Small Molecule Adsorption on Colloidal Alumina and Zirconia Abrasives Used in Chemical-Mechanical Planarization (CMP) Slurries

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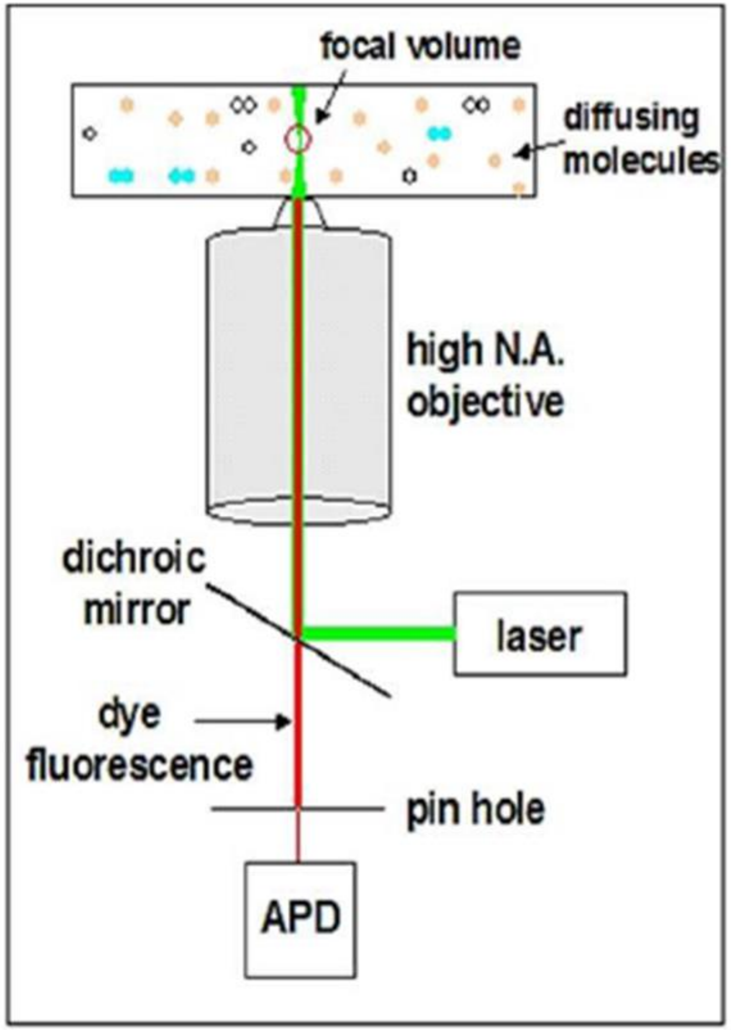
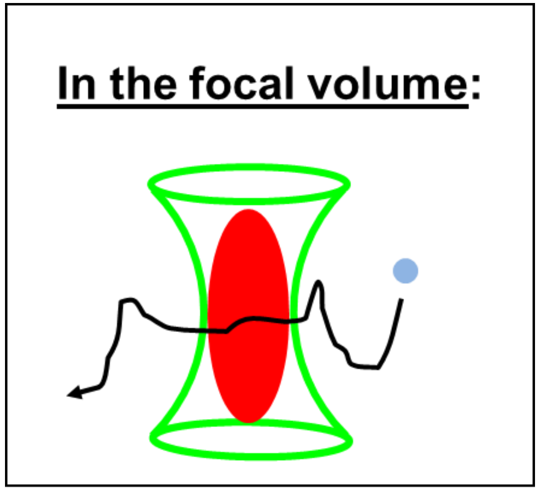
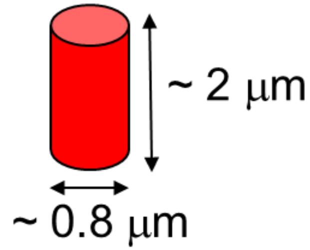
Outline

- Introduction to Fluorescence Correlation Spectroscopy (FCS)
- FCS Analysis of Dye Adsorption on Colloidal α-Alumina Abrasive Particles
- Application of Attenuated Total Internal Reflectance / Fourier Transform Infrared Spectrometry (ATR/FT-IR) in the Analysis of Small Molecule Adsorption on Colloidal Particle Thin Films
- ATR/FT-IR Characterization of Picolinic Acid Adsorption on a Thin Film of Colloidal Zirconia Abrasive Particles
- Directions for Future Studies

Single-Molecule Spectroscopic Analysis
Fluorescence Correlation Spectroscopy (FCS)

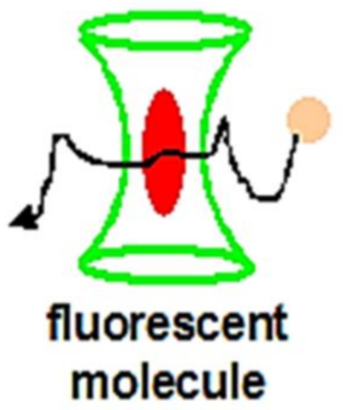


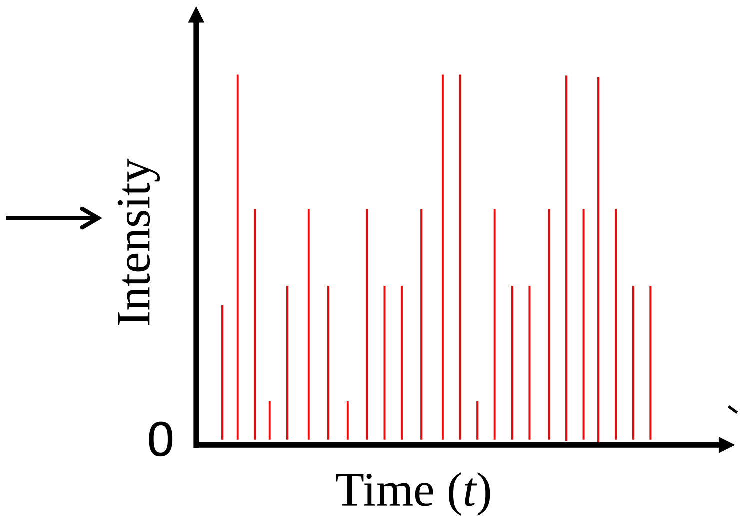




$$V = \pi r^2 h$$
$$= 1.00\ \mu m^3$$
$$= 1.00\ fL$$

FCS Measurements: Intensity Fluctuation Autocorrelation Function, $G(\tau)$





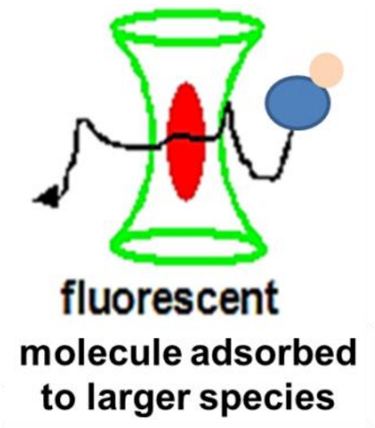
Define the *normalized autocorrelation function*, $G(\tau)$:

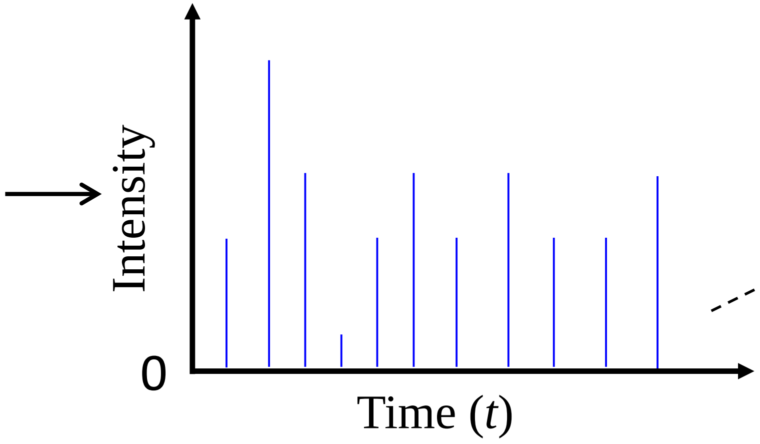
$$G(\tau) = \frac{\langle \delta F(t) \bullet \delta F(t+\tau) \rangle}{\langle F(t) \rangle^2}$$

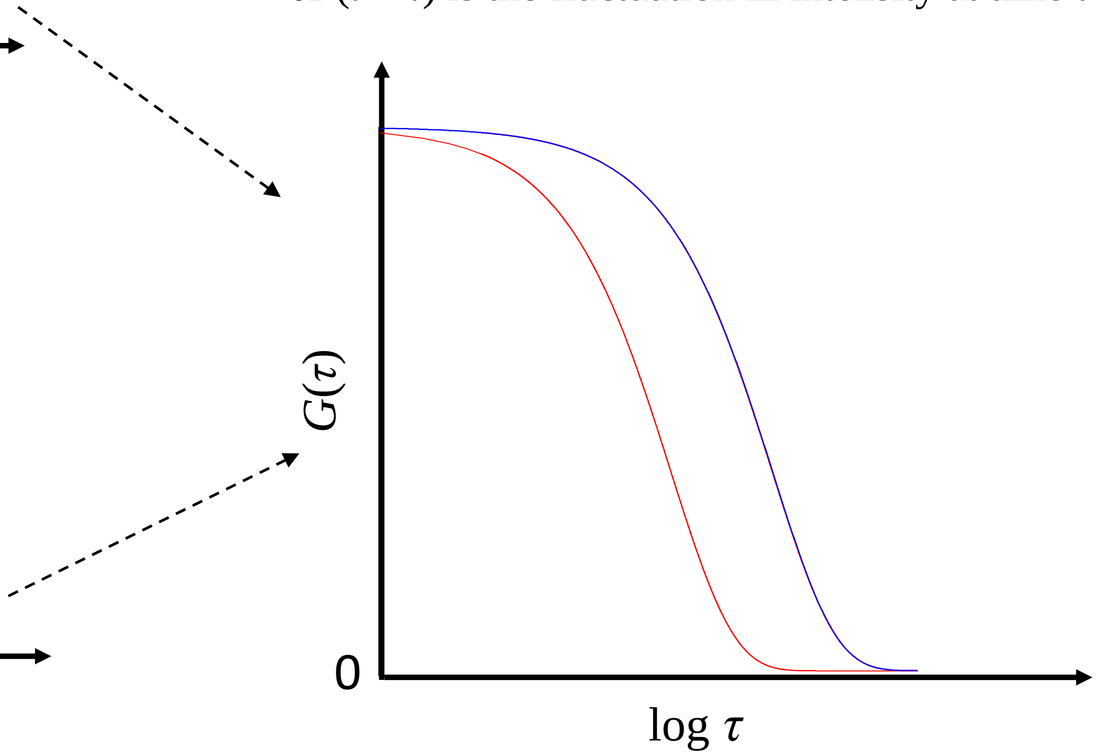
where: $F(t)$ is the intensity at time t

