

Theoretical approaches for the spectroscopy and dynamics of of mixed clusters

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Short time excited states dynamics : Pump-Probe photoelectron spectrum of Na_2F

LPQ Toulouse: M.C. Heitz, G. Durand

LCAR Toulouse: C. Meier

Long experience in Berlin for pump-probe experiments, control and theory, Na_2F : Phys. Rev. Lett. 2002

F.U. Berlin : L. Wöste

Von Humboldt U. Berlin: V. Bonaćić-Koutecký

LCAR Toulouse P.Labastie, J.M.Lhermite, A.Le Padellec, B.Girard, V.Blanchet, B. Chatel Na_3F

Treatment of absorption and long time dynamics in the ground state : CaAr_n

LPQ Toulouse: F. Calvo,

U. Cambridge D. Wales

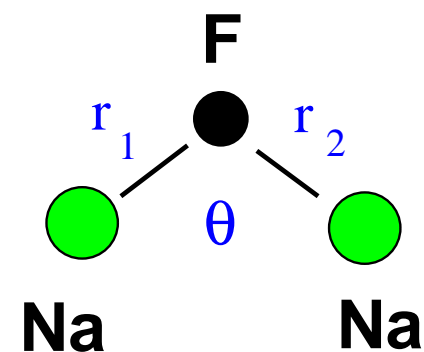
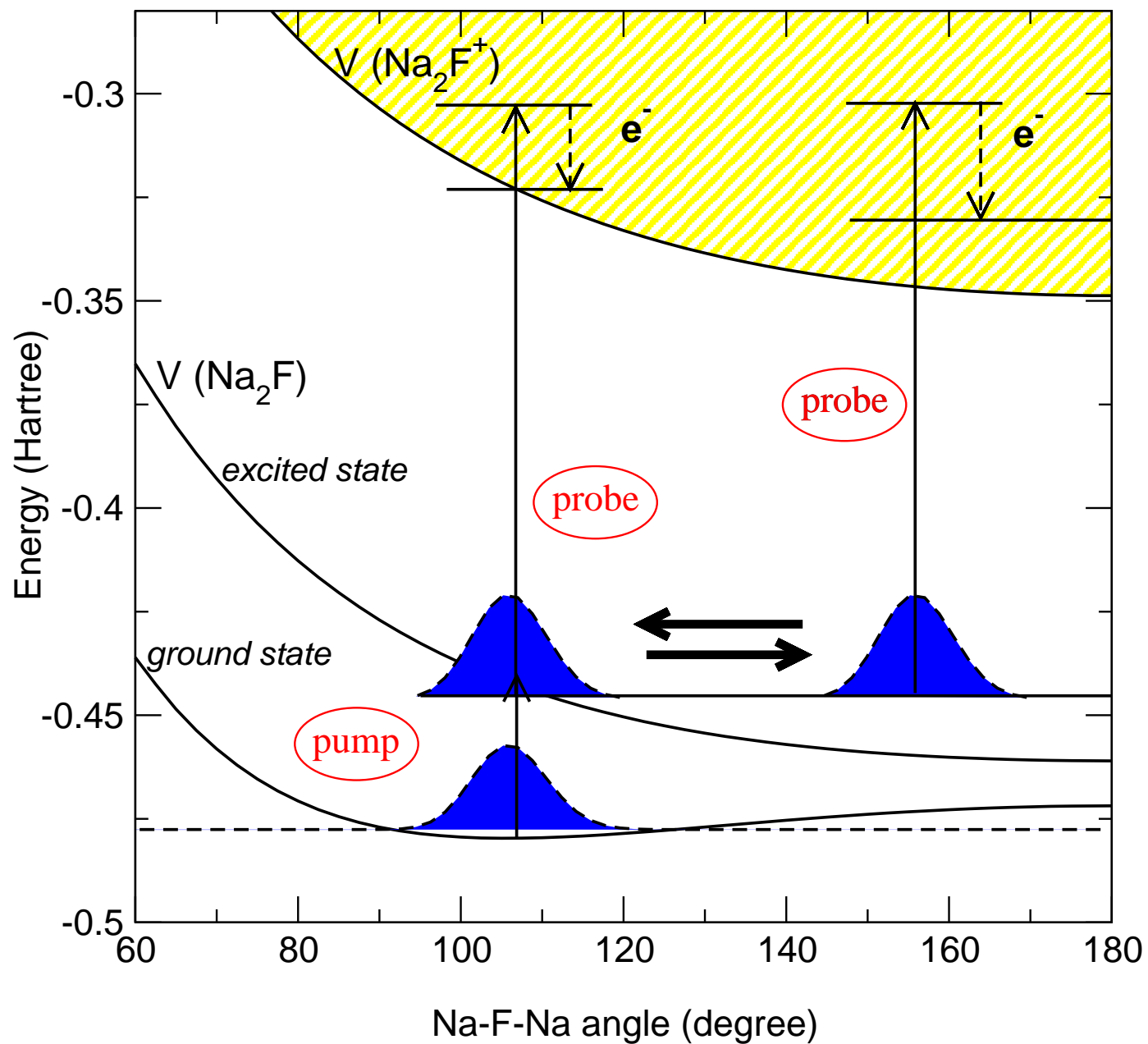
CEA/Saclay : J. M. Mestdagh Cluster Induced Chemical Reaction experiments

Rydberg states: NaAr_n

U. Monastir/Tunisie: H. Berriche, M. El Hadj Ben Rhouma

Principle of pump-probe experiment

Time-dependent photoelectron spectroscopy



Description of Na₂F

Electronic problem: quantal one-electron model

$$H = h_{el} + V_{coul} + V_{rep}$$

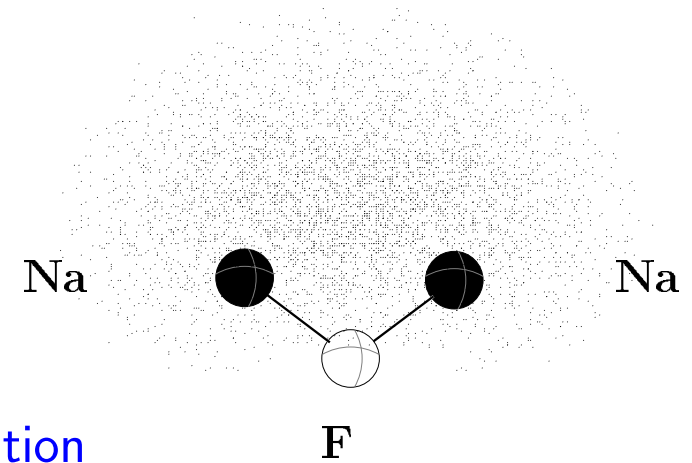
h_{el} : electron in the electric field of Na⁺ and F⁻ ions

Electron-ion pseudopotentials

Perturbative account of core-valence polarization and correlation

$V_{coul} + V_{rep}$: Classical Coulomb and Born-Mayer potentials for ion-ion interactions

G. Durand, F. Spiegelman, J.Chem. Phys., 1999



Nuclear Hamiltonian with bond coordinates : NaF lengths r_1, r_2 , NaFNa angle : θ

$$H(r_1, r_2, \theta) = \frac{p_1^2}{2\mu_1} + \frac{p_2^2}{2\mu_2} + \frac{j^2}{2\mu_1 r_1^2} + \frac{j^2}{2\mu_2 r_2^2} + \frac{p_1 p_2 \cos\theta}{m_F} - \frac{p_1 p_\theta}{m_c r_2} - \frac{p_2 p_\theta}{m_c r_1} - \frac{\cos\theta j^2 + j^2 \cos\theta}{2m_F r_1 r_2} + V(r_1, r_2, \theta)$$

Excited state dynamics

Pump excitation

- pump-pulse: 40 fs(FWHM), 1.02 eV \rightarrow excitation to the first excited state of Na₂F
- described by first order time-dependent perturbation theory

$$\psi_e(r_1, r_2, \theta, t) \propto \int_0^t e^{-iH_e(t-t')} (\mu_{eg}\mathcal{E}_{pu}(t')) e^{-iH_g t'} \psi_g(r_1, r_2, \theta, 0) dt'$$

with laser pulse: $\mathcal{E}_{pu}(t') = \mathcal{E}_0 f(t') e^{-i\omega_L t'}$

Wavepacket Propagation

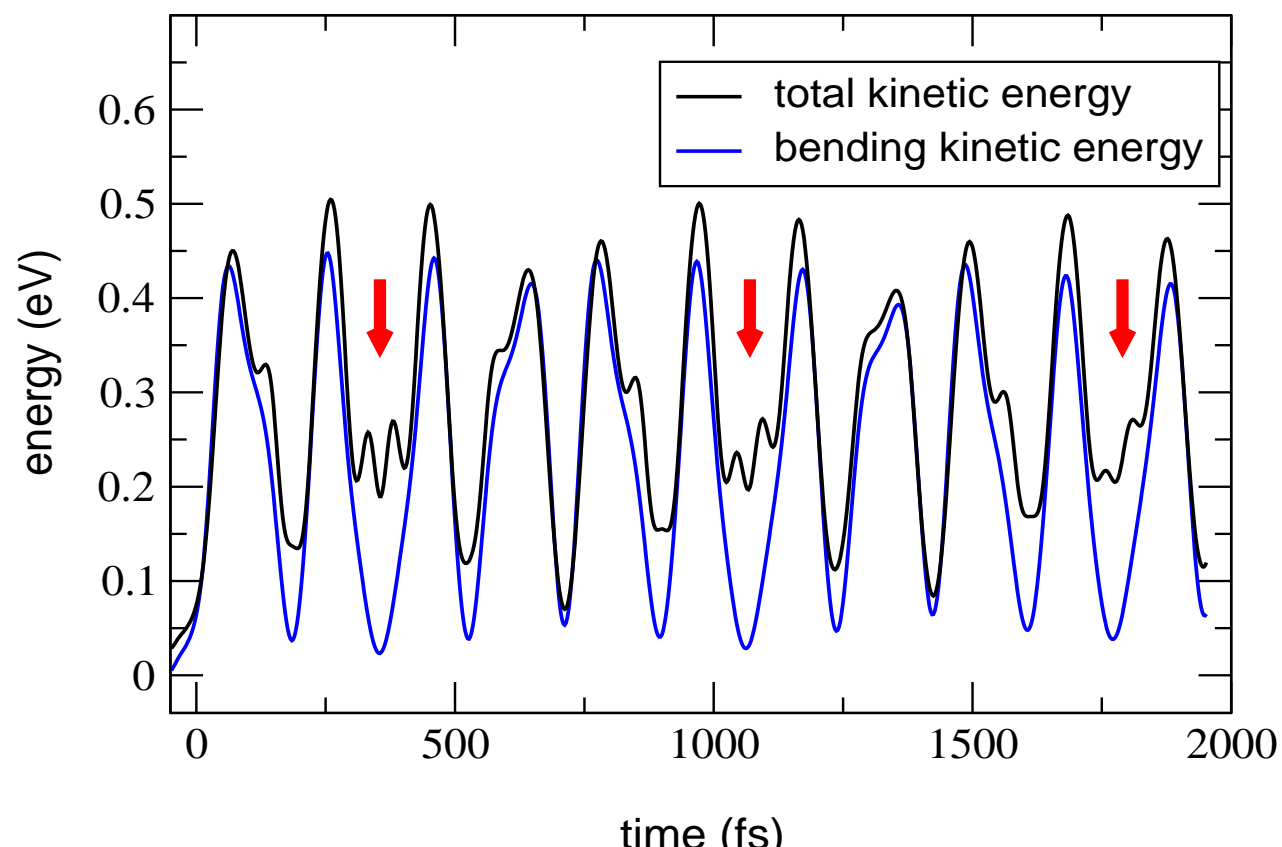
- 3-D quantum propagation, $\mathbf{J} = 0$

basis sets: r_1, r_2 : Fourier grid, 96 points

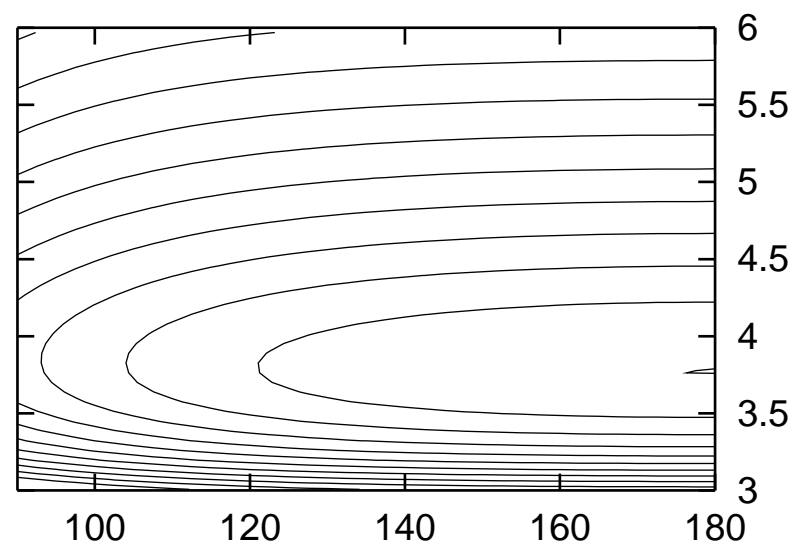
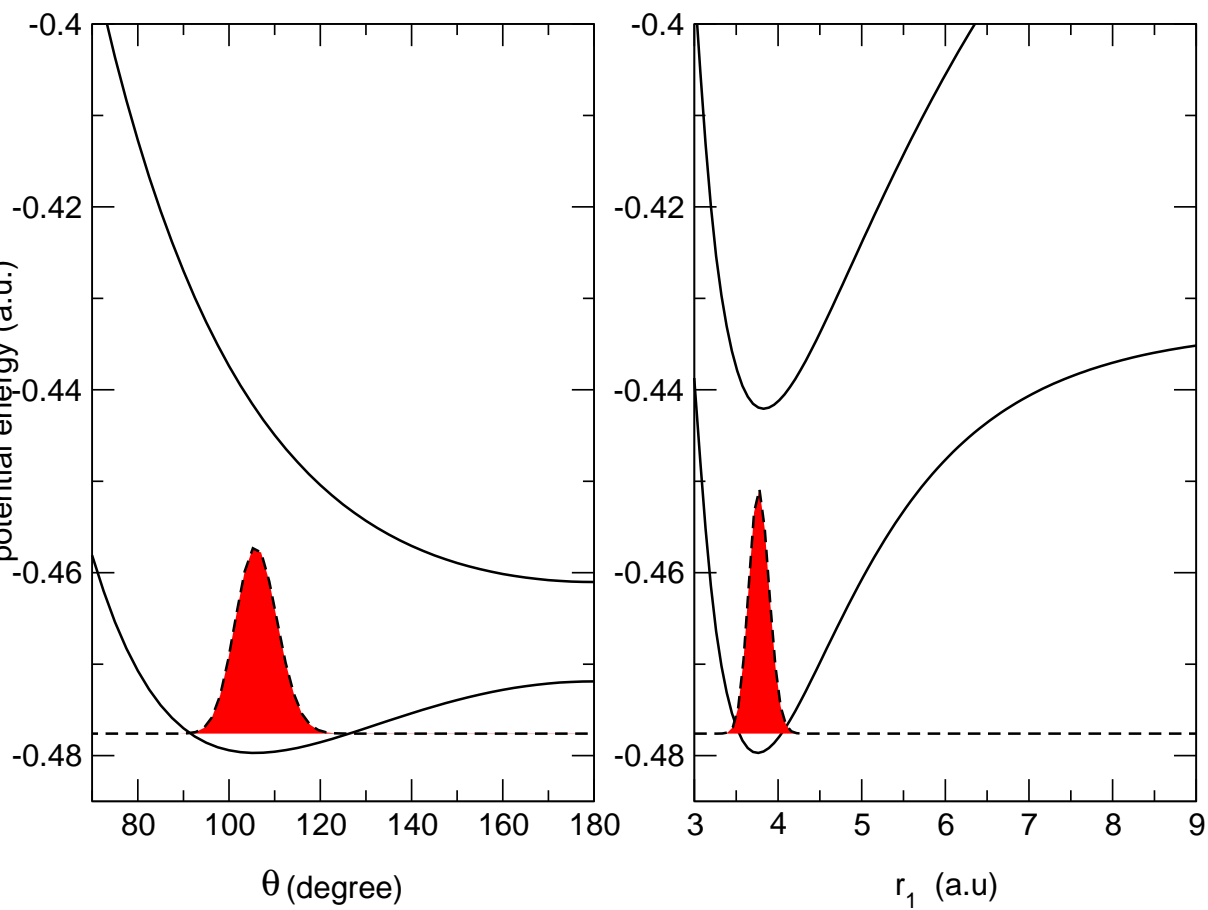
θ : Legendre DVR, 100 basis functions

