STICKING OF AN H ATOM ON A GRAPHITE SURFACE

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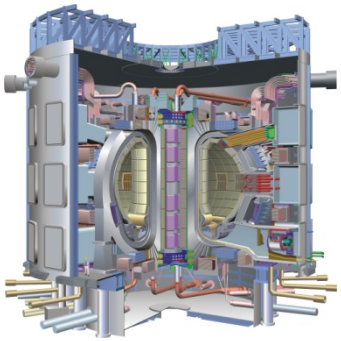


DOMAINS OF INTEREST

High energy domain (>10 eV)

Tokamak

=> the inner walls are in graphite

=> H retention is observed

=> Fusion reaction: T will used

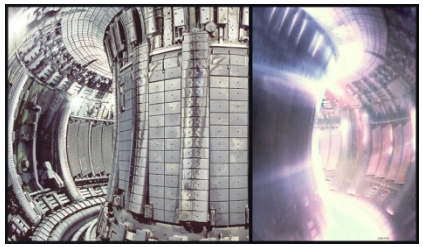
=> safety problems

Low energy domain (<1eV)

Interstellar Medium

=> H_2 formation on a dust grain (graphite) through a Eley Rideal (ER) mechanism can explain the molecular abundance

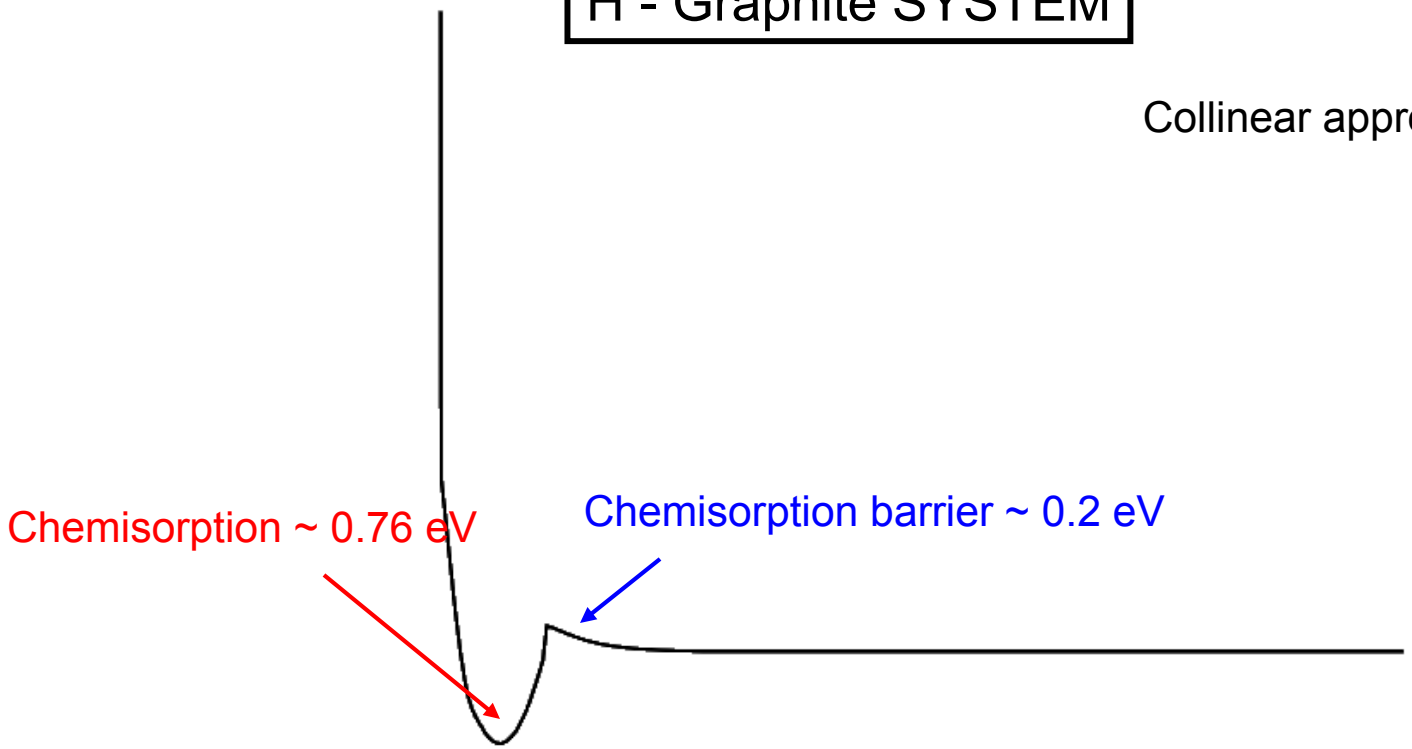
=> H must initially be chemisorbed



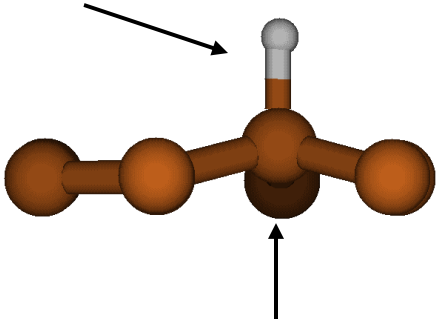
How does the H atom stickon a graphite surface ?

H - Graphite SYSTEM

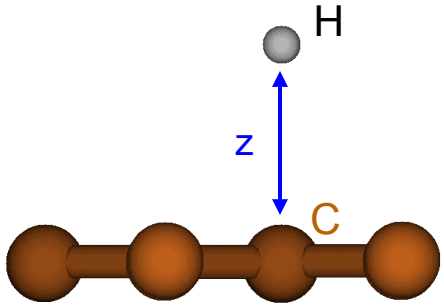
Collinear approach (z coordinate)



