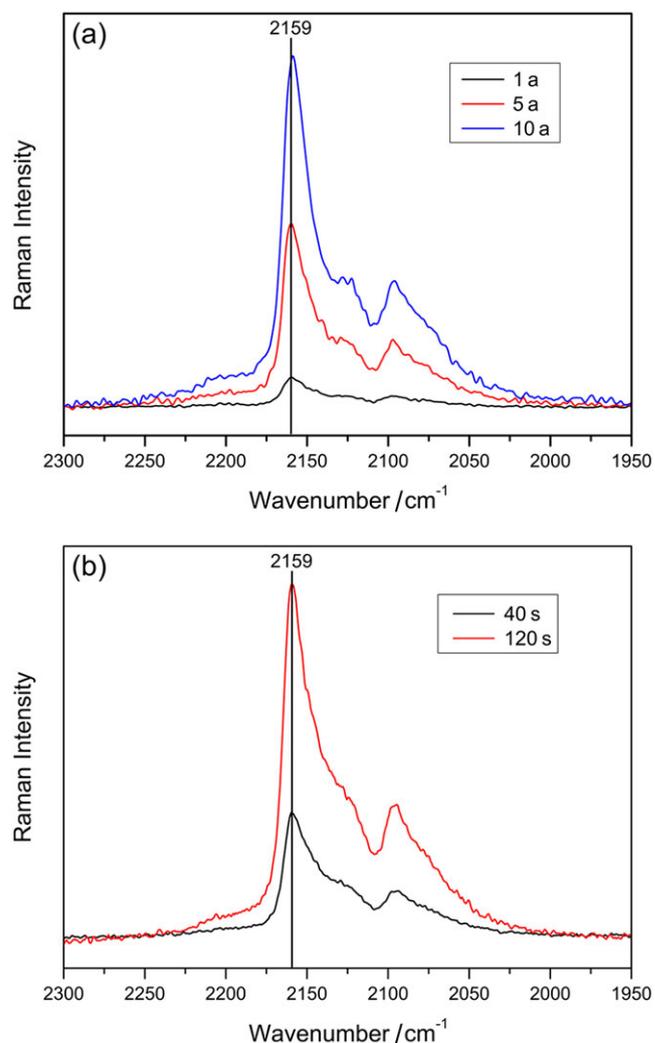


**FIGURE 4** Raman spectra of soluble Prussian blue powder collected progressively at 0.012, 1.21, and 0.012 mW again, excitation wavelength 785 nm. The shift of  $\nu(CN)$  band is related to the intensity of the laser excitation [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

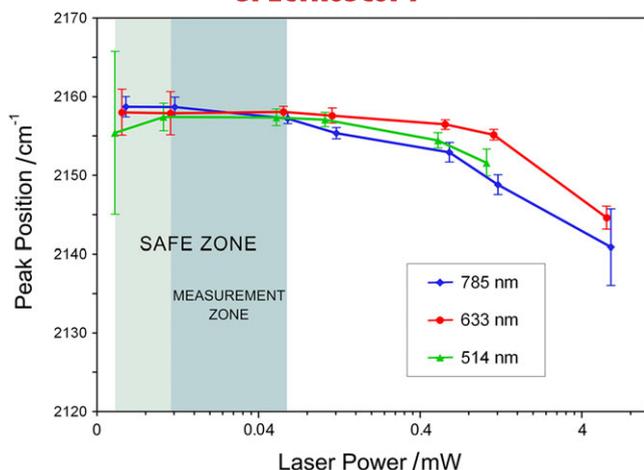
## 4 | DISCUSSION

### 4.1 | Raman spectrum of Prussian blue

The first step of this study was the identification and attribution of each Raman band of PB using the settings given in Section 2. To monitor the variations of the  $\nu(CN)$  band position as a function of power and wavelength of the laser, focus was set on the spectral window between 2000 and 2200  $\text{cm}^{-1}$  (Figure 7). Within this spectral range, stretching vibrations of the triple CN bond, characteristic for PB, occur between 2070 and 2200  $\text{cm}^{-1}$ [15]. The  $\text{C}\equiv\text{N}$  group, being coordinated with iron ions of different valence state, exhibits various wavenumber of  $\nu(CN)$  stretching in this range. The main peak around 2155 to