Excited state dynamics

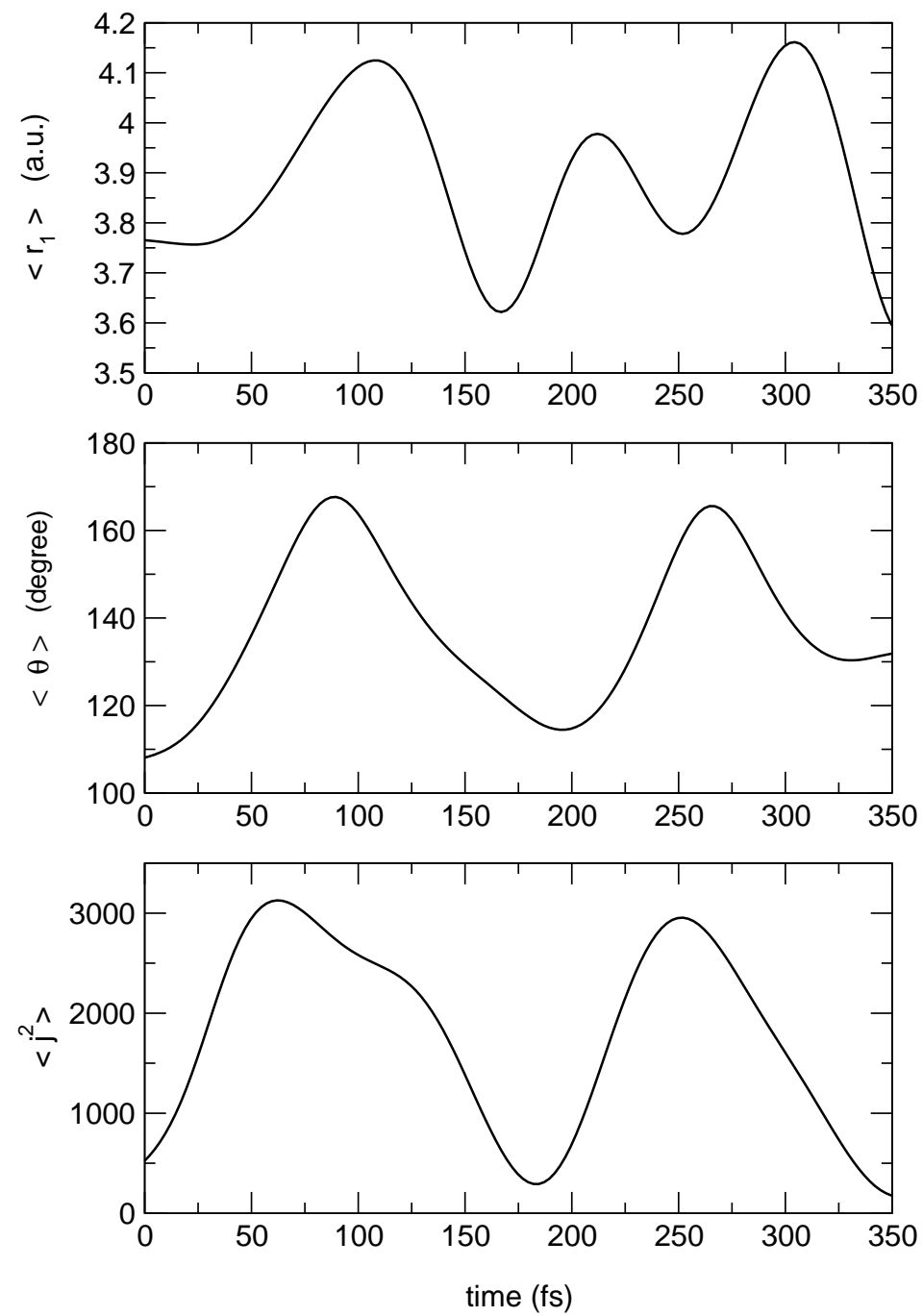
- oscillations along the bending coordinate θ , changing from bent to linear geometry with a periodicity of 180 fs (cf V. Bonacic-Koutecký/ L. Wöste)
- excitation of the symmetric stretch, due to kinetic coupling to the bending mode
- reversible flow of kinetic energy between the modes:
maximum transfer to the stretching mode at 355 fs, 1067 fs and 1780 fs (see arrows)



Initial excitation



Centrifugal acceleration



Probe: ionisation

- probe pulse at delay time T : 50 fs(FWHM), 3.5 eV
→ ionization of Na_2F
- described by first order time-dependent perturbation theory
- model of ionization continuum: Seel+Domcke (1996)
- no ion-core/electron interactions

$$P(E, T) \propto \int \left| \int_{-\infty}^{\infty} dt' e^{i(H_I + E)t'} (\mu_{eg} \mathcal{E}_{pr}(t')) e^{-iH_e t'} \psi_e(r_1, r_2, \theta, T) \right|^2 dr_1 dr_2 d\cos\theta$$

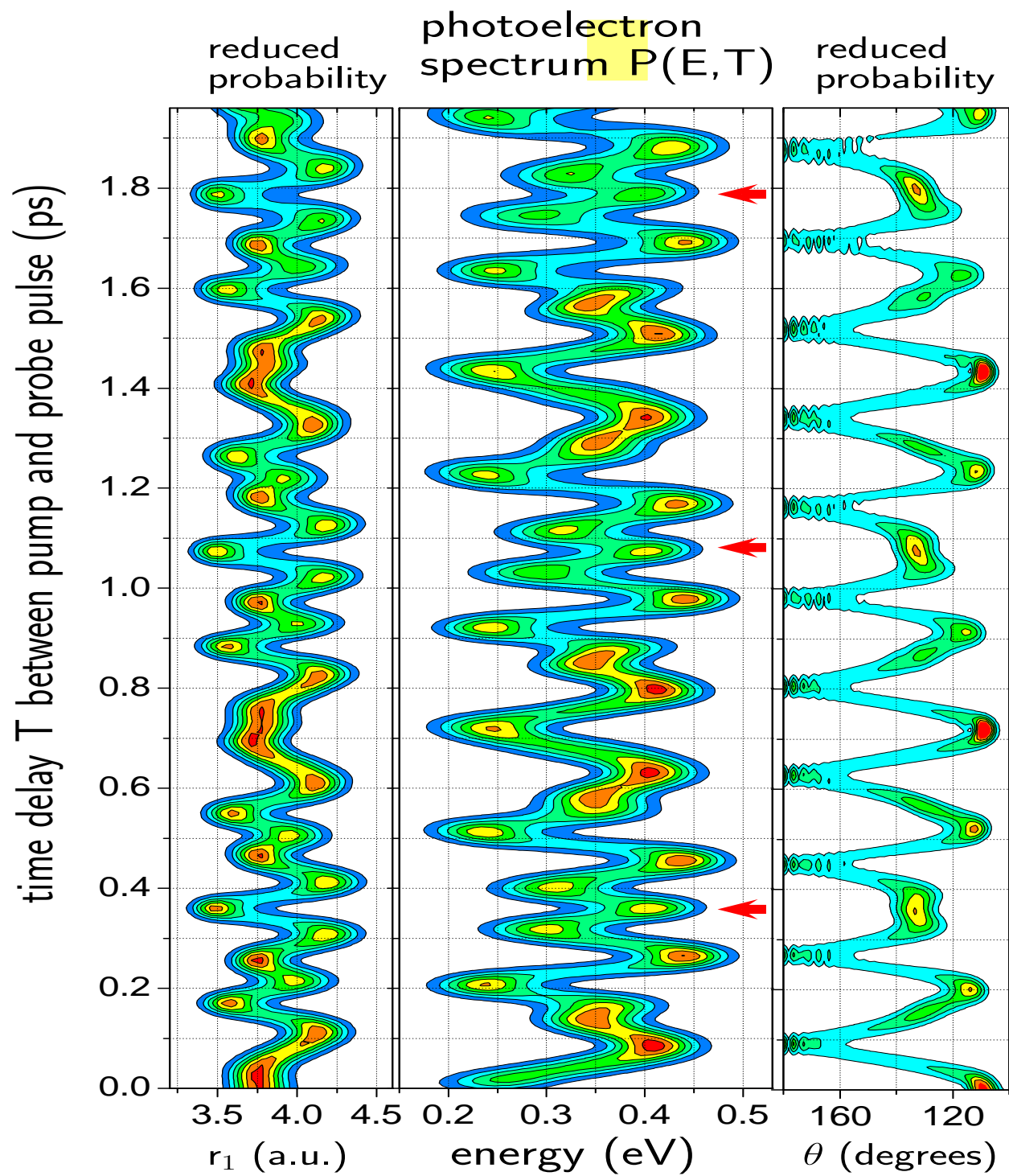
with probe pulse: $\mathcal{E}_{pr}(t') = \mathcal{E}_0 f(t') e^{-i\omega_L t'}$

- impulsive approximation: Meier+Engel (1996): pulse duration \ll nuclear dynamics

$$P(E, T) \approx \int |\mathcal{F}(V_I + E - V_e - \omega_L) \psi_e(r_1, r_2, \theta, T)|^2 dV$$

with $\mathcal{F}(\Omega)$ Fourier transform of pulse envelope $f(t)$.

⇒ time-dependent photoelectron spectrum maps nuclear dynamics

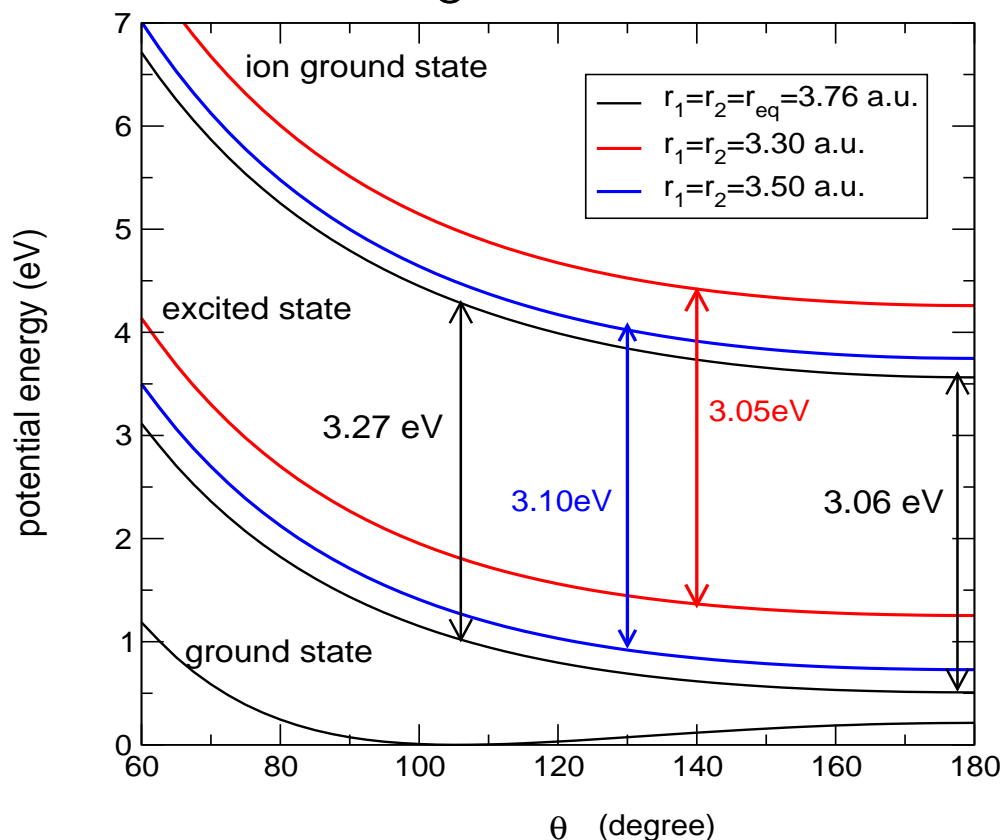


Time-Dependent Photoelectron Spectrum

- As an approximation, we can say : $E_{electron} \approx \omega_{pr} - (V_{excited} - V_{ion})$
- the time dependence of the photoelectron spectrum reflects the concerted motion of the internal modes:

photoelectrons with high energy correspond either to:

- linear configurations of the cluster
- or bent geometries with contraction of the Na-F bonds.



