

An Atomistic Simulation Study of the Interaction of Organic Adsorbates with Fluorapatite Surfaces

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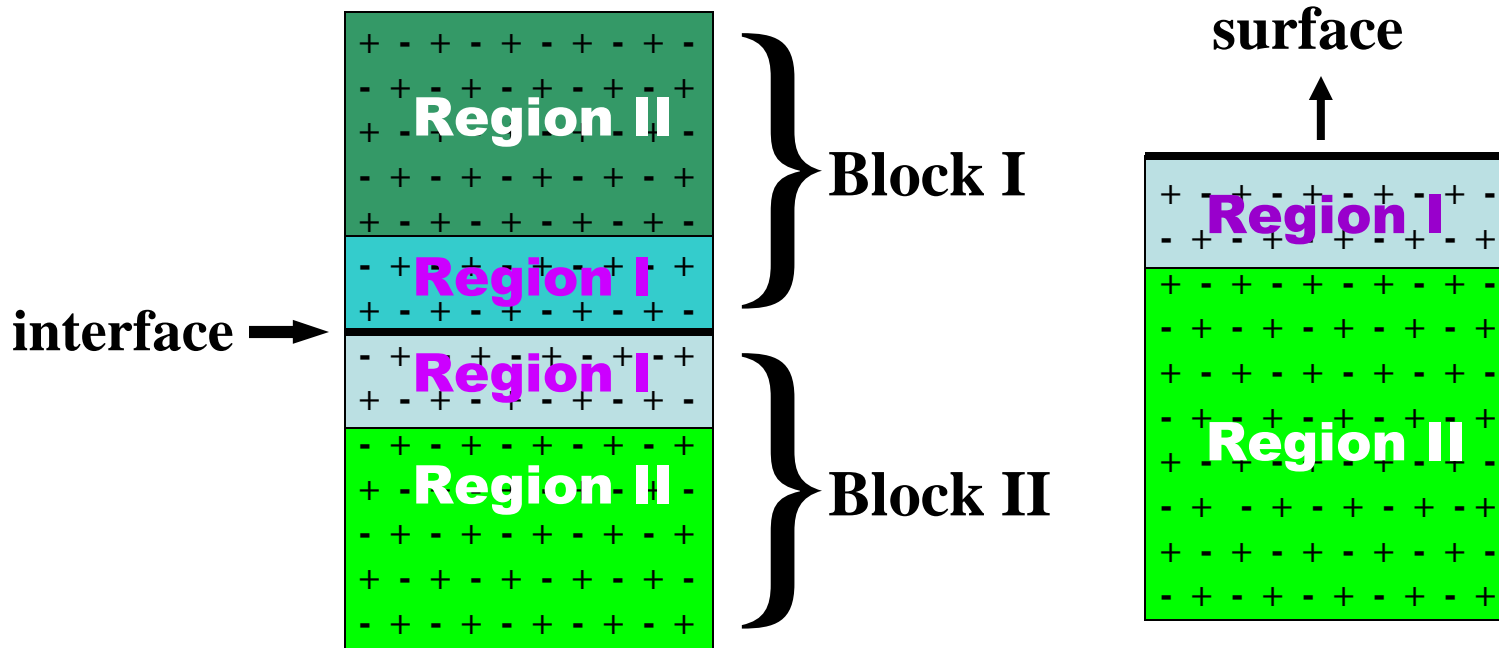


FLUORAPATITE

Methodology

Metadise program

- Static lattice minimisation technique
- Forces between species described by potential model



- Region I : ions relaxed
- Region II : ions kept at bulk equilibrium position

Potential Model

Components to interatomic forces:

- Long range electrostatic $E_{ij} = q_i q_j / r_{ij}$
- Short range repulsions and Van der Waals interactions, e.g