H chemisorbed on the C atom

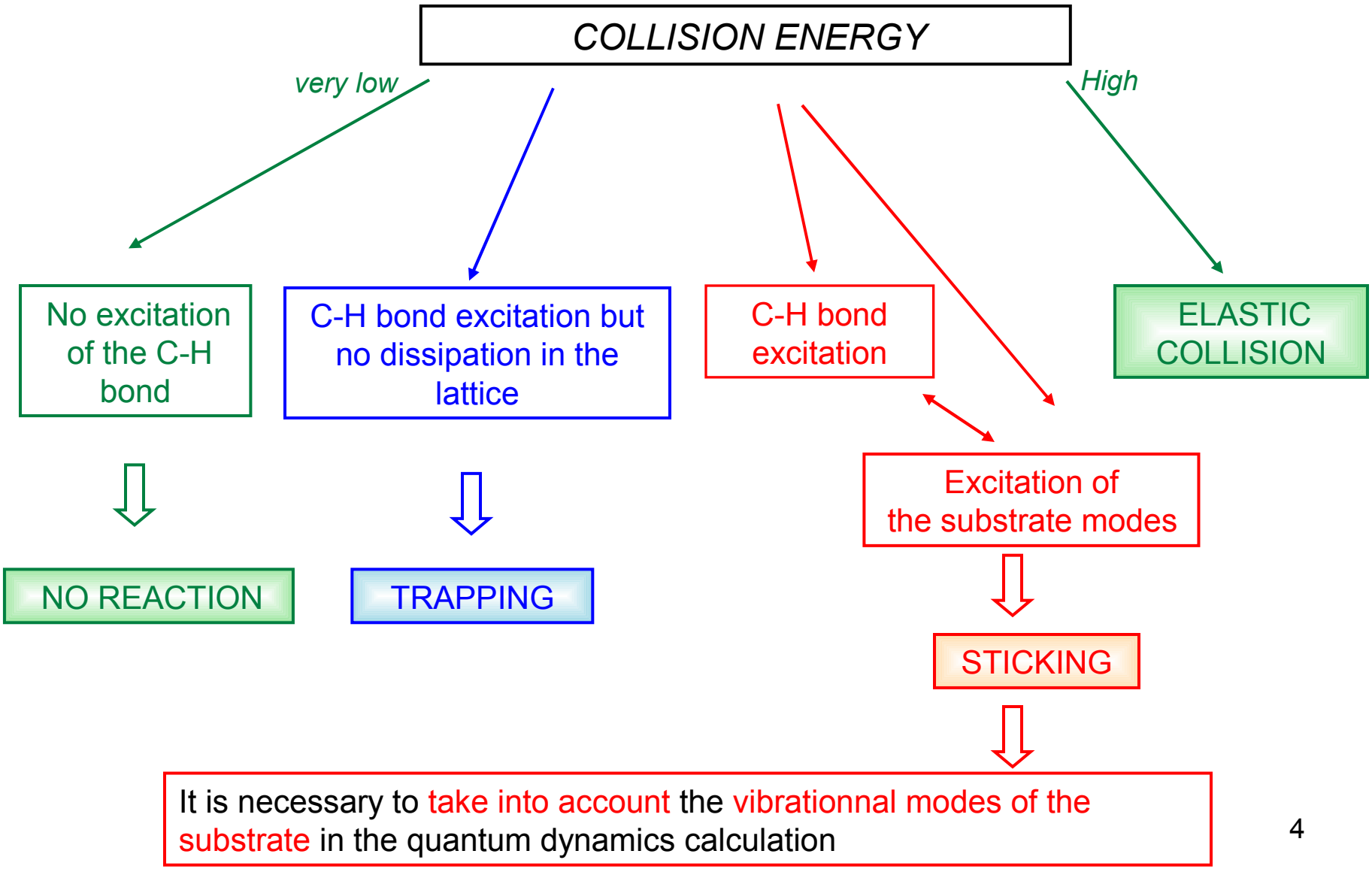


Surface reconstruction



L. Jeloaica & V. Sidis Chem. Phys. Lett. 300 157 (1999)
X. Sha, B. Jackson, D. Lemoine J. Chem. Phys. 116 7158 (2002)
Y. Ferro & A. Allouche Chem. Phys. Lett. 368 609 (2003)

SYSTEM


COLLISION ENERGY
very low
High
No excitation of the C-H bond
C-H bond excitation but no dissipation in the lattice
C-H bond excitation
ELASTIC COLLISION
Excitation of the substrate modes
NO REACTION
TRAPPING
STICKING
It is necessary to take into account the vibrationnal modes of the substrate in the quantum dynamics calculation

METHODS OF COMPUTATION

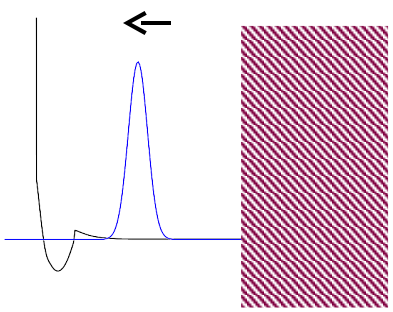
Density Functional Theory (DFT)

→ H - graphite interaction potential

→ phonons modes of graphite and H - graphite systems

Close Coupling Wave Packets (CCWP)

→ Numerical Resolution of the time dependant Schrödinger equation



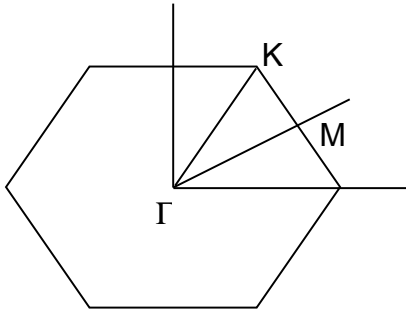
→ Time propagation: Lanczos method

→ Action of the kinetic operator on wave function : Fourier method

→ To avoid reflections on the edge on the grid: absorbent potential

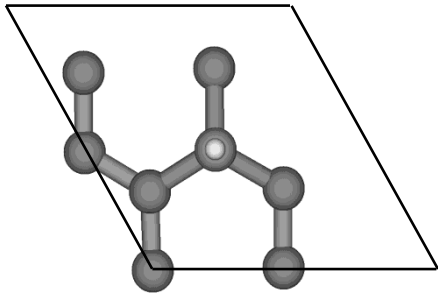
→ WP is analyzed in the asymptotic zone: flux analysis method