Conclusions

- Time-Resolved Photoelectron Spectroscopy is a sensitive tool for studying intracluster motion
- the pump probe signal is dominated by the bending motion of the cluster with a periodicity of 180 fs
- the detailed structures of the spectra are explained by excitation of the symmetric stretch vibration, induced by the coupling to the bending mode
- the time dependence of the photoelectron spectrum reflects the concerted motion of the internal modes:
photoelectrons with high energy correspond either to:
 - linear configurations of the cluster
 - or bent geometries with contraction of the Na-F bonds.⇒ the signature of the two-dimensional motion is visible
in the one-dimensional time-dependent spectrum

Introduction

Interpretation of experimental results in the group of J.-M. Mestdagh at LFP, CEA Saclay

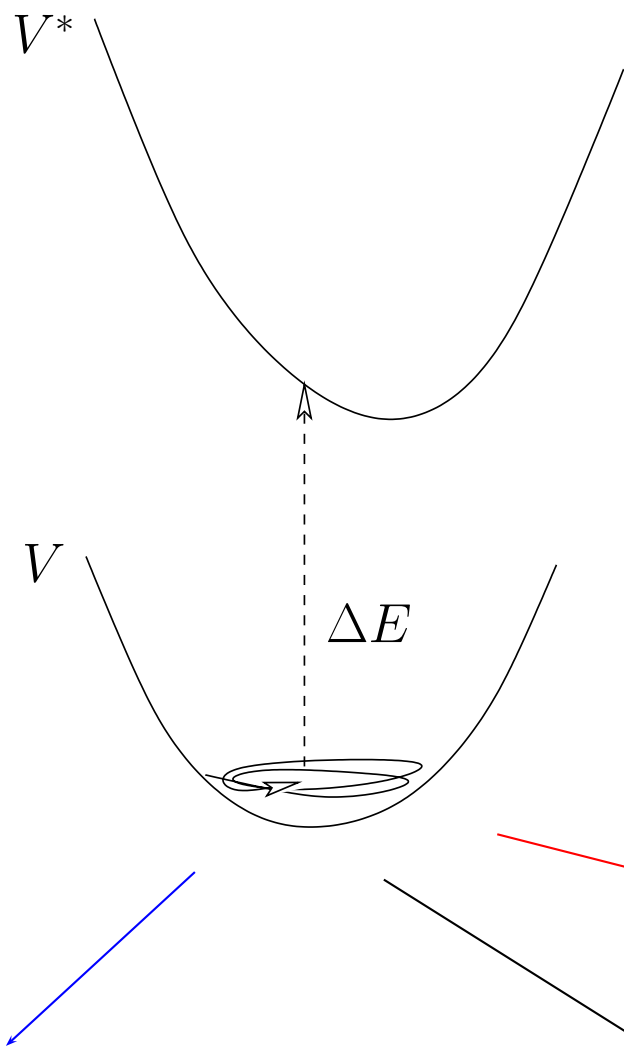
- excitation and fluorescence **spectra**
- dynamics and **reactivity** of $\text{Ca}+\text{O}_2\dots$

Systems investigated: Clusters Ar_nX , Ne_nX , $n \sim 100 - 1000$

Ingredients in the calculations

- **potential energy surfaces** obtained via a DIM model (Diatomics-In-Molecules) parameterized from *ab initio* calculations on CaAr
[DIM : Gaveau *et al.*, EPJD 21, 153 (2002) ;
ab initio : Spiegelman *et al.*, JCP 117, 7534 (2002)]
- Exact quantal calculation of the absorption spectrum only feasible for $n \ll 10 - 100$

Semi-classical approaches for the absorption of polyatomic molecules



Vertical transitions in the Condon approximation

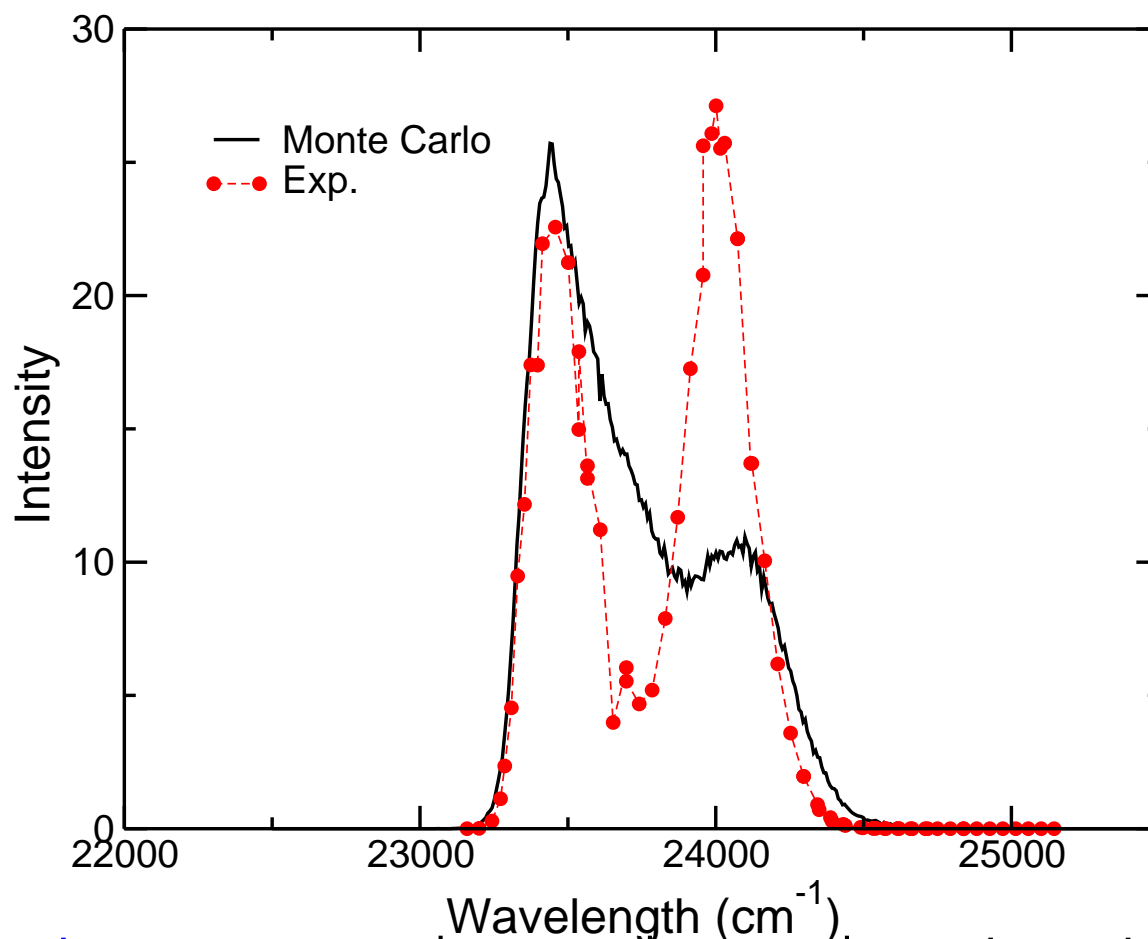
$$\sigma^2(R) = \frac{4\pi^2 \mu^2(R) \Delta E(R)}{3c \delta E}$$

Direct simulation

Superposition

Effective coordinate?

Simulation : Monte Carlo or Molecular Dynamics, constant E or T , vibrational treatment **classical or semi-classical** (path integrals, corrective terms)

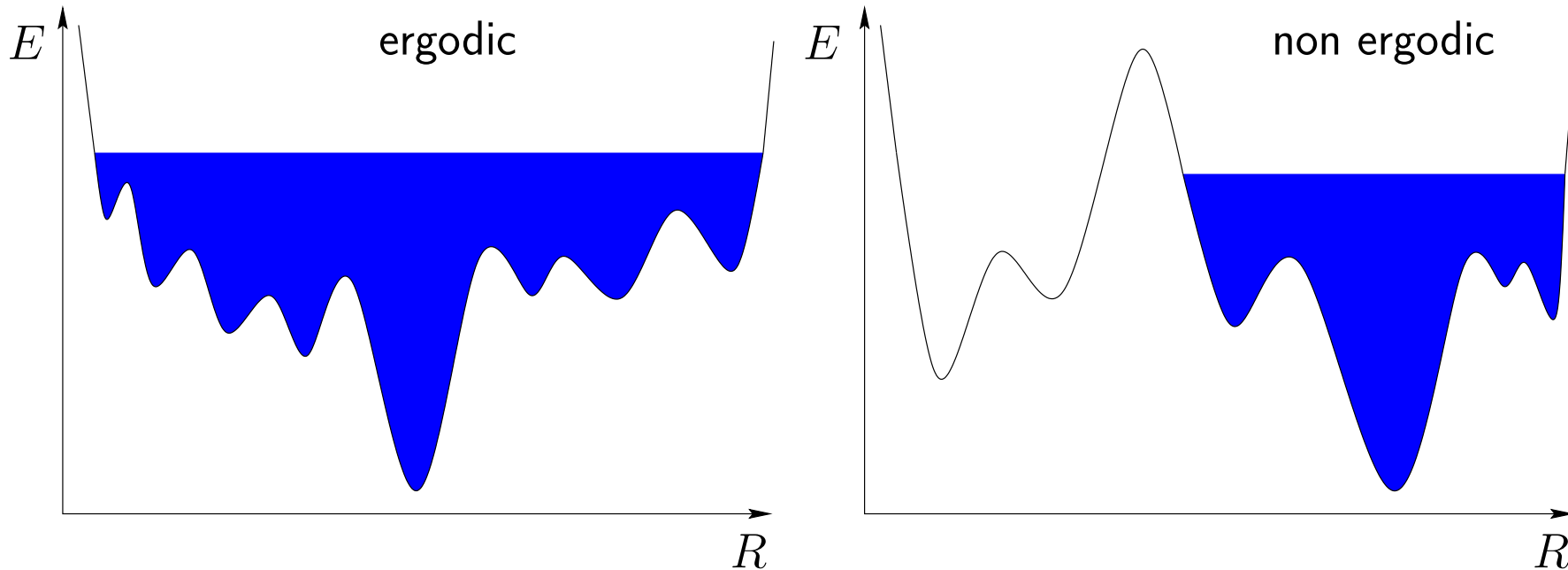


→ semi-quantitative agreement between theory and experiment in concern with excitation $4s^2 \rightarrow 4s4p$

Current problems in simulations

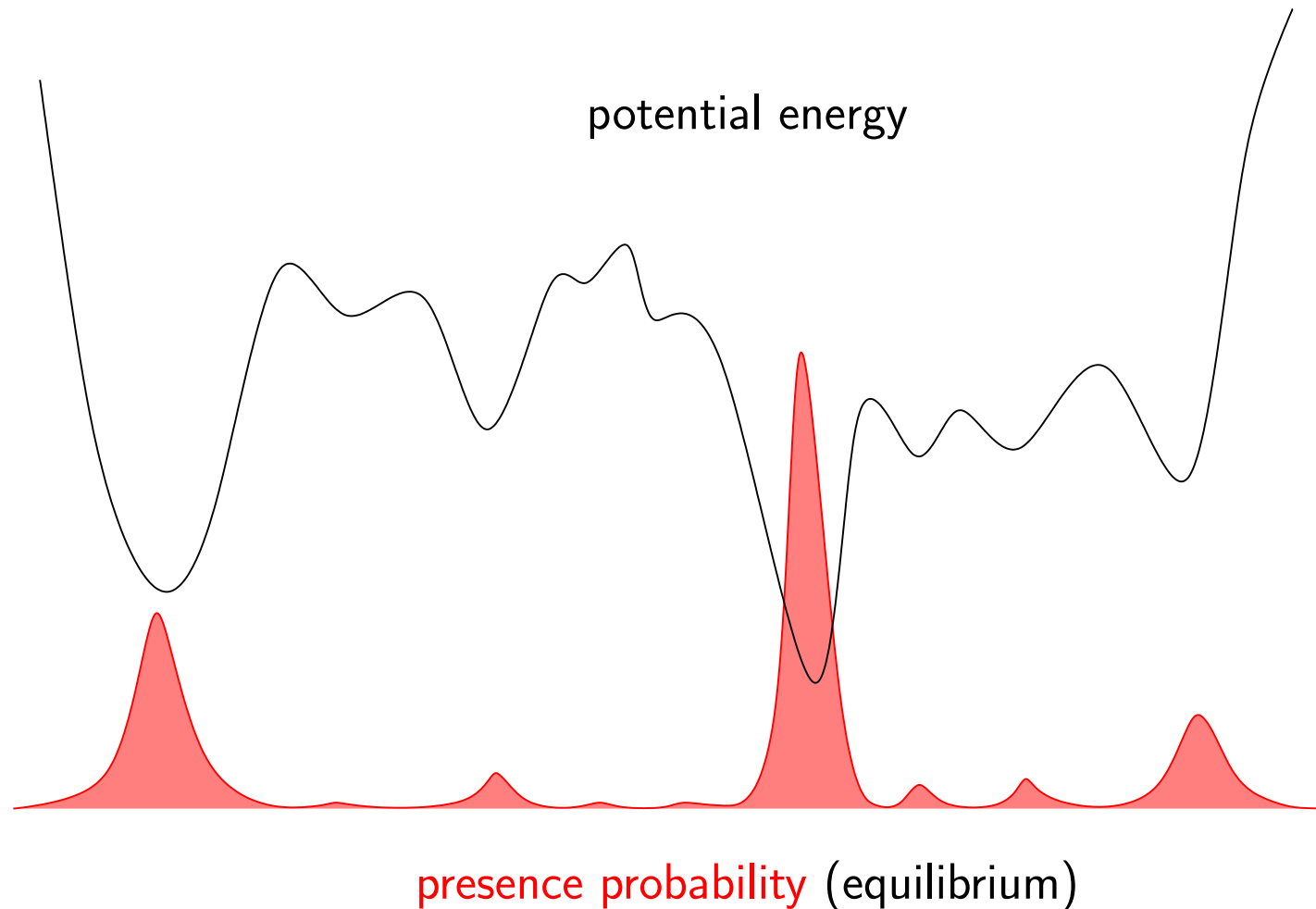
Monte Carlo : stochastic, but **no access to real time** informations

Molecular Dynamics : sensitive to **broken ergodicity**



In general : quantal vibration calculations **strongly time-consuming** numerically ;
structural analysis more delicate (via quenching)

2. Superposition of inherent structures : principle



A **physical property** is recovered from its knowledge on isomer basins or **inherent structures**

Harmonic superposition

At thermal equilibrium, the cluster visits a large number of isomers $\{\alpha\}$. In the **harmonic** approximation, the weight of isomer α is given by

$$Z_\alpha(\beta = 1/k_B T) = n_\alpha e^{-\beta E_\alpha} \prod_i \frac{2}{\sinh \beta \hbar \omega_\alpha^i}$$

symmetry

Boltzmann

vibrational

$$(n_\alpha = 2(n-1)!/O_\alpha)$$

Problem : the number of degrees of freedom approximately varies with size N within **exponential** increase!

⇒ For large systems, it becomes impossible to **find the complete set of minima**

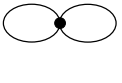
⇒ **reweighting** from classical simulation

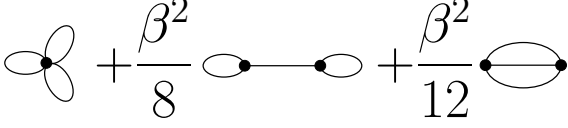
$$Z(\beta) \propto \sum'_\alpha p_\alpha(\beta_0) \frac{Z_\alpha(\beta)}{Z_\alpha(\beta_0)}$$

Beyond harmonic approximation, **perturbative correction** can be implemented

$$Z_\alpha(\beta) = \text{Tr} e^{-\beta H_\alpha} \approx Z_\alpha^h(\beta) [1 + \gamma_4 + \gamma_6 + \dots]$$

γ_i is the corrective term coming from the contribution of Q^i to the **anharmonic** potential. For instance :

$$\gamma_4 = -\frac{\beta}{24} \sum_{i_1 \dots i_4} \Gamma_{i_1 \dots i_4}^{(4)} \langle Q_{i_1} \times \dots \times Q_{i_4} \rangle = -\frac{\beta}{8} \text{diagram}$$


$$\gamma_6 = \sum_{i_1 \dots i_6} \left[\frac{-\beta}{720} \Gamma_{i_1 \dots i_6}^{(6)} + \frac{\beta^2}{72} \Gamma_{i_1 i_2 i_3}^{(3)} \Gamma_{i_4 i_5 i_6}^{(3)} \right] \langle Q_{i_1} \times \dots \times Q_{i_6} \rangle = -\frac{\beta}{48} \text{diagram} + \frac{\beta^2}{8} \text{diagram} + \frac{\beta^2}{12} \text{diagram}$$


where a **diagrammatic notation** has been introduced and

$$\langle Q_i^2 \rangle = \frac{\hbar}{\omega_i} \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega_i} - 1} \right)$$

For any observable A at **canonical equilibrium canonique** one has

$$\langle A \rangle(\beta) = \frac{\sum_\alpha Z_\alpha(\beta) A_\alpha(\beta)}{\sum_\alpha Z_\alpha(\beta)}$$

Problem : compute property $A_\alpha(\beta)$ corresponding to isomer α

Gaussian theory for the absorption of polyatomic molecules

- valid in the harmonic regime ;
- From Wadi et Pollak, JCP 110, 11890 (1999).

