# Interacciones en la interfaz dermatan sulfato - calcita

Rodrigo González
Doctorado en Ciencias de la Ingeniería
mención Ciencia de los Materiales,
Universidad de Chile.

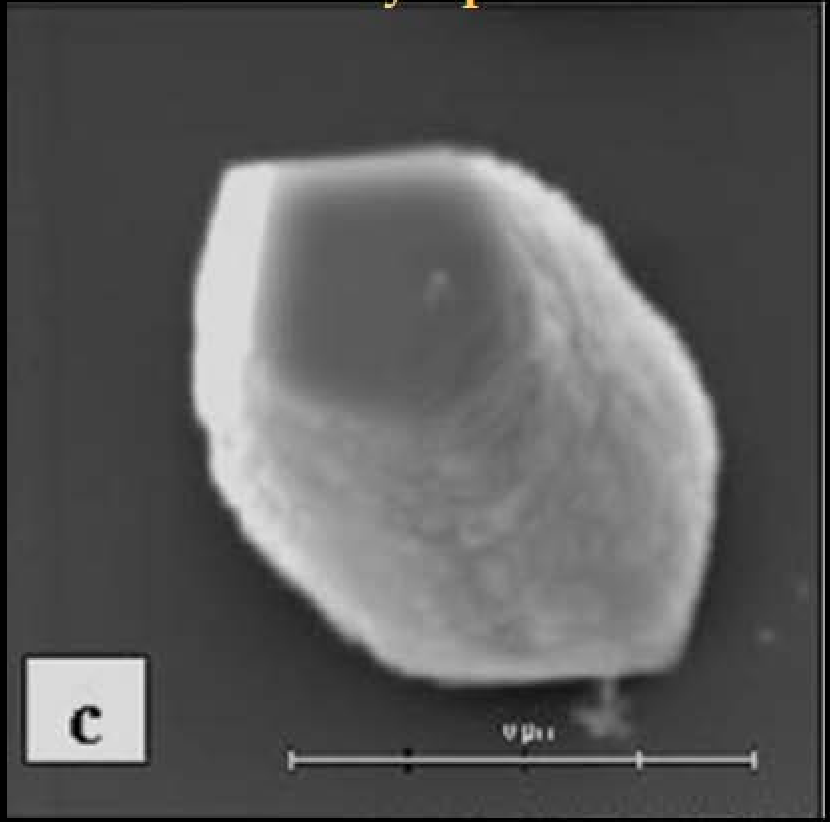
Leonardo Caballero & Francisco Melo.
Laboratorio de Física no Lineal,
Universidad de Santiago de Chile.

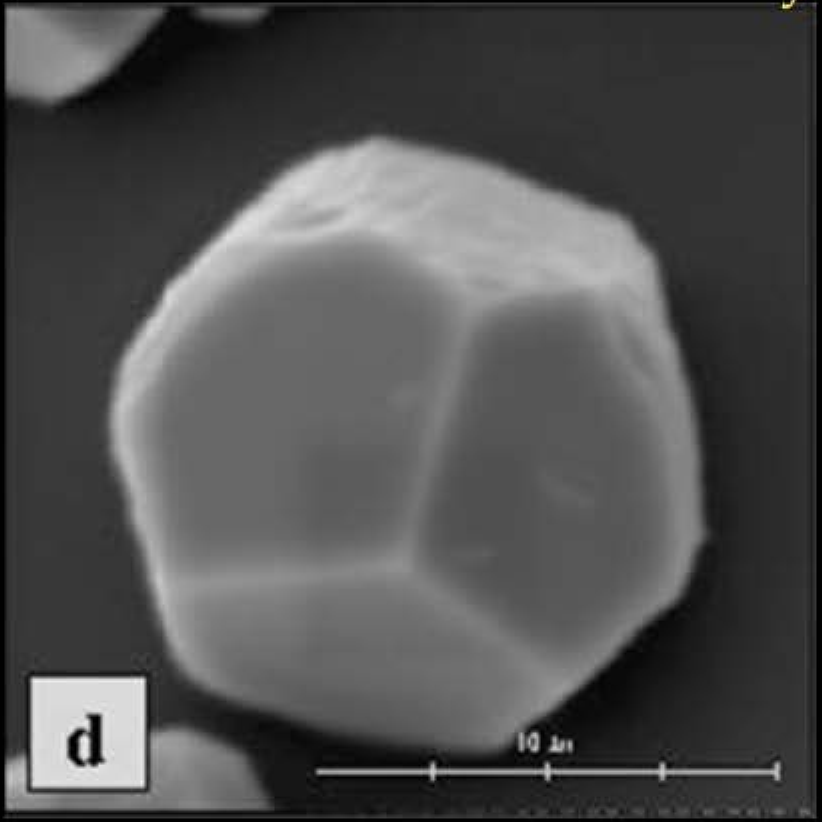
# Motivación

**Effect of Sulfate Content of Biomacromolecules on the Crystallization of Calcium Carbonate**

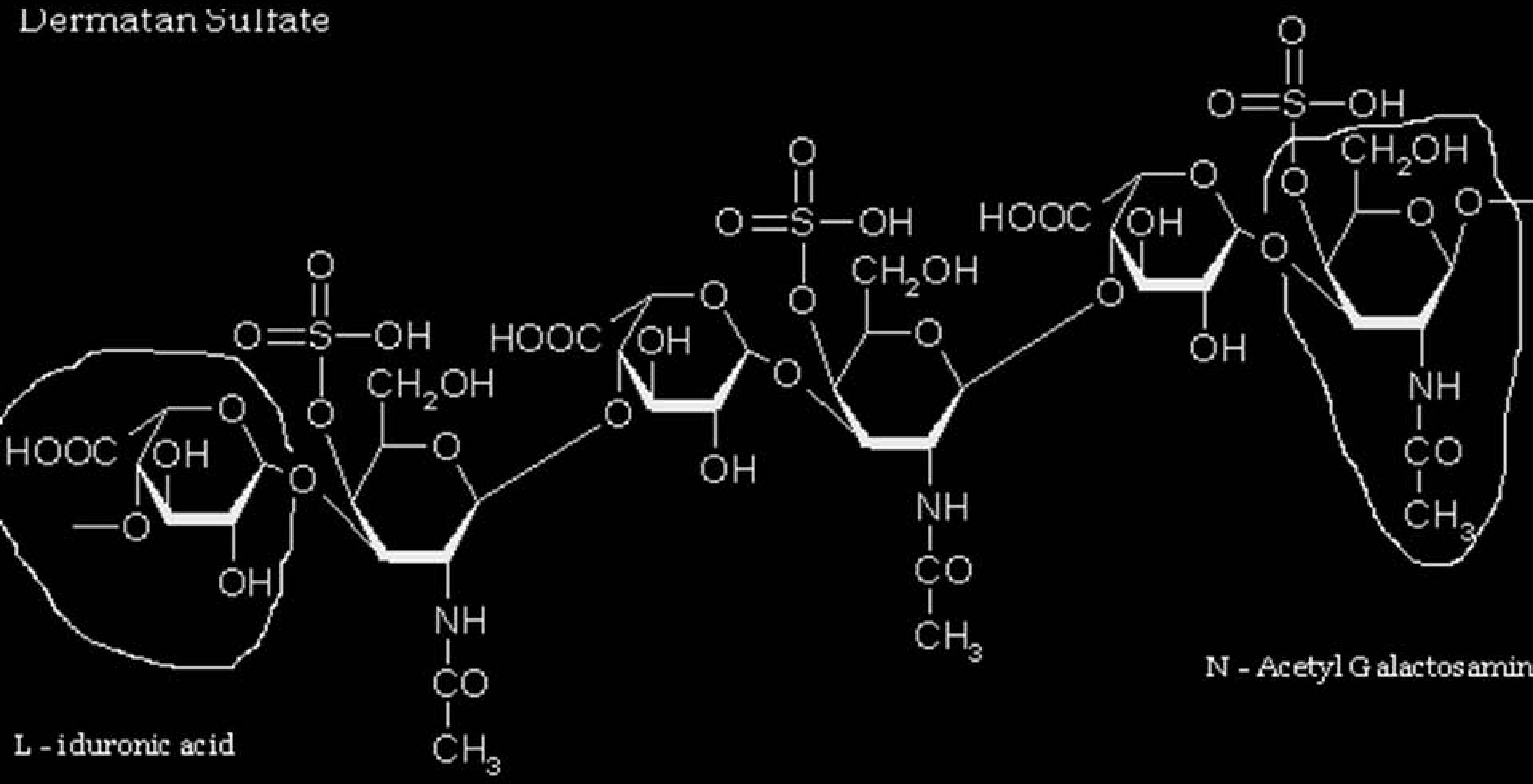
José I. Arias, Carolina Jure, Juan P. Wiff, María S. Fernández, Víctor Fuenzalida and José L. Arias

**Mat. Res. Soc. Symp. Proc. Vol. 711 © 2002 Materials Research Society**

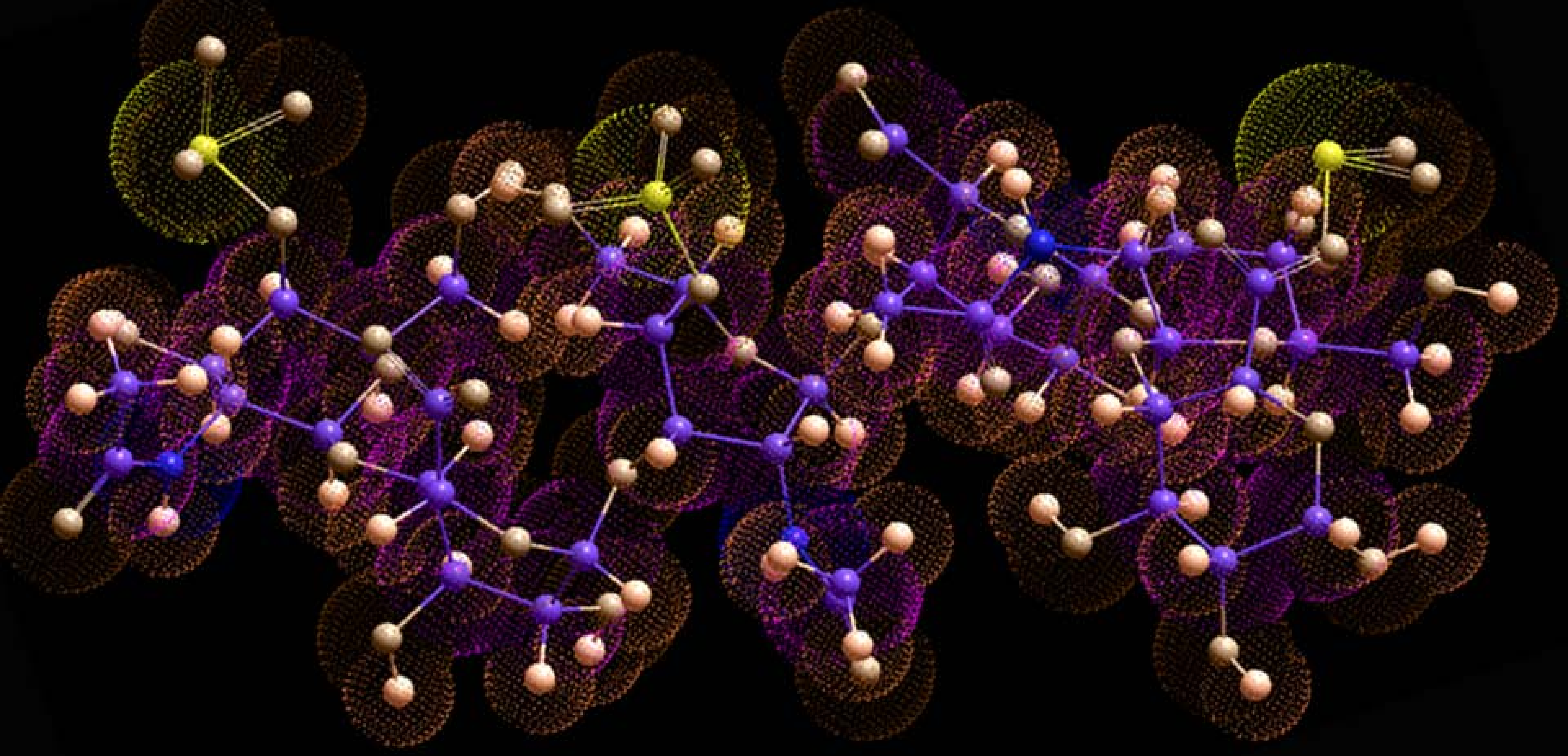




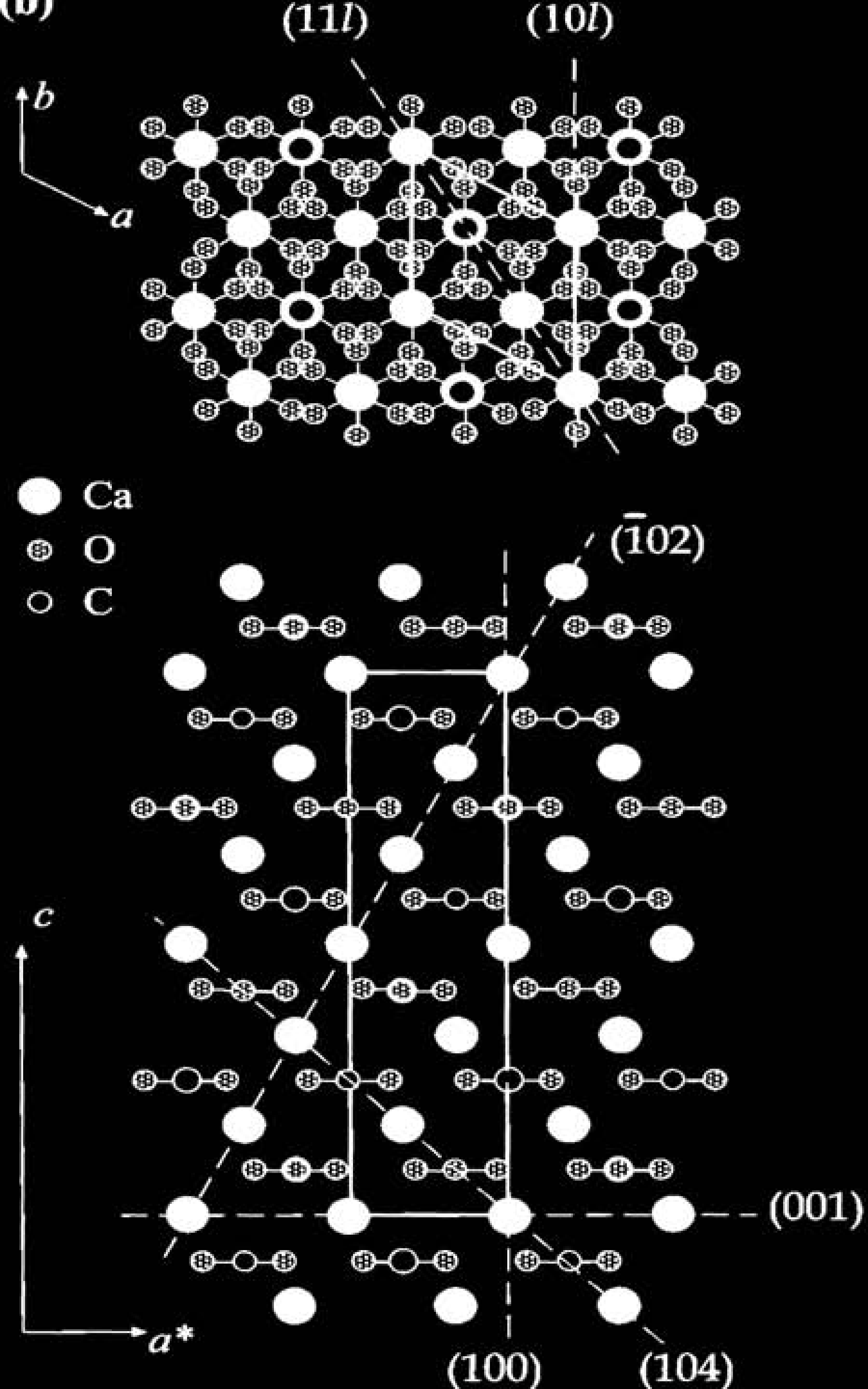
# dermatan sulfato



# dermatan sulfato



# Calcita



*J. Am. Chem. Soc.* **1999, 121, 4500-4509**

# Estrategia experimental

Se investiga la relación entre el cristal iónico calcita romboédrica y el oligosacárido polianiónico dermatan sulfato, ambos presentes en la cáscara de huevo de las aves.