$\delta F(t)$ is the fluctuation in intensity at time t

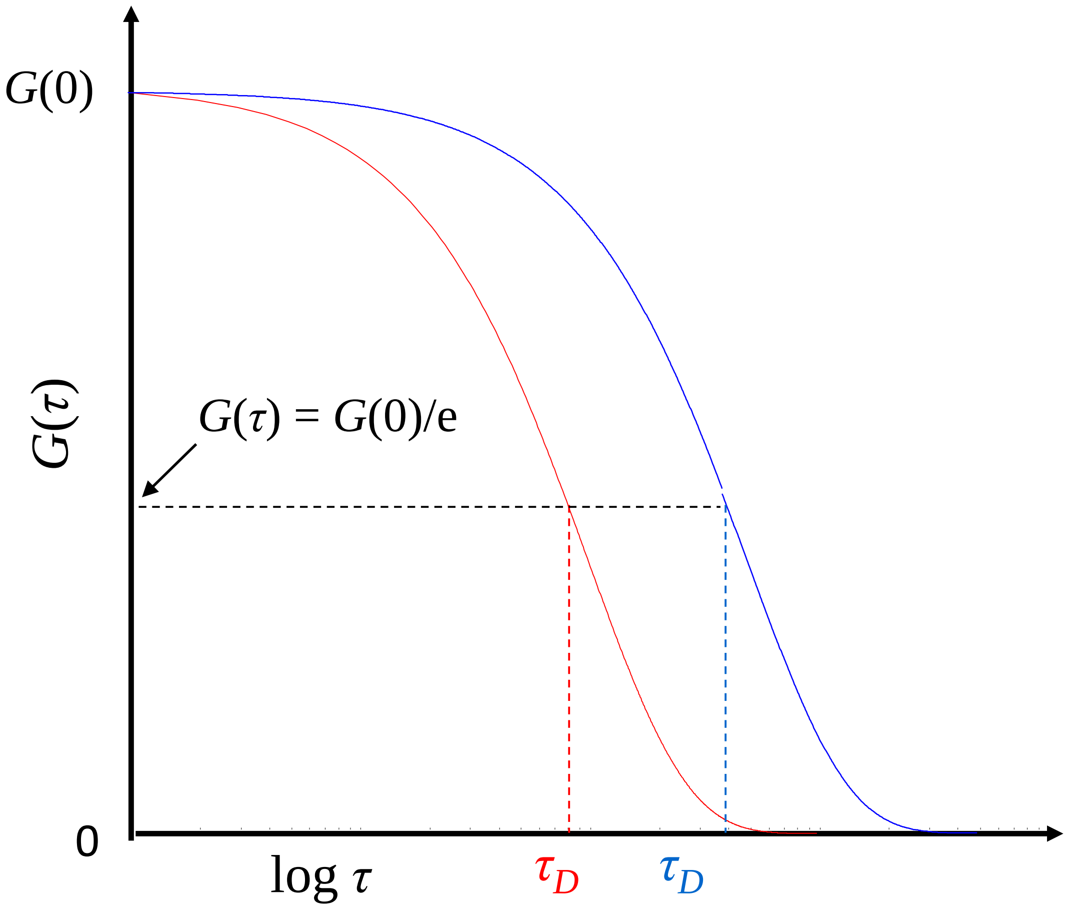
$\delta F(t+\tau)$ is the fluctuation in intensity at time $t+\tau$







Evaluate the Diffusion Coefficient, D_T, and Number of Fluorophores, N



$$G(\tau) = \frac{1}{N}\,\frac{1}{1 + 4D_T\tau/r_0^2}\left[\frac{1}{1+4D_T\tau\,/(z_0/2)^2}\right]^{1/2}$$

τ_D is related to the *translational diffusion coefficient*, D_T:

$$\tau_D = r_0^2 / 4D_T$$

where: r_0^2 is the radius of focal volume (~0.5 μm)

D_T is related to the *hydrodynamic diameter*, d_h :

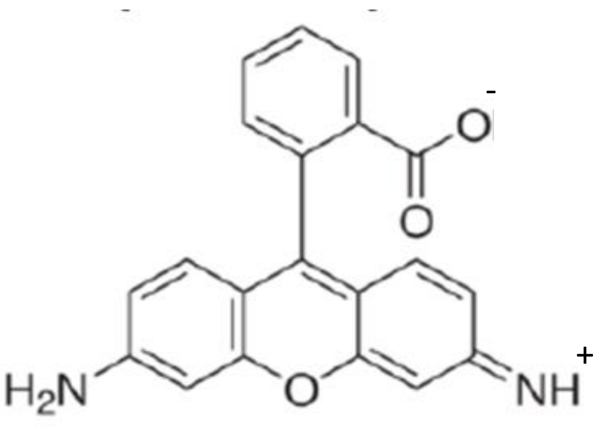
$$D_T = kT / 3\pi\eta d_h \quad \text{(Stokes-Einstein equation)}$$

where: k is the Boltzmann constant.
T is the absolute temperature.
η is the solvent viscosity.

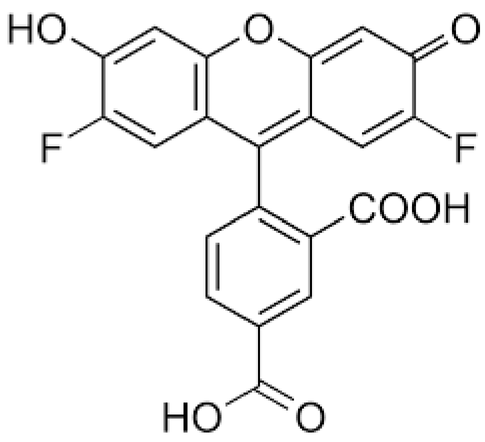
$G(0)$ is related to the *average number of fluorophores in the focal volume*, N:

$$G(0) = 1 / N$$

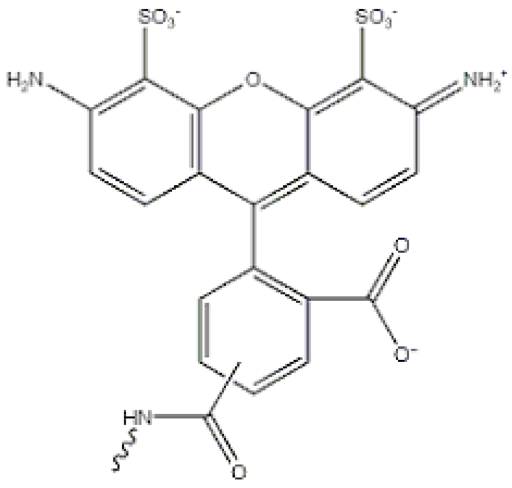
Representative Fluorophores Commonly Employed for FCS Studies



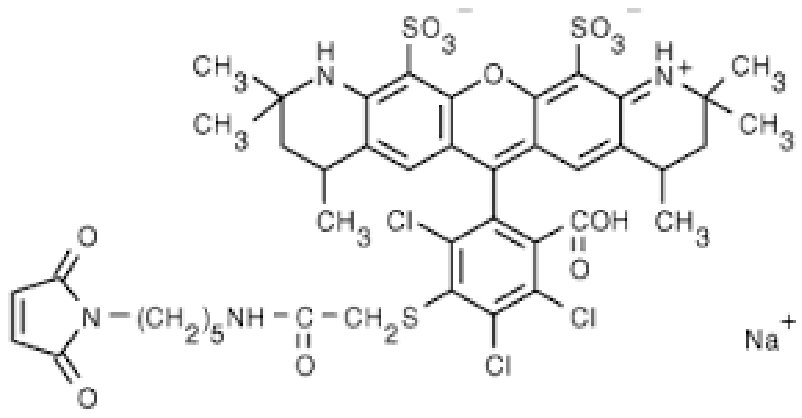
R110, λ_{ex} = 496 nm, λ_{em} = 520 nm



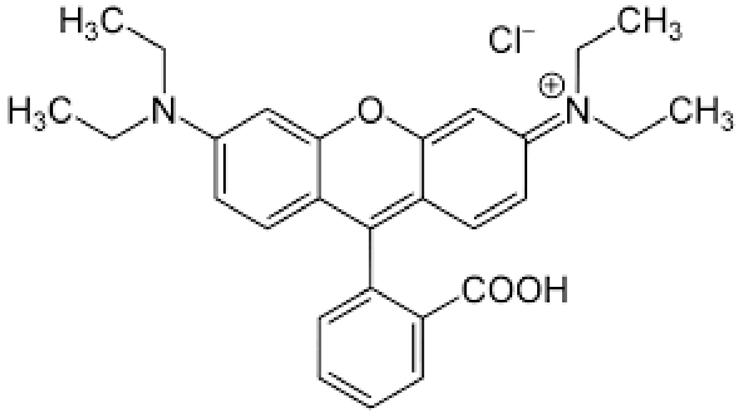
OG 488, λ_{ex} = 501 nm, λ_{em} = 526 nm



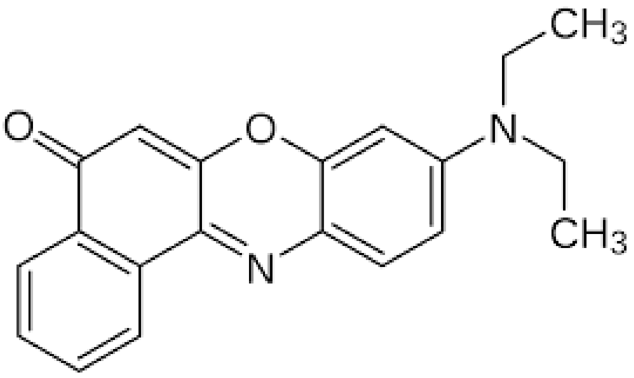
Alexa 488, λ_{ex} = 490 nm, λ_{em} = 525 nm



Alexa 546, λ_{ex} = 556 nm, λ_{em} = 573 nm



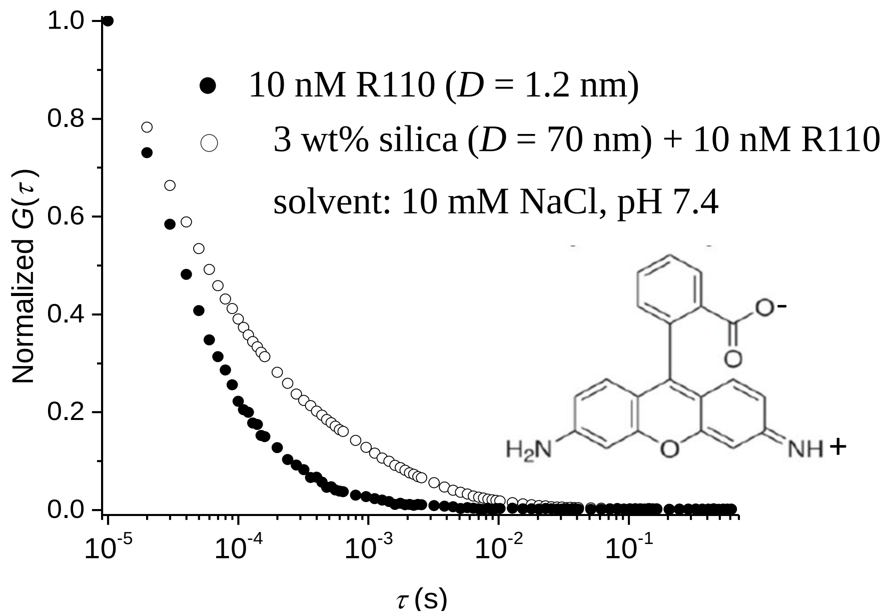
Rhod B, λ_{ex} = 553 nm, λ_{em} = 627 nm

