Characterization of Small Molecule Adsorption on Metal Oxide Colloidal Abrasives Used in Chemical-Mechanical Planarization (CMP) Slurries

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Outline

- Introduction to Fluorescence Correlation Spectroscopy (FCS) - A Single-Molecule Spectroscopic Analysis Technique

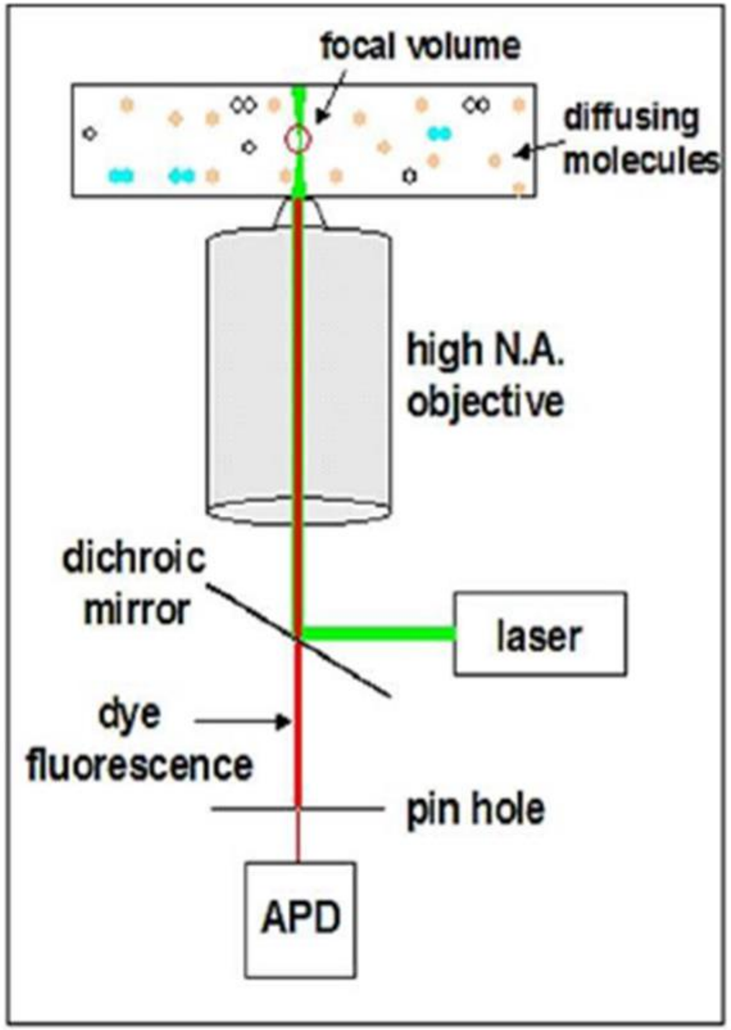
- FCS Analysis of Dye Adsorption on Colloidal Silica and Alumina Abrasive Particles

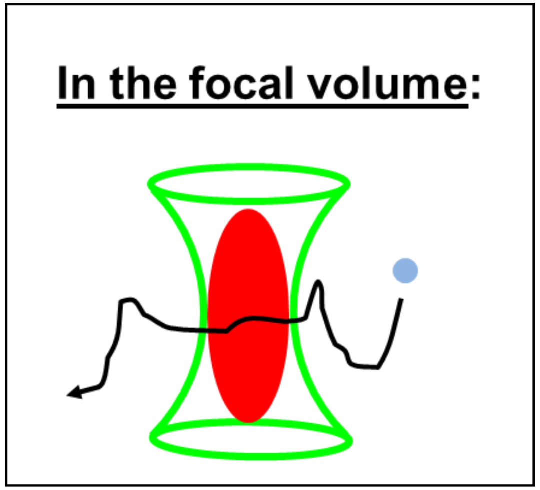
- Application of Attenuated Total Internal Reflectance / Infrared Spectrometry (ATR/FTIR) for the Analysis of Molecular Adsorption

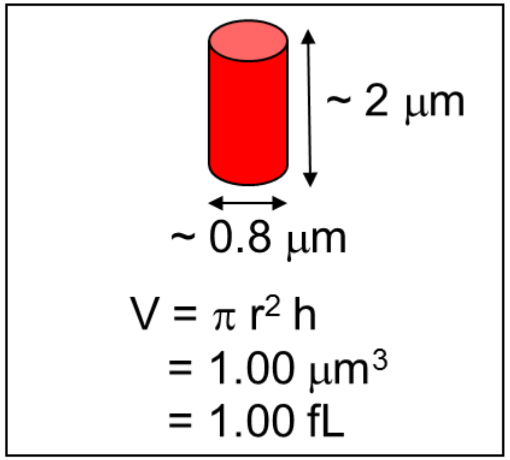
- ATR/FTIR Analysis of Small Molecule Adsorption on Thin Films of Colloidal Ceria and Silica Abrasive Particles

- Directions for Future Studies

Single-Molecule Spectroscopic Analysis
Fluorescence Correlation Spectroscopy (FCS)







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

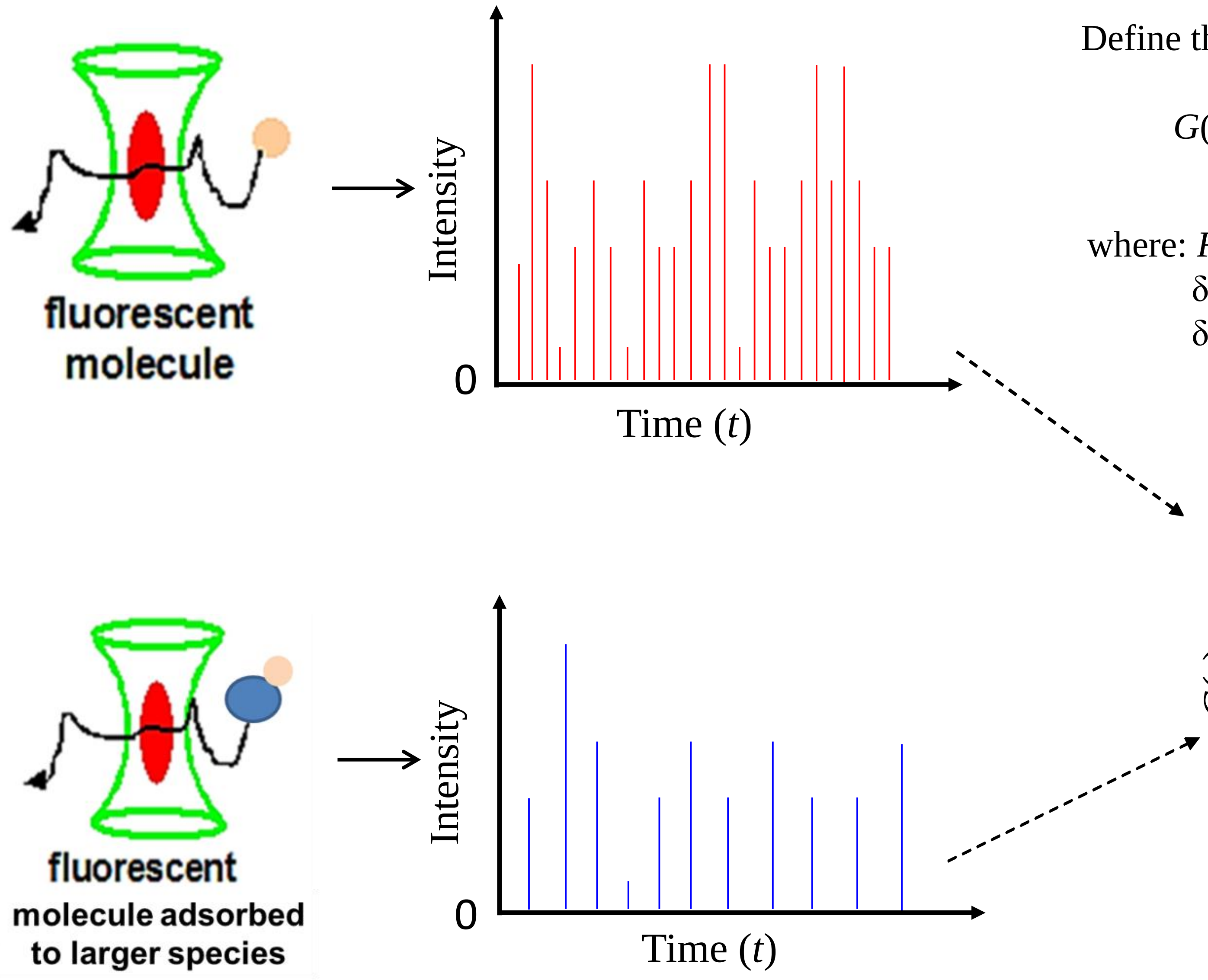
Define the *normalized autocorrelation function*, $G(\tau)$:

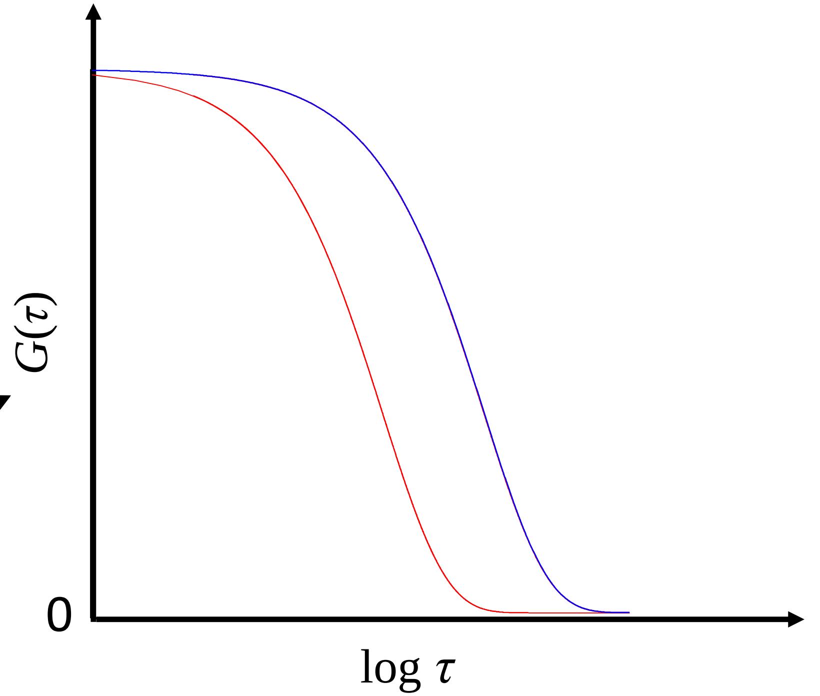
$$G(\tau) = \frac{\langle \delta F(t) \bullet \delta F(t+\tau) \rangle}{\langle F(t) \rangle^2}$$

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

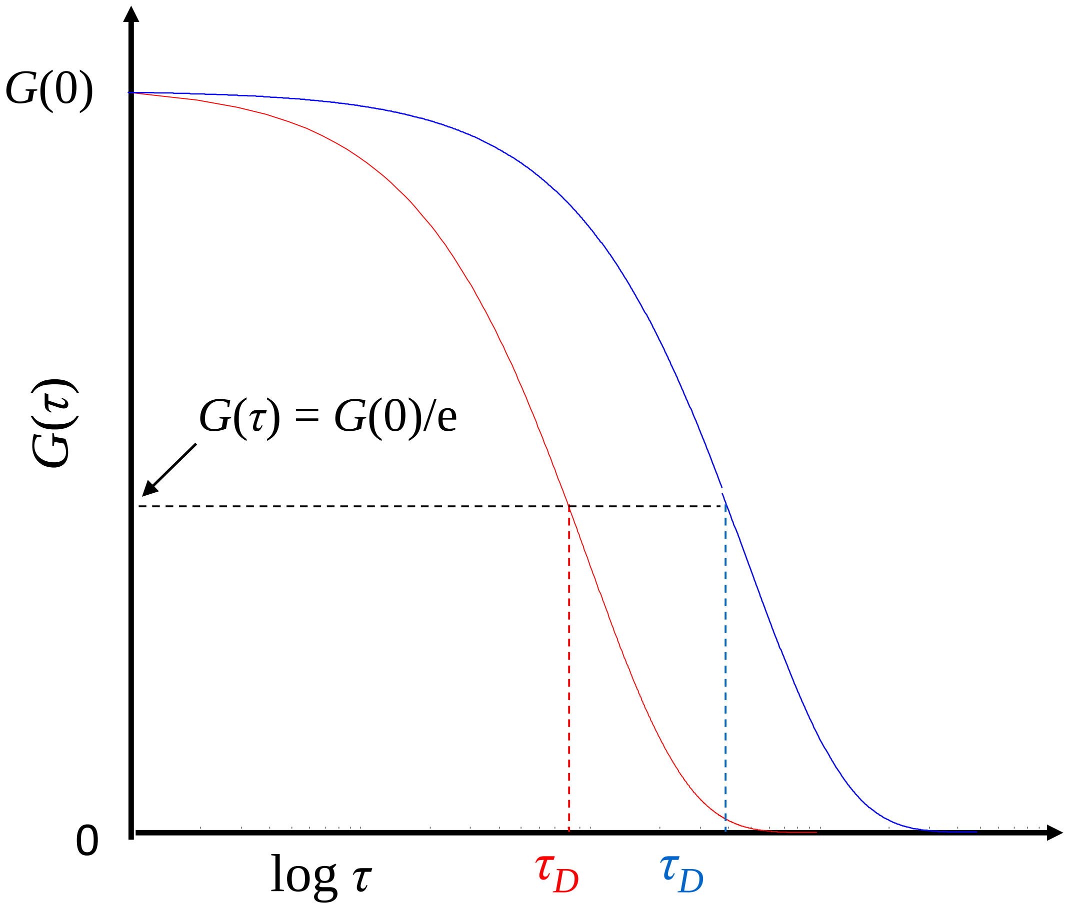
$\delta F(t)$ is the fluctuation in intensity at time t