Hamiltonians in **normal coordinates** :

$$H_g = \frac{1}{2} \sum_i p_i^2 + \frac{1}{2} \sum_i \omega_{gi}^2 q_i^2 \quad H_e = \frac{1}{2} \sum_i p_i^2 + \sum_i G_i q_i + \frac{1}{2} \sum_{ij} w_e^{ij} q_i q_j + \Delta E$$

the **absorption intensity** for excitation $\hbar\omega$ is given by

$$\mathcal{I}(\omega, \beta) = \frac{\mathcal{I}_0 \hbar}{\bar{\omega} \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\omega - \omega_0 + \Delta\omega}{\bar{\omega}} \right)^2 \right]$$

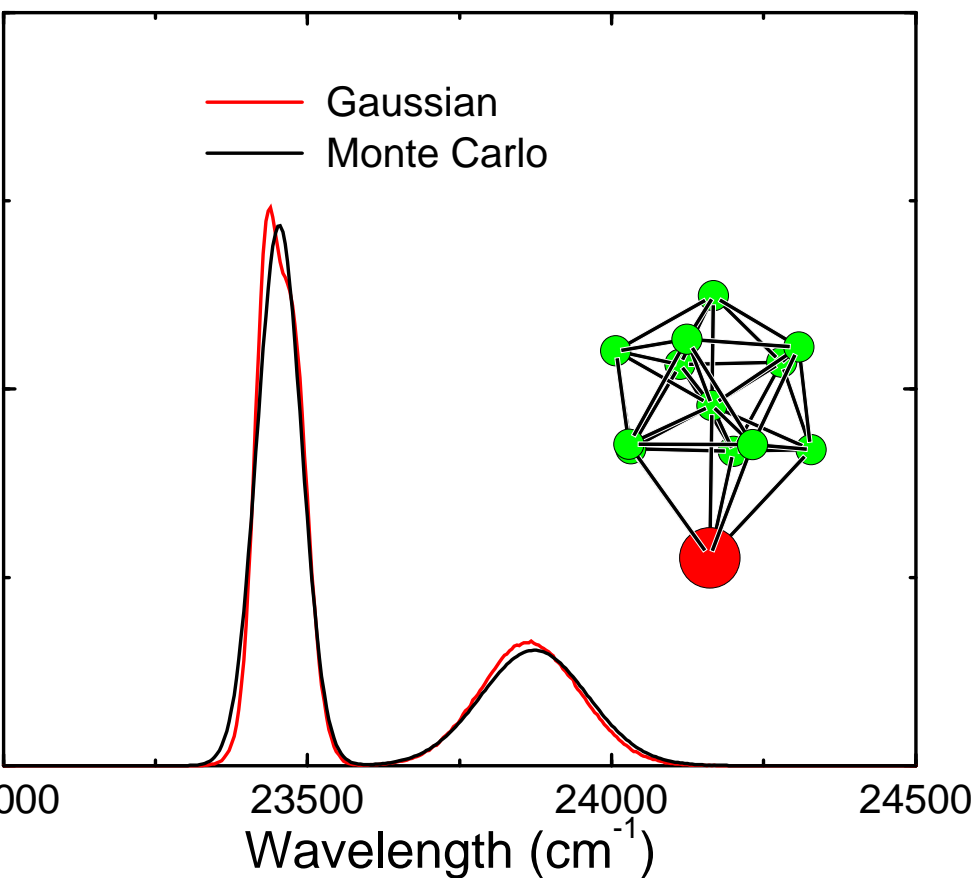
with $\omega_0 = \Delta E / \hbar$, $\gamma_i = \omega_{gi} \tanh \beta \hbar \omega_{gi} / 2$ et

$$\Delta\omega = \frac{1}{4} \sum_i \frac{\omega_{gi}^2 - \omega_e^{ii}}{\gamma_i}, \quad \bar{\omega}^2 = \frac{1}{8} \sum_i \left(\frac{\omega_{gi}^2 - \omega_e^{ii}}{\gamma_i} \right)^2 + \frac{1}{8} \sum_{i \neq j} \frac{(\omega_e^{ij})^2}{\gamma_i \gamma_j} + \frac{1}{2} \sum_i \frac{G_i^2}{\hbar \gamma_i}$$

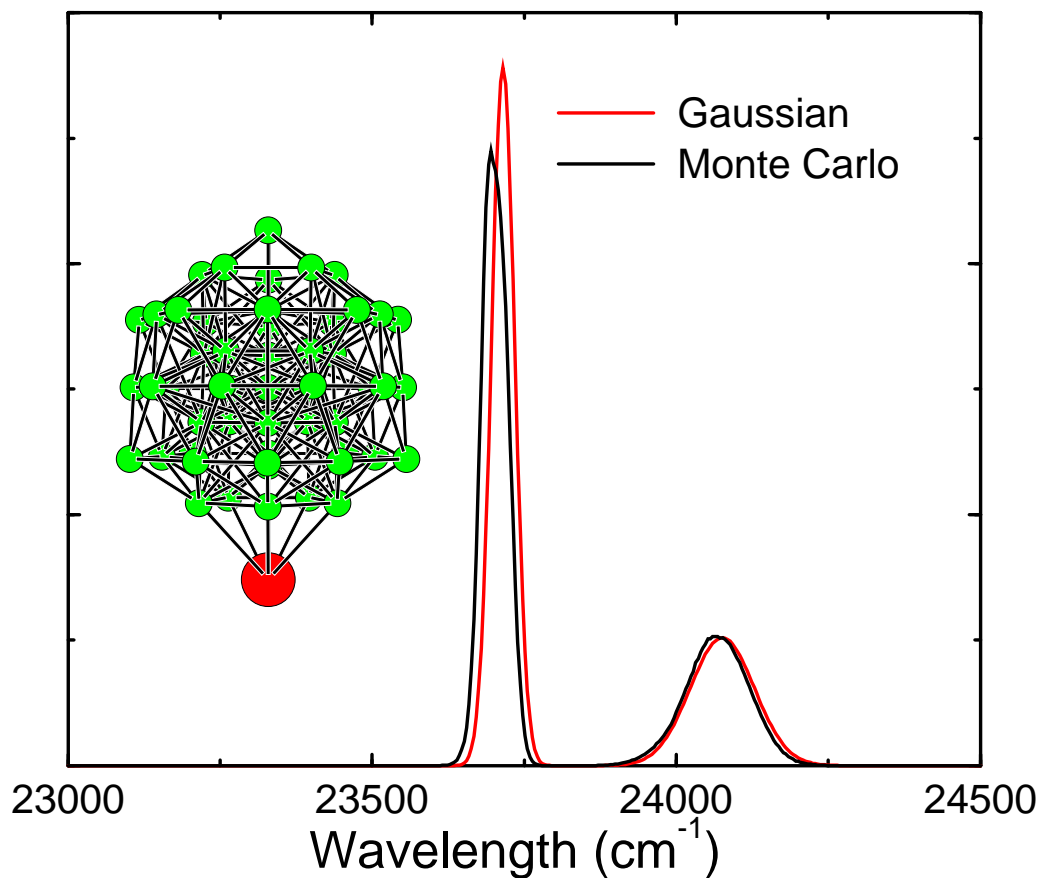
Tests : classical regime

Comparison of **classical MC** simulations with Gaussian theory **at the limit $\hbar \rightarrow 0$** .

CaAr₁₂, T=10 K



CaAr₅₄, T=5 K



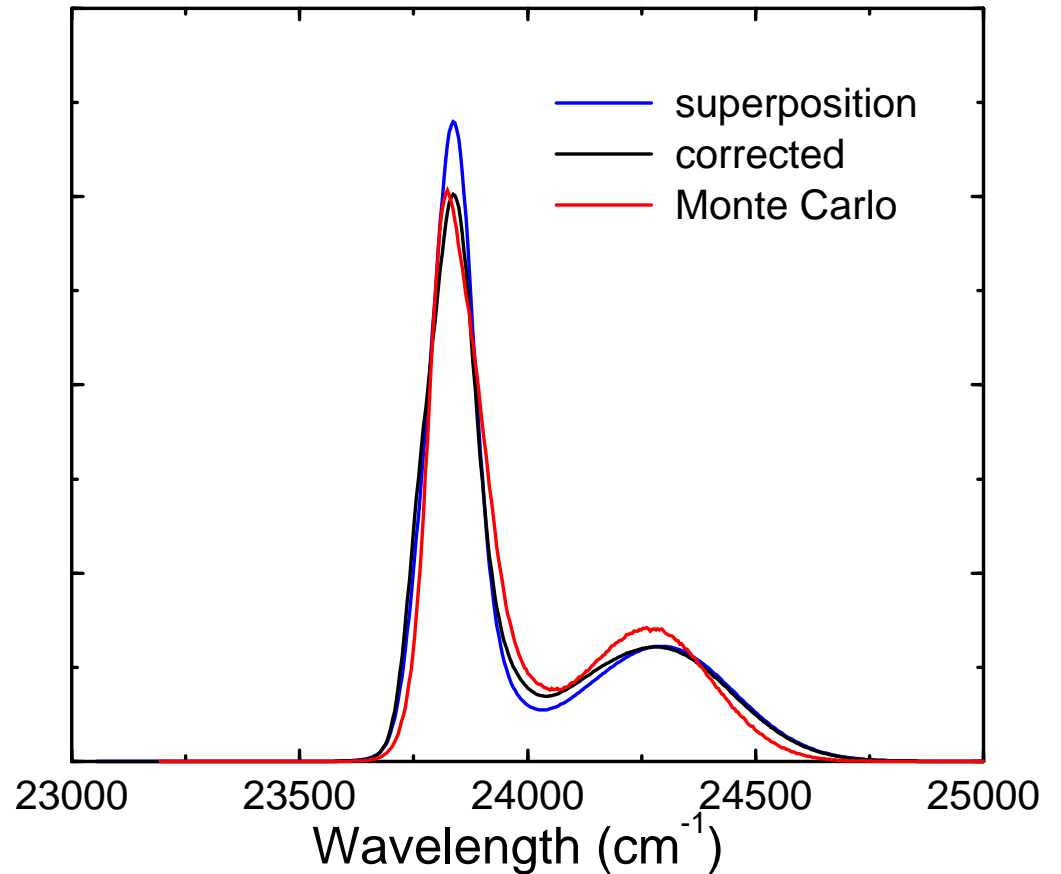
Validity of harmonic superposition

Comparison of **harmonic** superposition with superposition including second order **perturbative corrections**, and quasiclassical MC simulations.

Feynman-Hibbs correction for pair potentials :