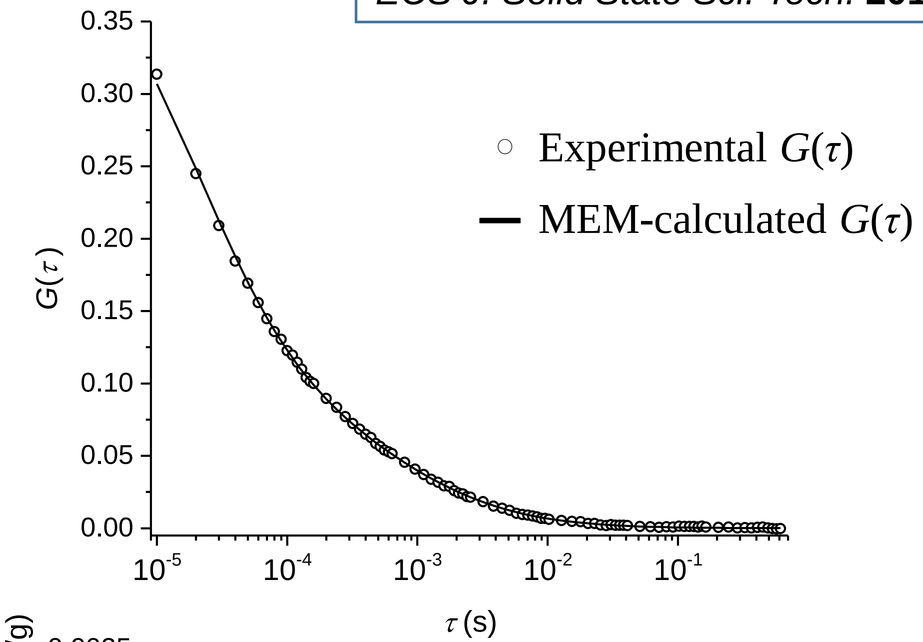


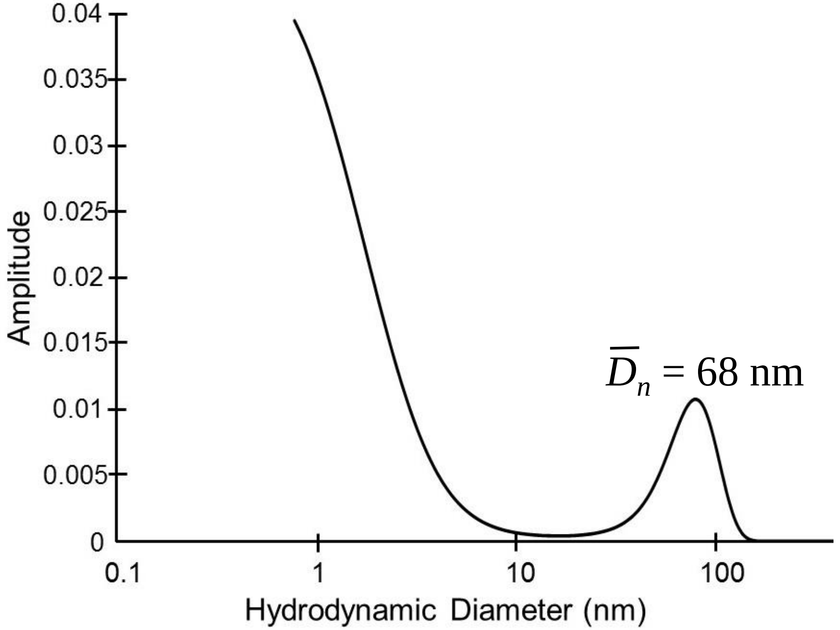
Nile Red, λ_{ex} ~ 540 nm, λ_{em} ~ 630 nm

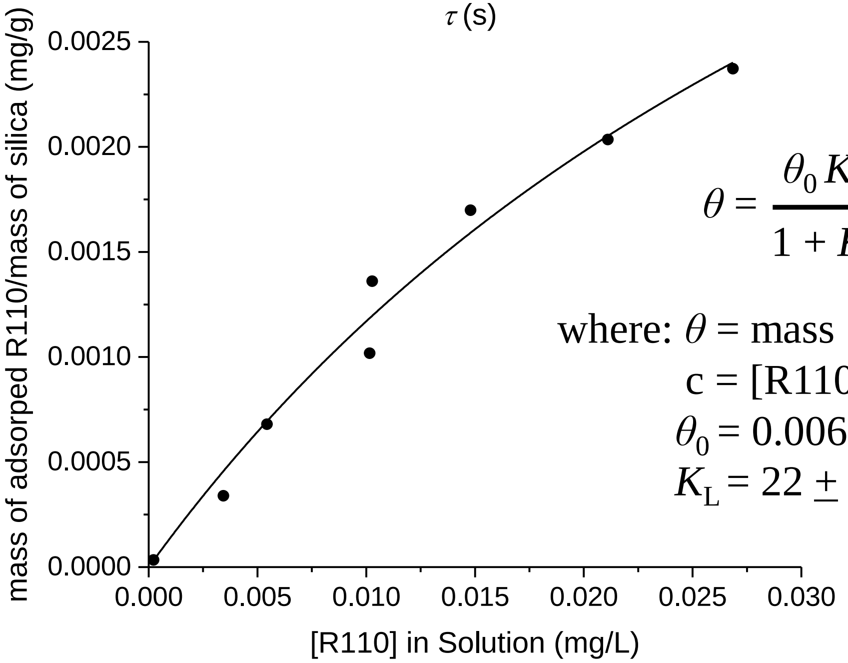
FCS Analysis of Dye Adsorption on SiO_2 Abrasives[1]

1. Jacobson, L.M.; Turner, D.K.; Wayman, A.E.; Rawat, A.K.; Carver, C.T.; Moinpour, M.; Remsen, E.E. *ECS J. Solid State Sci. Tech.* **2015,** *4,* P5053-P5057.









$$\theta = \frac{\theta_0 K_L c}{1 + K_L c}$$

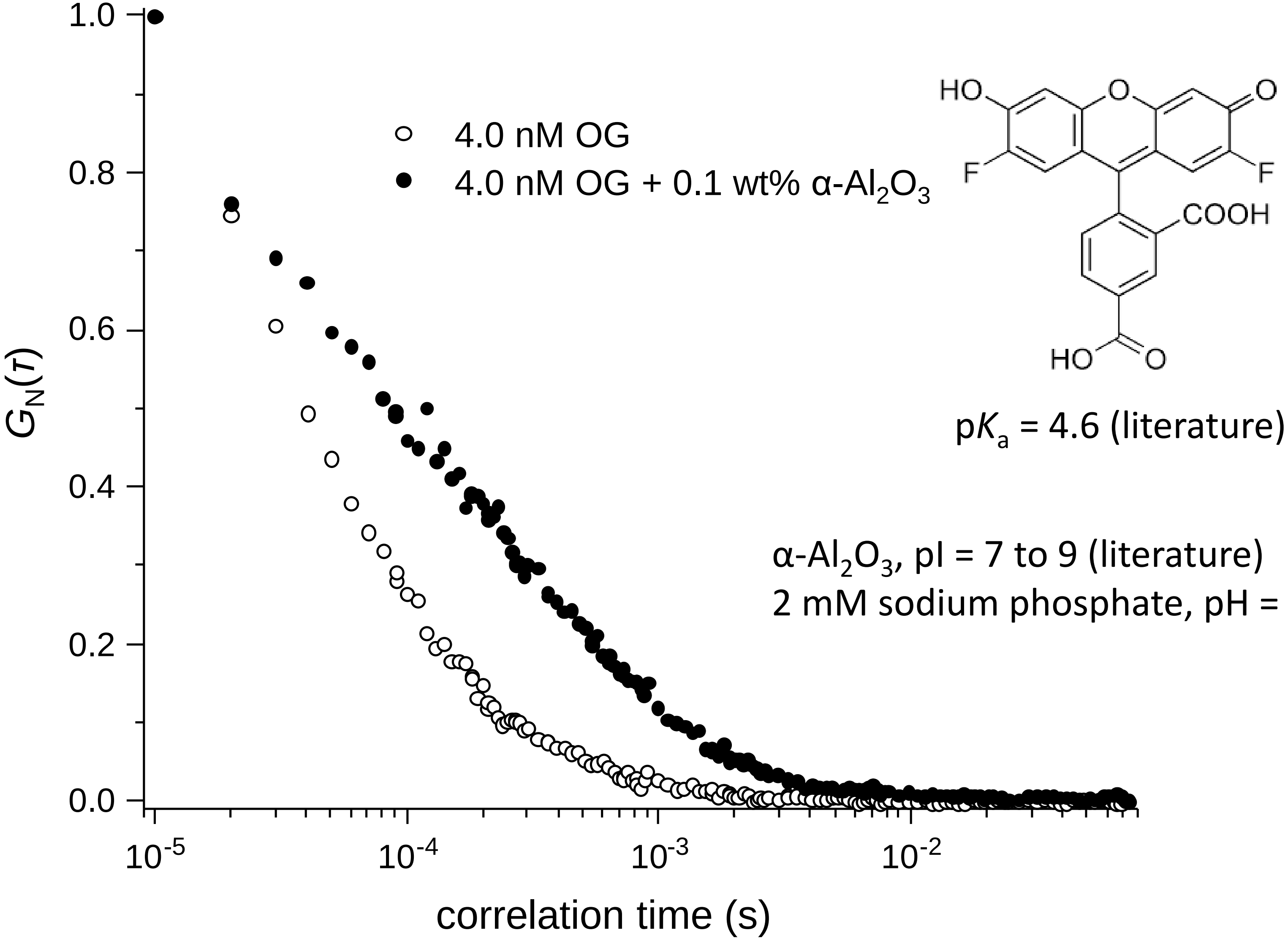
where: θ = mass adsorbed R110/mass of silica

