# NIR Dynamic Light Scattering for Quantum Dot particle size measurements

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***Key words:*** *VASCO Kin, Dynamic Light Scattering, Quantum Dots, particle size measurements, NIR laser*

# I. Context

## *1. Quantum Dots (QDs)*

Quantum dots (QDs) are nanocrystals made from semiconductor materials (usually, transition metal selenides, sulfide, or tellurides such as CdSe, CdS, ZnS, CdTe) whose size induces unique optical properties [1]. At the nanoscale, a quantum confinement appears in these particles, resulting in a discretization of the energy levels and, thus, in luminescent properties for the material. Especially, quantum dots exhibit fluorescence in the visible range of light, when excited with UV (*Figure 1*). The wavelength of the emitted light is directly link to the size of the nanoparticle (NP), since the gap between the conduction

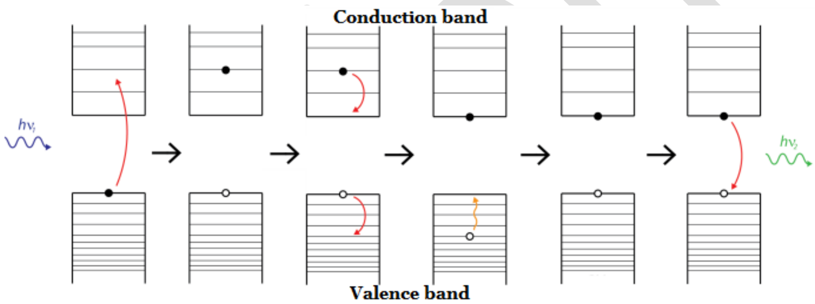



***Figure 1:*** *Scheme of the fluorescence process in quantum dots. An exciton (electron/hole pair) is formed with the UV excitation and, during its recombination, produces light in the visible range*

and the valence band depends on the NP size. It is then possible to tune the emission by changing the QD size, toward a very precise wavelength. The QD emission wavelength (*i.e.* the color of the produced light) will be directly link to the size polydispersity in the suspension, for each class of size will generate a specific wavelength. Typical Cd-based QDs have a characteristic size between 5 and 25 nm, for an emission in the visible range of light. Therefore, QDs constitute a very interesting field of research, due to these properties, and can lead to a wide range of applications such as screen development, photovoltaic material, or biomedical imagery.

## *2. Dynamic Light Scattering (DLS)*

Dynamic Light Scattering (DLS) is a technique based on the measurement of the fluctuation of light scattering through colloidal suspension, in order to get information on the NP size [2]. By analyzing the particles Brownian motion, it is possible to retrieve the NP diffusion coefficient (D) and therefore the hydrodynamic diameter (d) of the NPs, thanks to the Stokes-Einstein equation:

$$\boldsymbol{D} = \frac{k.T}{3.\pi.\eta.\boldsymbol{d}}$$

where D is expressed in $m.s^{-1}$, k is the Boltzmann constant (in $J.K^{-1}$), T is the medium temperature (in Kelvin), η is the medium viscosity (in $J.m^{-3}.s$) and d is the particle diameter (in m); DLS devices correlate fluctuations of the scattered laser light intensity with an exponential-like correlogram, whose decay rate can be linked to the diffusion coefficient and the scattering angle between the collected beam direction and the incident laser beam direction. Current DLS analysis can give a value of the NP size as well as an idea of the polydispersity in sizes for a given colloidal suspension. As such, DLS technique has become an ideal characterization technique for NP size measurement, often associated with complementary imaging techniques, such as Electronic Microscopies (TEM, SEM). While electronic microscopy shows NP shapes and sizes at the local scale, DLS give an indication on the NP size and size polydispersity over the whole suspension.

## 3. DLS for QD size measurement

DLS has already proven valuable in the characterization of various nano-sized species (metallic nanoparticles, vesicles, protein and polymeric compounds). However, its use for QDs raises some technical issues, despite the major advantages it could bring in the characterization of such nanocrystals.