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





Evaluate the Diffusion Coefficient, D, 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 is related to the *diffusion coefficient*, D:

$$\tau = r_0^2 / 4D$$

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

D is related to the *hydrodynamic diameter*, d:

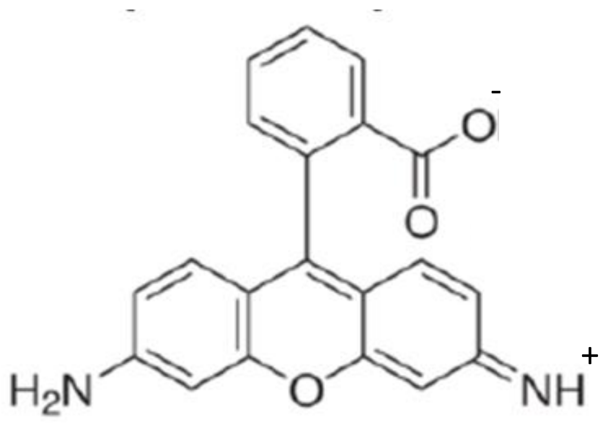
$$D = kT / 3\pi\eta d \quad \text{(Stokes-Einstein equation)}$$

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

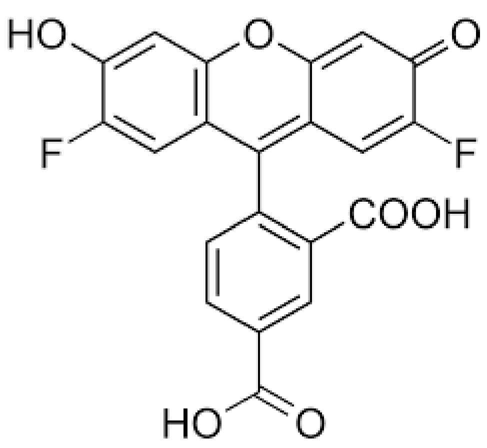
$G(0)$ is related to the *average number of fluorophores in the focal volume*, N:

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

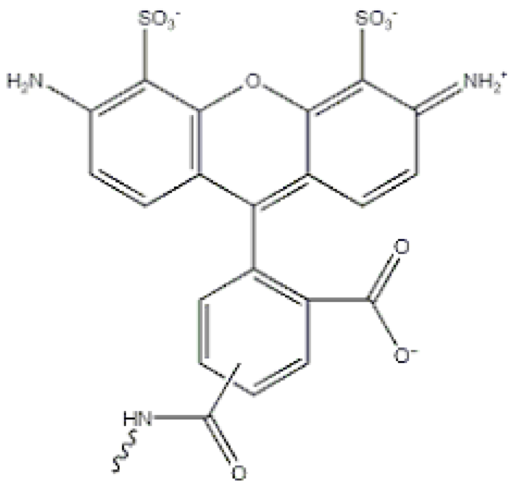
Representative Fluorophores Commonly Employed for FCS Studies



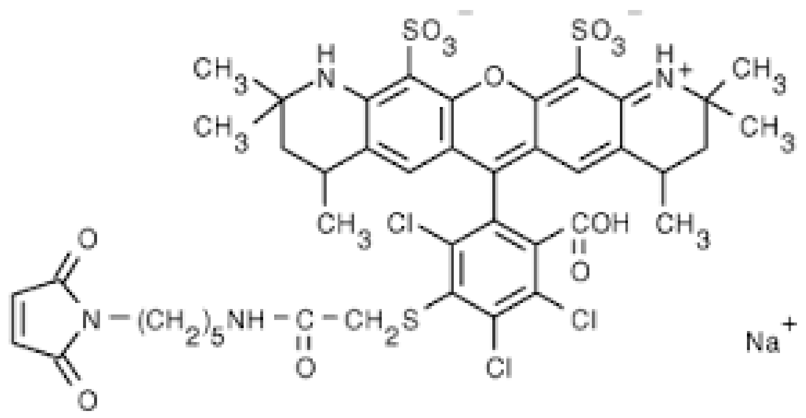
R110, λ_{ex} = 496 nm, λ_{em} = 520 nm



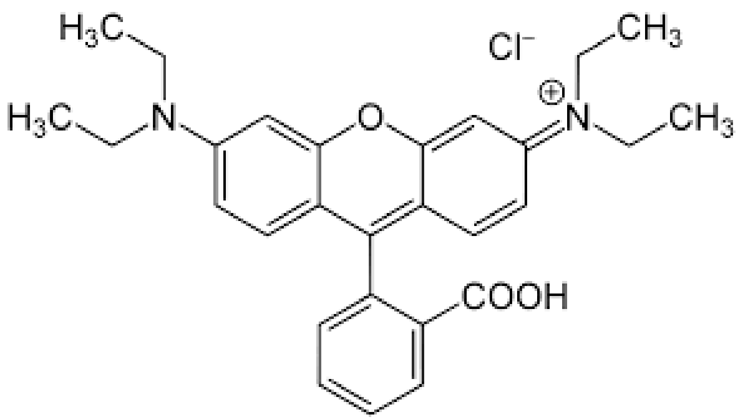
OG 488, λ_{ex} = 501 nm, λ_{em} = 526 nm



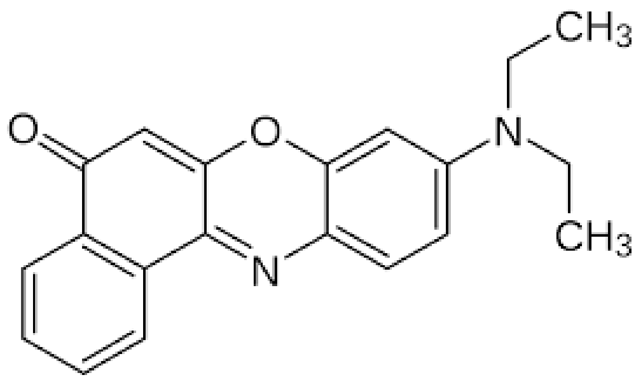
Alexa 488, λ_{ex} = 490 nm, λ_{em} = 525 nm



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



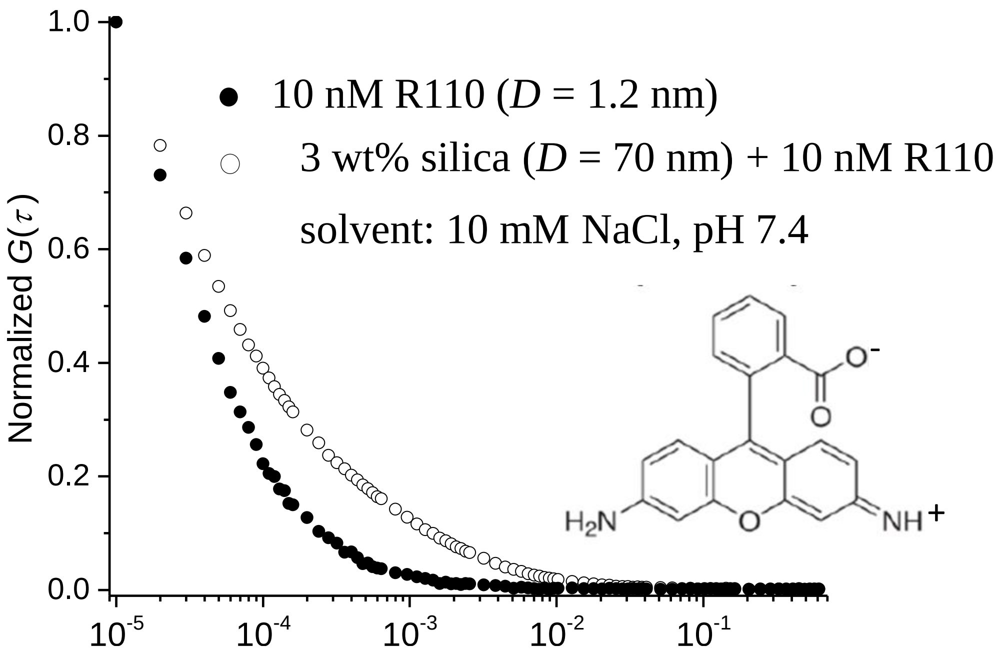
Rhod B, λ_{ex} = 553 nm, λ_{em} = 627 nm

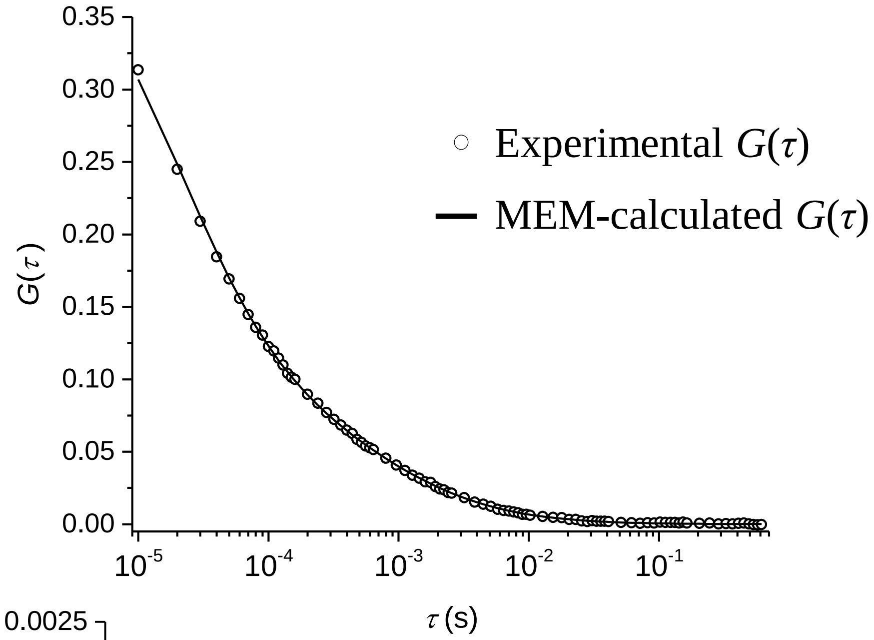


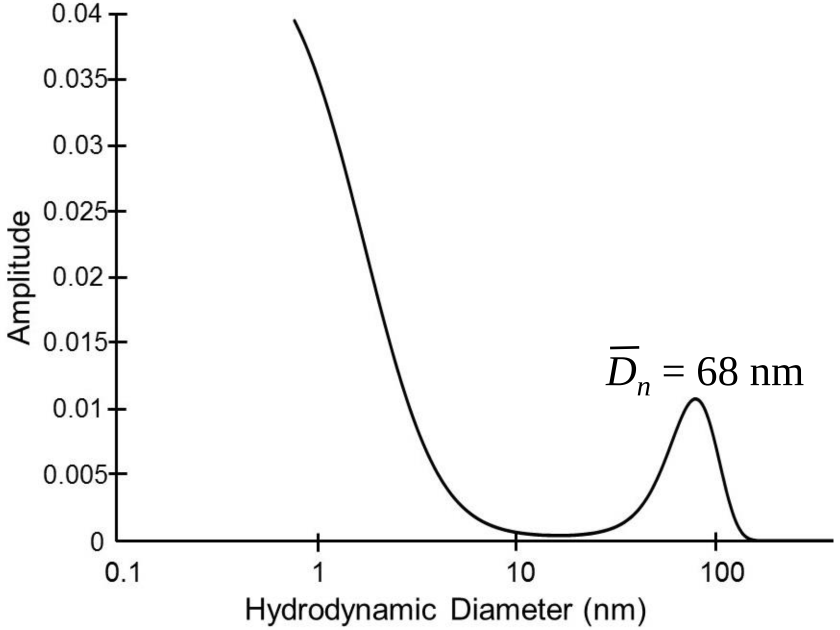
Nile Red, λ_{ex} ~ 540 nm, λ_{em} ~ 630 nm

