

Determining the binding energy of aromatic compounds on particle-like carbonaceous surfaces from the signal decay in two-step laser mass spectrometry

D. Duca¹, M. Vojkovic¹, Y. Carpentier¹, M. Ziskind¹, A. Faccinnetto², C. Focsa¹

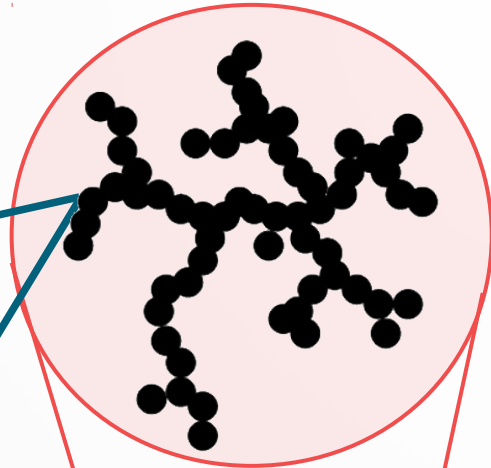
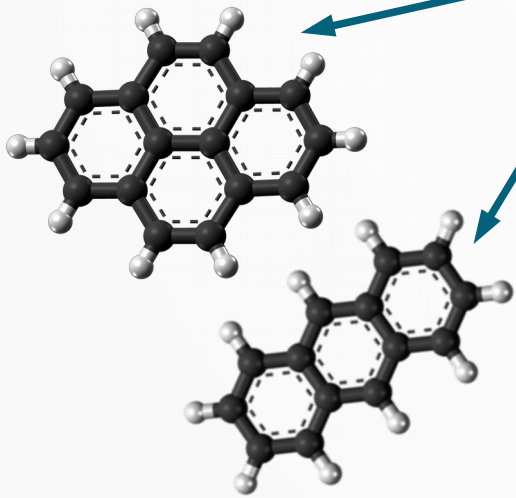
¹University of Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers, Atomes et Molécules, Lille F-59000, France

²University of Lille, CNRS, UMR 8522 - PC2A - Physicochimie des Processus de Combustion et de l'Atmosphère, Lille F-59000, France



Motivation

Polycyclic aromatic hydrocarbons (PAH)
adsorbed on the surface



SOOT:
residue of the
combustion
process



CLIMATE EFFECTS

**Radiation
absorption**



**Cloud
formation**



HEALTH EFFECTS

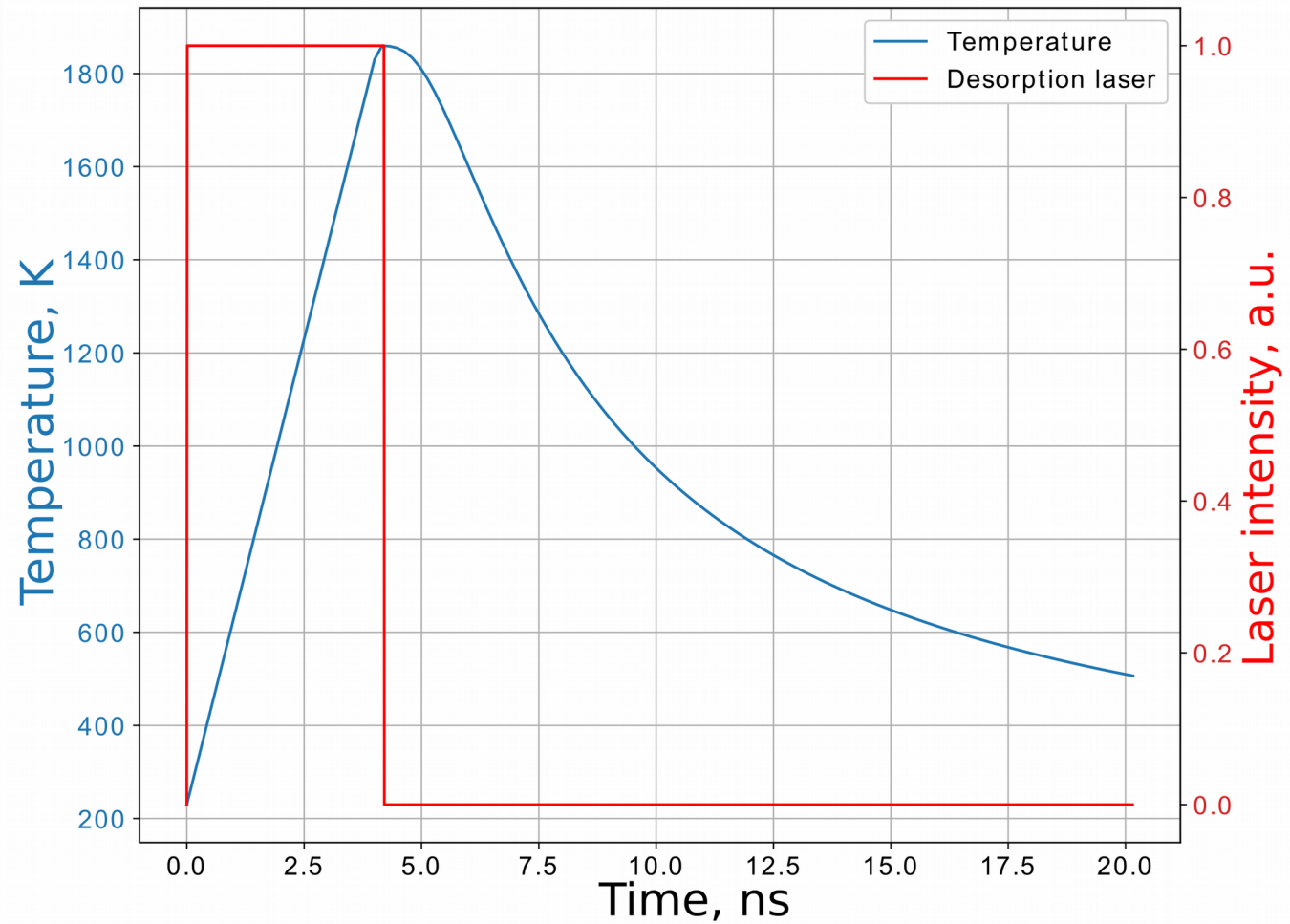
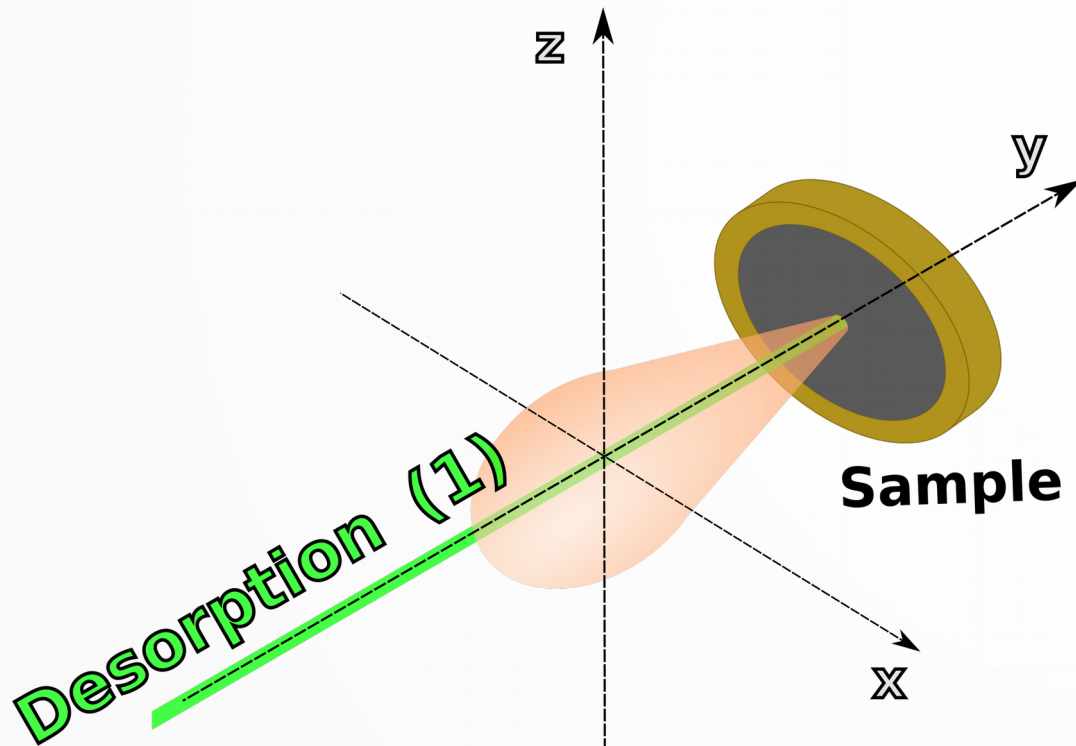


**Carcinogenic
potential**

Experimental setup

Two step laser mass spectrometry (L2MS) can be divided into three key stages^[1]:

- 1) **Laser desorption ($\lambda=532\text{nm}$)**
- 2) **Laser ionisation ($\lambda=266\text{nm}$)**
- 3) **Time-of-flight mass spectrometry**

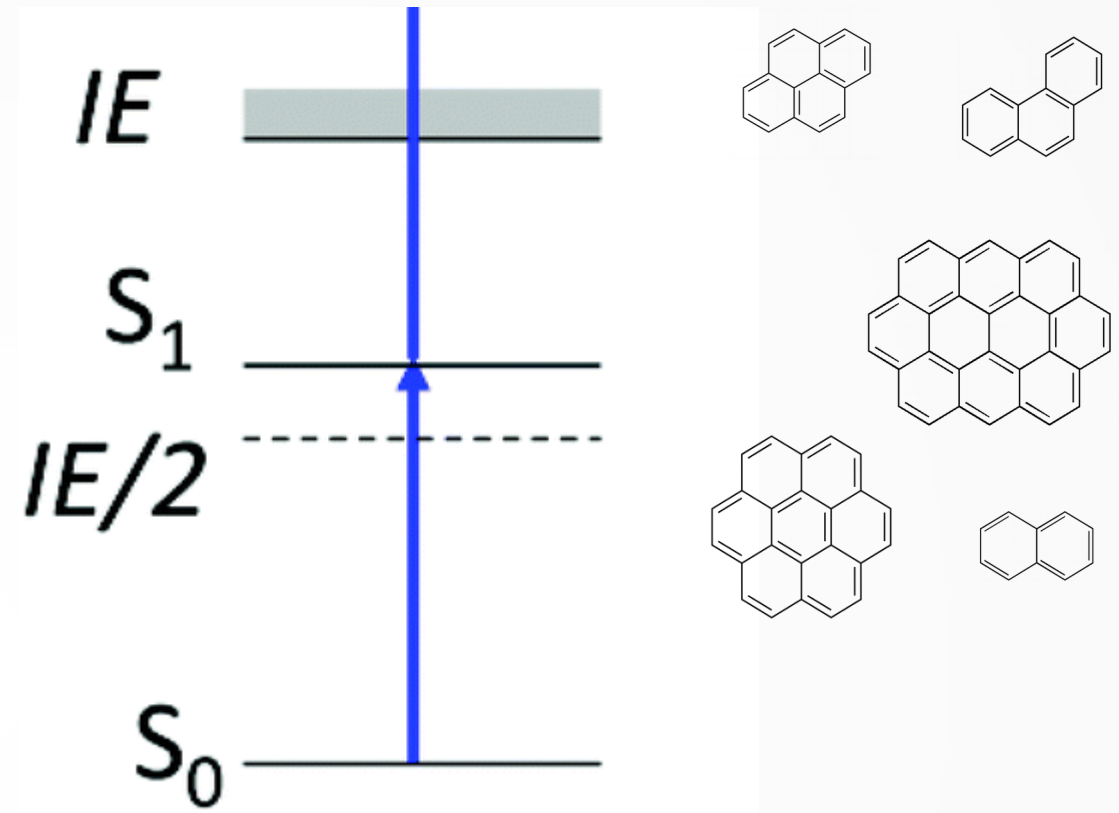
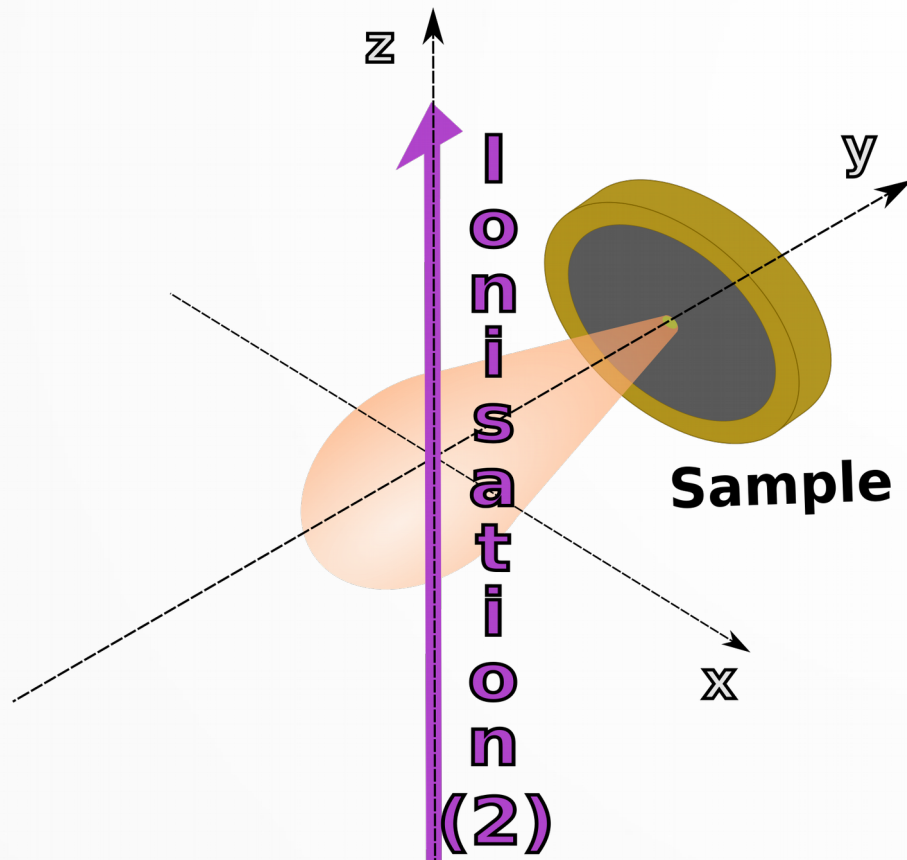


The increase in surface temperature promotes thermal desorption of the adsorbates

Experimental setup

Two step laser mass spectrometry (L2MS) can be divided into three key stages:

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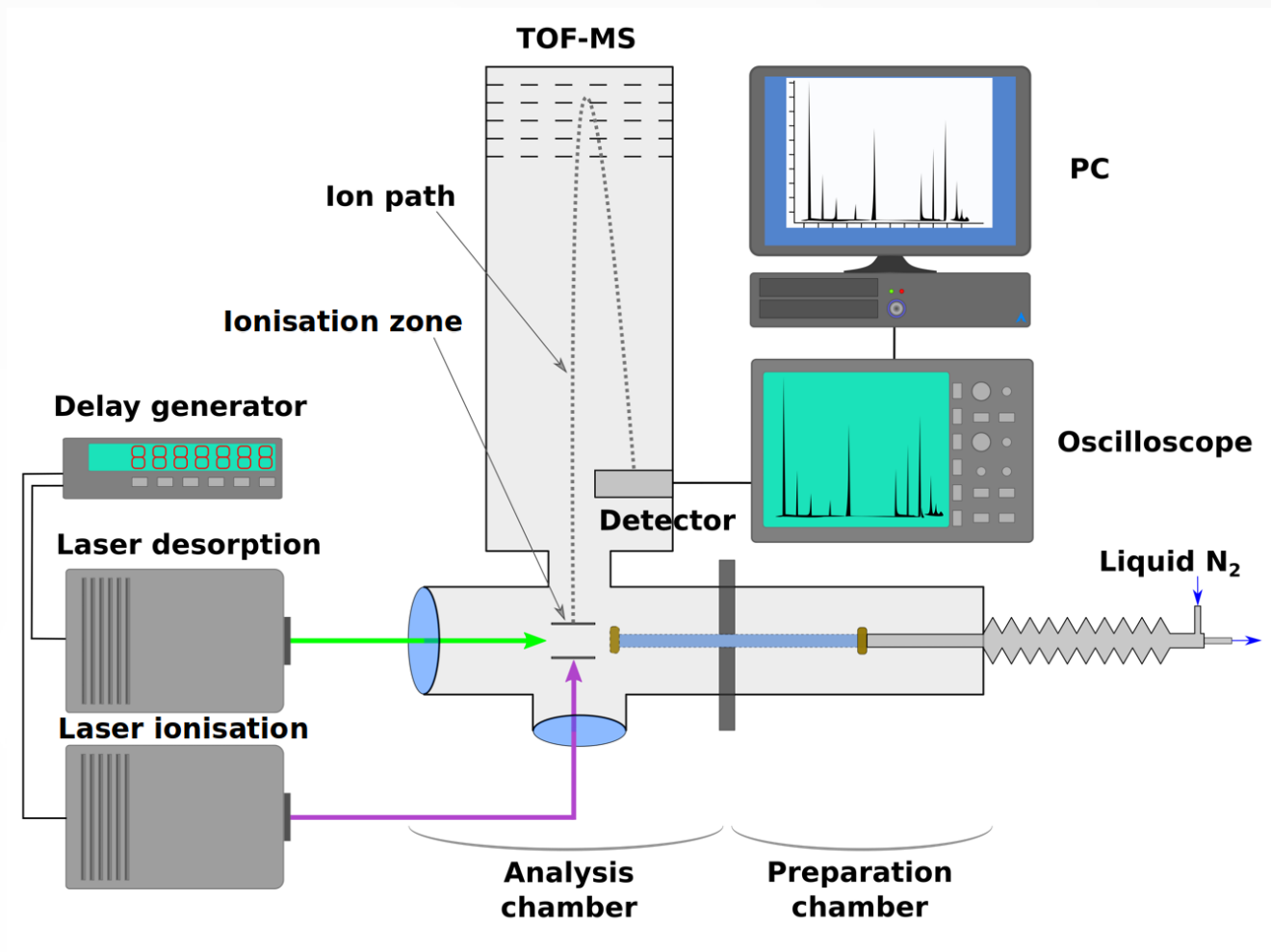
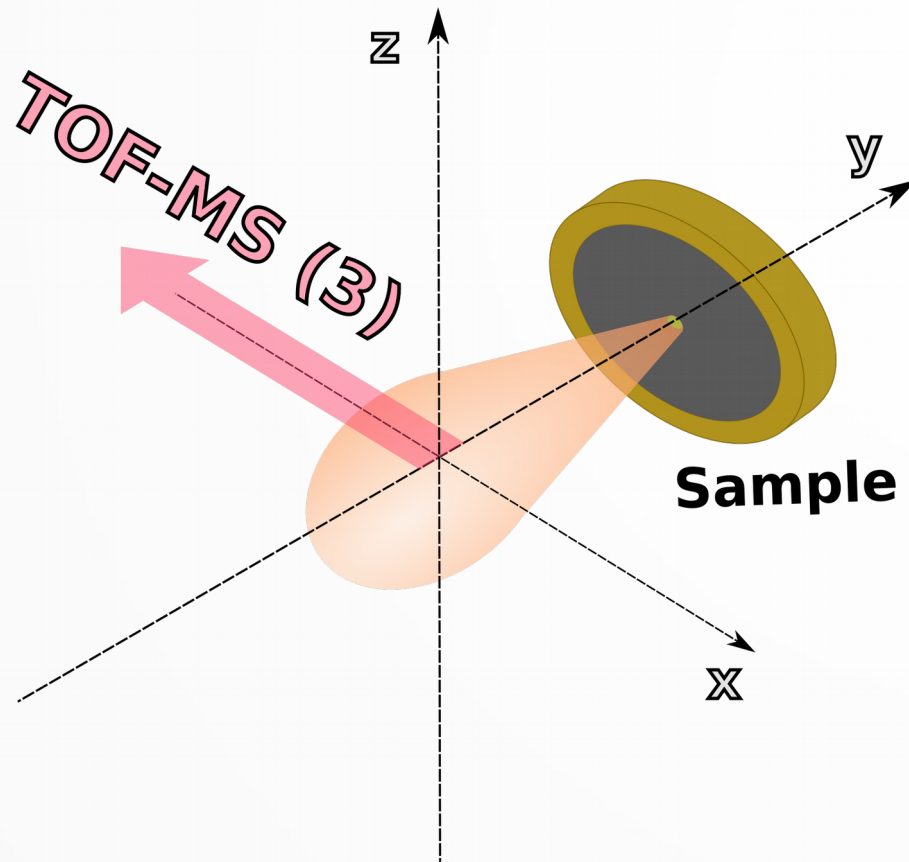


Desorbed species will be ionised via a resonant two photon process

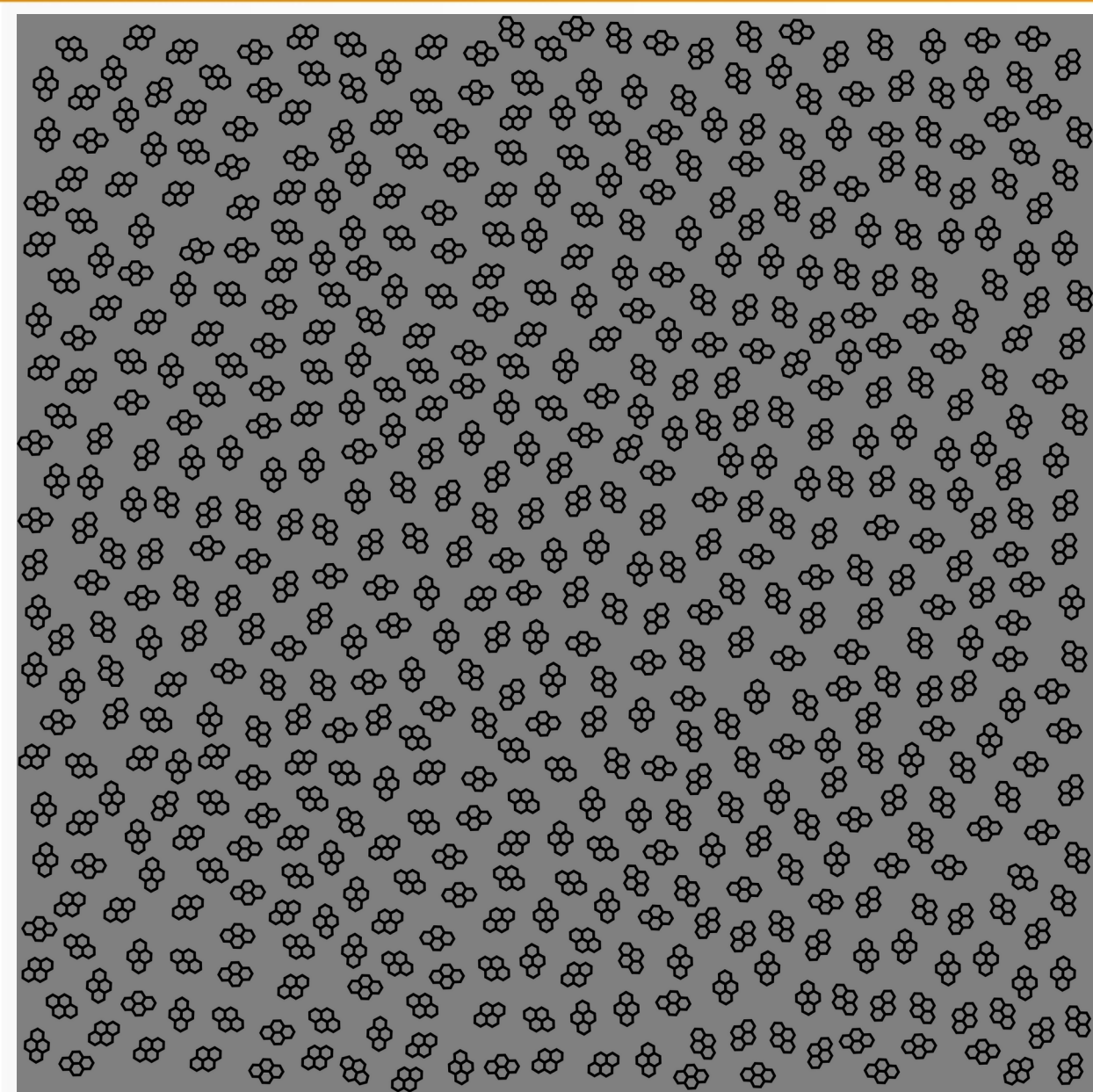
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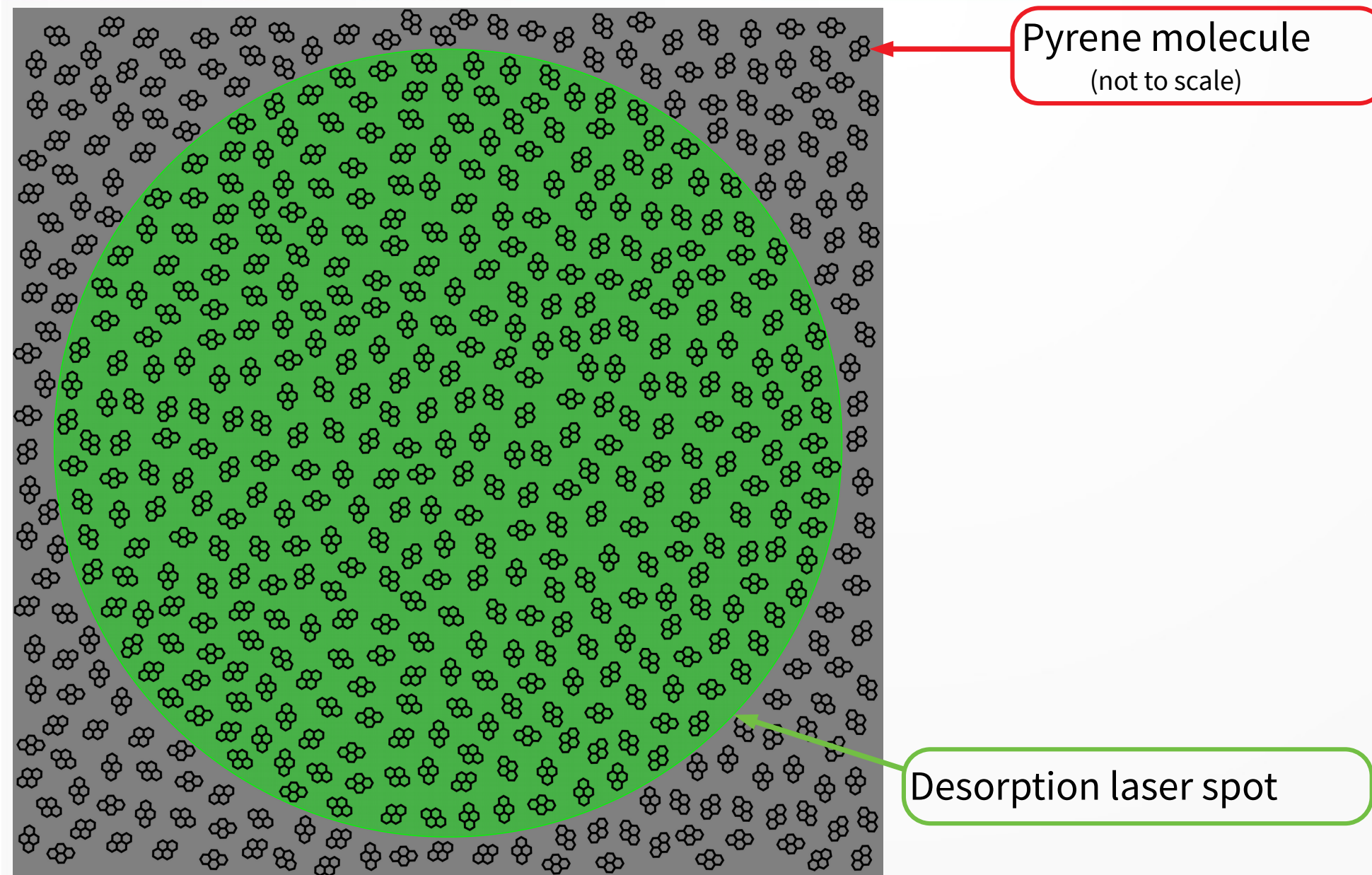
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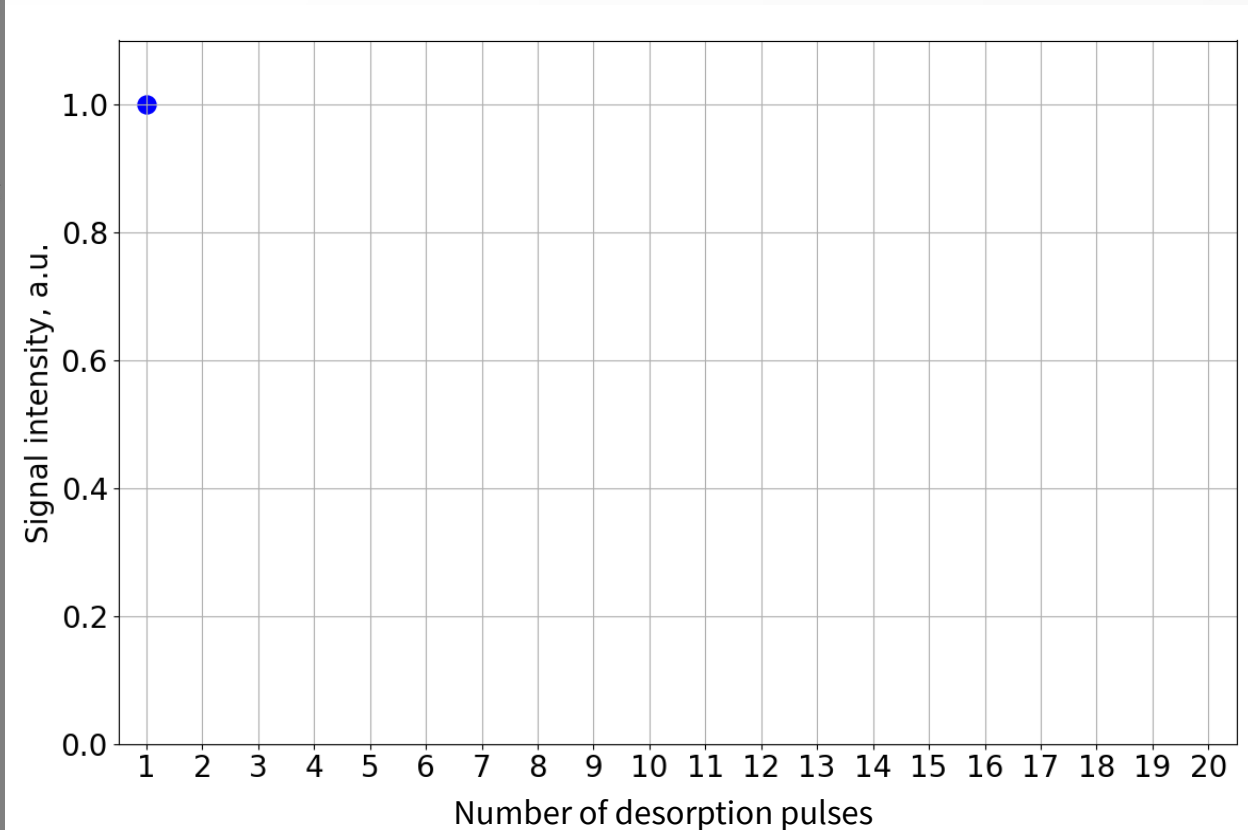
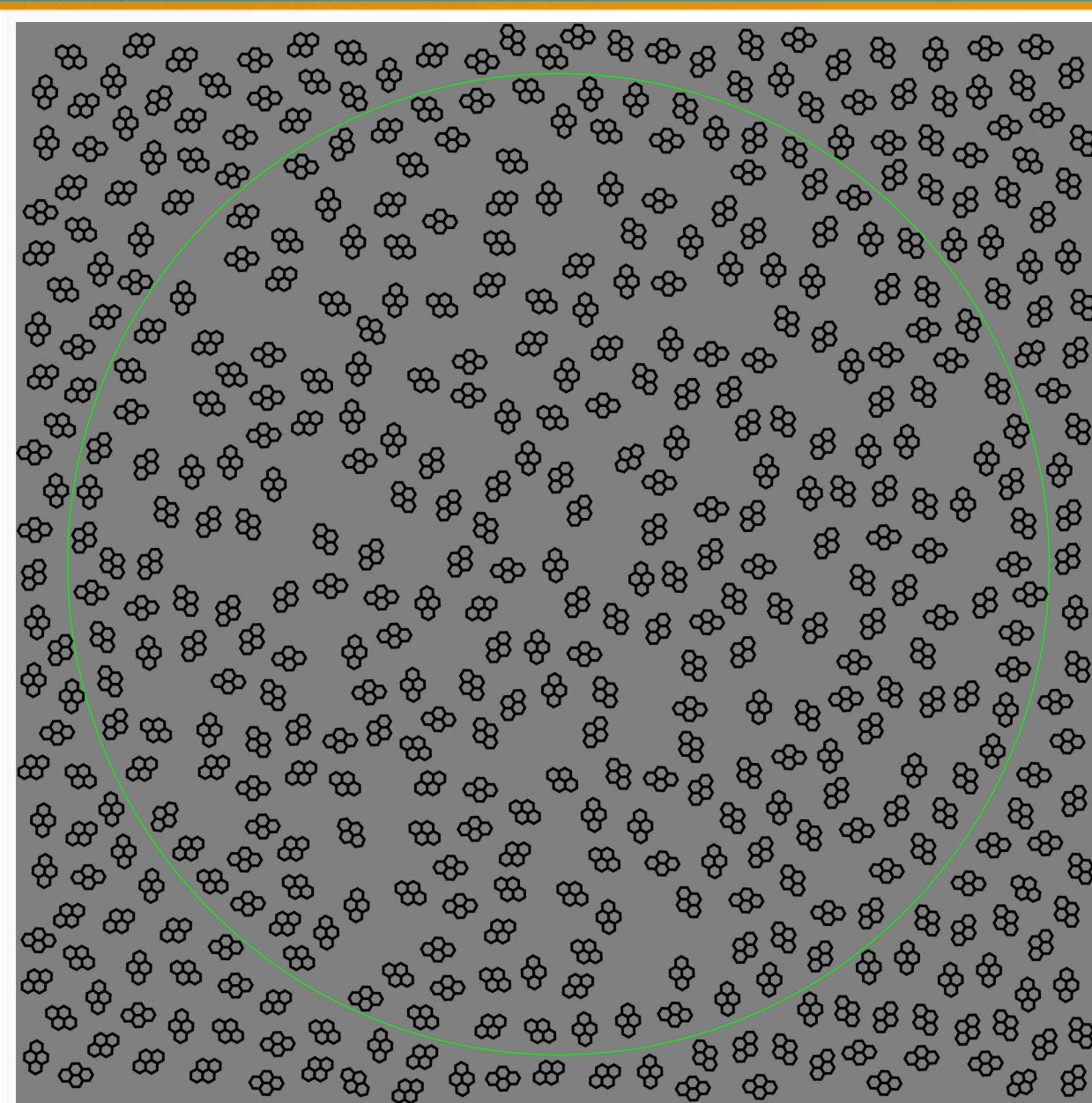
From Laser Induced Thermal Desorption to Adsorption Energy