First, the size of the QDs, especially the smaller ones (2-10 nm) can prove difficult to see when bigger particles (or aggregates) are in suspension. Indeed, in first approximation, the light scattering cross-section is proportional to $d^6$, so the smaller the particle, the less intense its signal will be.

The second issue is directly related to the QD optical properties. As they emit in the visible range of light, they also have a strong absorbance band, which also depends on the QD size. This band is shifted towards higher wavelengths with the size increase. For instance, in the case of red-emitting CdSe QDs (typical size around 15 nm), the absorbance band is located around 600-650 nm, which is the wavelength of a classical DLS laser (635 nm). A strong decrease in the collected signal is then correlated to this absorbance and, thus, a less easy size measurement.

In order to tackle these issues, we propose an experimental protocol based on the use of a Near-Infrared (NIR) laser as the core of our classical DLS experiment.

# II. Experimental protocol

## *1. Colloidal suspensions*

Two batches of CdSe@CdS core/shell QDs have been studied: the first batch emits green-light fluorescence, while the second is red-emitting. For the following description, these batches will be called "green QDs" and "red QDS", respectively.

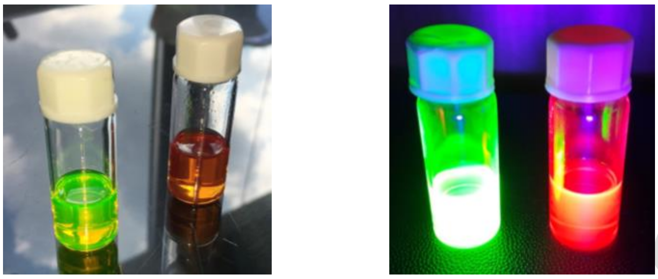


***Figure 2:*** *Camera picture of the green (left) and red (right) QDs non exposed (left) and exposed (right) to UV irradiation*

Theses QDs have been provided in powder form. QD suspensions (1 g/L) were prepared by dissolving the powders in toluene.
Sonication (10 min, with an Emmi H22 sonicating bath; 120 W) was performed before DLS measurements.

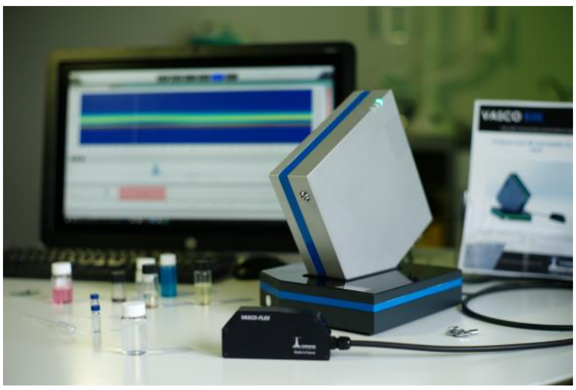
## *2. UV-visible and fluorescence spectroscopies*

QD suspension absorbance and fluorescence bands were analyzed at the Laboratoire de Chimie des Polymères Organiques (LCPO)(Pessac, France) with a Spectra Max M2 from Molecular Devices.

## *3. Transmission Electronic Microscopy (TEM)*

TEM analysis was performed on a LVEM-5 bench top TEM [3] , in Cordouan Technologies facilities.

## *4. DLS set-up*



DLS measurements were made with a **Vasco Kin**™ apparatus, developed by Cordouan Technologies [4], with either the "classical" 635-nanometers laser, or a **780-nanometers** laser (NIR), for comparison sake. Measurements were made with the "*in situ*" head, with a scattering angle of 170° (back-scattering). It is worth noting that with the *In-situ* remote probe, the measurement can be achieved directly into the vial without any contact with the sample. Thus thanks to the remote probe it was not necessary to batch the QDs samples which are highly toxic. Two multimodal analysis algorithms implemented by Cordouan Technologies have been used to evaluate the size of the QDs: a discrete size algorithm named "Pade-Laplace" and a continuous multimodal algorithm named "SBL".