DFT + CCWP ⟶ allow obtaining sticking probabilities

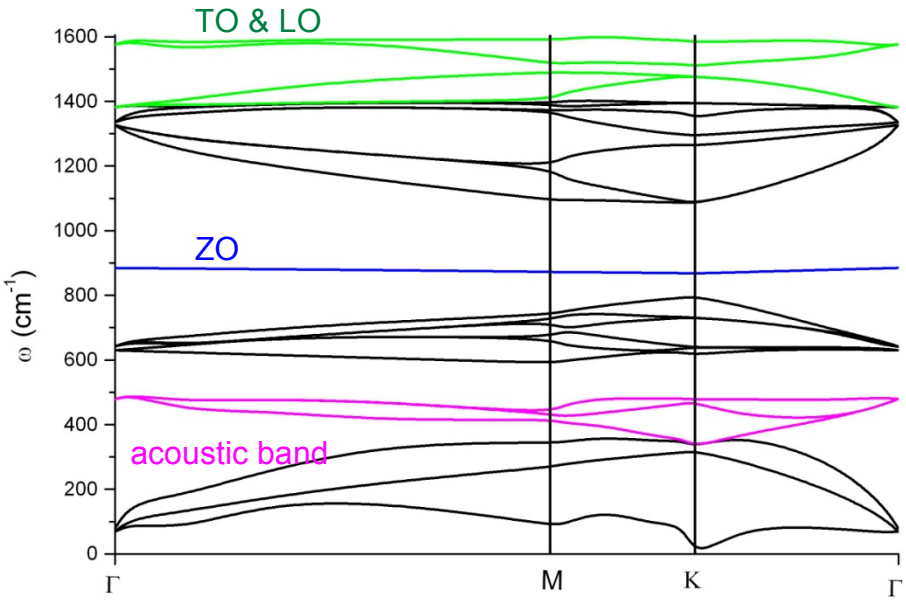


DFT Calculation

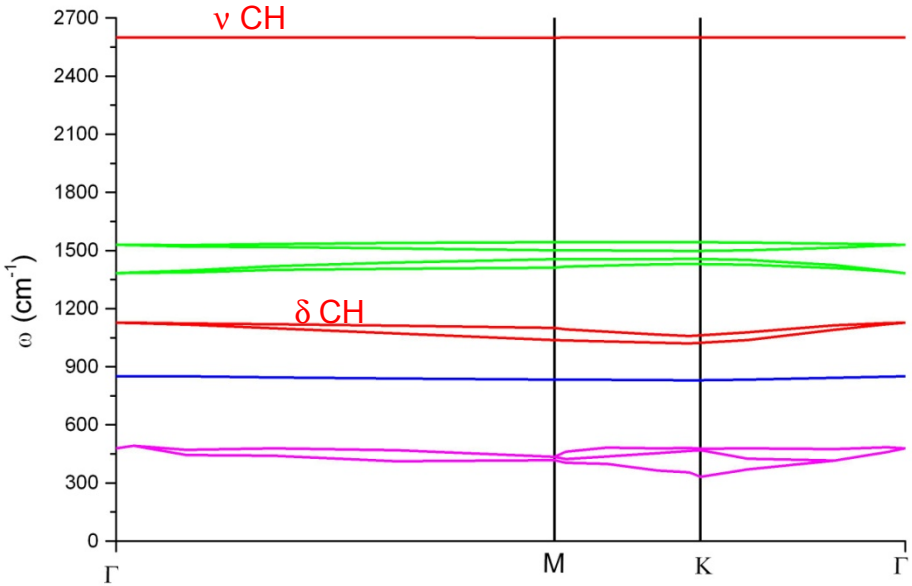
Phonons Dispersion (harmonic approximation)



Graphite



Hydrogen - Graphite



⇒11 phonon bands include in dynamic

⇒ 61 phonon modes by bands include in dynamic

Quantum Dynamics Calculations
Hamiltonian

One-phonon approximation

Kinetic energy operator

$$T = \frac{P^2}{2m}$$

Lattice dynamics Hamiltonian

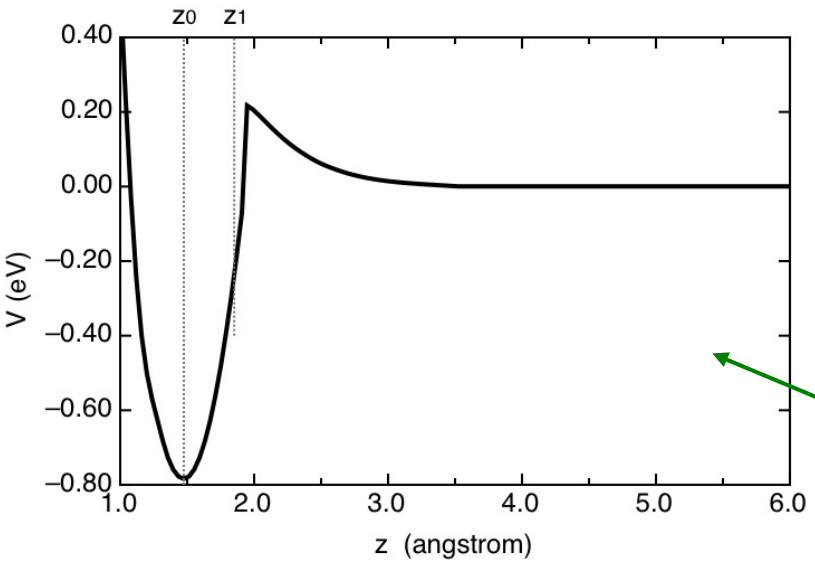
$$H_b = \sum_{\vec{k},j} \hbar w_j(\vec{k}) \left(a^{+}_{\vec{k}j} a_{\vec{k}j} + \frac{1}{2} \right)$$

$$H = T + \underbrace{V_0 + V_{mb}}_{\text{Potential Operator}} + H_b$$

$$V_{mb} = \sum_{\vec{k},i} g_{\vec{k}i}(z) \left(a^{+}_{\vec{k}i} + a_{\vec{k}i} \right)$$