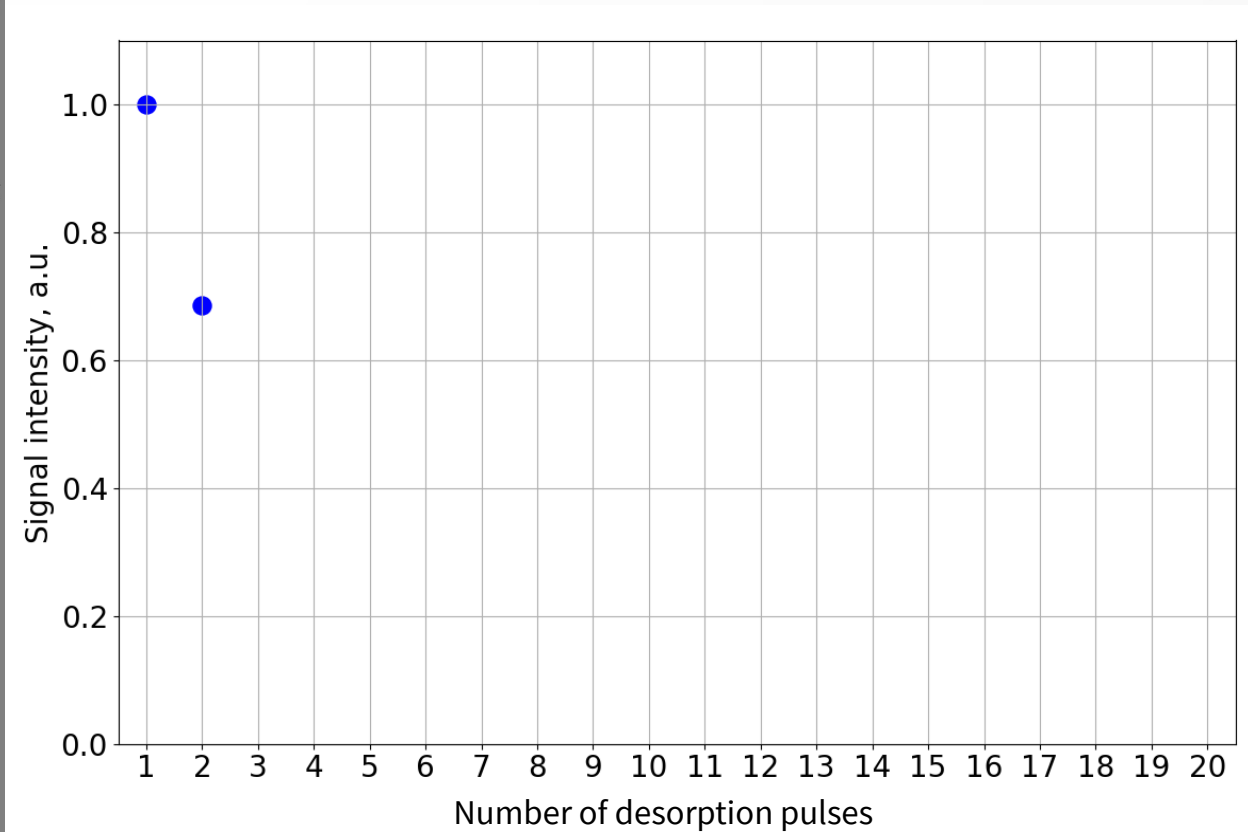
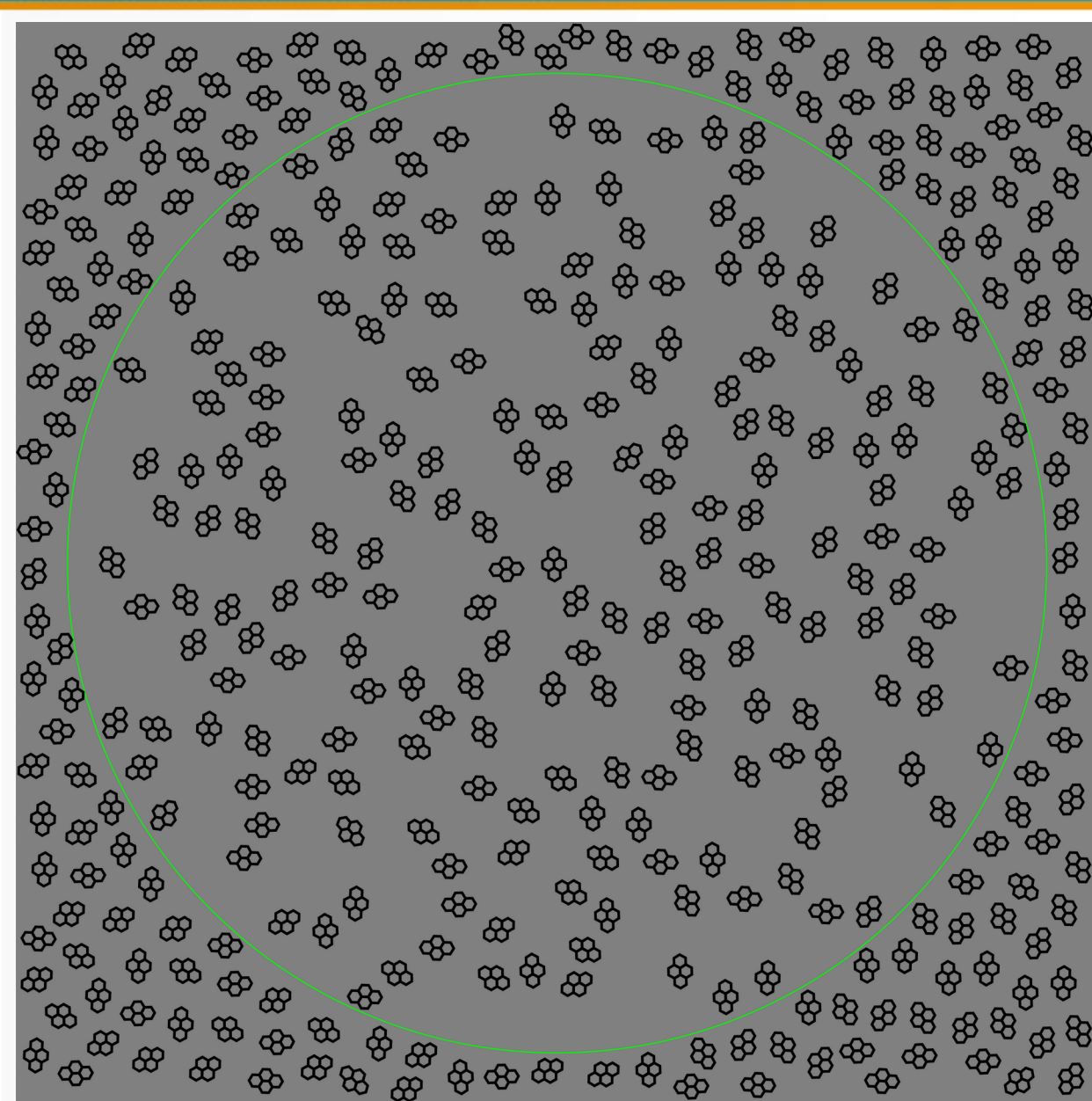
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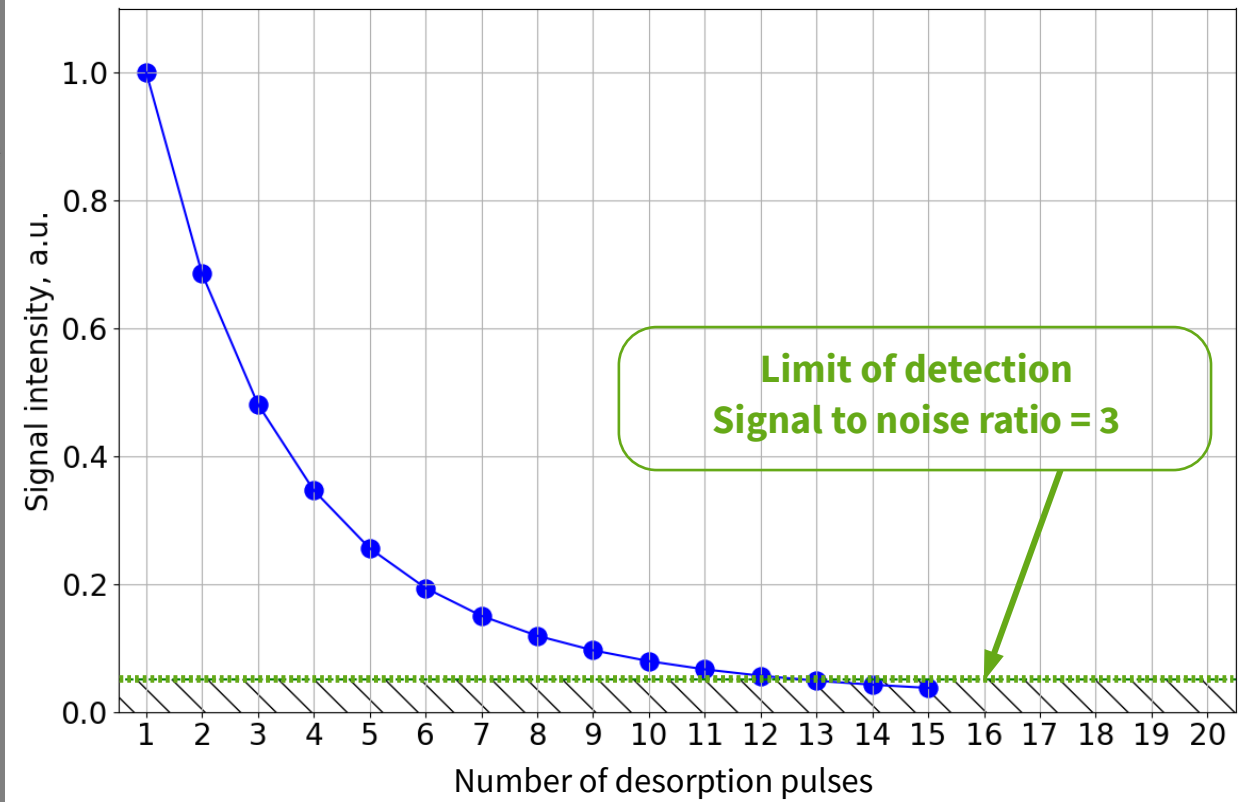
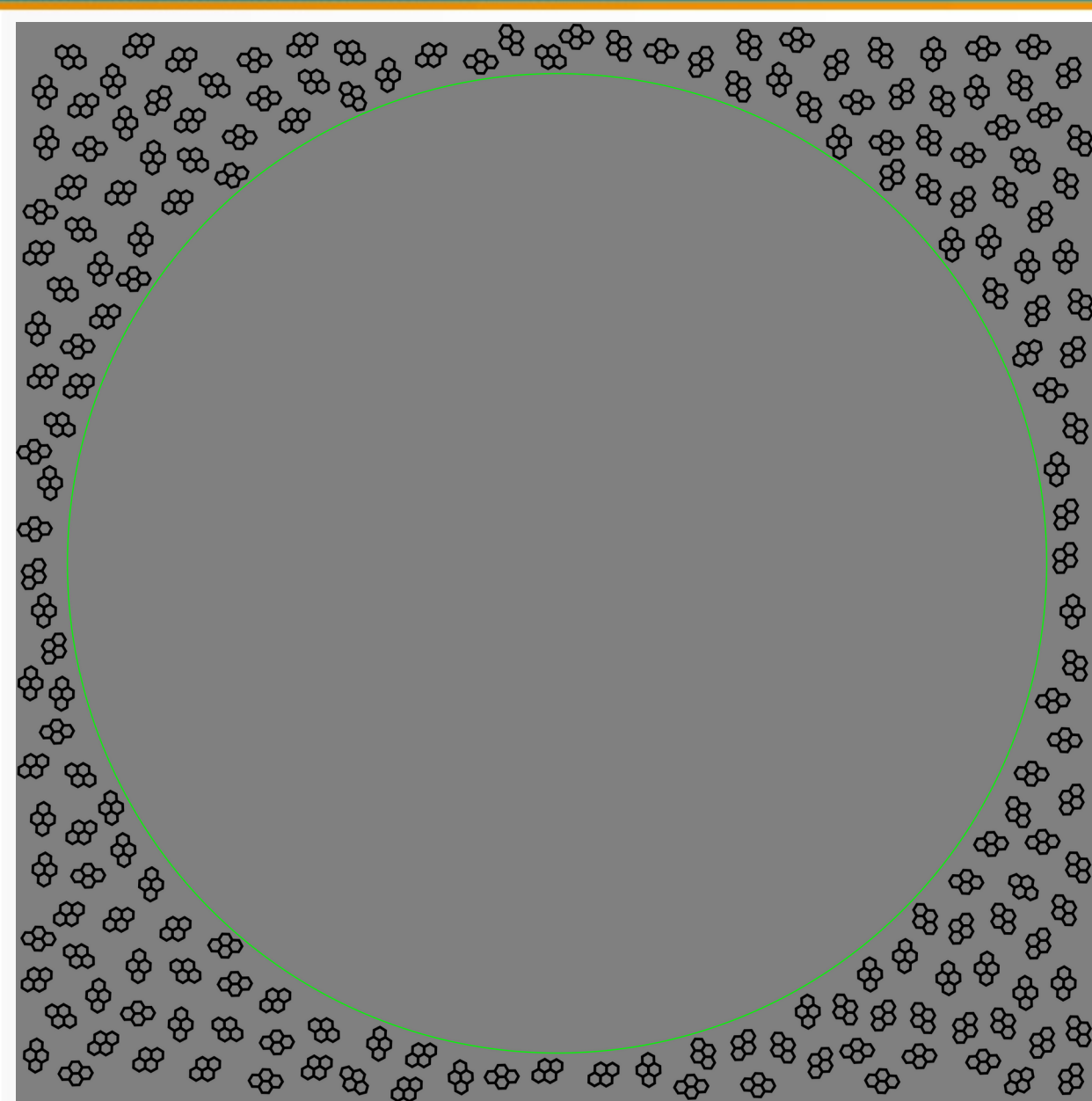
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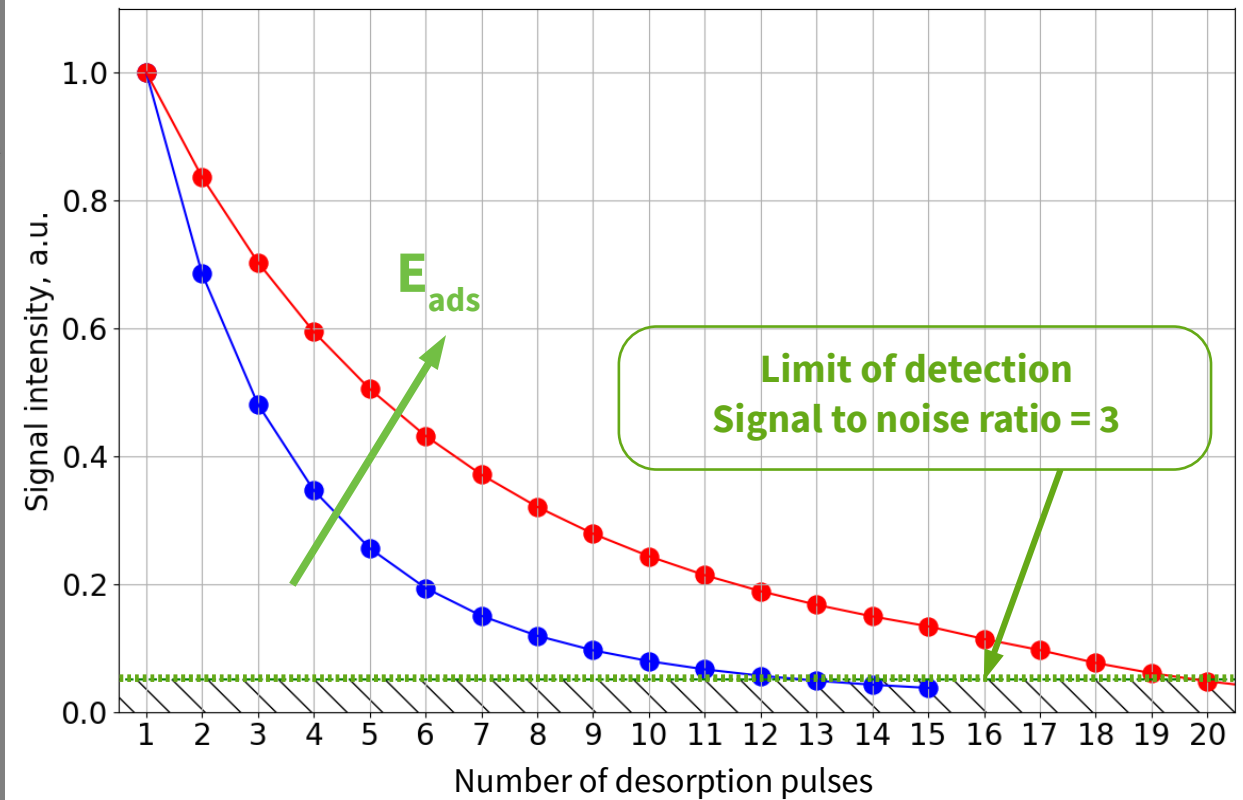
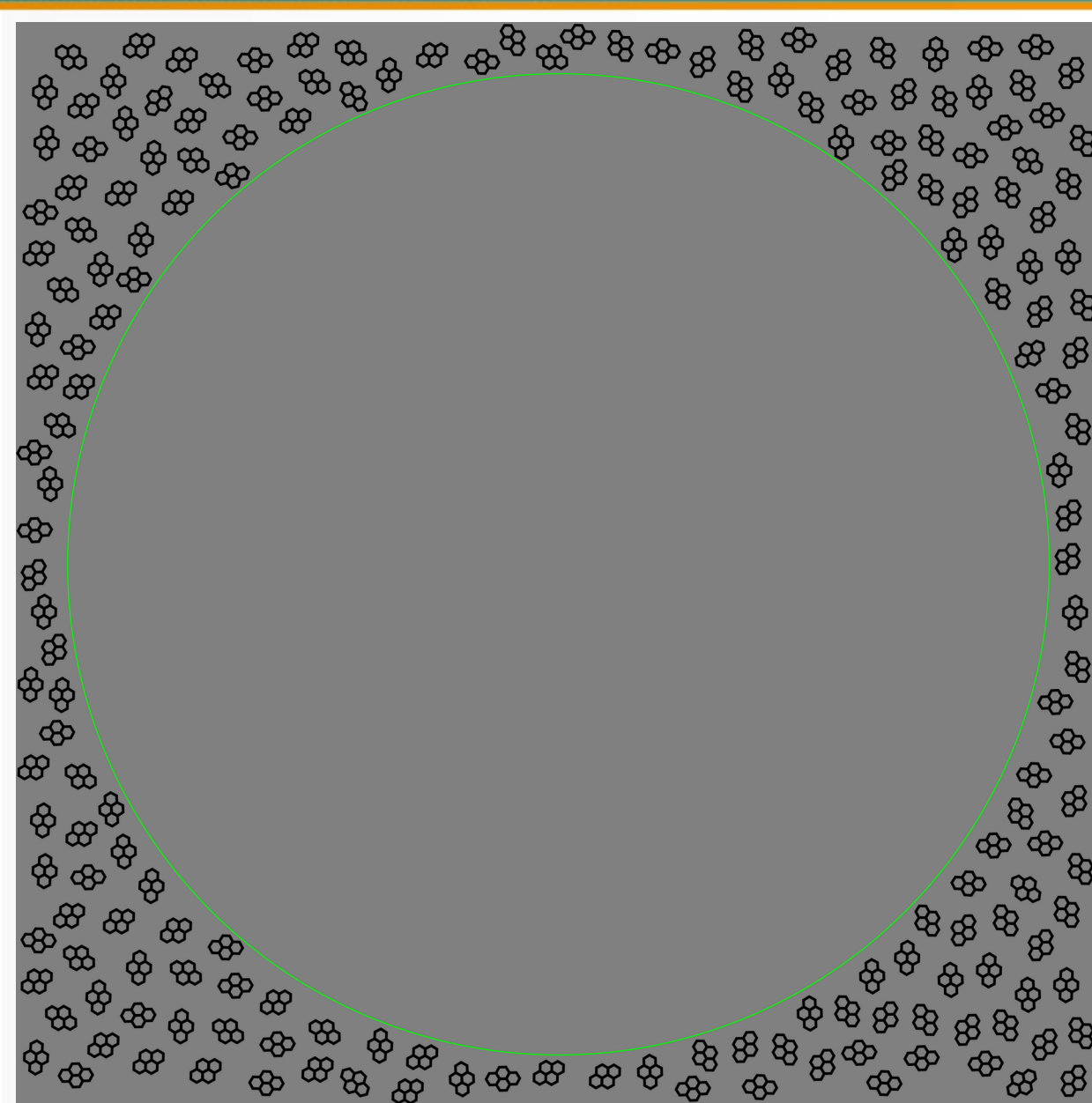
From Laser Induced Thermal Desorption to Adsorption Energy



