Discrete breathers and low temperature reconstructive transformations

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Nuclear waste and silicate barriers

•Nuclear waste is projected to be isolated permanently in deep geological repositories by a combination of natural and engineered barriers

- Clays are used as engineered backfill barriers due to:
    - Marked swelling
    - Cation exchange capacity (CEC) to retain radioactive nuclides
- **Some of the authors (MDA, MN, JMT) have observed that clays in contact with a lanthanide salt (simulating radionuclides) in aqueous solution transform in a lanthanide disilicate phase** [Becerro et al, J. Mater. Chem **13**, (2003)]
- This mechanism might be effective at immobilizing the radionuclides but it is necessary to know if it is independent of the CEC and swelling
- Muscovite, as a nonexpandable silicate is appropriate for that study

Reconstructive transformations in layered silicates

- In the laboratory the long times of ageing are simulated with higher temperatures
- Activation energies range typically about 200-400 kJ/mol
- They involve the breaking of the Si-O bond, stronger than that between any other element and oxygen
- Reconstructive transformations are observed in silicates only about 1000 C
- A condition for the transformation to take place is that sufficient atoms have enough energy to achieve a transition *activated state*.
- **Some of the authors (MDA, MN, JMT) have recently achieved low temperature reconstructive transformations (LTRT) at temperatures 500 C lower than the lowest temperature reported before** [Becerro et al, J. Mater. Chem **13**, (2003)]
- **THERE IS PRESENTLY NO EXPLANATION**

Reconstructive transformation of muscovite

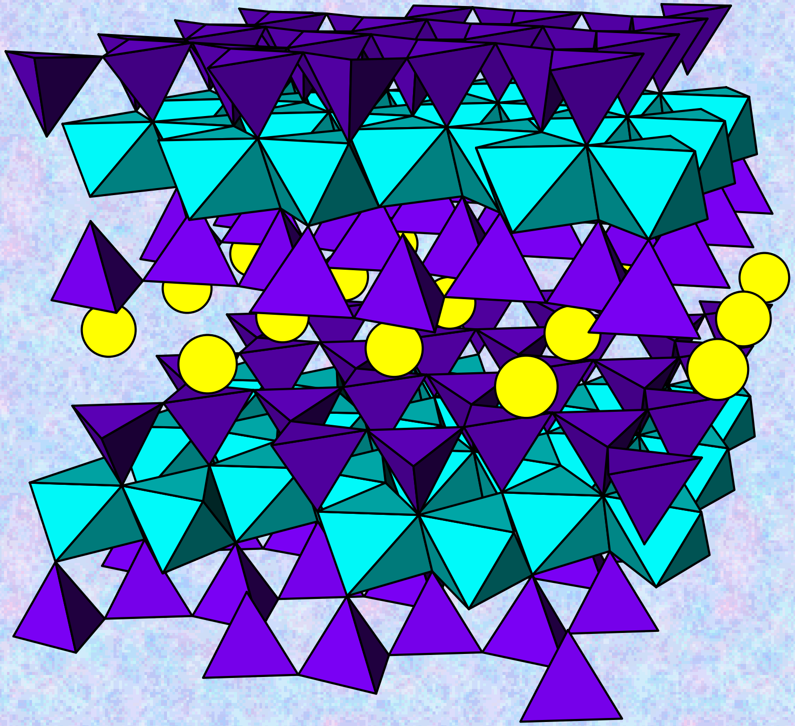
Muscovite

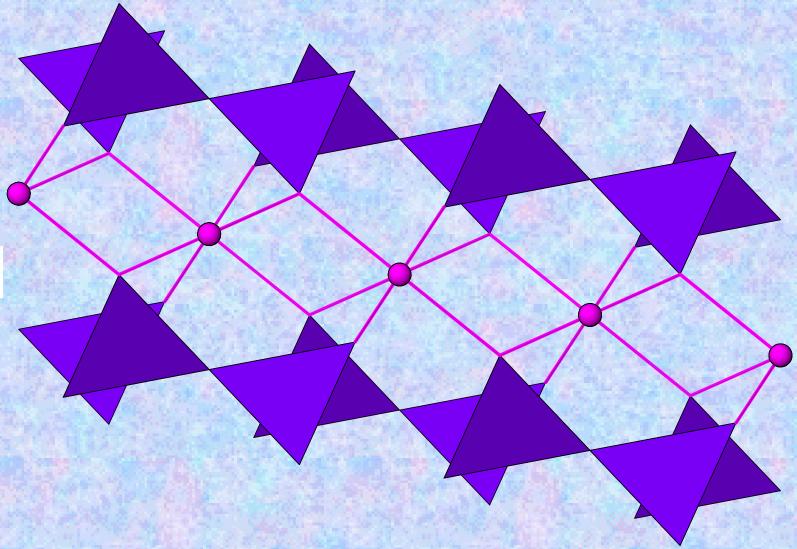
$K_2[Si_6Al_2]^{IV}[Al_4]^{VI}O_{20}(OH)_4$

Disilicate of Lutetium

$Lu_2Si_2O_7$

Lu^{3+}





300° C, 3 days

About 36% of muscovite is transformed

K^+

Some facts about LTRT

LTRT can be described by:

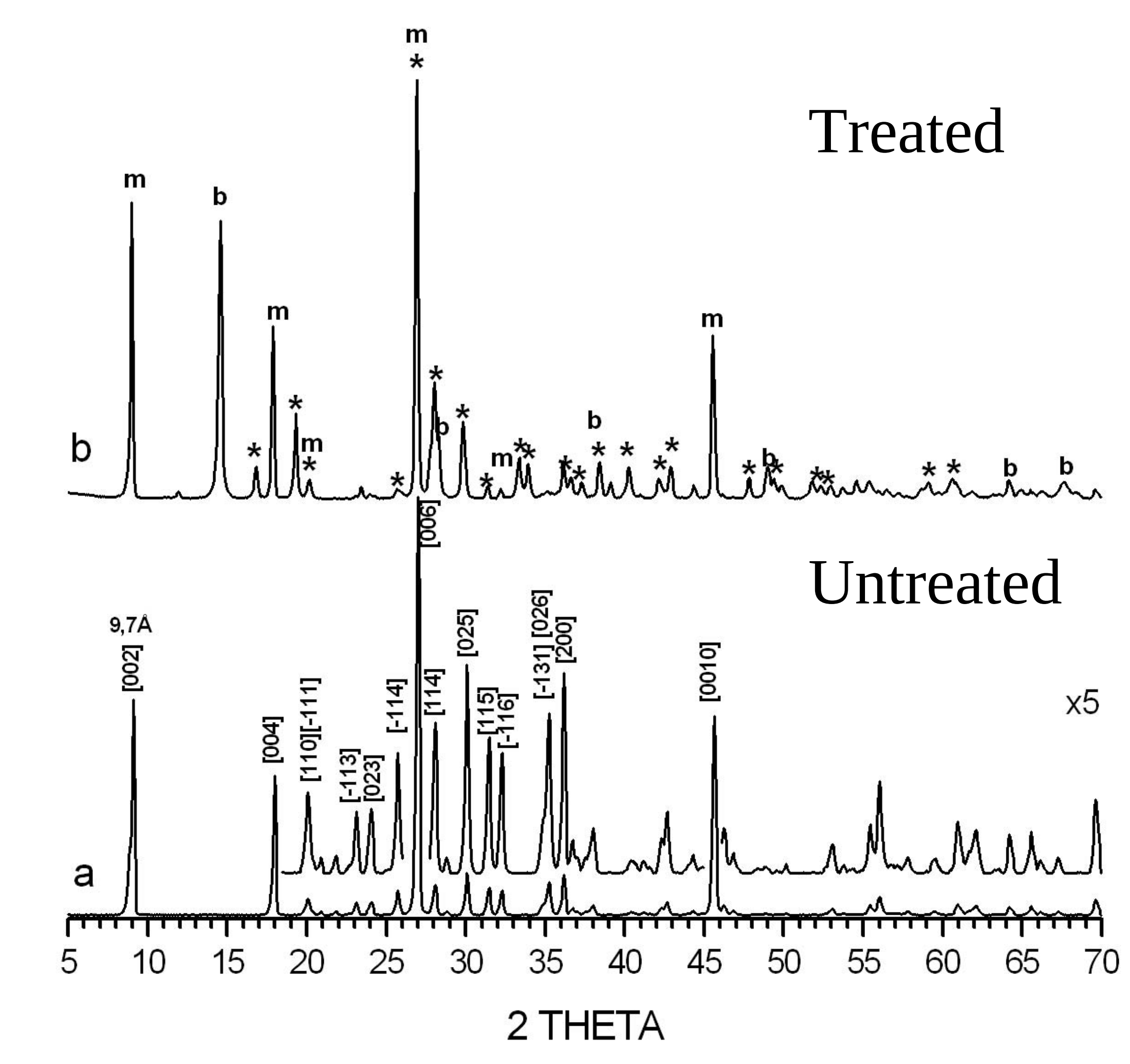
- Breaking of the Arrhenius law
- An increase of the reaction rate
- A diminution of the activation energy

No explanation has been provided for LTRT

Mackay and Aubry [Nonlinearity, **7**, 1623 (1994)] suggested the breaking of Arrhenius law as a consequence of discrete breathers