$$v_{\text{FH}}(r) = v(r) + \frac{\beta\hbar^2}{24\mu} \nabla^2 v(r)$$

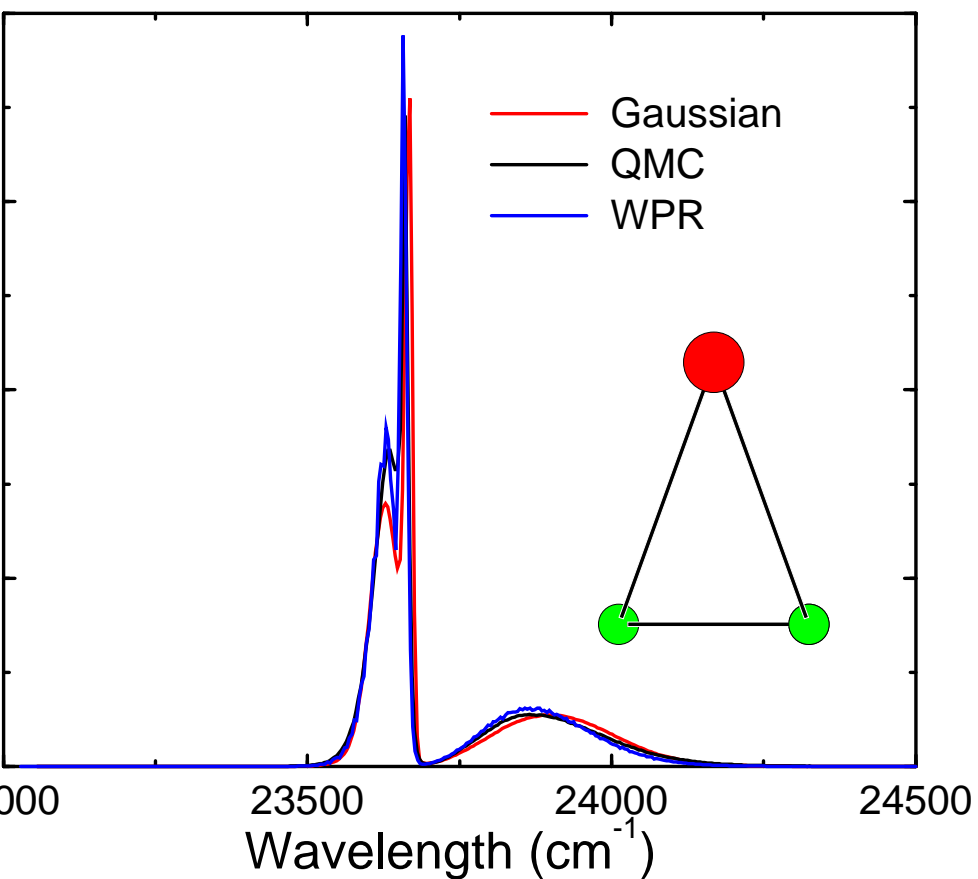
quasiclassical CaAr_{37} $T=25$ K



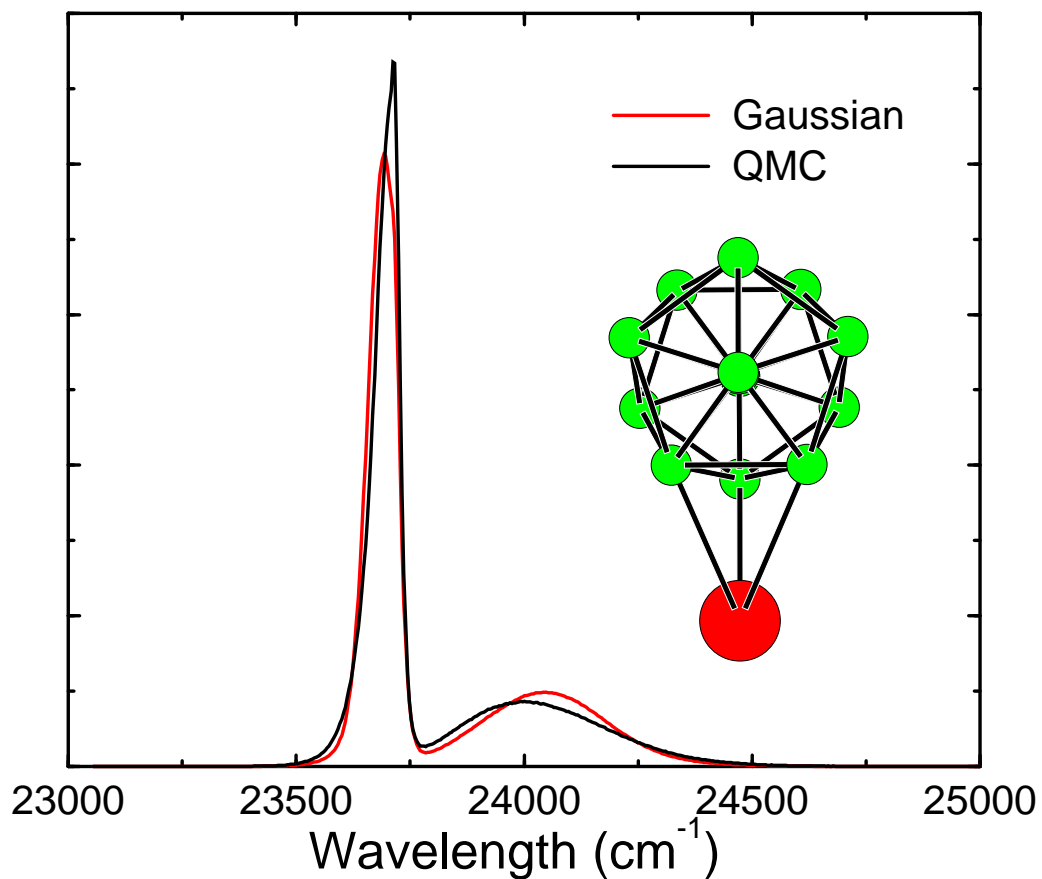
Tests : quantal regime

Comparison of MC quantal (DMC) simulations with Gaussian Theory *dans la limite* $\beta \rightarrow \infty$, and to wavepackets simulations (CaAr_2).

CaAr_2 T=0 K

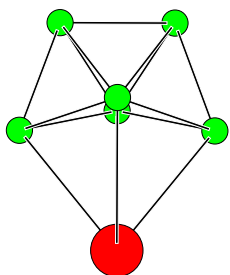


Quantum CaAr_{13} T=0 K

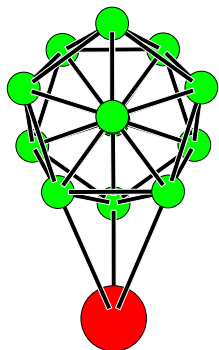


4. Application to isomerization in CaAr_n clusters

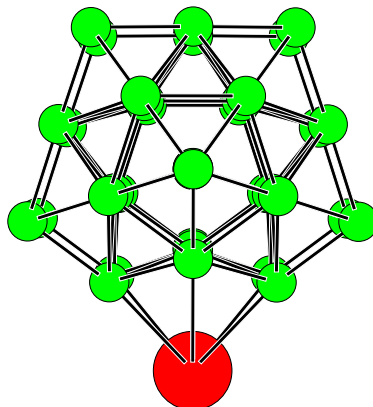
CaAr_7



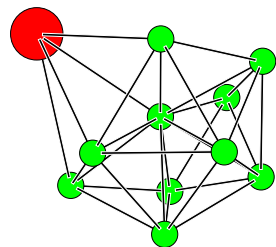
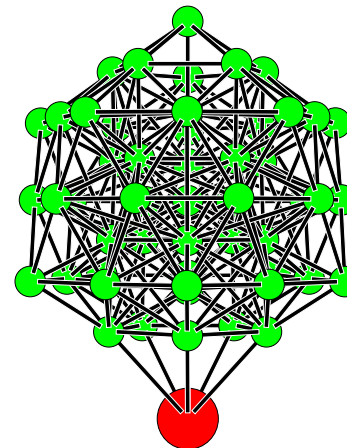
CaAr_{13}



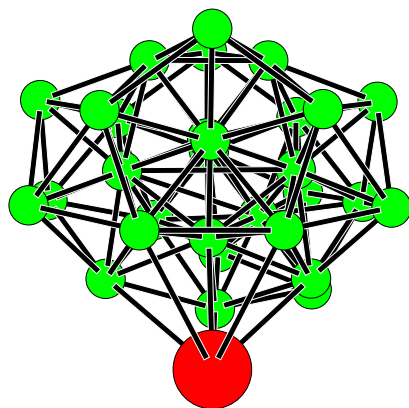
CaAr_{37}



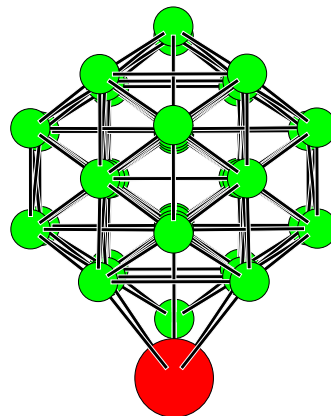
CaAr_{54}



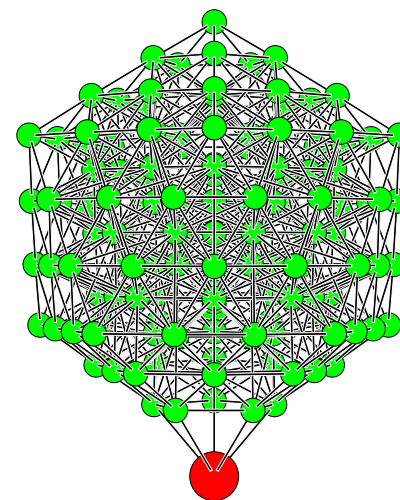
CaAr_{10}



CaAr_{30}

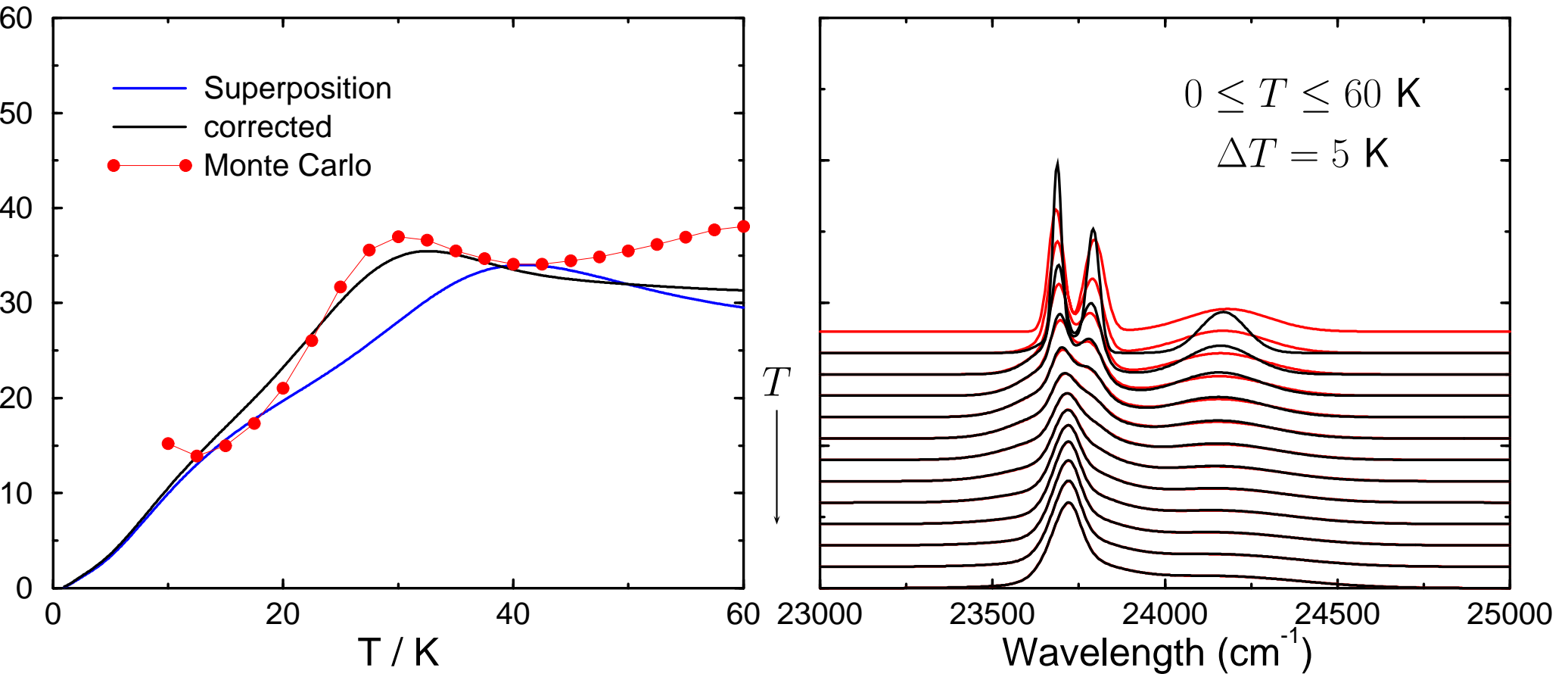


CaAr_{37}^*



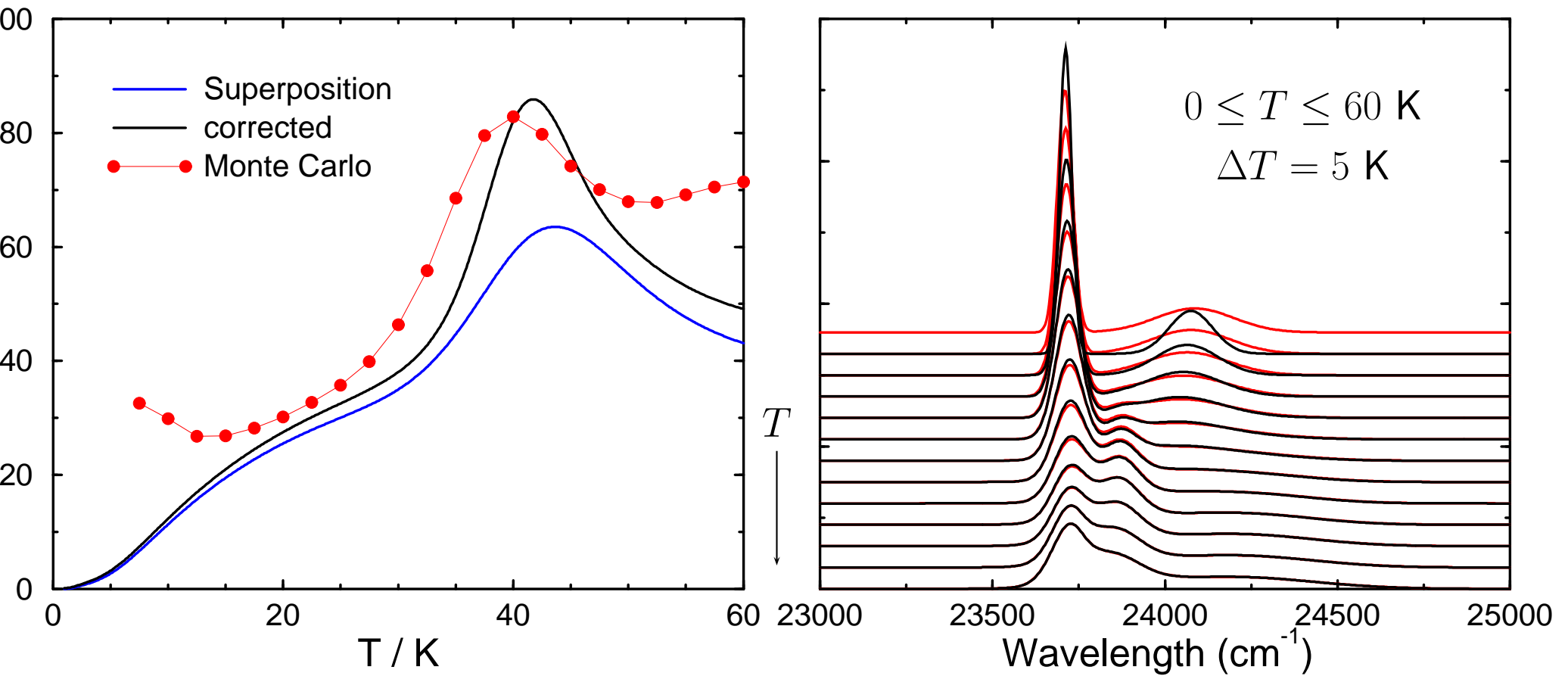
CaAr_{146}

Isomerization in CaAr₁₀



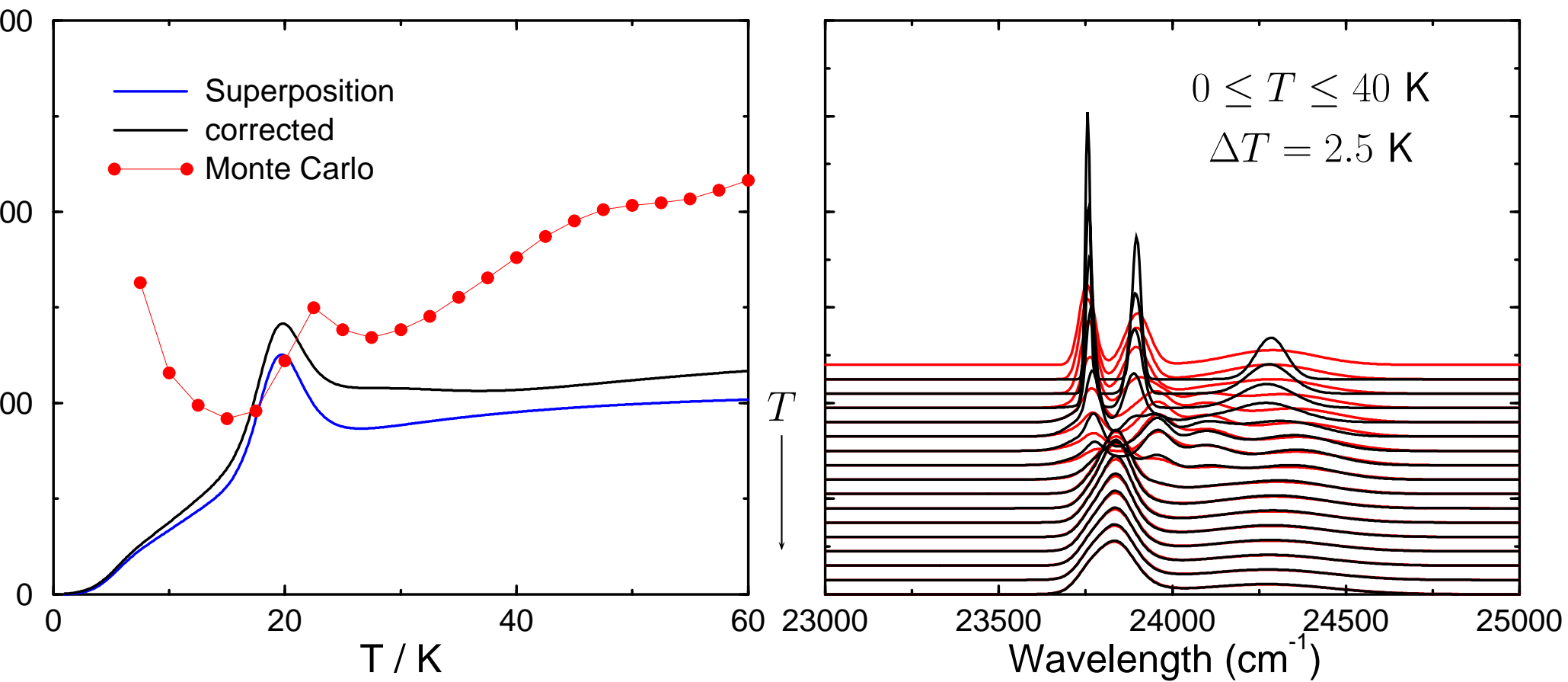
- Thermodynamics sensitive to isomerization, characterized by **spectroscopic signature** ;
- spectra smoothed by **quantal** effects