c = [R110] in solution

$\theta_0 = 0.0064 \pm 0.0016$ mg/g

$K_L = 22 \pm 8$ L/mg

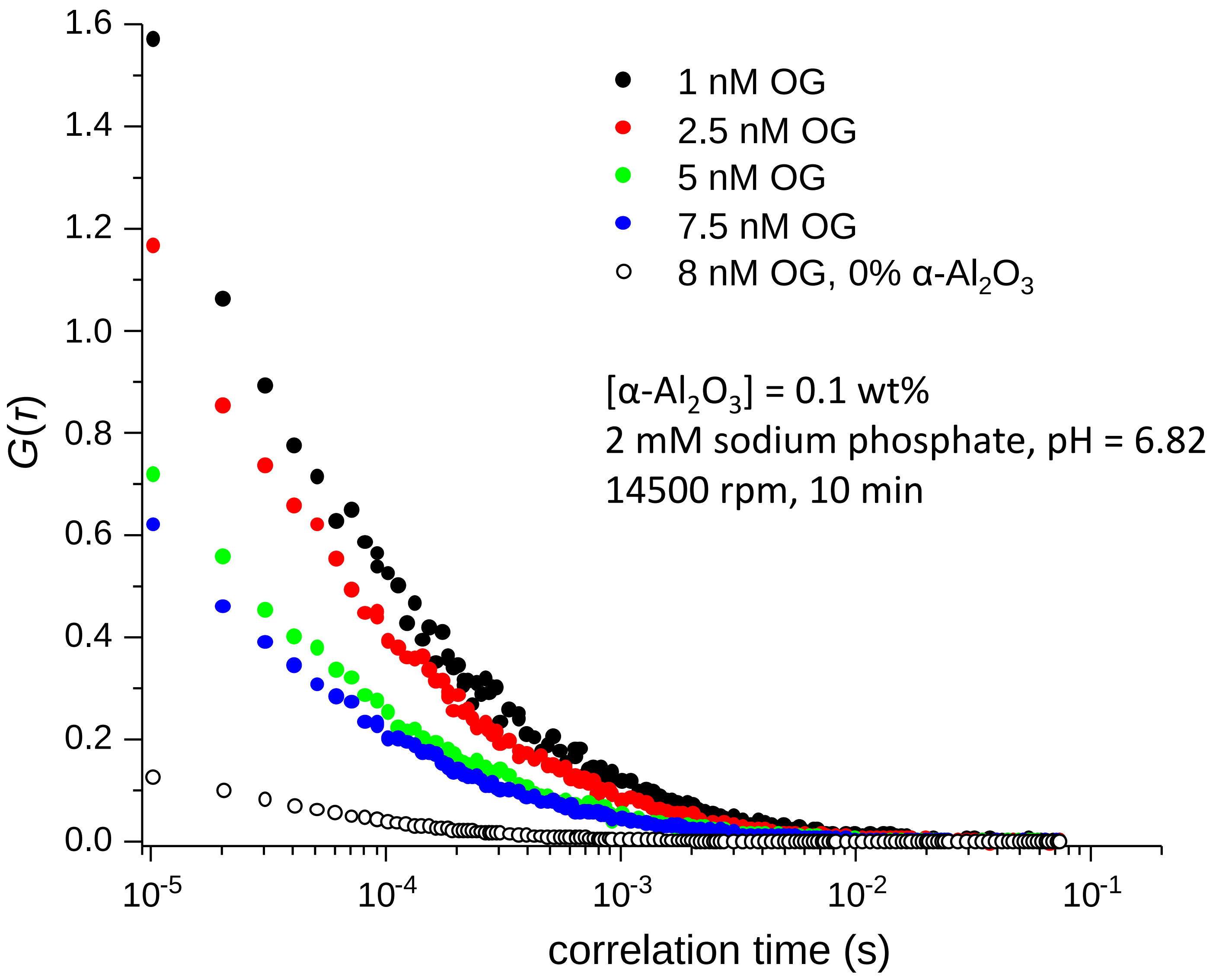
Representative Normalized ACFs for Oregon Green 488 (OG) and a Mixture of OG and α-Al_2O_3



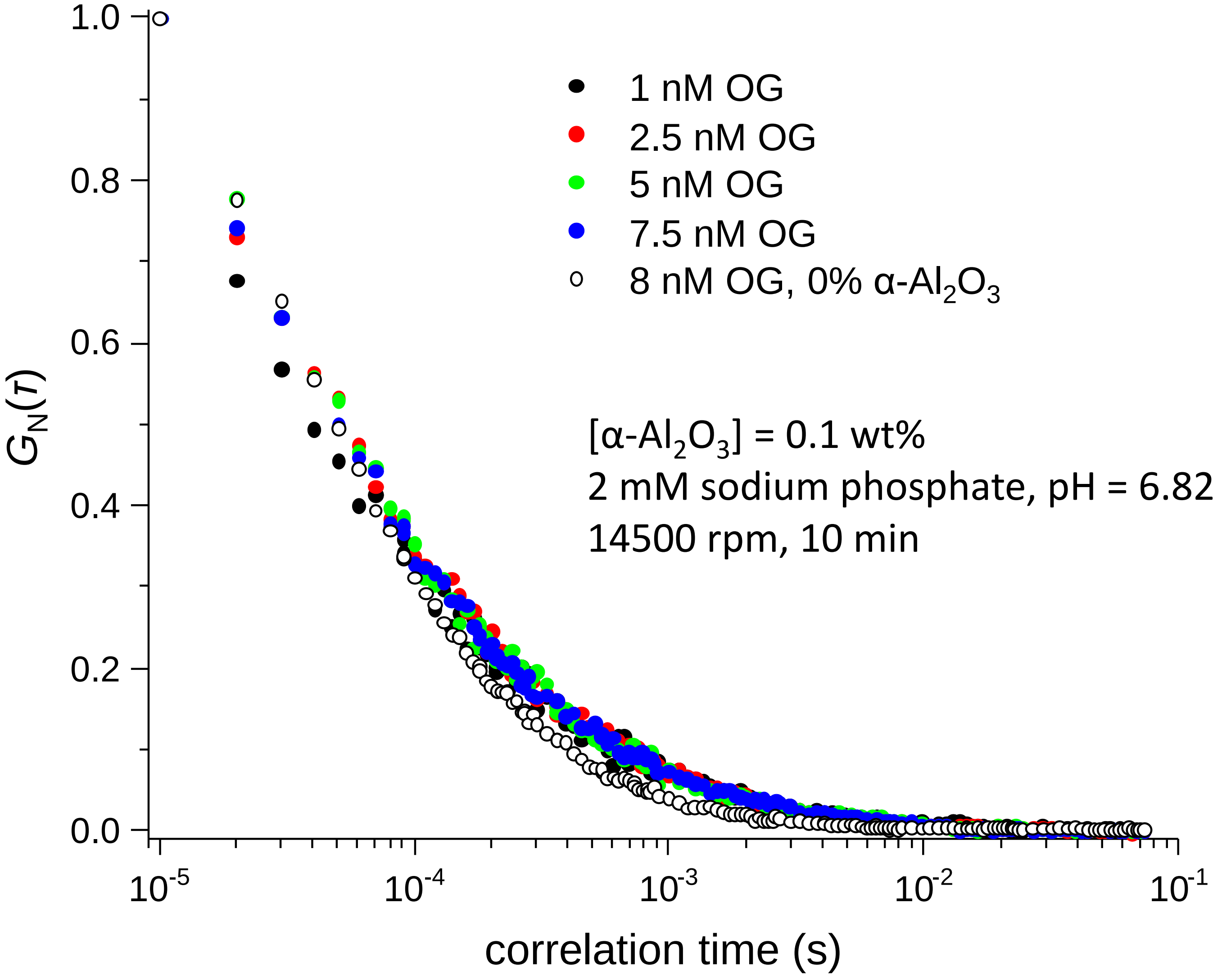
pK_a = 4.6 (literature)

α-Al_2O_3, pI = 7 to 9 (literature)
2 mM sodium phosphate, pH = 6.82

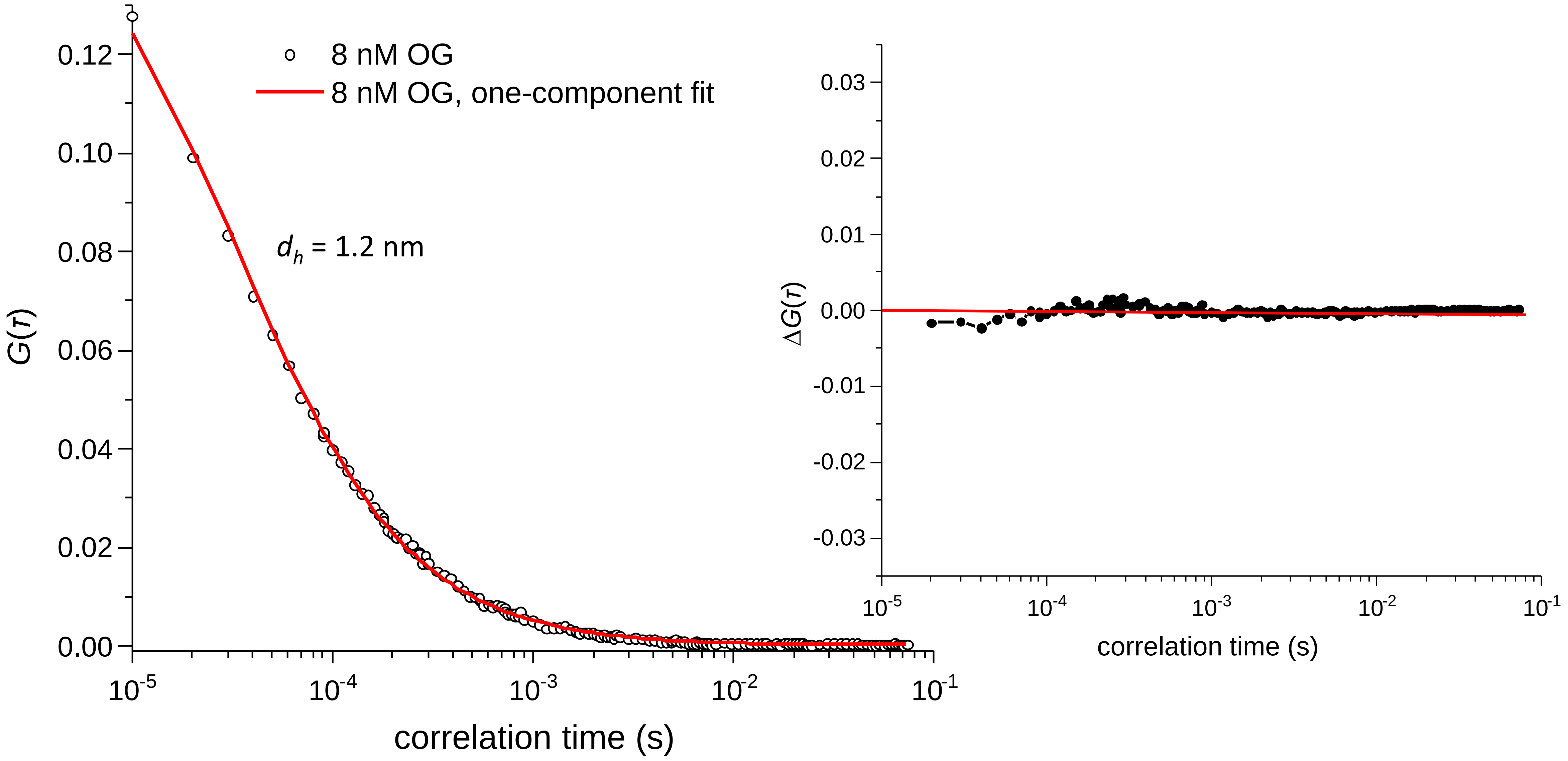
Representative ACFs for Supernatants of Centrifuged Mixtures of Oregon Green 488 (OG) and α-Al_2O_3



