Dynamics of clusters and molecules in contact with an environment

Molecules/clusters + environment (embedded, deposited)

Fundamental studies on mechanisms (irradiation, deposition)

(Nano)Technological applications (size controlled deposition…)

Contacts with insulators (ionic crystals, rare gases…)

Low energy dynamics (optical response, deposition)

Laser irradiation

M. Baer, P. G. Reinhard (Erlangen), M. Dinh, ES (Toulouse)

Model for free clusters

➢ Electrons

- Time Dependent Density Functional Theory (TDDFT)

Ensemble of orbitals (1 electron) / no correlation $\{\phi_i(\mathbf{r}), i = 1, ...\}$

One body density $\rho(\mathbf{r}) = \sum_j |\phi_j(\mathbf{r})|^2 = \sum_j \rho_j(\mathbf{r})$

Effective mean field theory (Kohn-Sham)

$$i\hbar\frac{\partial\phi_i}{\partial t} = h[\rho]\phi_i \qquad h[\rho] = -\frac{\hbar^2}{2m}\Delta + U_{\rm KS} + U_{\rm ext}(\mathbf{r},t)$$

Kohn-Sham potential | Ions + ext.

- Local Density Approximation (LDA) $U_{\rm KS} = U_{\rm H} + U_{\rm xc}[\rho]$

Hartree | Exch. + Corr.

- Self Interaction Correction (SIC) $U_i^{\rm SIC} = U_{\rm KS} - [U_{\rm H}(\rho_i) + U_{\rm xc}(\rho_i)]$

Time Dependent (TD)LDA → TDSIC !?

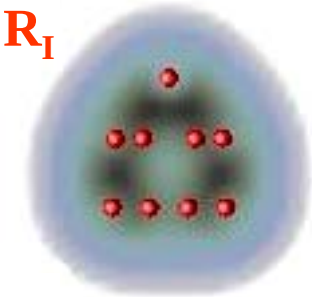
➢ Ions

- Explicit ions via pseudo potentials
- Detail of structure + ionic Molecular Dynamics (MD)

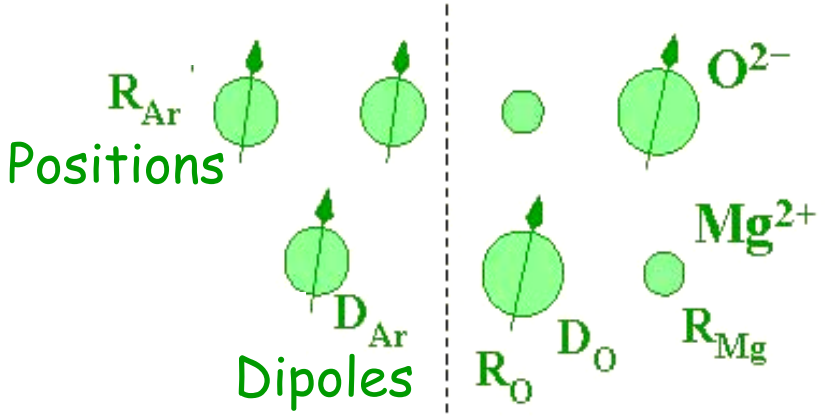
Metal cluster in an environment

Hierarchical approach:
Model for free clusters
+
Polarizable matrix
+
Couplings

Ions Na, K (Cs, Ag…)