LTRT take place in the presence of a cation layer

X-Ray powder diffraction



m=muscovite, b=bohemite, *$Lu_2Si_2O_7$

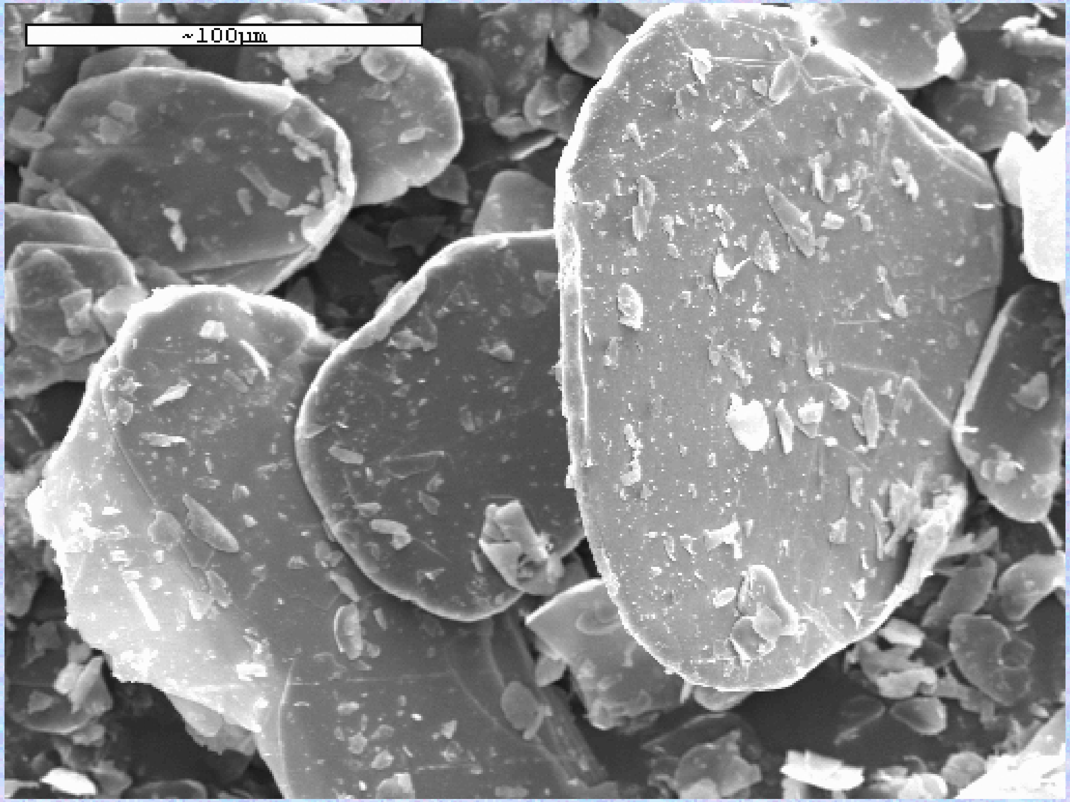
Consistent with:

- Untreated:
  - Perfect ordering
- Treated
  - Two new phases:
    - $Lu_2Si_2O_7$
    - Bohemite
- Uncomplete transformation

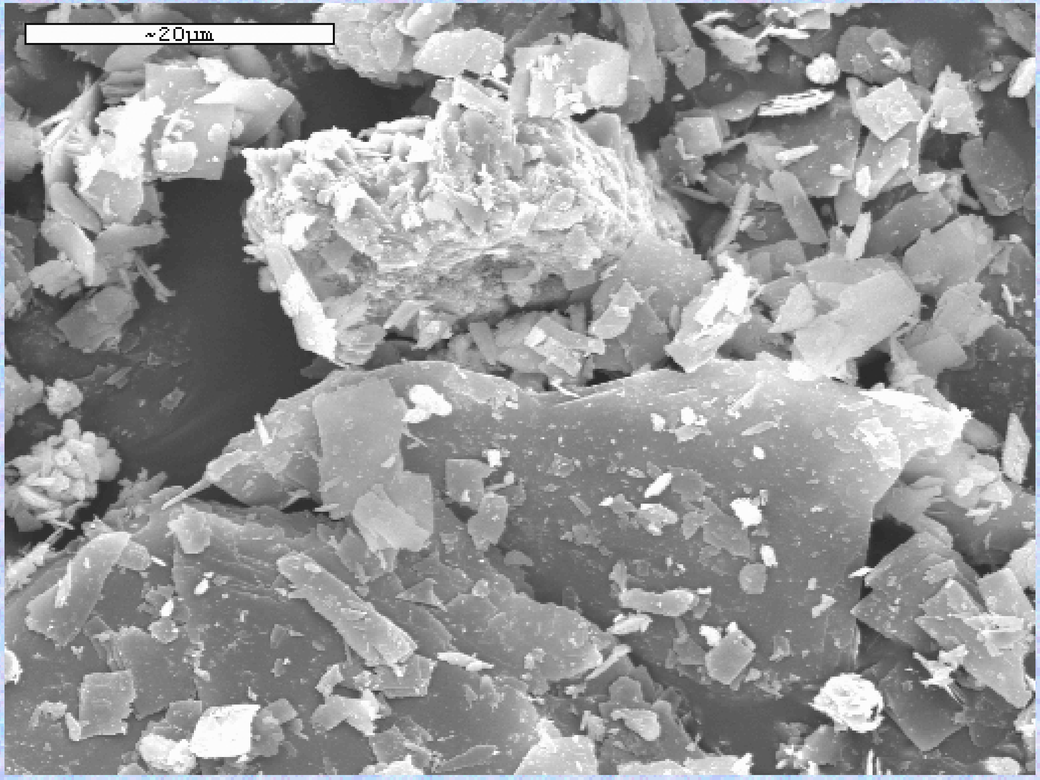
[Alba and Chain, Clays Clay Min. **53**. 39 (2005)]

