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Rapid shifted excitation Raman difference spectroscopy with a distributed feedback diode laser emitting at 785 nm

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ABSTRACT A distributed feedback (DFB) laser diode emitting at 785 nm was tested and applied as a light source for shifted excitation Raman difference spectroscopy (SERDS). Due to the physical properties of the laser diode, it was possible to shift the emission wavelength by 8 cm^{-1} (0.5 nm) required for our SERDS measurements by simply changing the injection current. The internal grating ensured single mode operation at both wavelength with the frequency stability of ± 0.06 cm^{-1} (0.004 nm) required for high resolution Raman spectroscopic applications. The shifted spectra were used for calculating enhanced Raman spectra being obscured by a strong scattering background. A 16 dB (≈ 38 fold) improvement of the signal-to-background noise $\overline{S}/\sigma_B$ was demonstrated using blackboard chalk as a sample. The tunable DFB laser is a versatile excitation source for SERDS, which could be used in any dispersive Raman system to subtract fluorescence contributions and scattering background.

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1 Introduction

In the past decade Raman spectroscopy has gained increasing attention as a contactless and *in situ* method for process control in industrial applications [1] and environmental monitoring [2]. However the occurrence of fluorescence or a strong scattering background reduces the signal-to-background noise. In some cases the Raman signal is completely masked. In particular for dispersive spectrometers with a CCD where a detector specific dark noise and a variation in quantum efficiency for each pixel, a so-called fixed pattern "noise" are additional noise sources reducing the $\overline{S}/\sigma_B$.

Several methods exist to extract the Raman signal from its background. An analytical approach to subtract the fluorescence background signal in Raman spectra by the use of a polynomial fit is presented by Lieber et al. [3]. A picosecond Kerr gate was used by Matousek et al. [4], which separates the analytical information in Raman spectra from its fluorescence signal. Among these techniques a method based on shifted excitation Raman difference spectroscopy (SERDS) is described to extract the Raman lines in spectra dominated by a background signal [5–7]. Two Raman spectra are recorded at slightly different excitation frequencies. In this case the heat sink temperature of a diode laser was changed [6]. Another method to shift the excitation wavelength of semiconductor lasers, which are frequently used in tunable diode laser absorption spectroscopy (TDLAS) are the direct modulation of the diode laser with the injection current, the temperature tuning, or to use an external cavity (EC) where the grating position is moved [9].

Here, we present the direct current modulation of a DFB laser emitting at 785 nm as a novel approach for SERDS. The physical properties of the DFB laser [10] allows the alternation of two current levels and provides the two excitation frequencies of the DFB laser with a necessary wavelength shift of 0.5 nm for the presented SERDS measurements.

Blackboard chalk which gives a high background signal in the Raman spectra was chosen as a test sample to illustrate the potential of this method. The improvement of the well known Raman signals of blackboard chalk ($CaSO_4 \cdot 2H_2O$) with this SERDS method will be discussed.

2 Experimental results

2.1 *DFB laser*

The design and layer structure of a DFB laser was described in detail in [10, 11]. Raman spectroscopy and surface-enhanced Raman spectroscopy (SERS) by the use of a DFB laser emitting at 785 nm as an excitation light source was demonstrated in [12].

The DFB laser for our Raman experiments is characterised by the power current diagram given in Fig. 1. The optical output power versus the injection current of the semiconductor laser was measured at a heatsink temperature of $T = 25\,^{\circ}$C. The threshold current I_{th} is 40 mA and the slope efficiency S is 0.88 W/A. The DFB laser has an optical output power of 140 mW and 224 mW at an injection current of $I_1 = 200$ mA and $I_2 = 300$ mA, respectively. The two injection currents were chosen to achieve a wavelength shift of 0.5 nm corresponding to 8 cm^{-1} in the Raman spectra. Figure 2 presents two optical spectra of the DFB laser in a continuous wave