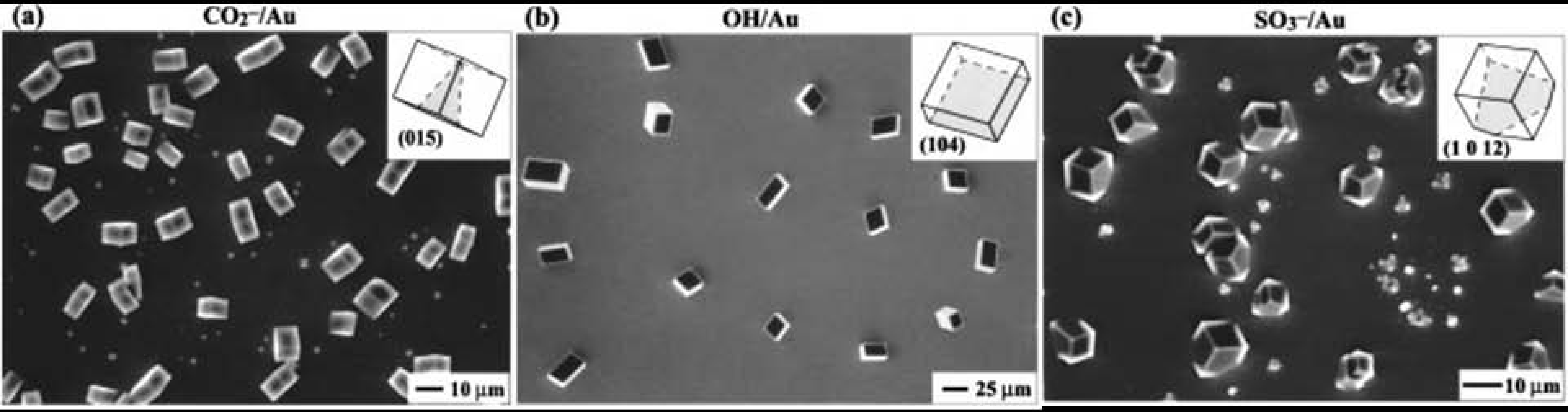
Exp.1: Para saber como DS se coordina sobre la superficie de los cristales de calcita, se hizo y caracterizó sustrato de DS, para sobre este realizar un proceso de nucleación de cristales de carbonato de calcio.

Exp.2: Estudio *in-situ* de la adición de DS al crecimiento cristalino de una dislocación helicoidal observada en el plano <104> de la calcita romboédrica mediante AFM en modo contacto para medio líquido....

# Motivación Exp1:

# Oriented Growth of Calcite Controlled by Self-Assembled Monolayers of Functionalized Alkanethiols Supported on Gold and Silver

**Joanna Aizenberg,*,† Andrew J. Black,‡ and George M. Whitesides*,‡**

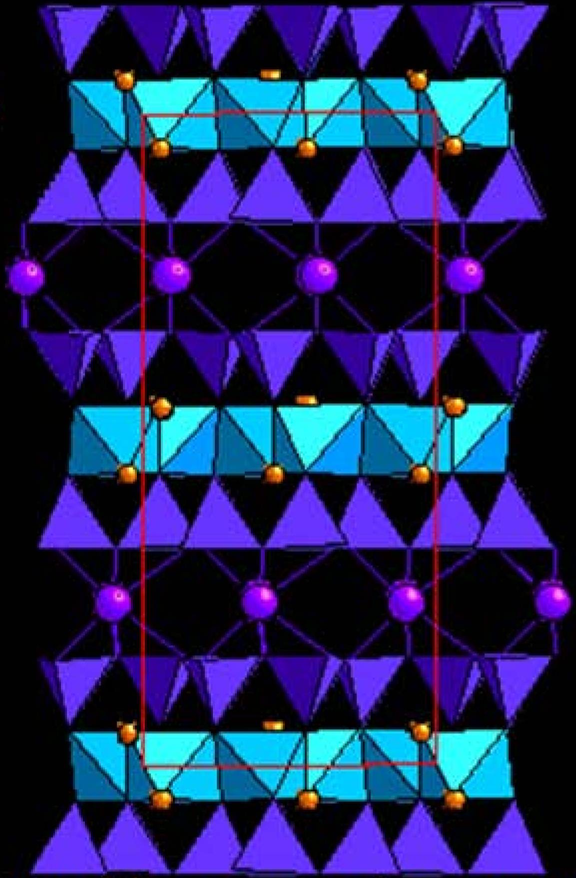


*J. Am. Chem. Soc.* 1999, 121, 4500-4509

# Sustrato

- Mica + 3 AminoPropilTriMetoxiSilano + Dermatan Sulfato

100



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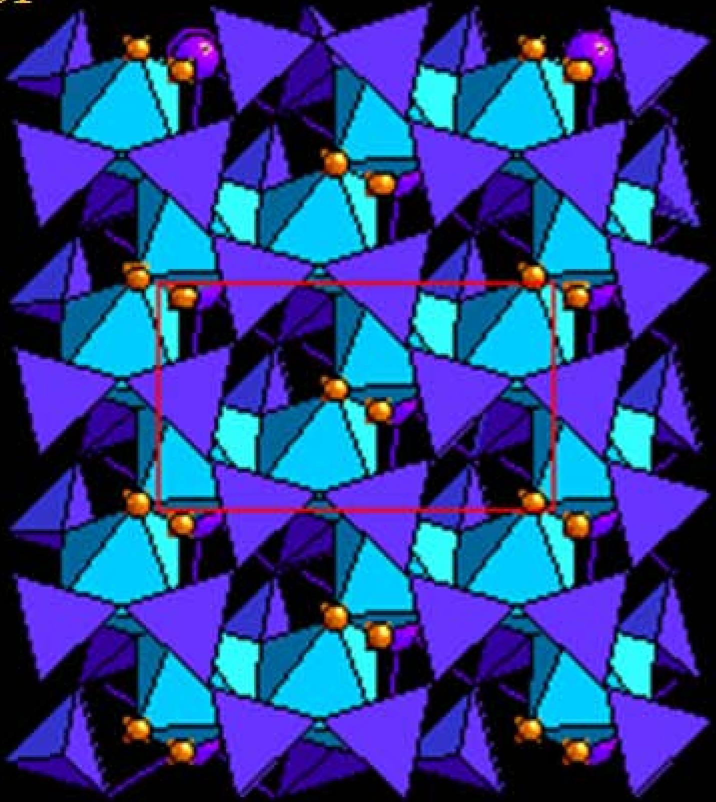
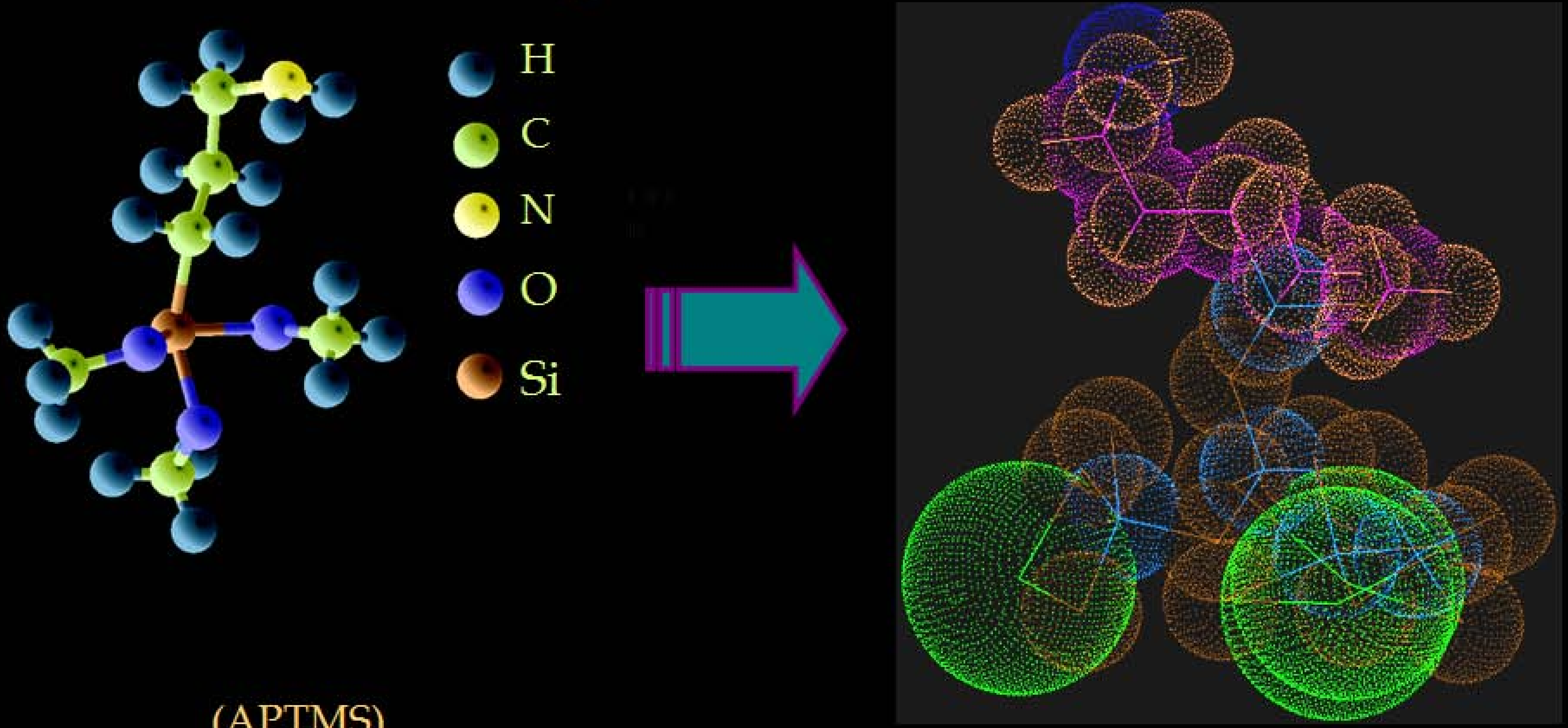


http://www.geoclassroom.com/mineralogy/phyllosilicates.html

# Sustrato

- Mica + 3 AminoPropilTriMetoxiSilano + Dermatan Sulfato

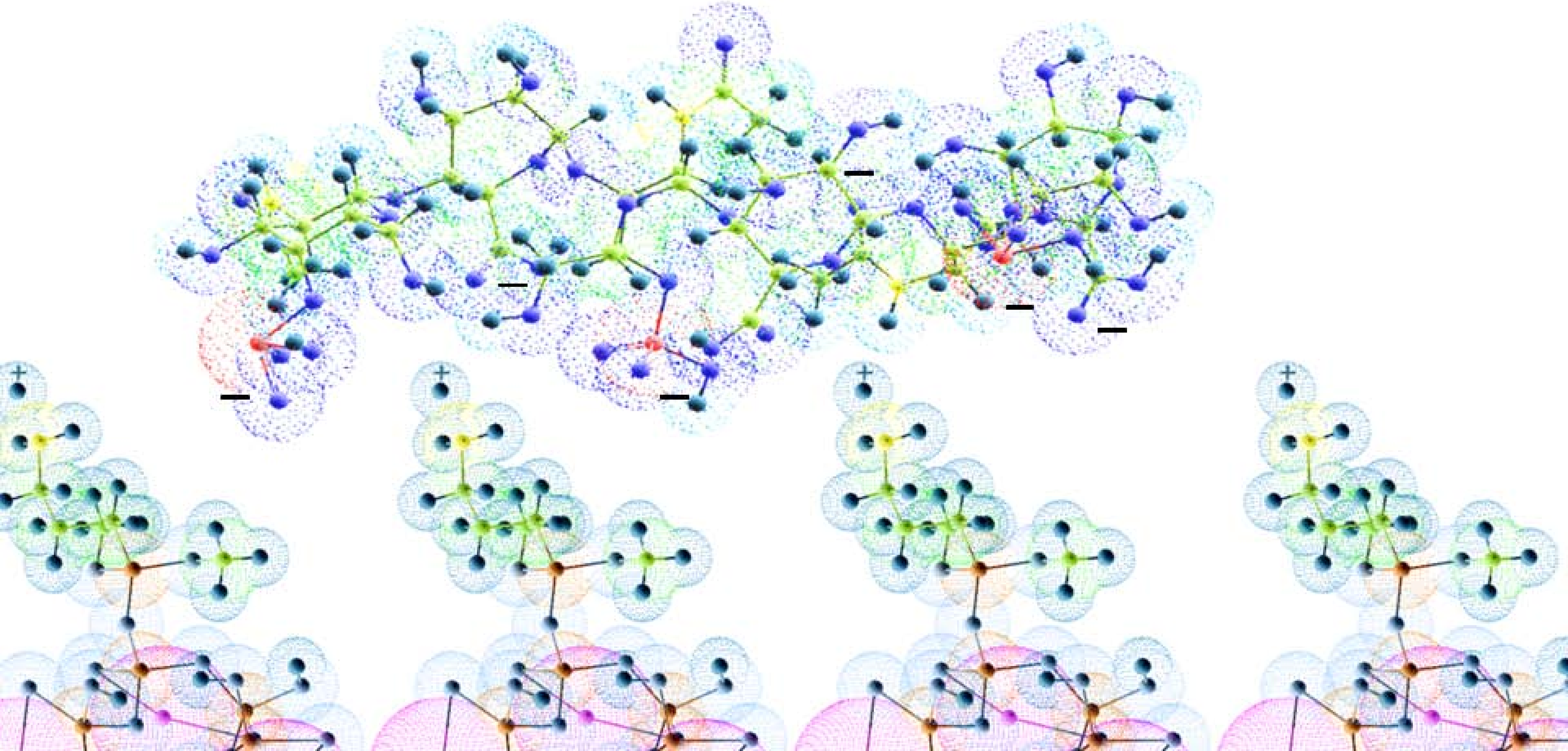


(APTMS)