# III. Results

## 1. Green QDs

The first sample to be analyzed with this DLS set-up was a suspension of green-emitting CdSe@CdS quantum dots in toluene. The typical size of these particles was determined by TEM, around 7 nm (*Figure 3.a*).

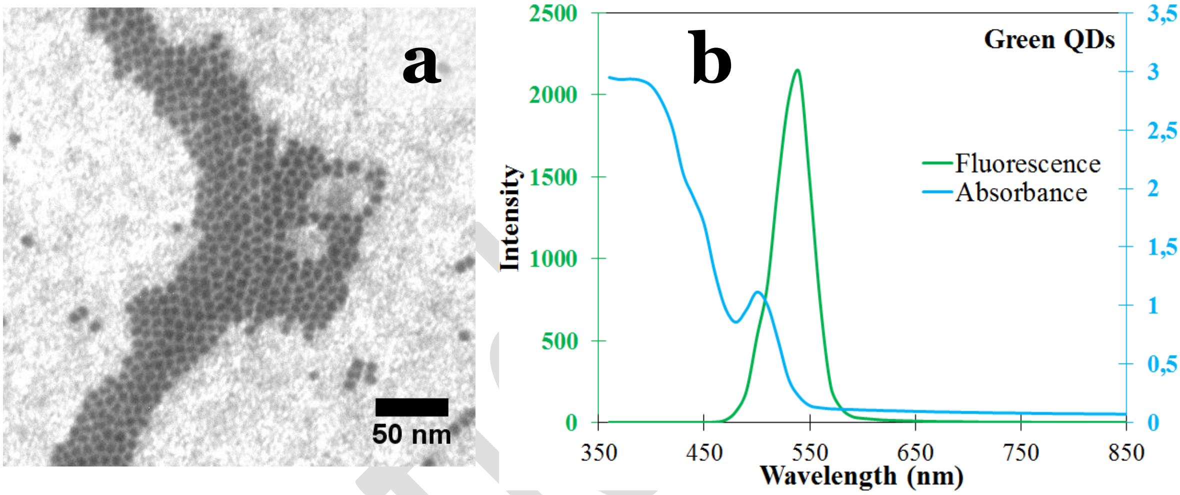



***Figure 3:*** *a/TEM picture of the green QDs; b/UV-visible and fluorescence spectra of the green QD suspension*

The absorbance band for this suspension is at 500 nm, which should not interfere too much with a classical DLS laser, even less with the 780-nanometers laser.
*Figure 4* shows the correlogram obtained for the green QDs when analyzed with both 635-nanometers and 780-nanometers lasers. The classical Kin laser (635 nm) has a better β, which come with no surprise since the higher wavelength laser is expected to have a stronger noise. *Table 1* summarizes the value of these β, as well as data relevant for determining the pertinence of the fit algorithms: the residues, which are corresponding to the difference between the fit curve and the correlogram, for both Pade-Laplace and SBL algorithms. We can already notice that the measures made by DLS, whatever the laser wavelength, and the algorithm fits are relevant since the residues are very small (<0.007).
Size distribution analysis made with the 635-nanometers laser and the 780-nanometers laser (*Figure 4*) show similar results, whatever DLS algorithm used ("Pade-Laplace" and "SBL").
The data, summarized in *Table 2* are relevant with the TEM size measurements, although a difference of some nanometers is found.

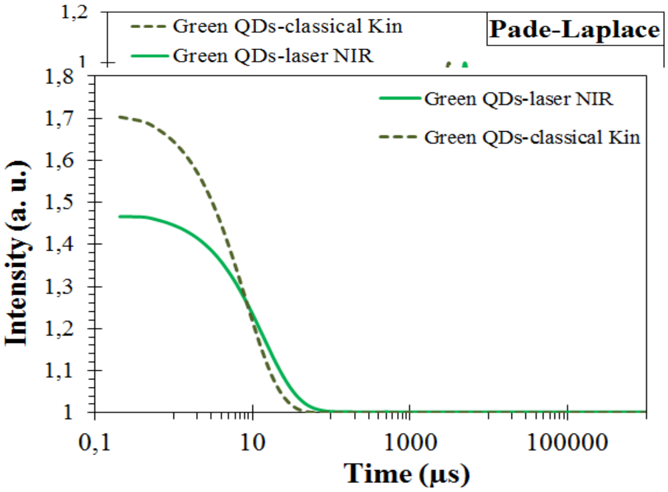
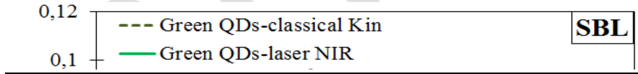