→ Coupling between the H motion with the bath of phonons

DFT calculation
Coupling between the H motion and the bath of phonons



One-phonon approximation

$$V\left(z_0,\{u_j\}\right) = V_0\left(z_0,\{u_j^{rel}\}\right) + \underbrace{\sum_{i=1} \left.\frac{\partial V\left(z_0,\{u_j\}\right)}{\partial u_j}\right|_{u_j = u_j^{rel}} \left(\vec{u}_j - \vec{u}_j^{rel}\right)}_{\text{DFT phonon calculation}}$$

static potential (DFT)

$$V_{mb} = \sum_j \nabla_j V\left(z_0,\{u_j\}\right)\left(\vec{u}_j - \vec{u}_j^{rel}\right)$$

$$\approx \sum_{j,k,i} \vec{\nabla}_j V\left(z_0,\{u_j\}\right)\sqrt{\frac{\hbar}{2m\omega(\vec{k})}}\,\varepsilon_i^j(\vec{k})\,e^{i\vec{k}.\vec{R}_j}\left(a_{\vec{k}i}^{+} + a_{\vec{k}i}\right) = \sum_{k,i} g_{\vec{k}i}(z_0)\left(a_{\vec{k}i}^{+} + a_{\vec{k}i}\right)$$

Dynamical matrix diagonalization

"COUPLING TERM"

DFT calculation
How calculated the « COUPLING TERMS » ?

DFT ⟶ dynamical matrix

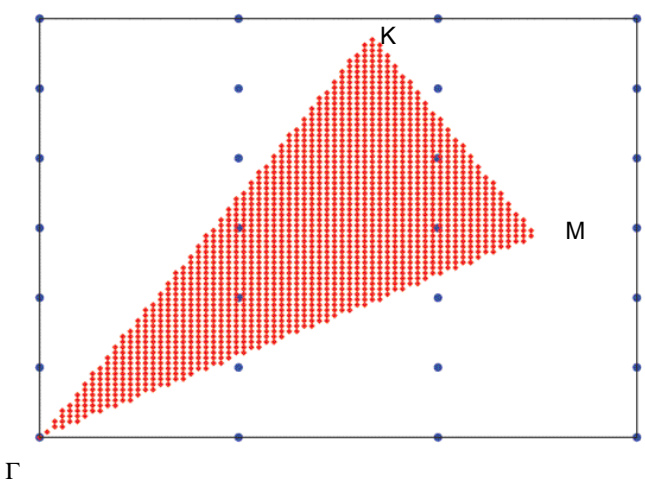
Quantum dynamic calculation : phonons dispersion in all the Irreducible Brillouin zone

→ Interpolation of the dynamical matrix by spline method

→ frequencies and polarization vectors obtained by this matrix diagonalization

→ construction of $u_j(k)$ => U

→ V= U^+ D U



Bleu : DFT
Rouge : Interpolation

$$g_{kj}^{\vec{}}(z_0) = \sum_j \left.\frac{\partial V\left(z_0,\{u_j\}\right)}{\partial u_j}\right|_{u_j = u_j^{rel}} \sqrt{\frac{\hbar}{2m\omega(\vec{k})}}\,\varepsilon_i^j(\vec{k})\,e^{i\vec{k}.\vec{R}_j}$$

Quantum Dynamics Calculation

Hamiltonian

Kinetic energy operator

Lattice dynamics Hamiltonian

$$H = T + \underbrace{V_0 + V_{mb}}_{\text{Potential Operator}} + H_b$$

$$V_{mb} = \sum_{k,i} g_{ki}^{\rightarrow}(z)\left(a_{ki}^{+} + a_{ki}^{\rightarrow}\right)$$

$$H_b = \sum_{k,j} \hbar w_j(\vec{k})\left(a_{kj}^{+} a_{kj}^{\rightarrow} + \frac{1}{2}\right)$$

Wave function

Sum = elastic wave function + creation of one-phonon + annihilation of one-phonon

$$|\Psi\rangle = \left[\left|\Psi^{(0)}\right\rangle + \sqrt{\frac{1}{N}}\sum_{k,j}\left(\left|\Psi_{kj}^{\rightarrow(+)}\right\rangle a_{kj}^{+} + \left|\Psi_{kj}^{\rightarrow(-)}\right\rangle a_{kj}^{\rightarrow}\right)\right]|p\rangle$$

=> Close Coupling Wave Packets (CCWP) approximation

Quantum Dynamics Calculation

System to resolve:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\vec{\Psi}$$

with : $\vec{\Psi} = \begin{pmatrix} \Psi^{(0)}(z,t) \\ \Psi_{11}^{(+)}(z,t) \\ \vdots \\ \Psi_{MN}^{(+)}(z,t) \\ \Psi_{11}^{(-)}(z,t) \\ \vdots \\ \Psi_{MN}^{(-)}(z,t) \end{pmatrix}$

Elastic channel function

Inelastic channel functions :
- creation of one-phonon
- annihilation of one-phonon

H matrix :

$$H = \begin{pmatrix} T+V & \frac{1}{N} g_{11}(z)(n_{11}+1) & \cdots & \frac{1}{N} g_{MN}(z)(n_{MN}+1) & \frac{1}{N} g_{11}(z) n_{q1} & \cdots & \frac{1}{N} g_{MN}(z) n_{MN} \\ g_{11}(z) & T+V+\hbar\omega_{11} & 0 & \cdots & \cdots & \cdots & 0 \\ \vdots & 0 & \ddots & \ddots & \ddots & \ddots & \vdots \\ g_{MN}(z) & \vdots & \ddots & T+V+\hbar\omega_{MN} & \ddots & \ddots & \vdots \\ g_{11}(z) & \vdots & \ddots & \ddots & T+V-\hbar\omega_{11} & \ddots & \vdots \\ \vdots & \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ g_{MN}(z) & 0 & \cdots & \cdots & \cdots & 0 & T+V-\hbar\omega_{MN} \end{pmatrix}$$

with the phonon population $n_{\vec{k}} = \left[e^{\hbar w(\vec{k})/k_B T} - 1 \right]^{-1}$

Quantum Dynamic Calculation
Hermiticity

Why is not H Hermitian ?