Silanización: $\mathrm{R\text{-}CH_3} + \textit{mica}\text{-}\mathrm{Si(OH)_2} + \mathrm{H_2O} \longrightarrow \textit{mica}\text{-}\mathrm{Si}{<}^{\mathrm{OH}}_{\mathrm{R}} + \mathrm{CH_2OH} + \mathrm{H_3O^+}$

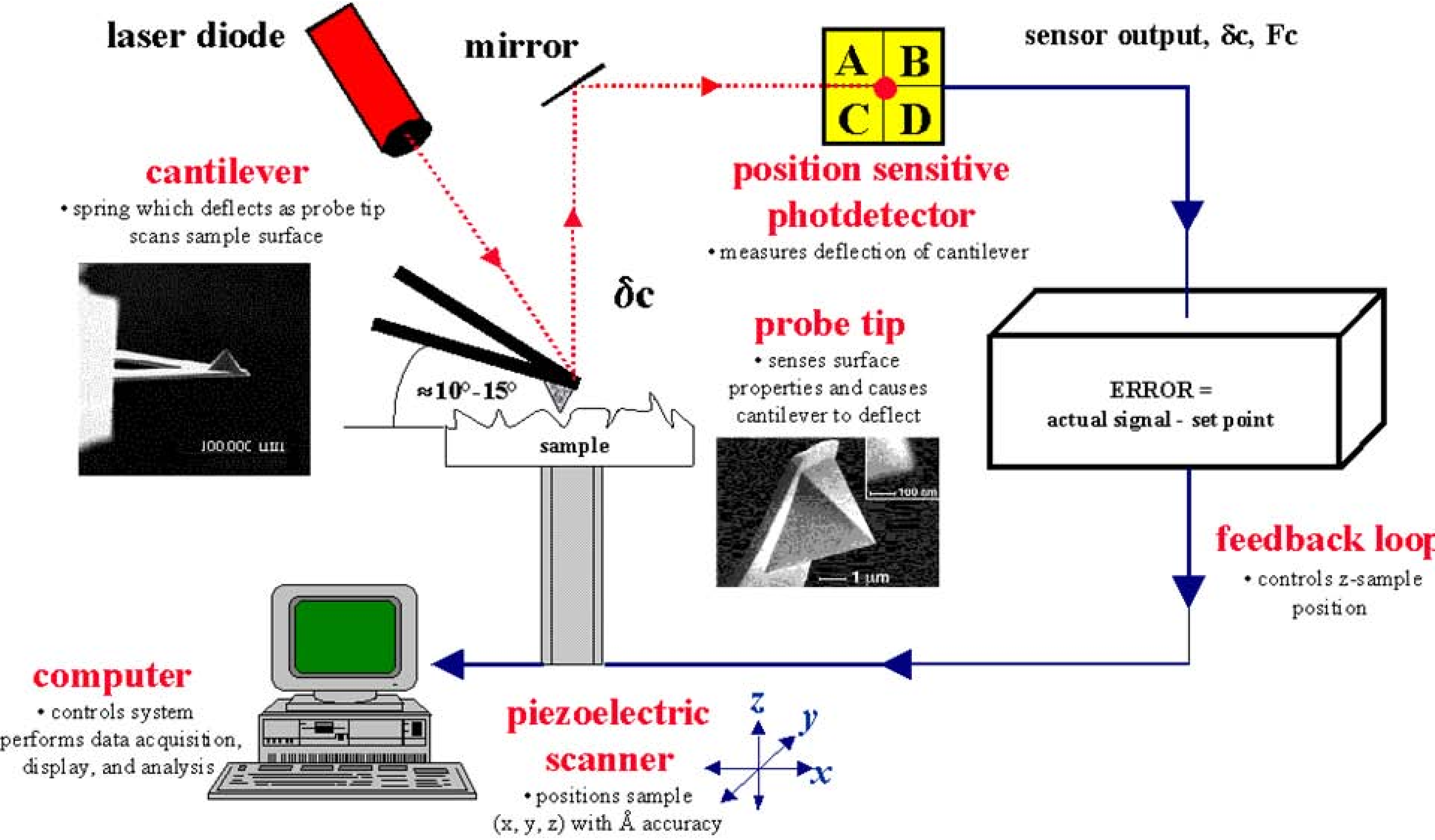
# Sustrato

- Mica + 3 AminoPropilTriMetoxiSilano + Dermatan Sulfato



# *Atomic Force Microscopy (AFM)* :

## General Components and Their Functions



**laser diode**

**mirror**

**cantilever**

- spring which deflects as probe tip scans sample surface

**position sensitive photdetector**

- measures deflection of cantilever

**sensor output, δc, Fc**

**probe tip**

- senses surface properties and causes cantilever to deflect

ERROR =
**actual signal - set point**

**feedback loop**

- controls z-sample position

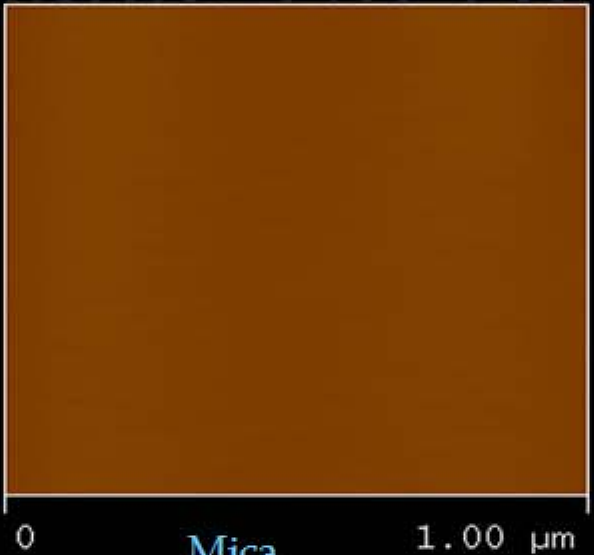
**computer**

- controls system performs data acquisition, display, and analysis

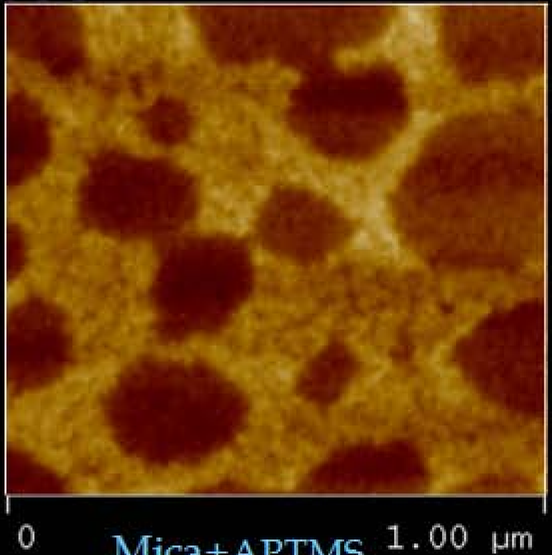
**piezoelectric scanner**

- positions sample (x, y, z) with Å accuracy

# Caracterización del sustrato mediante TM-AFM

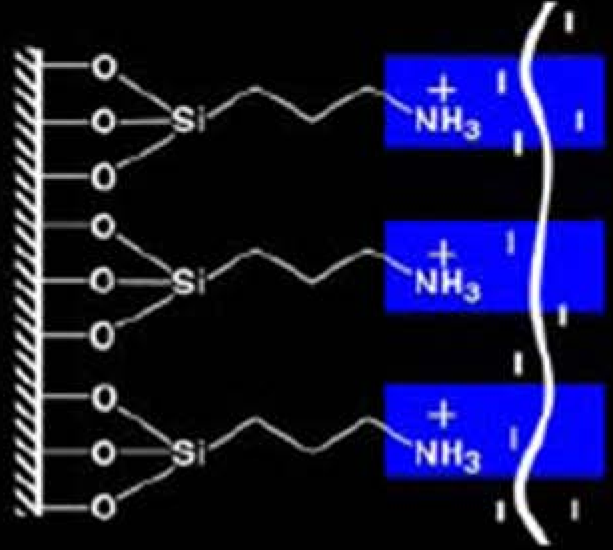