**Figure 4:** *DLS correlogram for the green QDs analysis either with the classical 635-nanometers laser or 780-nanometers laser*




| | Laser 635 nm | Laser 780 nm |
|---|---|---|
| β | 0.72 | 0.48 |
| Pade-Laplace residues | <0.006 | <0.006 |
| SBL residues | <0.005 | <0.005 |

*ometers laser, measured with Pade-Laplace*

**Table 1:** *β and residues values for the DLS measurements made with both laser wavelengths*

| *Intensity distribution* | Laser 635 nm | Laser 780 nm |
|---|---|---|
| **Pade-Laplace** | 12.3 | 12.8 |
| **SBL** | 11.7 | 11.2 |

**Table 2:** *DLS size measurements for the green QDs before and after sonication*

It is highly probable that the species on the particle surface (stabilizer) add to the NP size without being seen with the TEM. Usual stabilizing agent, such as polymeric chains, can add up to 2 nm to a NP radius.

The analysis in <u>numbers</u> is a traditional way to have a better account of small particles in DLS measurements, since, with <u>intensity</u>, the bigger particles tend to hide the signal of smaller ones.

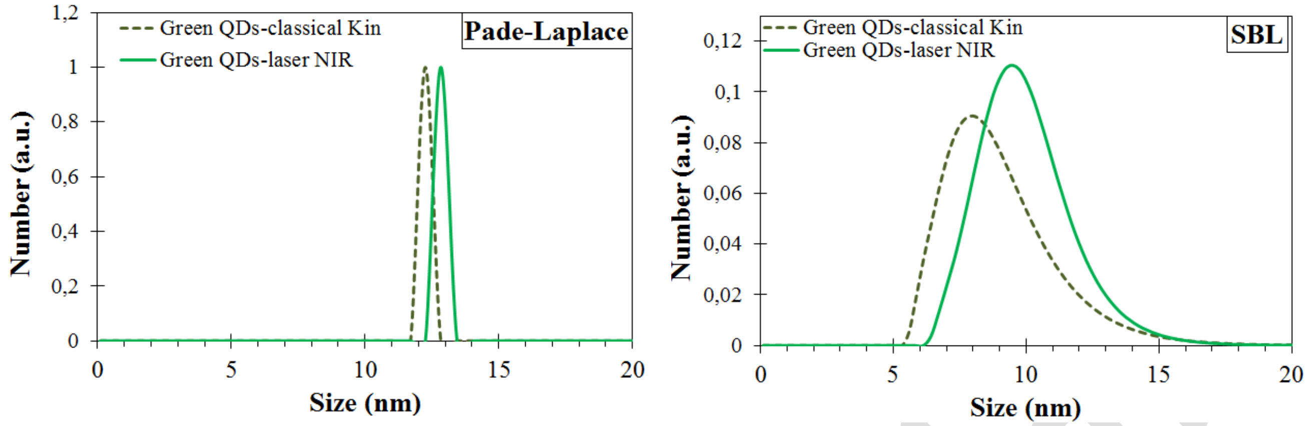



***Figure 6:*** *DLS size distribution* ***<u>in numbers</u>*** *of the green QDs suspension either with the classical 635-nanometers laser or 780-nanometers laser, measured with Pade-Laplace (left) and SBL (right) algorithms*

