



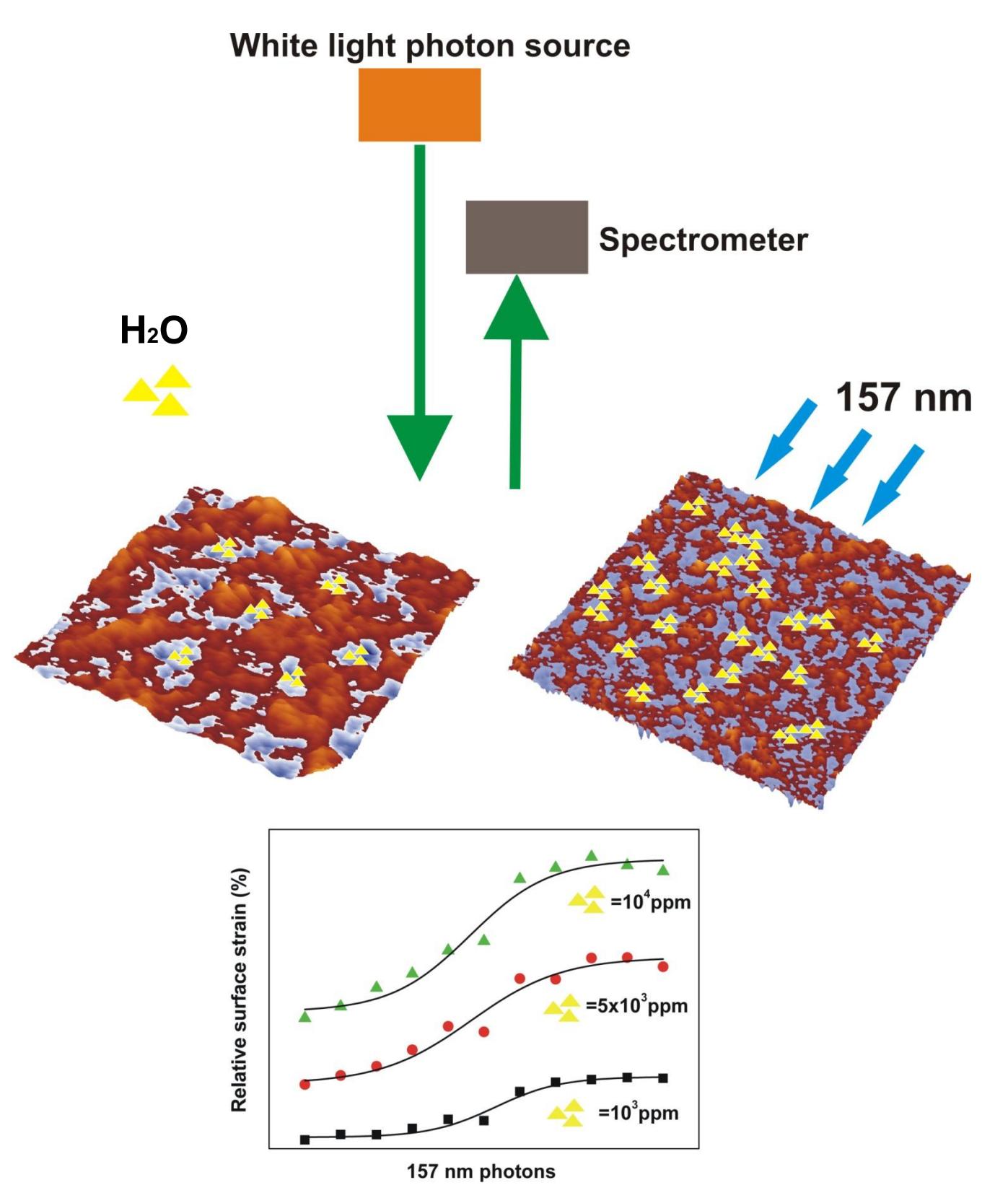
# Nanothermodynamic sensors: Novel devices to probe polar-entropic competition and energy flow at the nanoscale.

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## ABSTRACT



Tiny dimensional systems brought the concept of "nanothermodynamic potential", which is proportional to the number of nano-entities in a macroscopic system, from either the presence of surface and edge effects at the boundaries of nanoentities or, the restriction of the translational and rotational degrees of freedom of molecules from nanovoids. The nanothermodynamic potential is directly correlated to a stress-strain response of a surface. By applying laser modification of surfaces, any morphological change should imply major entropic variation of any matrix-analyte system during sorption of analytes, due to molecular trapping within photon induced nano-voids.

