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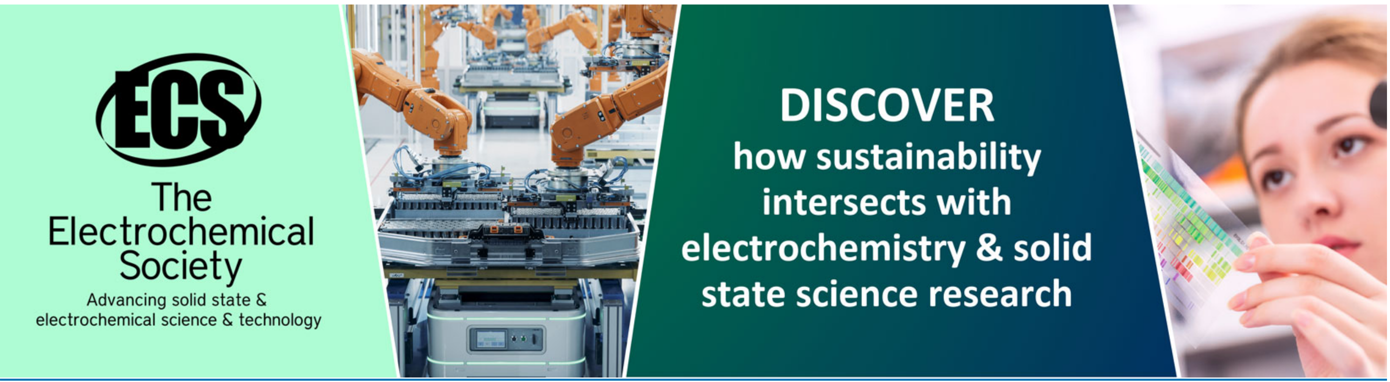

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Optical referencing in differential reflectance spectroscopy

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Abstract
We report a new optical set-up for difference reflectance spectroscopy (DRS) measurements based on a two-beam configuration. By normalizing the reflected intensity from the sample surface with a reference signal that is directly proportional to the incident beam intensity, the calculated DR spectra become insensitive to the instability of the light source. As a result, a significantly improved signal-to-noise ratio is obtained and DR signals in the low 10^{-4} range can be measured reliably. This enables an extremely high sensitivity for surface studies using optical spectroscopy.

Keywords: differential reflectance spectroscopy, optical spectroscopy, signal-to-noise ratio

(Some figures may appear in colour only in the online journal)

1. Introduction

Differential reflectance spectroscopy (DRS) measures the normalized change in reflectance of a surface upon physical or chemical modification, such as during absorption or growth. By subtracting the reflectance spectrum of the pristine surface from the one after modification, the optical contribution from the bulk substrate is effectively suppressed, such that the DR signal emphasizes the optical changes induced at the surface. The DRS technique has been successfully applied to probe the surface optical changes upon thin film growth on metals and semiconductors with monolayer sensitivity [1–6]. On the other hand, due to the large penetration depth of light in the visible range, the change of the optical signal induced by a single monolayer is quite small, typically in the range of 10^{-3} of the total reflectance. In order to study the adsorption or the early stages of thin film growth, an even higher (submonolayer) sensitivity is desired. There are several issues that can limit the sensitivity of the DRS technique, namely, the performance of the photon detector, mechanical stability of the experimental set-up as well as the intensity fluctuations of the light source. Due to the fact that the DR signal is calculated from the reflected intensity rather than the reflectance of the sample, the stability of the light source imposes a strict limitation on the signal-to-noise ratio (SNR) of the spectra and, hence, on the surface sensitivity of the DRS technique.

In this study, a design for a DR spectrometer including an optical referencing path, called the two-beam set-up for short, is introduced. We will show that this set-up significantly improves the SNR of the DR spectra induced by both short-term fluctuations and long-term drift of the light source. The proposed design relies on the normalization of the reflected intensity by a reference signal, which is strictly proportional to the incident beam intensity. As a result, a signal that is directly related to the reflectance of the sample is obtained. The DR spectra deduced on the basis of these normalized intensities are insensitive to fluctuations of the output intensity of the light source. The so improved signal-to-noise ratio of the new design reaches error levels as low as 10^{-4}, thus enabling unprecedented submonolayer sensitivity [1, 2, 6]. In fact, a two-beam configuration has been used previously by Selci and co-workers in their DRS set-up [7]. In this case, the intensity of the incident monochromatic beam was modulated by an optical chopper rotating at a distinct frequency