In order to do the conversion from intensity to number, one must first know the refractive index of its material. In the case of cadmium selenide (CdSe), the data were modeled by Ninomiya and Adachi (1995). The real and imaginary parts of the refractive index at 780 nm are: n=2.5286 and k=0.092265, respectively. The DLS size distributions in numbers are shown in *Figure 5*. *Table 3* summarizes these size results with, once again, a size very close to the 7 nm measured in TEM. As expected, the laser wavelength as no impact on the size measurement of the green QDs since their absorption is not affecting any of the wavelengths considered.

| ***Number distribution*** | **Laser 635 nm** | **Laser 780 nm** |
|---|---|---|
| **Pade-Laplace** | 12.3 nm | 12.8 nm |
| **SBL** | 8.1 nm | 9.3 nm |

***Table 3:*** *Green QDs size measurements, in* ***numbers****, with both types of laser wavelengths*

## 2. *Red QDs*

Bigger red-emitting QDs have been investigated with the same NIR-laser DLS technique. Although their bigger size, seen in TEM around 12 nm (*Figure 6.a*), makes them easier to be detected, their absorbance band (600-650 nm) is now right in the usual DLS laser wavelength (*Figure 7.b*).

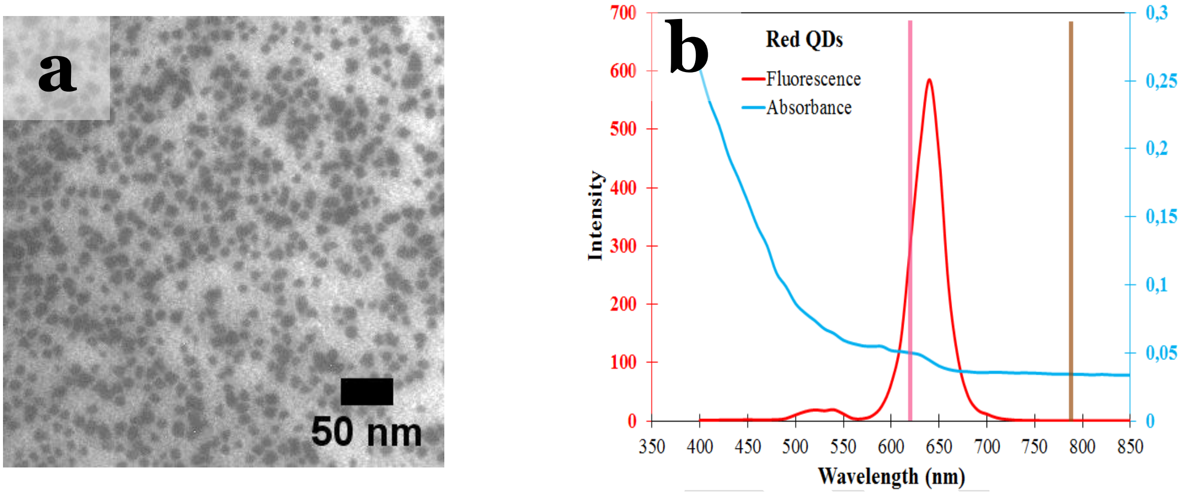



***Figure 7:*** *a/TEM picture of the red QDs; b/UV-visible and fluorescence spectra of the red QD suspension. The laser wavelengths are represented in pink (635 nm) and brown (780 nm) to show how they can be taken into the red QD absorption.*

By using a higher wavelength, it is possible to prevent the absorption of the laser. The NIR-laser is then an adapted method to tackle this absorption issue, although the collected signal stays very noisy. *Figure 7* shows the correlograms obtained with both kinds of laser. It is noticeable that, in this case, the 635-nanometers laser is not adapted for the measurement, with such a small β; while the 780-nanometers laser result in a proper correlogram. The β value of 0.38, although a little noisy, is quite good given the high laser wavelength used here. The residues for both algorithms confirm this tendency, and underline the pertinence of the