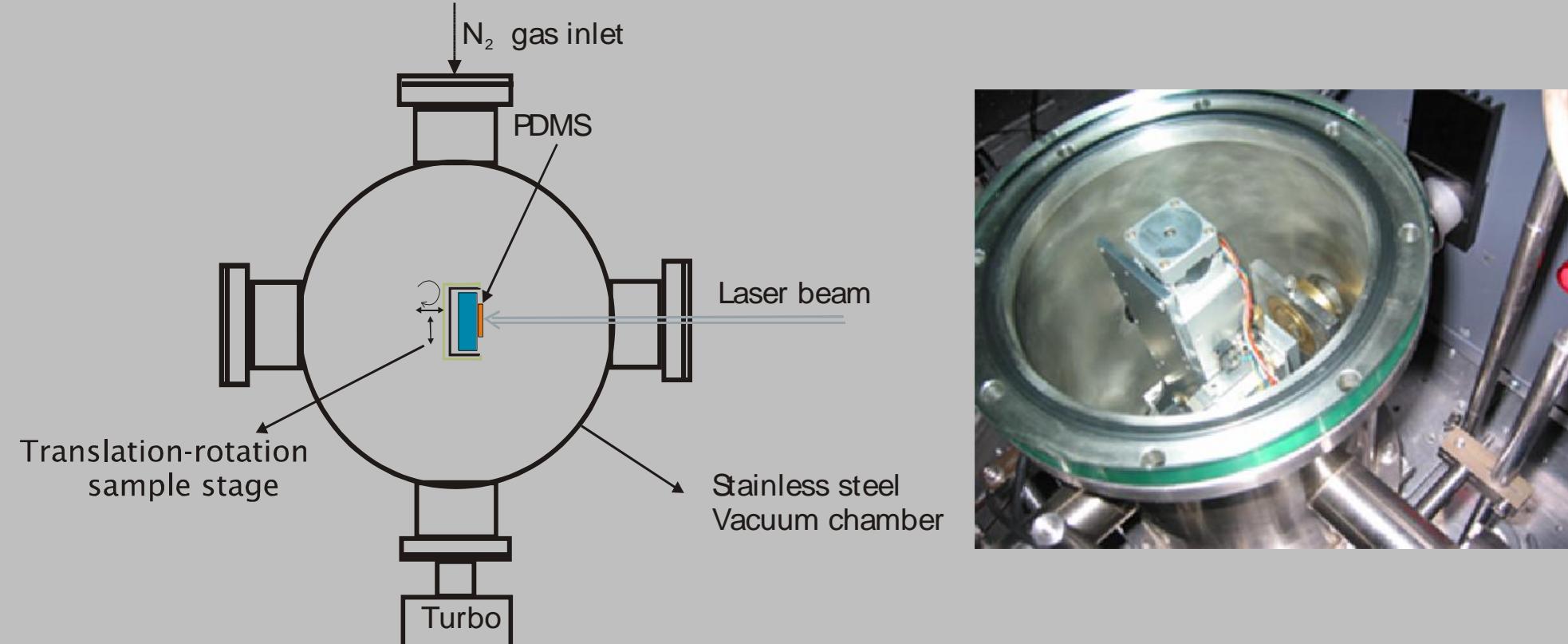
The stressing field allows the identification of thermodynamic state variations under well controllable conditions and maps polar-entropic fields.

In this work, polar and entropic energy variation during sorption of gas analytes and the strain in PHEMA and Polyacrylamide polymeric matrixes is measured. It is shown that the confinement of adsorbed analytes within photon induced nano-voids in matrices, is the source of an entropic nanothermodynamic potential, proportional to the number of nano-voids.

The experimental methodology is based on establishing the relation between the stressing field and the free energy difference during sorption of analytes in a thin polymer layer, processed with a molecular fluorine laser at 157 nm. The polar and entropic, energy of the matrix is measured with white light reflectance spectrometry that monitors the relative stress (swelling) of the matrix by using as an external variable the number of laser photons that modify the matrix and the analyte concentration.

The methodology allows the development of nanothermodynamic sensors that monitor polar-entropic completion and nanothermodynamic energy flow in the pJ level.