f_1. Additionally, the light reflected from the sample surface and a dummy surface was detected alternatively at a frequency f_2 using a two-channel lock-in amplifier [7]. However, our design differs from the one in reference [7] in the following two respects: (1) In the set-up of Selci *et al*, the signals reflected from the dummy and the sample surfaces, respectively, are detected alternatively, whereas in our design the reference spectra are recorded in a fully synchronized way. As we will demonstrate later, the synchronization is essential for the improvement of the SNR. (2) Due to the utilization of a monochromator and the lock-in detection scheme in reference [7], the reflected intensity can only be measured for a single wavelength at a time. Only recently has the need for synchronous full spectral data acquisition been recognized [8].

In this paper we will first describe the principle of our conventional differential reflectance spectroscopy measurement and quantify the influence of the lamp instability on the quality of the DR spectrum. Subsequently, we will present our new set-up based on a two-beam configuration and its stability against fluctuations and drift of the light source. Finally, a short conclusion will be given.

Figure 1(*a*) illustrates the working principle of our conventional DRS experiment. The reflectance at a photon energy E from the clean surface at $t = 0$ and at a later time t are denoted as $R(E, 0)$ and $R(E, t)$, respectively. In case that changes of the surface optical properties have occurred during this time interval, the corresponding change in the DR spectrum is given by:

$$\frac{\Delta R}{R}(E,t) = \frac{R(E,t) - R(E,0)}{R(E,0)}. \quad (1)$$

In the actual measurement, it is not the reflectance $R(E, t)$ but the intensity of the beam reflected from the surface $I_r(E, t)$ which is recorded and used to calculate the DR spectrum:

$$\mathrm{DRS}(E,t) = \frac{I_r(E,t) - I_r(E,0)}{I_r(E,0)}. \quad (2)$$

Since $R(E, t) = I_r(E, t)/I_i(E, t)$, equation (2) is only identical to equation (1) if the intensity of the incident light beam $I_i(E, t)$ is the same as $I_i(E, 0)$ at time $t = 0$. However, in reality, the light sources used in a DRS measurement always suffer from intensity fluctuations. In particular, if short-arc discharge lamps are employed, such instabilities may be caused by the internal structure of the light bulb, the power supply or a lack of temperature stabilization. The resulting instability of the incident beam intensity $I_i(E, t)$ leads to a proportional variation of the reflected beam intensity, independent of the change of the reflectance of sample, and thus introduces a systematic error in the DRS signal.

The incident beam intensity at time t can be written as:

$$I_i(E,t) = I_i(E,0) + \delta I_i(E,t), \quad (3)$$

where $\delta I_i(E, t)$ represents the deviation of the incident beam intensity at time t with respect to the intensity at $t = 0$. Thus, the measured DRS signal can be rewritten as:

$$\mathrm{DRS}(E,t) = \frac{\Delta R}{R}(E,t) + R(E,t)\,\frac{\delta I_i(E,t)}{I_i(E,0)}. \quad (4)$$