Electrons ϕ_i



Equations of motion by variation of total energy

TDLDA for electrons

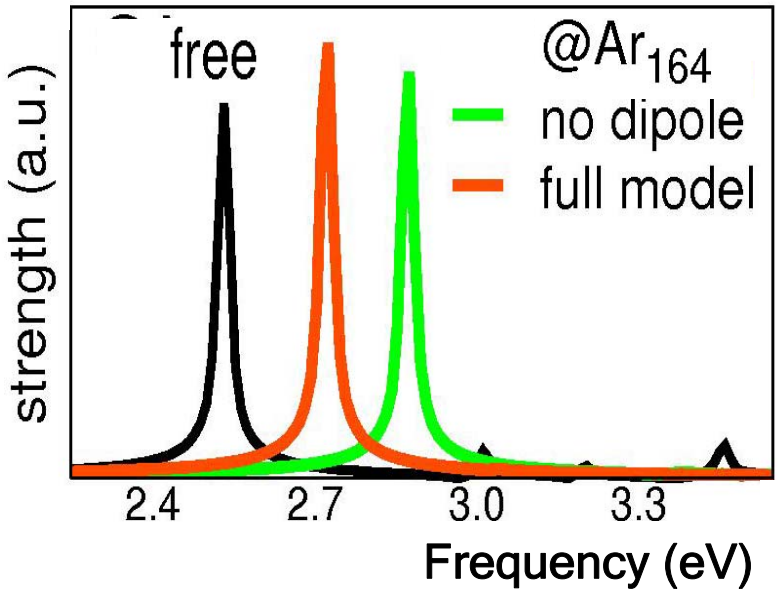
MD for ions

MD for atoms (positions AND dipoles)