-Morse for bonded interactions (OH, PO₄)

$$E_{ij} = D[1 - \exp(-\alpha(r_{ij} - r_0))]^2 - D$$

-Lennard Jones potential functions for non bonded species of organic molecules

$$E_{ij} = A/r_{ij}^{12} - B/r_{ij}^6$$

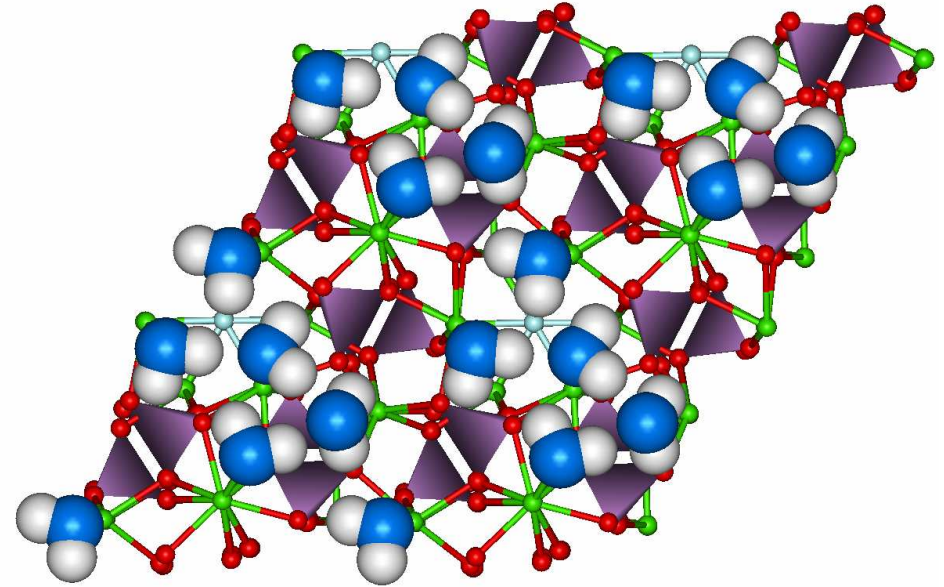
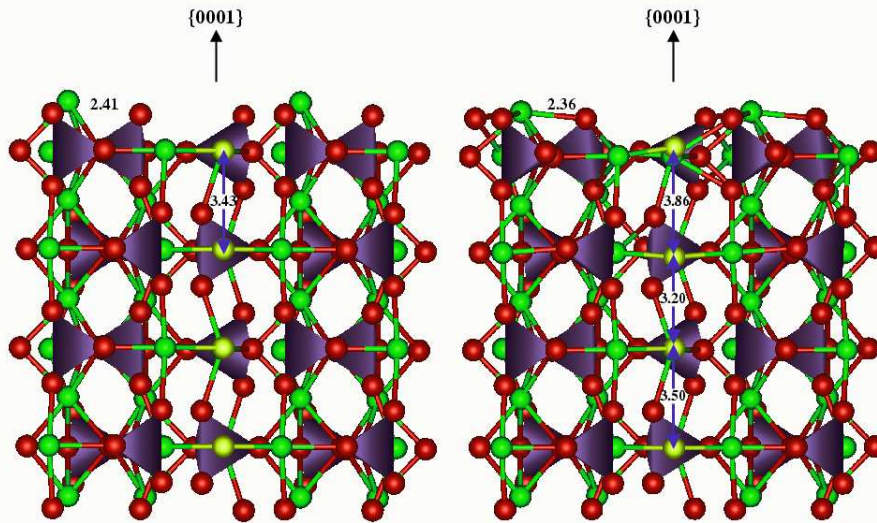
-Buckingham for non-bonded and bonded (Ca-O, Ca-F)

$$E_{ij} = A \exp(-r_{ij}/\rho) - C_{ij}/r_{ij}^6$$

-Bond bending term (PO₄)

$$E_{ij} = \frac{1}{2} k_{ijk} (\theta_{ijk} - \theta_0)^2$$

Dry and Hydrated (0001) Surface



- Side view: (a) bulk terminated and
- (b) geometry optimised (0001) surface
- Surface Ca move into the bulk Ca-O shorter.
- Alternating lengthening and shortening of F-F distances into the bulk.

- Series of partial coverages up to full monolayer coverage
- Ca-O_w strongest interaction
- Clustering of H₂O molecules.