From Laser Induced Thermal Desorption to Adsorption Energy



From Laser Induced Thermal Desorption to Adsorption Energy



Steady state approximation – estimation of the desorption rate

The number of desorbed molecules per desorption pulse is [2,3]:

$$N \simeq A \cdot n_0 \cdot \exp\left(-\frac{E_{ads}}{k_B(T_0 + BF)}\right)$$

where E_{ads} is the adsorption energy,

n_0 – surface concentration of the adsorbate

F - laser fluence (J/cm²) and

B is a conversion factor of the deposited energy into an increase of the surface temperature

Effective temperature is:

$$T_{eff} = T_0 + BF$$

B coefficient depends on the optical and thermal properties of the sample

For the used desorption fluence values, the effective temperature is:

$$T_{eff} \approx 2400 \text{ K}$$

[2] Klaus Dreisewerd et al., International Journal of Mass Spectrometry and Ion Processes 141 (1995), pp. 127–148.

[3] L V Zhigilei and B J Garrison, Applied Physics Letters 74 (1999)

Steady state approximation – estimation of the desorption rate

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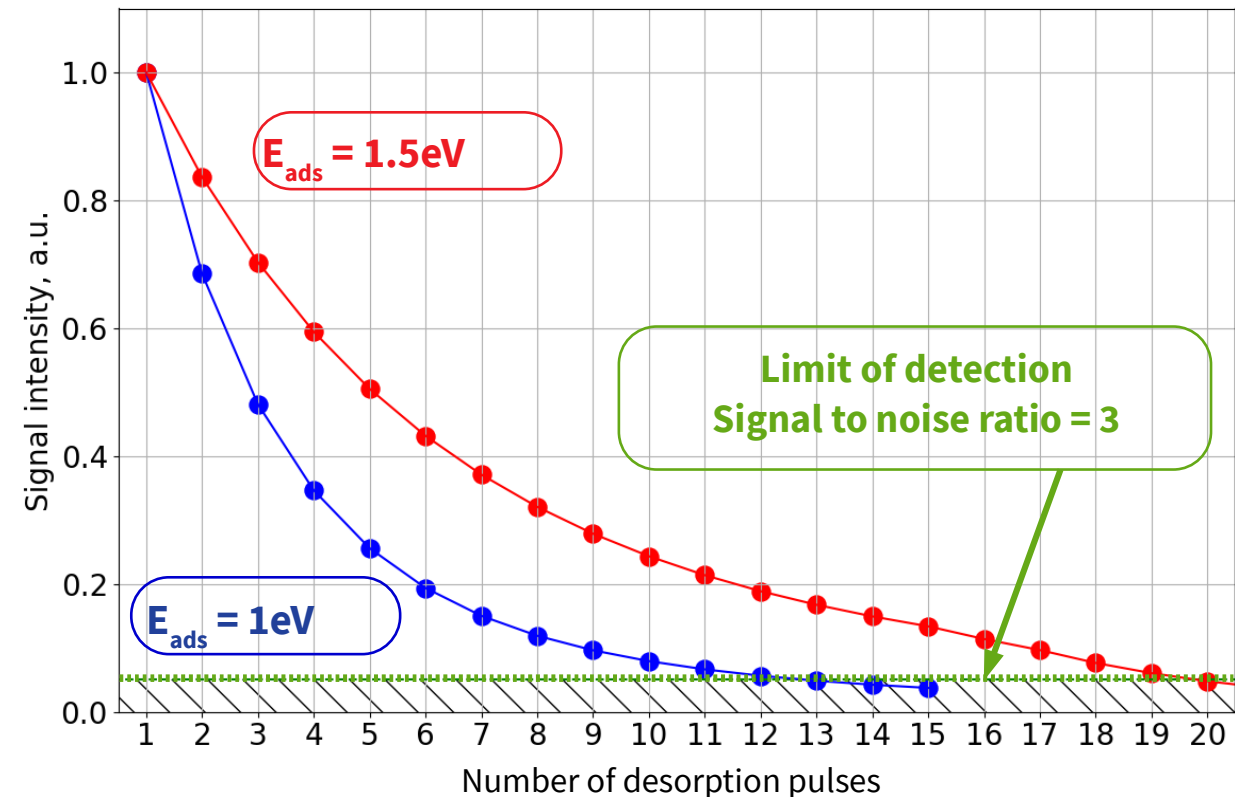
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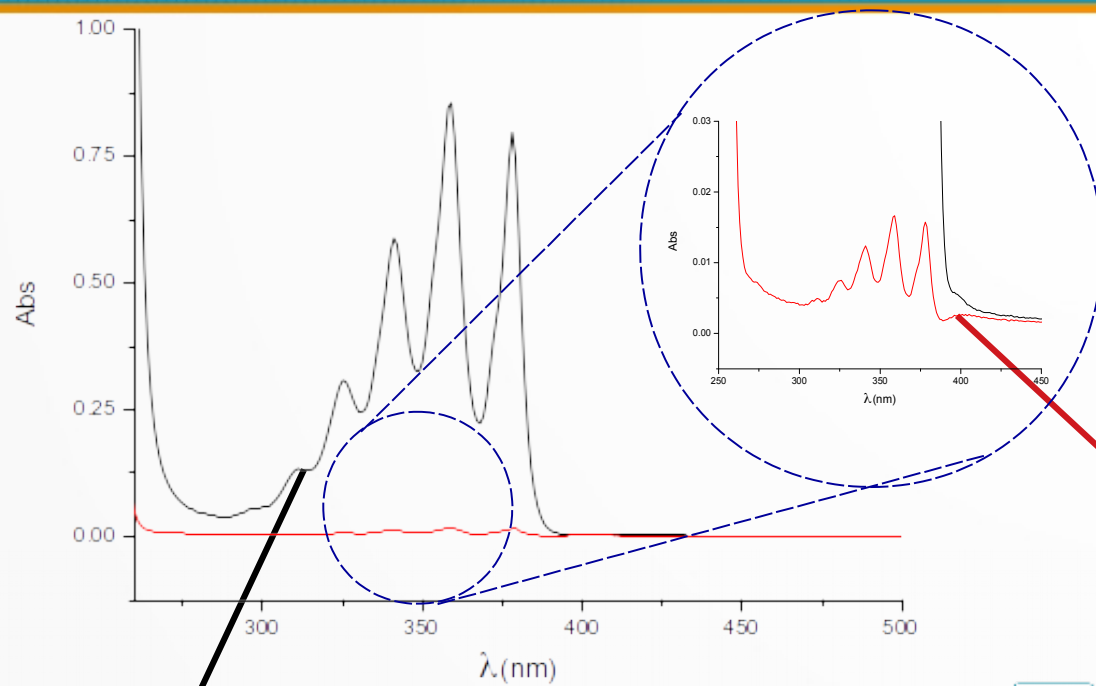


The shape of the signal decay curve depends on the adsorption energy E_{ads}

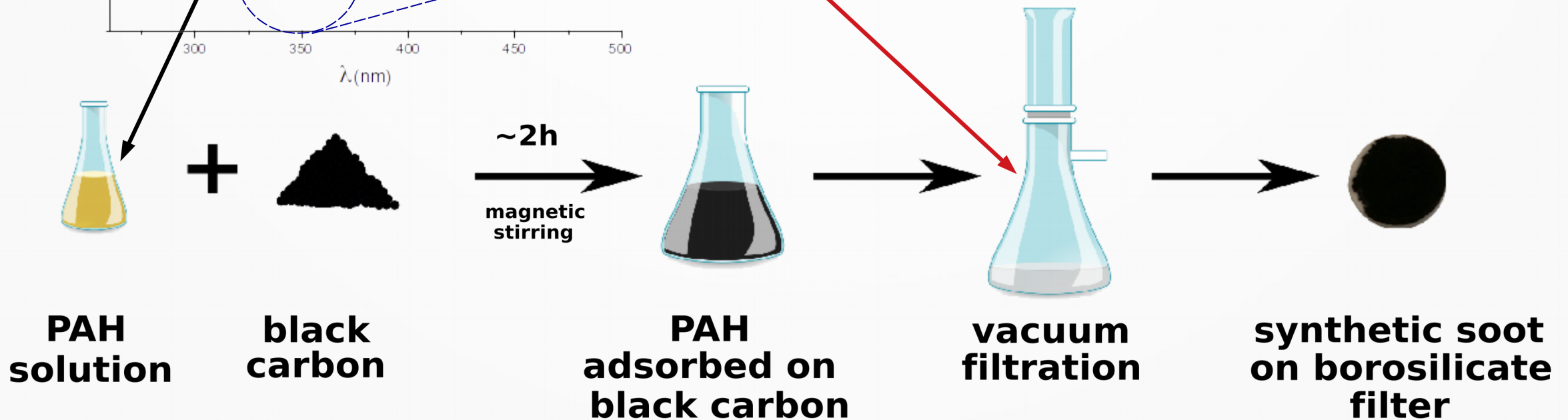
[2] Klaus Dreisewerd et al., 141 (1995), pp. 127–148.