## EXPERIMENTAL SET UP

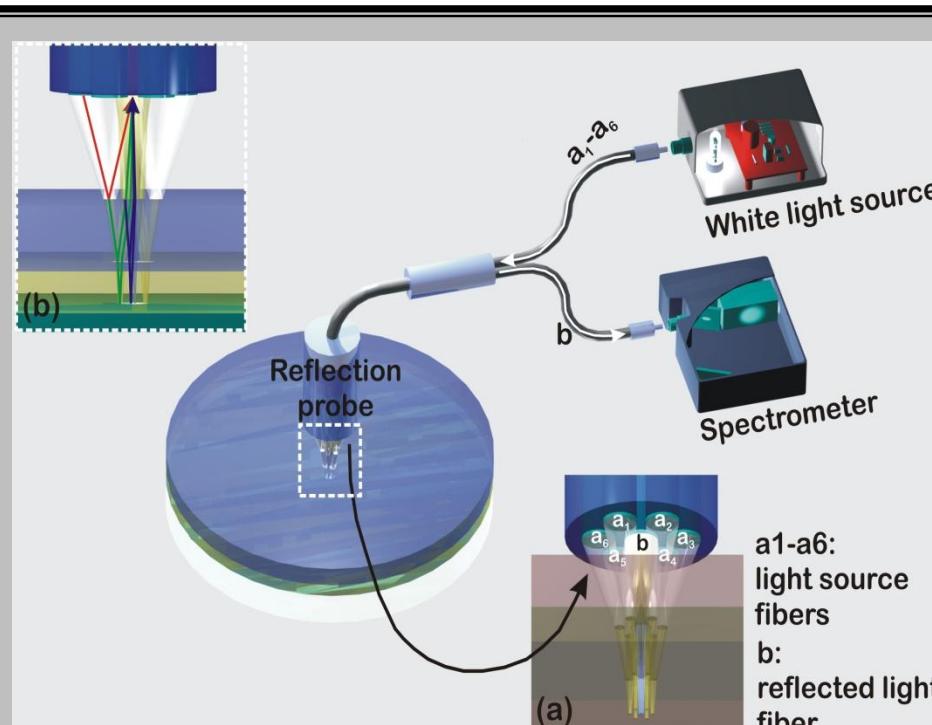


### Material:

PHEMA & Polyacrylamide films (PAM)  
Film thickness ~ 345nm, 379nm respectively.

### VUV exposure set up:

Molecular fluorine F<sub>2</sub> (Lambda Physik, LPF 200): 157nm, 15 Hz rep. rate, 15 ns at FWHM, E= 22 mJ, Fluence= 110 J/m<sup>2</sup>. Background pressure: N<sub>2</sub> (99.999%) ~1 bar X-Y-Z-θ computer-controlled translation stage.