Fluorapatite Surfaces

Surface energies of un-relaxed, relaxed and hydrated surfaces.

$$\gamma = \frac{E_s - E_b}{A} \quad \gamma_w = \frac{E_h - (E_b + nE_{H_2O})}{A} \quad E_{hydr} = \frac{E_h - (E_{dry} + nE_{H_2O})}{n}$$

PLANE	$\gamma_{unrel.}(\text{J}\cdot\text{m}^{-2})$	$\gamma_{rel}(\text{J}\cdot\text{m}^{-2})$	$\gamma_w(\text{J}\cdot\text{m}^{-2})$	$E_{hydration}(\text{kJ}\cdot\text{mol}^{-1})$
(0001)	1.19	0.77	0.45	-73
(10 $\bar{1}$ 0)	2.71	1.32	0.75	-97
(10 $\bar{1}$ 1)	2.28	1.00	0.61	-83
(11 $\bar{2}$ 0)	2.28	1.12	0.72	-97
(10 $\bar{1}$ 3)	2.98	1.94	1.67	-78
(11 $\bar{2}$ 1)	2.62	1.11	0.88	-81

The hydration energies are used for competitive adsorption with organic molecules

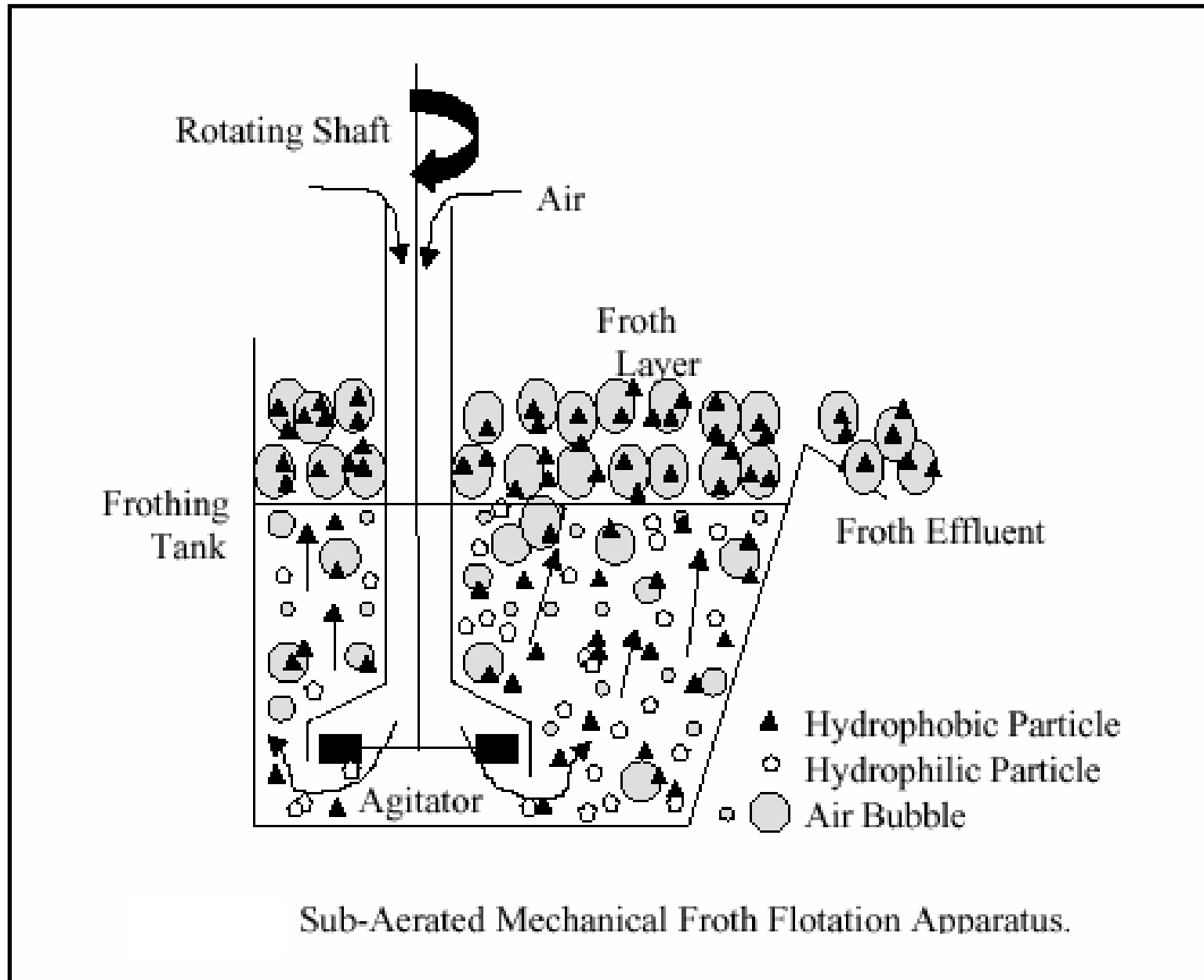
D. Mkhonto, N.H. de Leeuw, *J. Mater. Chem.* **12**, 2633 (2002)