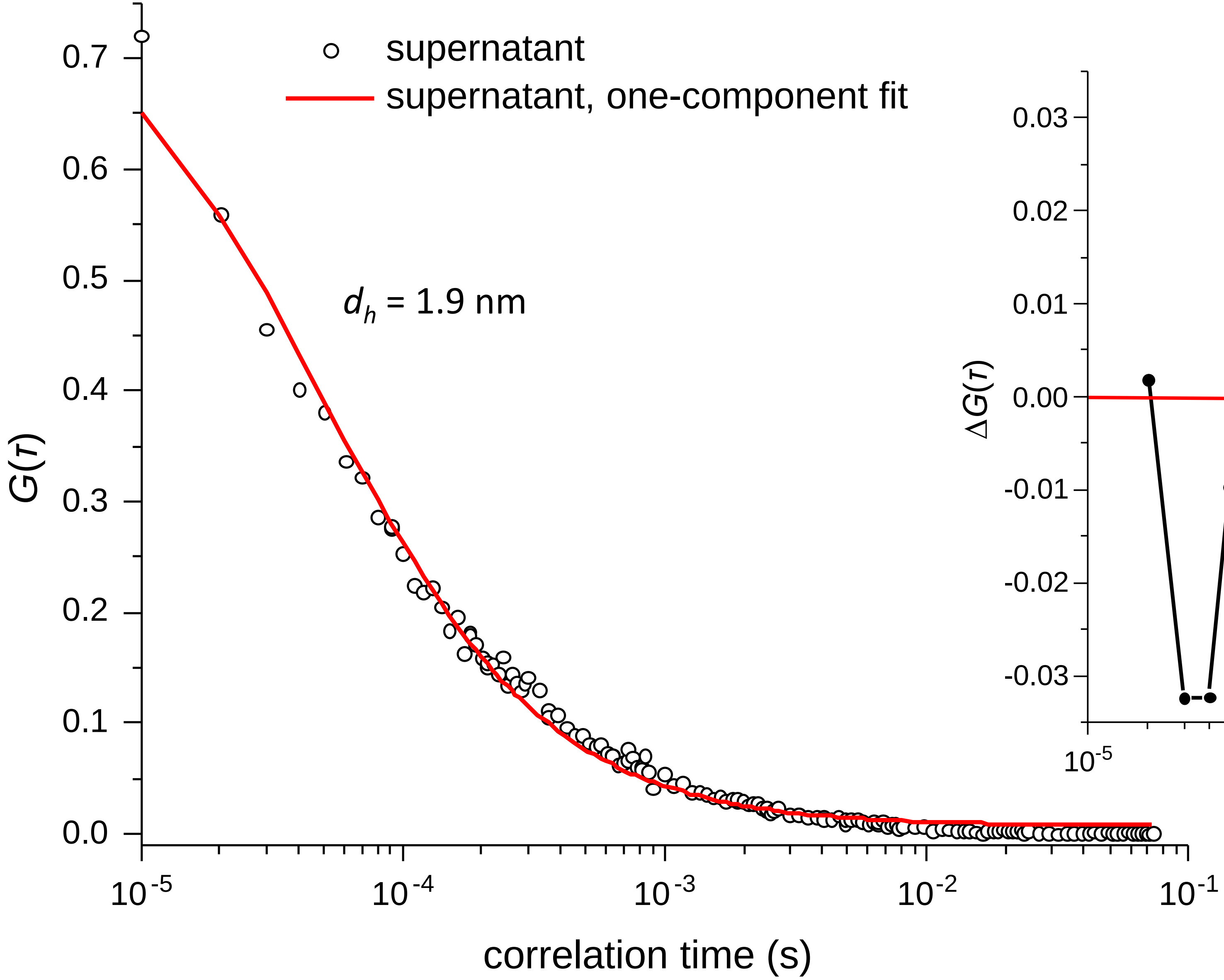
Representative Normalized ACFs for Supernatants of Centrifuged Mixtures of Oregon Green 488 (OG) and α-Al_2O_3

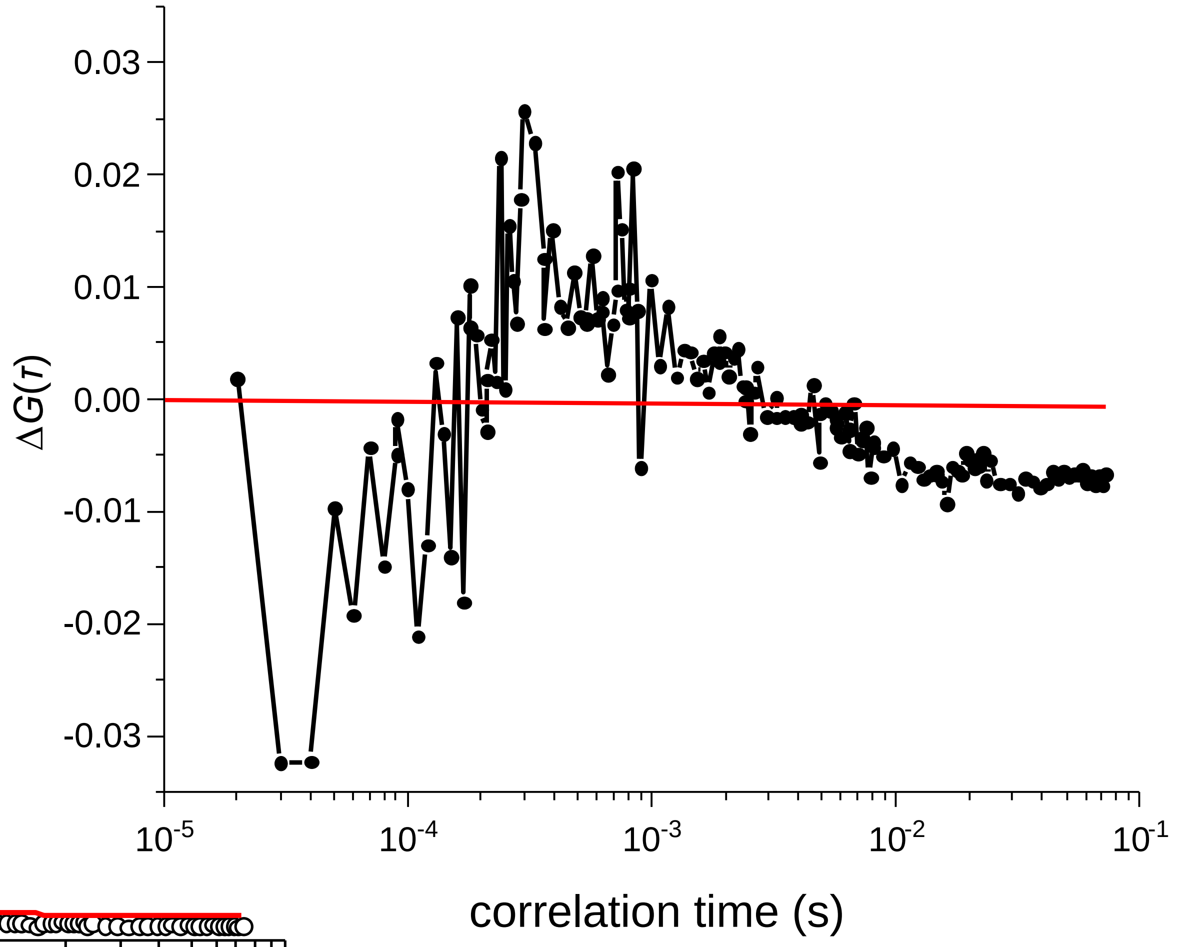


One-Component Analysis of ACF for Oregon Green 488 (OG)

