NONLINEAR DOUBLE DAY, *Sevilla, May 17-18, 2004*

Macroscopic effects of anharmonic excitations

Discrete breathers for understanding low temperature reconstructive tranformations

JFR Archilla, J Cuevas, JM Trillo and F Palmero

Nonlinear Physics Group (GFNL).
University of Sevilla, Spain.
http://www.us.es/gfnl

Known facts

LTRT can be described by:

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

No explanation has been provided for LTRT

Mackay and Aubry [Nonlinearity, 1994] suggested the breaking of Arrhenius law as a consequence of discrete breathers

LTRT take place in the presence of a cation layer

Discrete breathers hypothesis

Adventurous but worth trying

Objectives:

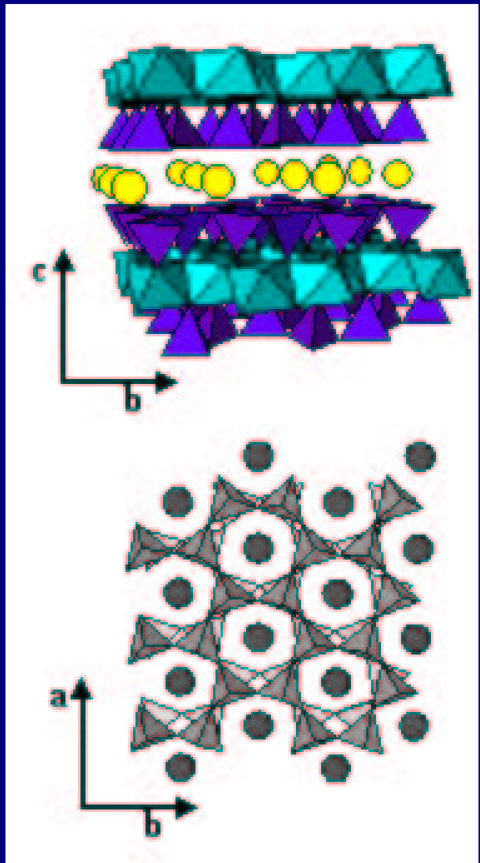
- Calculate 2D breathers in the cation layer for mica muscovite
- Obtention of their energies
- Are those energies enough to provide the increase of the reaction rate?

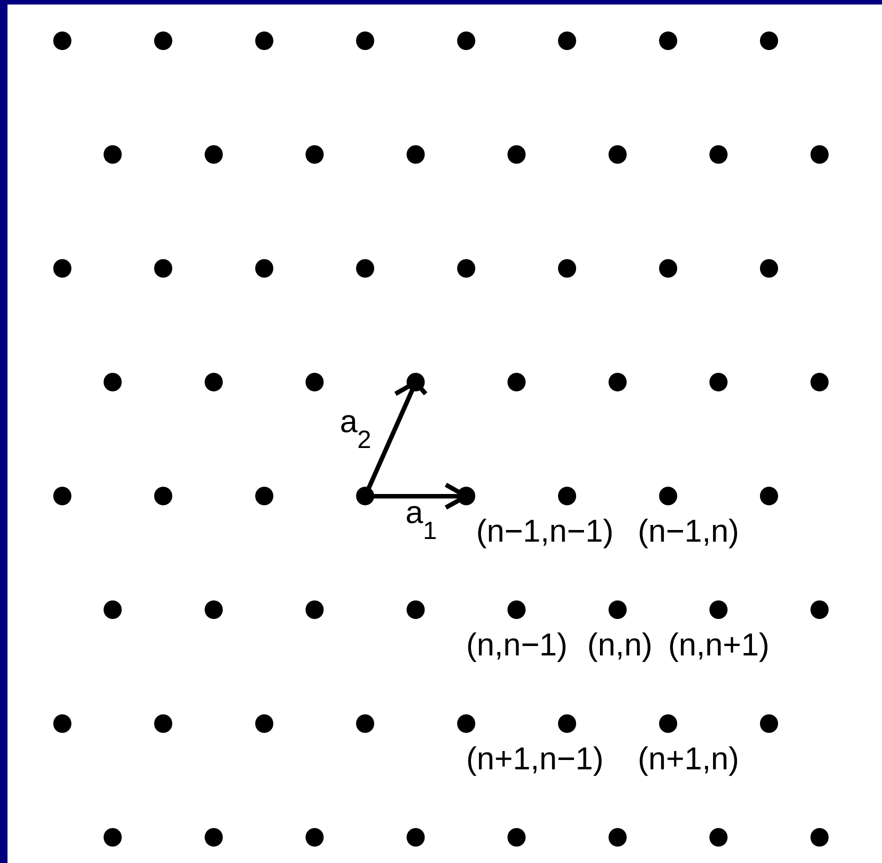
Problems:

- Choose a vibration mode
- Construct the model
- Obtain the parameter values

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

Geometry of the K^+ layer





Mathematical model

Hamiltonian

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

Harmonic coupling

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

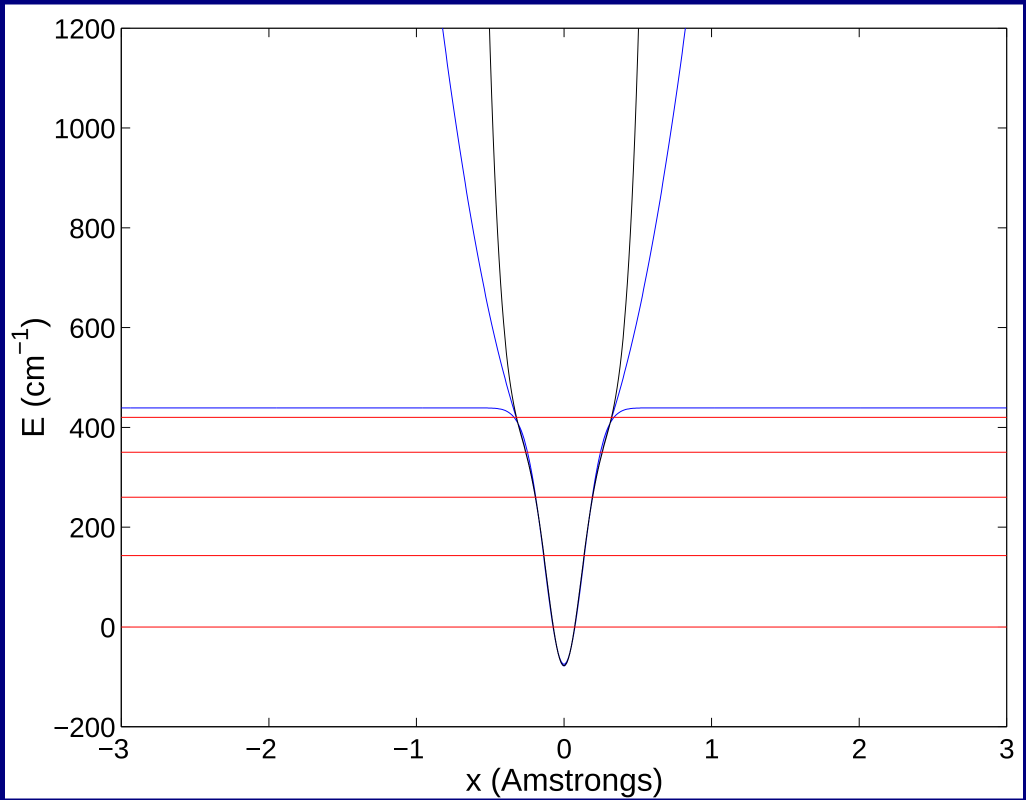
On-site potential V

- Assignment of far infrared (30-230 cm^{-1}) bands through dichroic experiments, [Diaz et al, *Clays and clay Miner.* **71**, 701]
- Linear frequency ω_o=143cm^{-1}
- Nonlinearity of the potential unknown