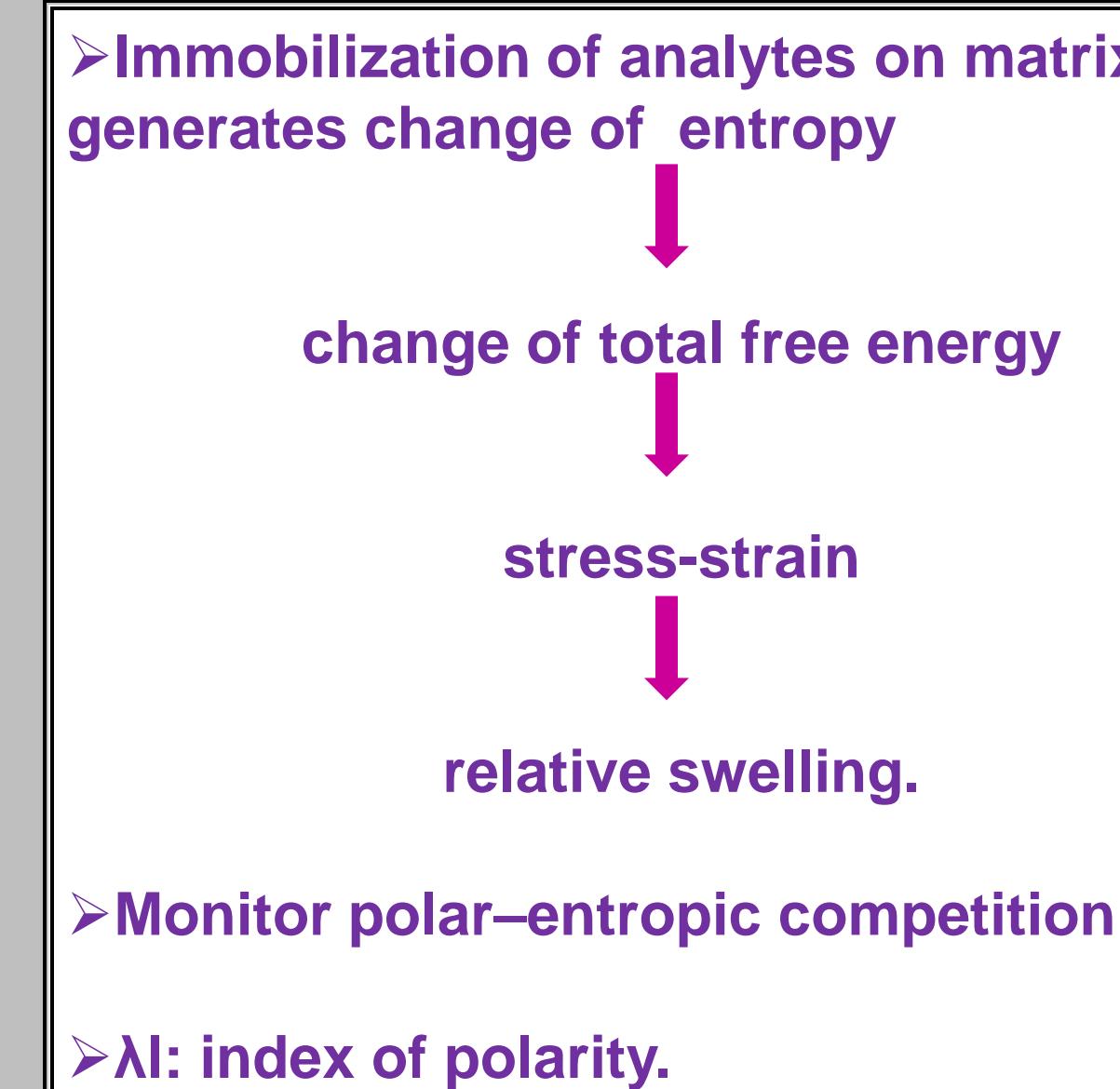
### Strain analysis -Chemical sensing:

White Light Reflection Spectroscopy (WLRS)

### Micro / nano structures characterization:

Atomic Force Microscopy: AFM (dilnovo, Bruker), tapping mode at ambient conditions. Nano-indentation: Scanning probe Microscope SPM (dilnovo, Bruker), phosphorus-(n)-doped silicon cantilever (RTESPA).

## BACKGROUND



### Gibbs Free Energy

$$\delta G = \delta \sigma_{ik} n_k \delta L_i = -\delta U - \delta(PV) + \delta(TS)$$

### Internal Energy variation during sorption

$$\delta U = \sum_{j=1}^k \lambda j \ln \Phi_a(r)_j = -(\lambda N_p(n) \ln \Phi_a)_p + \lambda N_\sigma \ln \Phi_a)_\sigma = -\lambda N_b(n) \ln \Phi = -\lambda N_b(n) \frac{5\epsilon_{xy}^4}{64\pi^4 \epsilon_0^2 \epsilon_1^2 k_B T r^6},$$