**FIGURE 5** Raman spectra of soluble Prussian blue powder collected at excitation wavelength 785 nm: increase the number of accumulations (a) or the exposure time (b) do not affect the accuracy of the peak position [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**FIGURE 6** Comparison of 514, 633, and 785 nm wavelength excitation applied to PBS with increasing laser power on PBS. The highlighted zone indicates where no laser-induced shift was observed [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

2160  $\text{cm}^{-1}$  refers to the  $1A_g \nu(\text{CN})$  stretching vibration and [Fe(II), Fe(III)] vibrational state.<sup>[5,9,14]</sup> This peak presents a shoulder towards lower wavenumbers at 2123  $\text{cm}^{-1}$ , characteristic for  $\text{CN}^-$ .<sup>[9]</sup>

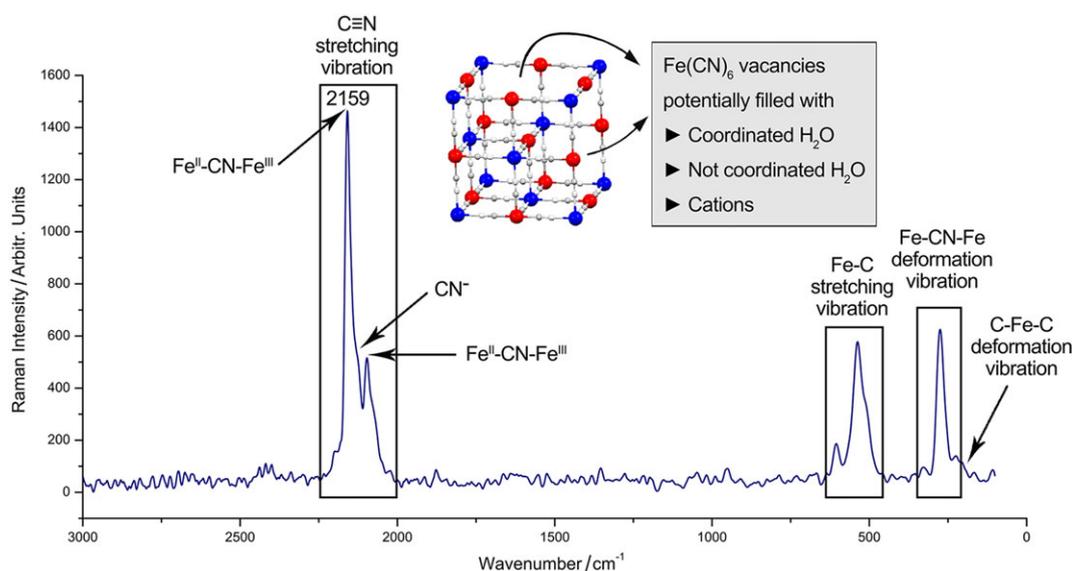
The second peak is localized at around 2090  $\text{cm}^{-1}$  and corresponds to the  $E_g$  mode of the  $\nu(\text{CN})$  stretching vibration<sup>[5]</sup> of the [Fe(II), Fe(III)] state. Other characteristic peaks are located in the lower part of the spectrum, in the range between 450–620  $\text{cm}^{-1}$  and 190–340  $\text{cm}^{-1}$ . The group of peaks in the higher spectral window (450–620  $\text{cm}^{-1}$ ) is characteristic for all the Fe–C stretching vibrations of the lattice and is defined by a major peak at 537  $\text{cm}^{-1}$  and a second one at 605  $\text{cm}^{-1}$ .<sup>[16]</sup> The lower spectral window (190–340  $\text{cm}^{-1}$ ) with peaks at 276  $\text{cm}^{-1}$

and two shoulders at 233 and 328  $\text{cm}^{-1}$  represents the Fe–CN–Fe bond deformation vibrations. Another shoulder present at 181  $\text{cm}^{-1}$  is characteristic for C–Fe–C deformations.<sup>[16]</sup>

In summary, the lowest part of the spectrum (1000–100  $\text{cm}^{-1}$ ) gives information about all the vibrations related to the PB structure. Structural modification thus can be identified by modification of the spectrum in this region. These bands have shown to be not sensitive to overexcitation of the pigment by the laser. The peaks in the region between 2070–2200  $\text{cm}^{-1}$ , however, are related to the electronic features of PB: PB cyanide ligands are coordinated to iron ions with different oxidation state ( $\text{Fe}^{\text{III}}\text{--CN--Fe}^{\text{II}}$ ) that influences the wavenumber of the vibrational stretching mode. When a modification in the oxidation state of iron occurs, as in case of laser-induced excitation, these vibrational modes change, giving rise to peaks with different characteristics.<sup>[5,6,9,10]</sup>