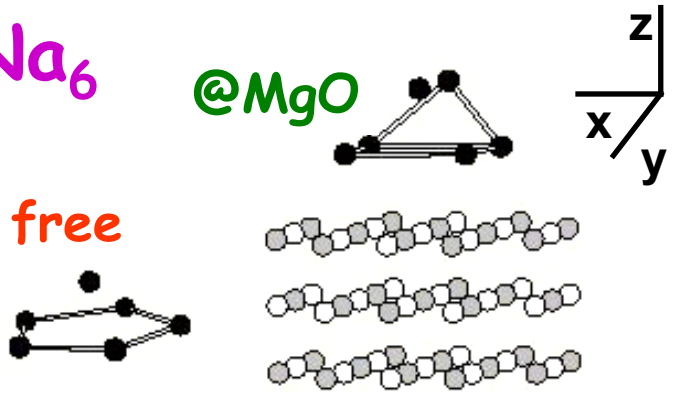
Ar, Ne, Kr atoms, MgO…

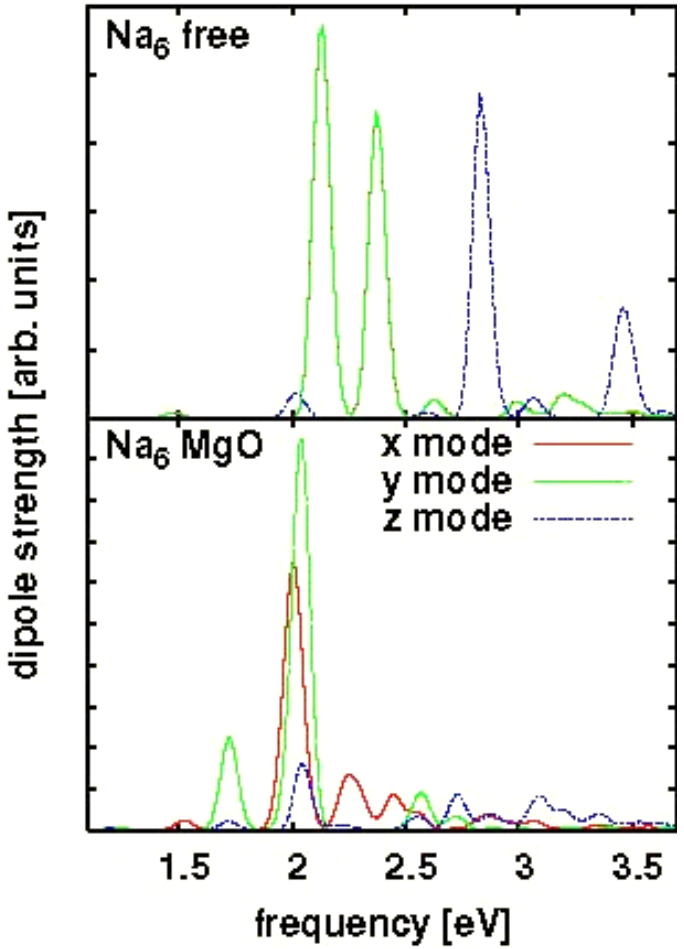
Optical response

Na_8



Na_6 @MgO



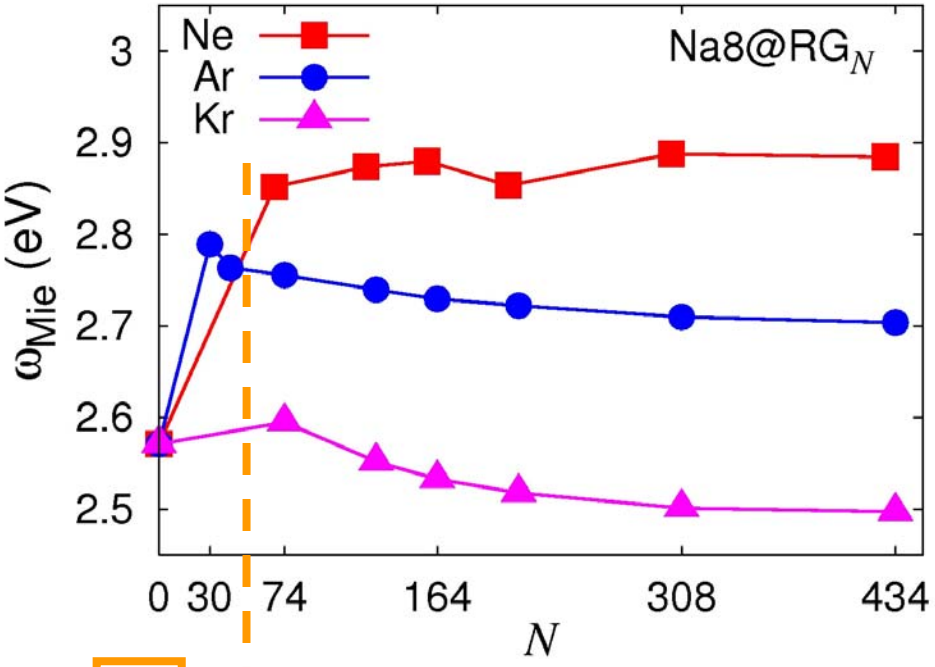


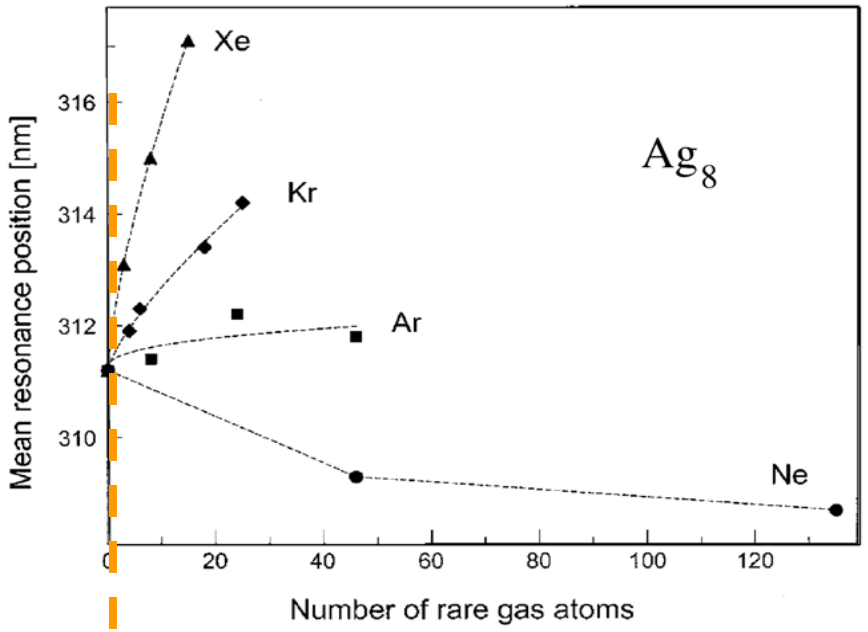
Delicate balance

Short range compression (blue shift)