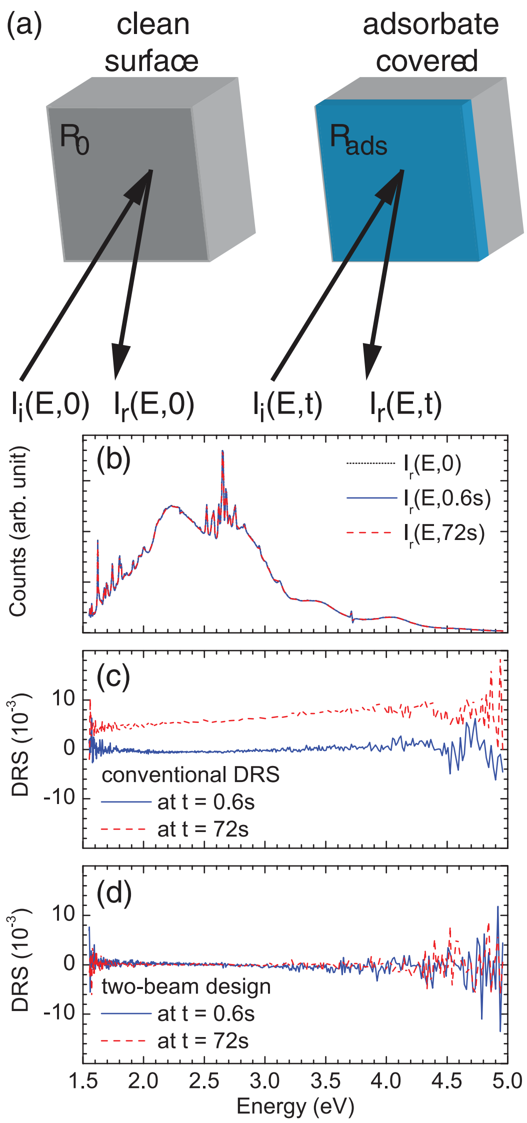

Figure 1. (*a*) Operation principle of differential reflectance spectroscopy (DRS). (*b*) Recorded intensity $I_r(E, t)$ of the light reflected from a UV enhanced Al mirror at $t = 0$, $t = 0.6$ s and $t = 72$ s (dotted black, solid blue and dashed red lines, respectively). (*c*) Calculated DRS spectra for $t = 0.6$ s and $t = 72$ s for our conventional DRS set-up (solid blue and dashed red lines, respectively). (*d*) Same DRS measurement as shown in (*c*) but using the two-beam design. In all cases, the acquisition time was 600 ms per spectrum.

The influence of the instability of the light source on the measured DRS signal is clearly evident from equation (4). Considering the fact that the $\Delta R/R$ signal is typically of the order of 10^{-2}, it is essential to reduce the influence of the instability $\delta I/I$ of the incident light beam well below this value.

In order to quantify the influence of the lamp instability $\delta I/I$ on the DRS signal, DR spectra were recorded over a long period of time while the reflectance of the sample was held constant. To this end a UV enhanced aluminum mirror was used as the reflecting surface. A Xe high-pressure arc lamp was used as the light source and the angle of incidence was set close to zero. Figure 1(*b*) shows the intensities $I_r(E, t)$ of the light beam reflected from the Al surface at $t = 0$ s, $t = 0.6$ s and

t = 72 s (dotted black, solid blue and dashed red lines, respectively). The line shape of the reflected spectra is a product of the reflectance of the Al mirror, the emission spectrum of the Xe arc lamp and the detection efficiency of the spectrometer. The corresponding DRS spectra at t = 0.6 s (solid blue line) and t = 72 s (dashed red line) calculated using equation (2) are plotted in figure 1(*c*). Under ambient conditions the reflectance of the Al mirror is constant at least on the timescale of our experiment. Therefore, at any time $\Delta R/R$ should be equal to zero over the whole photon energy range. Indeed, the DR spectra presented in figure 1(*c*) are featureless and almost straight lines. However, the intensities of the DR spectra are not equal to zero. In particular, the DR spectrum recorded at t = 72 s shows an offset as large as $\sim 5 \times 10^{-3}$ over the whole spectral range. The observed deviation of the latter from the expected $\Delta R/R = 0$ signal is obviously induced by the variation of the incident beam intensity. Furthermore, with a closer look at the line shape of the DR spectra, one can recognize a wavelength dependence of the intensity fluctuations of the Xe lamp.

To eliminate the errors in the DR spectra induced by the instability of the light source, we propose a new configuration for the differential reflectance set-up based on two detectors (figure 2). A beam splitter, which is a fused silica plate, is inserted in the path of the incident beam. It splits the primary beam into two beams: the one with most of the original intensity is transmitted to the sample surface, gets reflected and is recorded by detector 1; the other beam (reflected from the silica plate) carries the rest of the intensity and goes directly to detector 2. The intensity recorded by detector 2 can be written as:

$$I_{r2}(E,t) = R_{bs}(E)\, I_i(E,t) \tag{5}$$

where $R_{bs}(E)$ is the reflectance of the beam splitter, which can be adjusted by varying the angle between its surface normal and the direction of the incident beam. The optical properties of fused silica in ambient conditions are very stable. Therefore, $R_{bs}(E)$ is constant in time as long as the incident angle of the primary light beam is fixed. Consequently, $I_{r2}(E, t)$ exclusively probes the variation of $I_i(E, t)$ and can thus be used as a reference of the incident beam intensity. On the other hand, the intensity measured by detector 1 is:

$$I_{r1}(E,t) = (1 - R_{bs}(E))\, I_i(E,t)\, R(E,t) \tag{6}$$

where $R(E, t)$ is the reflectance of the sample surface which changes during the experiments performed on the surface.