[3] L V Zhigilei and B J Garrison, Applied Physics Letters 74.9 (1999)

Sample preparation – synthetic soot

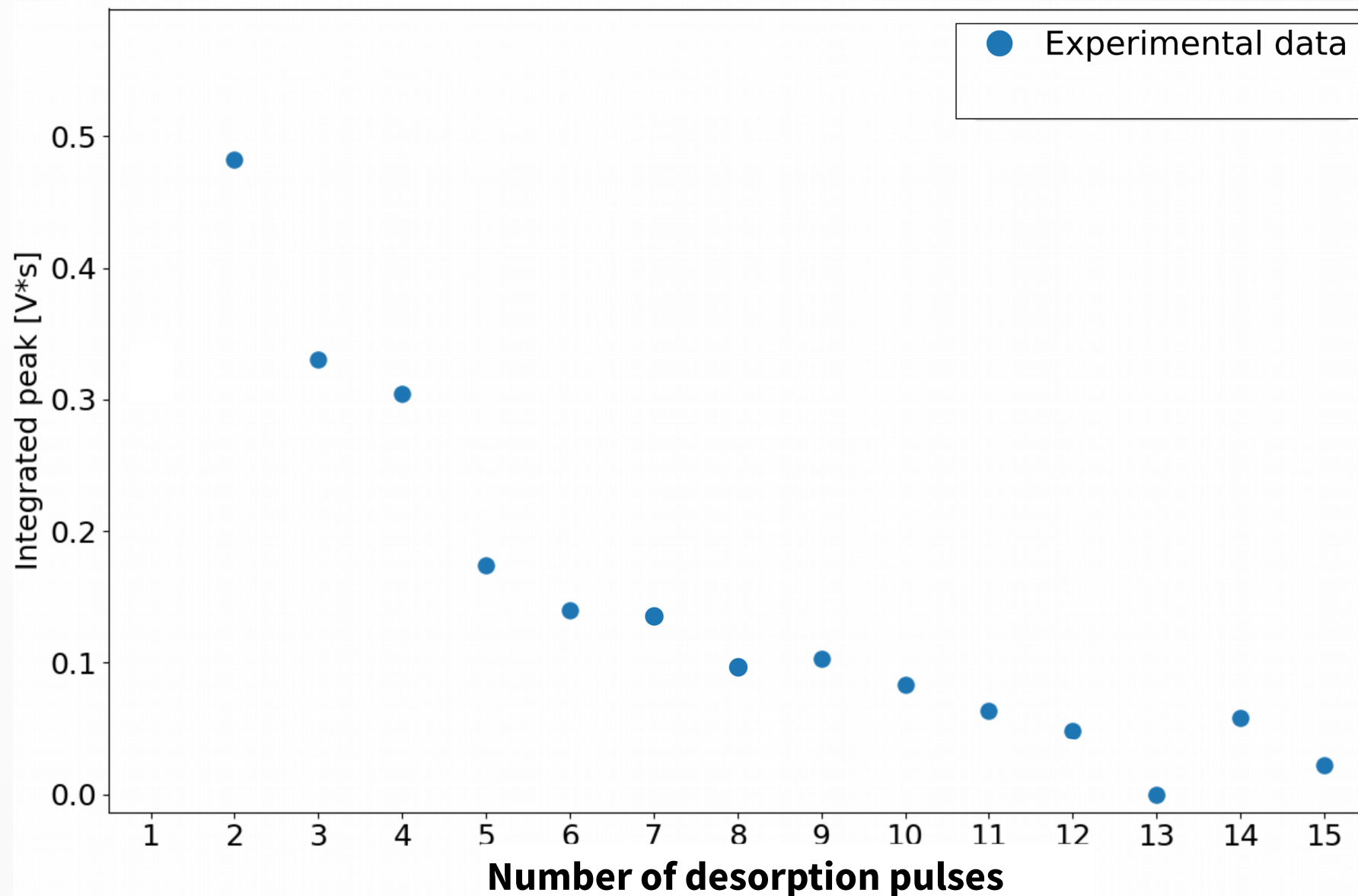
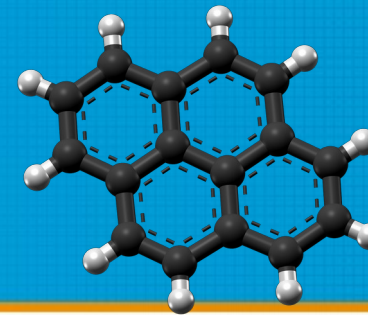


- Synthetic soot was prepared by adsorbing single PAHs from a solution of known concentration on fine carbon particles.
- The adsorbed amount of PAH was calculated from the absorption spectra^[1].
- Analysed samples had a surface concentration of $\sim 10^{-3}$ monolayers.



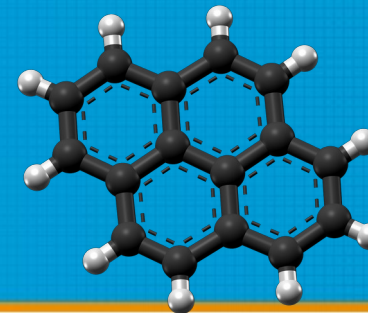
First approach (from Signal decay)

Adsorption Energy of Pyrene ($C_{16}H_{10}$)



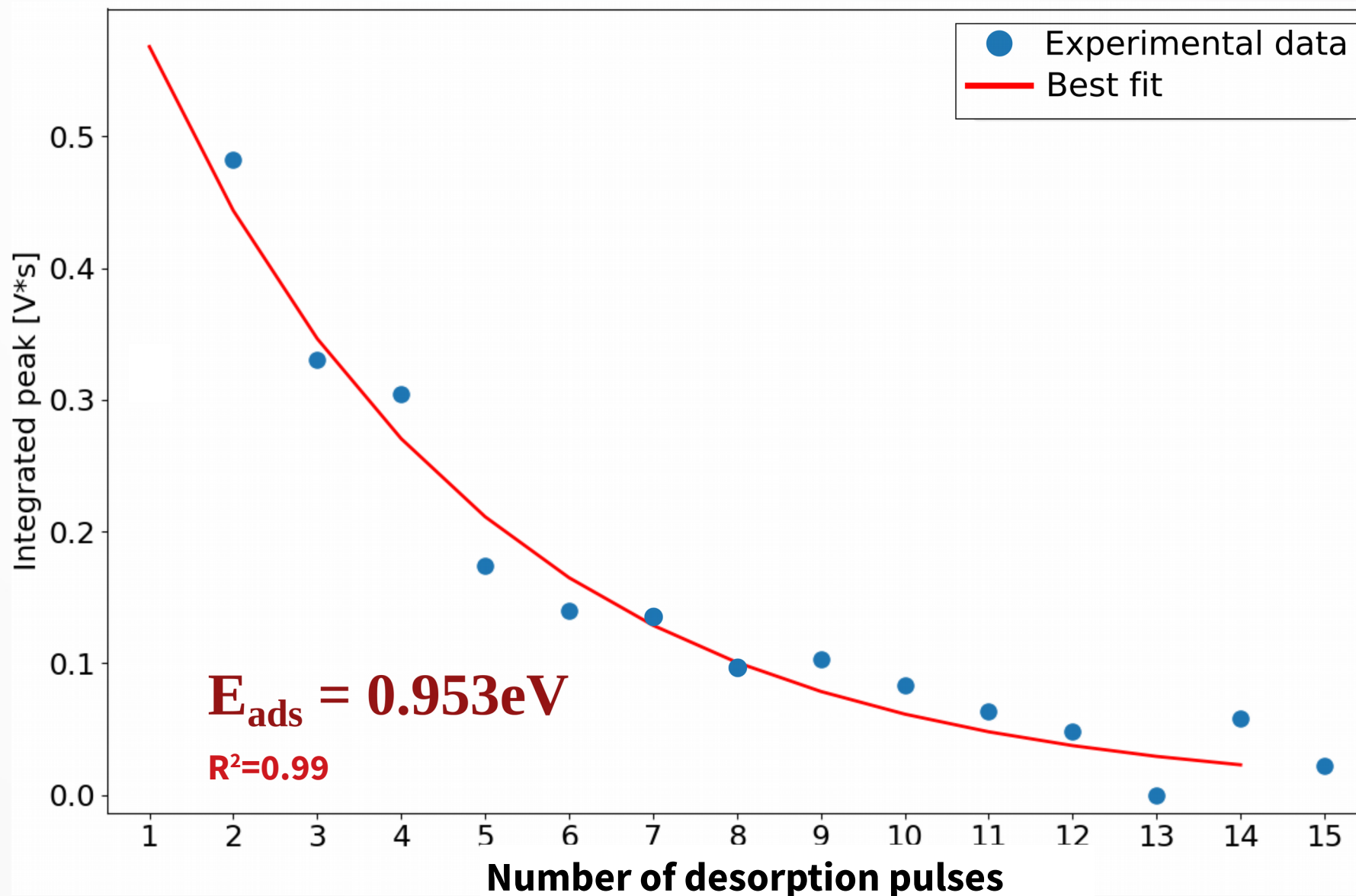
First approach (from Signal decay)

Adsorption Energy of Pyrene ($C_{16}H_{10}$)



The adsorption energy was retrieved by fitting the experimental data

The obtained value is close to the one found in literature **0.986eV**^[4,5]

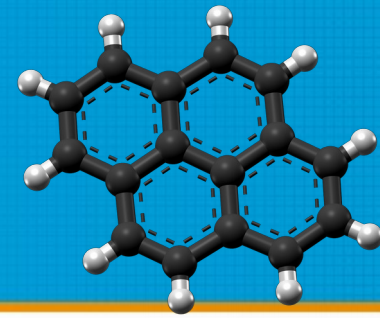


[4] Y Bedjanian et al., J. Phys. Chem. 114.10 (2010), pp. 3533–3539

[5] A Guilloteau et al., J. Phys. Chem. A 112.42 (2008), pp. 10552–10559

First approach (from Signal decay)

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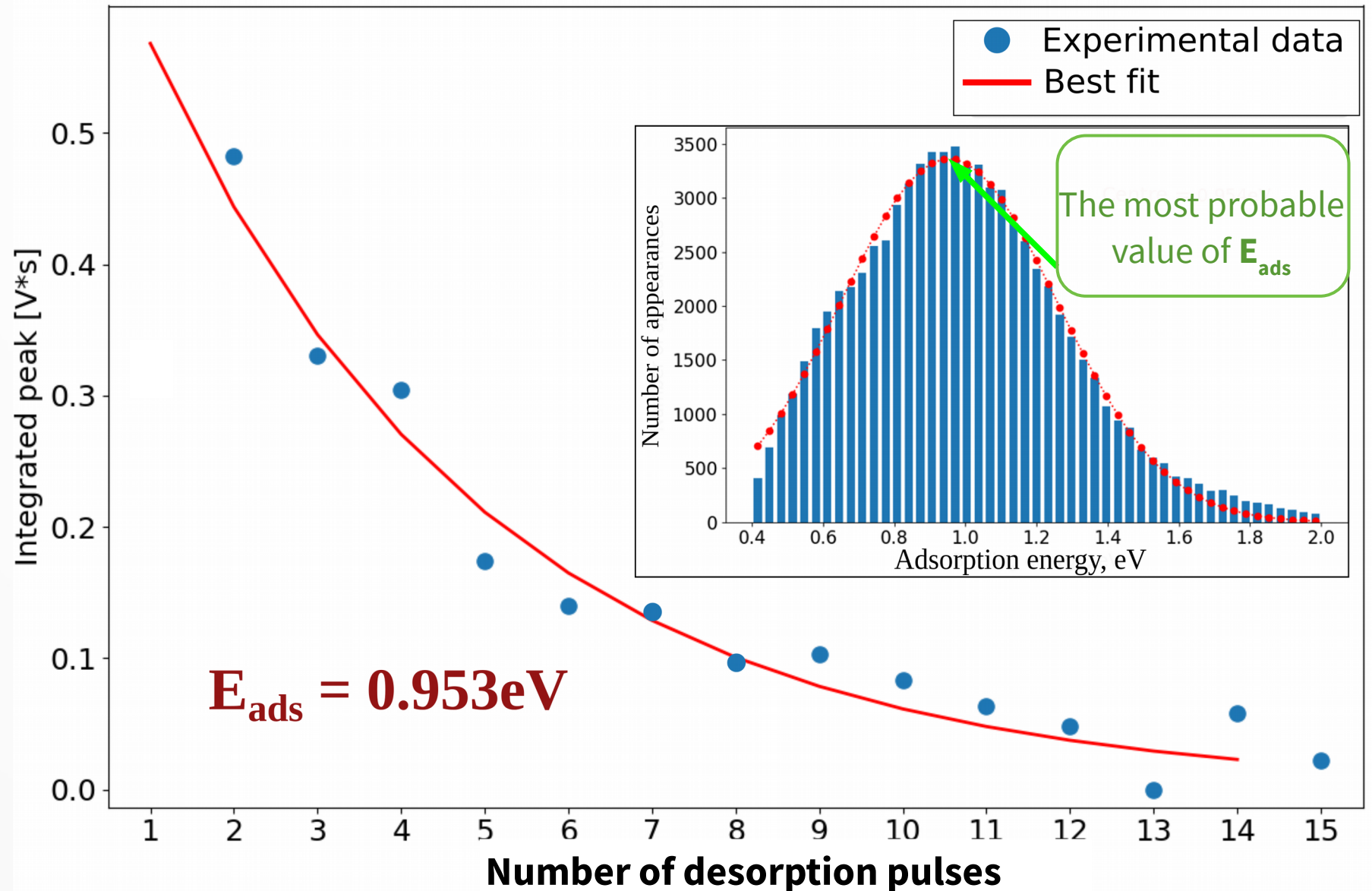


$$N \simeq A \cdot n_0 \cdot \exp\left(-\frac{E_{ads}}{k_B(T_0 + BF)}\right)$$

There is a high correlation between E_{ads} and B

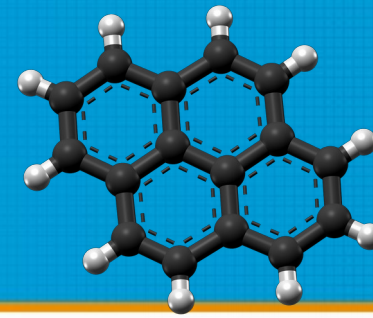
Solution:

Multiple fits with different initial values for the fit



First approach (from Signal decay)