Long range polarization (red shift)

Optical response (cont'd)





Compression

Polarization

Caution:
« Helium blue shift »

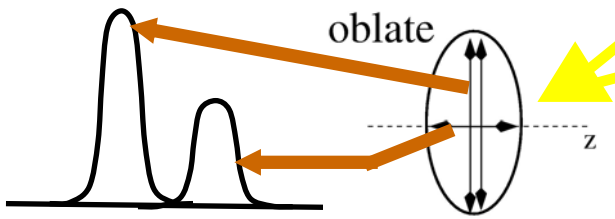
Exp: Rostock

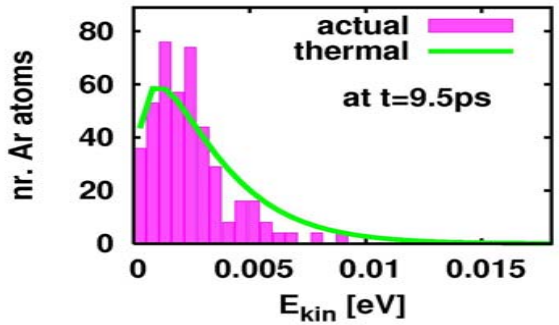
More detailed investigations …

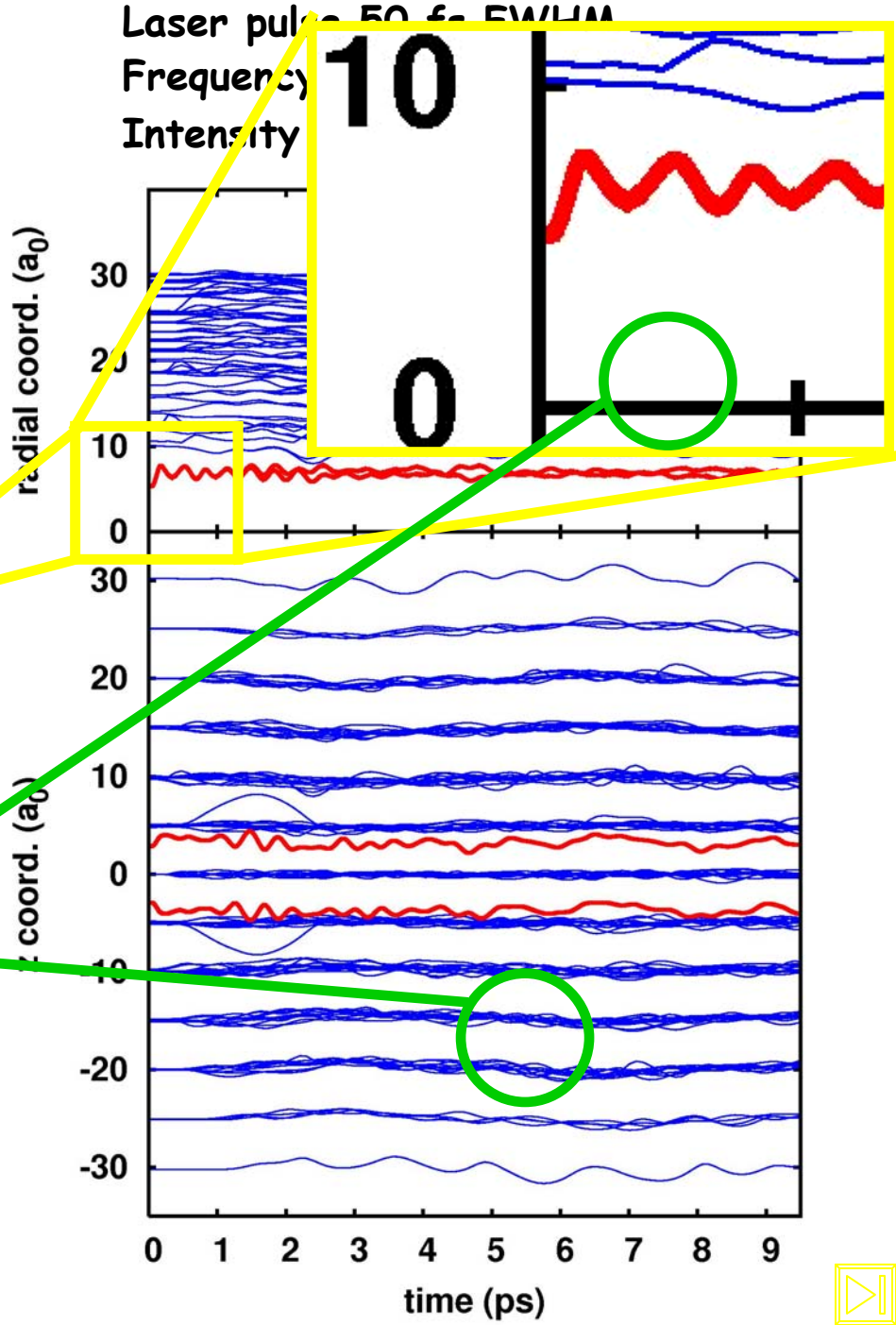