Finally, the DR spectra can be calculated by using the ratio I_{r1}/I_{r2} between the reflected intensity from the surface I_{r1} and the reference intensity I_{r2} from the beam splitter instead of using the intensity I_{r1} only:

$$\frac{\Delta R}{R_0}(E,t) = \frac{\frac{I_{r1}(E,t)}{I_{r2}(E,t)} - \frac{I_{r1}(E,0)}{I_{r2}(E,0)}}{\frac{I_{r1}(E,0)}{I_{r2}(E,0)}} \tag{7}$$

Inserting the expressions in equations (5) and (6) and introducing a lamp instability according to equation (3), yields:

$$\frac{\Delta R}{R_0}(E,t) = \frac{R(E,t) - R(E,0)}{R(E,0)}. \tag{8}$$

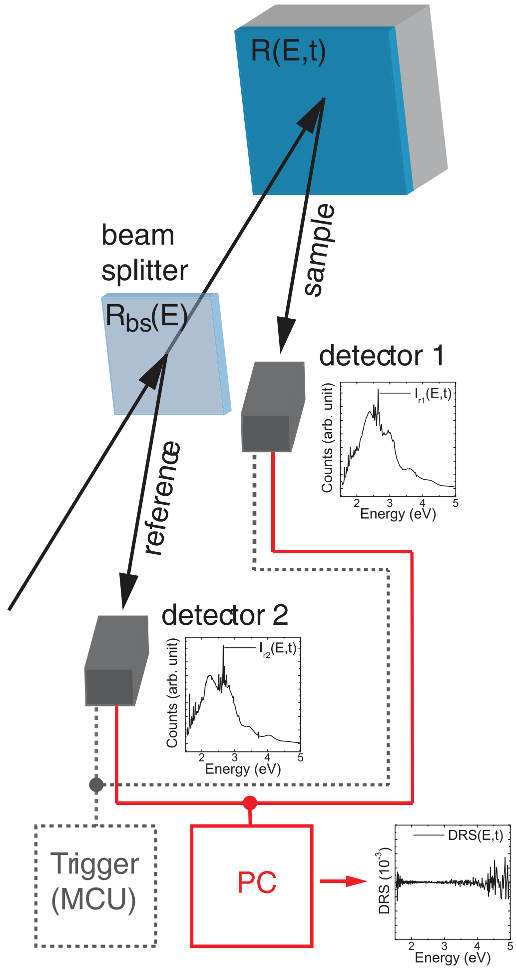

Figure 2. Two-beam DRS set-up, allowing the correction of lamp instabilities. A fraction of the incident beam (reference) is coupled out into detector 2 using a beam splitter. The transmitted beam is reflected from the sample and collected by detector 1. To correct also for high frequency fluctuations the two detectors are synchronized by a hardware trigger (MCU). Both spectrometers are then read out by a personal computer (PC).

From equation (8) one can see that the error $\delta I/I$ introduced via equation (3) cancels out, i.e. the instability of the light source can be completely removed. The variation of the incident beam intensity is effectively compensated by normalizing the reflected intensity from the sample surface with a reference signal that is strictly proportional to the incident light beam intensity. Figure 1(*d*) demonstrates the spectral stability of the DRS signal for the very same measurement as shown in figure 1(*c*). The corrected DR spectra show no offset of the spectrum and yield a flat line shape as expected for a sample with constant reflectance.

2. Results and discussion

In order to compare the stability of our conventional DRS and the proposed two-beam design, long time stability measurements were performed for different acquisition parameters. All measurements were conducted after an adequate warm-up time of the optical set-up of at least 2 h. While the integration time of the two spectrometers was kept constant at 60 ms, the