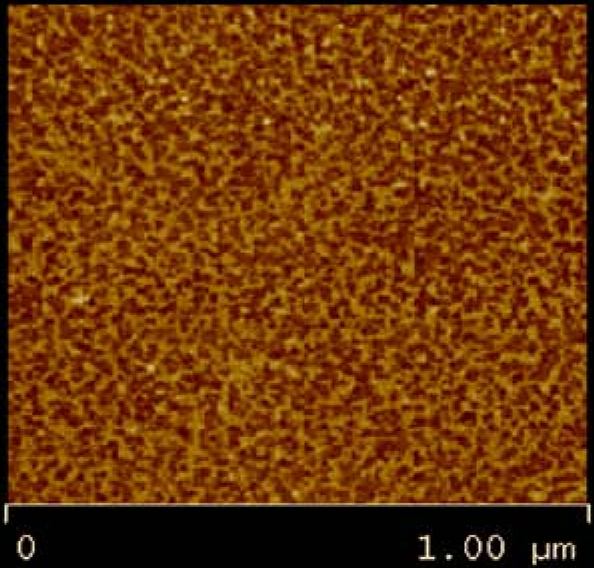
Mica



Mica+APTMS

mica-aptms-ds



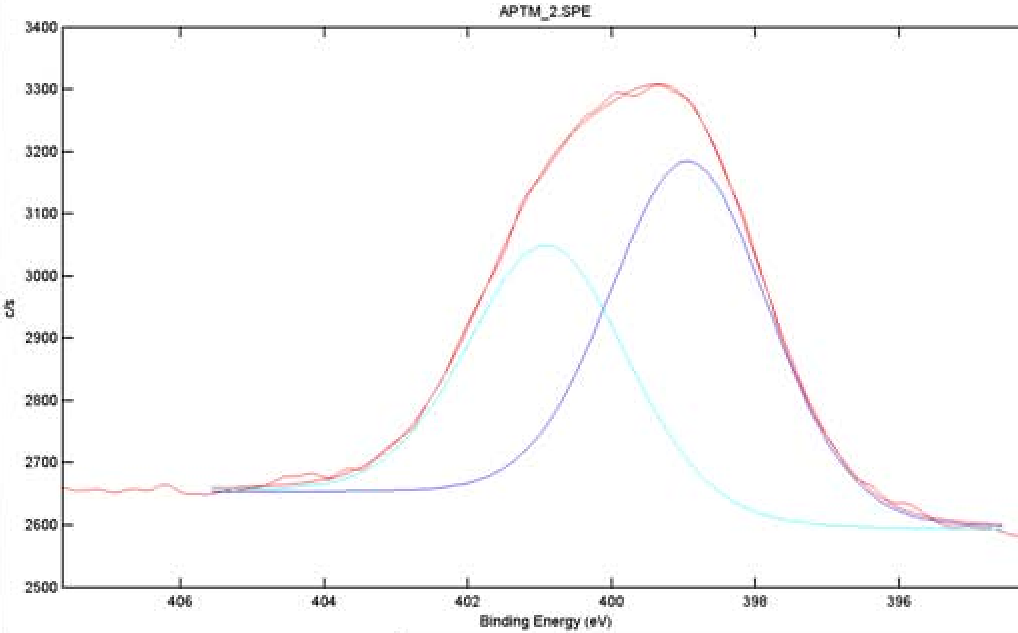


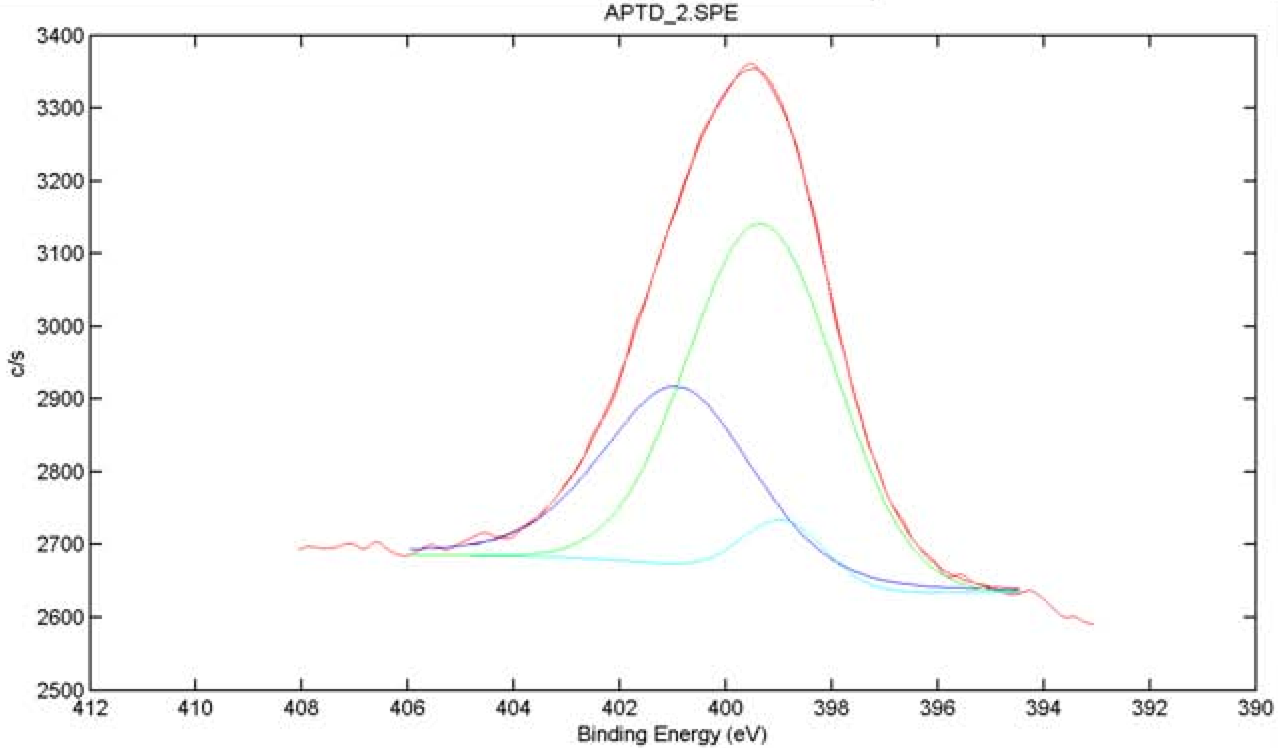
Mica+APTMS+DS

# XPS

Boris Chornik

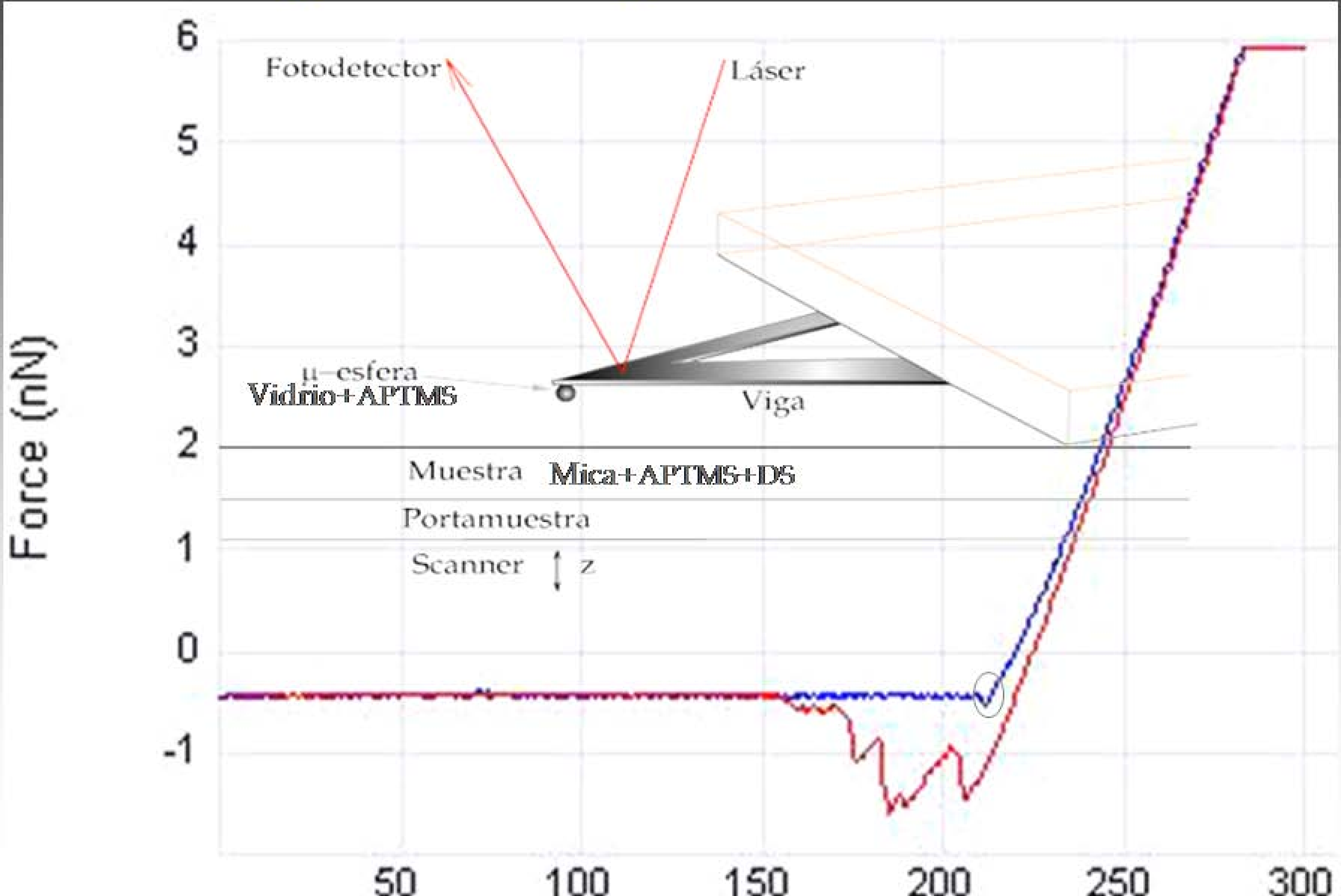
Ajuste del peak del nitrógeno 1s, en sustrato mica+APTMS





Ajuste del peak del nitrógeno 1s, en sustrato mica+APTMS+DS

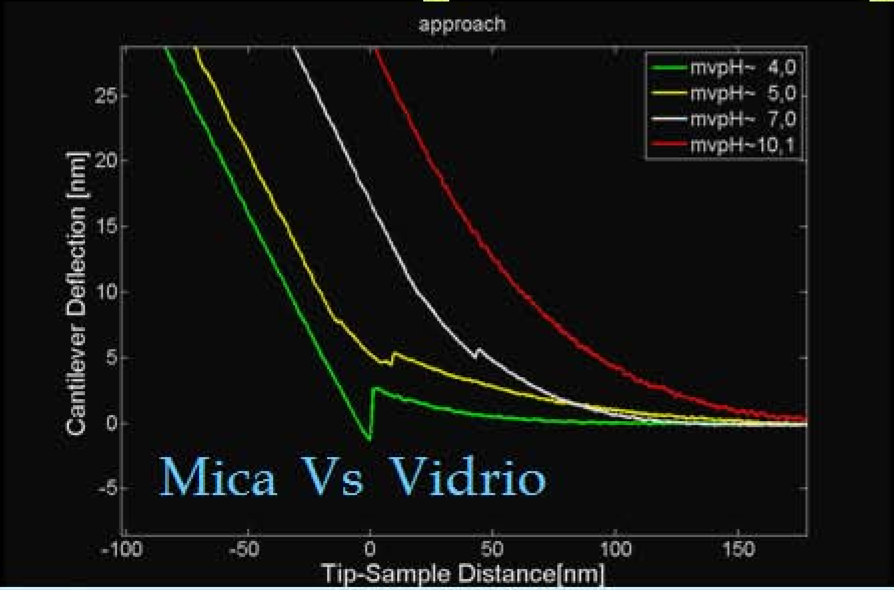
# Espectroscopia de fuerzas

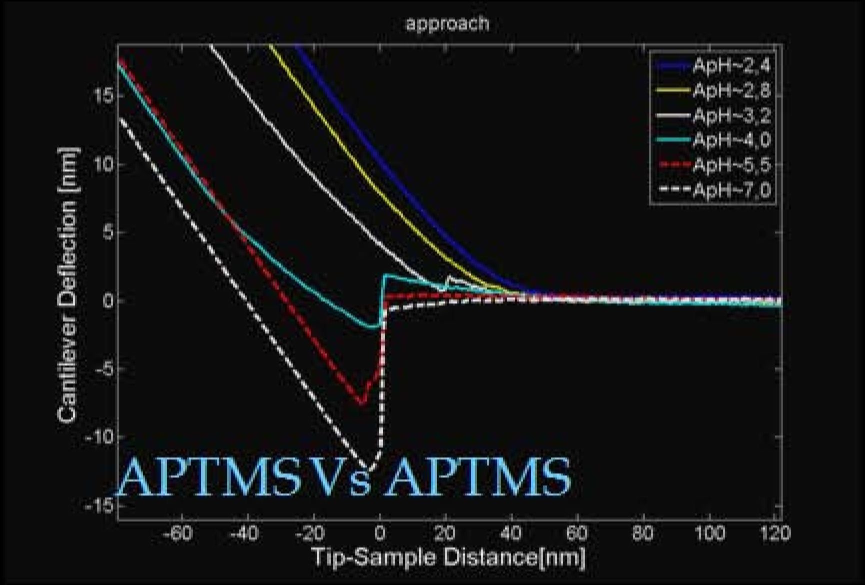


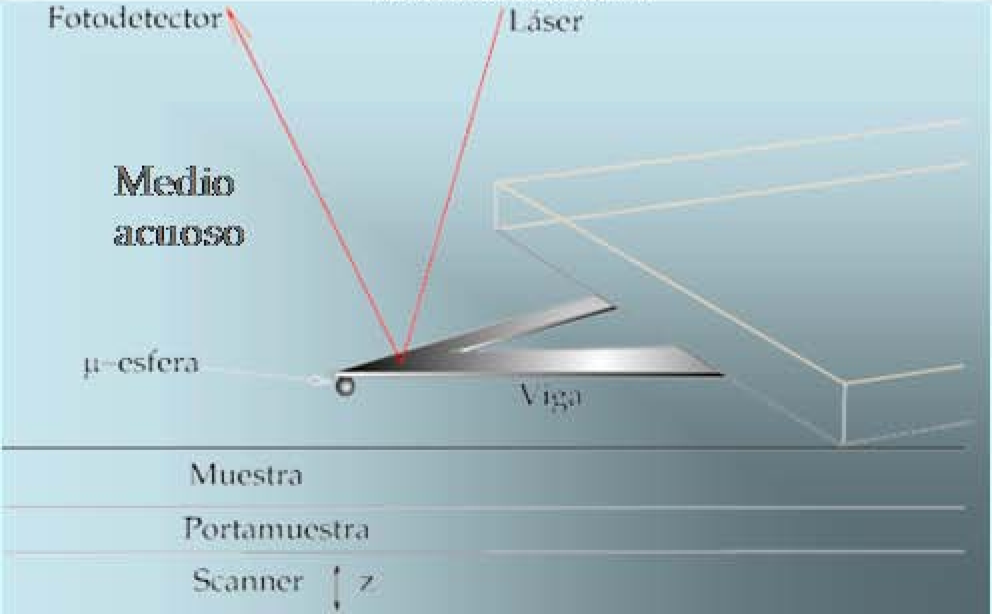
# Reacciones

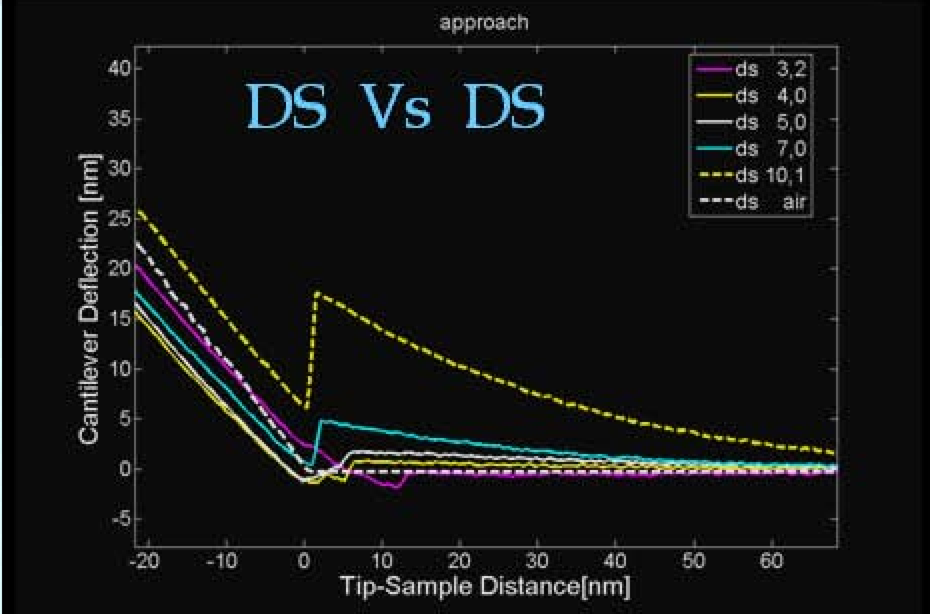
- $2H_2O + X\text{-}Si(OH)_2 \leftrightarrow H_2O + H_3O^+ + X\text{-}Si<^{OH}_{O^-} \leftrightarrow$ $2H_3O^+ + X\text{-}Si(O^-)_2$ , donde X = mica o vidrio
- $H_2O + HCl + R'\text{-}NH_2 + X\text{-}Si(OH)_2 \leftrightarrow$ $H_2O + Cl^- + R'\text{-}NH_3^+ + X\text{-}Si(OH)_2$
- $H_2O + 2NaOH + R'\text{-}NH_3^+ + X\text{-}Si(OH)_2 \leftrightarrow$ $2Na^+ \cdot 3H_2O + R'\text{-}NH_2 + X\text{-}Si(O^-)_2$
- $R''\text{-}COOH + H_2O \leftrightarrow R''\text{-}COO^- + H_3O^+$
- $R'''\text{-}SO_2OH + H_2O \leftrightarrow R'''\text{-}SO_3^- + H_3O^+$