Scanning electron microscopy with energy dispersive X-ray (EDX) analysis

Untreated muscovite

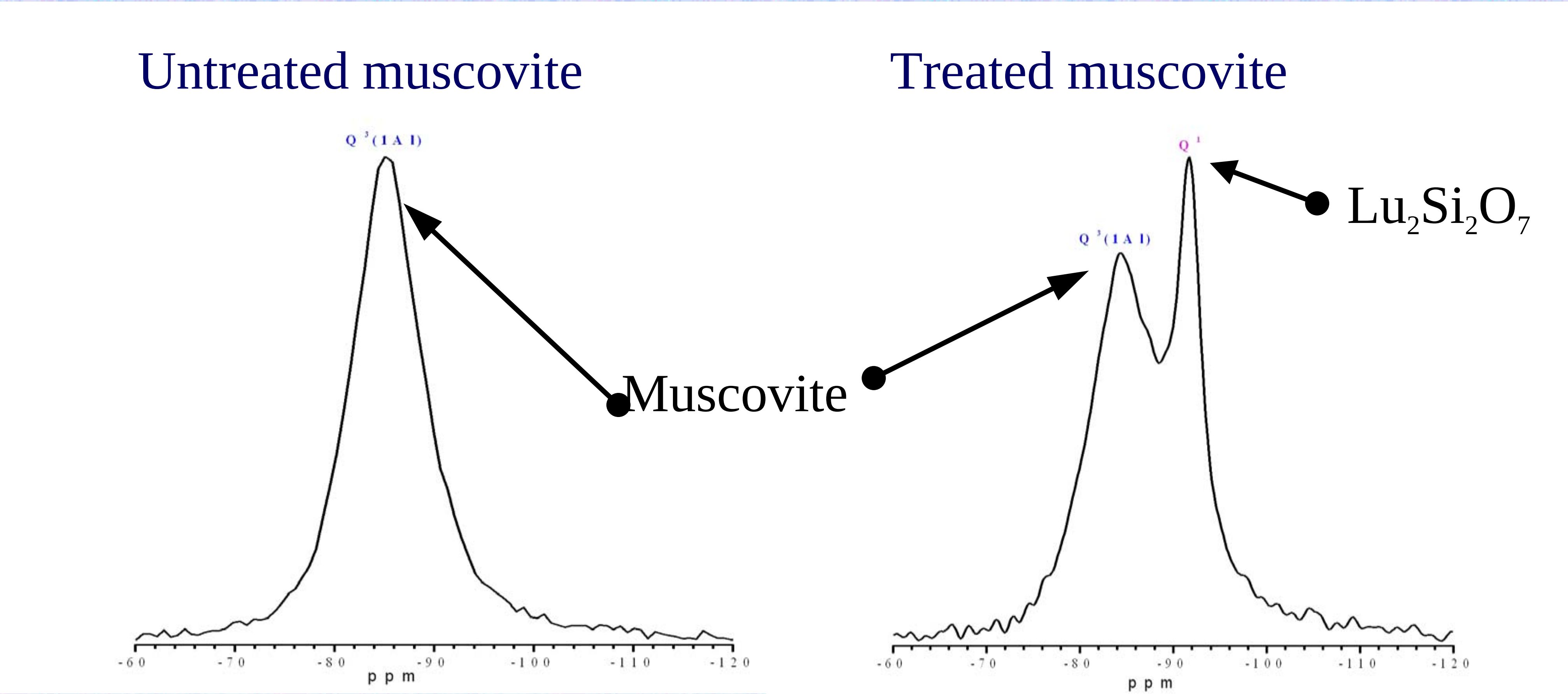


Treated muscovite



Three different types of particles: muscovite, $Lu_2Si_2O_7$ and boehmite

Nuclear Magnetic Resonance
Magic Angle Spinning for silicon



36.6% of Si has changed to the $Lu_2Si_2O_7$ phase

Discrete breather hypothesis

Adventurous but worth trying

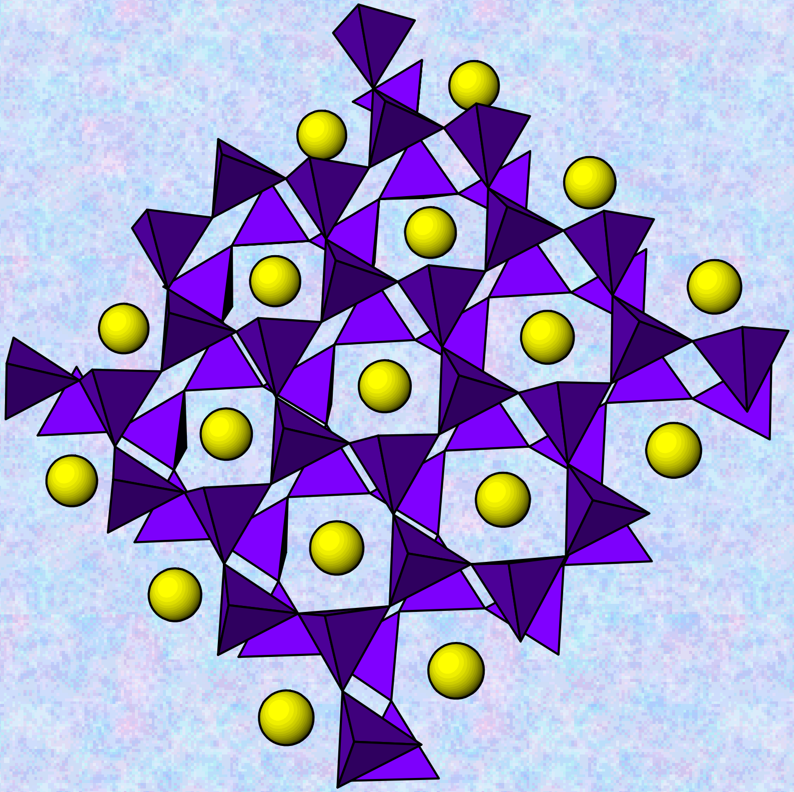
Objectives:

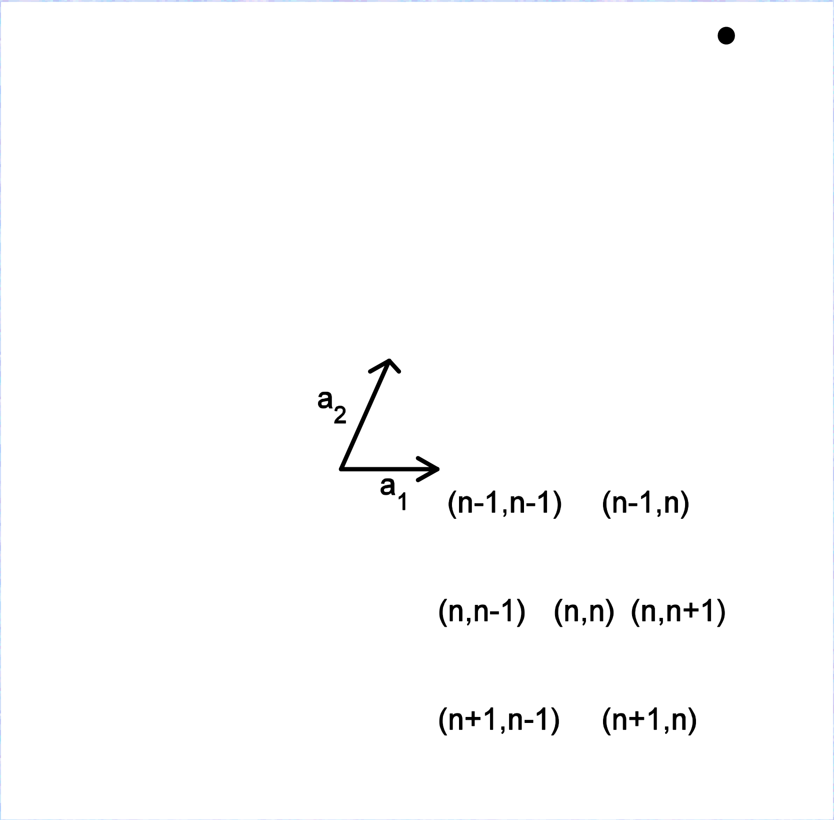
- Calculate 2D breathers in the cation layer for mica muscovite
- Obtention of their energies
- Are those energies enough to provide the increase of the reaction rate?

Problems:

- Find the vibration mode
- Construct the model
- Obtain the parameter values

Mode: vibration of K^+ perpendicular to the cation layer





Mathematical model

Hamiltonian

$$H = \sum_{\vec{n}} \left[\frac{1}{2} m \dot{u}_{\vec{n}}^{2} + V(u_{\vec{n}}) + \frac{1}{2} k \sum_{\vec{n}'} (u_{\vec{n}} - u_{\vec{n}'})^{2} \right]$$

Harmonic coupling

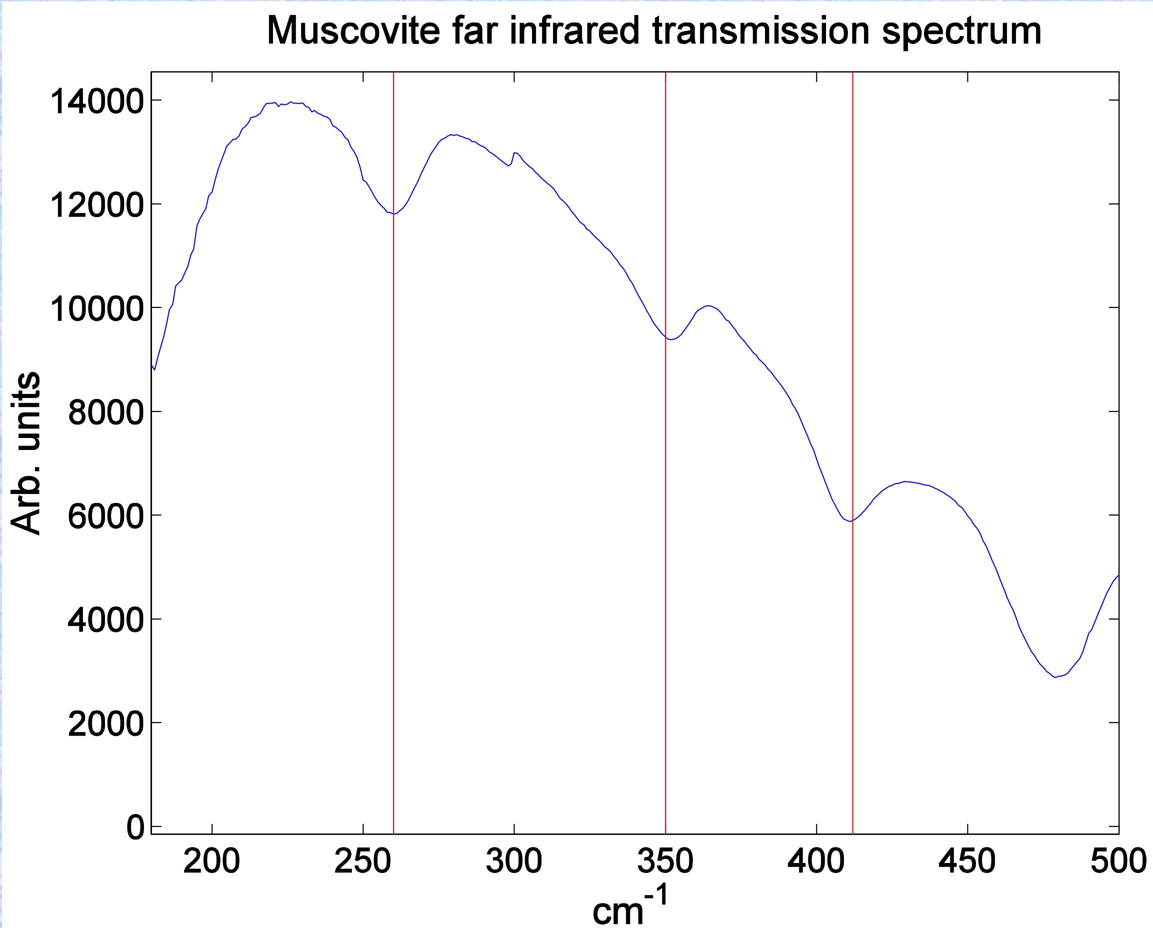
• k=10±1 N/m (D. R. Lide Ed., *Handbook of Chemistry and Physics*, CRC press 2003-2004)