## 4.2 | Study of the shift

The shift of the  $\nu(\text{CN})$  band in Prussian blue usually takes place when there is a reduction of the  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$ , and the charge transfer between  $\text{Fe}^{\text{III}}\text{--CN--Fe}^{\text{II}}$  cannot take place.<sup>[5,17,18]</sup> Within the context of Raman spectroscopy analysis, this shift is sometimes not associated to an effective change in the structure of Prussian blue but to an excitation induced by the Raman laser radiation in particular analytical conditions that can be related both to laser power and laser wavelength. As shown in Figures 1 and 4, in absence of a concrete structural difference, the shifting position of the peak at 2159  $\text{cm}^{-1}$  is directly proportional



**FIGURE 7** Typical Raman spectrum of soluble Prussian blue (PBS) powder collected at excitation wavelength 785 nm (0.012 mW). Peak attribution according to Kettle et al., Mazeikien et al.<sup>[14]</sup> and Nakamoto<sup>[15]</sup> [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

to the increase of the laser power, and it reverses to the original position when the source of excitation is removed. This behavior confirms thus that Prussian blue is not only a pigment very sensitive to visible light and X-ray radiation but to every type of radiation, and it needs specific care in the choice of analytical conditions to obtain reliable measurements.

Modern instrumentation allows choosing between a huge variety of lasers, different in type, source, power, and wavelength. As seen, laser wavelength can also be an important shift-inducing factor. Nevertheless, different laser wavelength means different S/N ratios and different excitation of Prussian blue. Spectra collected with 785 nm laser and with 514 nm show a comparable behavior of the  $\nu(\text{CN})$  band shift, suggesting that the effects of the laser excitation on Prussian blue are similar. The most relevant difference between spectra collected with these two lasers is the higher S/N ratio of the first respect to the second, due to the different energetic type of laser.

On the other side, 633 nm laser shows to induce a different behavior on PB, manifested by a shift that is less enhanced than the ones observed with other lasers. The different behavior of the shift observed during Raman spectroscopy analysis with 633 nm laser can have its origin in the nature of the  $\text{Fe}^{\text{III}} - \text{C} \equiv \text{N} - \text{Fe}^{\text{II}}$  bond responsible of the blue color of this pigment. In fact, Prussian blue's color is due to intervalence charge transfer between low-spin  $\text{Fe}^{\text{II}}$  and high-spin  $\text{Fe}^{\text{III}}$  centers, leading to absorption around 640 nm<sup>[5,17]</sup>: in the case of the red laser with 633 nm wavelength, the radiation could have been absorbed, as for the light, avoiding overexcitation and keeping the charge transfer mechanism unaltered until a certain dose of energy. The shift occurred on PB powder, known to be more stable to radiation than on-substrate artifacts, can also be influenced by the thermal response of the material to the laser beam, but further research is needed.