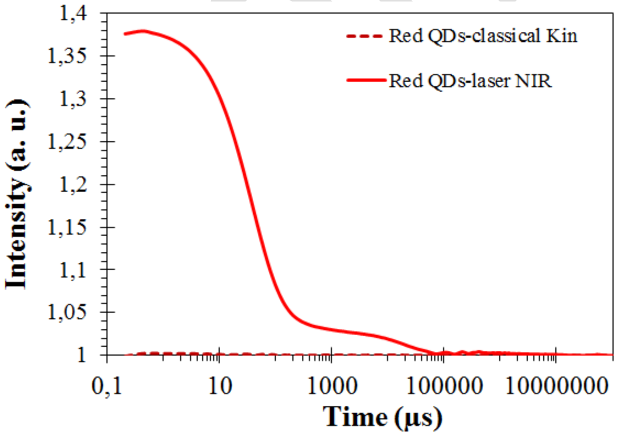



***Figure 8:*** *DLS correlogram for the red QDs analysis either with the classical 635-nanometers laser or 780-nanometers laser*

| | Laser 635 nm | Laser 780 nm |
|---|---|---|
| **β** | 0.01 | 0.38 |
| **Pade-Laplace residues** | <0.181 | <0.002 |
| **SBL residues** | <0.027 | <0.005 |

***Table 4:*** *β and residues values for the DLS measurements made with both laser wavelengths, onto the red QDs*

measurement done with the NIR laser. The size distributions in intensity, with Pade-Laplace and SBL algorithms, for both lasers are shown in *Figure 9*. We were able to collect a QD size quite relevant with the SBL algorithm, while using the 635-nanometer laser but the data

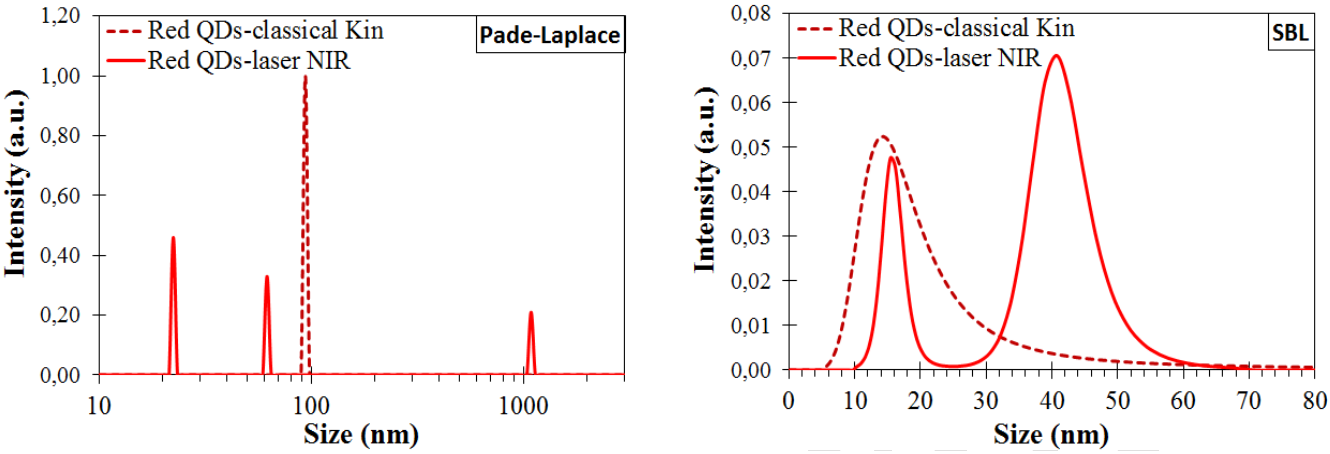



***Figure 9:*** *DLS Intensity size distribution of the red QDs suspension either with the classical 635-nanometers laser or 780-nanometers laser, measured with Pade-Laplace (left) and SBL (right) algorithms*

were quite easier to get with the NIR laser.