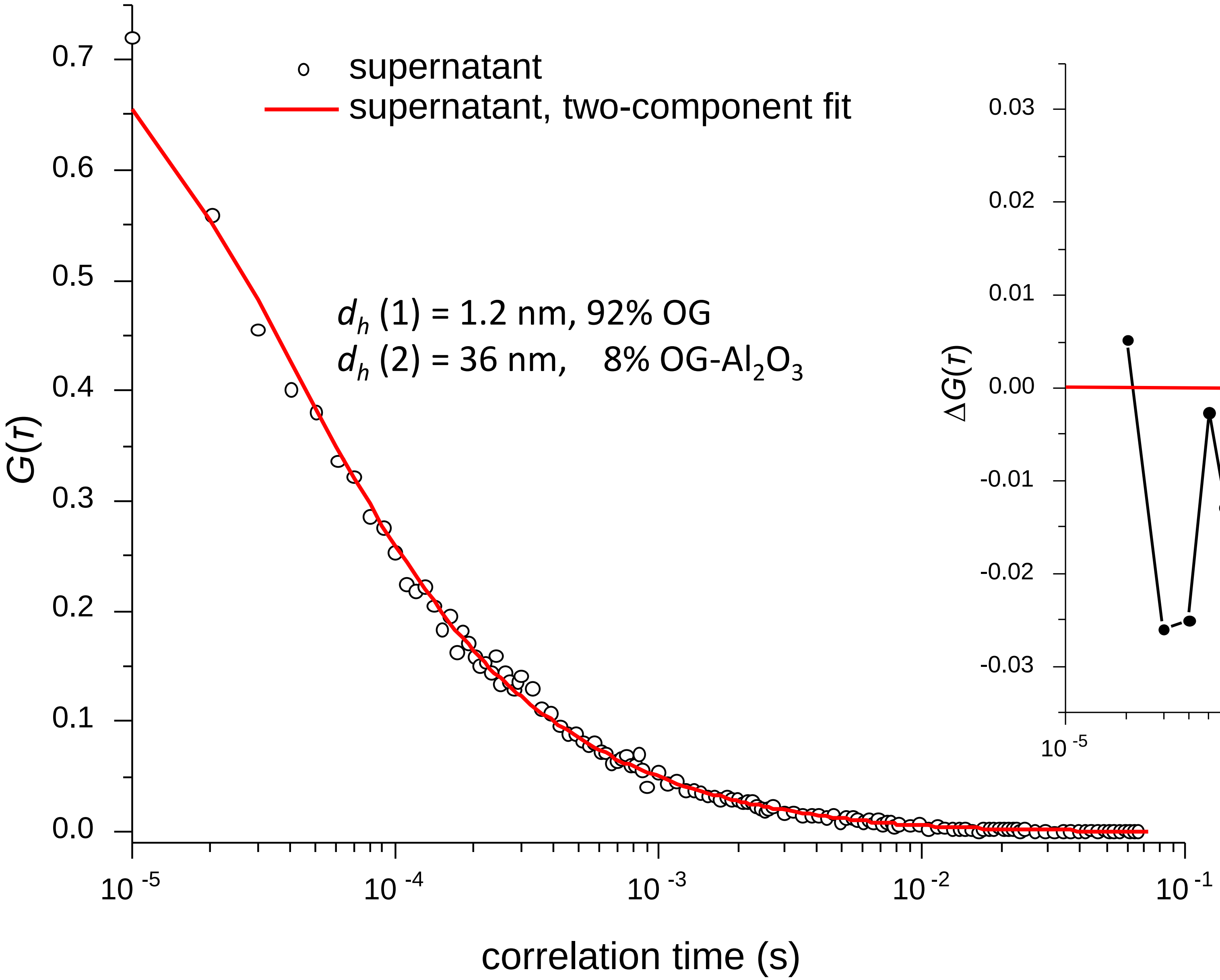


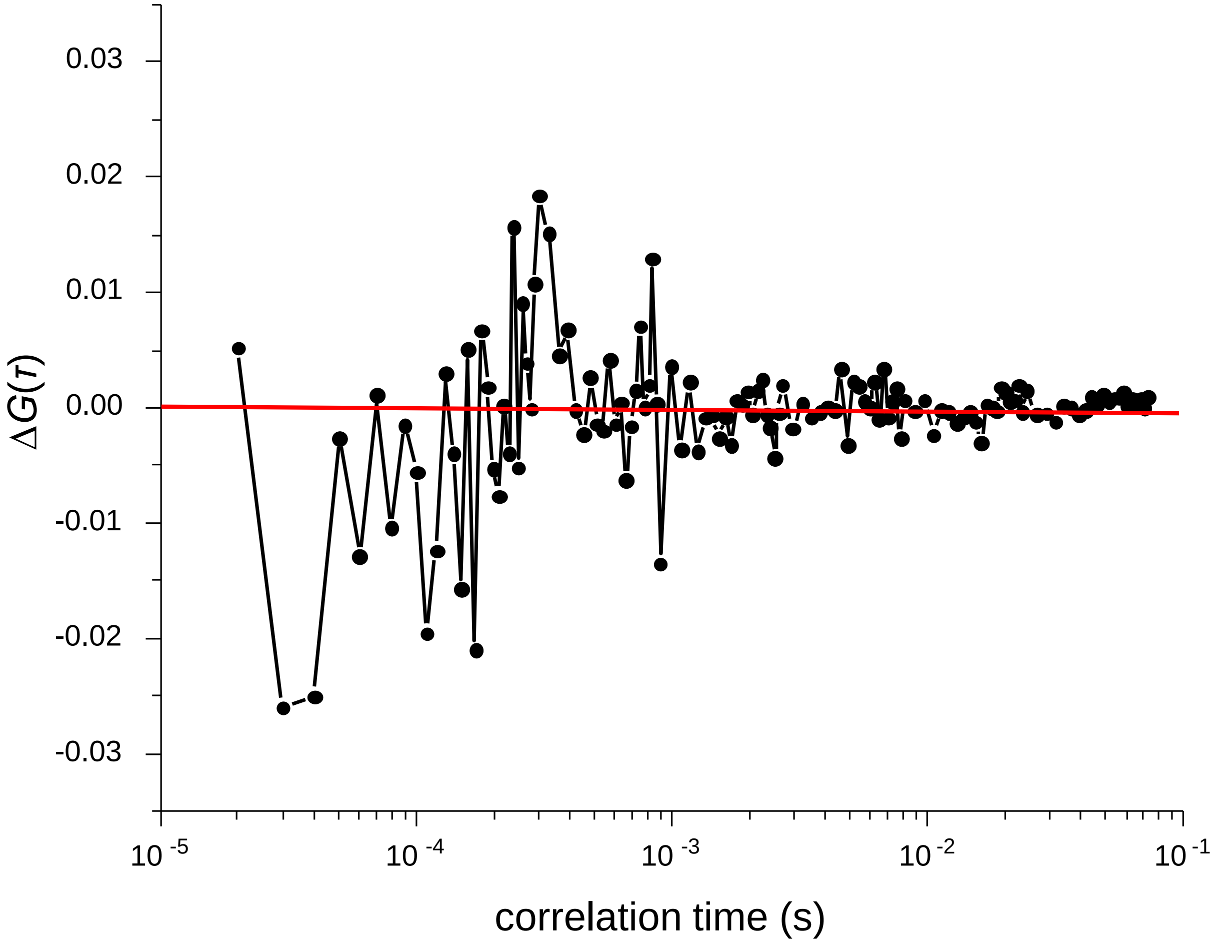
One-Component Analysis of ACF for Supernatant of Centrifuged 5 nM OG + 0.1 wt% α-Al_2O_3 Mixture





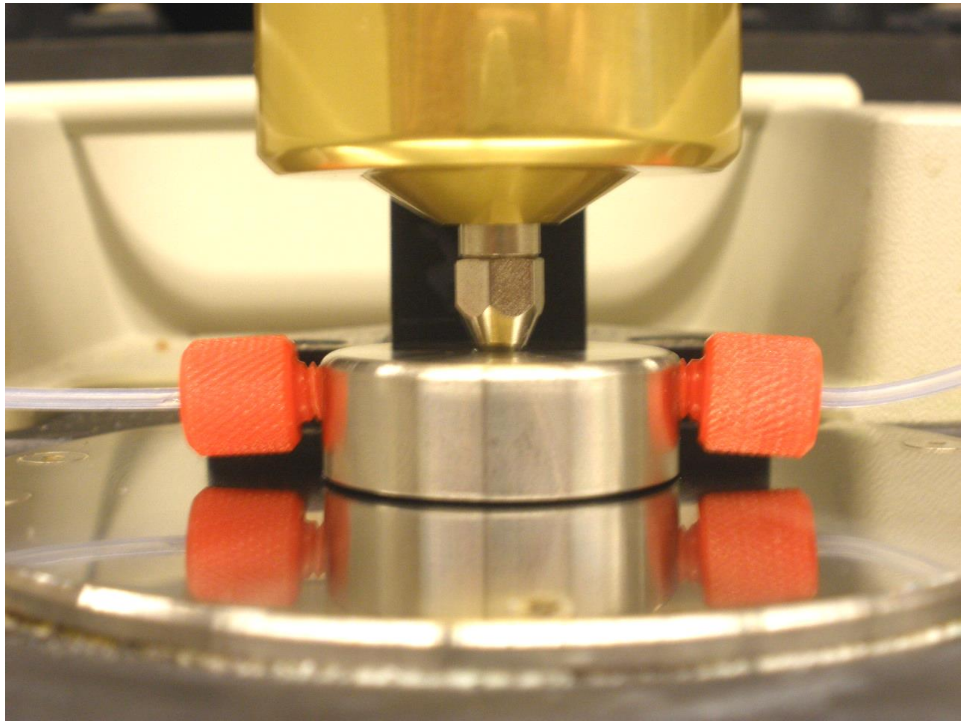
Two-Component Analyses of ACF for Supernatant of Centrifuged 5 nM OG + 0.1 wt% α-Al_2O_3 Mixture

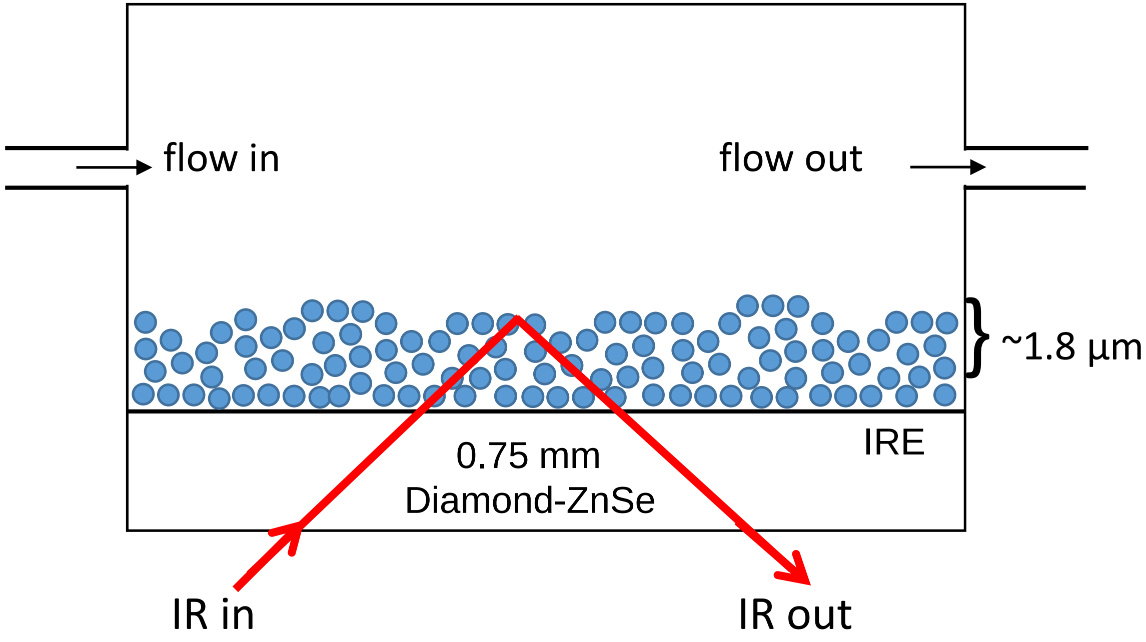




Characterization of Abrasive Particle Surface Chemistry and Molecular Interactions During Adsorption

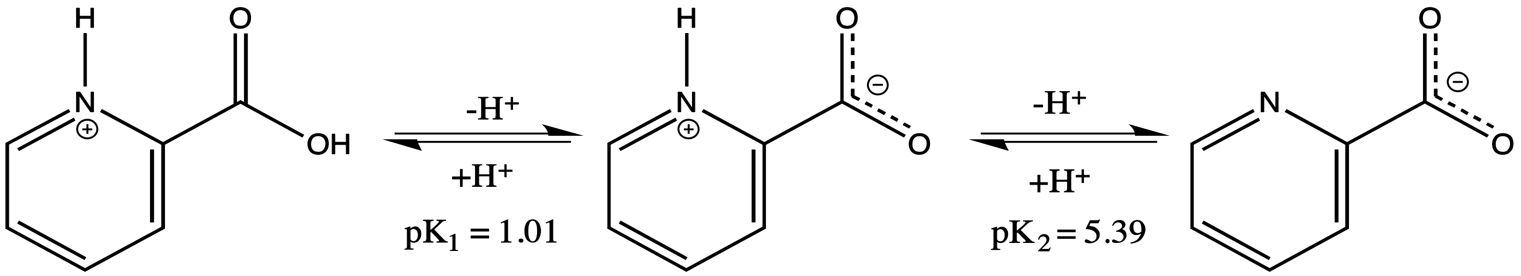
Approach: Attenuated Total Reflectance / Fourier Transform Infrared Spectrometry (ATR/FT-IR)