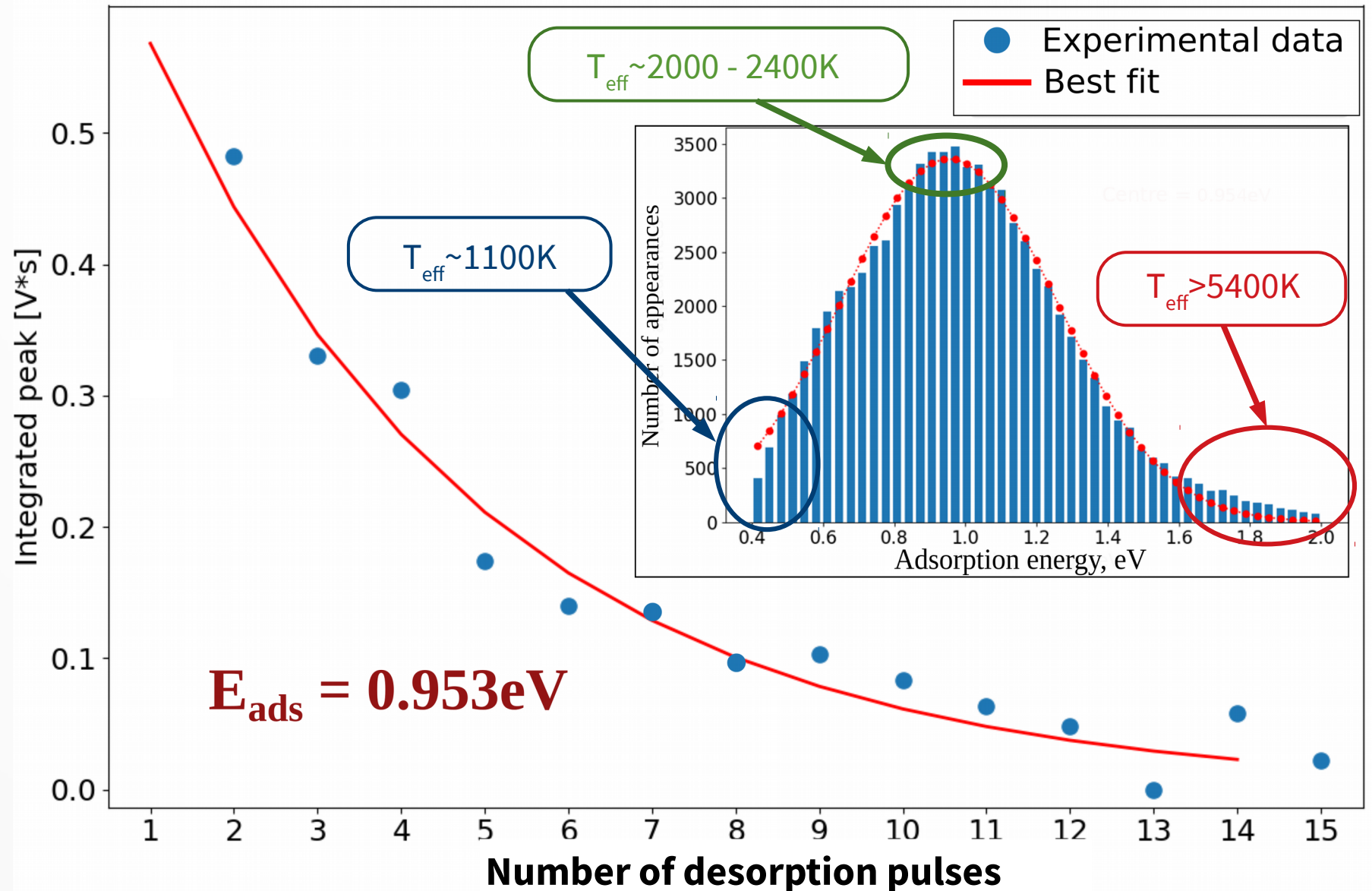
Adsorption Energy of Pyrene ($C_{16}H_{10}$)



$$N \simeq A \cdot n_0 \cdot \exp\left(-\frac{E_{ads}}{k_B(T_0 + BF)}\right)$$

Effective temperature is:

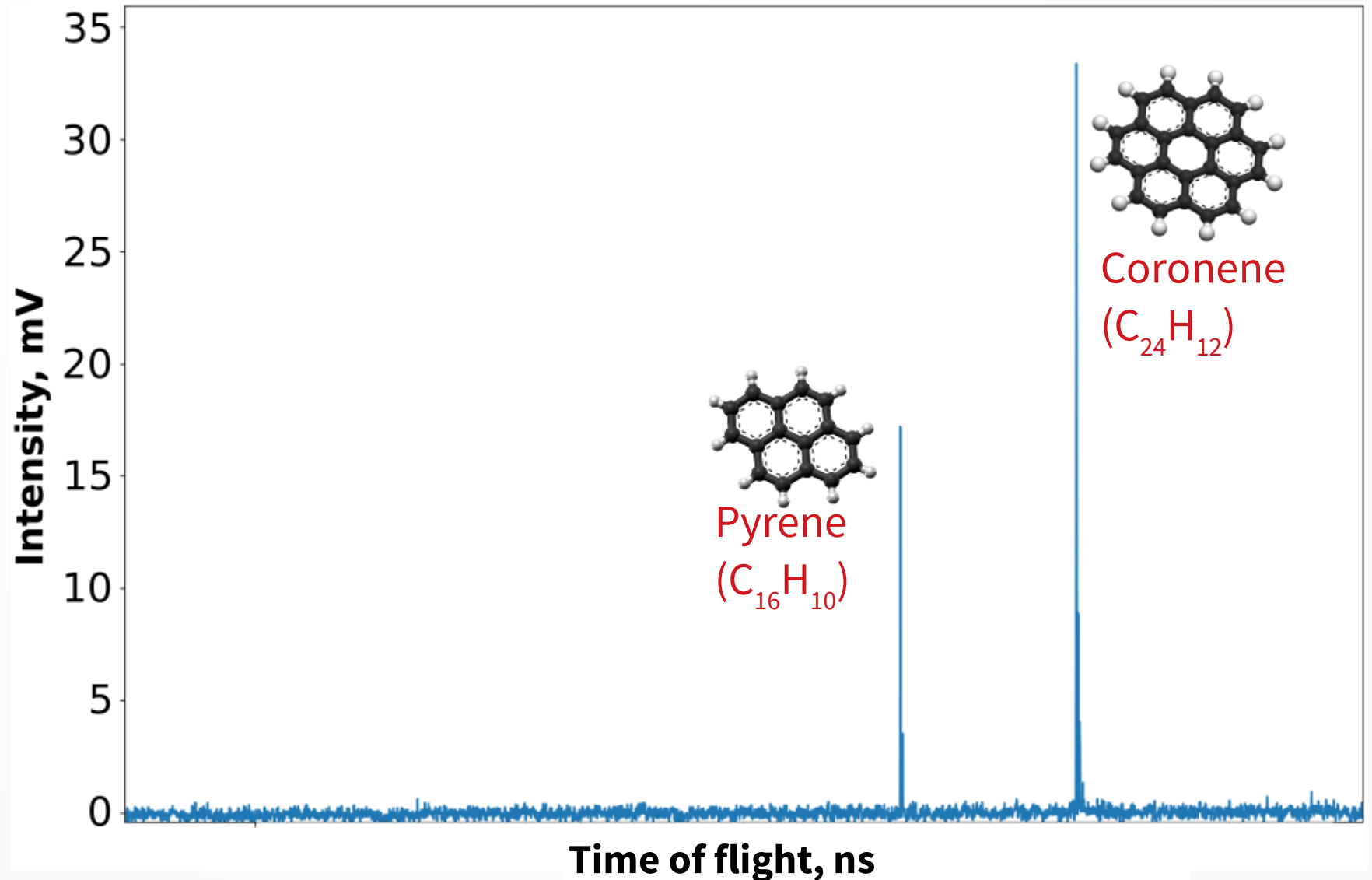
$$T_{eff} = T_0 + BF$$



Retrieval of adsorption energy - sample with multiple PAHs

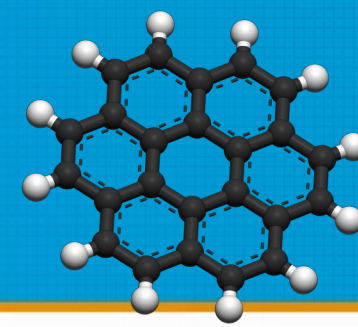
Synthetic soot with two PAHs adsorbed on the surface was analysed (**pyrene and coronene**)

The adsorption energy retrieval is independent for different molecules

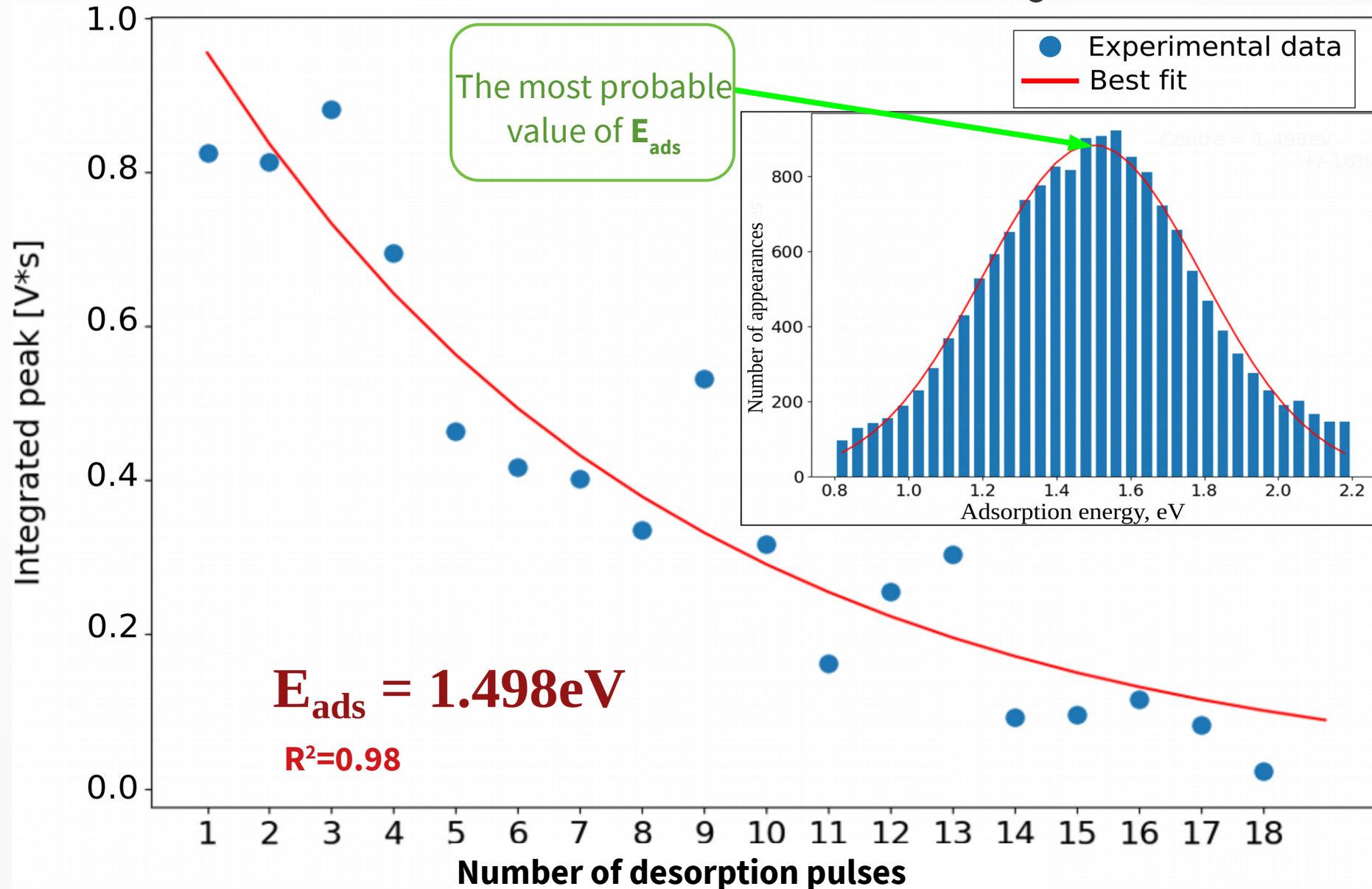


First approach (from Signal decay)

Adsorption Energy of Coronene ($C_{24}H_{12}$)



The obtained value is close to the one found in literature - from **1.32 to 1.48eV**^[6]



Second approach (from fluence curve)

Adsorption Energy of Pyrene ($C_{16}H_{10}$)



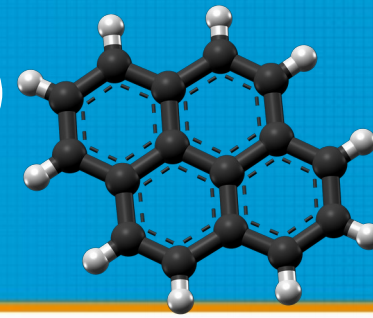
$$N \simeq A \cdot n_0 \cdot \exp\left(-\frac{E_{ads}}{k_B(T_0 + BF)}\right)$$

The fluence curve –
variation of the signal
corresponding to the first
desorption shot with laser
fluence.

Each shot was taken on a
different spot on the sample
(same initial surface
concentration)

Second approach (from fluence curve)

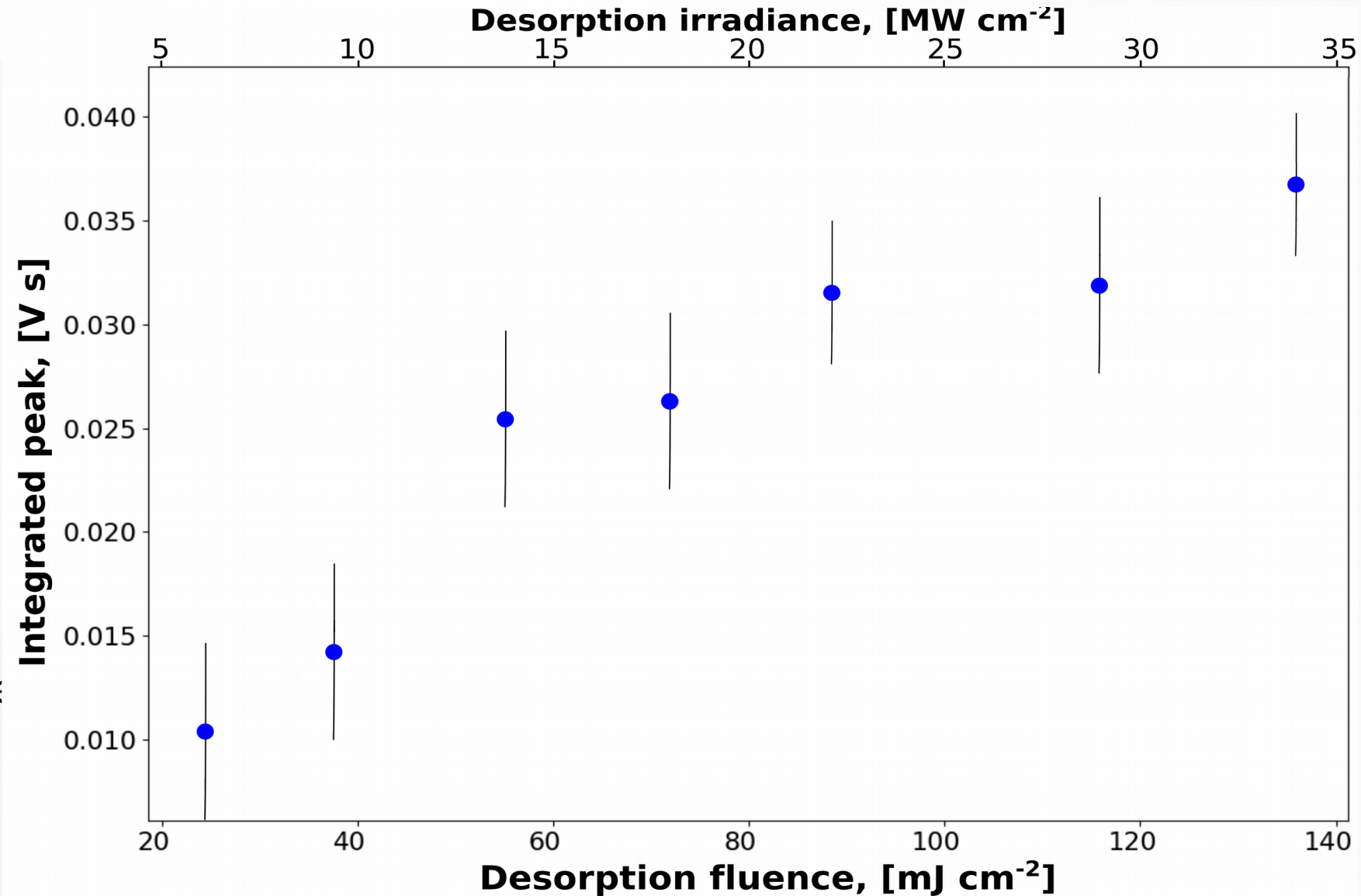
Adsorption Energy of Pyrene ($C_{16}H_{10}$)



$$N \simeq A \cdot n_0 \cdot \exp\left(-\frac{E_{ads}}{k_B(T_0 + BF)}\right)$$

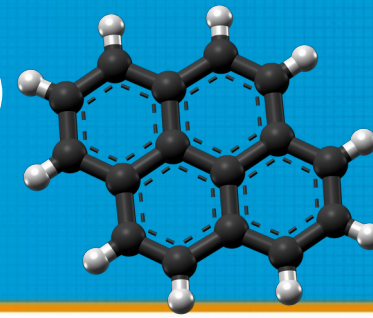
The fluence curve – variation of the signal corresponding to the first desorption pulse with laser fluence.