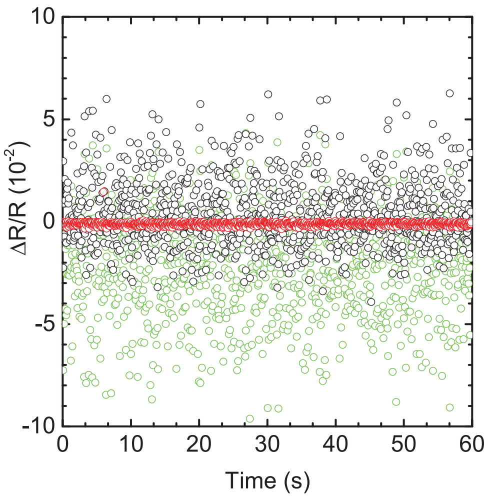

Figure 3. DRS signal at a photon energy of 2.82 eV (wavelength: 440 nm) for an acquisition time of 60 ms per spectrum (60 ms integration time, no averaging) plotted as a function of time. The black circles are the results obtained on the basis of the measured intensity I_{r1}, only (our conventional DRS), whereas the red circles were obtained by taking the reference signal I_{r2} into account (two-beam design). The green circles were obtained with the two-beam design but an asynchronous referencing with a time delay $\Delta t = 60$ ms.

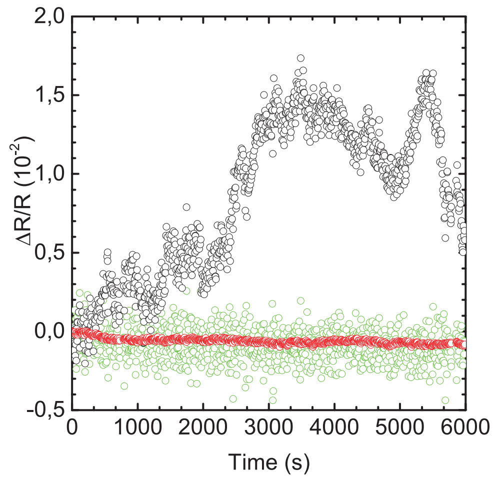

Figure 4. DRS signal at a photon energy of 2.82 eV (wavelength: 440 nm) for an acquisition time of 6 s per spectrum (60 ms integration time, 100 times averaging) plotted as a function of time. The black circles are the results obtained on the basis of the measured intensity I_{r1}, only (our conventional DRS), whereas the red circles were obtained by taking the reference signal I_{r2} into account (two-beam design). The green circles were obtained with the two-beam design but an asynchronous referencing with a time delay $\Delta t = 6$ s.

number of spectra used for averaging was varied from 1 to 10 and 100, resulting in acquisition times of 60 ms, 600 ms and 6 s, respectively. For all three cases, at least 1000 DR spectra were acquired.

Figure 3 shows the DR signal at a photon energy of 2.82 eV (corresponding to a wavelength of 440 nm) as a function of time for an acquisition time of 60 ms. 1300 DR spectra were recorded over a total time of 80 s. As mentioned earlier, the reflectance of the Al mirror used in this test should be constant during the whole measurement; consequently the DR signal should be zero. In the case of our conventional DRS set-up, the signal (black circles) shows strong fluctuations around zero with a mean value of 9.94×10^{-4} and a standard deviation of 1.65×10^{-2}. On the other hand, the two-beam design (red circles) yields a mean value of -1.59×10^{-4}, which is closer to zero and a standard deviation of 8.43×10^{-4}, which is reduced by a factor of ~20 as compared to our conventional DRS set-up. This result clearly demonstrates that the error signal of the DR spectrum induced by short-term fluctuations of the light source can be very efficiently removed by using the two-beam set-up. The fluctuation frequency of the light source has not been systematically investigated in this study. However, significant fluctuations occur over a time-scale shorter than 60 ms, which is the minimum acquisition time used in this study. Therefore a synchronous referencing is mandatory.

In order to test the performance of the new DRS design concerning the long-term drift of the incident light intensity, the DRS measurement was carried out over a period of more than 2 h. The DR signals at a photon energy of 2.82 eV (black circles for our conventional DRS, red circles for the two-beam set-up, respectively) are plotted in figure 4 as a function of time. In order to emphasize the long-term drift effect, each data point presented in figure 4 was averaged over 100 integrations of 60 ms leading to an effective sampling time of 6 s per point. In the case of our conventional DRS, the deviation around the mean value due to the high frequency fluctuation is reduced to 4.64×10^{-3} by this averaging. However, the mean value of the DRS signal shows a slow variation with a deviation as large as 1.5×10^{-2} from the zero line. The observed slow change of the DR signal is due to the drift of the light intensity emitted from the Xe lamp. Obviously, the influence on the DR signal due to this intensity drift cannot be corrected by increasing the sampling time. However, the drift of the light intensity can, again, be successfully removed using the two-beam set-up. In this case, the mean value of the DR signal at 2.82 eV changes slowly by about 1×10^{-3} within the 2 h of the measurement. Besides, the standard deviation has been further reduced to 3.08×10^{-4}, which is more than one order of magnitude smaller than with our conventional DRS design. For the long-term stability measurement, a drift of the DR signal can be recognized in both our conventional and the two-beam DRS set-ups. The complex variation of the DR signal over a larger time span obtained with our conventional DRS set-up is due to the drift of the incident beam intensity, which can be effectively removed by the two-beam design. The small monotonic evolution of the DR signal observed with the two-beam DRS set-up is related to mechanical instabilities of other optical components, excluding the light source, which react in a much slower fashion.