On-site potential *V*

• Assignment of far infrared (30-230 cm−1) bands through dichroic experiments, [Diaz et al, *Clays Clay Miner.*, **48**, 433 (2000)] with linear frequency ν_0=143 cm^{-1}

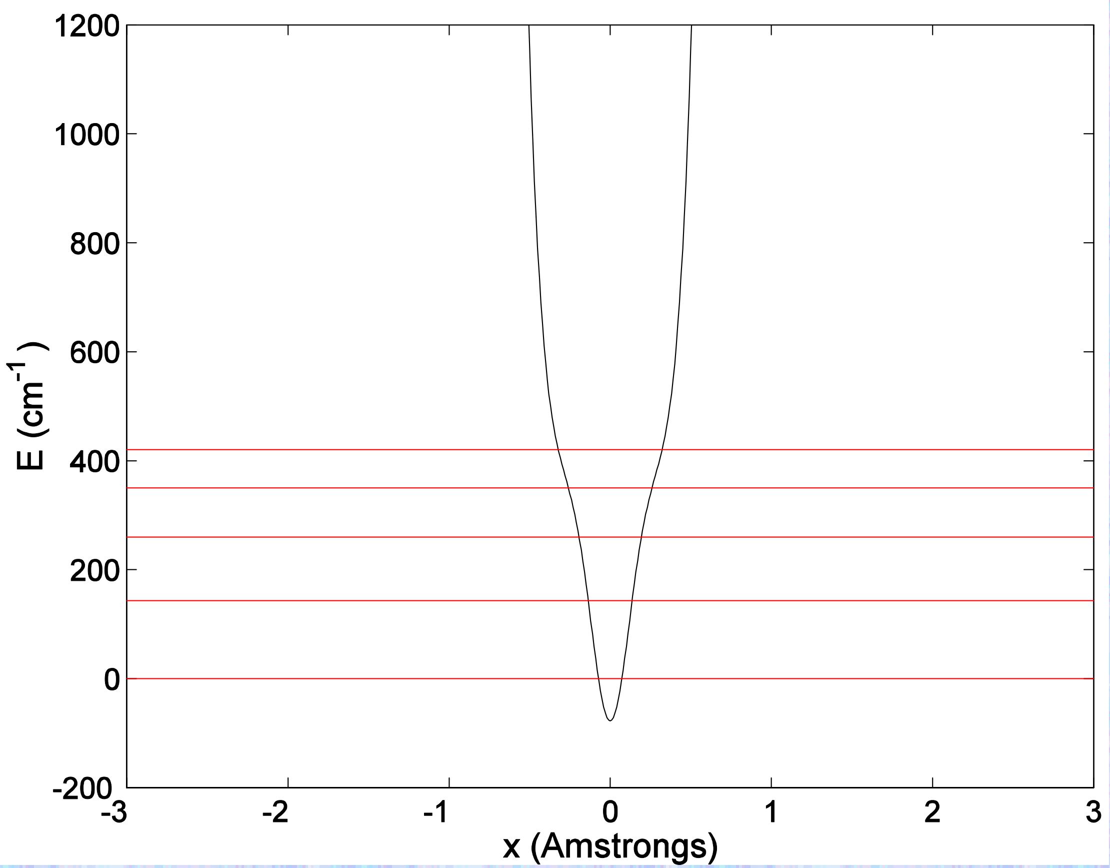
• Nonlinearity of the potential unknown

Infrared spectrum performed at LADIR-CNRS



Bands are assigned tentatively to K^+ higher order transititions

Fitting of the nonlinear on-site potential



$$V(x) = D\left([1 - \exp(- b^2 x^2)] + \gamma x^6 \right)$$

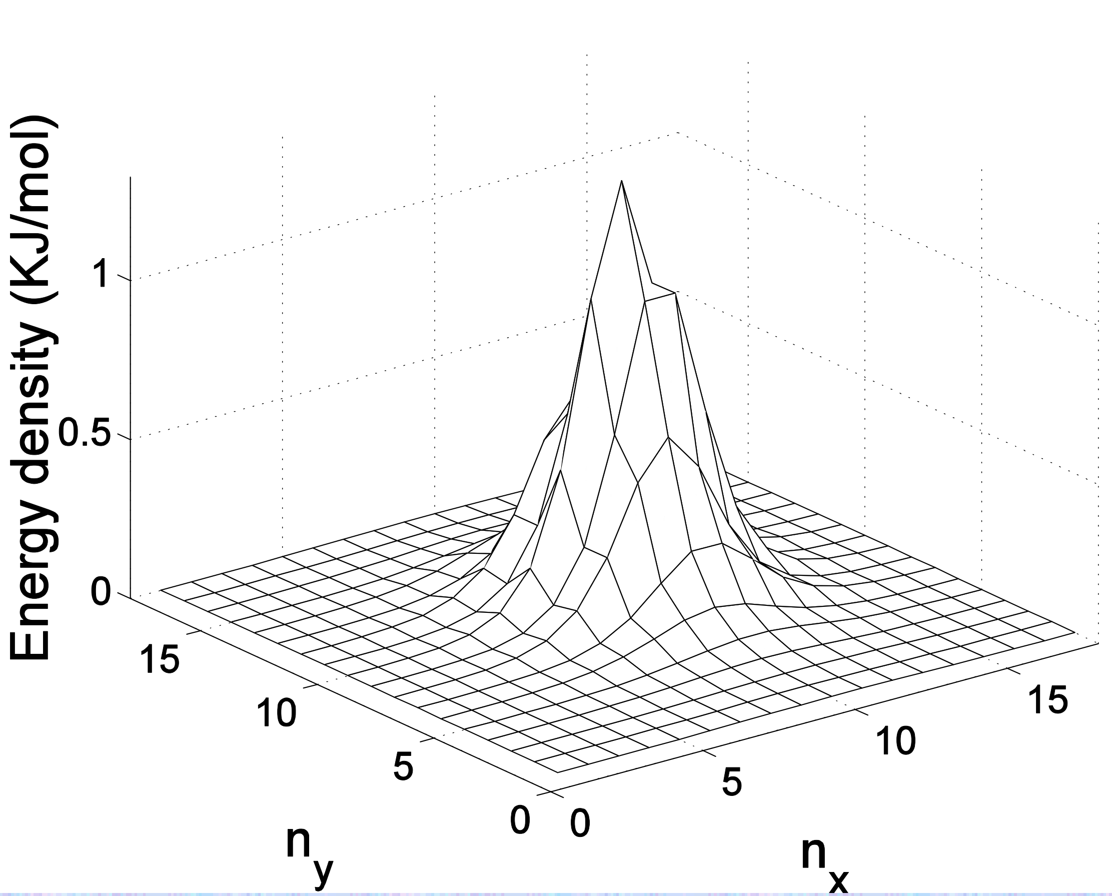
$D = 453\ cm^{-1}$

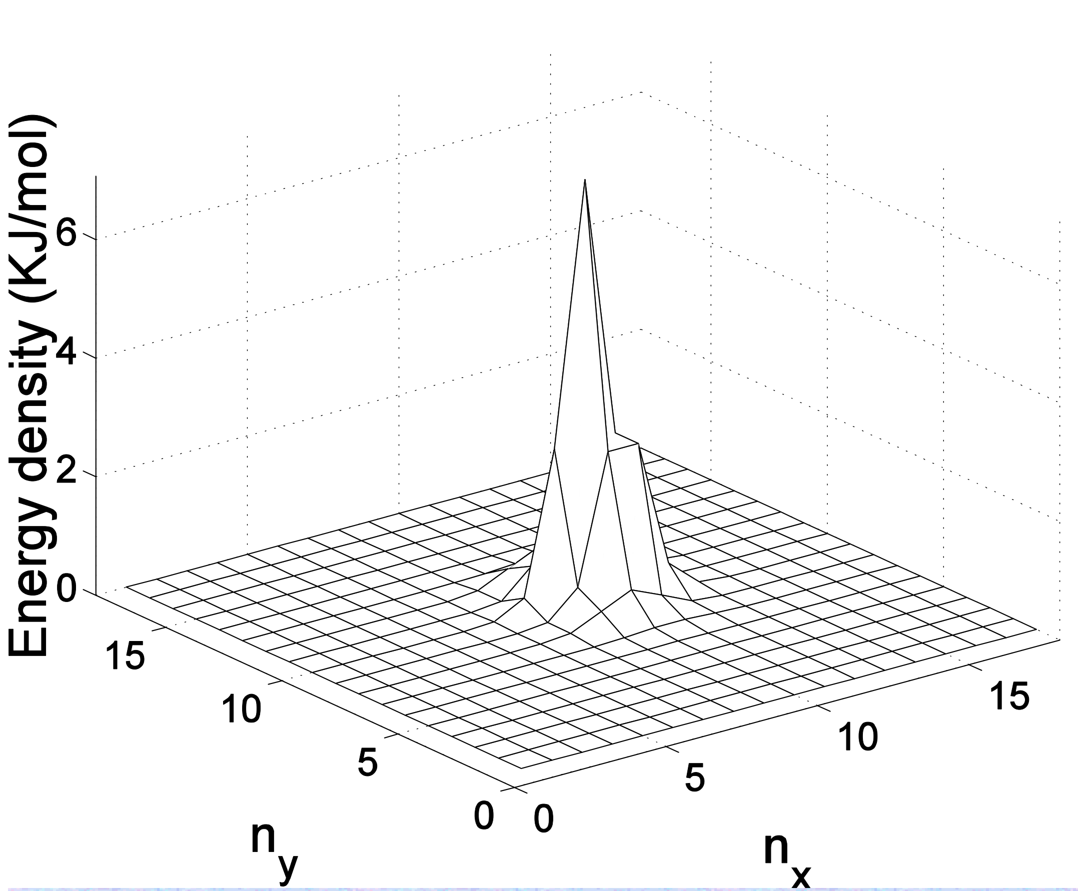
$b^2 = 36\ Å^{-2}$

$\gamma = 49884\ cm^{-1}\ Å^{-6}$

Choice consistent with the space available for K^+ 2x1.45 Å

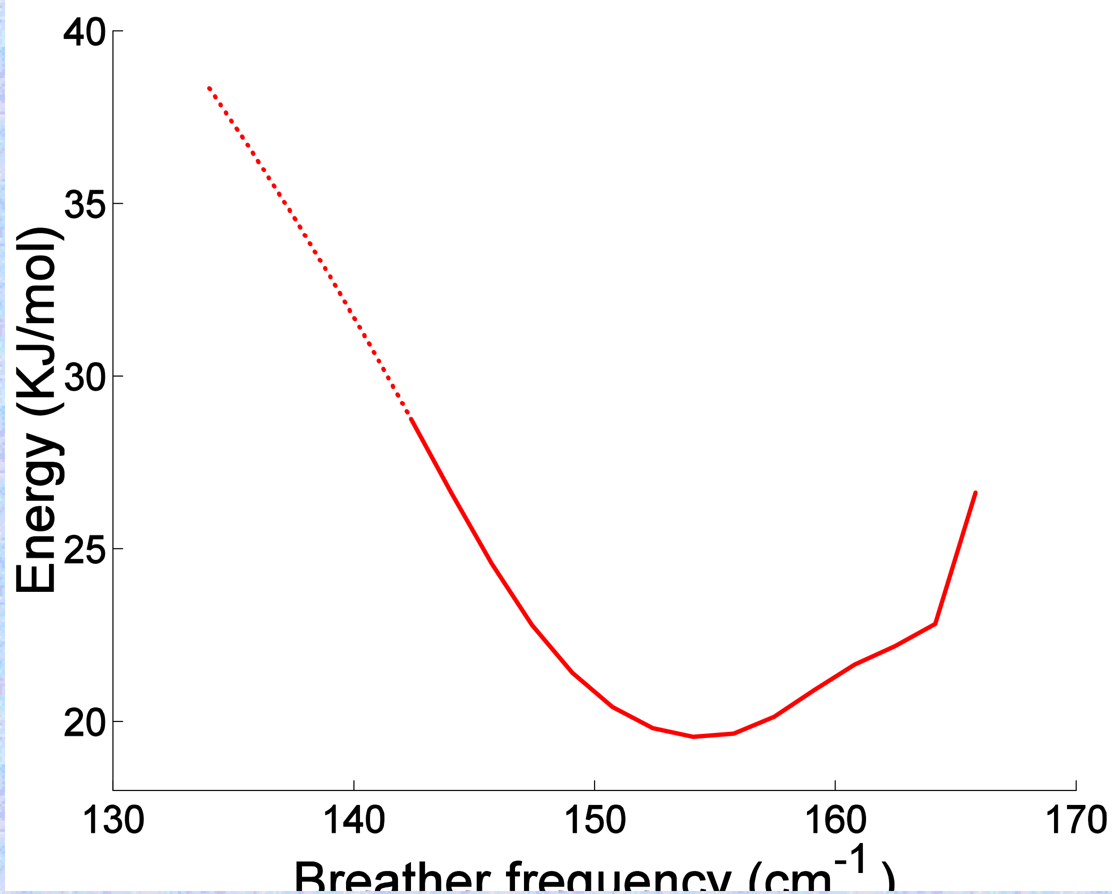
Energy density profiles for two breathers





ν_b=164.15 cm^{-1}, E =22.82 kJ/mol ν_b =142.38 cm^{-1}, E =28.75 kJ/mol

Breather energy with respect to the frequency