Laser irradiation : embedded cluster

Na_8 @ Ar_{434} ➡ Na_8^{3+} @ Ar_{434}

Optical response







- Hindered explosion
- Cluster expansion/deformation
- Matrix vibrations/heating

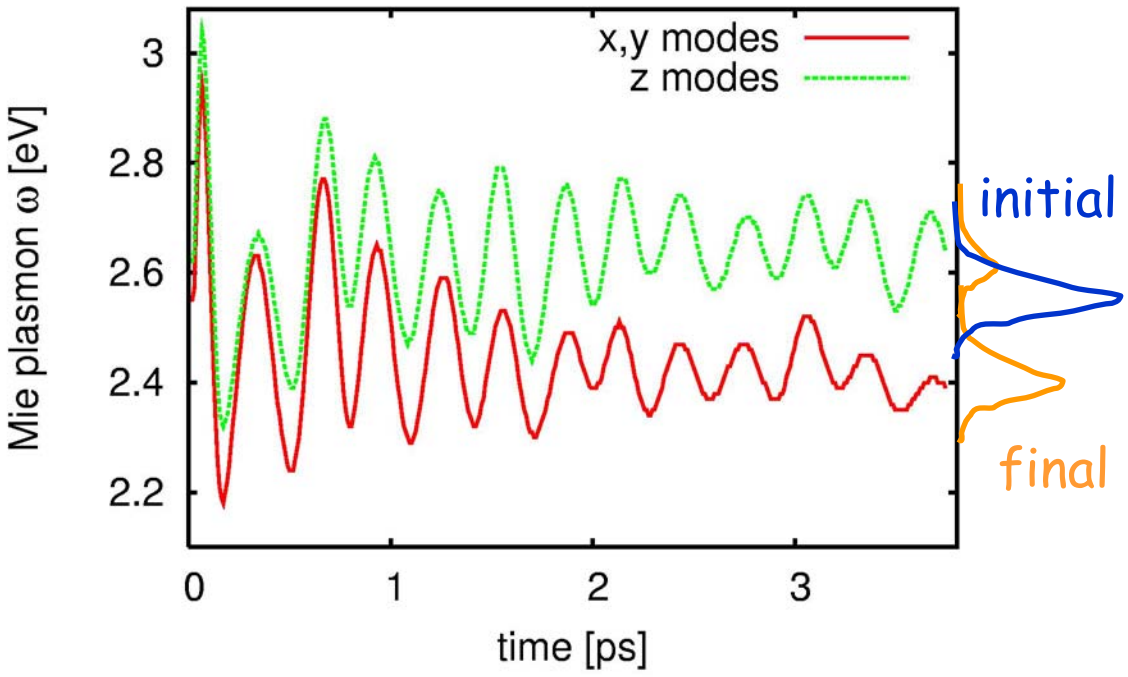
Optical analysis of the embedded cluster