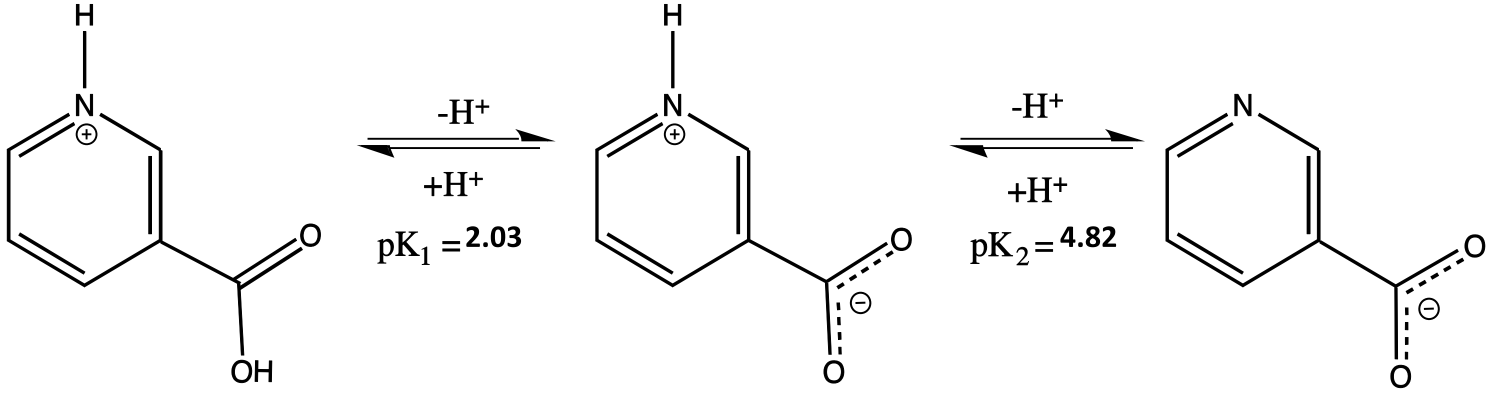


Dissociation Equilibria of Pyridine Carboxylic Acids

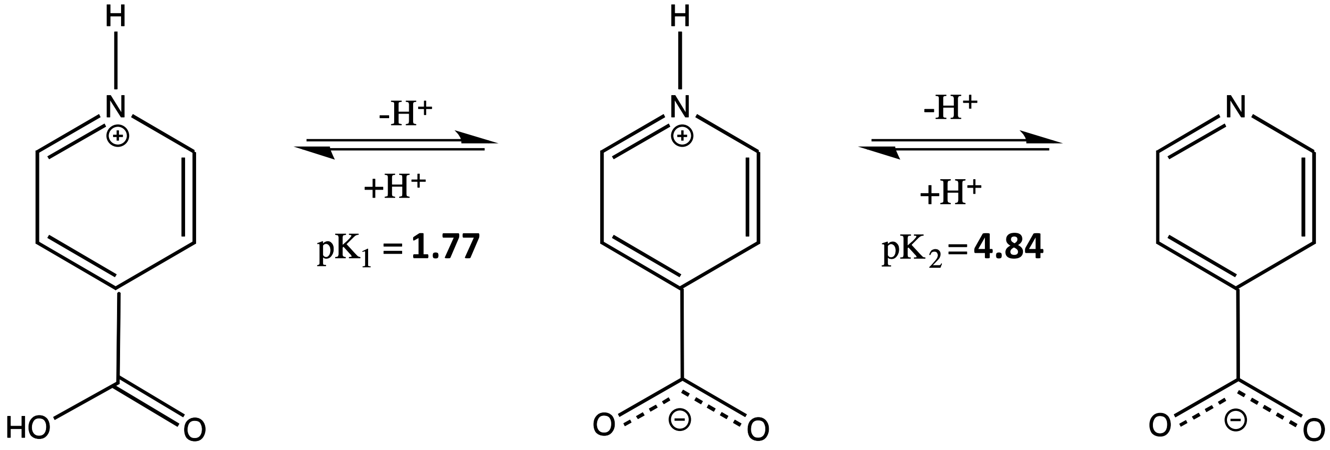
pyridine-2-carboxylic acid (picolinic acid)



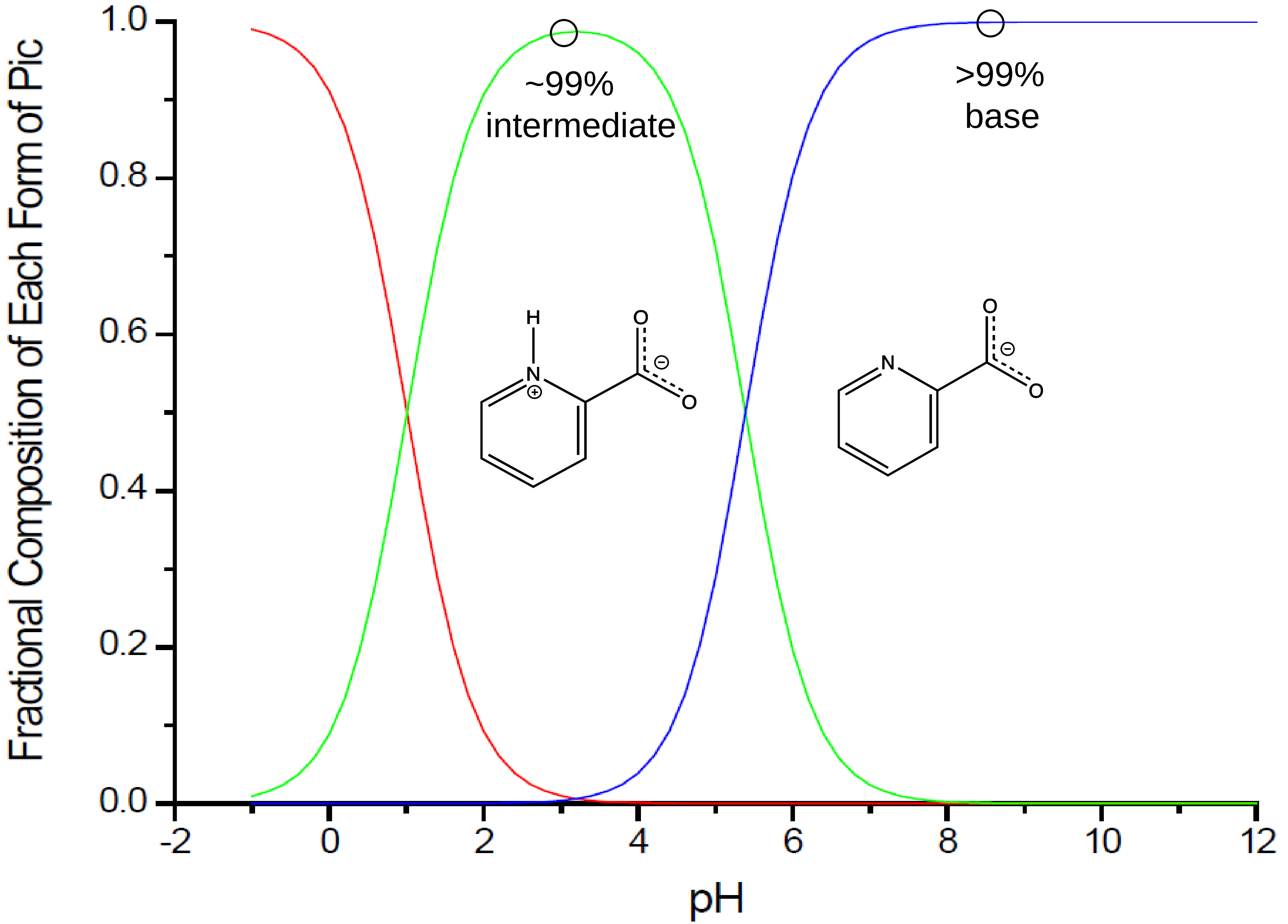
pyridine-3-carboxylic acid (nicotinic acid)

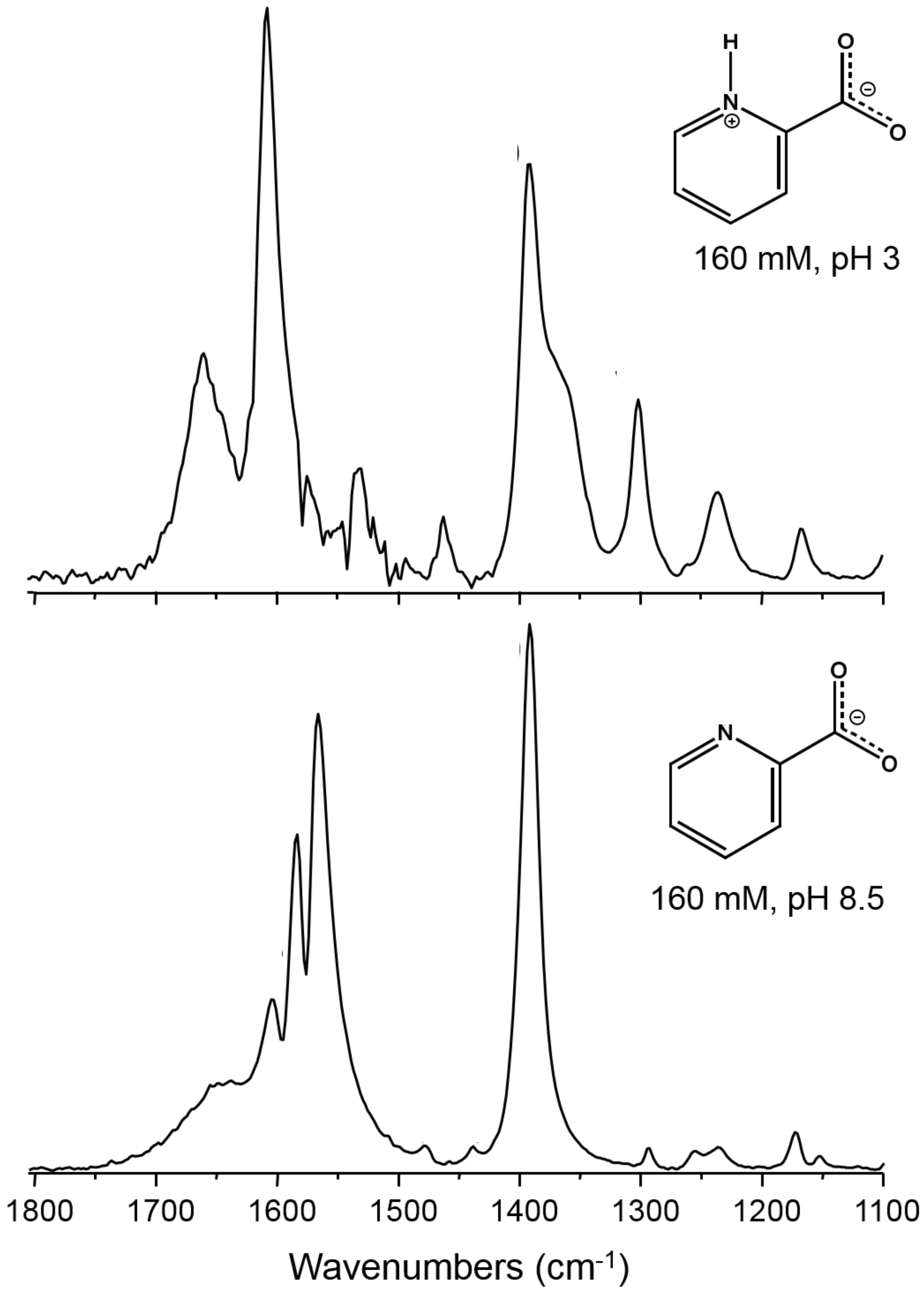


pyridine-4-carboxylic acid (isonicotinic acid)



Fractional Composition of Pyridine-2-Carboxylic Acid (Picolinic Acid)





Assignment of IR spectra[2]:

IR spectra were calculated using Density Functional Theory (B3LYP/6-311++G**).