Adsorption of Some Organic Molecules on Apatite

- **Apatite coexist in mineral ore deposits with other calcium-bearing minerals such as calcium phosphate, calcium carbonate, calcium fluorite.**
- **Apatite need to be separated from these e.g. by flotation process.**
- **Surfactant molecules with long hydrophobic chains are attached to make mineral surfaces hydrophobic.**
- **They are attached either by physisorption or ionic bonding.**
- **We have modelled selection model of collector molecules using atomistic simulation.**

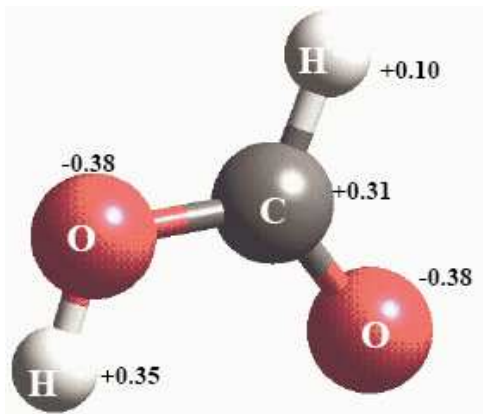
Phys. Chem. Min. (2006) in press

Flotation



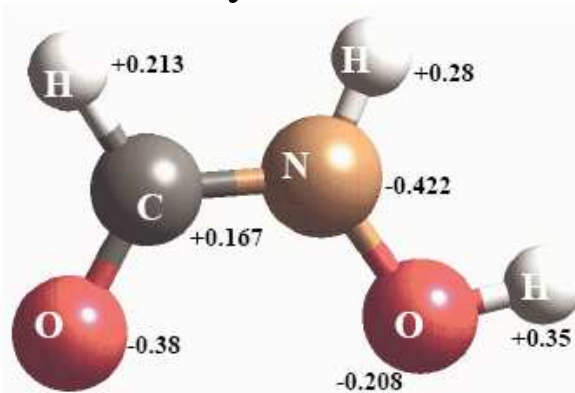
Molecule models

Methanoic Acid



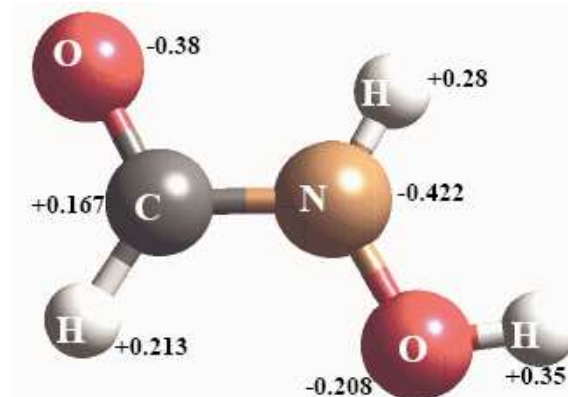
[CHOOH]
model of carboxylic acid.