# Espectroscopia de fuerzas

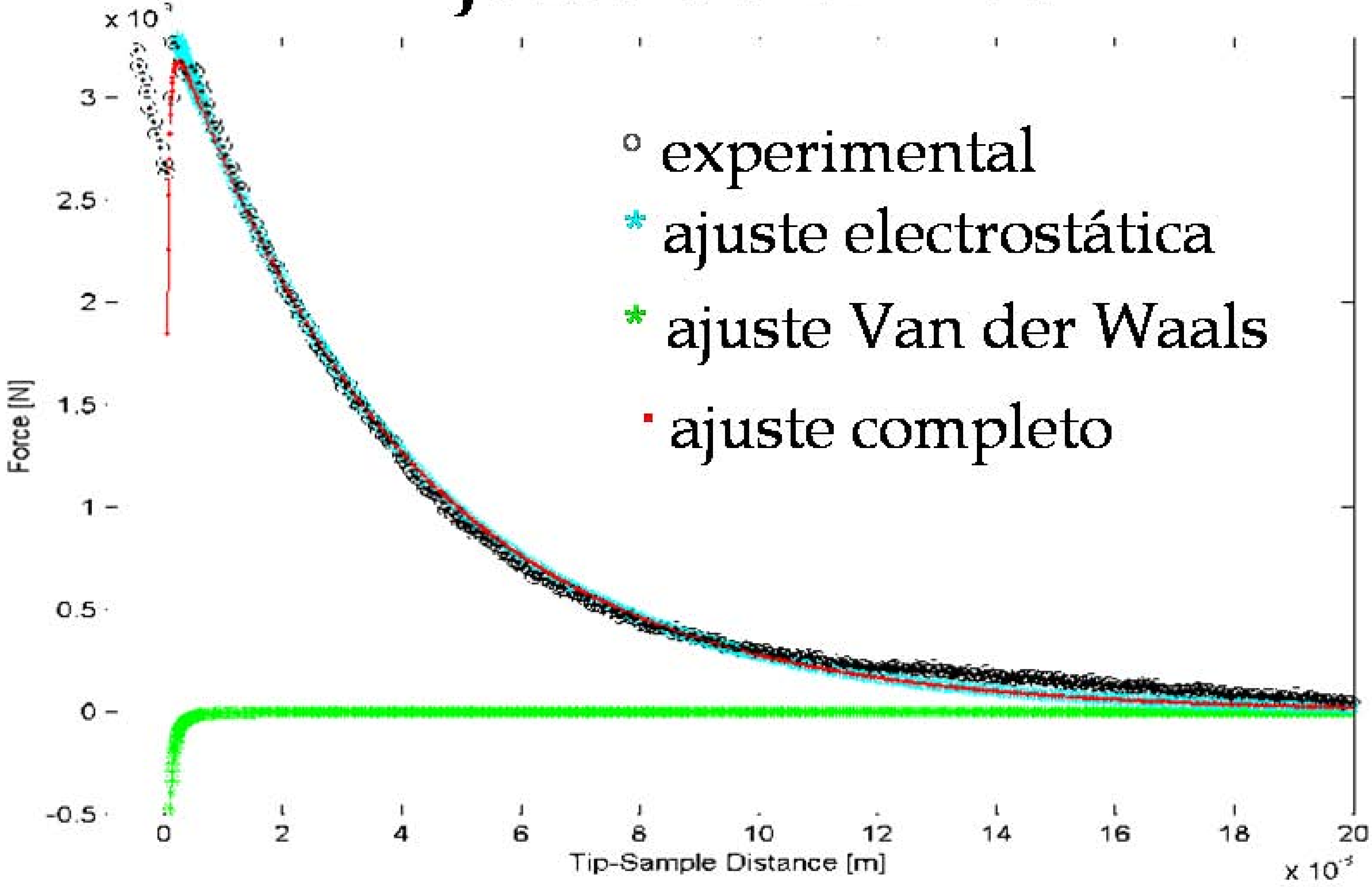

Mica Vs Vidrio


APTMS Vs APTMS



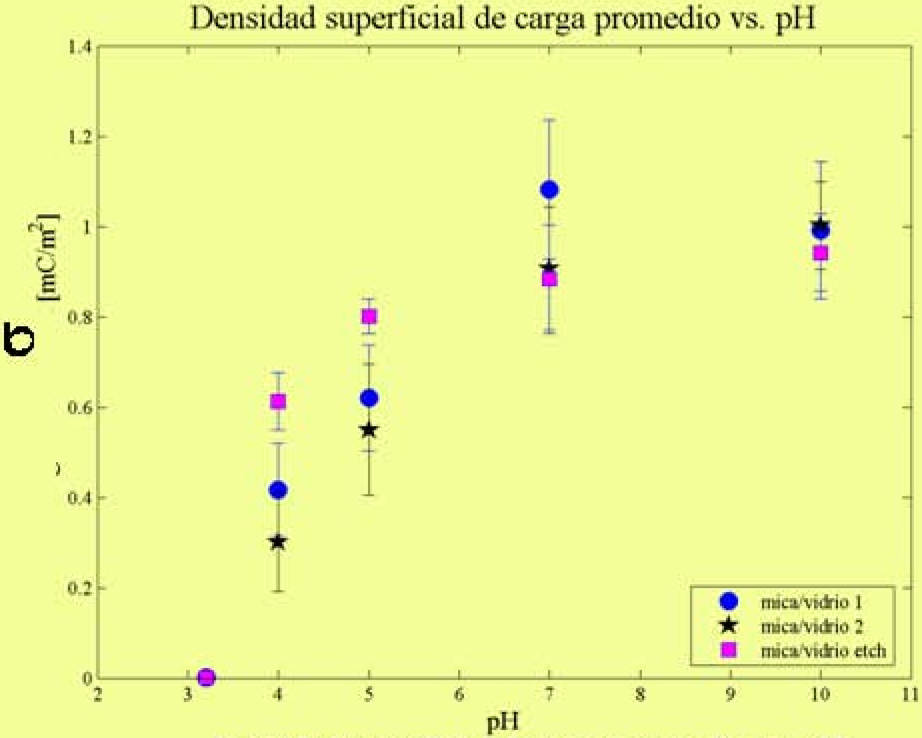

DS Vs DS

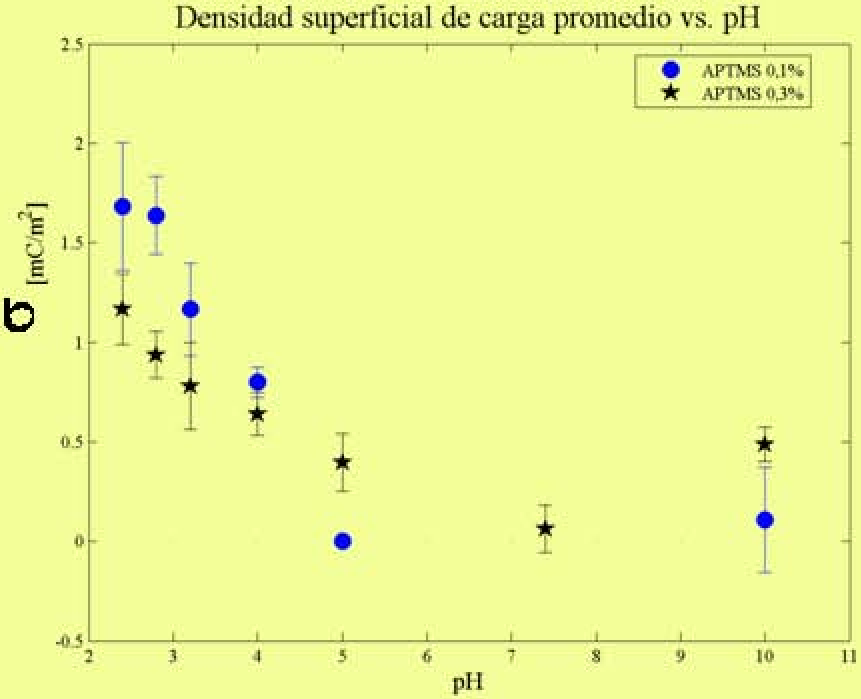
# Ajuste de curvas

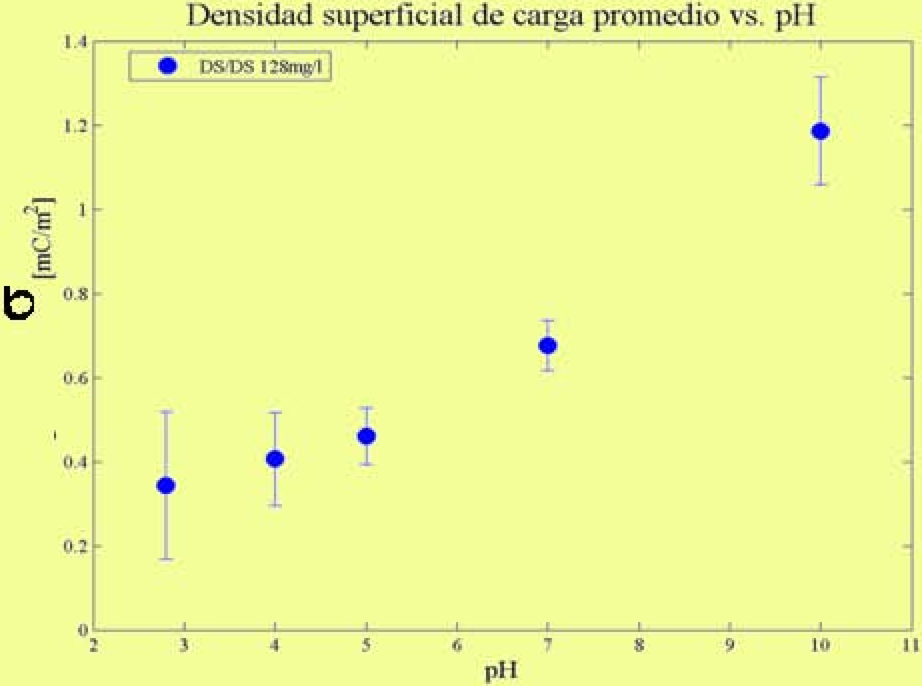


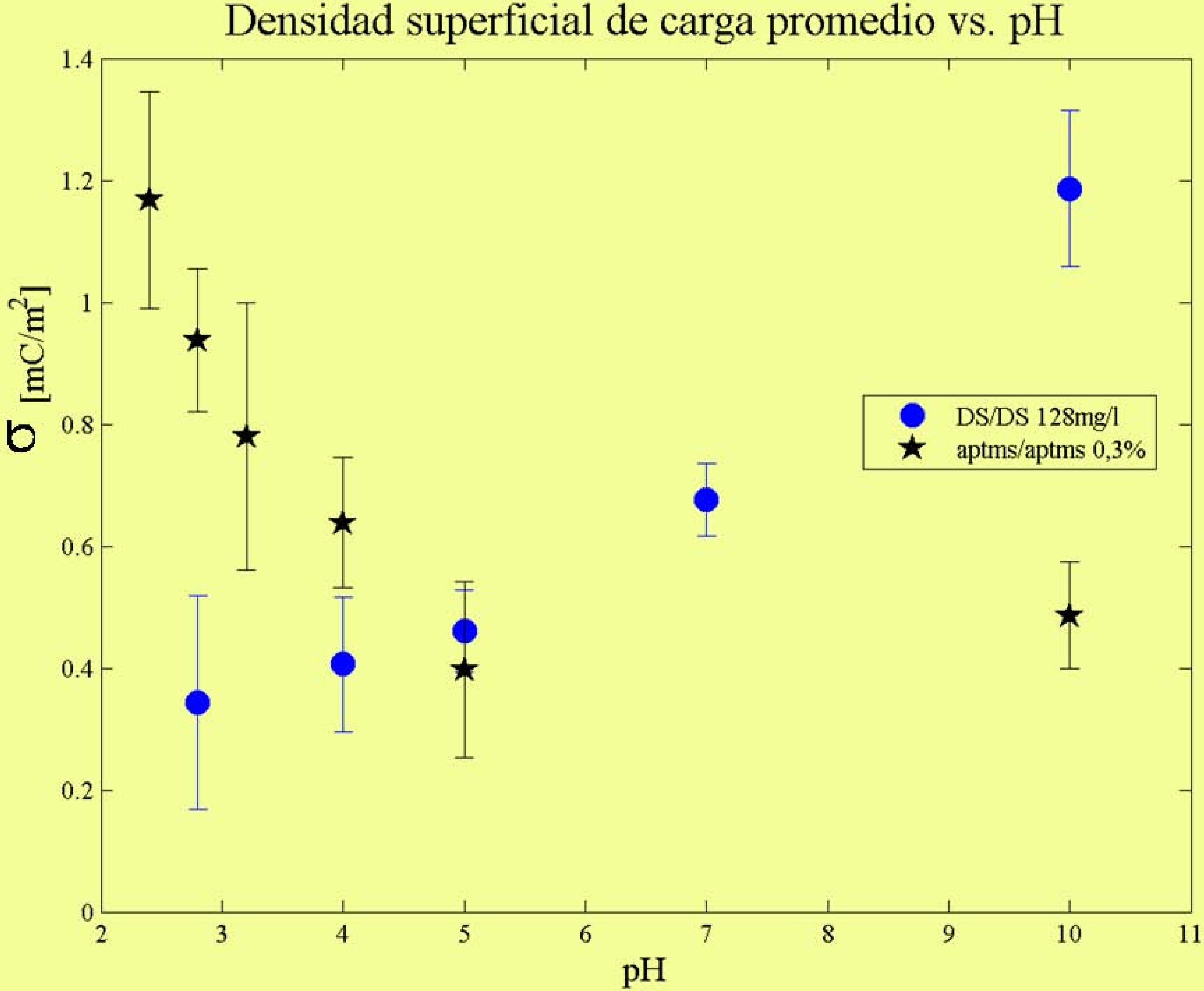
$$F = F_{Elec} + F_{VdW} + F_{Elas} = \frac{4\pi \cdot R \cdot \sigma_1 \cdot \sigma_2 \cdot \lambda}{\varepsilon \cdot \varepsilon_0} \cdot e^{-D/\lambda} - \frac{\mathcal{A} \cdot R}{D^2} + k(D - z) = 0$$