Each pulse was taken on a different spot on the sample (same initial surface concentration)



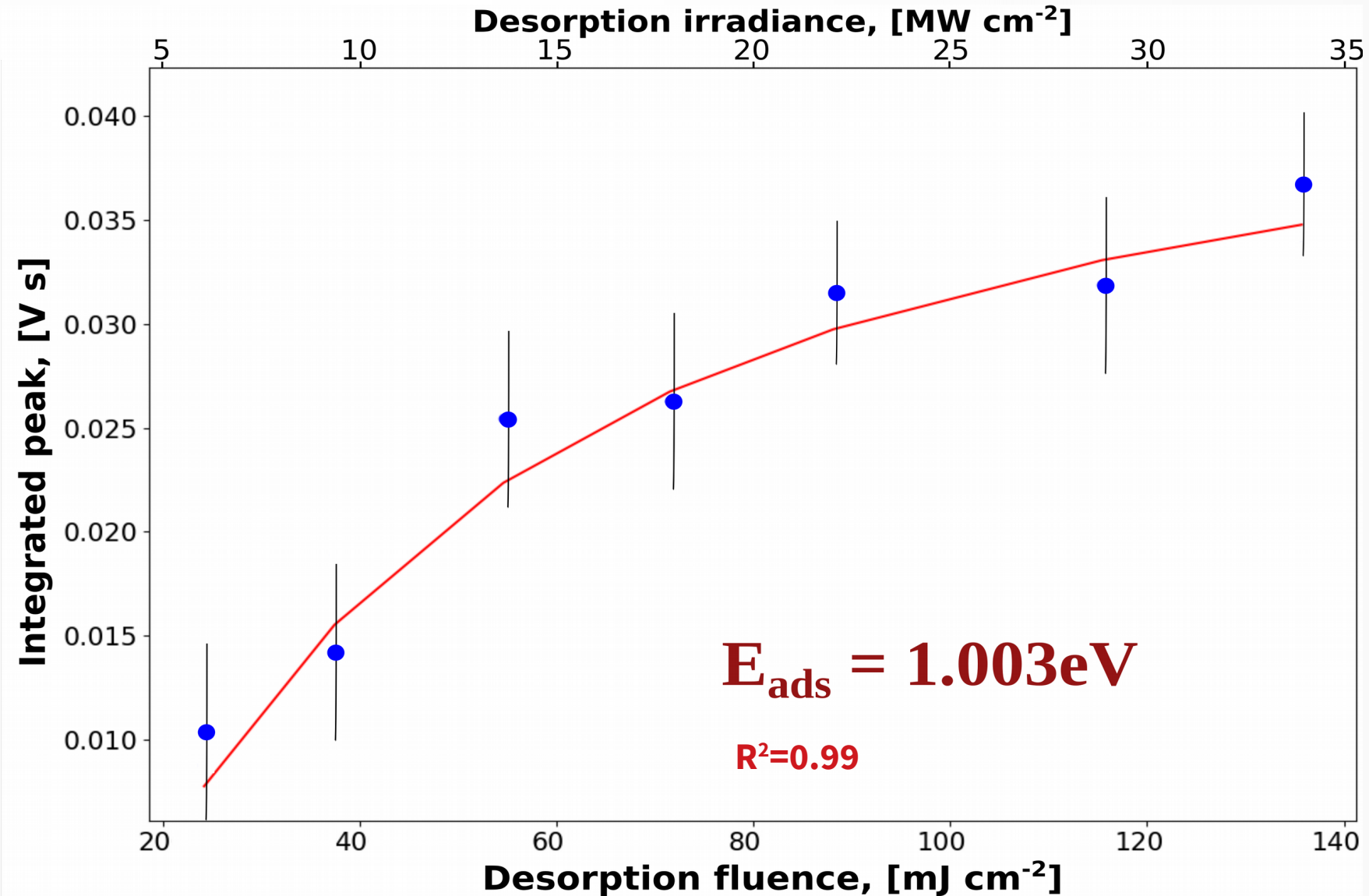
Second approach (from fluence curve)

Adsorption Energy of Pyrene ($C_{16}H_{10}$)



The adsorption energy was retrieved by fitting the experimental data

The obtained value is close to the one retrieved from the signal decay (**0.953eV**) and the one found in literature (**0.986eV**)^[4, 5]

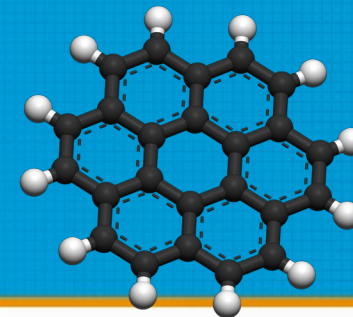


[4] Y Bedjanian et al., J. Phys. Chem. 114.10 (2010), pp. 3533–3539

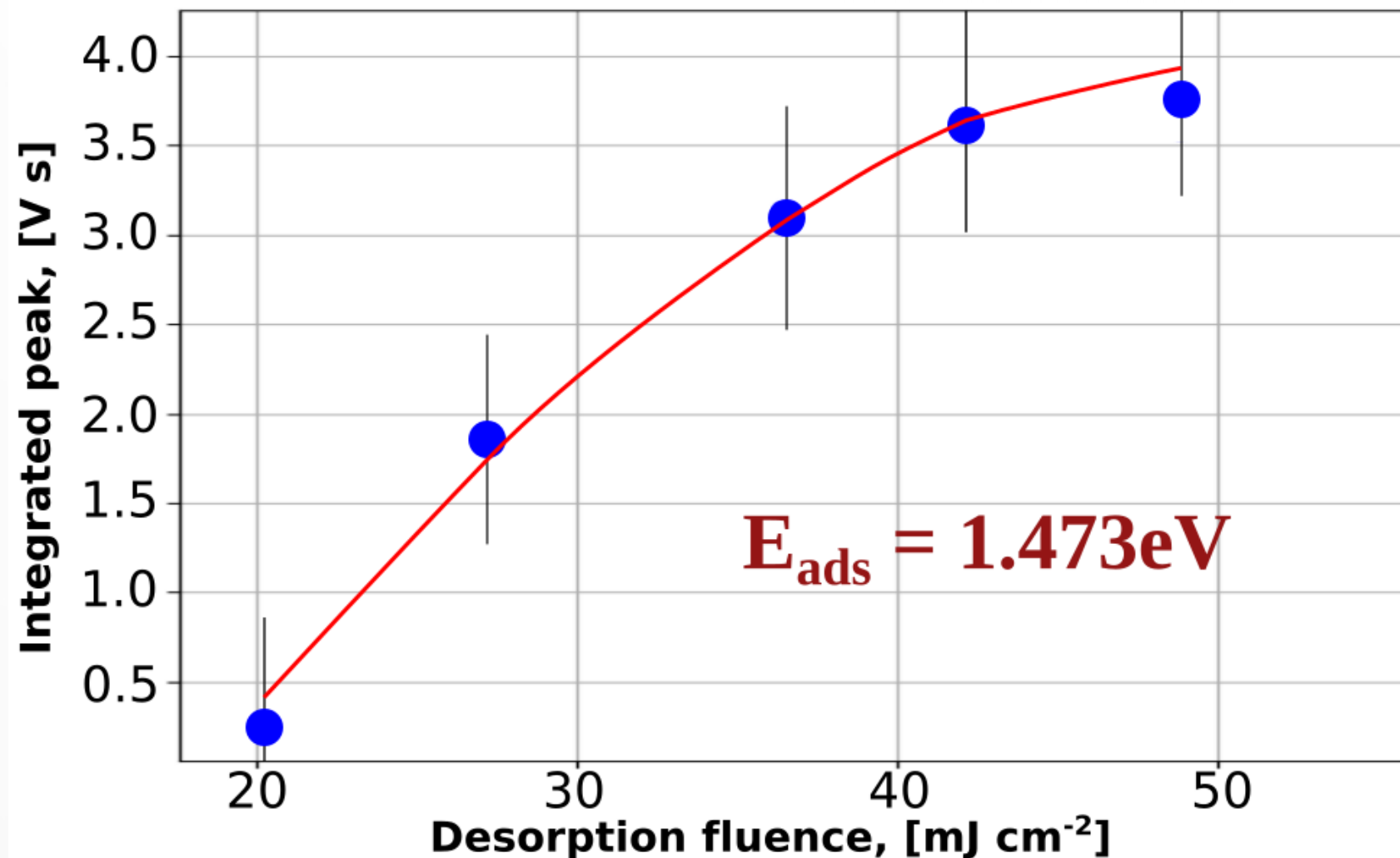
[5] A Guilloteau et al., J. Phys. Chem. A 112.42 (2008), pp. 10552–10559

Second approach (from fluence curve)

Adsorption Energy of Coronene ($C_{24}H_{12}$)



The obtained value is close to the one retrieved from the signal decay (**1.498eV**) and the one found in literature (**1.32 to 1.48eV**)^[6]



Transient temperature approach

Determining the adsorption energy from the temperature profile

Determining the temperature variation

A two-dimensional heat equation was considered:

$$\rho_{app} c_p \frac{\partial T(x, y, t)}{\partial t} = k_{app} \left(\frac{\partial^2 T(x, y, t)}{\partial x^2} + \frac{\partial^2 T(x, y, t)}{\partial y^2} \right) + q_H(x, y, t)$$

where

$$q_H(x, y, t) = (1 - R) \alpha I_0 f(x, y) g(t)$$

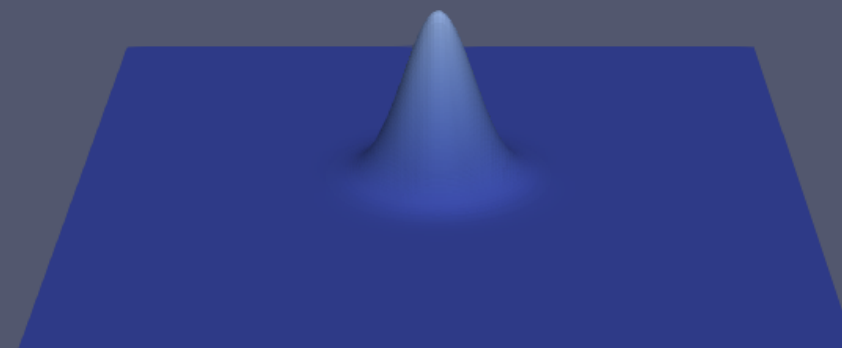
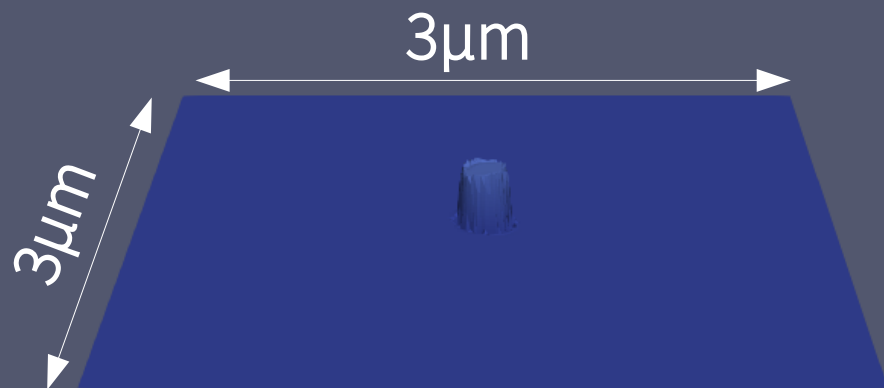
$$f(x, y) = \begin{cases} 1 & \sqrt{x^2 + y^2} \leq d_{des}/2 \\ 0 & \text{otherwise} \end{cases}$$

$$g(t) = \begin{cases} 1 & t \leq \tau_{des} \\ 0 & \text{otherwise} \end{cases}$$

Boundary conditions:

$$\begin{cases} T(x, y \rightarrow \infty, t) = T_i \\ T(x, y, t=0) = T_i \end{cases}$$

Temperature variation



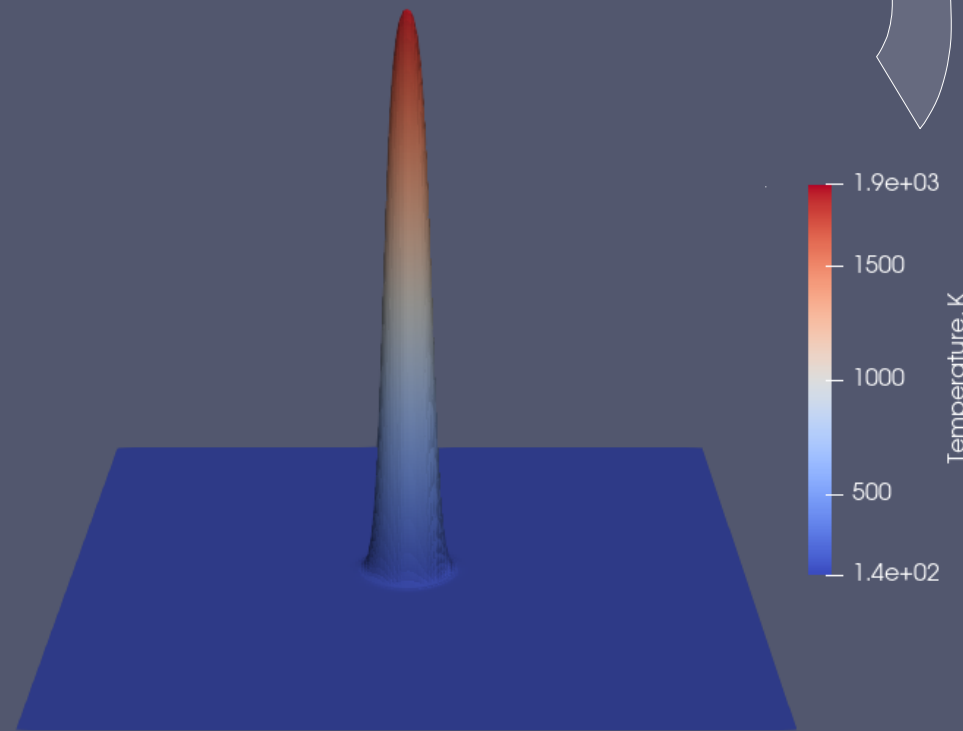
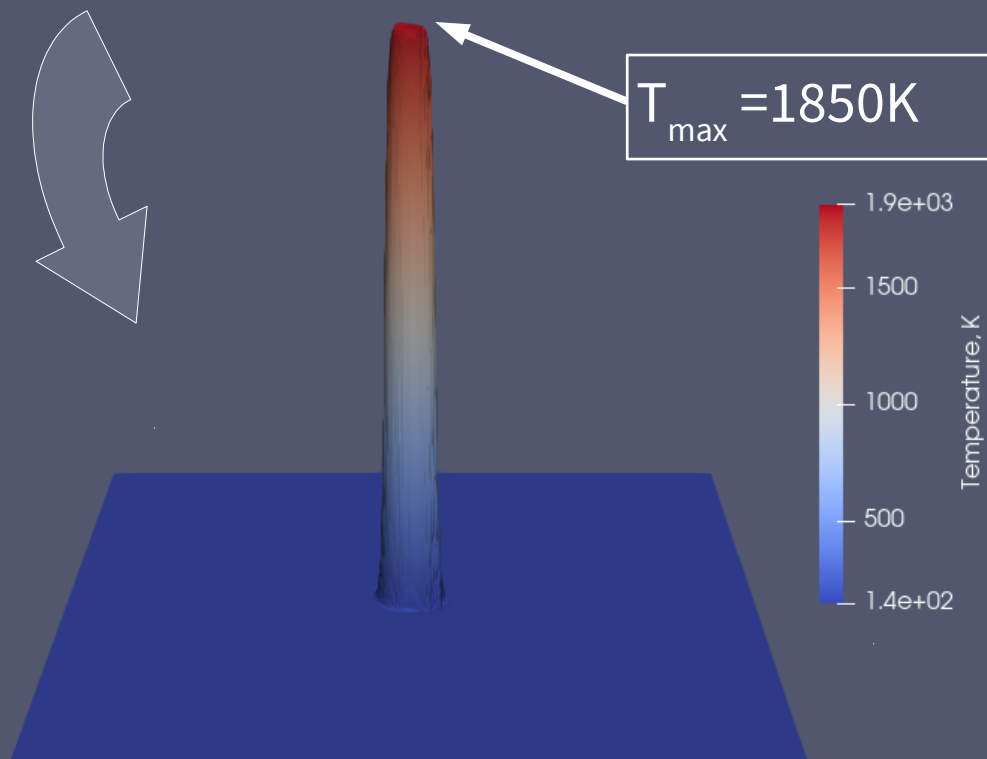
Time: 0.20 ns