Cis-Hydroxamic

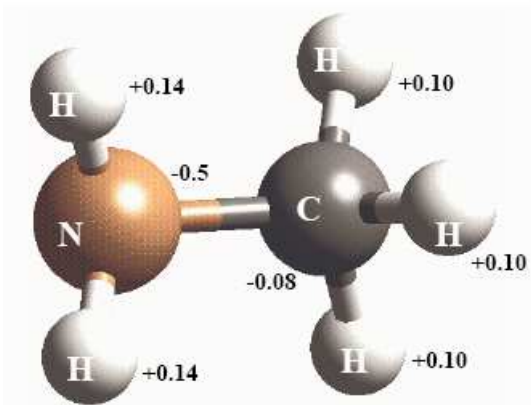


[RC(=O)NHOH] Hydroxyl amide and carbonyl functional group

Trans-Hydroxamic

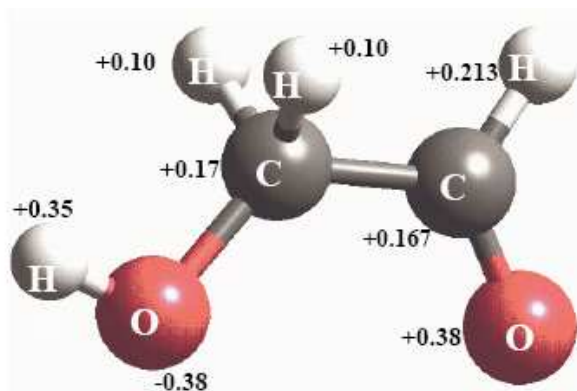


Methylamine



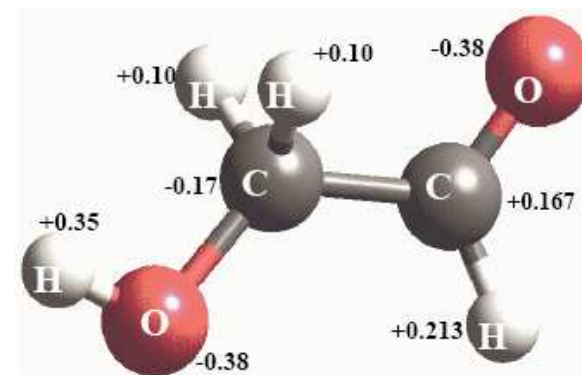
[H₂CNH₃]
Amine and methyl group
functional group

Cis-Hydroxyethanal



HC(=O)CH₂OH Contain hydroxyl and aldehyde functional groups

Trans-Hydroxyethanal



Adsorption Energies (kJmol⁻¹)

$$E_{\text{ads}} = E_{\text{system}} - (E_{\text{surf}} + E_{\text{adsorbate}})$$