Existence of an energy threshold $\Delta = 20$ kJ/mol

Reaction rate and breather statistics

Arrhenius law: reaction rate: $\kappa = A \exp(-\beta E_a)$

E_a activation energy; β=1/RT

A depends on the reaction kinetics

Boltzmann factor: $\exp(-\beta E_a)$: fraction of vibrational modes above E_a

Breather statistics [Piazza et al, Chaos **13,** 589 (2003)]

Mean number of breathers per site: $\langle n_B \rangle = D \exp(-\beta\Delta)$

Fraction of breathers above E: $C(E)=\Gamma(z+1)^{-1}\,\gamma(z+1,E-\Delta)$

γ : incomplete gamma function, z~2

Fraction of breathers above E_a: $\langle n_B \rangle\, C(E_a)$

Reaction rate due to breathers:

$\kappa' = A' \langle n_B \rangle\, C(E_a)$

Approximation: $C(E_a)=B \exp(-\beta\,(E_a - \Delta'))$, B, $\Delta' > \Delta$ constants

Approximate breather reaction rate: $\kappa' = A'DB \exp(-\beta(E_a - \Delta' + \Delta))$

consistent with Arrhenius law with activation energy $E_a' = E_a - \Delta'$

Estimations

Suppose A'~A, E_a~100 kJ/mol, <n_B>~0.01, T=573 K, then:

$E_a' = E_a - 8.7$ kJ/mol, $C(E_a) \sim 10^4 \exp(-\beta E_a)$

The reaction rate with breathers is about 100 times faster

Reaction time with breathers: 3 days

Reaction time without breathers: 1 year, unobservable as occurs with most silicates

THERE ARE MUCH LESS BREATHERS THAN LINEAR MODES, BUT MUCH MORE ABOVE THE ACTIVATION ENERGY

More, A' should be greater than A as breathers can deliver energy in a more localized way, which would increase the reaction rate

CONCLUSIONS

1. Breathers in the cation layer have enough energy to overcome the activation barrier
2. There are more breathers than linear excitations with enough energy which accounts for the increase of the reaction rate observed

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