# Fuerza electrostática


Densidad superficial de carga promedio vs. pH

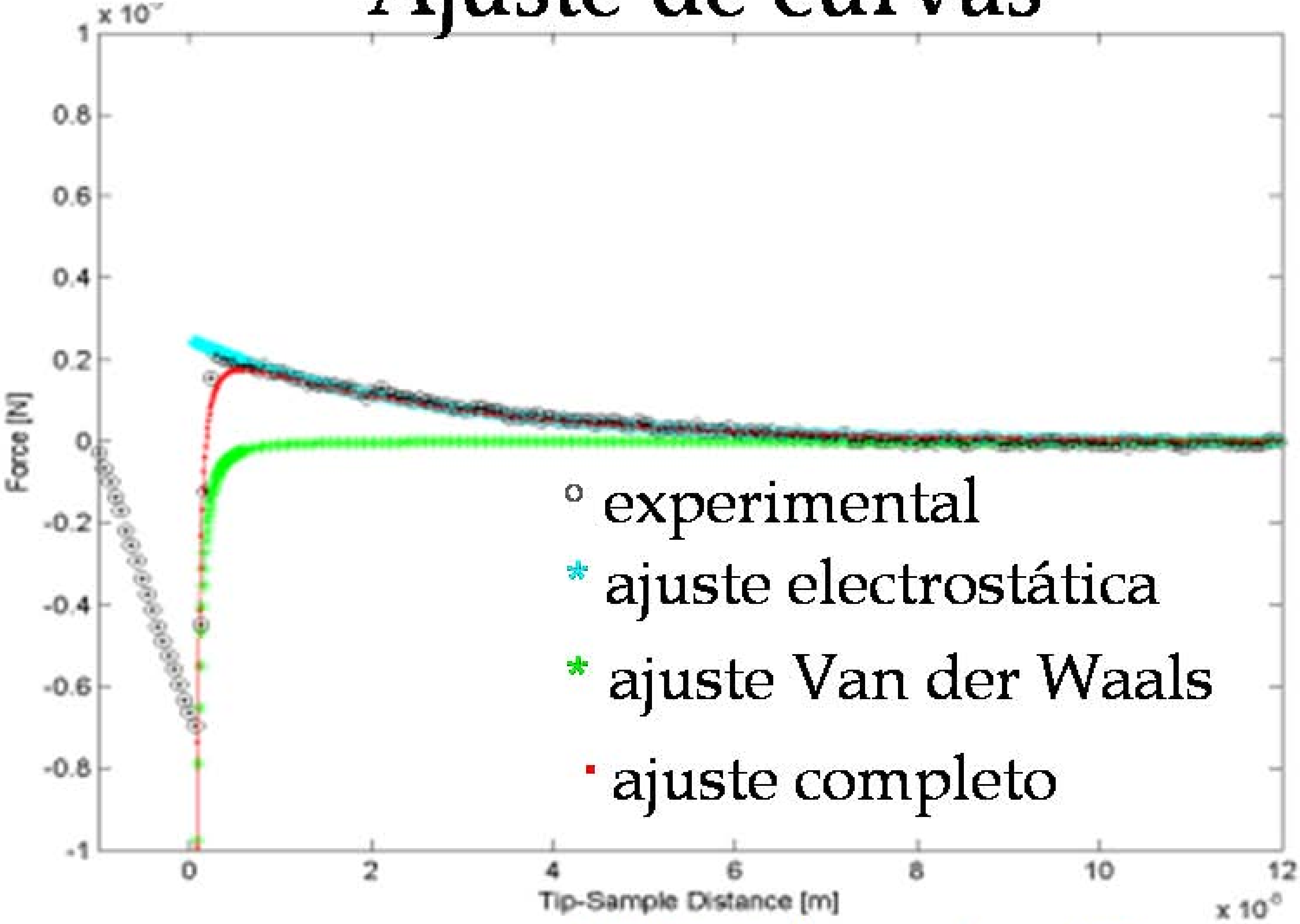

Densidad superficial de carga promedio vs. pH


Densidad superficial de carga promedio vs. pH



Densidad superficial de carga promedio vs. pH

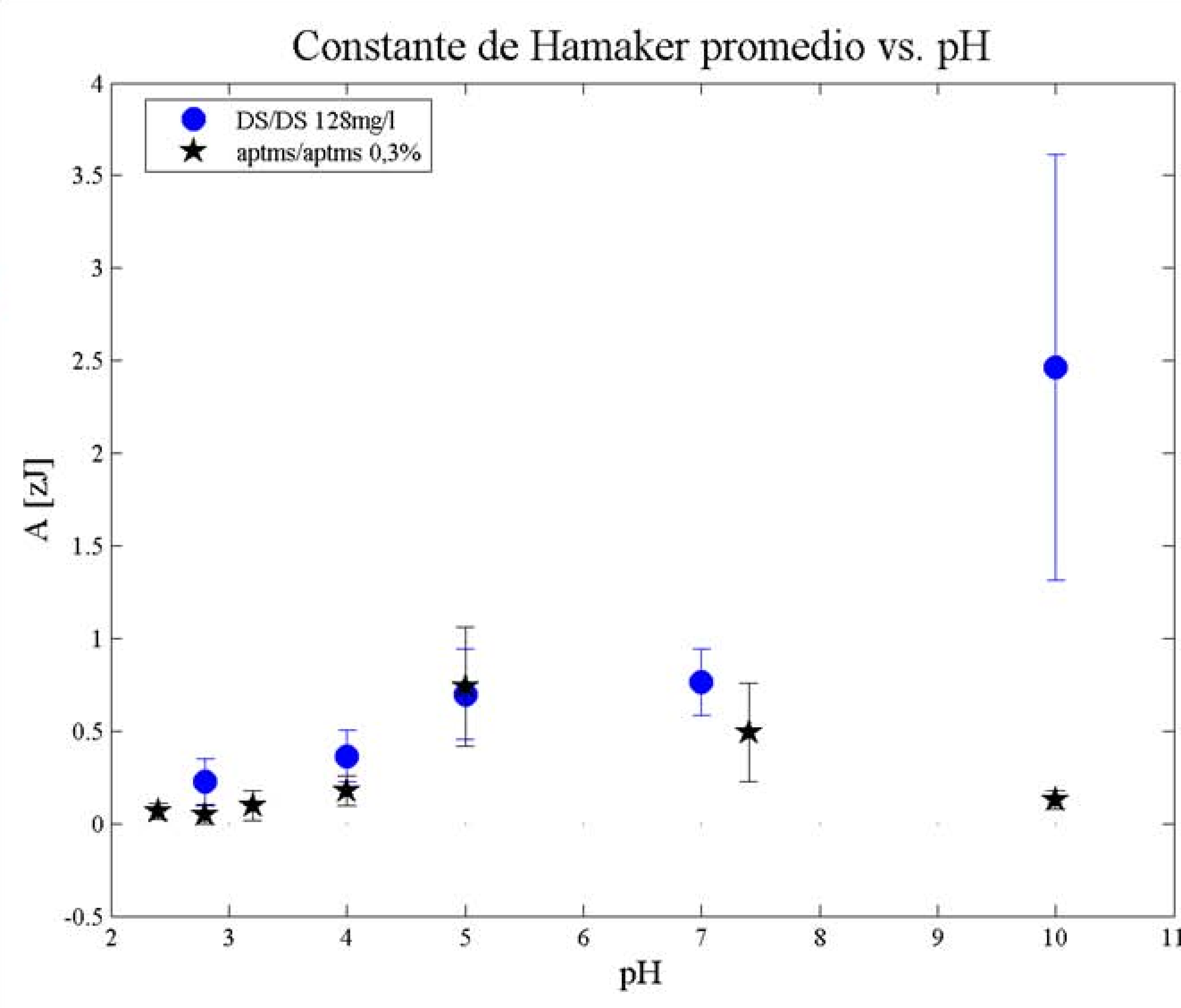
# Ajuste de curvas



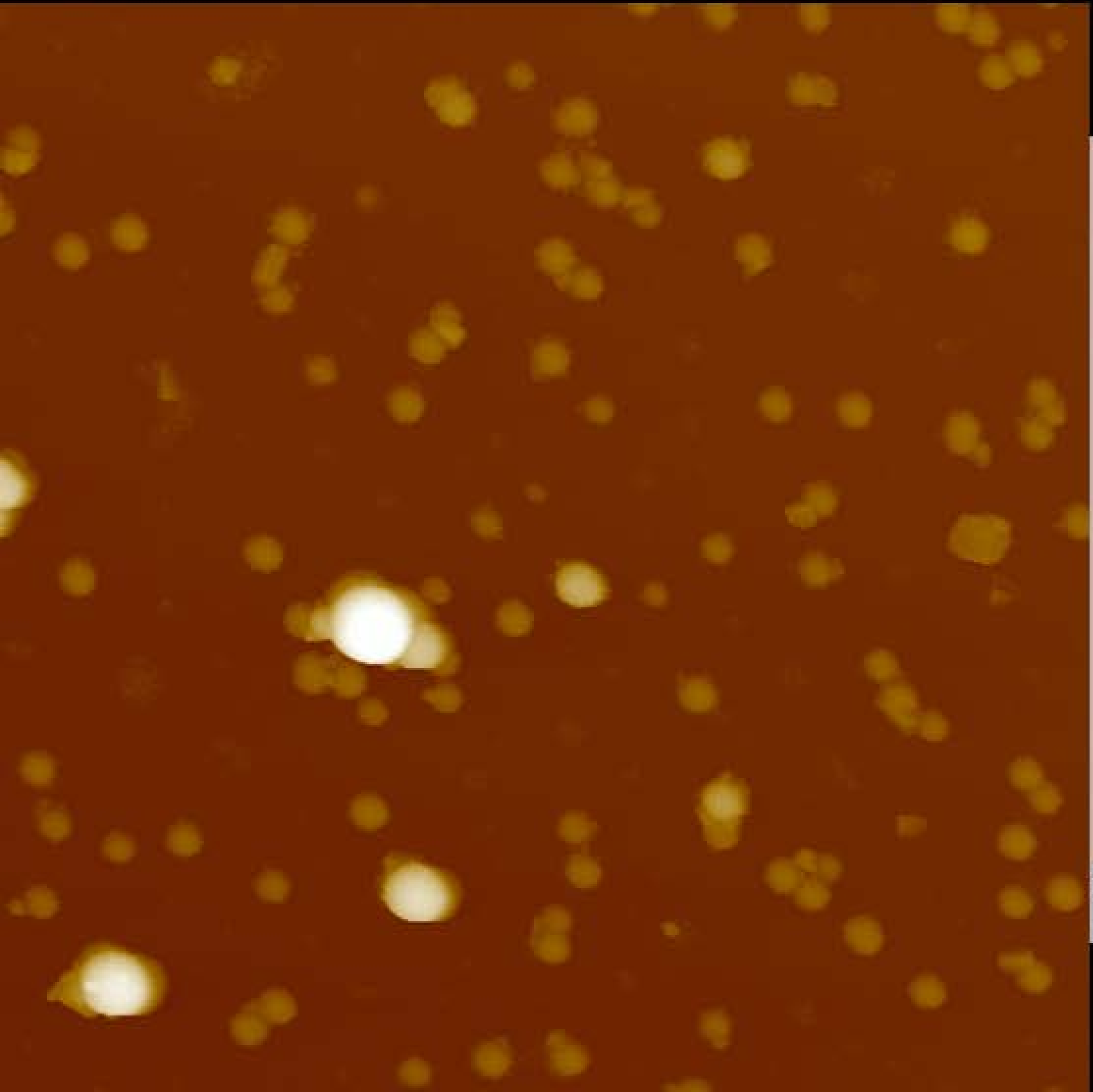
$$F = F_{Elec} + F_{VdW} + F_{Elas} = \frac{4\pi \cdot R \cdot \sigma_1 \cdot \sigma_2 \cdot \lambda}{\varepsilon \cdot \varepsilon_0} \cdot e^{-D/\lambda} - \frac{\mathcal{A} \cdot R}{D^2} + k(D - z) = 0$$