$\longrightarrow$ choice of development $|\Psi\rangle$ $\longrightarrow$ one phonon exchange approximation

$$|\Psi^{(0)}\rangle = |\Phi^{(0)}\rangle$$

Transformation of H non-Hermitian into Hermitian :

$$|\Psi^{(+)}\rangle = \sqrt{\frac{N}{(n_{qj}+1)}}\,|\Phi^{(+)}\rangle$$

$$|\Psi^{(-)}\rangle = \sqrt{\frac{N}{n_{qj}}}\,|\Phi^{(-)}\rangle$$

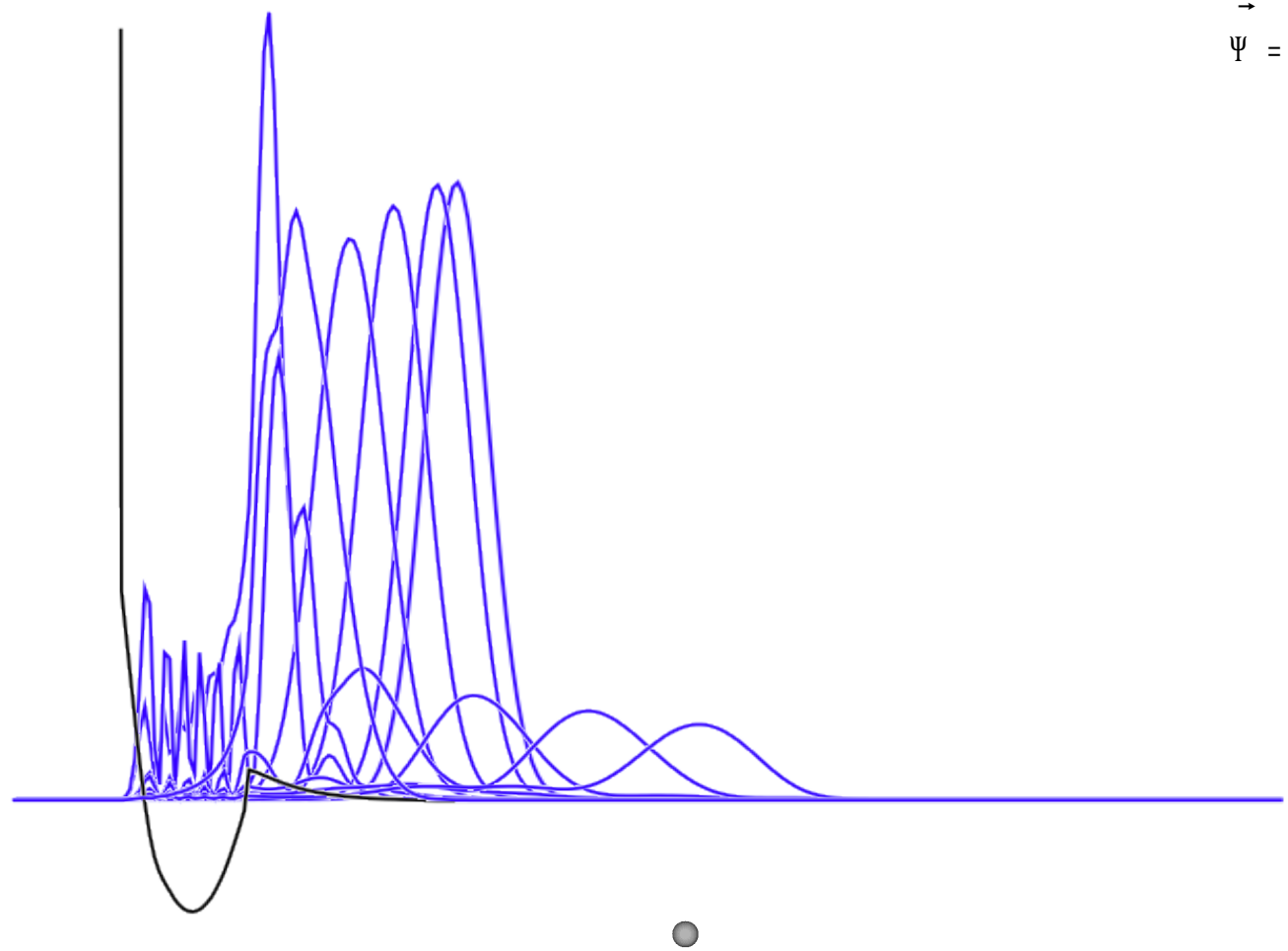
H has the following form :

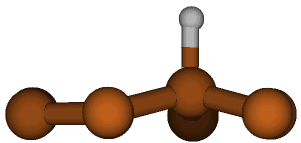
$$H = \begin{pmatrix} T+V & g_{11}(z)\sqrt{\frac{(n_{11}+1)}{N}} & \cdots & g_{MN}(z)\sqrt{\frac{(n_{MN}+1)}{N}} & g_{11}(z)\sqrt{\frac{n_{11}}{N}} & \cdots & g_{MN}(z)\sqrt{\frac{n_{MN}}{N}} \\ g_{11}(z)\sqrt{\frac{(n_{11}+1)}{N}} & T+V+\hbar\omega_{11} & 0 & \cdots & \cdots & \cdots & 0 \\ \vdots & 0 & \ddots & \ddots & \ddots & \ddots & \vdots \\ g_{MN}(z)\sqrt{\frac{(n_{MN}+1)}{N}} & \vdots & \ddots & T+V+\hbar\omega_{MN} & \ddots & \ddots & \vdots \\ g_{11}(z)\sqrt{\frac{n_{11}}{N}} & \vdots & \ddots & \ddots & T+V-\hbar\omega_{11} & \ddots & \vdots \\ \vdots & \vdots & \ddots & \ddots & \ddots & \ddots & 0 \\ g_{MN}(z)\sqrt{\frac{n_{MN}}{N}} & 0 & \cdots & \cdots & \cdots & 0 & T+V-\hbar\omega_{MN} \end{pmatrix}$$

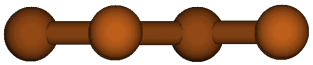
Wave Packets Propagation

Elastic wave function

$$\vec{\Psi} = \begin{pmatrix} \Psi^{(0)}(z,t) \\ \Psi_{11}^{(+)}(z,t) \\ \vdots \\ \Psi_{MN}^{(+)}(z,t) \\ \Psi_{11}^{(-)}(z,t) \\ \vdots \\ \Psi_{MN}^{(-)}(z,t) \end{pmatrix}$$