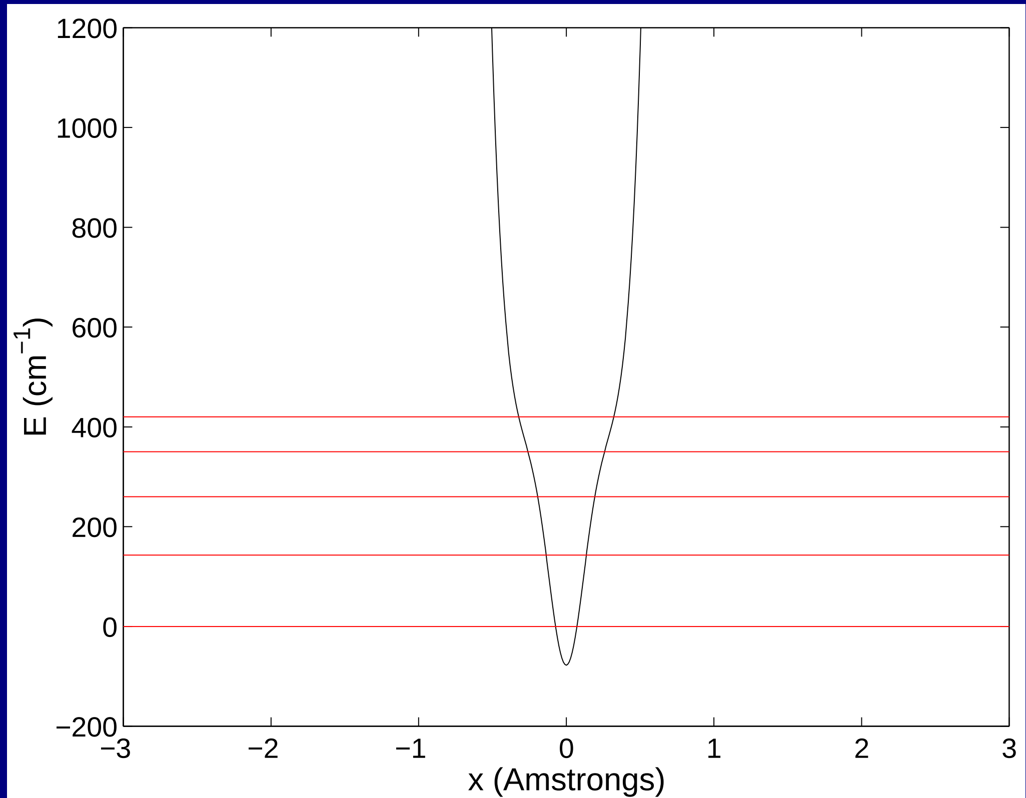
Infrared spectrum at LADIR-CNRS

On site potentials

- Fitting of the on-site potentials to the observed IR bands
- Method: *Crystal structures and proton dynamics in potassium and cesium hydrogen bistrifluoroacetate salts with strong symmetric hydrogen bonds* A Cousson, JFR Archilla, J Tomkinson and F Fillaux, submitted `physics/0404083`.