To emphasize the importance of a *synchronous* detection of the sample and the reference signal, an artificial time shift was introduced as follows:

$$\frac{\Delta R}{R_0}(E, m, l) = \frac{\frac{I_{r1}(E,m)}{I_{r2}(E,m+l)} - \frac{I_{r1}(E,0)}{I_{r2}(E,m+l)}}{\frac{I_{r1}(E,0)}{I_{r2}(E,m+l)}}, \tag{9}$$

where m denotes the mth spectral acquisition of the two spectrometers and l the artificially introduced time shift. Equation (9) mathematically describes a subsequent measurement of the sample and reference spectrometer instead of a synchronous acquisition as used in equation (7). The green circles in figures 3 and 4 demonstrate the time dependence for the time-delayed reading of the sample and reference signals with $l = 1$ ($\Delta t = 60$ ms and $\Delta t = 6$ s, in figures 3 and 4, respectively). Comparing figures 3 and 4 illustrates that the asynchronous referencing corrects well for low frequency intensity deviations (long-term drift), whereas high frequency fluctuations do not. Compared to our conventional DRS mode, (black circles in figures 3 and 4), the high frequency noise is even increased by the asynchronous referencing. Therefore, an accurate synchronization of the two detectors used in the two-beam design is of utmost importance in order to generate the highest profit from the optical referencing.

3. Conclusion

We have presented a new optical set-up for differential reflectance spectroscopic measurements based on a two-beam configuration. The errors in the DR signal induced by the instability of the light source can be efficiently removed by normalizing the reflected intensity from the sample surface (beam one) with a reference signal that is proportional to the incident beam intensity (beam two). The improved performance of the two-beam design is based on the fact that the normalized intensity spectra used subsequently for the calculation of the DR spectra are equivalent to the *reflectance*, instead of the *reflected intensity* of the sample surface. We further demonstrate the importance of an exact synchronization of the two detectors. With the two-beam design, an improved signal-to-noise ratio can be obtained for very short integration times. The method to reduce the errors induced by the intensity fluctuations proposed in this work is quite general and applicable for DRS systems based on other types of light sources. The results indicate a very promising future for its application in the field of *in situ* surface science and ultrathin film growth.

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Appendix. Instrumentation

As the optical set-up is intended to cover a broad energy range from 1.5–5 eV (corresponding to a wavelength range of 250–600 nm), Zerodur coated UV enhanced aluminum mirrors from Newport were used for collimation and focusing of the light beam. As a light source, a 35 W high-pressure Xe short-arc lamp, covering a spectral range from 0.6 to 6.7 eV (185–2200 nm), from Ocean Optics (Mikropack HPX-2000) was used. For spectral acquisition two deep well spectrometers (Ocean Optics S1024DW), which are based on NMOS-type Si diode arrays with 1024 channels (Hamamatsu S3904), were used as detectors. The entrance slit widths were 50 μm and 100 μm for detector 1 and detector 2, respectively. These spectrometers show a very low dark noise of 1–2 counts RMS, have a high signal-to-noise ratio (SNR) of 4000 : 1 and a well depth of 1.56×10^8 electrons. The A/D conversion is done via a 12-bit converter. A home-built hardware trigger based on an ATmega328P micro-controller unit from Atmel was used to synchronize the measurements of the two spectrometers. A combined low-pressure mercury and argon lamp (Mikropack Cal-2000) was used for the wavelength calibration of both spectrometers. As a beam splitter, a 1 mm thick fused silica plate was mounted in the path of the incident beam. The surface normal of the plate is aligned with an angle of ≈10° to the incident beam.

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