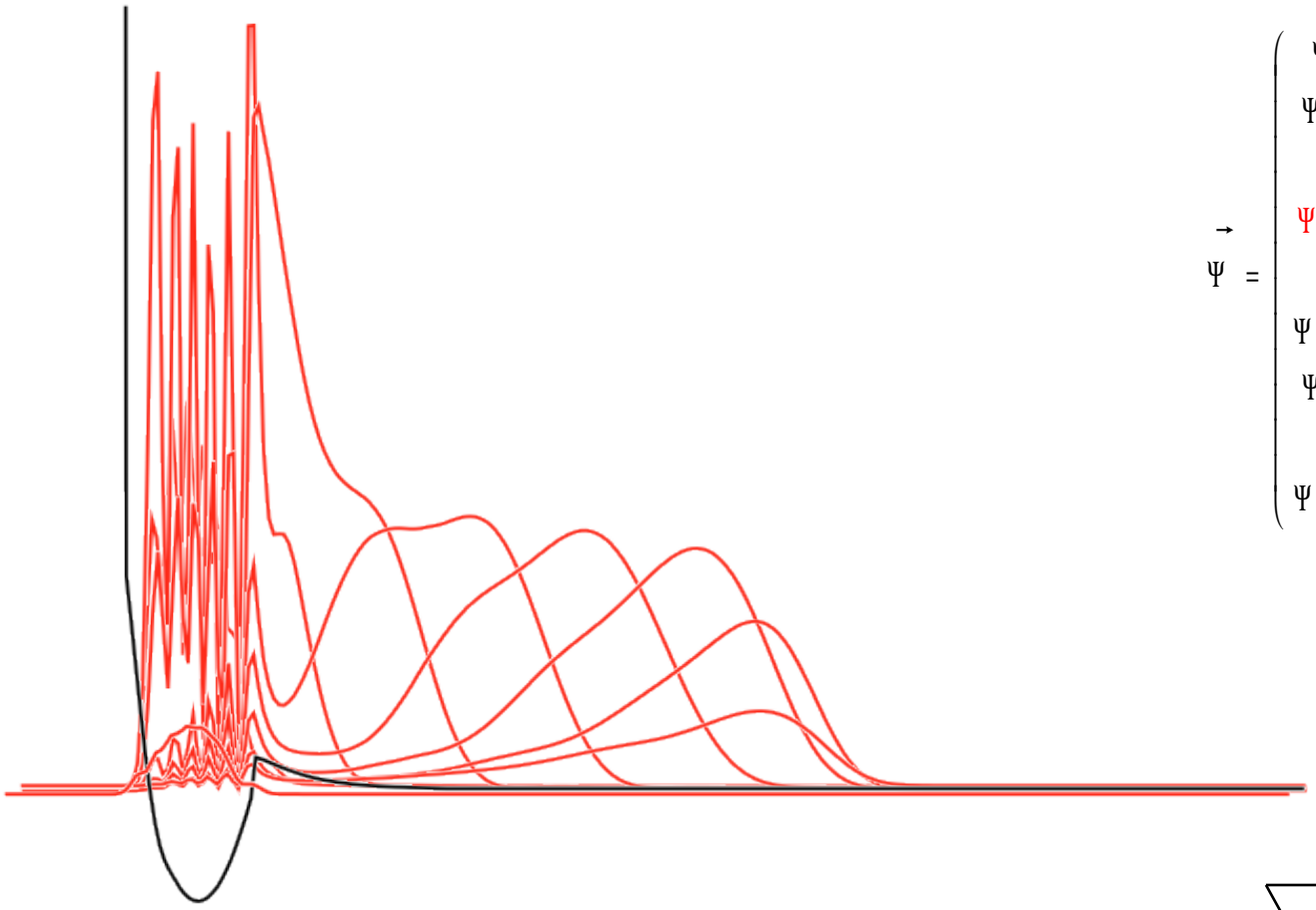


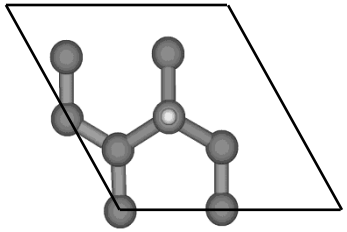
Wave Packet Propagation

Inelastic wave function

→ creation of one phonon
→ C-C mode

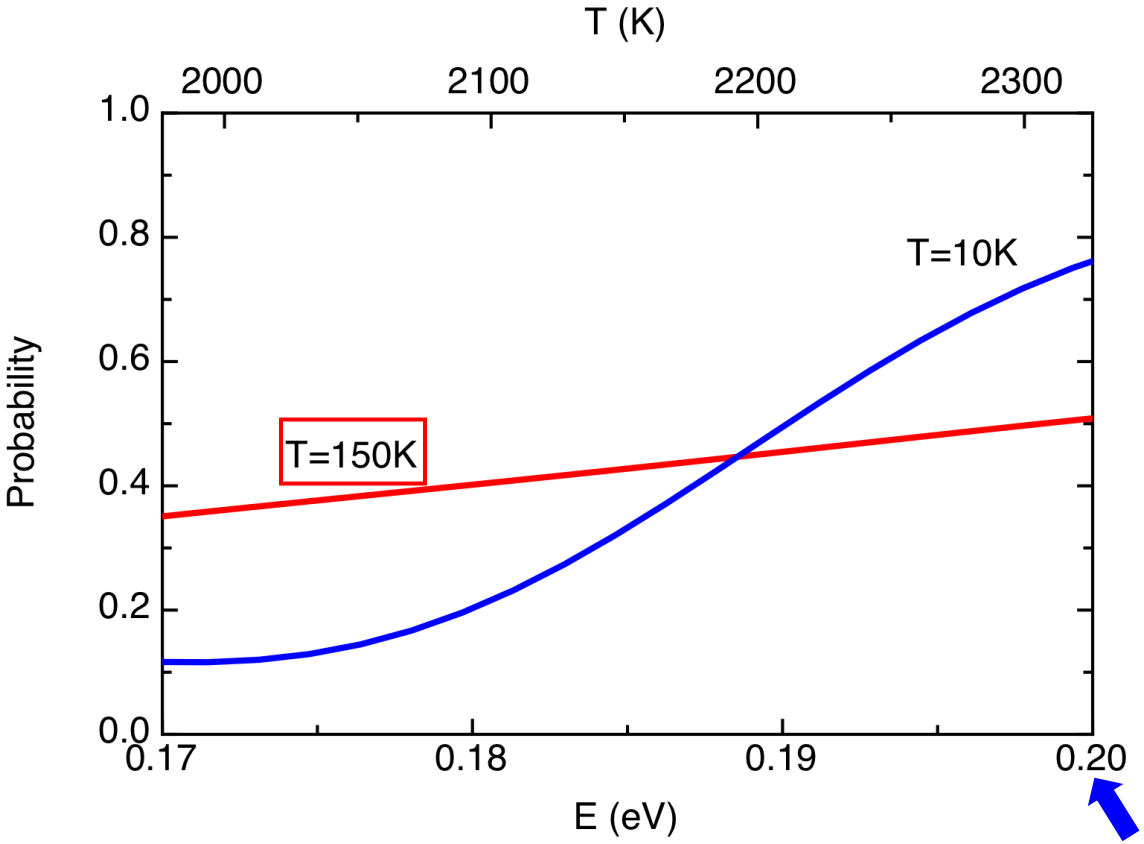
$$\vec{\Psi} = \begin{pmatrix} \Psi^{(0)}(z,t) \\ \Psi_{11}^{(+)}(z,t) \\ \vdots \\ \Psi_{mn}^{(+)}(z,t) \\ \vdots \\ \Psi_{MN}^{(+)}(z,t) \\ \Psi_{11}^{(-)}(z,t) \\ \vdots \\ \Psi_{MN}^{(-)}(z,t) \end{pmatrix}$$