CaAr₁₃



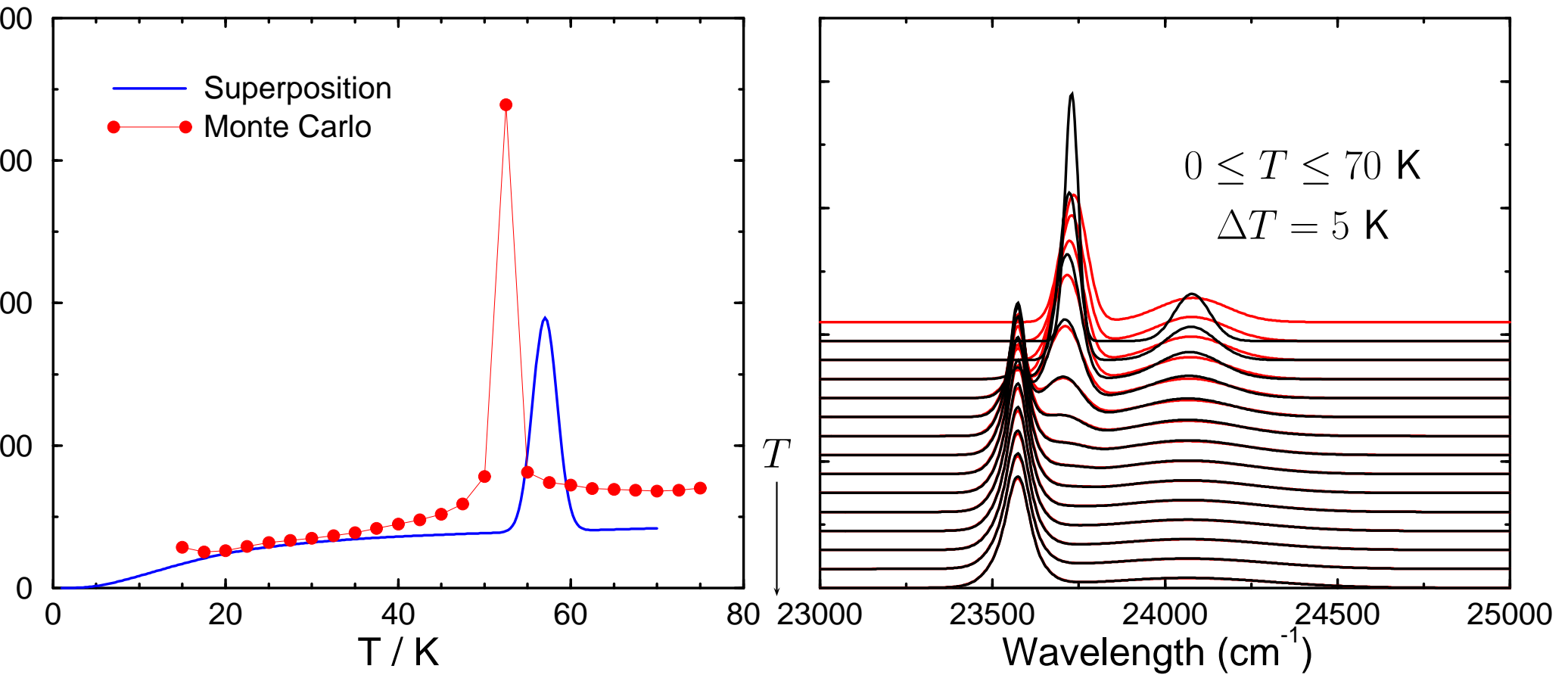
- Phase change more sharply defined , different spectroscopic signature :
1 peak \rightarrow 2 peaks.

CaAr₃₇



- multiple isomerizations, complex spectroscopic signature ;
- qualitative quantal effects

CaAr₁₄₆



- Spectroscopy sensitive to **surface fusion** transition , but not to solid-liquid transition

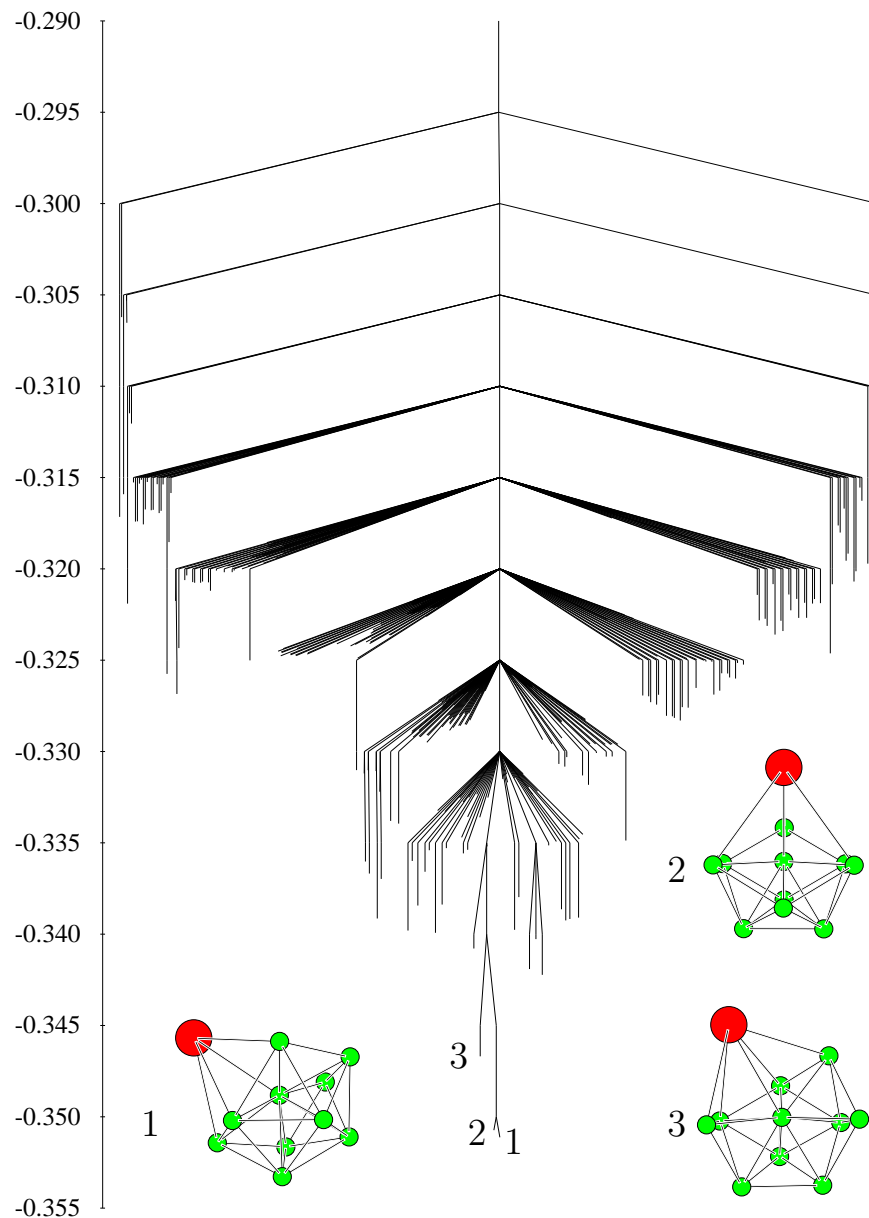
Interpretation with the help of energy landscapes

Using **disconnectivity** graphs, one can visualize the **topography of the potential energy surface**.

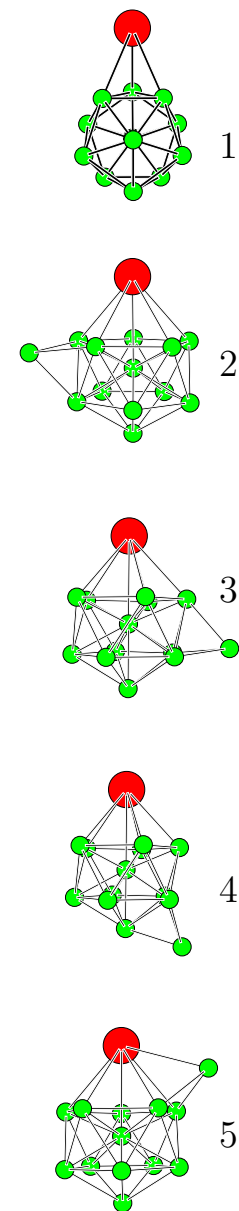
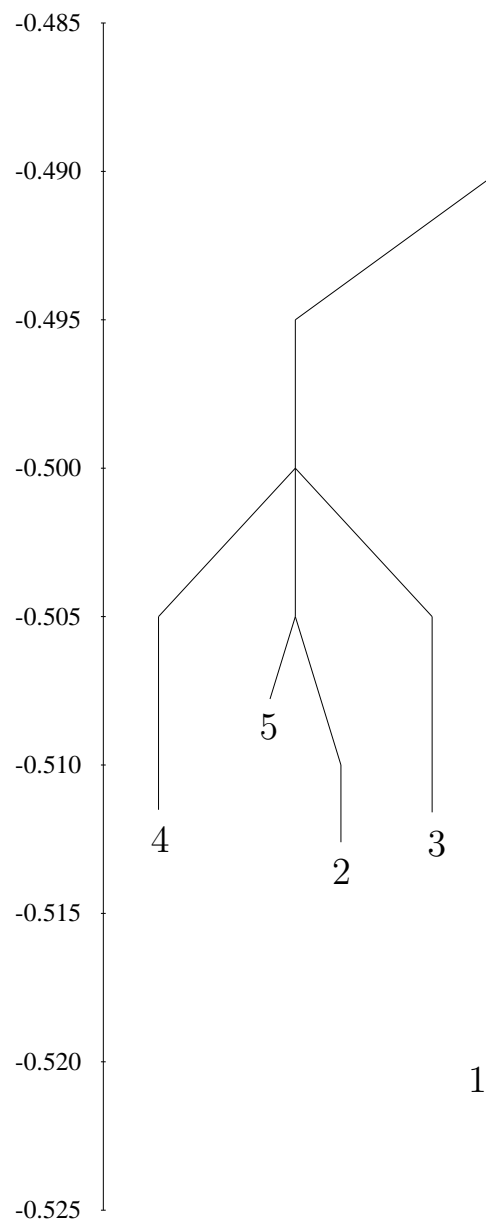
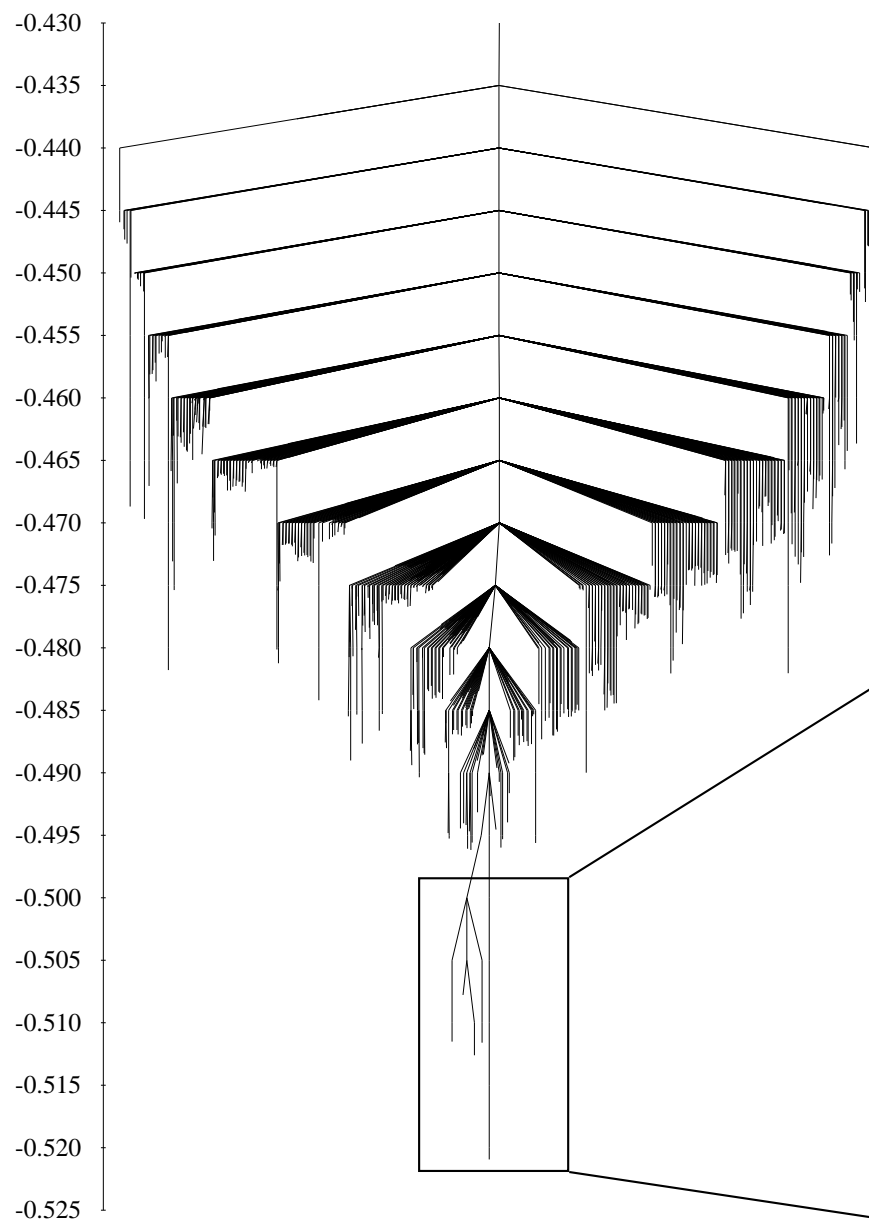
Ref: Becker and Karplus, JCP 106, 1495 (1997).