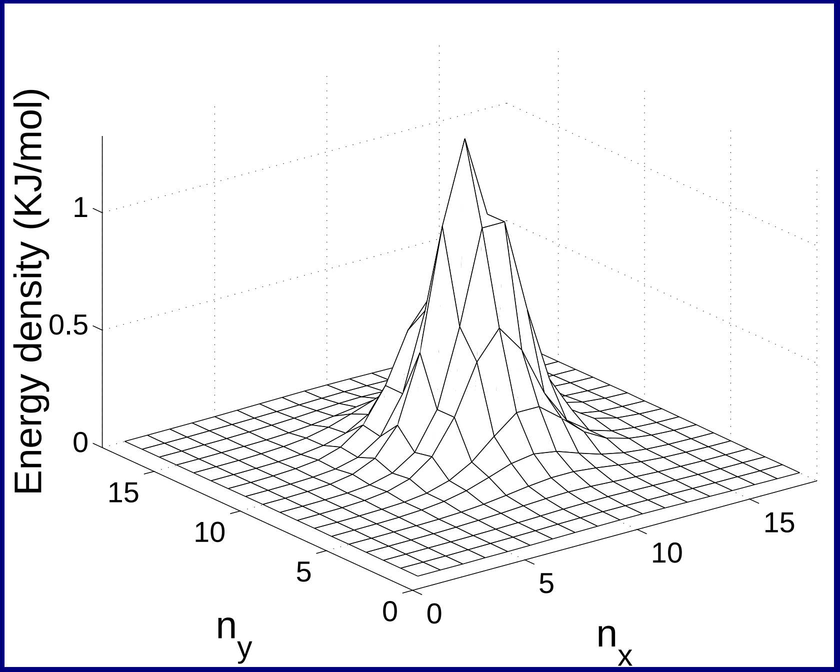
Choice of the on-site potential

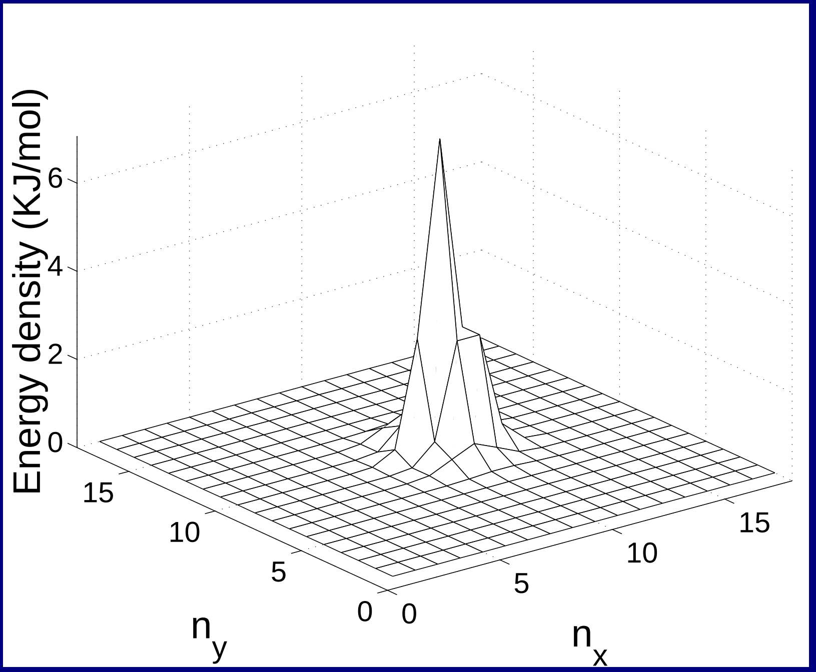


- $V(x) = D(1 - \exp(-b^2x^2)) + \gamma x^6$
- D=453cm^{-1}, b^2=36 Å^{-2}, γ=49884cm^{-1}Å^{-6}
- Consistent with the space available to the K$^+$: 2×1.45Å