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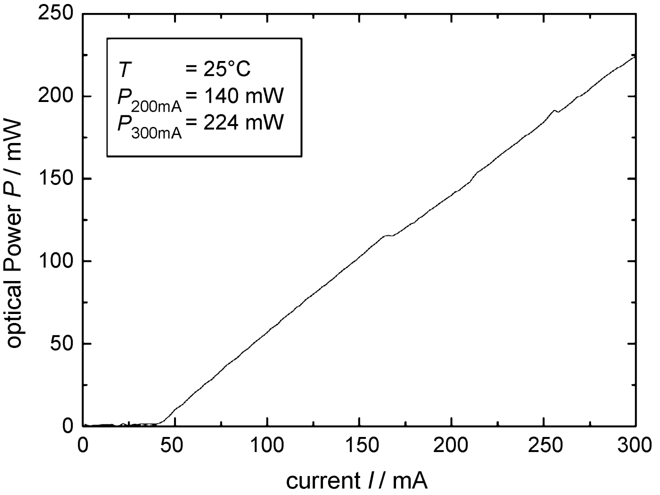

FIGURE 1 Power current characteristic of the DFB laser emitting at 785 nm for $T = 25\,°C$

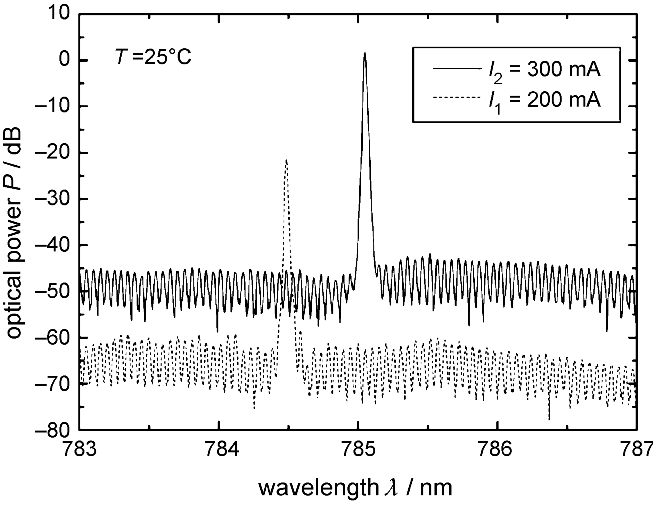

FIGURE 2 Optical spectra of the DFB laser at injection currents $I_1 = 200\,mA$ and $I_2 = 300\,mA$ for $T = 25\,°C$

(cw) operation mode measured with an Advantest Q8384 spectrometer at a spectral resolution of 0.01 nm. The spectra are shifted in intensity for clarity and show a single mode operation with a side-mode suppression ratio of more than 40 dB. The observed linewidth of 0.03 nm at FWHM was limited by the resolution of the spectrograph. Typical spectral linewidth for a DFB laser emitting at 785 nm were measured to be smaller than 3 MHz corresponds to 6 fm [12].

To illustrate the single mode operation of a DFB laser during the direct current modulation optical spectra are shown in Fig. 3. The noise is due to the detector system. The injection current was alternated between 200 mA and 300 mA with a frequency of 1 Hz. The pulses were of rectangular profile with a duty cycle of 50%. The observed spectral linewidth of 10 pm was limited by the resolution of the spectrograph (Jobin Yvon THR 1000). A typical frequency stability of a DFB laser emitting at 785 nm of $\pm 0.06\,cm^{-1}$ over 12 hours required for high resolution Raman spectroscopic measurements is presented in [12]. This allows the integration of a DFB laser emitting at 785 nm as an excitation light source in a Raman spectroscopic setup for SERDS.

2.2 *Raman measurements*

The Raman spectra were recorded with a 320 mm Cerny-Turner spectrograph equipped with a 600 lines/mm grating and a red-enhanced back illuminated EHRB CCD (256 × 1064 pixel) from Princeton Instruments. The CCD is liquid nitrogen cooled and operated at −80 °C. For excitation and collection of the Raman scatter an in-house constructed backscattering optode was utilized [13, 14]. The laser radiation was delivered by a 50 µm core optical fiber to the optode and passed a dielectric bandpass filter (PWL 785 nm, FWHM 8 nm, Quarterwave Berlin) before being focused onto the sample. The laser power at the sample was 38 mW at 784.5 nm and 60 mW at 785 nm. The loss of 73% of optical power compared to the optical power shown in Fig. 1 was mainly due to the optical isolator (60 dB), which was used to prevent the laser from back reflections. Backscattered light was Rayleigh-filtered by means of two dielectric edge filters (OD 4 @ 785 nm, cut-off wavelength 809 nm OD 0.3, Quarterwave Berlin). The Raman scattered radiation was launched into a 104 µm core optical fiber which was coupled via an optical fiber adapter to the spectrograph. This set up had a spectral resolution of $10\,cm^{-1}$.