Ex: CaAr_{10} :

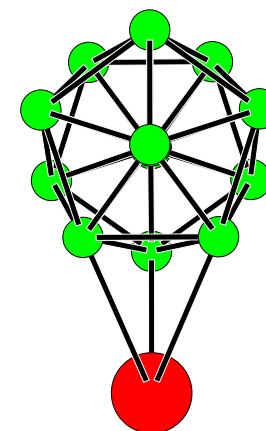
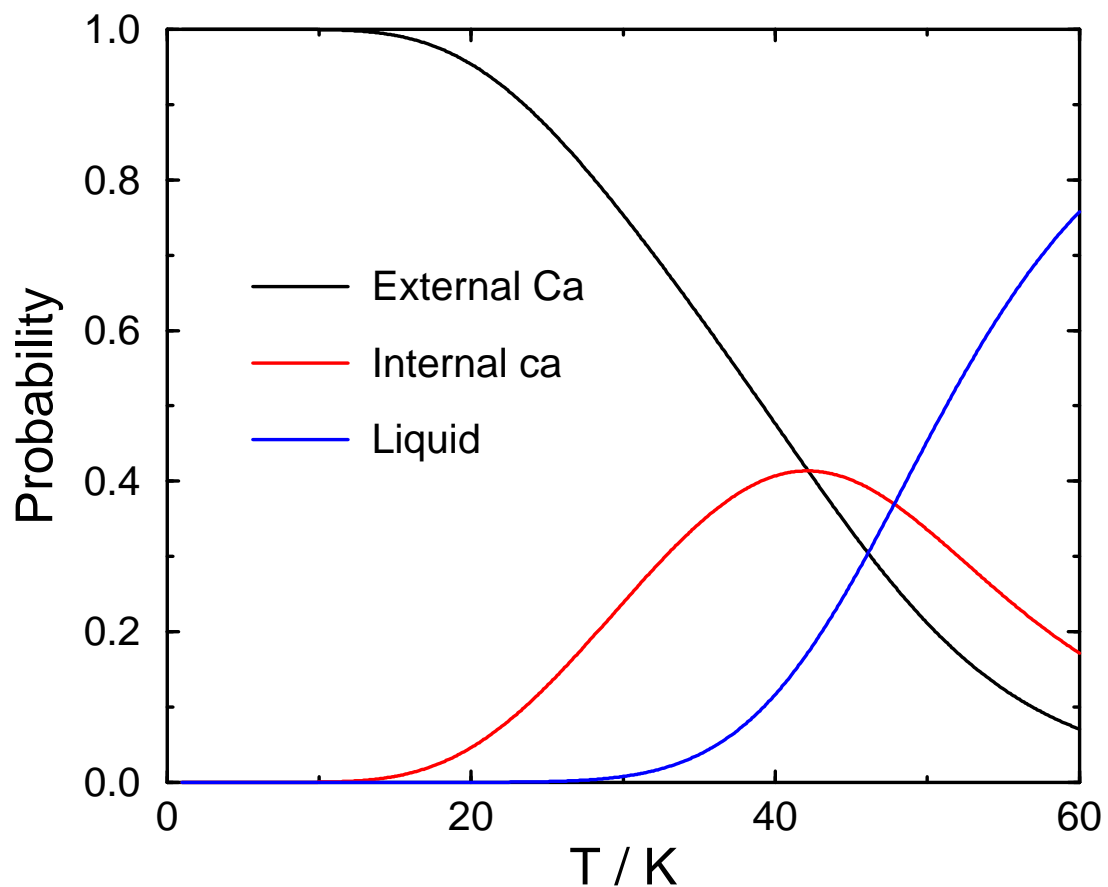
The spectroscopic signature at 30 K is that of isomer **3**



CaAr₁₃ case : secondary funnel

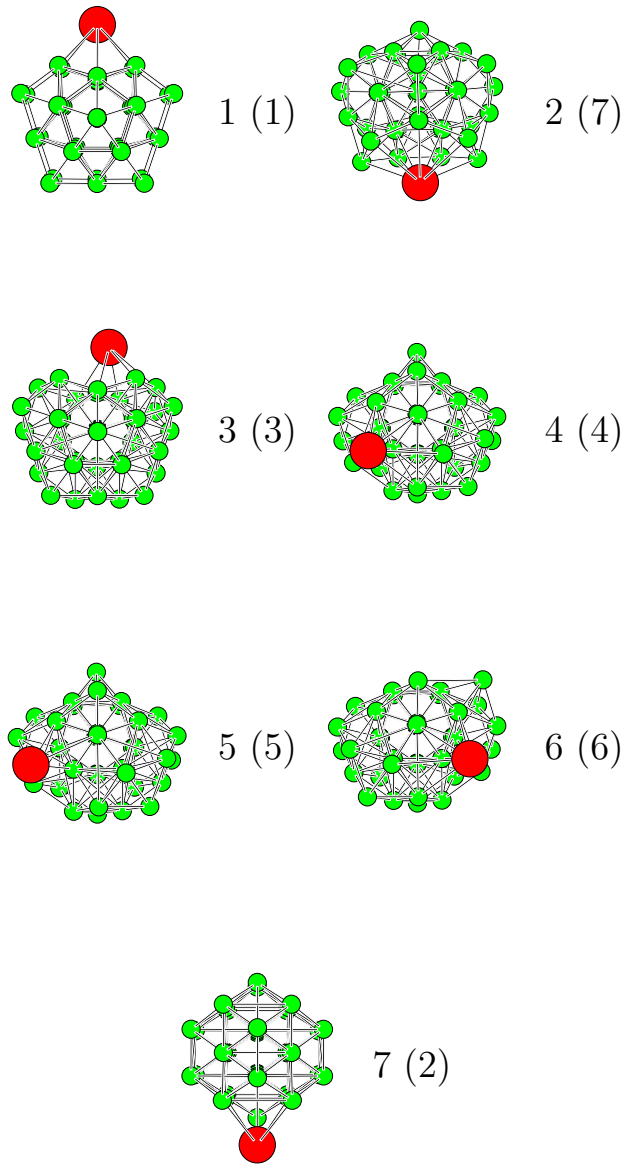
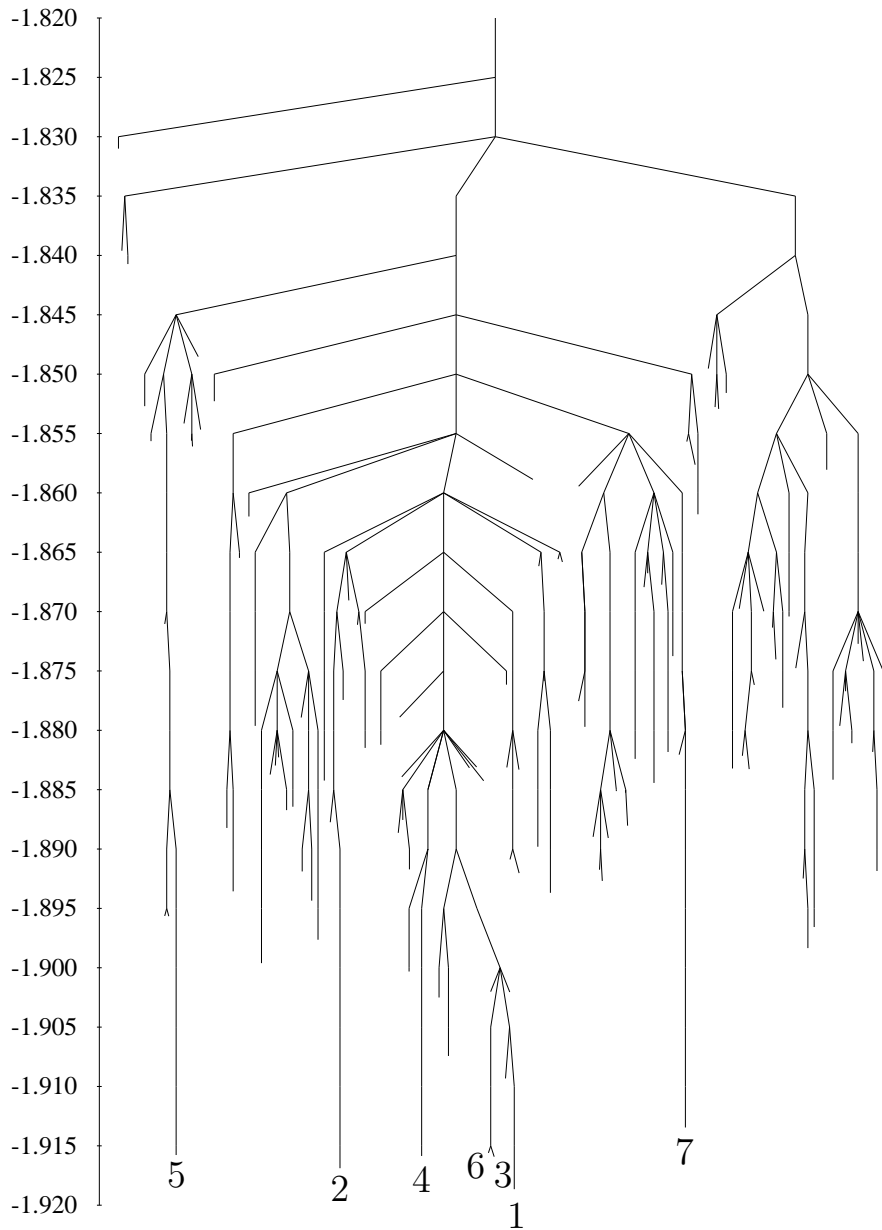


Origin of absorption peak doubling



The cluster undergoes multiple **preliminary** isomerization corresponding to the chromophore **inserted in the "rigid" icosahedral shell**.

The CaAr_{37} case : multiple funnels

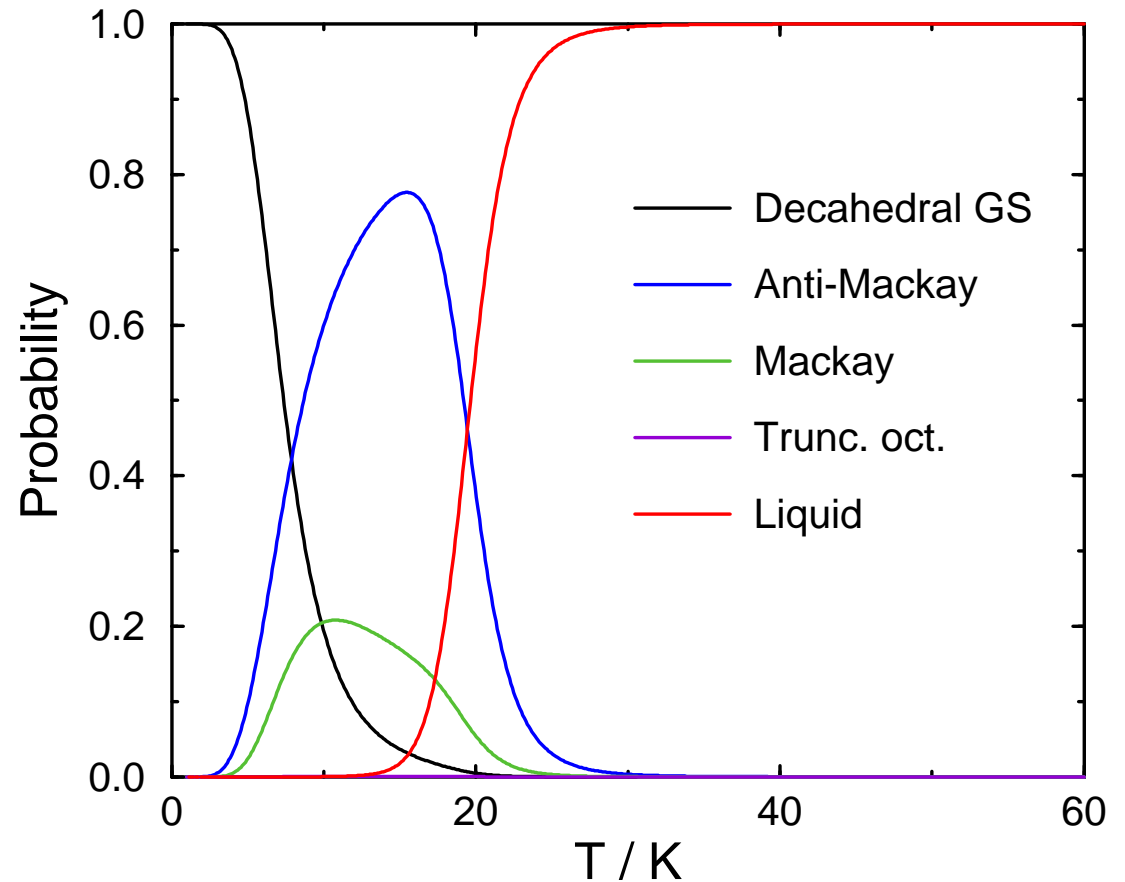


Consequences for isomerization

Case **unique** of structural isomerizations between main shape families known for van der Waals clusters: decahedral, cubic, multi-shell icosahedral (**Mackay**) and polyicosahedral (**anti-Mackay**).

The variations in the absorption spectra reflect the successive transitions :

- **decahedral** → **anti-Mackay** and **anti-Mackay** → **liquid** in the quantal regime ;
- **decahedral** → **cubic**, **cubic** → **Mackay** et **Mackay** → **liquid** in the classical regime.



Relaxation towards equilibrium

Given a **connex** set of minima $\{\alpha\}$ and linking saddle points between them, one can characterize the time evolution of the **probability** for the system to be in one of the isomers.