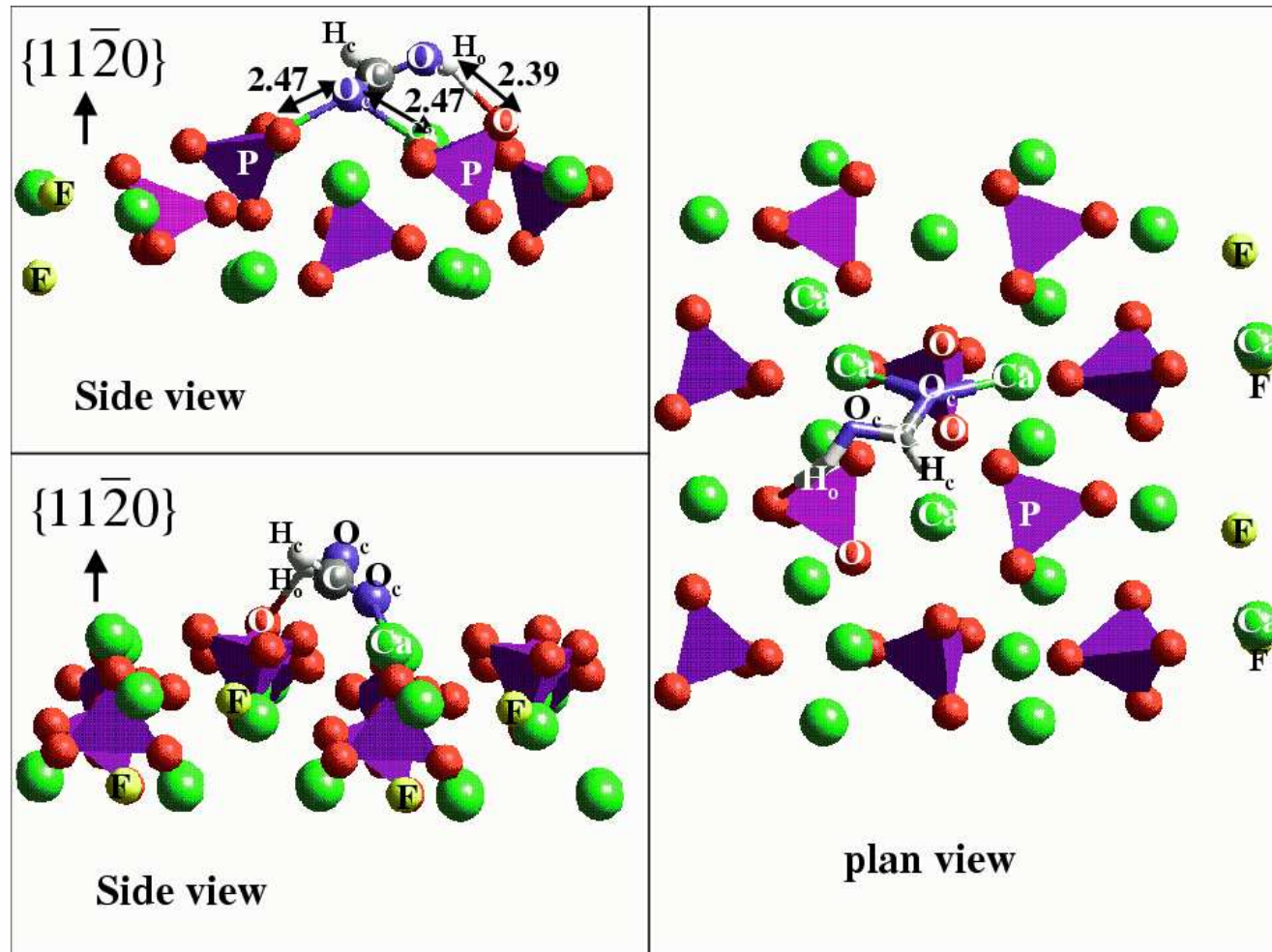
surface	Methanoic acid	hydroxamic cis	Hydroxamic trans	methylamine	Hydroxyethanal cis	hydroxyethanal trans
{0 0 0 1}	-105.2	-112.2	-112.4	-30.3	-142.1	-122.8
{1 0 $\bar{1}$ 0}	-170.1	-203.0	-116.4	-83.0	-196.3	-214.6
{1 0 $\bar{1}$ 1}	-136.0	-185.8	-132.9	-52.0	-193.0	-135.9
{1 1 $\bar{2}$ 0}	-171.5	-185.4	-172.0	-95.3	-212.6	-159.6
{1 1 $\bar{2}$ 1}	-138.0	-169.7	-115.5	-51.3	-185.8	-187.3
{1 0 $\bar{1}$ 3}	-105.3	-98.4	-99.4	-25.0	-134.8	-137.4

H₂O(hydration energies) ranges between -73 to -97 kJmol⁻¹

- Generally (100) and (110) are preferable adsorption surface.
- They have relatively high surface energies and would be reactive.
- (103) has large surface area and adsorbate has little effect to surface geometry.
- Methylamine is weakest, because only N and H interact with surfaces and partly steric hindrance.
- Availability of O on surfactants to interact on surface contribute to stability.
- Also flexibility due to C-C on other molecules plays a role.
- Methylamine will not displace water thus, not suitable for flotation

Adsorbate Structures.

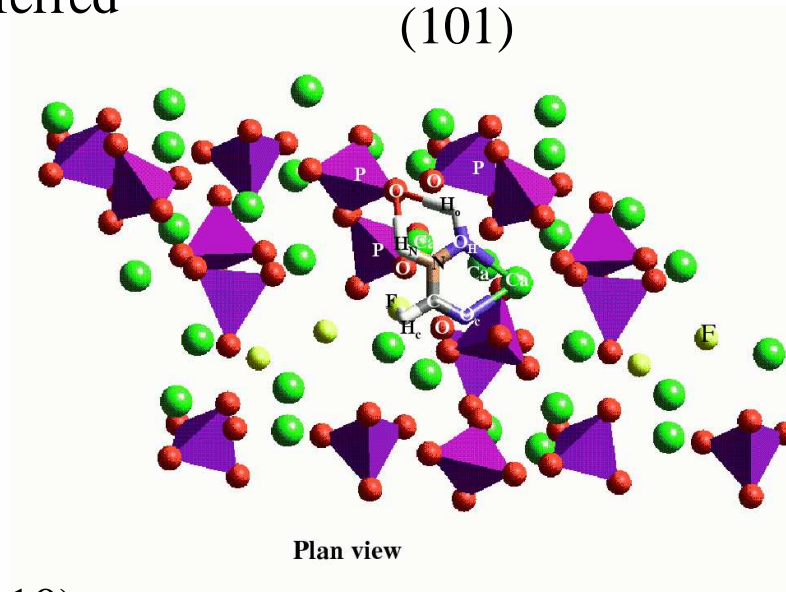
Methanoic acid on (110) surface.