Optical analysis

Charge/Shape/Size

Balance
Charge → Blue shift
Expansion → Red shift
Deformation → Splitting

Red Shift
Spreading/splitting



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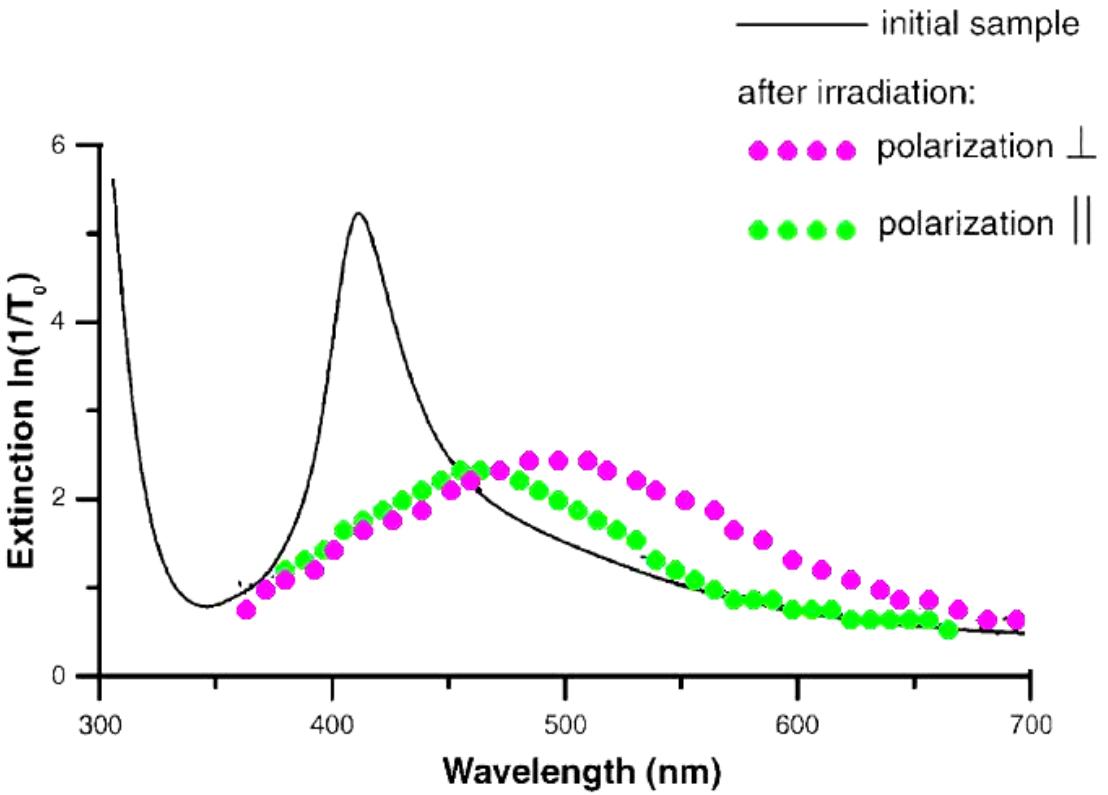
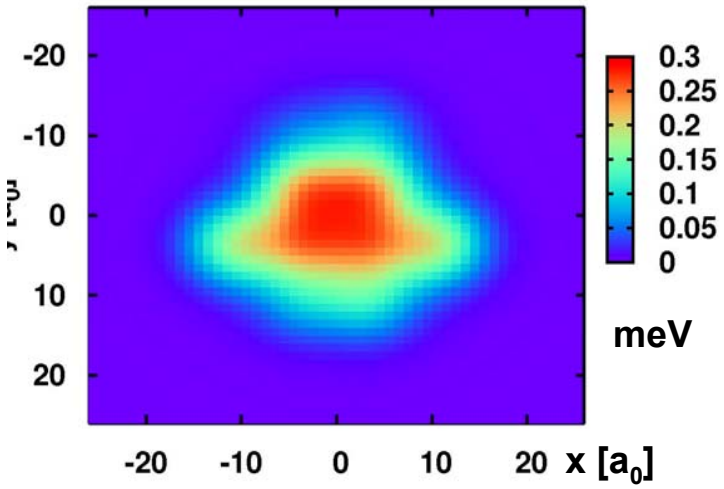