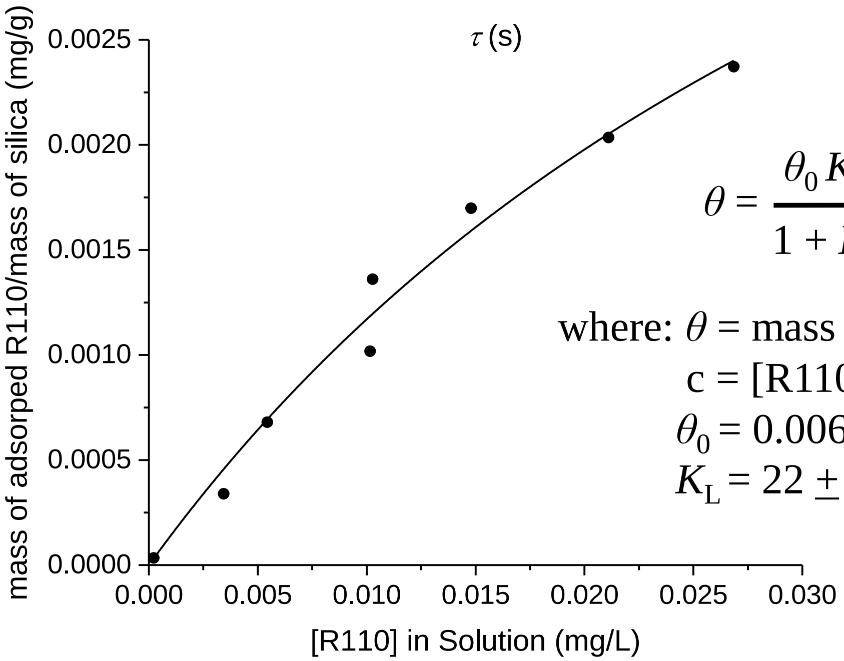
FCS Analysis of Dye Adsorption on SiO_2 Abrasives[1]

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.





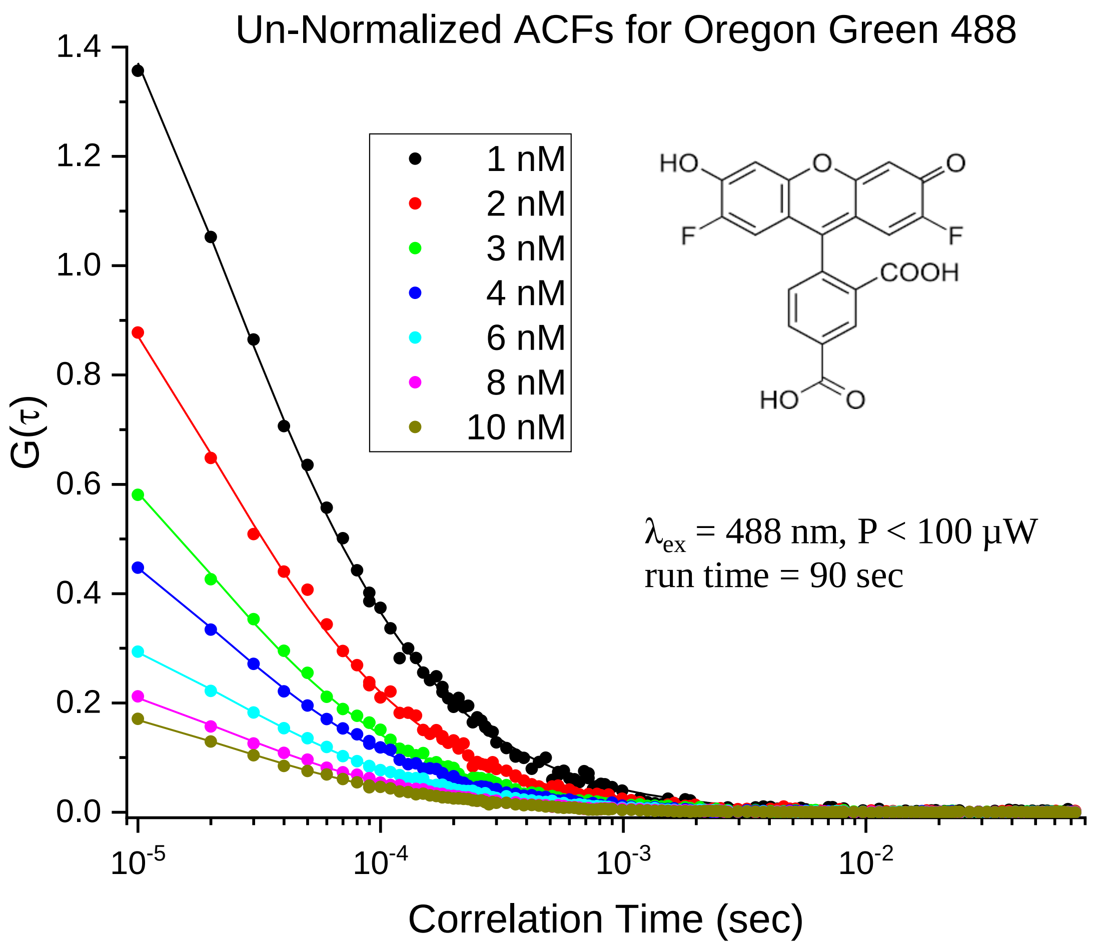


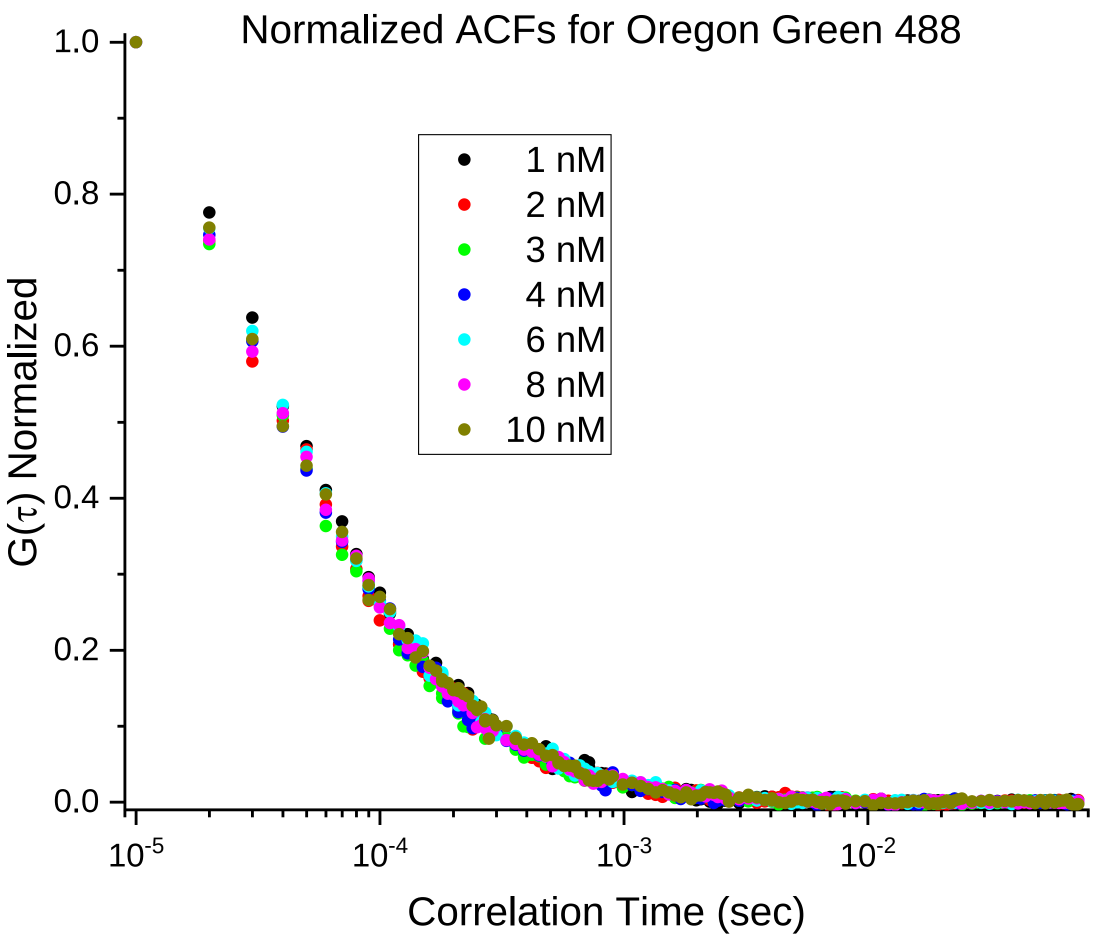


$$\theta = \frac{\theta_0 K_L c}{1 + K_L c}$$

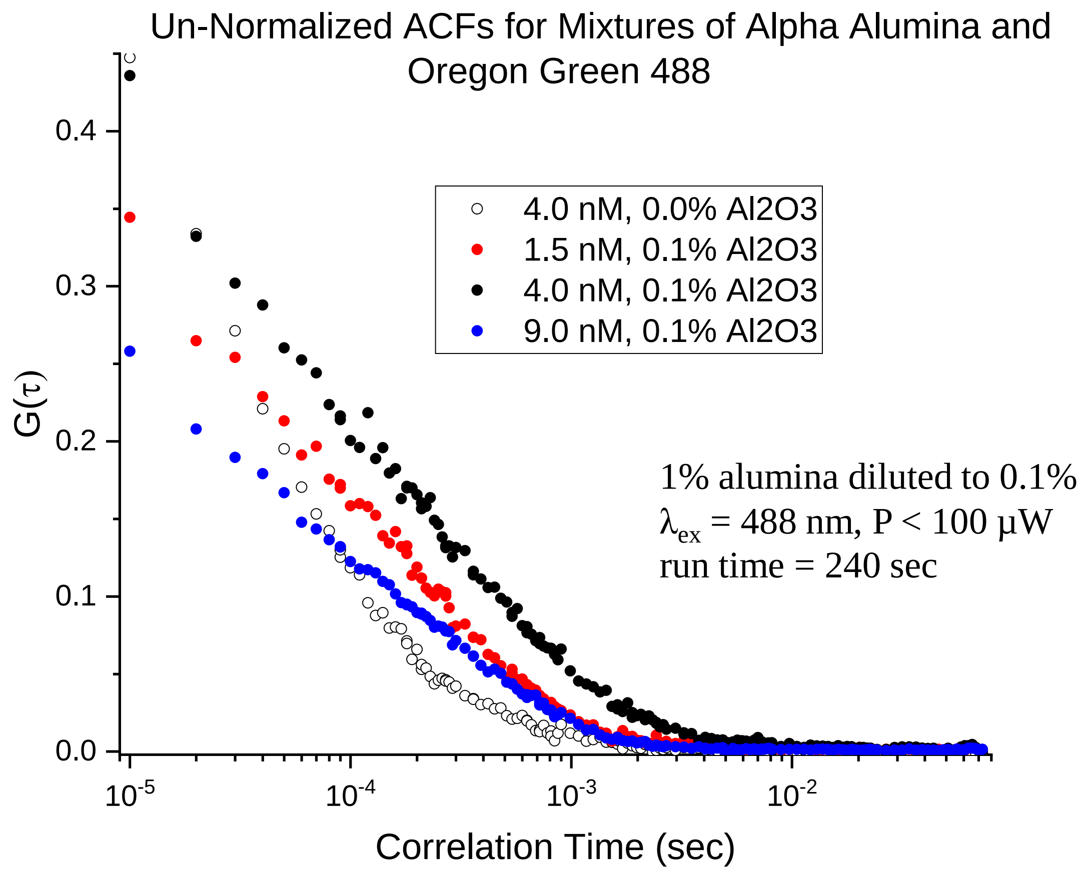
where: θ = mass adsorbed R110/mass of silica
c = [R110] in solution
$\theta_0 = 0.0064 \pm 0.0016$ mg/g
$K_L = 22 \pm 8$ L/mg