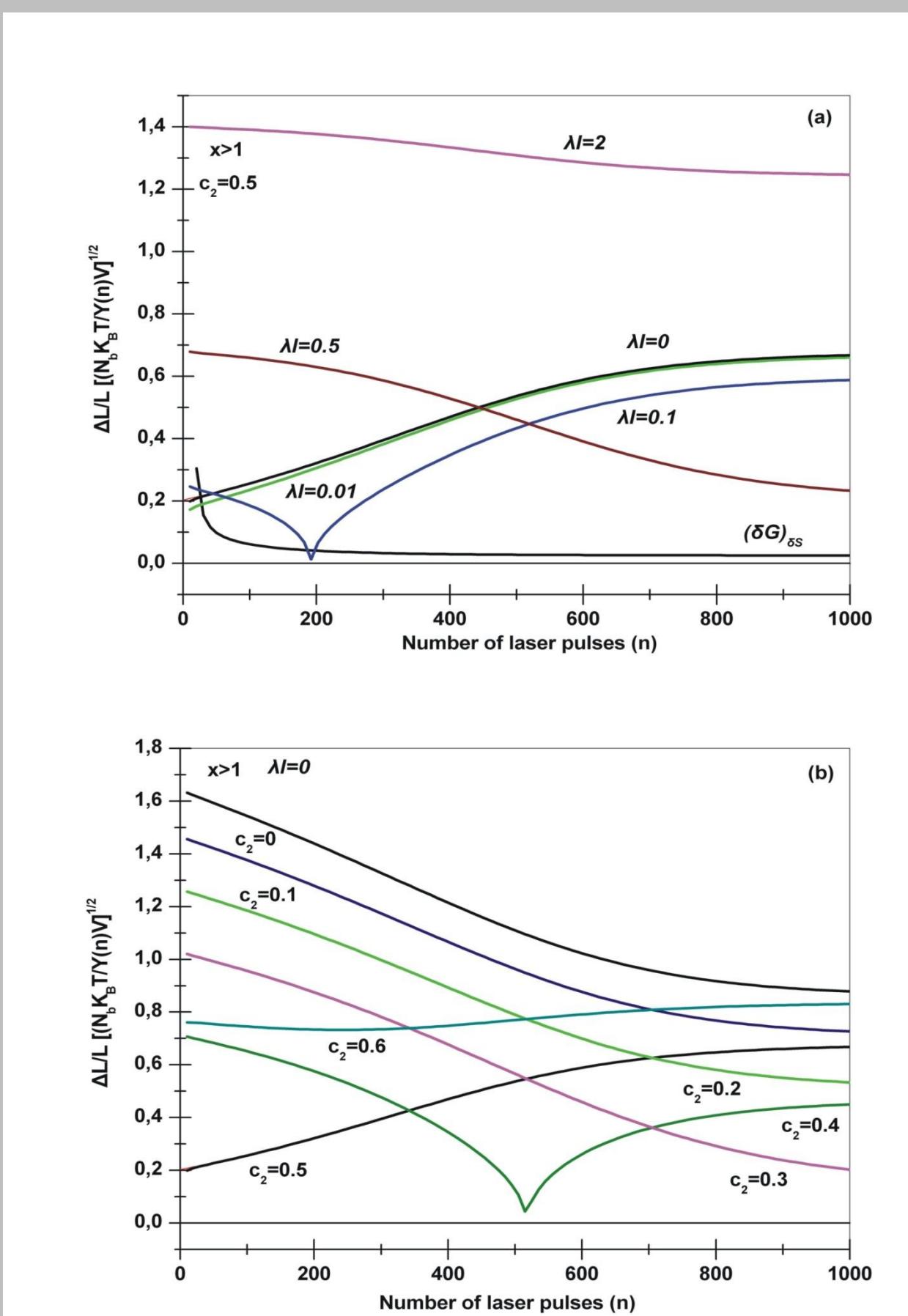
For  $N_b \ll N_a$  and  $\ln \Phi \approx k_B T$

### Entropic variation during sorption

$$\delta S = \delta S^{ph} + \delta S^e = k_B N_b \left[ \ln \left( \frac{x}{x-1} \right) + \frac{1}{x} \ln ((x-1)m) \right] + k_B N_v \left[ \ln \left( \frac{x}{x-1} \right) + \frac{1}{x} \ln ((x-1)m) \right], x > 1$$