The data (Table 4) give a size of 15 nm with the SBL algorithm, a little higher than the one measured with TEM (12 nm), but still accurate if we consider the potential stabilizing layer surrounding the nanocrystal.

| ***Intensity distribution*** | **Laser 635 nm** | **Laser 780 nm** |
|---|---|---|
| **Pade-Laplace** | 93.7 nm | 22.4 nm<br>61.8 nm<br>1086.8 nm |
| **SBL** | 14.1 nm | 15.4 nm<br>40.8 nm |

***Table 4:*** *Red QDs size measurements, with classical 635-nanometers laser and 780-nanometers laser*

The analysis in **numbers** (*Figure 10*) leads to a similar statement, with the SBL algorithm unable to fit the correlogram in the case of the classical laser (*Table 5*), while it reaches an expected value in the case of the NIR laser.

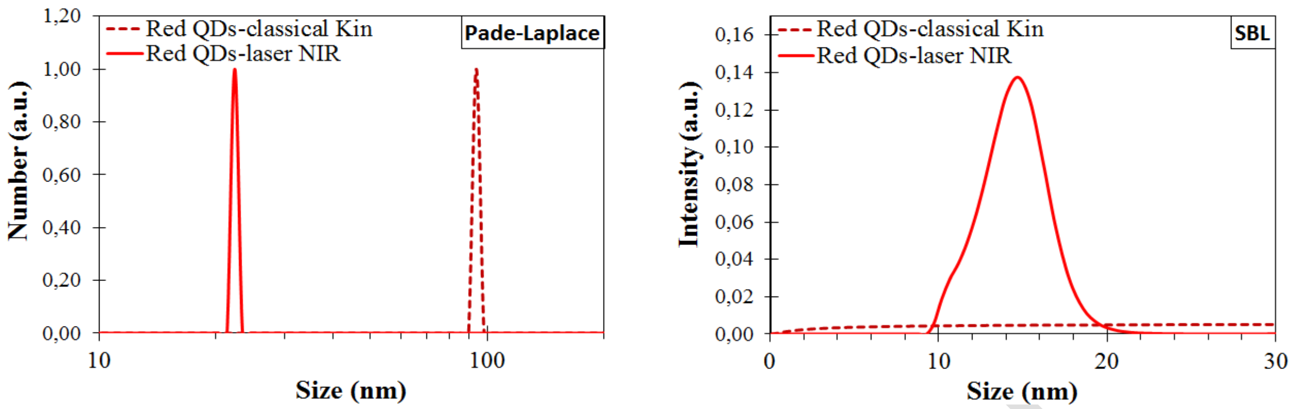



***Figure 10:*** *DLS size distribution <u>in numbers</u> of the red QDs suspension either with the classical 635-nanometers laser or 780-nanometers laser, measured with Pade-Laplace (left) and SBL (right) algorithms*

| ***Number distribution*** | **Laser 635 nm** | **Laser 780 nm** |
|---|---|---|
| **Pade-Laplace** | 93.7 nm | 22.4 nm |
| **SBL** | undetermined | 14.7 nm |

***Table 5:*** *Red QDs size measurements, in* ***numbers****, with both laser wavelengths*

# IV.Conclusion

We have shown here that the NIR-laser can be a valuable asset in the DLS measurement of Cd-based QDs. The laser wavelength at 780 nm prevents most of the absorption effects in the case of red-emitting QDs, in order to get a strong signal for size-retrieving, thanks to adapted algorithms. The comparison with the green-emitting QDs has shown that the DLS is already a potent instrument for characterizing small object (<10 nm) such as these nanocrystals and that the addition of the NIR laser can extent is potential towards absorbing materials.
This study is but the first step in the DLS characterization of fluorescent nanoparticles. Already, we applied the same methodology with red-emitting gold nanoclusters (3 nm in size), with very promising results that would ensure the durability and viability of such a characterization technique. This would surely enlarge the field of application for DLS to new domains, such as the bio-medical imagery/treatments, and to the characterization of strong visible-absorbing particles such as plasmonic NPs or various dyes/fluorophores used in the biological field.

# References

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*[4] VASCO Kin : https://www.cordouan-tech.com/products/vasco-kin/*



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