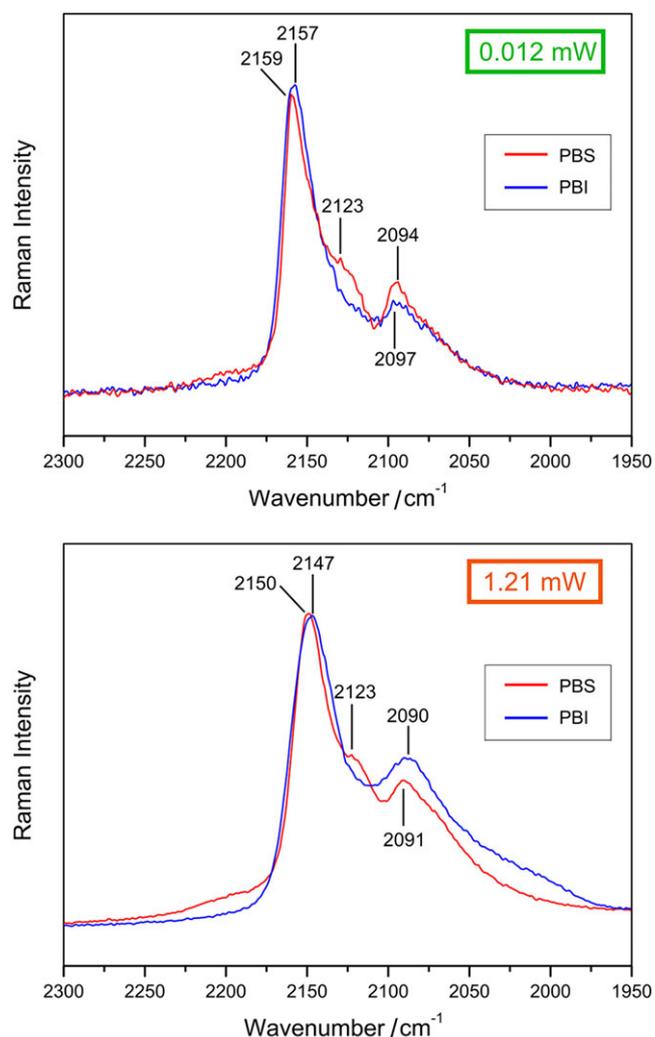
### 4.3 | Definition of safe zone

In order to have a set of reliable measurements, a safe zone has been defined from these values: each measurement in the range of the safe zone, from 0.005 to 0.06 mW, can be considered to be unaffected by the analytic conditions. This safe zone is valid for all the three laser wavelengths that we have taken into consideration for this study, because it has been evaluated in absolute power (mW) and not in percentage depending on the type of laser (Figure 6). In the first fragment before lower limit of the safe zone, measurements can not be considered as reliable because of the low S/N ratio of the spectra: the low resolution and accuracy of the spectrum do not allow a good reading and interpretation of the peaks. After the upper limit of the safe zone, analytical conditions can induce shift of the characteristic

$\nu(\text{CN})$  band of PB and, at higher values of power, can also provoke irreversible damage.

### 4.4 | PBI versus PBS

Raman spectroscopy can be a useful tool to individuate different spectral signatures in different form of Prussian blue. PBS and PBI can show Raman spectra with some differences, indicator of possible alterations in the charge transfer mechanism due, for example, to the amount of vacancies inside the structure,<sup>[19]</sup> the presence of cations<sup>[19,20]</sup>, or coordinated water within vacancies.<sup>[21]</sup> As shown in Figure 8, spectra collected inside the safe zone (0.0121 mW) on these two types of PB present some differences not only in the shape of the  $\text{C} \equiv \text{N}$  related peak but also at the level of the shoulder,



**FIGURE 8** Raman spectra collected inside (0.012 mW) and outside (1.21 mW) the safe zone (from up to down) on PBS and PBI: The different signature of the two forms of Prussian blue is clear inside the safe zone; spectral differences observed at 1.21 mW are an artifact originated by laser-induced excitation of the pigment. PBI = insoluble Prussian blue; PBS = soluble Prussian blue [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

present only in PBS, correspondent to  $\text{CN}^-$  stretching. These differences are altered on spectra collected outside the safe zone: in addition to the shift of characteristic peaks for both PB types, a variation in the ratio between peaks and appearance of new shoulders are also visible. This suggests the features associated to electronic and structural difference undergo a modification induced by the laser radiation. Knowing the specific safe zone for analysis of Prussian blue allows thus not only to configure a proper and adequate experimental setup but also to avoid measurement artifacts that may lead to a wrong interpretation of the difference between the two Prussian blue.

## 5 | CONCLUSIONS

Prussian blue is a very sensitive pigment, susceptible even to low frequency radiations as visible light and that can undergo transformation during Raman measurements. Therefore, it is recommended that each measurement falls inside the safe zone defined by this study for this pigment (0.005–0.06 mW), paying attention in the setting of the experimental conditions to the choice of adequate laser wavelength and power. Too low laser power values can affect the S/N ratio, which can otherwise be improved by increasing the number of accumulations (not more than five to grant the accuracy of the measurement in the range of the spectral resolution). On the other side, it is recommended to keep the laser power under 1 mW. In every case, the factor that must be always taken into consideration is the total dose of energy to which the sample is exposed. In cultural heritage studies, the destruction of the sample can not be accepted, but even in the range of laser power values between the end of the safe zone and the irreversible damage of the pigment, the interpretation of subtle shifts of characteristic bands can be affected by the susceptibility to the laser radiation, and characteristic features of the compound, as the different spectral signature for PBS and PBI, may slip away.

## ACKNOWLEDGEMENTS

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