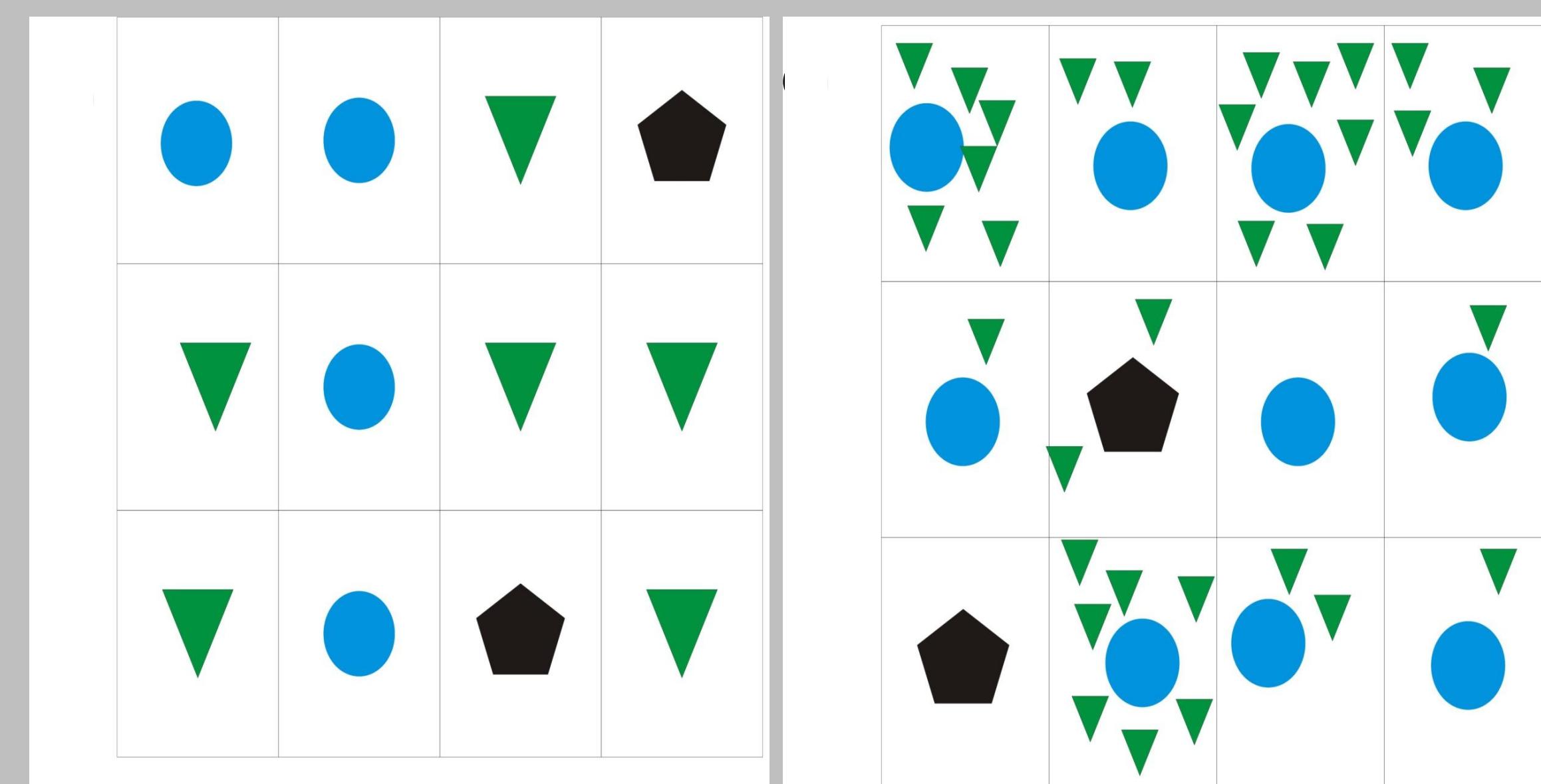
### Relative Swelling

$$\left( \frac{\delta L}{L} \right) = \left( \frac{N_b(n)}{Y(n) V} \right)^{\frac{1}{2}} \left\{ -\lambda \ln \Phi + \frac{\mu_a M_a}{x(n) N} + k_B T \left[ (1 + c_2(n)) \ln \left( \frac{x(n)}{x(n)-1} \right) + \frac{(1 + c_2(n))}{x(n)} \ln ((x(n)-1)m) \right] \right\}^{\frac{1}{2}}$$