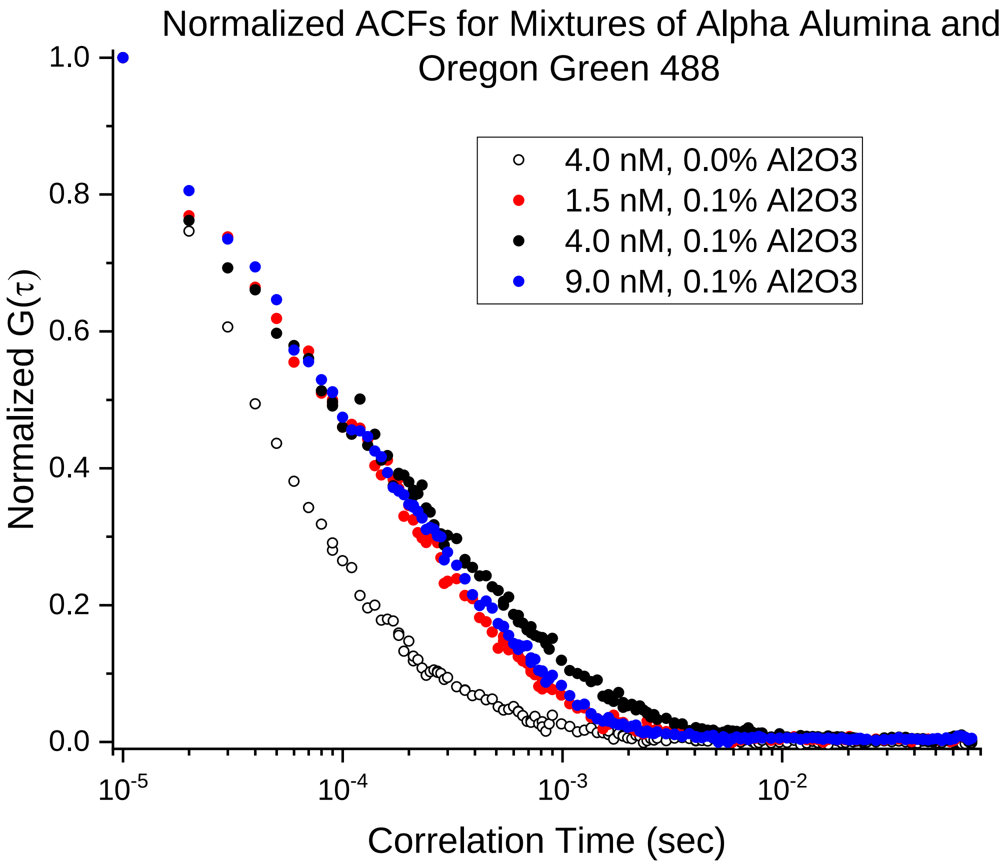
Comparison of Un-normalized and Normalized ACFs for Oregon Green 488 as a Function of Concentration



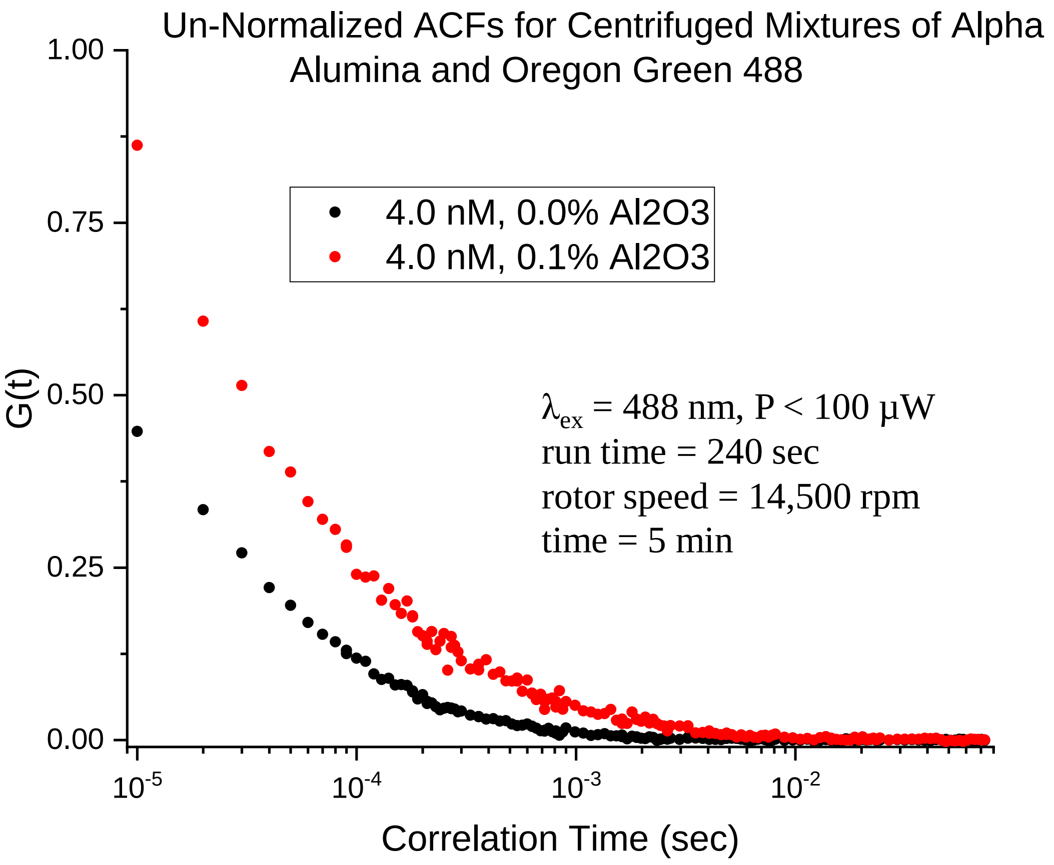


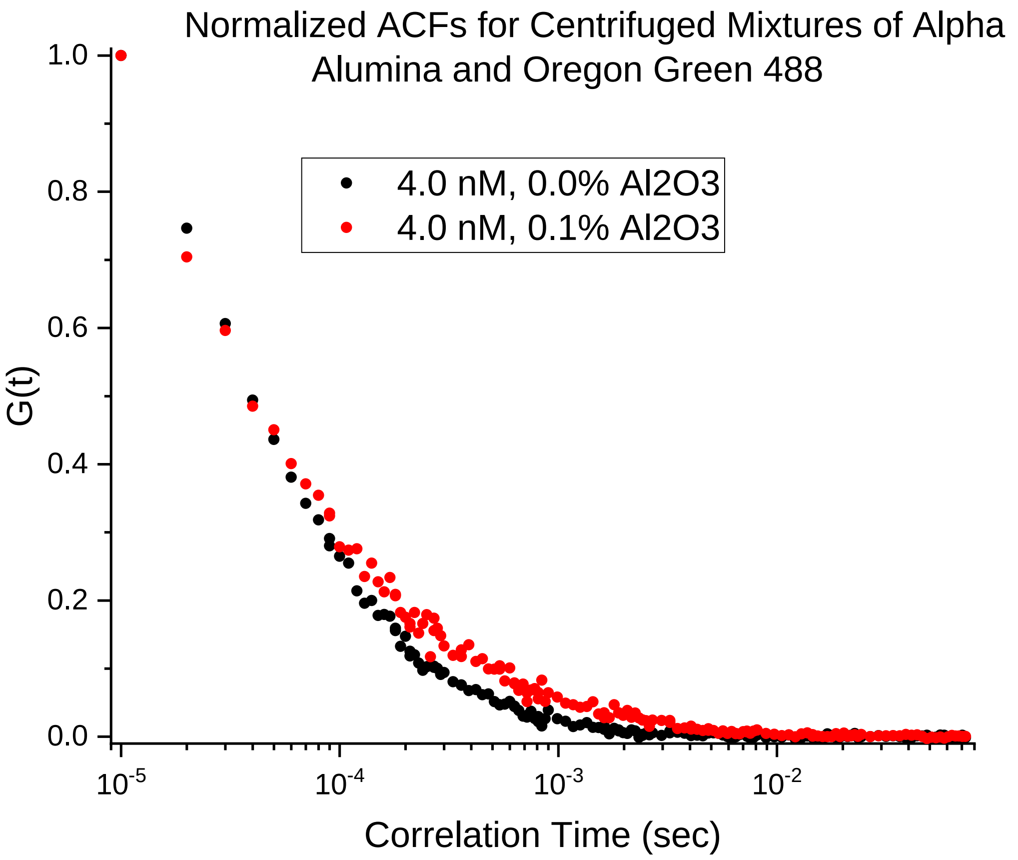
Comparison of Un-normalized and Normalized ACFs for Mixtures of Oregon Green 488 and Alpha Alumina





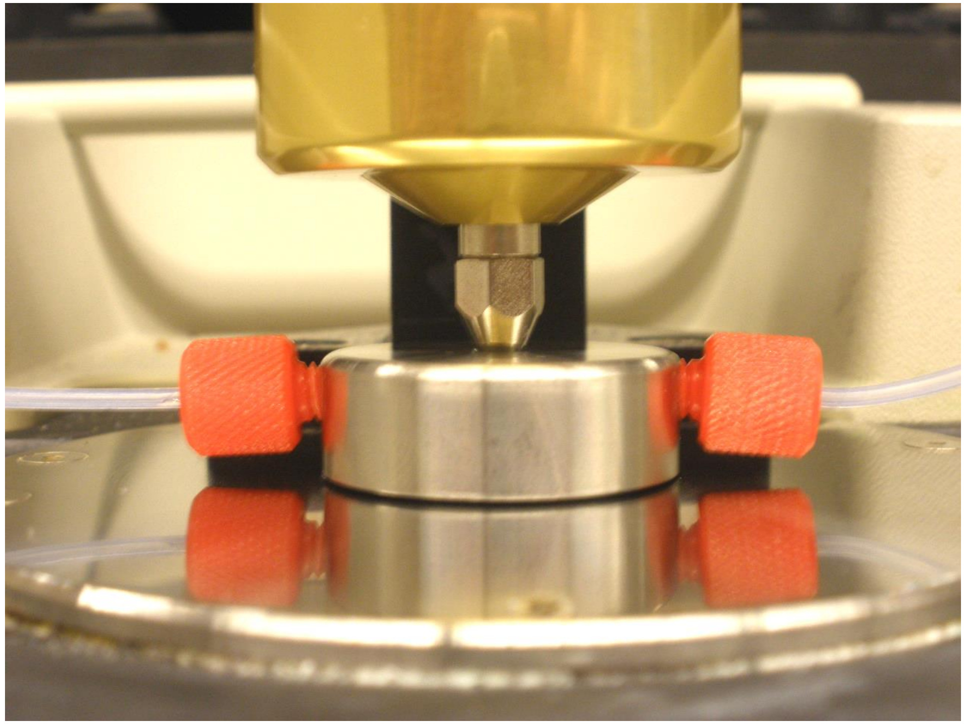
Comparison of Un-normalized and Normalized ACFs for Supernatants of Centrifuged Mixtures of Oregon Green 488 and Alpha Alumina

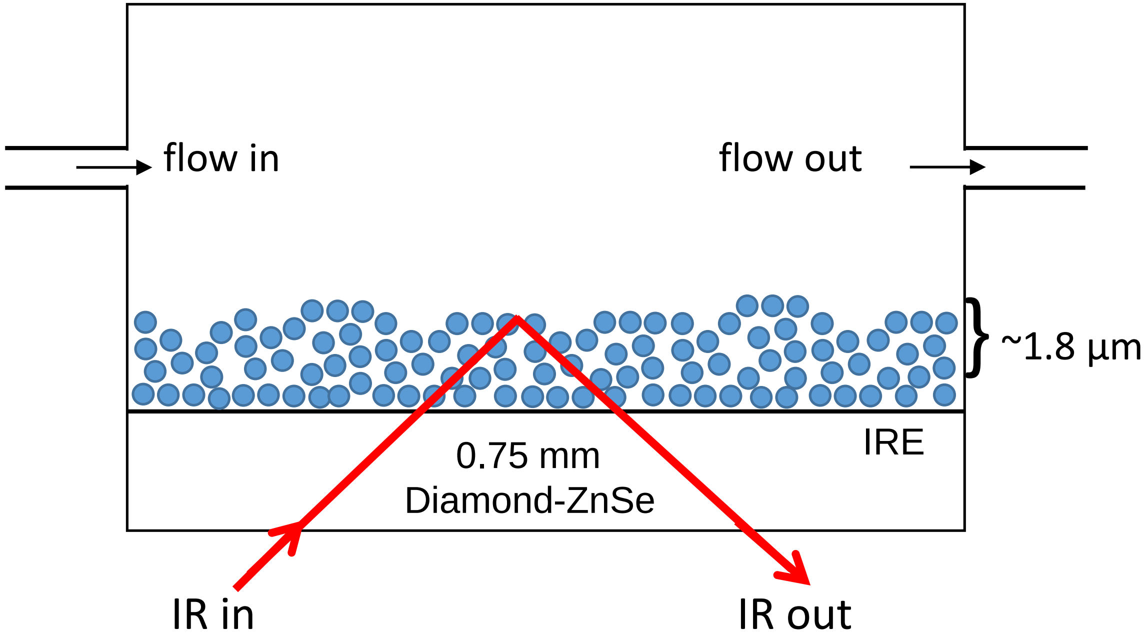




Characterization of Abrasive Particle Surface Chemistry and Molecular Interactions During Adsorption