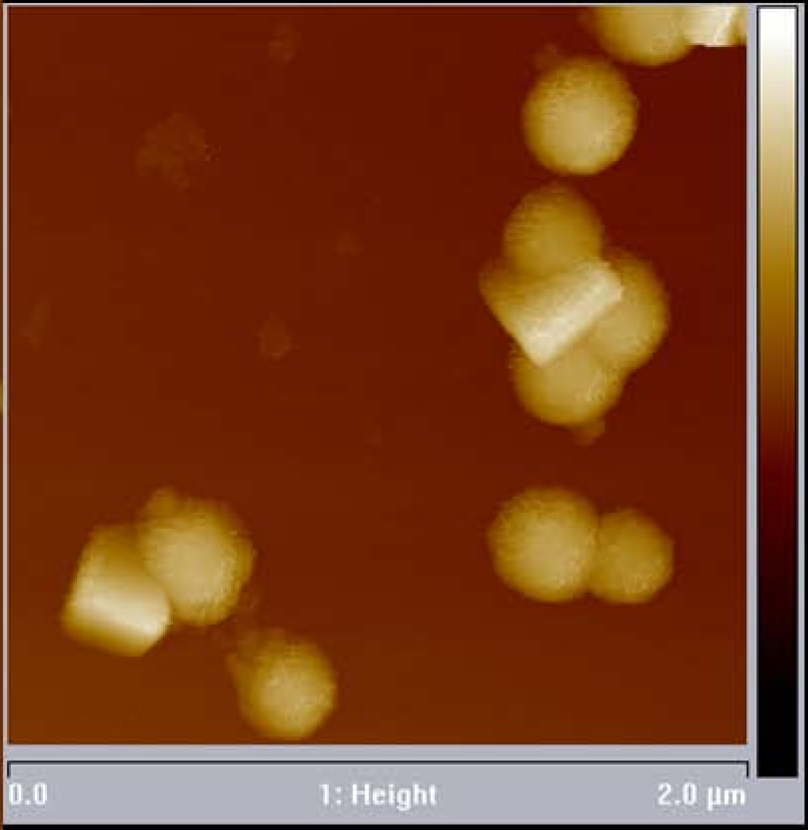
# Van der Waals

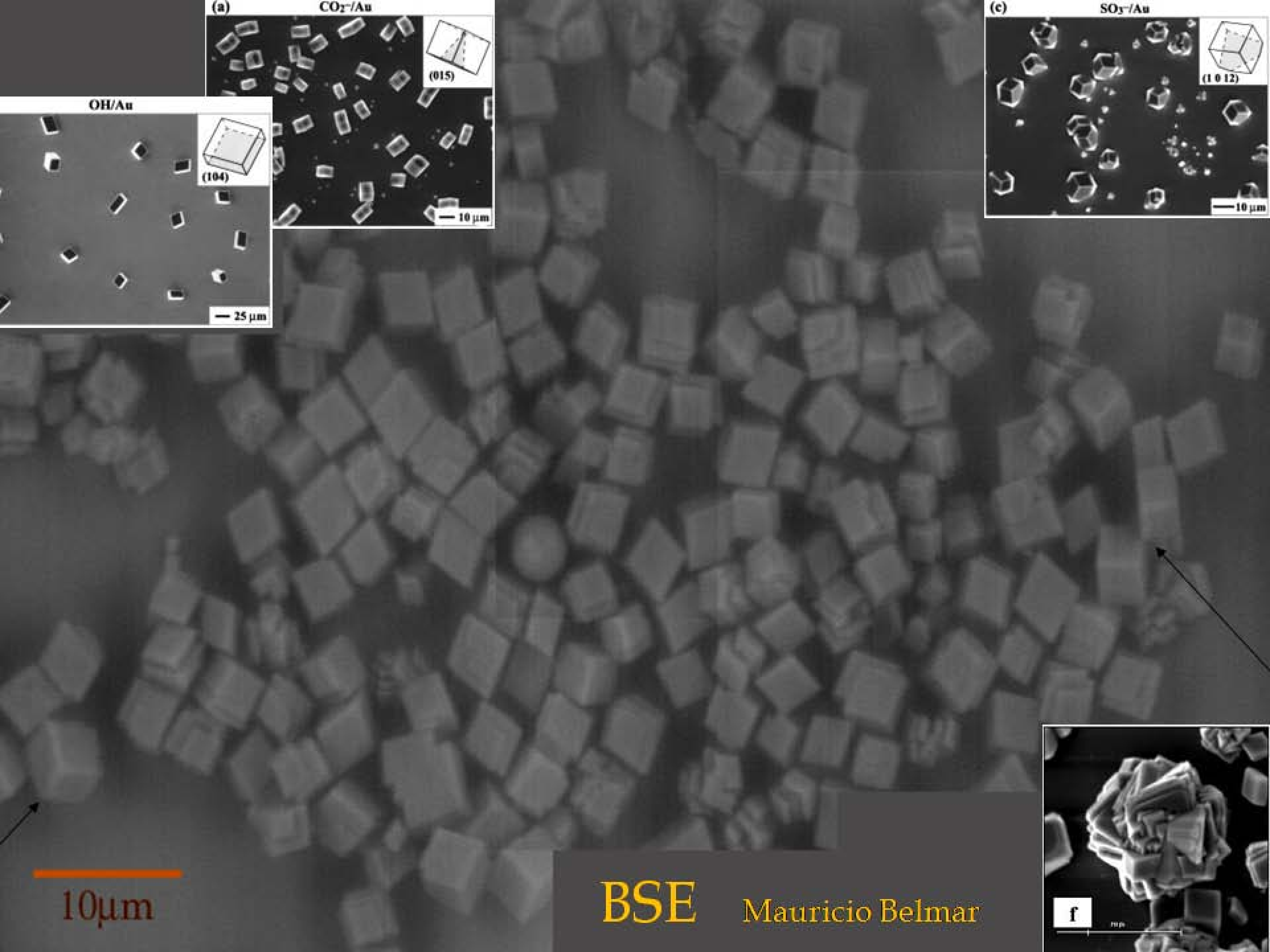
$$A = \pi^2 C \rho_1 \rho_2$$



# AFM *in-situ: n*ucleación







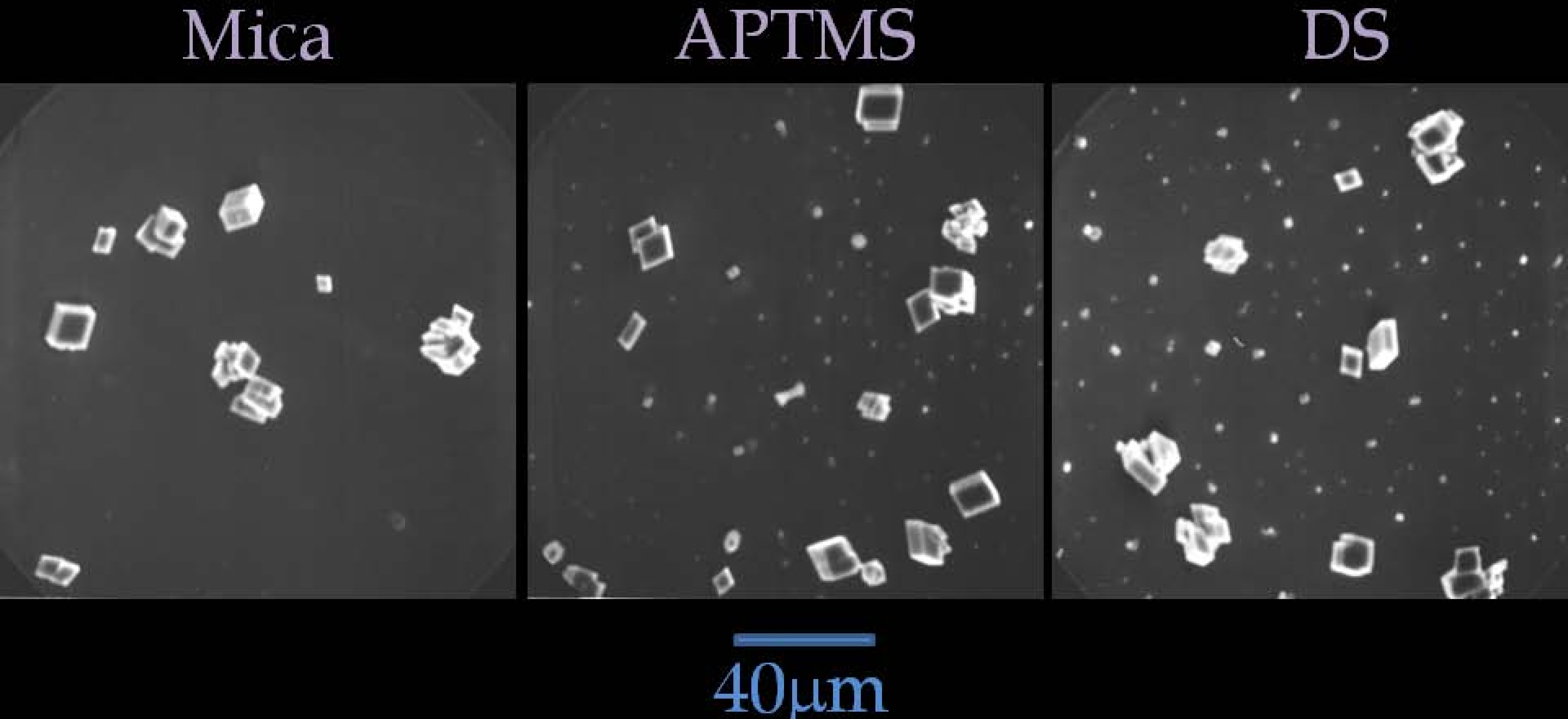
# BSE

Mauricio Belmar

# Cristales nucleados sobre diferentes superficies

SEM

Jaime Bravo



Mica

APTMS

DS

40μm

# Estrategia experimental

Se investiga la relación entre el cristal iónico calcita romboédrica y el oligosacárido polianiónico dermatan sulfato, ambos presentes en la cáscara de huevo de las aves.

Exp.1: Para saber como DS se coordina sobre la superficie de los cristales de calcita, se hizo y caracterizó sustrato de DS, para sobre este realizar un proceso de nucleación de cristales de carbonato de calcio.

Exp.2: Estudio *in-situ* de la adición de DS al crecimiento cristalino de una dislocación helicoidal observada en el plano <104> de la calcita romboédrica mediante AFM en modo contacto para medio líquido....

# Formation of chiralmorphologies through selective binding of amino acids to calcite surface steps

C.A. Orme*, A. Noy*, A. Wierzbicki², M. T. McBride*, M. Grantham³, H.H. Teng§, P.M. Dove³ & J.J. DeYoreo*

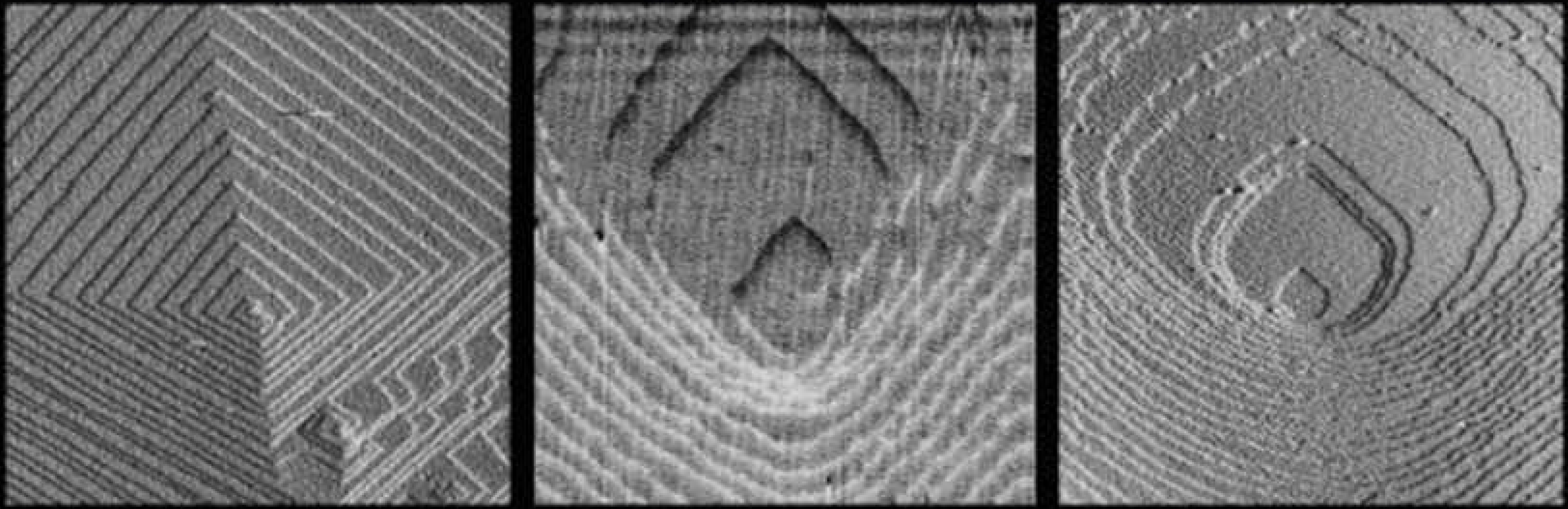


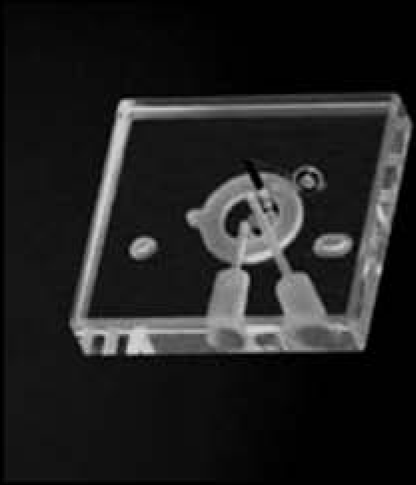
Figure 1 Images showing the effect of amino acids on calcite morphology. a±c, AFM images showing the effect of amino acids on growth-hillock and dissolution-pit geometry. a, A pure calcite growth hillock. b, Growth hillocks following addition of supersaturated solutions with 0.01M glycine, an achiral amino acid (b); 0.01M L-aspartic acid (c);