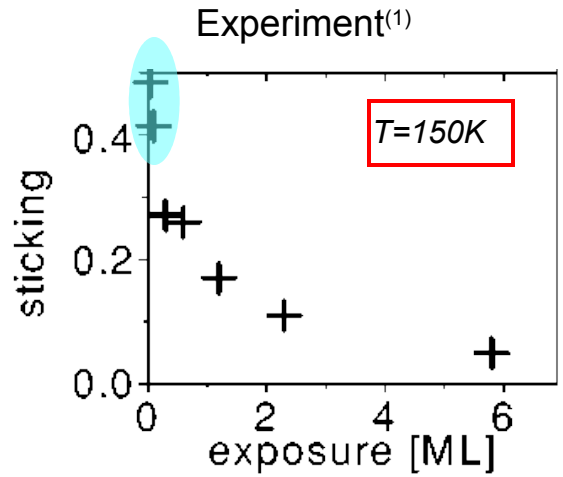




Absorption of phonons modes of the lattice surface → energy dissipation

Sticking Probabilities





Saturation coverage 0.3
--> sticking probability about 0.4

Chemisorption barrier

→ T=150K : good agreement theory - experiment

→ T=10K (ISM conditions) : ER mechanism does not seem efficient to explain the abundance of H_2

(ER = H coming from gas phase collides an H initially absorded on the surface)

(1) T. Zecho, A. Güttler, X. Sha, B. Jackson, and J. Kuppers, J. Chem. Phys. 117 8486 (2002)

Sticking Probabilities

T=150K

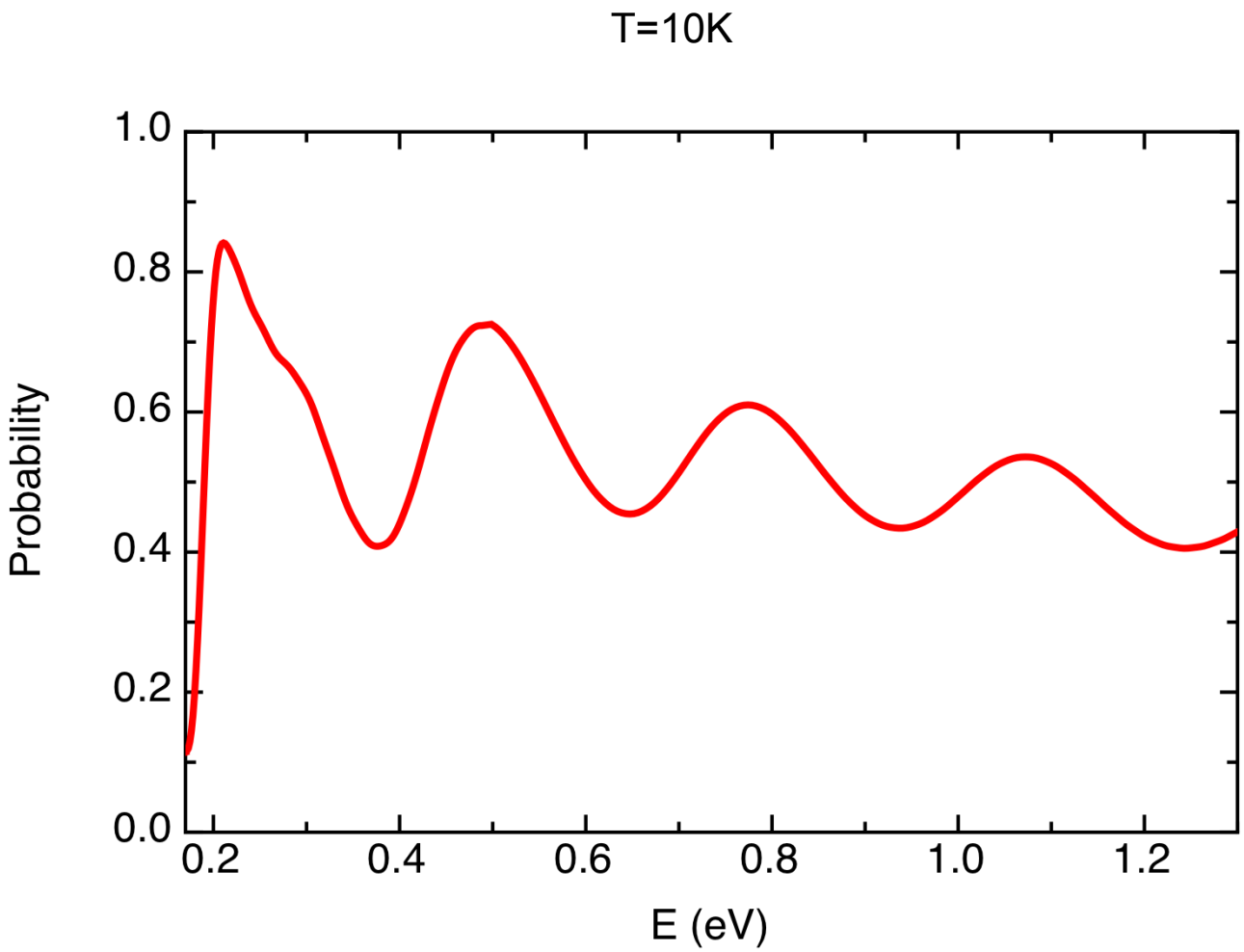
	Experiments Zecho et al.[1]	Quantum method Sha et al.[2]	Classical method Kerwin et al.[3]	This work
Energy (eV)	Centered around 0.2	0.1 - 0.9	0.1 - 0.9	0.2
Sticking coefficient	0.25 - 0.5	0.1	0.024 - 0.05	0.5