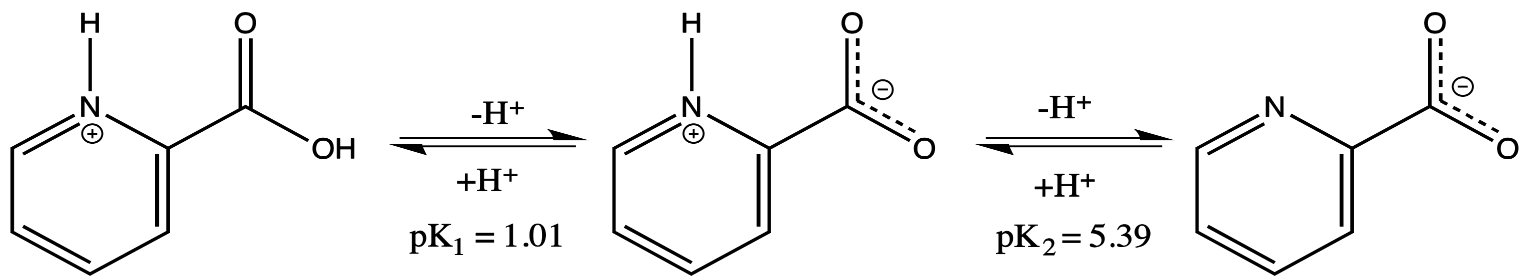
Approach: Attenuated Total Reflectance / Fourier Transform Infrared Spectrometry (ATR/FTIR)



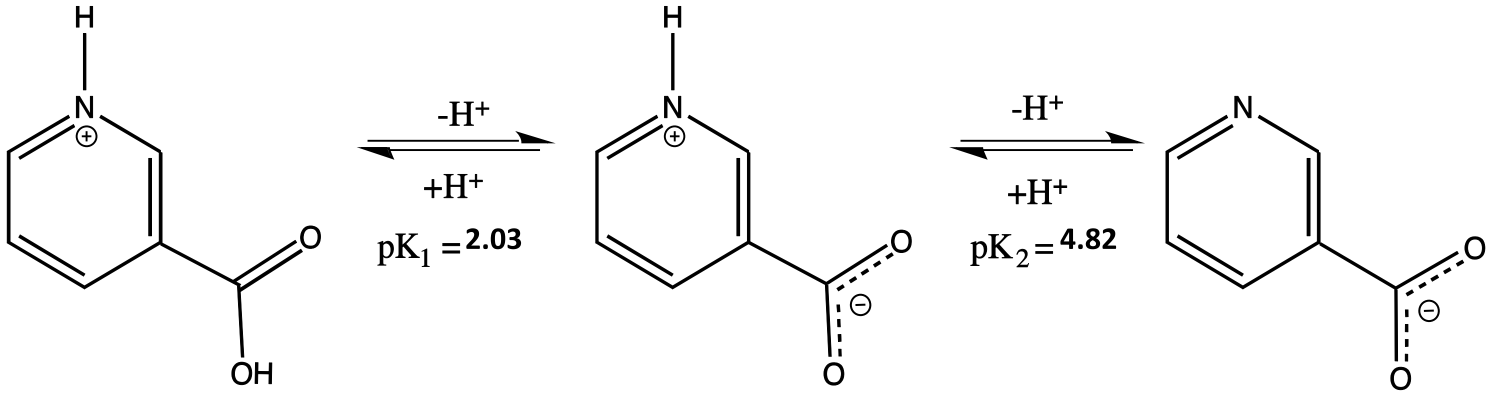


Dissociation Equilibria of Pyridine Carboxylic Acids

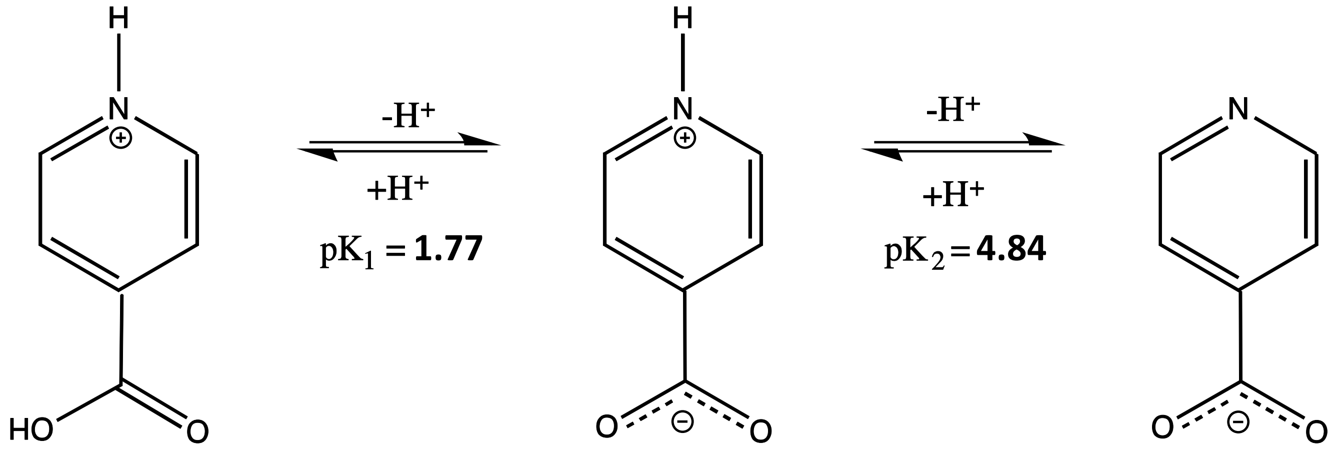
pyridine-2-carboxylic acid (picolinic acid)



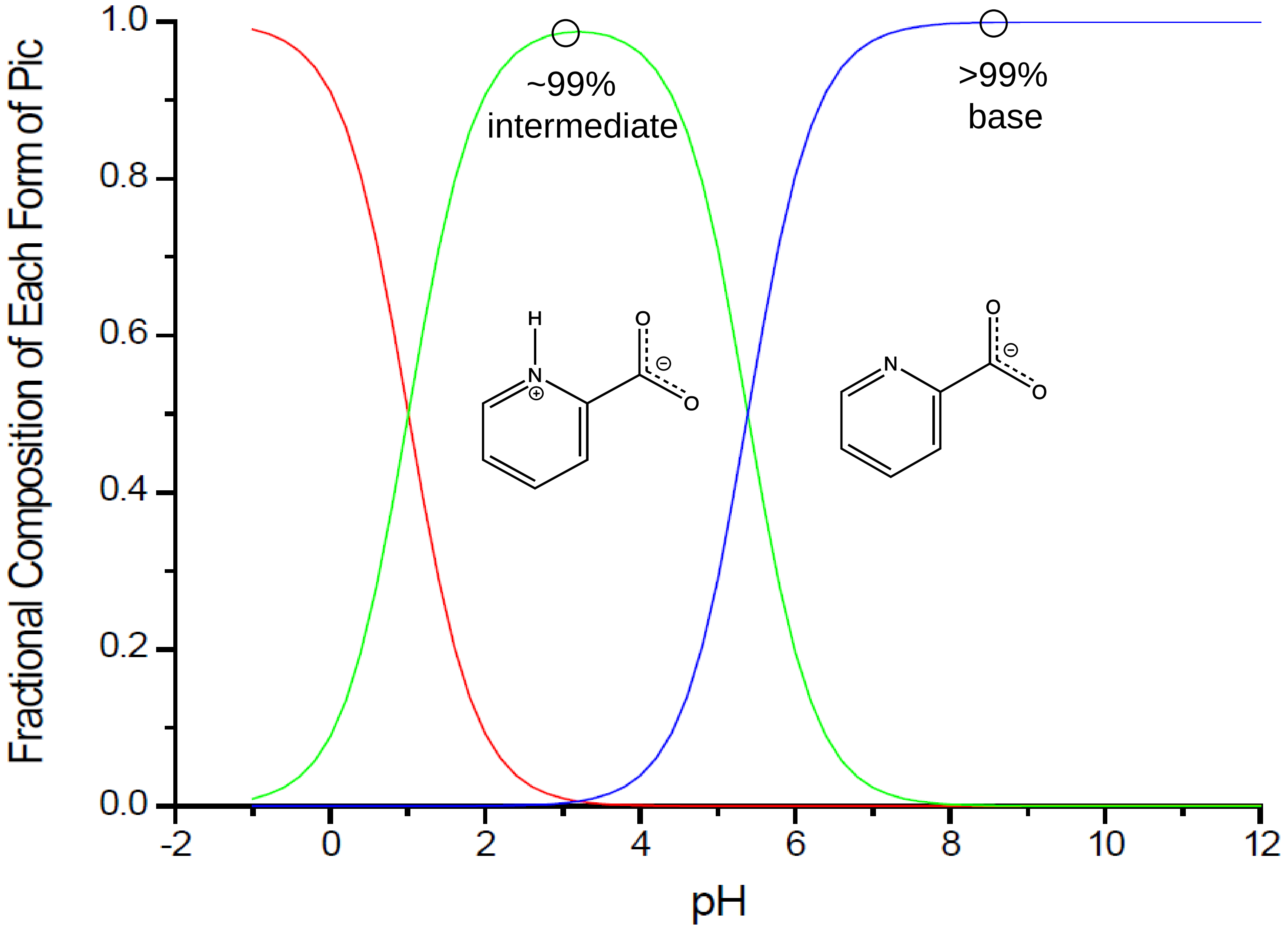
pyridine-3-carboxylic acid (nicotinic acid)



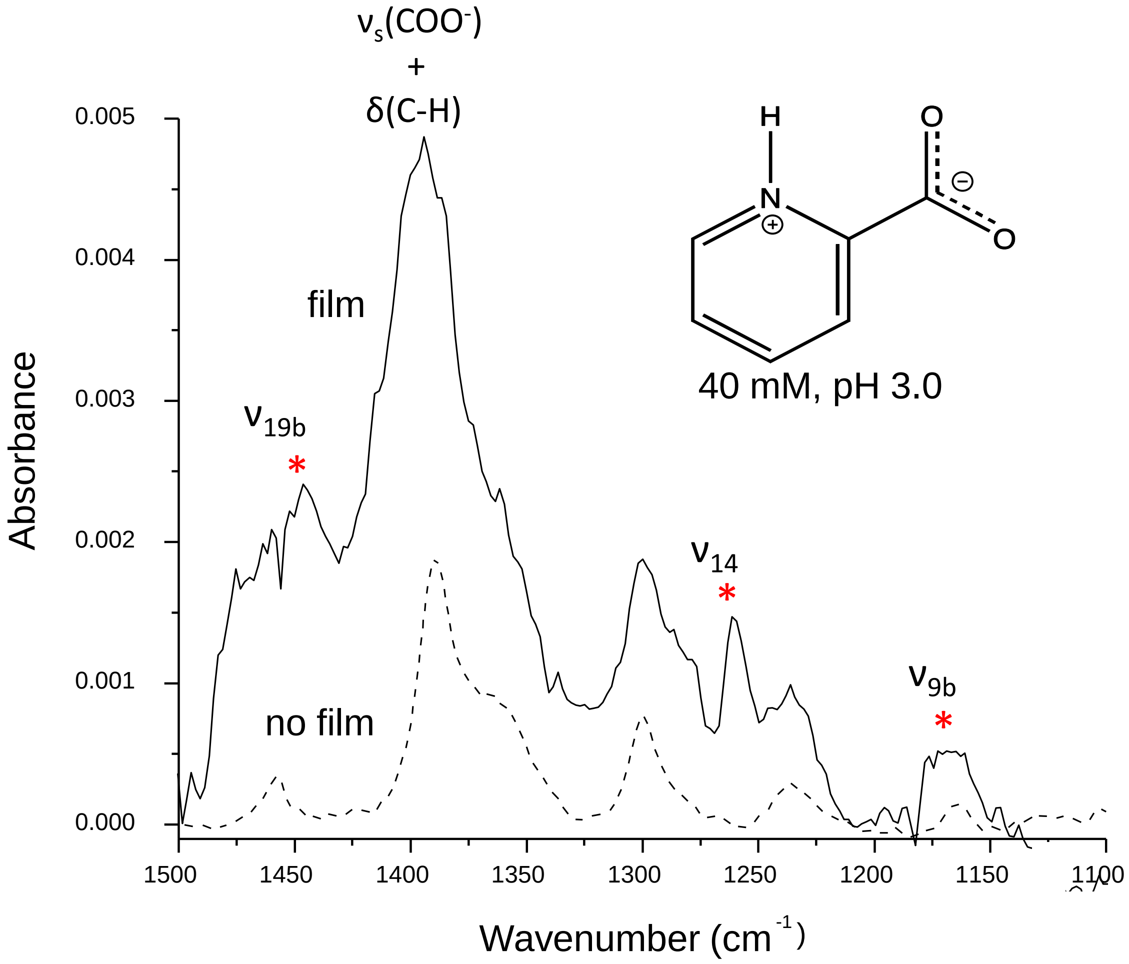
pyridine-4-carboxylic acid (isonicotinic acid)