Conventional black board chalk was used as model for a sample, which exhibits a strong scattering background signal due to the small particle size and is almost completely masking the Raman lines. Unlike the name "chalk" implies it consists of gypsum ($CaSO_4 \cdot 2H_2O$).

The excitation wavelength shift was chosen as a compromise between favorable displacement of the Raman spectra and intensity in the Raman lines of both spectra as a function of the laser power. While the largest scattering intensity in both spectra would imply the shortest possible displacement e.g., 1 pixel. The largest effect in the difference spectrum is expected at a $\Delta\tilde{\nu}$ approximates the original FWHM in the Raman lines of the measured Raman spectra [6]. Furthermore, both wavelengths have to be in keeping with the cut-off specifications of the bandpass and the Rayleigh rejection filters. In our case the shift of 0.5 nm is one order of magnitude smaller than the bandwidth acceptable by the filter and the same is true if a notch filter would be used.

In Fig. 4a the two shifted excitation Raman spectra of blackboard chalk are presented. The spectra are an average of ten spectra with an integration time of 1 s. The intensity is normalised to unity, and both spectra are shifted for

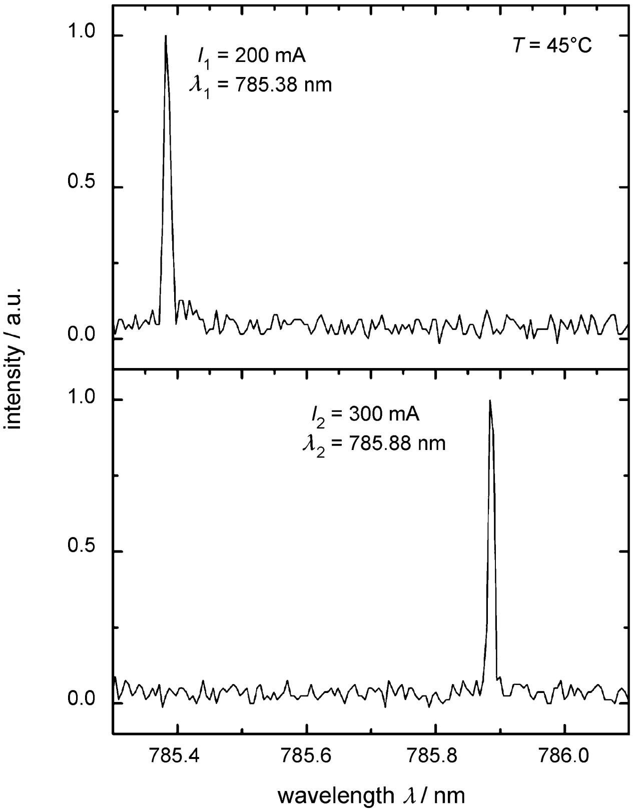

FIGURE 3 Optical spectra of a DFB laser at alternated injection currents $I_1 = 200\,\text{mA}$ and $I_2 = 300\,\text{mA}$ with a frequency of 1 Hz and a duty cycle of 50%