(1) T. Zecho, A. Güttler, X. Sha, B. Jackson, and J. Kuppers, J. Chem. Phys. 117 8486 (2002)

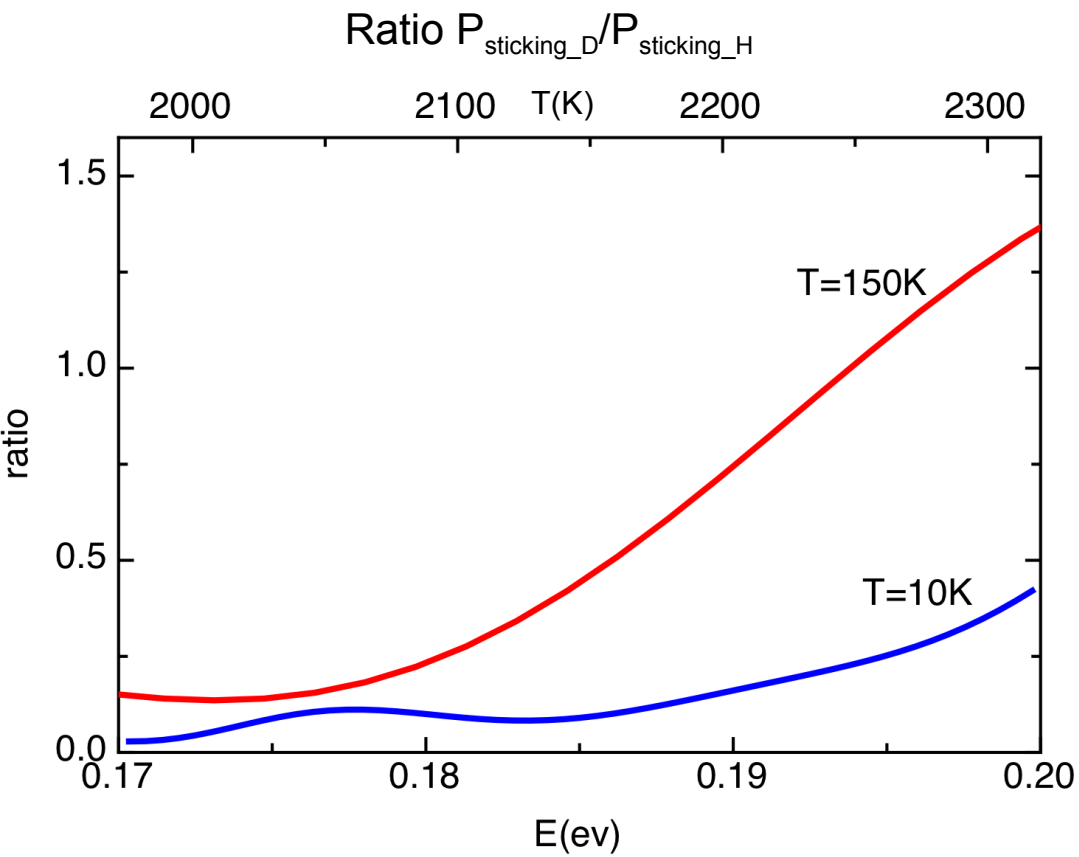
(2) X. Sha, B. Jackson, D. Lemoine, B. Lepetit J. Chem. Phys. 122 014709 (2005)

(3) J. Kerwin, X. Sha, B. Jackson J. Phys. Chem. B 110 18811 (2006)

Sticking Probability



Isotopic Effect Deuterium



T=10K $P_{sticking\_D} < P_{sticking\_H}$

T=150K $P_{sticking\_D} < P_{sticking\_H}$ $E < 0.195eV$

Calculation concludes to an Isotopic effect ⇒ consequence in the ISM :

→ graphite grain absorbed differently H and D atom

→ ER mechanism does not seem to be efficient to explain the deuterated hydrogen molecules formation HD and D_2 .

Model : the coupling between the D motion and the bath of phonon < coupling between the H motion and the bath of phonon

$$g_{\vec{k}j}(z_0) = \sum_j \left.\frac{\partial V\left(z_0,\{u_j\}\right)}{\partial u_j}\right|_{u_j = u_j^{rel}} \sqrt{\frac{\hbar}{2m\omega(\vec{k})}}\,\varepsilon_i^j(\vec{k})\,e^{i\vec{k}.\vec{R}_j}$$

CONCLUSION & PROSPECTS

CONCLUSION

- Taking into explicit account of vibrationnal modes of the lattice in the dynamic calculation
- Study of the H sticking on graphite in the chemisorption well
- Development of a model to extract coupling term with DFT calculation
- Good agreement theory - experiment
- Chemisorption barrier governs the sticking at low collision energy
- Important isotopic effect is observed

- One-phonon approximation is not sufficient
  --> it is not possible to transfer energy in n-phonons processes

PROSPECTS

Develop the model to take into account the n-phonons processes

To Increase the number of degree of freedom

Thanks you for your attention