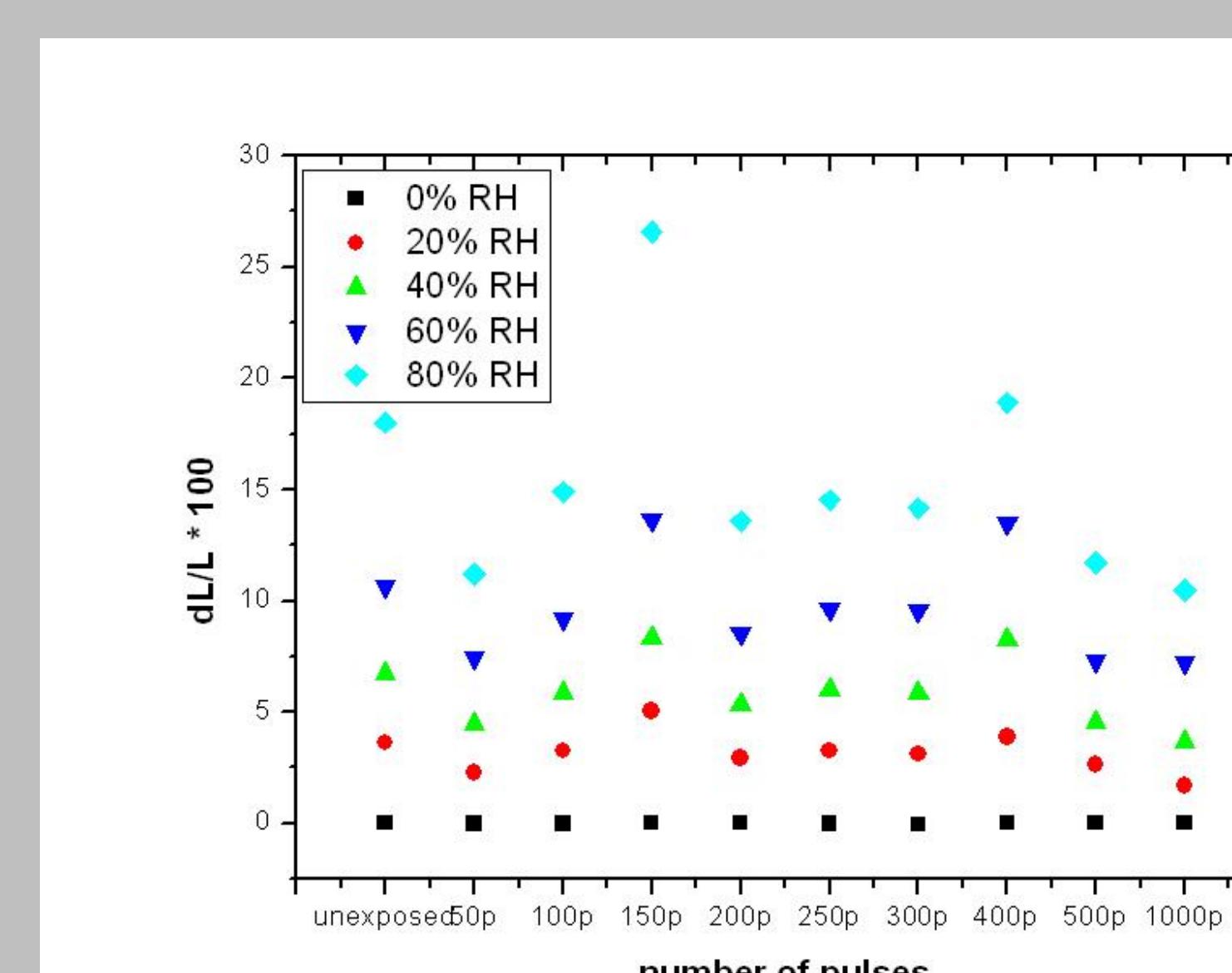
(a) Relative strain is a function of laser energy (entropic modulation) and dipole interactions ( $I\Delta$ ) for constant ratio of laser induced nano-voids to polymeric sites ( $c_2 = N_b/N_a$ ).

(b) Relative strain is a function of  $c_2$  at constant polar energy ( $I\Delta \sim 0$ ). ( $x = (N_v + N_b)/N_a$ )).