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



Infrared Spectra Indicate Picolinic Acid Adsorption to Ceria[2]



Assignment of IR spectra:

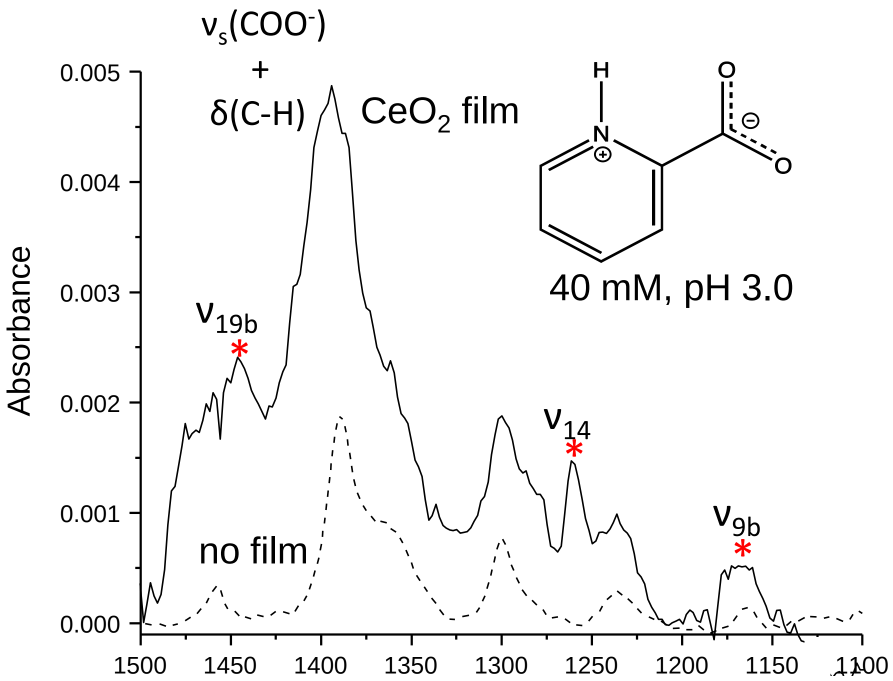
IR spectra were calculated using Density Functional Theory (B3LYP/6-311++G**).

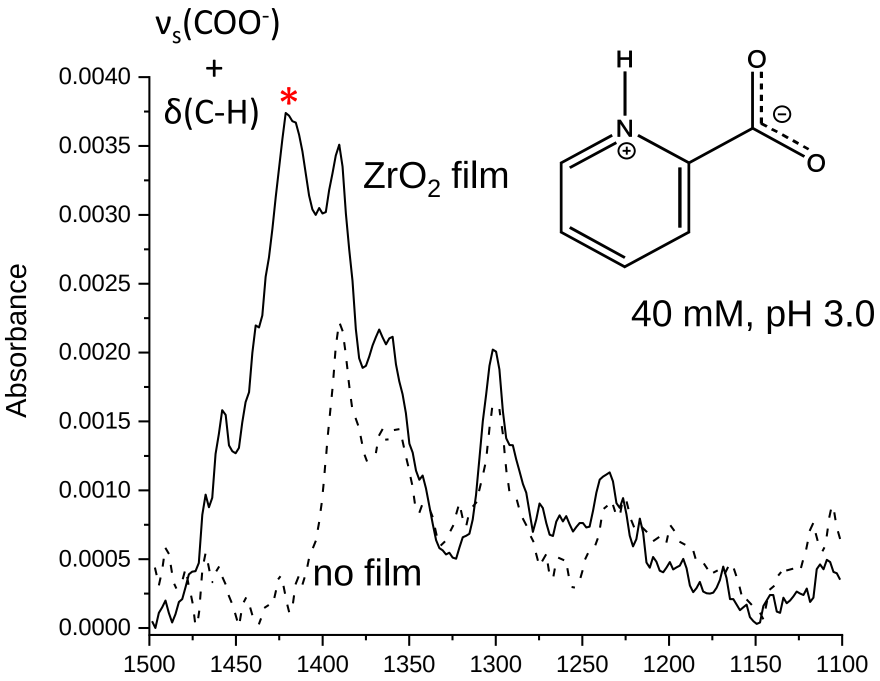
Solvation was incorporated using the COSMO model; four explicit water molecules were also included.

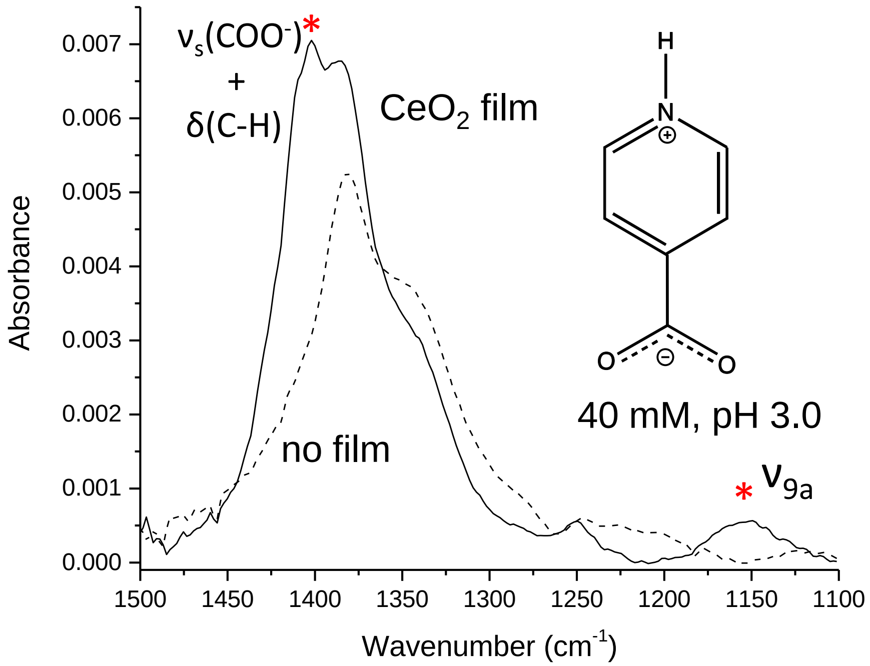
Explicit water molecules bridged molecular hydrogen bonding sites.

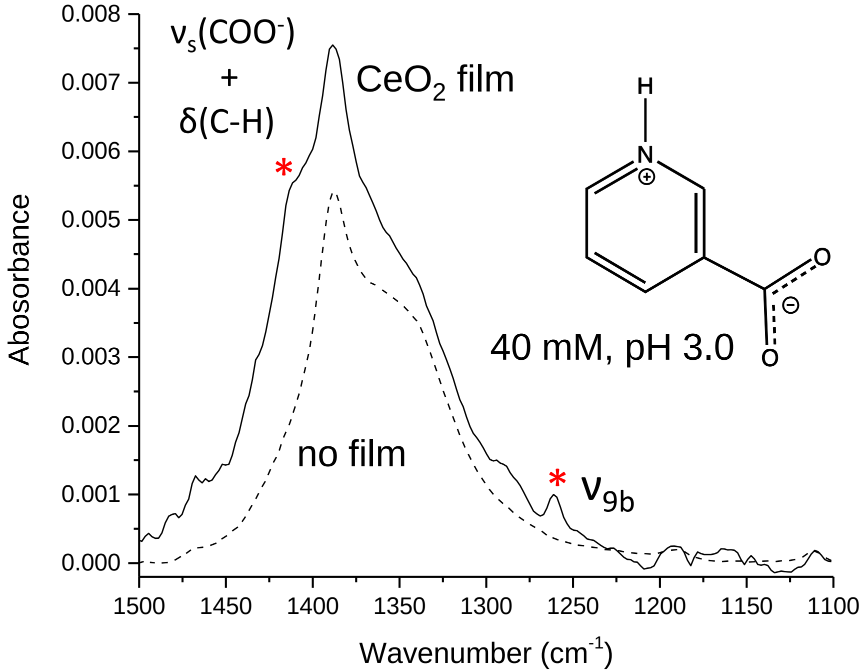
Assignments were made by comparing with benzene, pyridine and pyridinium ion.

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**.**


νs(COO-)
+
δ(C-H)
CeO2 film
40 mM, pH 3.0
ν19b
ν14
ν9b
no film
Absorbance
0.005
0.004
0.003
0.002
0.001
0.000
1500 1450 1400 1350 1300 1250 1200 1150 1100

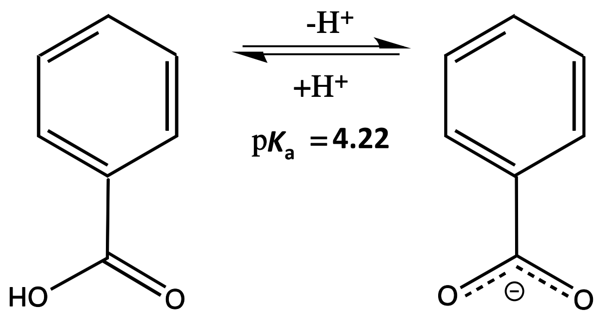

νs(COO-)
+
δ(C-H)
ZrO2 film
40 mM, pH 3.0
no film
Absorbance
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
1500 1450 1400 1350 1300 1250 1200 1150 1100

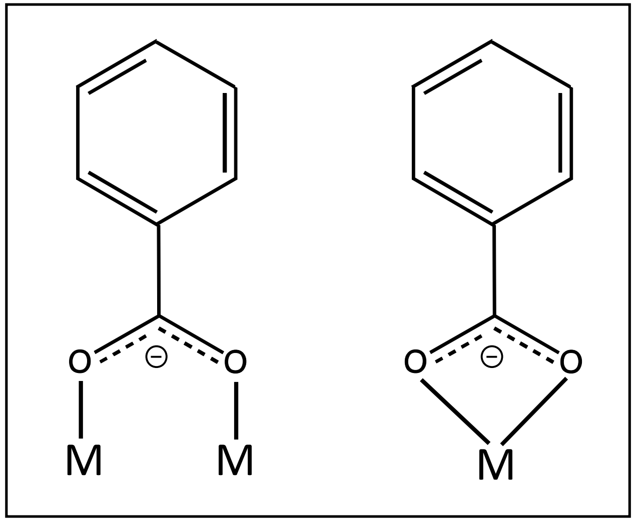

νs(COO-)
+
δ(C-H)
CeO2 film
40 mM, pH 3.0
no film
ν9a
Absorbance
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
1500 1450 1400 1350 1300 1250 1200 1150 1100
Wavenumber (cm-1)