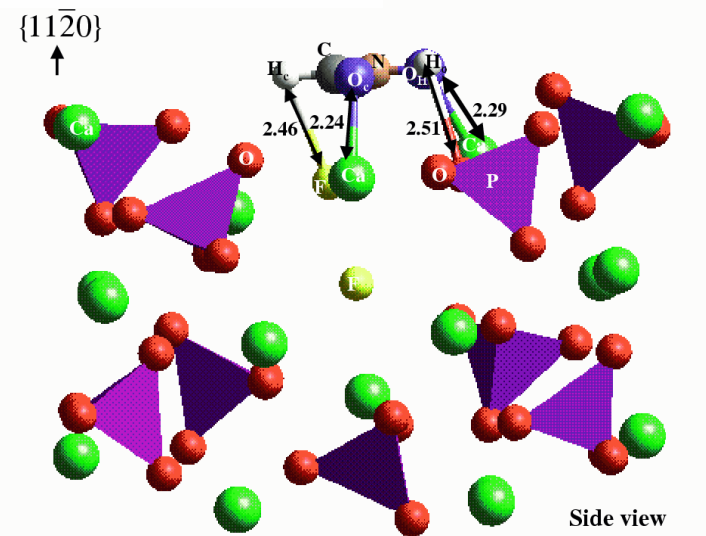
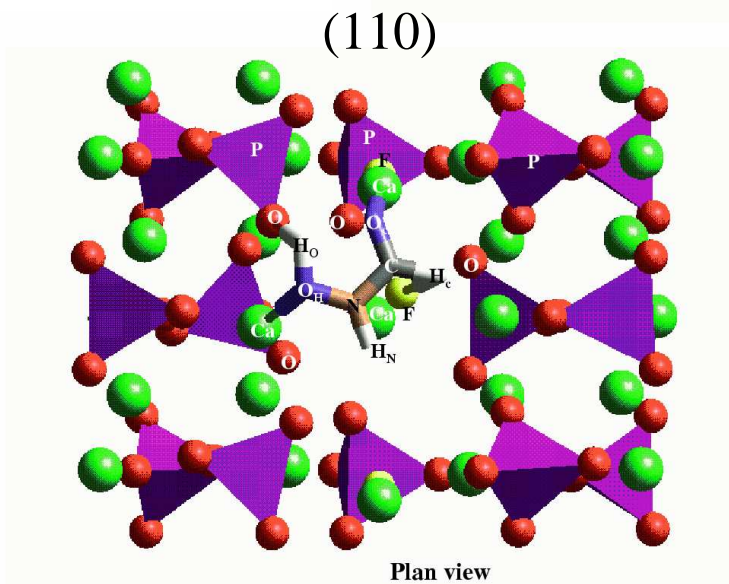
- carboxyl Oxygen bindate to two closer Ca ions.
- Hydroxyl Oxygen not interact in favour of H-O_A