Breather profiles

Energy density profiles for breathers



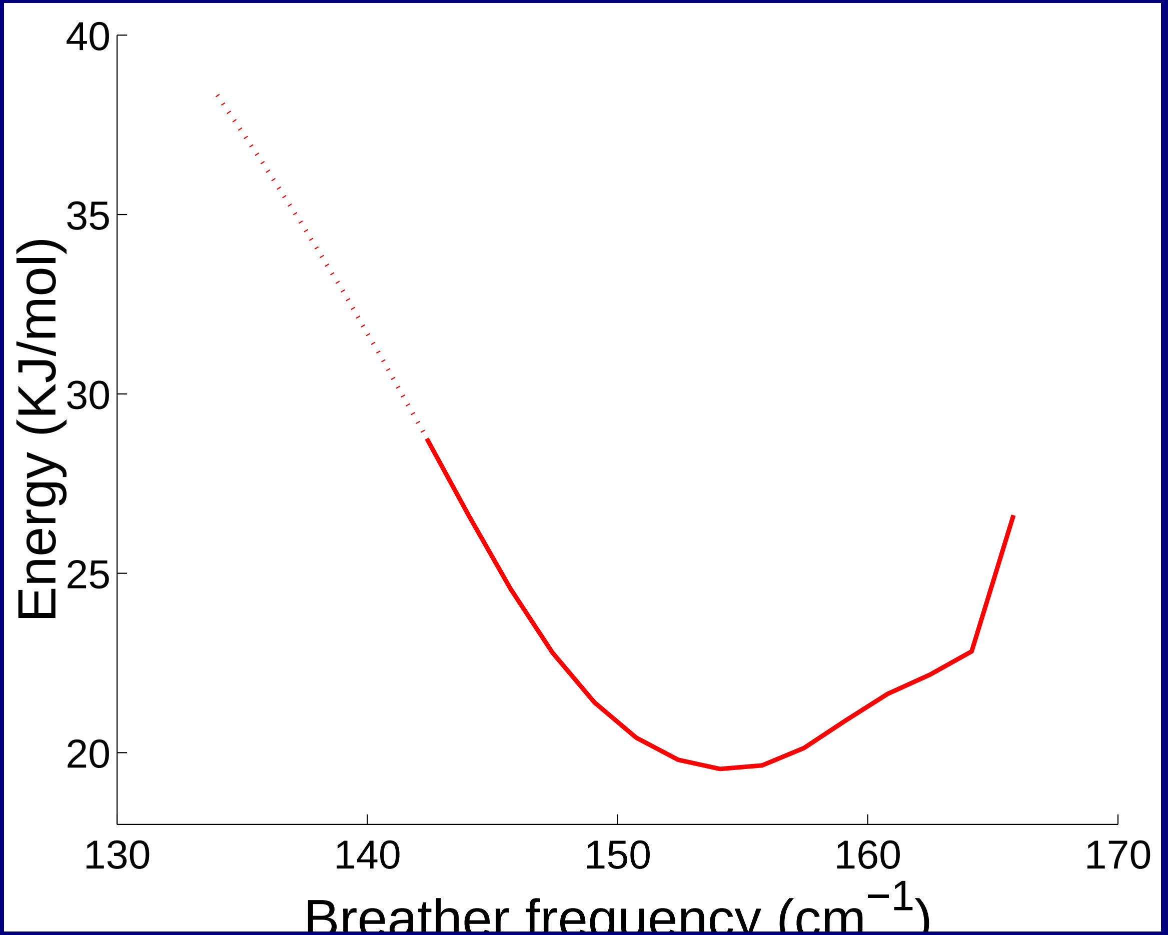


$\nu_{\mathrm{b}} = 164.15\,\mathrm{cm}^{-1}$ E=22.82 KJ/mol

$\nu_{\mathrm{b}} = 142.38\,\mathrm{cm}^{-1}$ E=28.75 KJ/mol

Breather energies

Energy with respect to the frequency



Decrease of the activation energy

Arrhenius law:

Reaction rate: $$k = A\exp(-\frac{E_a}{RT})$$

Breather energy: ΔE_a

New reaction rate: $$k' = A\exp(-\frac{E_a - \Delta E_a}{RT})$$

Increase of the reaction rate

$$\frac{k'}{k} = \exp(\frac{\Delta E_a}{RT})$$

Several hundreds of times faster

CONCLUSION

Breathers in the K^+ layer have enough energy to provide the observed increase of the reaction speed

PROBLEMS

Quantum breathers?

Is the band assignment correct?

Mechanism for the transmission of energy?

Discrete breathers for understanding reconstructive mineral processes at low temperatures, J Cuevas, JFR Archilla, MD Alba, M Naranjo and JM Trillo. Submitted, `arXiv:nlin.PS/0404030`.