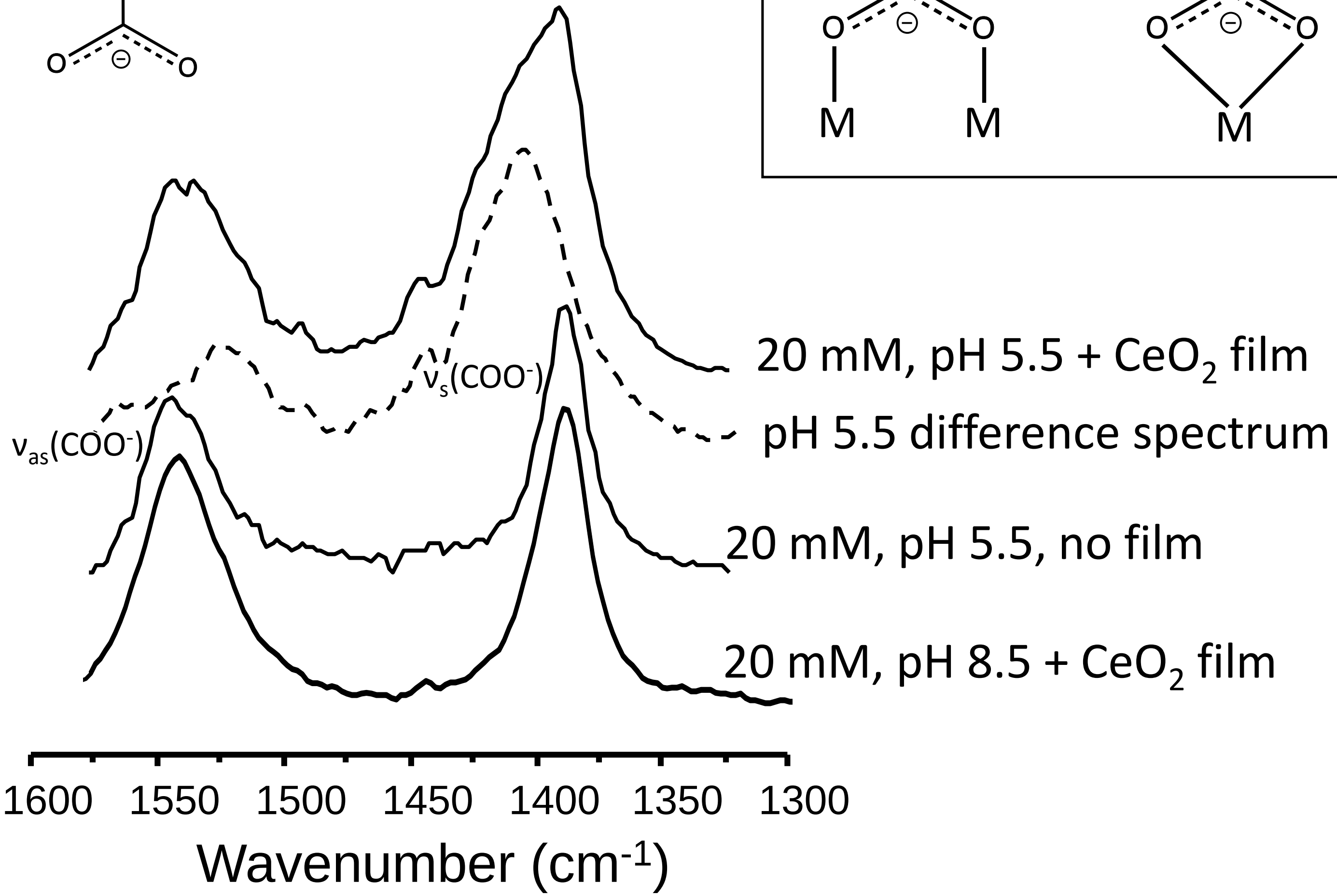

νs(COO-)
+
δ(C-H)
CeO2 film
40 mM, pH 3.0
no film
ν9b
Abosorbance
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
1500 1450 1400 1350 1300 1250 1200 1150 1100
Wavenumber (cm-1)

Carboxylate Binding Interactions with a Metal Oxide Film

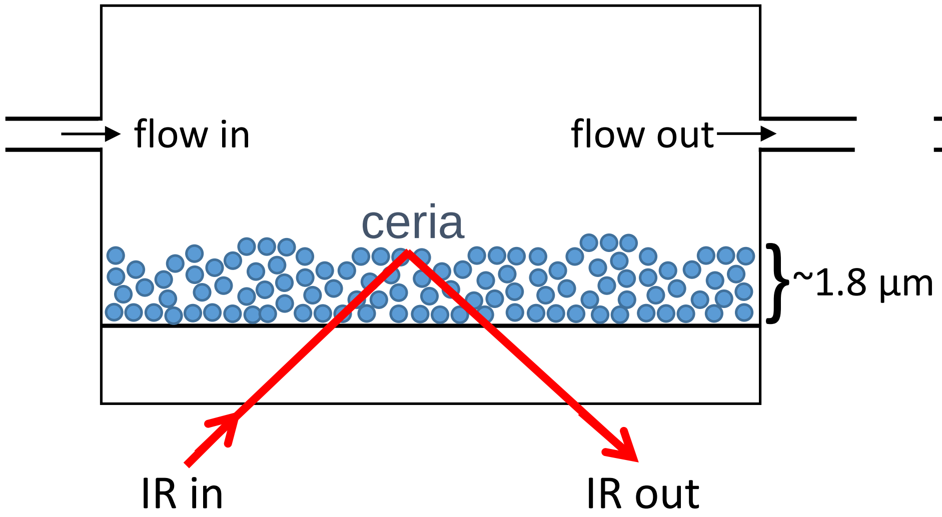
Use benzoic acid as a model compound:

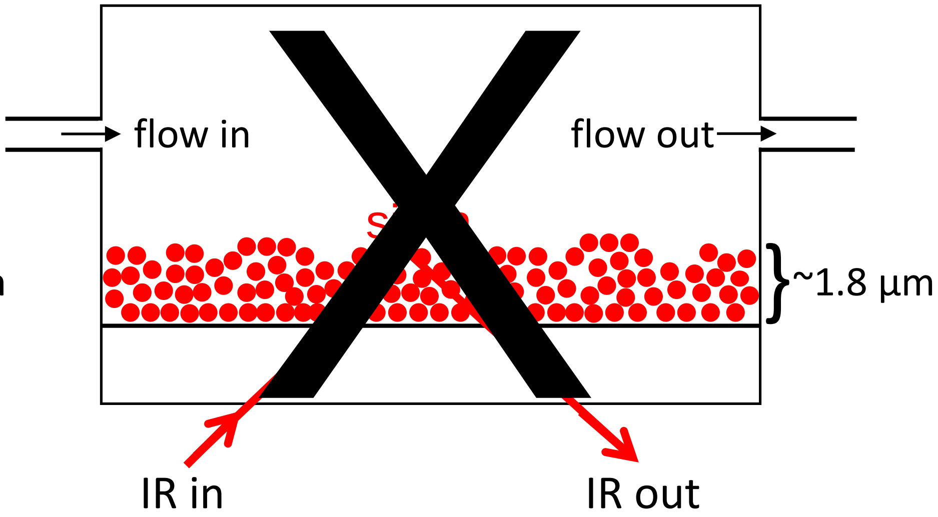






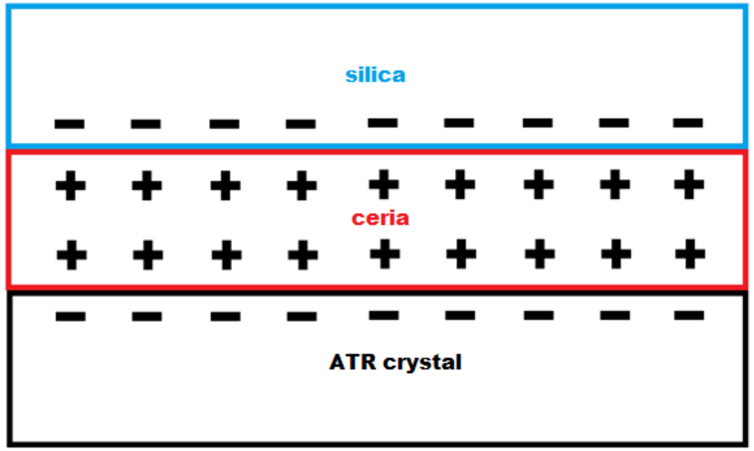
Analysis of Adsorption on Colloidal Silica Abrasive Particles