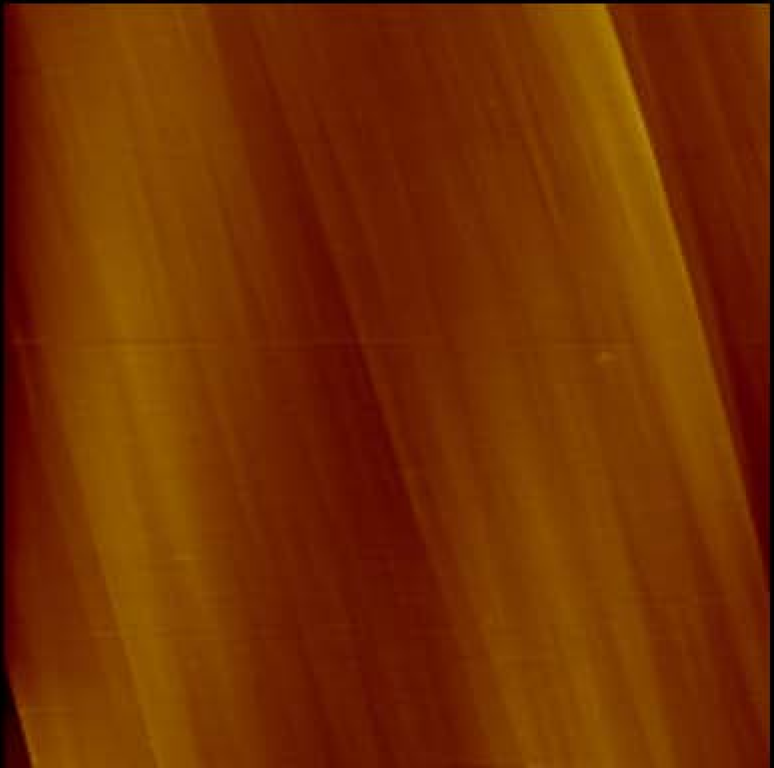
# Clivaje de la calcita

Elección del plano

Tamaño de la muestra

Limpieza y frescura de la superficie

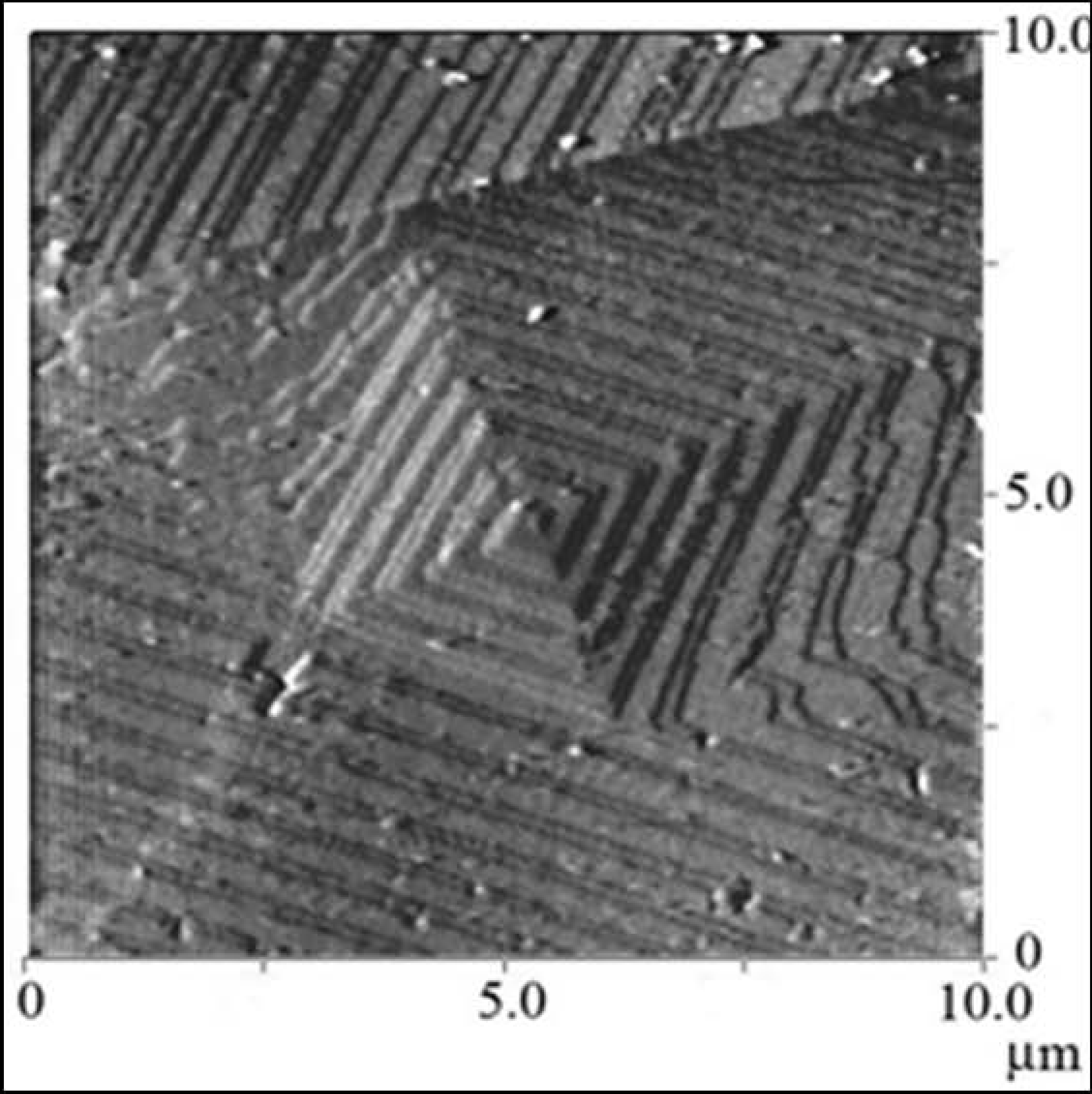




# Seguimiento con AFM *in-situ*

Crecimiento de calcita, solución sobresaturada de $CaCl_2$, $NaHCO_3$ y NaCl

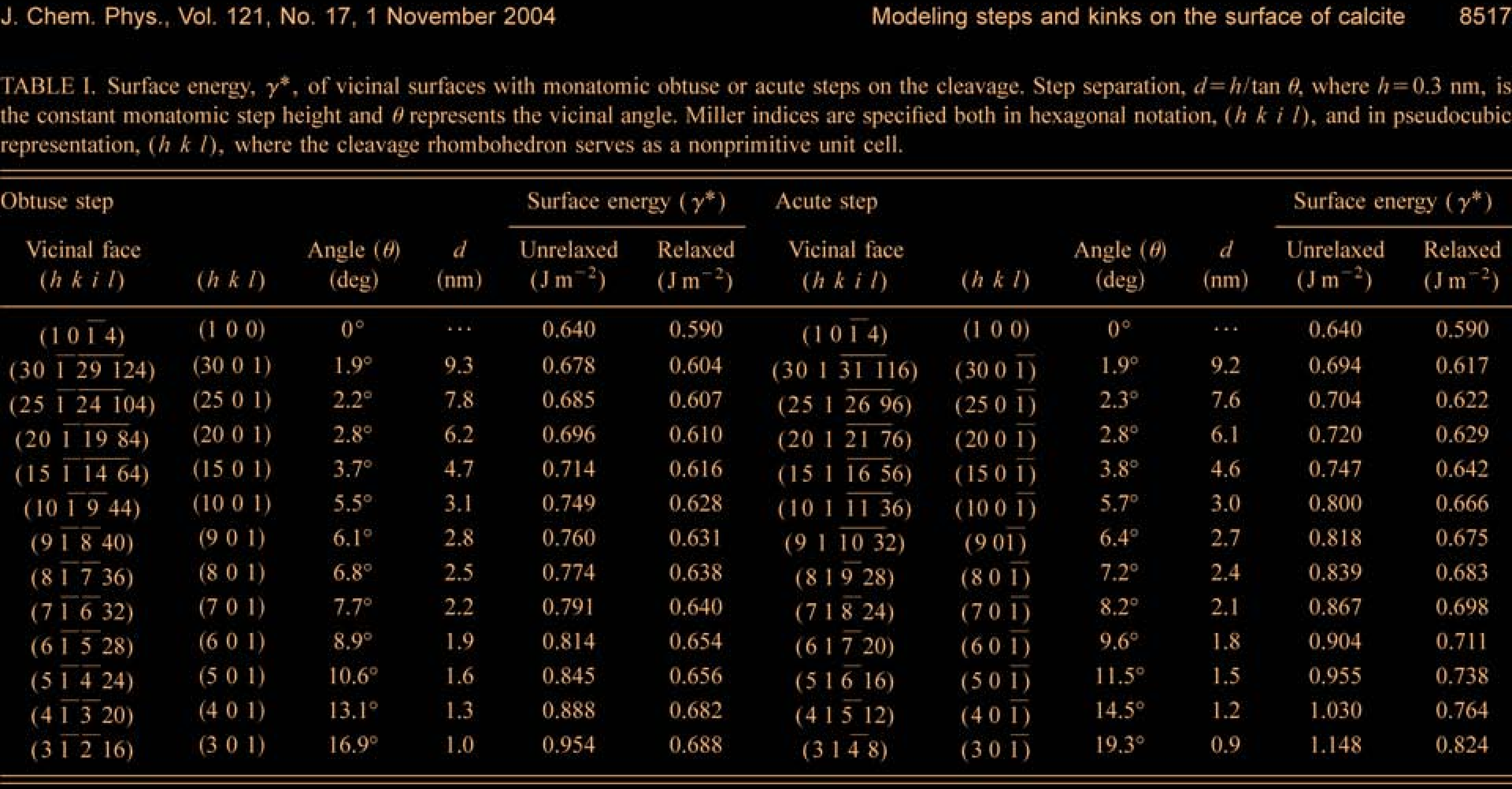
Crecimiento cristalino de una dislocación helicoidal normal al plano <104> de calcita romboédrica



# Adición de DS a la calcita

Se requiere comparar las dimensiones de los sitios donde se localizaría preferentemente el DS, teniendo en cuenta el tamaño y espaciamiento entre cargas en el DS y en la superficie de calcita en sus distintos planos.

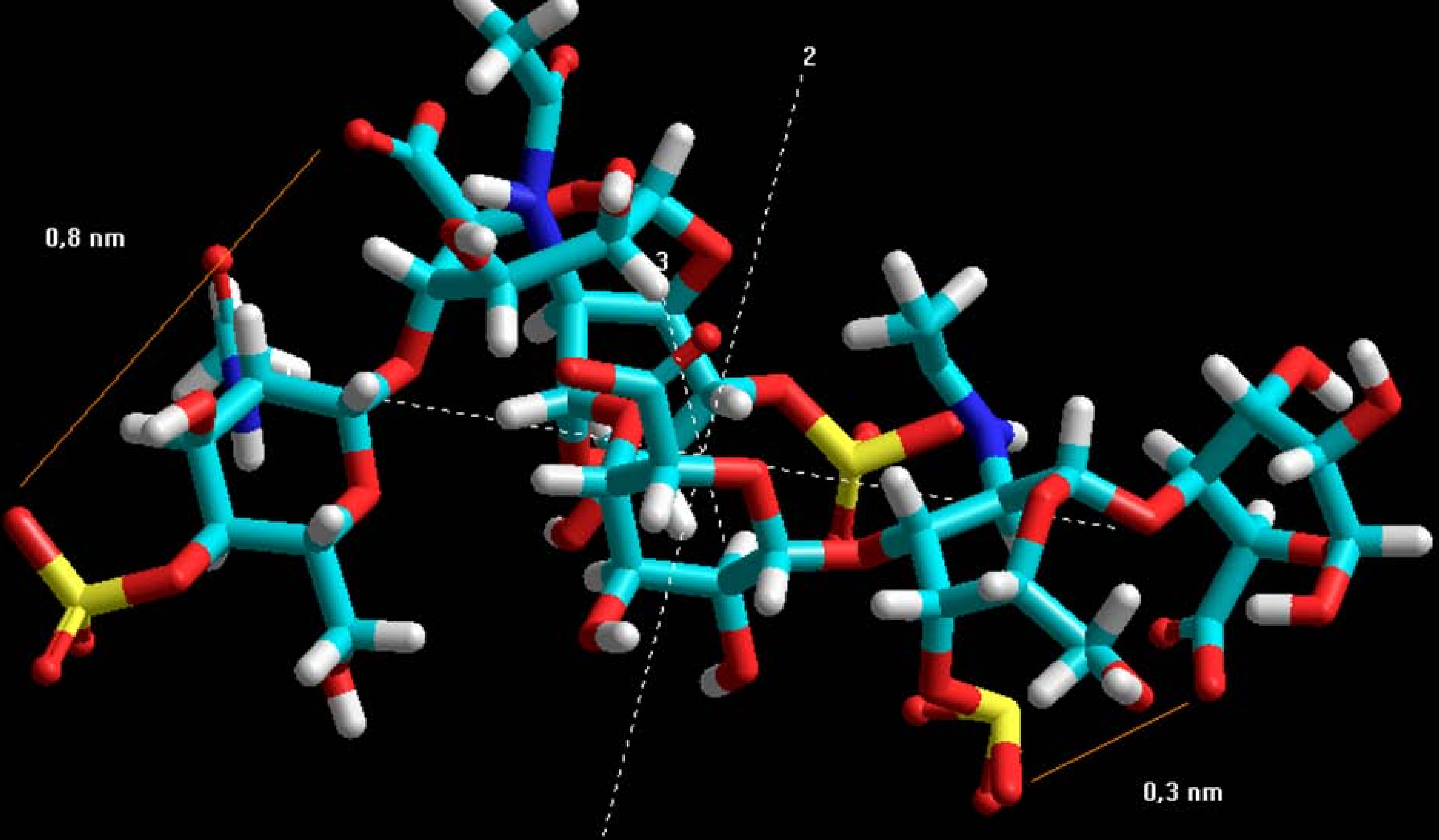
# Espaciamiento de cargas en calcita



J. Chem. Phys., Vol. 121, No. 17, 1 November 2004 Modeling steps and kinks on the surface of calcite 8517

TABLE I. Surface energy, $\gamma^*$, of vicinal surfaces with monatomic obtuse or acute steps on the cleavage. Step separation, $d = h/\tan\theta$, where $h = 0.3$ nm, is the constant monatomic step height and $\theta$ represents the vicinal angle. Miller indices are specified both in hexagonal notation, $(h\ k\ i\ l)$, and in pseudocubic representation, $(h\ k\ l)$, where the cleavage rhombohedron serves as a nonprimitive unit cell.

| Obtuse step | | | | Surface energy ($\gamma^*$) | | Acute step | | | | Surface energy ($\gamma^*$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Vicinal face $(h\ k\ i\ l)$ | $(h\ k\ l)$ | Angle ($\theta$) (deg) | $d$ (nm) | Unrelaxed ($\mathrm{J\ m^{-2}}$) | Relaxed ($\mathrm{J\ m^{-2}}$) | Vicinal face $(h\ k\ i\ l)$ | $(h\ k\ l)$ | Angle ($\theta$) (deg) | $d$ (nm) | Unrelaxed ($\mathrm{J\ m^{-2}}$) | Relaxed ($\mathrm{J\ m^{-2}}$) |
| $(1\ 0\ \bar{1}\ 4)$ | (1 0 0) | 0° | ⋯ | 0.640 | 0.590 | $(1\ 0\ \bar{1}\ 4)$ | (1 0 0) | 0° | ⋯ | 0.640 | 0.590 |
| $(30\ \bar{1}\ \overline{29}\ 124)$ | (30 0 1) | 1.9° | 9.3 | 0.678 | 0.604 | $(30\ 1\ \overline{31}\ 116)$ | $(30\ 0\ \bar{1})$ | 1.9° | 9.2 | 0.694 | 0.617 |
| $(25\ \bar{1}\ \overline{24}\ 104)$ | (25 0 1) | 2.2° | 7.8 | 0.685 | 0.607 | $(25\ 1\ \overline{26}\ 96)$ | $(25\ 0\ \bar{1})$ | 2.3° | 7.6 | 0.704 | 0.622 |
| $(20\ \bar{1}\ \overline{19}\ 84)$ | (20 0 1) | 2.8° | 6.2 | 0.696 | 0.610 | $(20\ 1\ \overline{21}\ 76)$ | $(20\ 0\ \bar{1})$ | 2.8° | 6.1 | 0.720 | 0.629 |
| $(15\ \bar{1}\ \overline{14}\ 64)$ | (15 0 1) | 3.7° | 4.7 | 0.714 | 0.616 | $(15\ 1\ \overline{16}\ 56)$ | $(15\ 0\ \bar{1})$ | 3.8° | 4.6 | 0.747 | 0.642 |
| $(10\ \bar{1}\ \bar{9}\ 44)$ | (10 0 1) | 5.5° | 3.1 | 0.749 | 0.628 | $(10\ 1\ \overline{11}\ 36)$ | $(10\ 0\ \bar{1})$ | 5.7° | 3.0 | 0.800 | 0.666 |
| $(9\ \bar{1}\ \bar{8}\ 40)$ | (9 0 1) | 6.1° | 2.8 | 0.760 | 0.631 | $(9\ 1\ \overline{10}\ 32)$ | $(9\ 0\ \bar{1})$ | 6.4° | 2.7 | 0.818 | 0.675 |
| $(8\ \bar{1}\ \bar{7}\ 36)$ | (8 0 1) | 6.8° | 2.5 | 0.774 | 0.638 | $(8\ 1\ \bar{9}\ 28)$ | $(8\ 0\ \bar{1})$ | 7.2° | 2.4 | 0.839 | 0.683 |
| $(7\ \bar{1}\ \bar{6}\ 32)$ | (7 0 1) | 7.7° | 2.2 | 0.791 | 0.640 | $(7\ 1\ \bar{8}\ 24)$ | $(7\ 0\ \bar{1})$ | 8.2° | 2.1 | 0.867 | 0.698 |
| $(6\ \bar{1}\ \bar{5}\ 28)$ | (6 0 1) | 8.9° | 1.9 | 0.814 | 0.654 | $(6\ 1\ \bar{7}\ 20)$ | $(6\ 0\ \bar{1})$ | 9.6° | 1.8 | 0.904 | 0.711 |
| $(5\ \bar{1}\ \bar{4}\ 24)$ | (5 0 1) | 10.6° | 1.6 | 0.845 | 0.656 | $(5\ 1\ \bar{6}\ 16)$ | $(5\ 0\ \bar{1})$ | 11.5° | 1.5 | 0.955 | 0.738 |
| $(4\ \bar{1}\ \bar{3}\ 20)$ | (4 0 1) | 13.1° | 1.3 | 0.888 | 0.682 | $(4\ 1\ \bar{5}\ 12)$ | $(4\ 0\ \bar{1})$ | 14.5° | 1.2 | 1.030 | 0.764 |
| $(3\ \bar{1}\ \bar{2}\ 16)$ | (3 0 1) | 16.9° | 1.0 | 0.954 | 0.688 | $(3\ 1\ \bar{4}\ 8)$ | $(3\ 0\ \bar{1})$ | 19.3° | 0.9 | 1.148 | 0.824 |



Espaciamiento de cargas en DS

# Agradecimientos

- Proyecto Fondap 11980002
- Doctorado en Ciencias de la Ingeniería mención Ciencia de los Materiales, Universidad de Chile.
- Laboratorio de Física no Lineal, Universidad de Santiago de Chile.