$T_{\text{max}} = 1850\text{K}$

Time: 18.00 ns

Heating

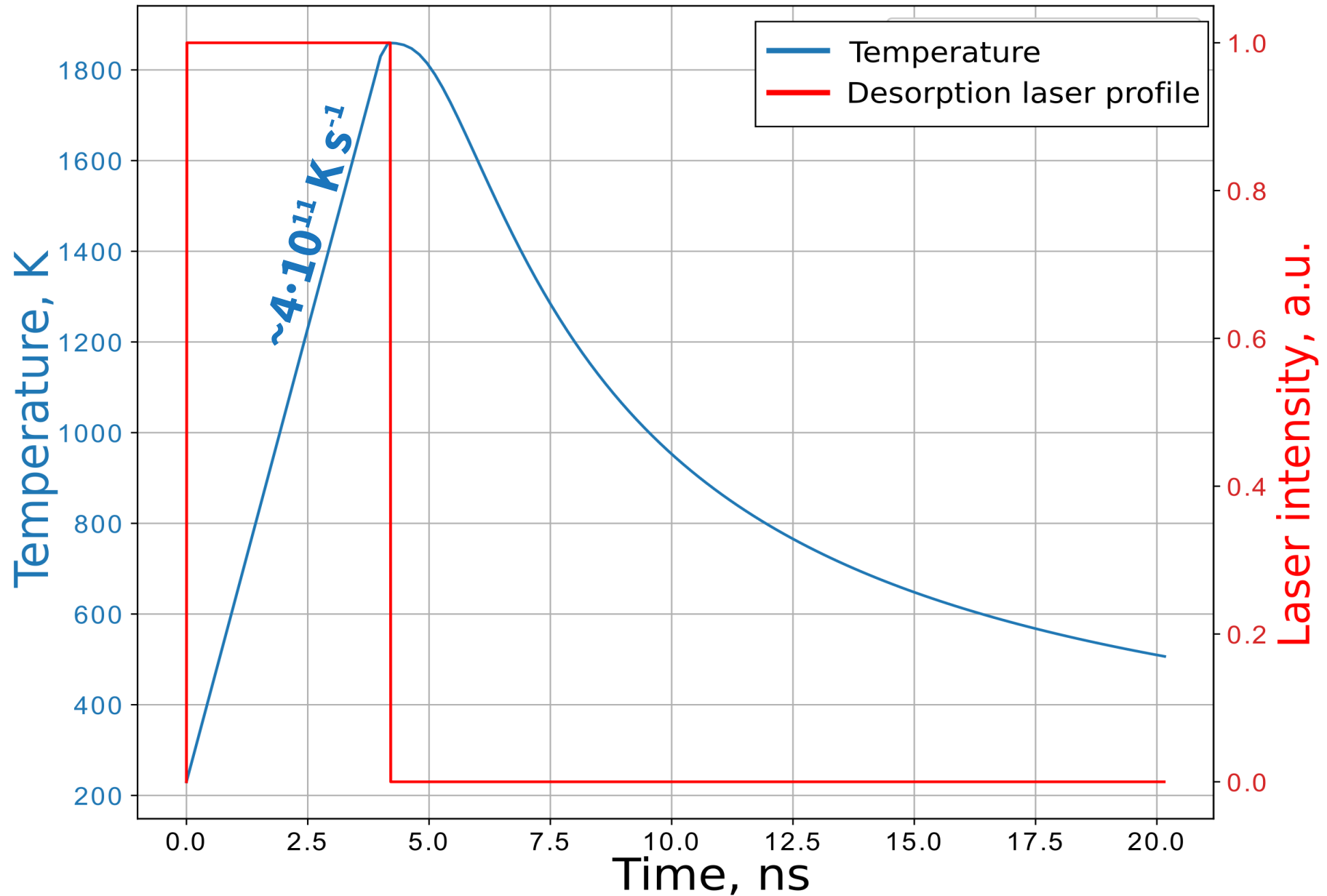
Cooling



Time: 4.00 ns

Time: 5.00 ns

Temperature variation in the centre of the desorption spot



Desorption rate

The desorption rate can be calculated from the Langmuir adsorption isotherm and is:

$$-\frac{d\theta}{dt} = \nu \theta \exp\left(-\frac{E_{ads}}{k_B T}\right)$$

Where θ is the surface coverage, ν is the pre-exponential factor.

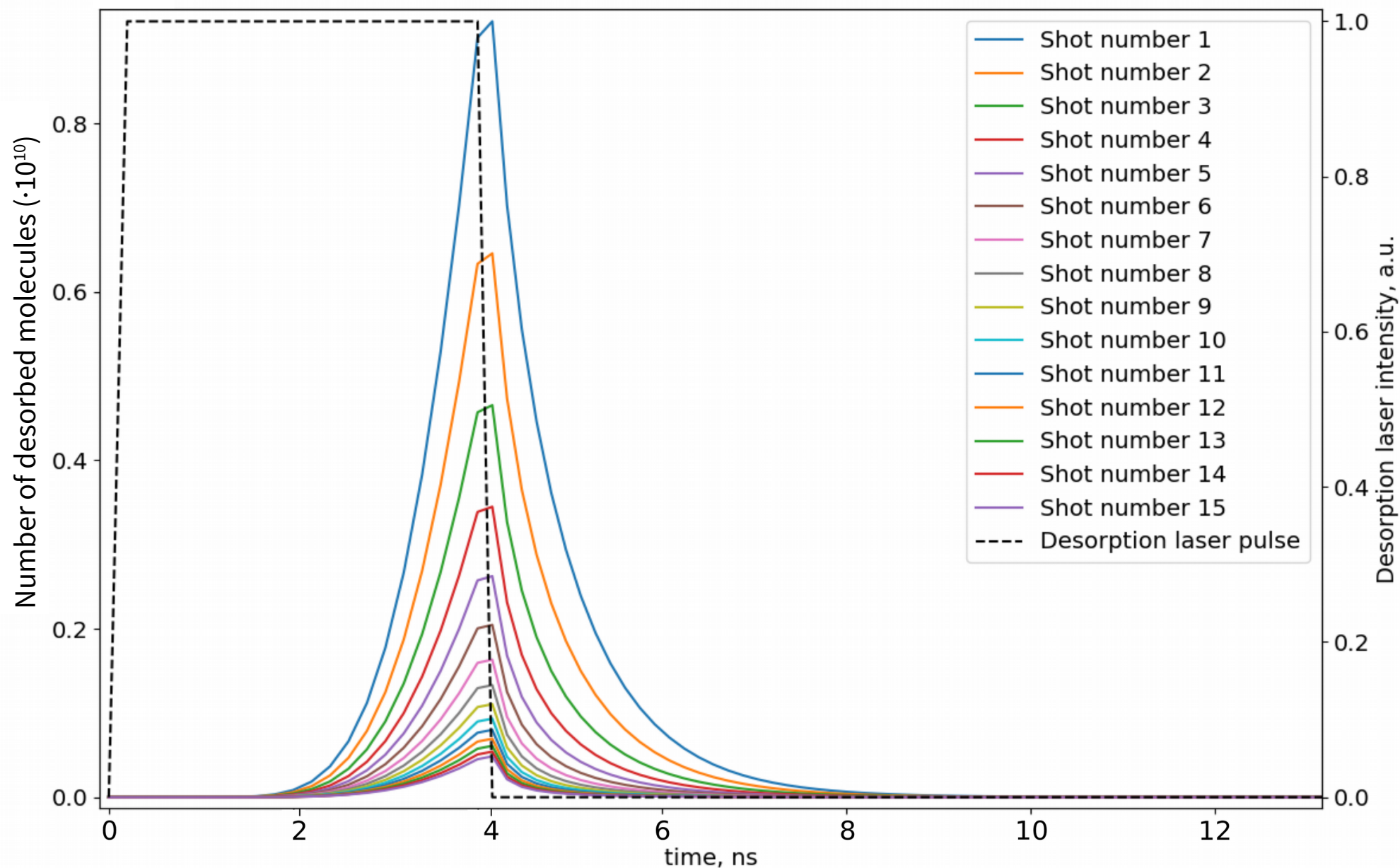
The surface concentration changes as follows:

$$\theta(t, T) = \theta_0 \exp\left(-\nu \cdot \exp\left(\frac{-E_{ads}}{k_B \cdot T(t)}\right) \cdot t\right)$$

Total number of molecules desorbed per desorption pulse is:

$$\Delta \theta = \theta_0 \left(1 - \int_0^{+\infty} \exp\left(-\nu \cdot \exp\left(\frac{-E_{ads}}{k_B \cdot T(t)}\right) \cdot t\right) dt\right)$$

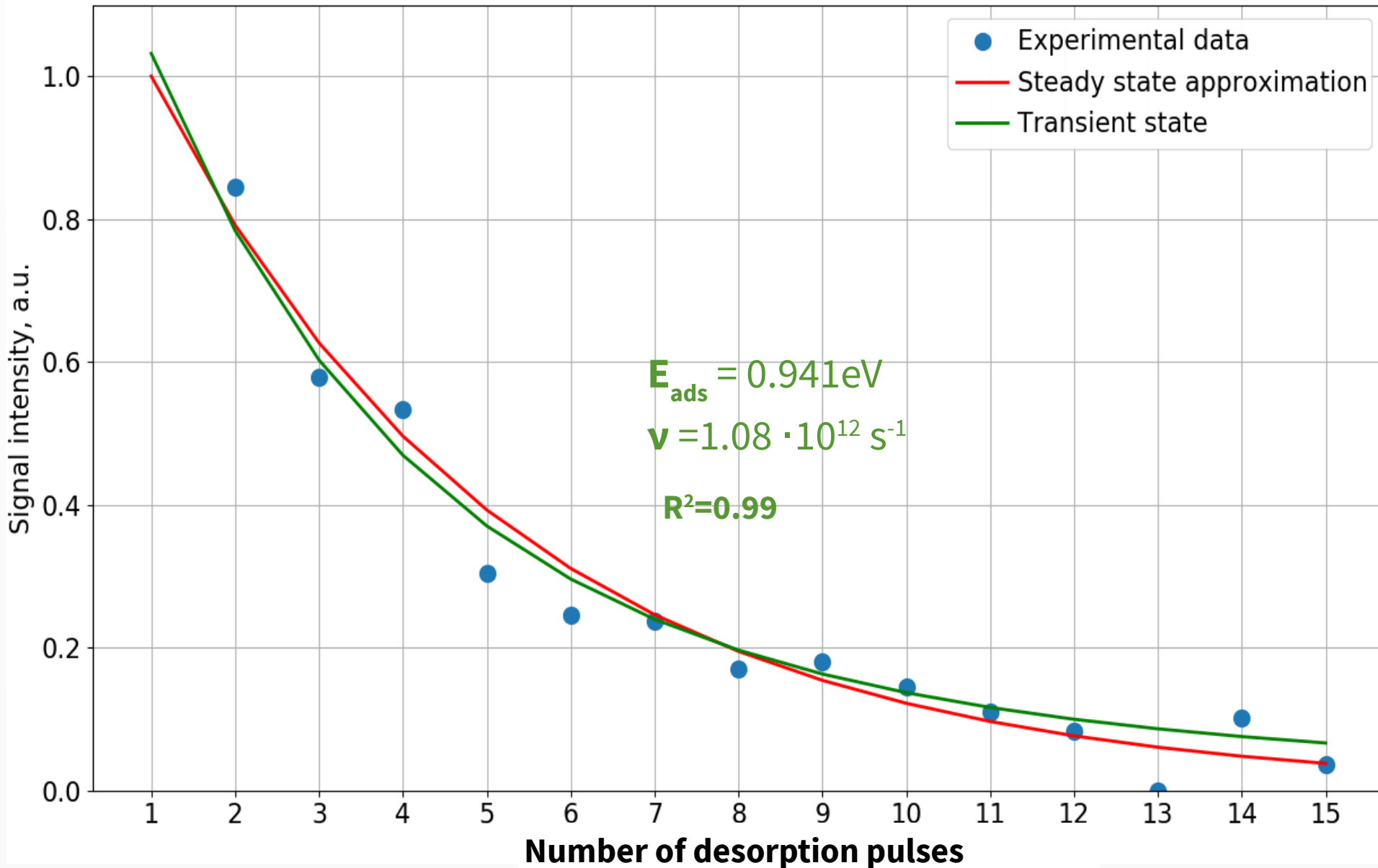
Desorption rate (pyrene)



Transient state approach (pyrene)

The shape of the signal decay obtained for the transient state (from the temperature variation) is similar to the one for the steady state approximation.

The value of the pre-exponential factor is lower than the one reported in the literature (different temperature ranges).



Work in progress...

Conclusions

- An original method for measuring the adsorption energy of PAHs, based on Laser Induced Thermal Desorption, was proposed.
- Two different approaches were derived from the steady state assumption and used to determine the adsorption energy of two PAHs of interest (pyrene and coronene).
- The results obtained from the steady-state assumption are in good agreement with ones calculated for a transient regime.
- The results are in good agreement with values reported in the literature, thus providing a *proof-of-concept* for the method.

Thank you

Questions?

Expressions used for fitting

The number of desorbed molecules on the j desorption pulse is:

$$N_j = k \cdot n_0 \cdot \left(1 - k \cdot \exp\left(\frac{-E_{ads}}{k_B(T_0 + BF)}\right) \right)^{j-1} \cdot \exp\left(\frac{-E_{ads}}{k_B(T_0 + BF)}\right)$$

Where k is a proportionality constant.

Total number of desorbed molecules is:

$$N_j = \sum_1^j \left(k \cdot n_0 \cdot \left(1 - k \cdot \exp\left(\frac{-E_{ads}}{k_B(T_0 + BF)}\right) \right)^{j-1} \cdot \exp\left(\frac{-E_{ads}}{k_B(T_0 + BF)}\right) \right)$$

The signal measured with a mass spectrometer will be:

$$S_j[V] = c \cdot N_j = c \cdot k \cdot n_0 \cdot \left(1 - k \cdot \exp\left(\frac{-E_{ads}}{k_B(T_0 + BF)}\right) \right)^{j-1} \cdot \exp\left(\frac{-E_{ads}}{k_B(T_0 + BF)}\right)$$

Expressions used for fitting

The number of desorbed molecules for the first laser pulse, as a function of laser fluence, is:

$$N_j = c \cdot k \cdot n_0 \cdot \exp\left(\frac{-E_{ads}}{k_B(T_0 + BF)}\right)$$

The logarithm of the signal was fitted with:

$$\ln(S1) \left(\frac{1}{k_B(T_0 + BF)} \right) = C_1 + E_{ads} \cdot \left(\frac{1}{k_B(T_0 + BF)} \right)$$

where $C_1 = \ln(c \cdot k \cdot n_0)$