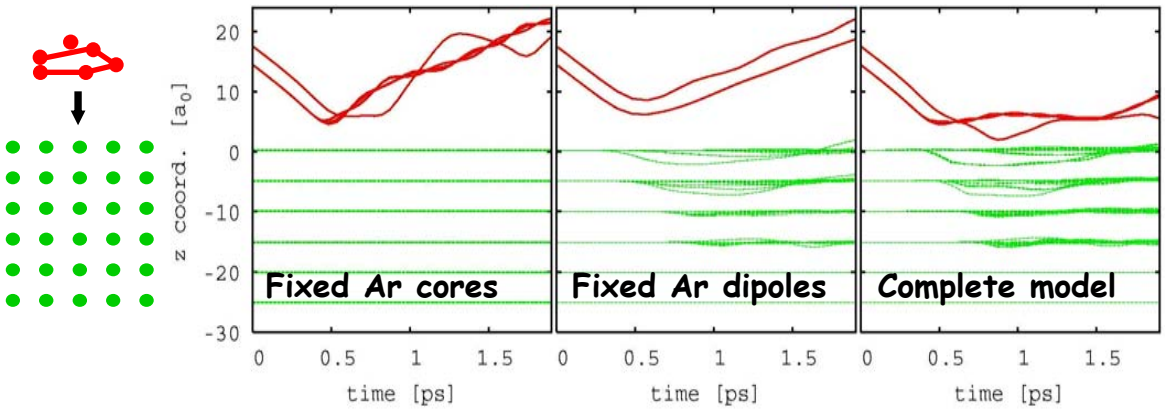
Exp: Seifert

Electronic Response of the environment : deposition

Na_6@Ar(100)
E_{kin} = 800 meV

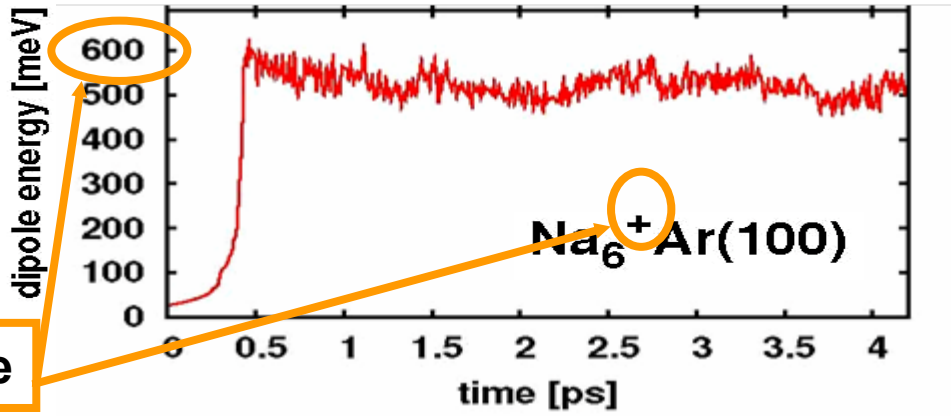
Distribution of dipole energy at time of impact





Key role of environment's degrees of freedom

Subtle energy exchanges



Some conclusions and perspectives

- Low energy response of cluster's in contact with an environment

  Hierarchical model

  Microscopic electrons, classical polarization… (Dynamical QM/MM)

  Delicate interplay of competing effects

  Subtle energy balance

  Key role of environment's degrees of freedom

- Some open questions

  - Towards irradiation dynamics

    Clusters and « bio » molecules under irradiation (laser, ions…)

  - Formal difficulties

    SIC and beyond…, TDSIC…