Hydroxamic

Cis/eclipse form preferred

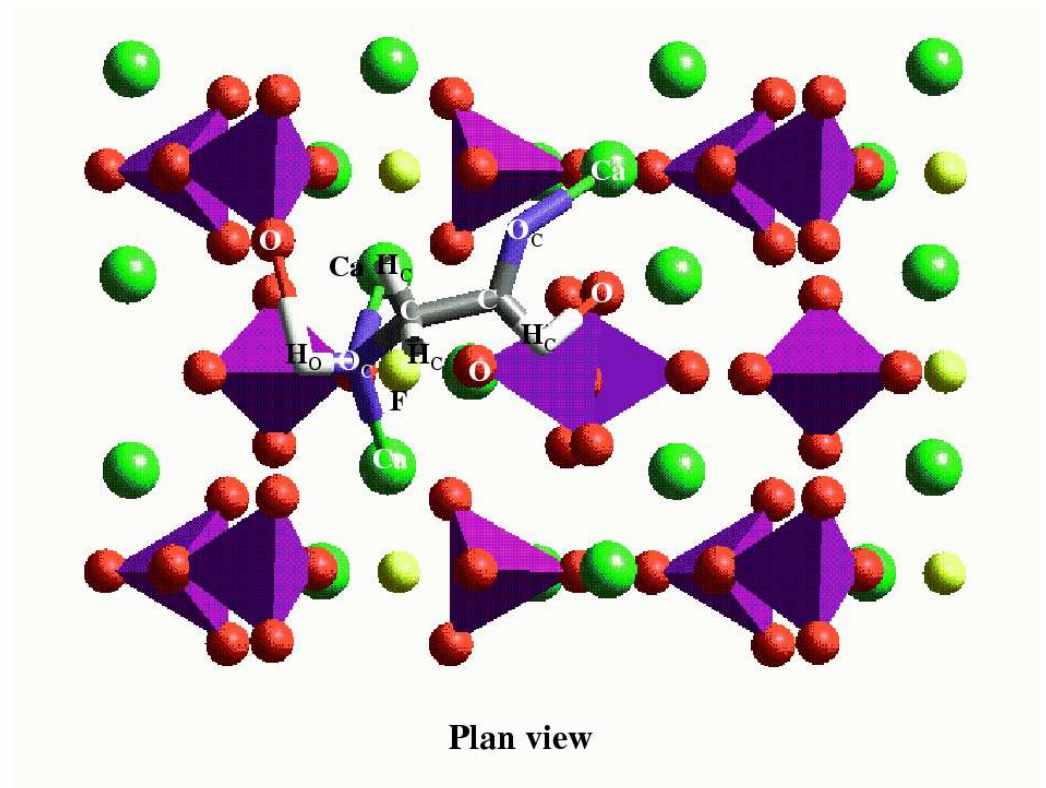
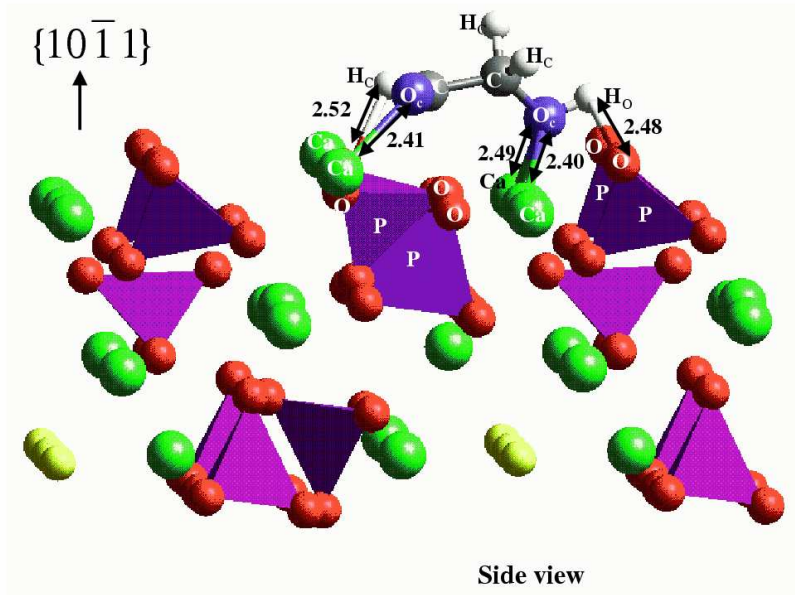


Ca bindate to the two oxygens.



Both cabonyl and hydroxyl O interact with Ca, also H to O_A and to some extent H-F

Hydroxyethanal



- Trans form preferred but rotate to mid way position between staggered and eclipse.
- Generally give the eclipse/Cis form to be most favourable interaction

Atomistic Summary

- Strongest attachments where multiple bonds are formed.
- Particularly where they can bridge between two surface Ca.
- Separating the carboxylic acid functional group into =O and –OH parts spread over two carbon atoms, lead to a greater flexibility of the molecule.
- It make the molecule better capable of forming bridging interactions between surface calcium atoms.
- Competitive adsorption with H₂O shows that methylamine will not displace water hence not suitable to be used in flotation
- Further modeling of coexisting minerals, (*tungstates, fluorides and phosphates*) will give better comparison of suitable separating molecules between them.

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