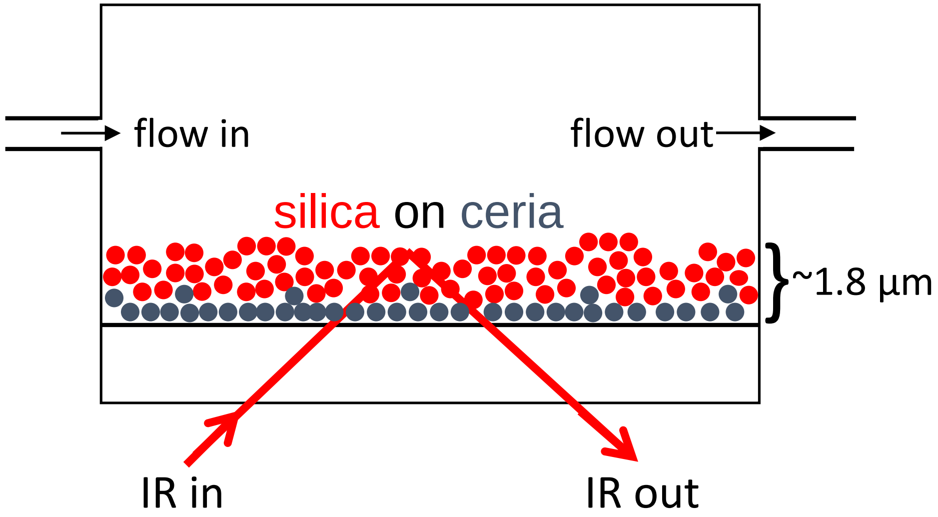




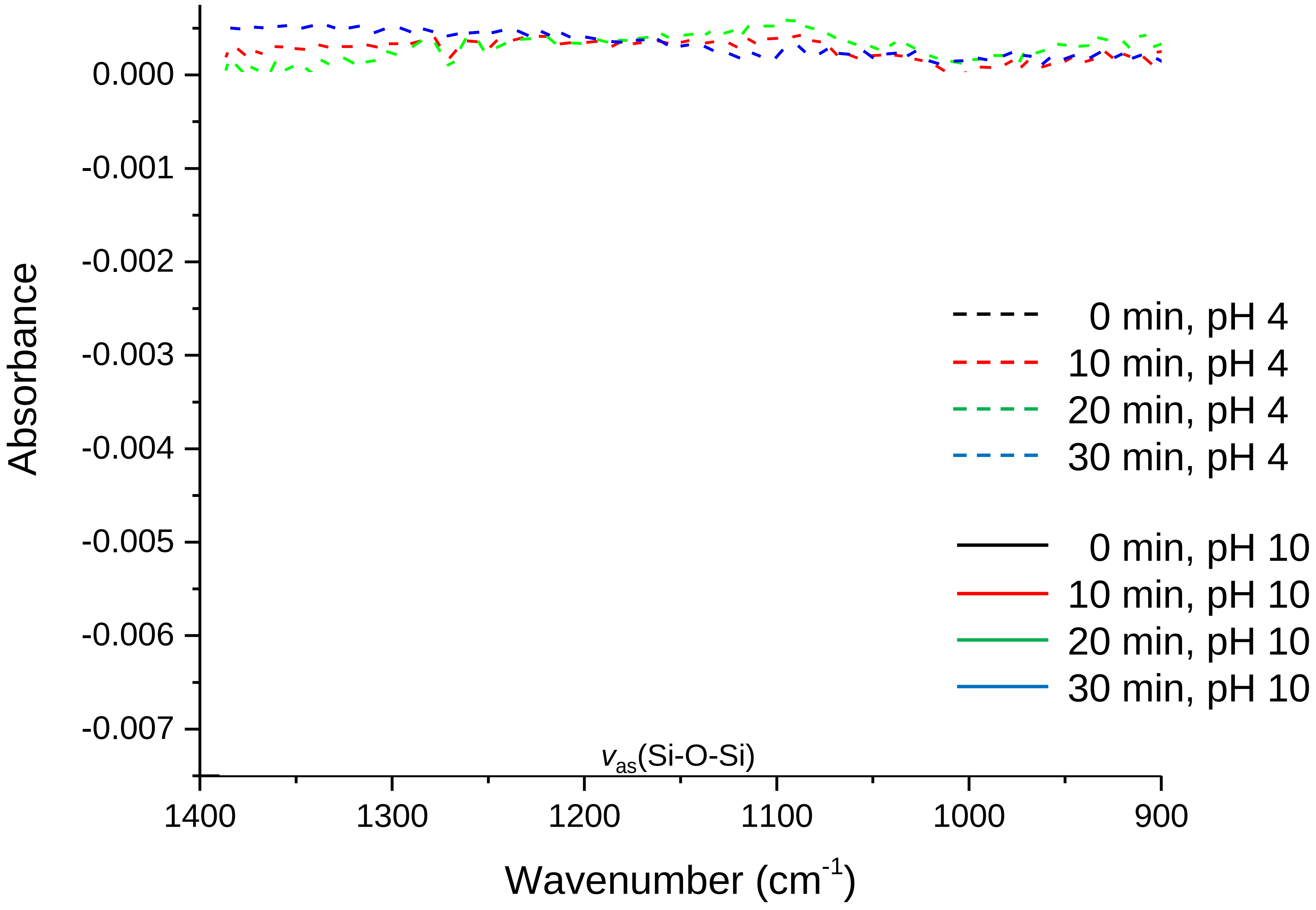
pI (silica): 2 to 3

pI (ceria): 8 to 9; pI (titania): 6 to 7

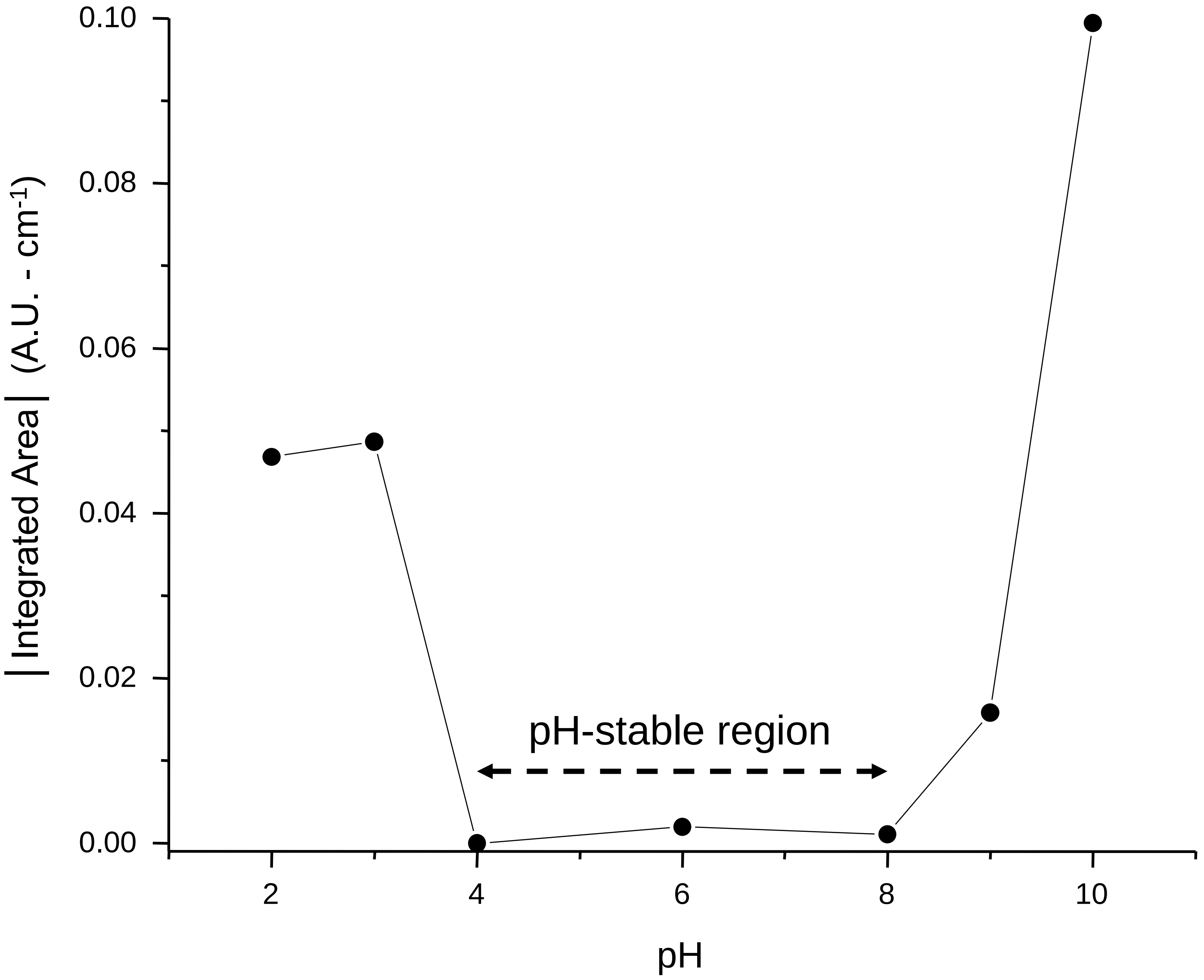




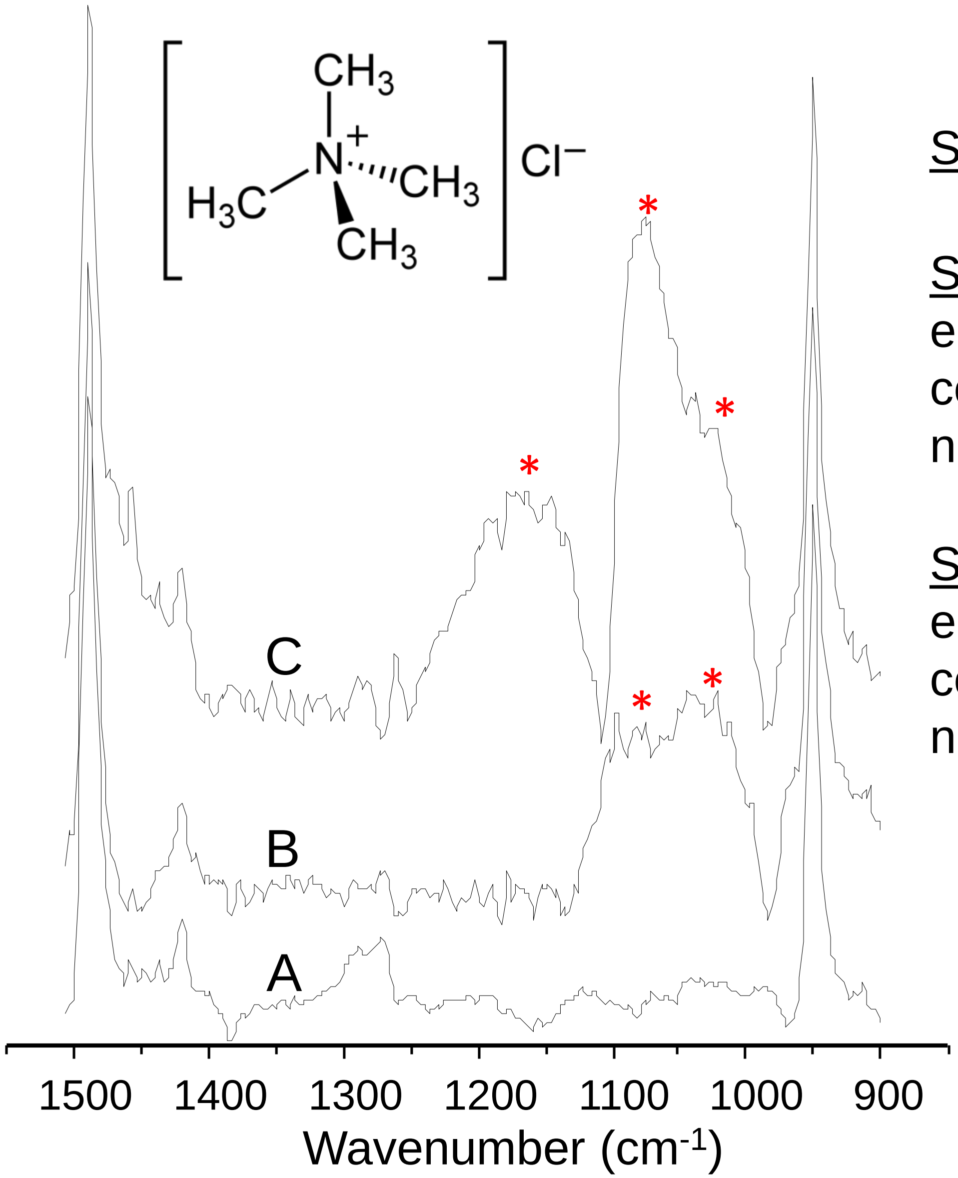
Desorption of SiO_2-CeO_2 Films on ATR Crystal



pH Stability of SiO_2-CeO_2 Films on ATR Diamond Crystal



IR Spectra of Tetramethylammonium (TMA) Ions Adsorbed to the SiO_2 Films on the SiO_2-CeO_2 Bilayer

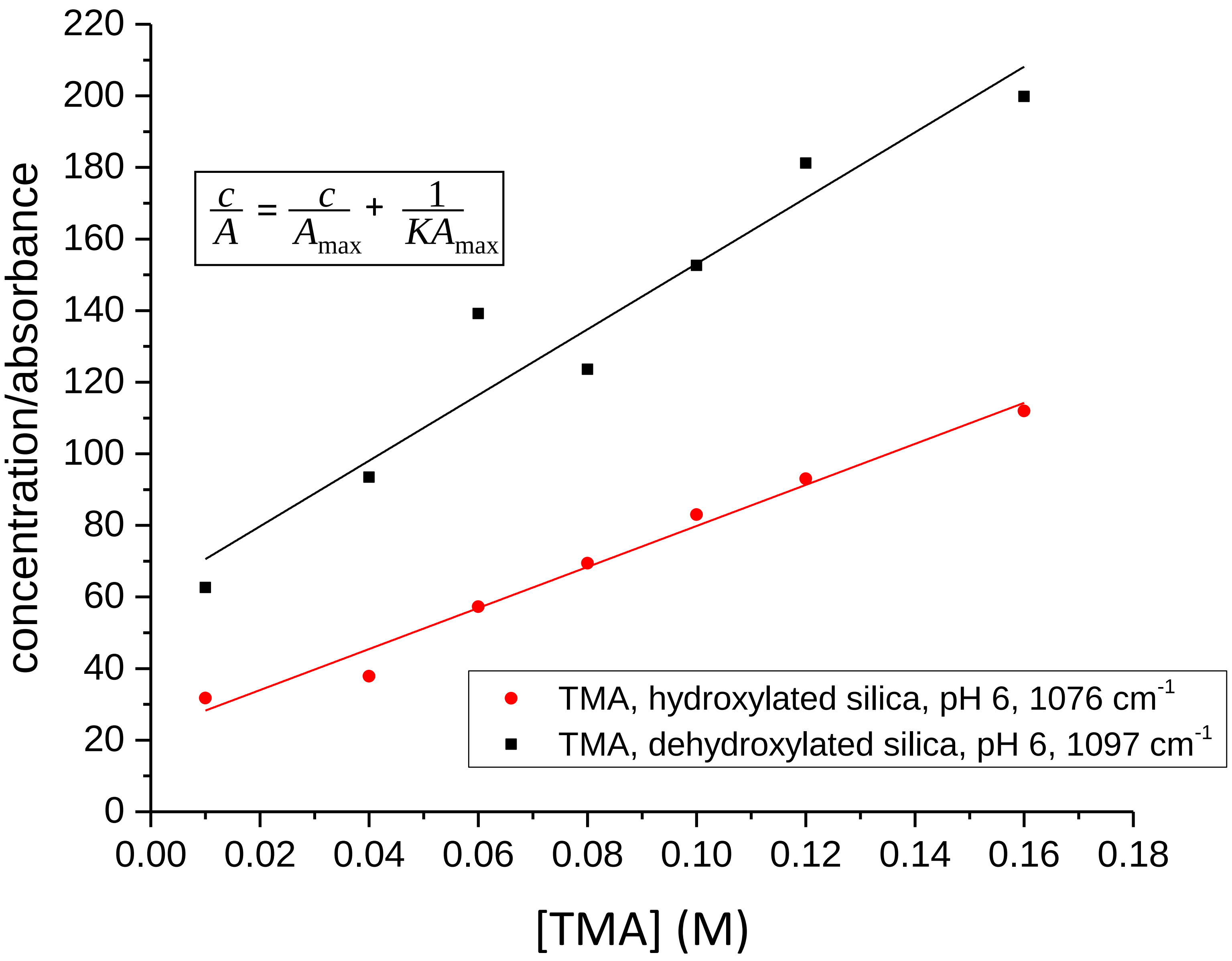


Spectrum A: 40 mM TMA, pH 6

Spectrum B: 40 mM TMA, pH 6, equilibrated with a dehydroxylated colloidal silica particle (D_n = 44 nm) film on the CeO_2 layer.

Spectrum C: 40 mM TMA, pH 6, equilibrated with a hydroxylated colloidal silica particle (D_n = 39 nm) film on the CeO_2 layer.

Langmuir Isotherms for TMA Ion Adsorption on Silica Films



Directions for Future Studies

- Using FCS and ATR/FTIR, quantitatively evaluate adsorption isotherms for CMP additive interactions with alumina (alpha and fumed) and zirconia abrasive particles

- Apply ATR/FTIR method to characterize the mode(s) of interaction of TMA with silica abrasive particles prepared by different synthetic methods to assess surface chemistry differences among different silica abrasives

- Extend ATR/FTIR method to characterize the mode(s) of interaction of CMP abrasives with alumina abrasive particles of different types (alpha, fumed, etc.) to assess surface chemistry differences among different alumina abrasives

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Cabot Microelectronics Corporation

Intel Corporation