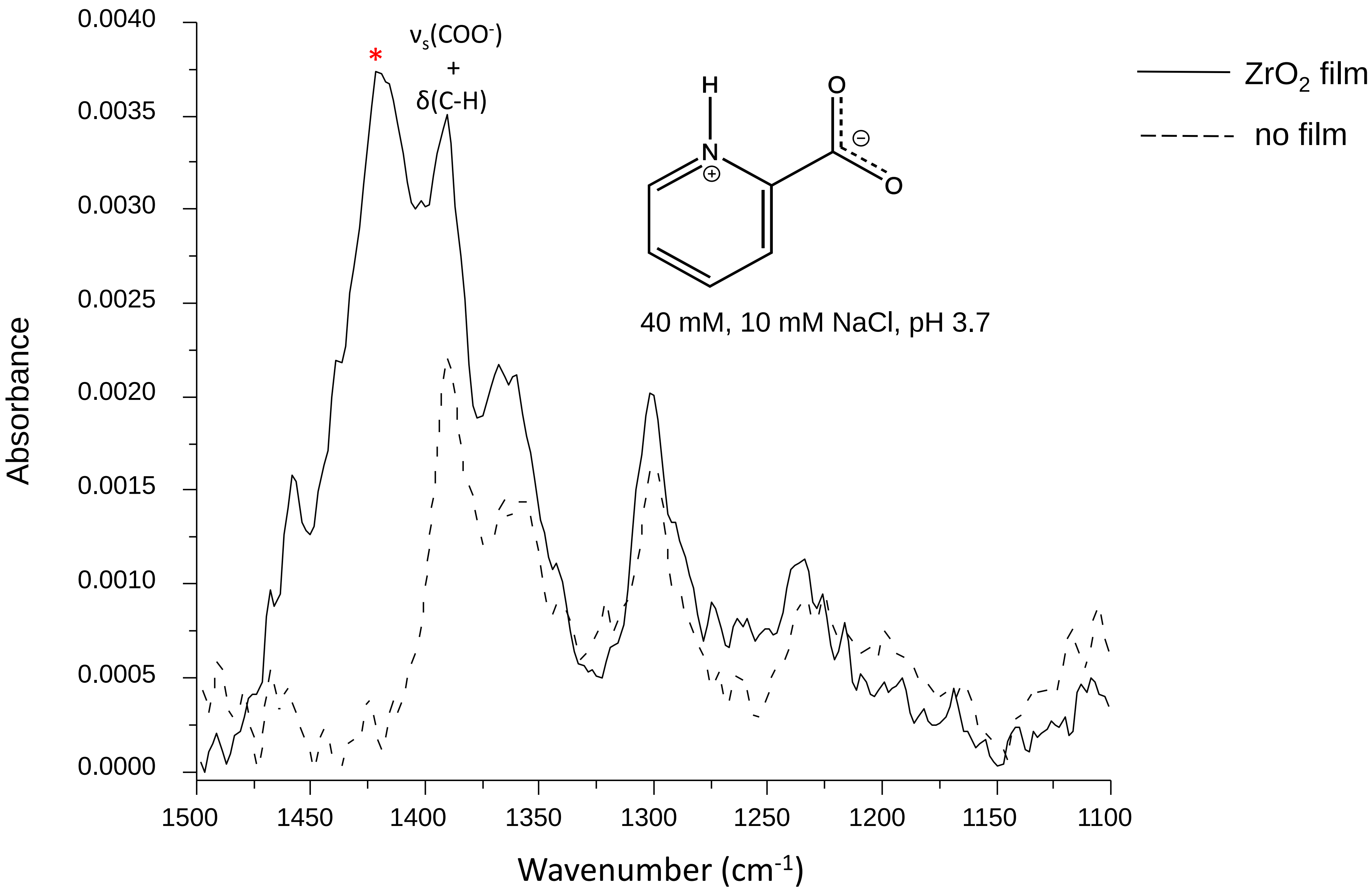
Solvation was incorporated using the COSMO model; four explicit water molecules were also included.

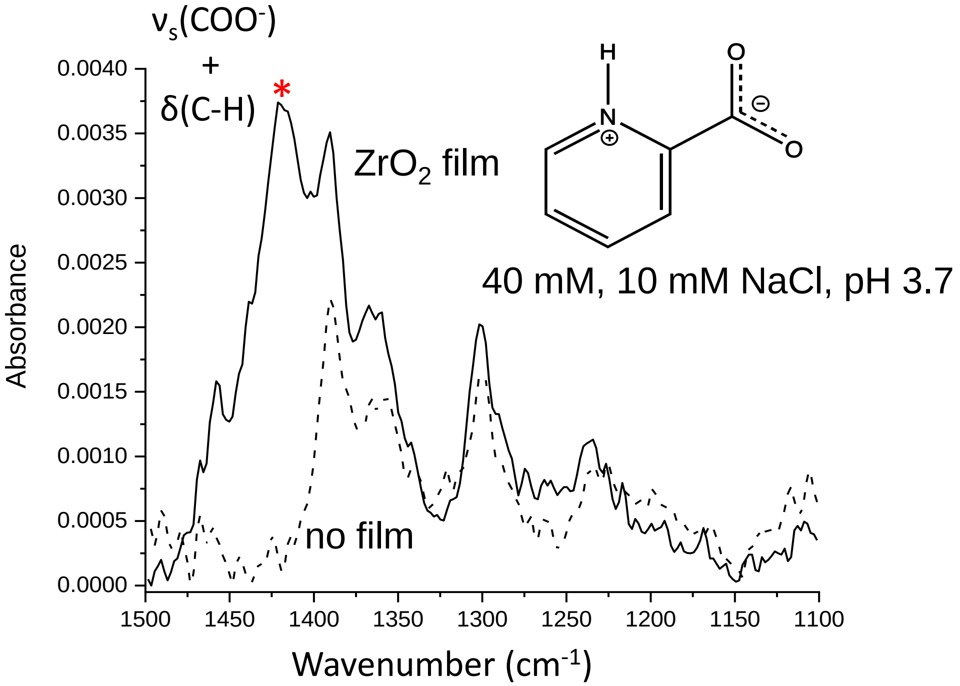
Explicit water molecules bridged molecular hydrogen bonding sites.

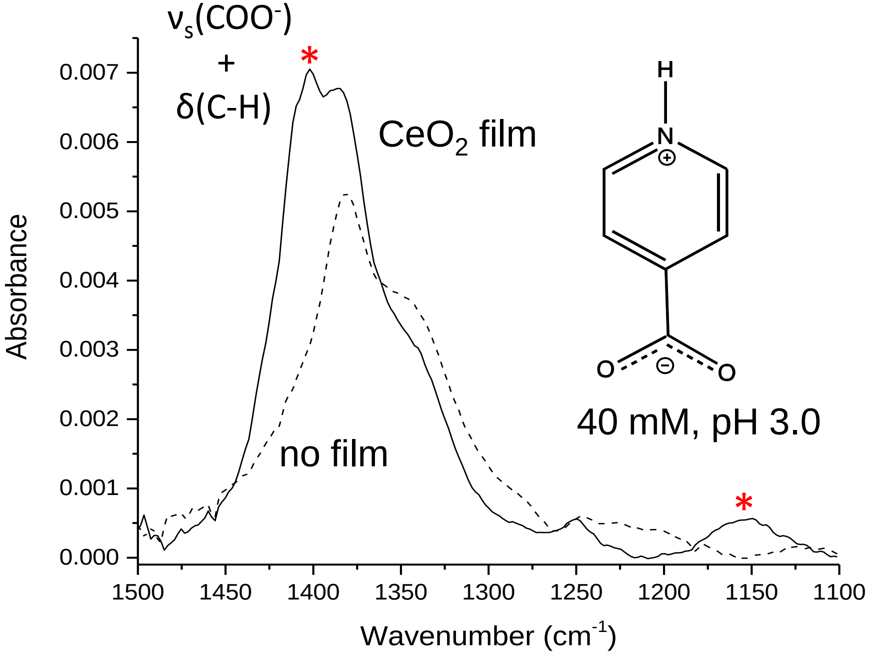
Assignments were made by comparing with benzene, pyridine and pyridinium Ion.

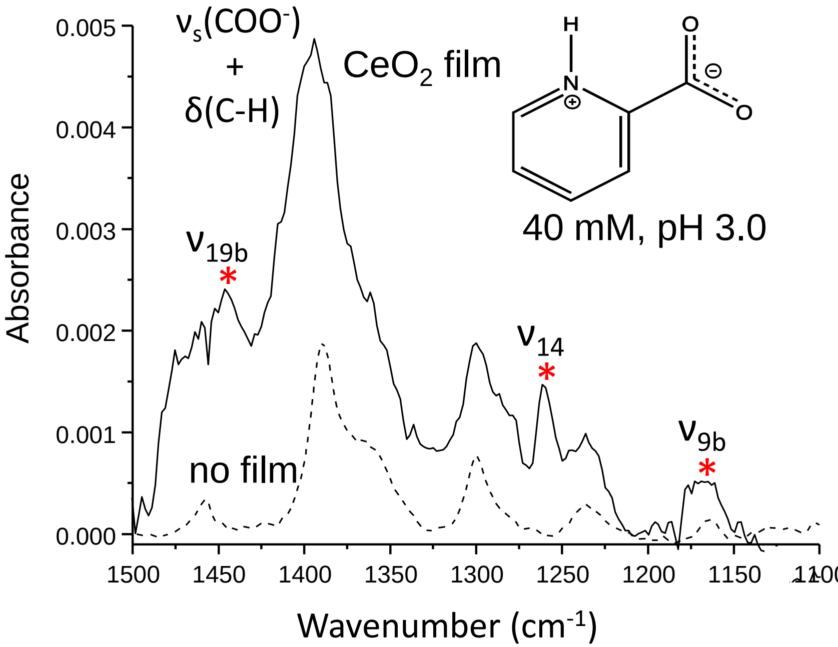
2. Marsh, J.L.; Wayman, A.E.; Smiddy, N.M.; Campbell, D.J.; Parker, J.C.; Bosma, W.B.; Remsen, E.E. *Langmuir* **2017,** *33,* 13224-13233**.**

IR Spectrum Picolinic Acid Adsorbed to ZrO_2 Film vs. IR Spectrum of Free Picolinic Acid (no film)

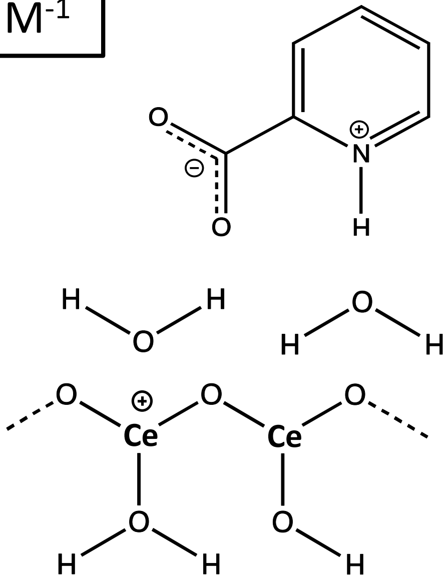


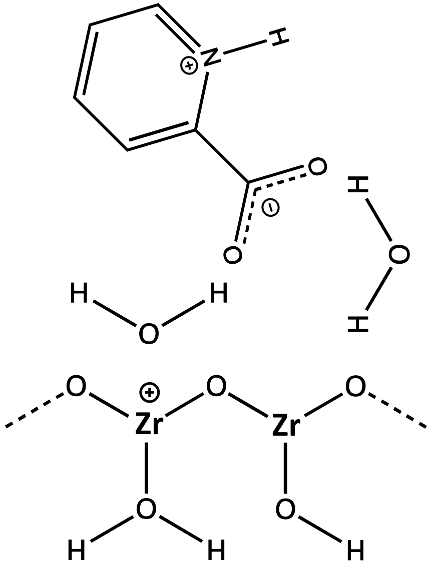






$K_L \approx 10^3\ M^{-1}$





Directions for Future Studies

- Use FCS to quantitatively evaluate adsorption isotherms for CMP additive interactions with α-alumina (and fumed alumina) and zirconia abrasives via competitive adsorption with Oregon Green 488

- Characterize alumina and zirconia abrasive surface chemistry via FCS analysis of adsorption for additional anionic dyes, such as Alexa fluor 488 and 546

- Determine using ATR/FT-IR, the functional groups of additional CMP additives, e.g. amino acids which produce adsorption on α-alumina abrasives

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