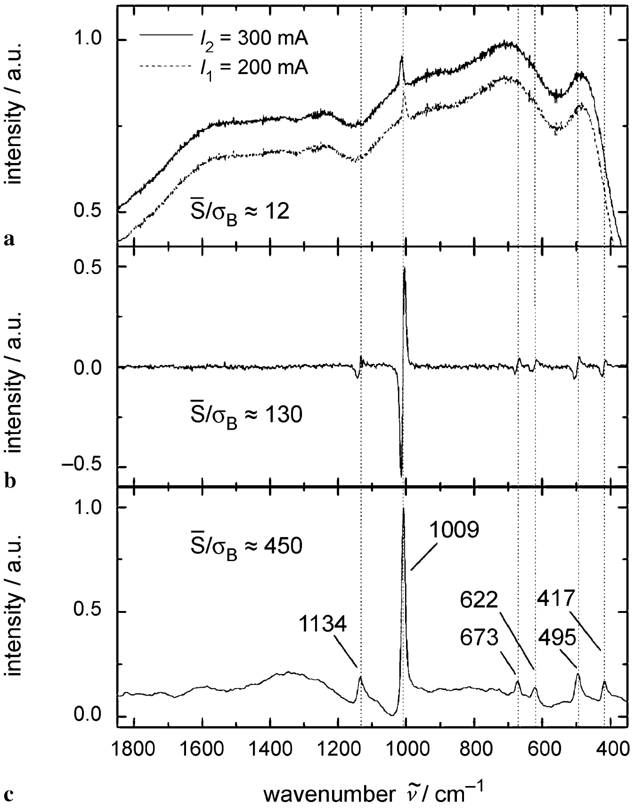

FIGURE 4 (**a**) Two Raman spectra of blackboard chalk at $I_1 = 200\,\text{mA}$ and $I_2 = 300\,\text{mA}, \Delta\lambda = 0.5\,\text{nm}$, average of ten spectra with an integration time 1 s, $\bar{S}/\sigma_B \approx 12$ at $1005\,\text{cm}^{-1}$ ($1015\,\text{cm}^{-1}$), (**b**) Raman difference spectrum, (**c**) Generated Raman spectrum of $CaSO_4 \cdot 2H_2O$, $\bar{S}/\sigma_B \approx 450$ at $1009\,\text{cm}^{-1}$

clarity. Only the very strong Raman line at $1005\,\text{cm}^{-1}$ and $1013\,\text{cm}^{-1}$ are clearly visible with a $\bar{S}/\sigma_B$ of 12.

The difference of the above spectra is shown in Fig. 4b. A polynomial fit was used to shift the baseline of the difference spectrum to zero. Five additional weaker Raman signals at $417\,\text{cm}^{-1}$, $495\,\text{cm}^{-1}$, $622\,\text{cm}^{-1}$, $673\,\text{cm}^{-1}$, and $1134\,\text{cm}^{-1}$ appear as derivative signals. The $\bar{S}/\sigma_B$ of the two strong Raman lines mentioned above is $\approx 11\times$ better than the $\bar{S}/\sigma_B$ in the measured spectra presented in Fig. 4a. For reconstruction the Raman spectrum various methods are known from literature [6–8]. Here an integration of the Raman difference spectrum was employed, presented in Fig. 4c. All Raman lines including the weak signals mentioned above of $CaSO_4 \cdot 2H_2O$ from $400\,\text{cm}^{-1}$ to $1800\,\text{cm}^{-1}$, which are well known from literature [13, 14], are clearly resolved with a spectral linewidth of $16\,\text{cm}^{-1}$ at FWHM. The integration of the stochastic noise in the difference spectrum implicate a decrease of its standard deviation and integrate the deterministic signal in the Raman lines. This causes a dramatically reduced background signal providing a 16 dB ($\approx 38\times$) better $\bar{S}/\sigma_B$ at $1009\,\text{cm}^{-1}$ than in the raw spectra.

3 Conclusion

The DFB laser emitting at 785 nm is a versatile excitation source for SERDS. It is compatible with most dispersive Raman systems because the required wavelength shift complies with the cut-off specifications of dielectric edge filters and holographic notch filters used as Rayleigh rejection filters. The wavelength shift is favorably chosen to be equal or slightly smaller than the observed line width of the Raman signal in the spectra. Single mode operation of the DFB laser during alternation of the injection current was demonstrated. With blackboard chalk as a high background scatterer, the potential of SERDS was shown implying the use of this technique for other samples were the spectra are obscured by a high background signal such as tissue/phantoms. This technique together with a straightforward integration of intensity in the Raman difference spectrum identified all Raman lines from 400 cm^{-1} to 1800 cm^{-1} of the sample as $CaSO_4 \cdot 2H_2O$ known from literature [15, 16] with a ≈ 38 fold improvement of the $\bar{S}/\sigma_B$.

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