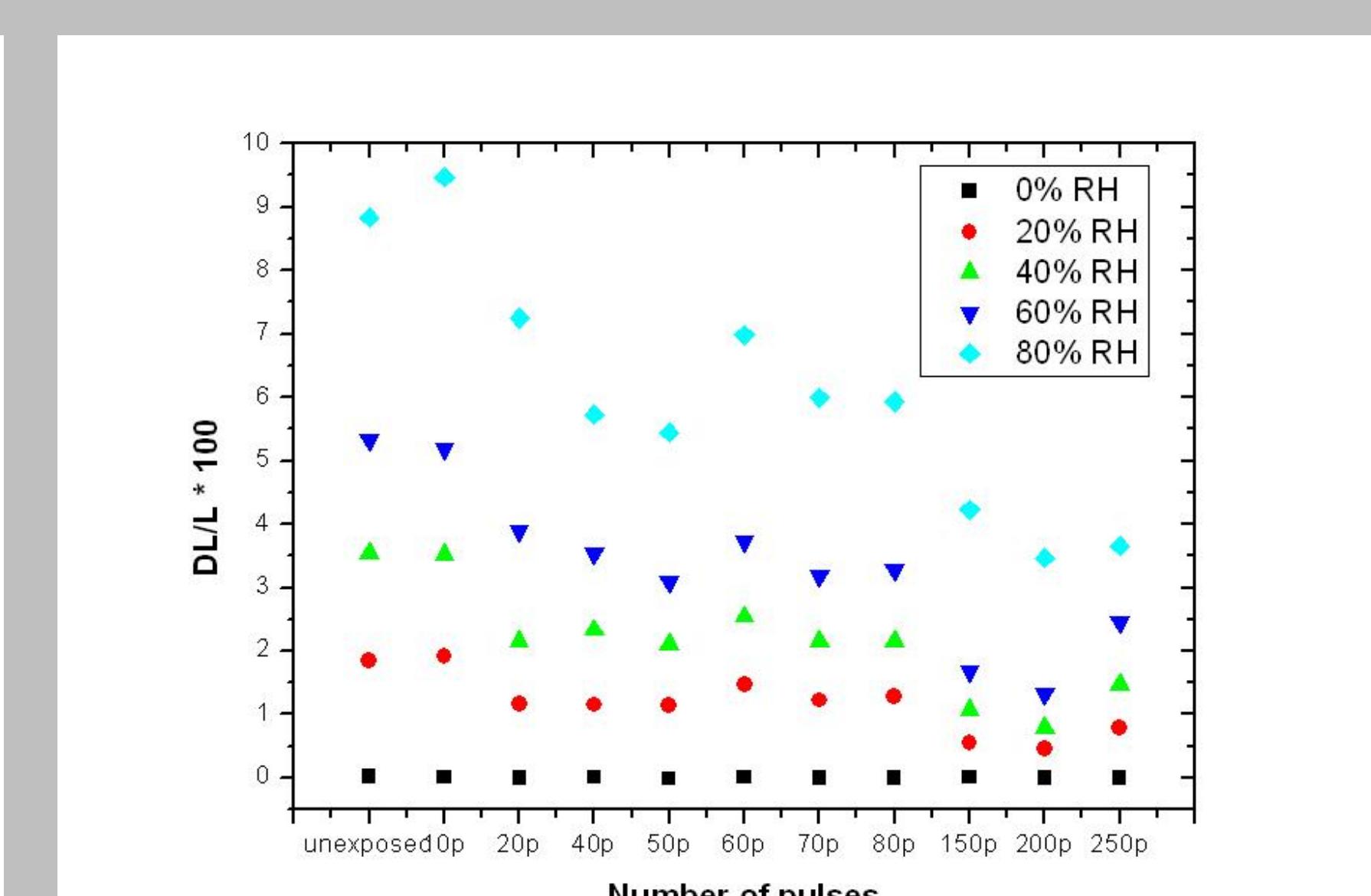


Polymeric site (●). Analyte (▼). nano-void (◆)

## RESULTS



Left: Relative strain of the ~345 nm thick PHEMA layer under different VUV laser irradiating conditions and concentrations of water analytes. RH: Relative Humidity. ( $I\Delta$ : 0.5-3).



Right: Relative strain of the ~379 nm thick PAM layer at different irradiating conditions and concentrations of water analytes. RH: Relative Humidity. ( $I\Delta$ : 0.2-4).

## CONCLUSIONS

- Sub-nm WLRS indicates that photon modified PHEMA and PAM polymeric layer during sorption of gas molecules exhibits free energy change due to polar-entropic competition due to the trapping of the gas molecules (analytes) within the photon induced nano-voids.
- The entropic term is proportional to the number of nano-voids, demonstrating thus the action of a pJ nanothermodynamic entropic potential in the stressing field from the confinement of the translational motion of the adsorbed molecules within the nano-voids.
- The work highlights the importance of entropy in nano-chemical sensing. It has the potential (1) to analyze polar-entropic competition in bio-surfaces (2) to decipher nano-thermodynamic energy flow at the pJ level.

## REFERENCES

- Entropic nanothermodynamic potential from molecular trapping within photon induced nano-voids in photon processed PDMS layers, A.C. Cefalas et al. *Soft Matter*, 2012, 8, 5561-5574.

- Nano-thermodynamics mediates drug delivery . A. L. Stefi et al. to be published in *Adv. Exp. Med. Biol.*