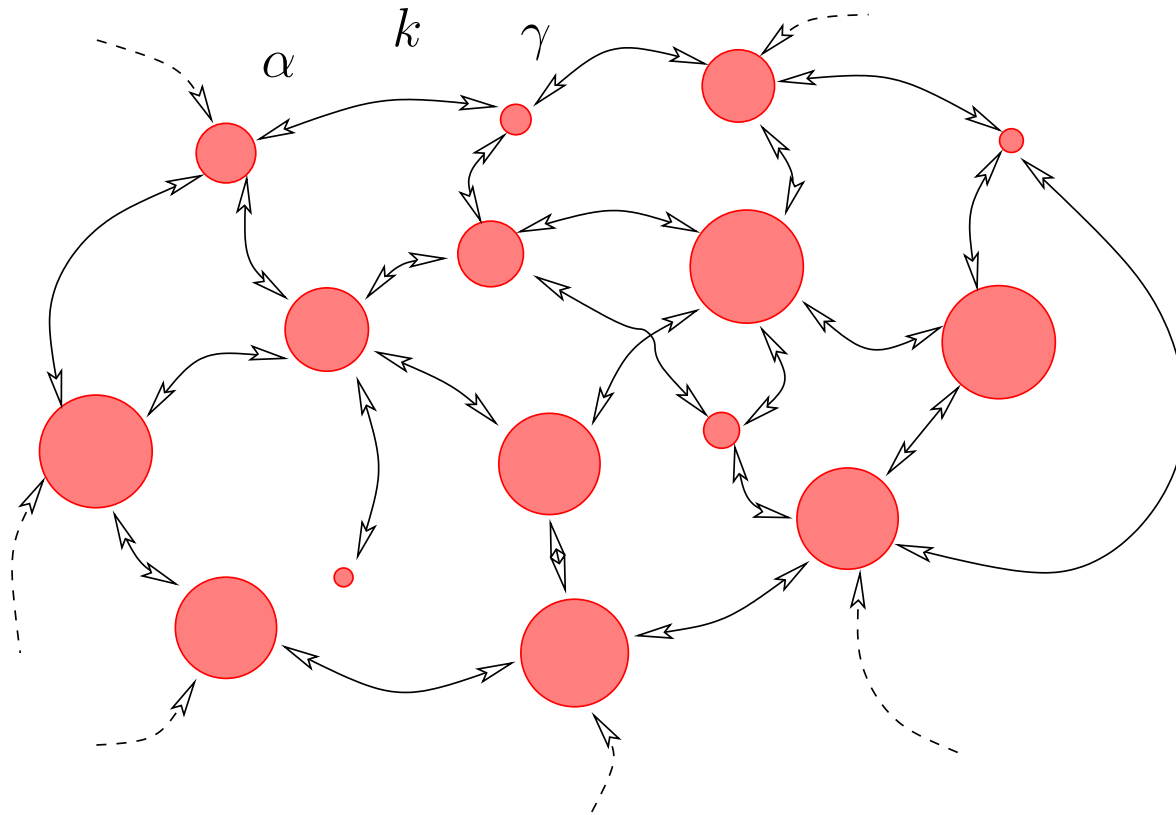
The **statistical** state of the system is defined at time t by a presence probability vector $\mathbf{P}(t)$ which evolves according to the **master equation** :

$$\frac{dP_\alpha}{dt} = \sum_{\gamma \neq \alpha} k_{\gamma \rightarrow \alpha} P_\gamma - \sum_{\gamma \neq \alpha} k_{\alpha \rightarrow \gamma} P_\alpha$$

Setting $W_{\alpha\gamma} = k_{\alpha\gamma} - \delta_{\alpha\gamma} \sum_{\nu} k_{\nu\alpha}$, the master equation can receive a matrix expression

$$\frac{d\mathbf{P}}{dt} = \mathbf{W}\mathbf{P}(t).$$

This equation is solved numerically via **exact diagonalization**.

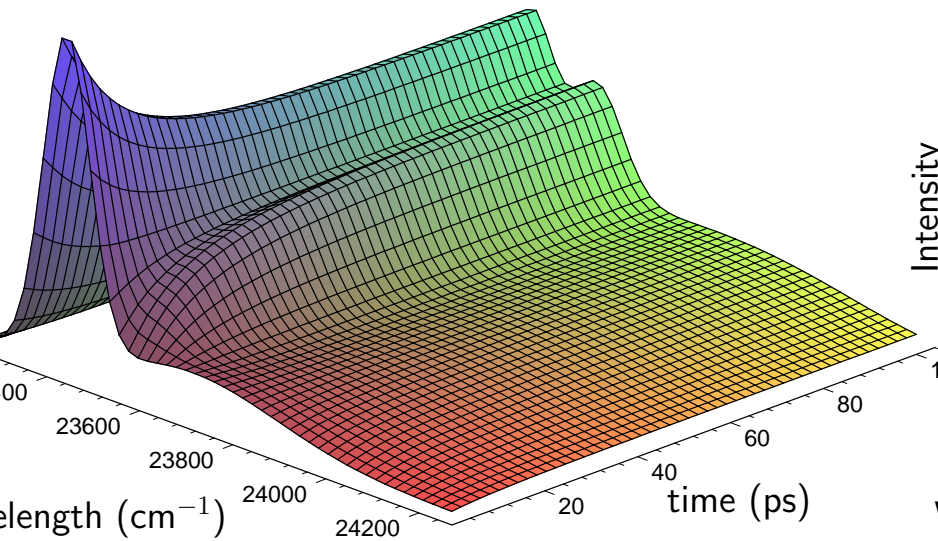


The transition rates $k_{\alpha \rightarrow \gamma}$ may be approximated, for example, according to [transition state theory](#) in the harmonic approximation :

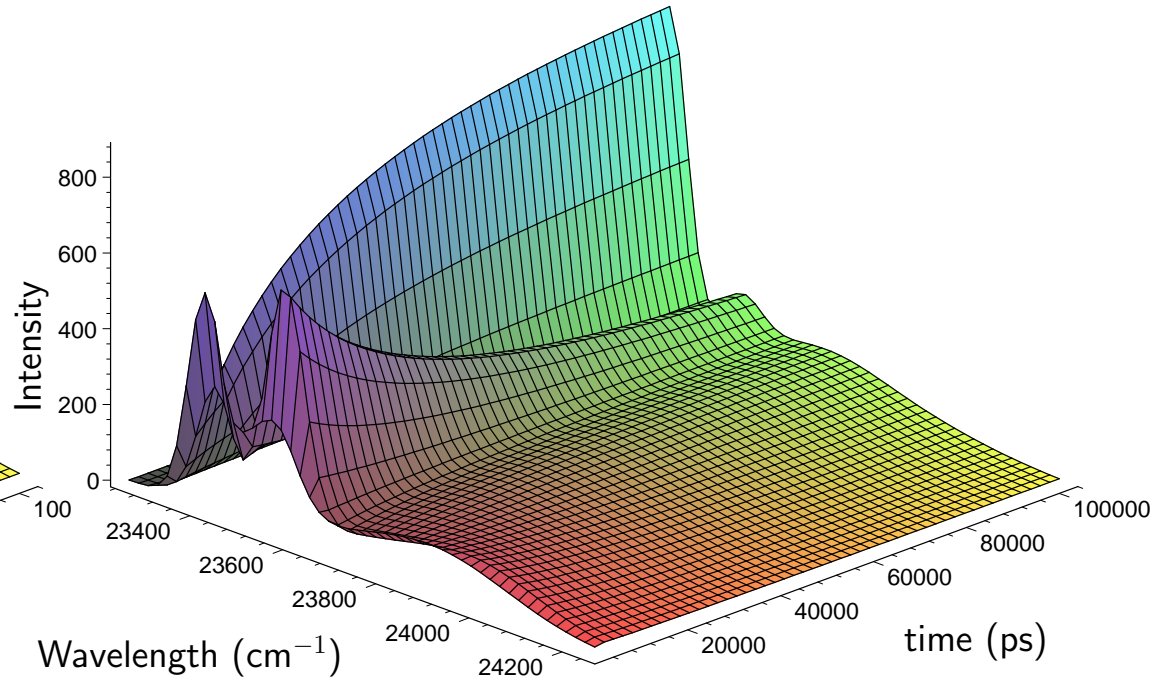
$$k_{\gamma \rightarrow \alpha}(\beta) = \frac{k_B T}{h} \frac{Z_{\gamma}^{\ddagger}(\beta)}{Z_{\alpha}(\beta)} = \frac{n_{\gamma}^{\ddagger}}{n_{\alpha}} \frac{k_B T}{h} e^{-(E_{\gamma}^{\ddagger} - E_{\alpha})/k_B T} \frac{\prod_{i=1}^{3N-7} \frac{2}{\sinh \hbar \omega_{\gamma\alpha}^{(i)}/k_B T}}{\prod_{i=1}^{3N-6} \frac{2}{\sinh \hbar \omega_{\alpha}^{(i)}/k_B T}}$$

Relaxation in CaAr₁₃

$T = 0 \text{ K} \rightarrow T = 40 \text{ K}$



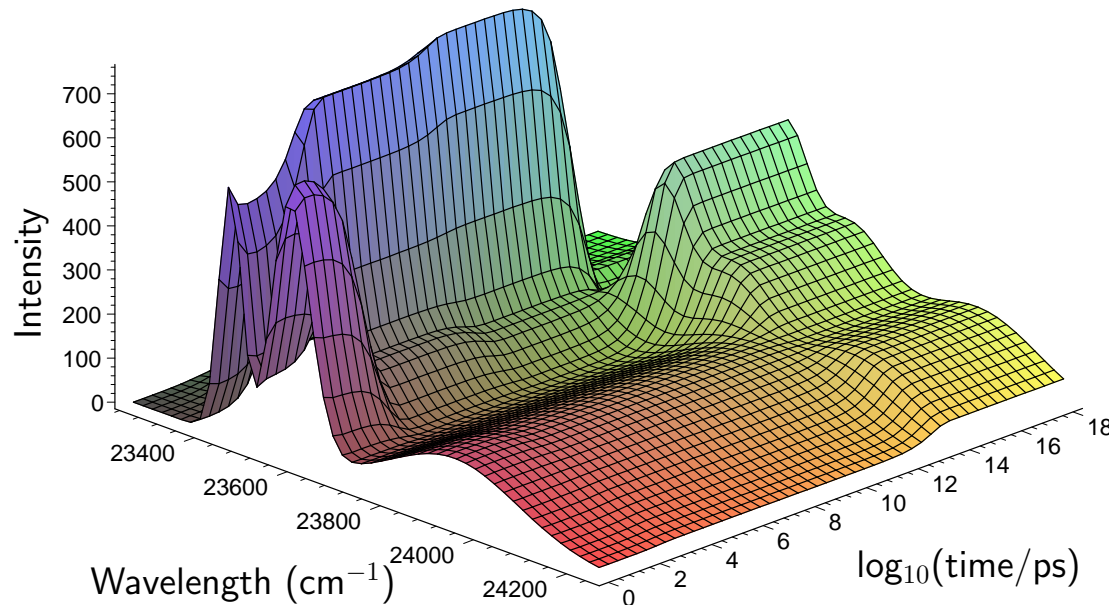
$T = 60 \text{ K} \rightarrow T = 20 \text{ K}$



- A $T = 40 \text{ K}$, the spectra reflect relaxation towards equilibrium within about 10 ps.
- At $T = 20 \text{ K}$, starting from a hot distribution at $T = 60 \text{ K}$, the system burries in the secondary funnel acting as a **kinetic trap**. The relaxation time (100 ns) increases significantly.

Slow relaxation in CaAr₃₇

$$T = 0 \text{ K} \rightarrow T = 40 \text{ K}$$



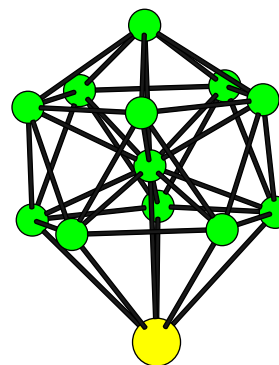
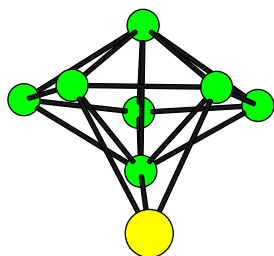
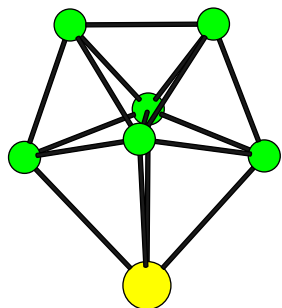
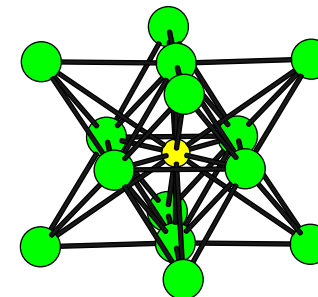
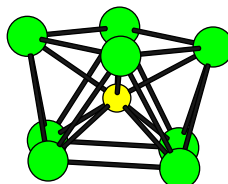
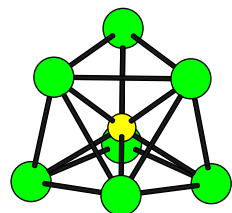
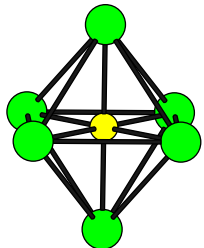
- The existence of **multiple funnels** strongly slows down cluster dynamics, and **macroscopic** relaxation times up to 10^3 seconds can be seen !

⇒ **glassy** behaviour

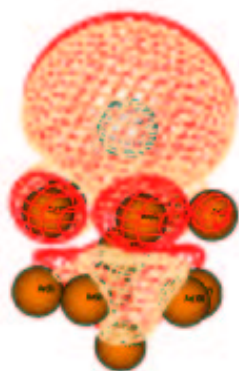
- The spectroscopic sensitivity to isomer structure and the **variety** of competing isomers make possible the following of the statistical evolution of the system with **time**.

Alkali atom solvated by a rare gas cluster

Geometry of ions: NaAr_n^+



Geometry of neutrals: NaAr_n



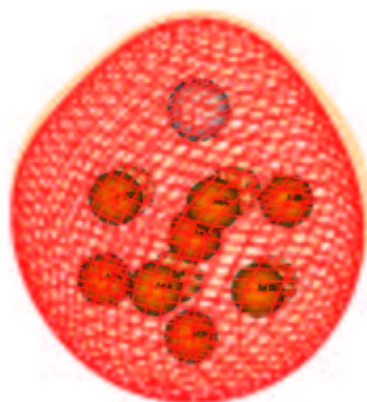
3px



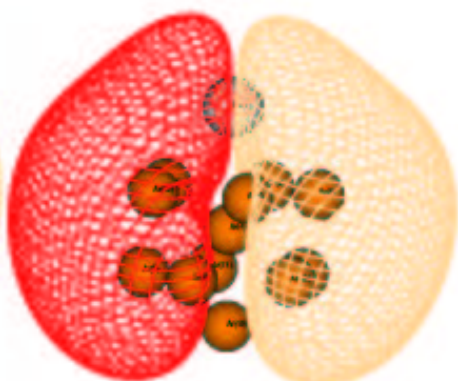
3py



3pz



4px



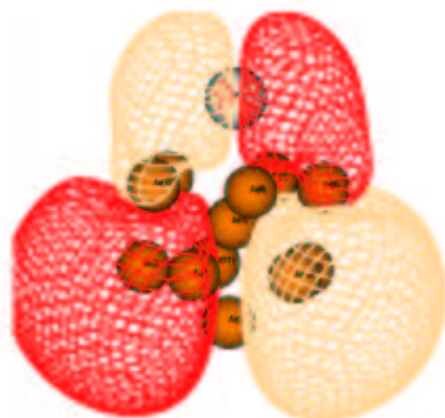
4py



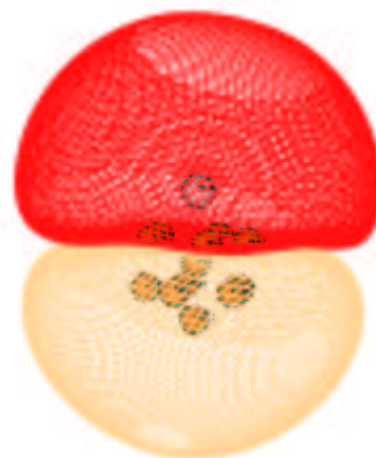
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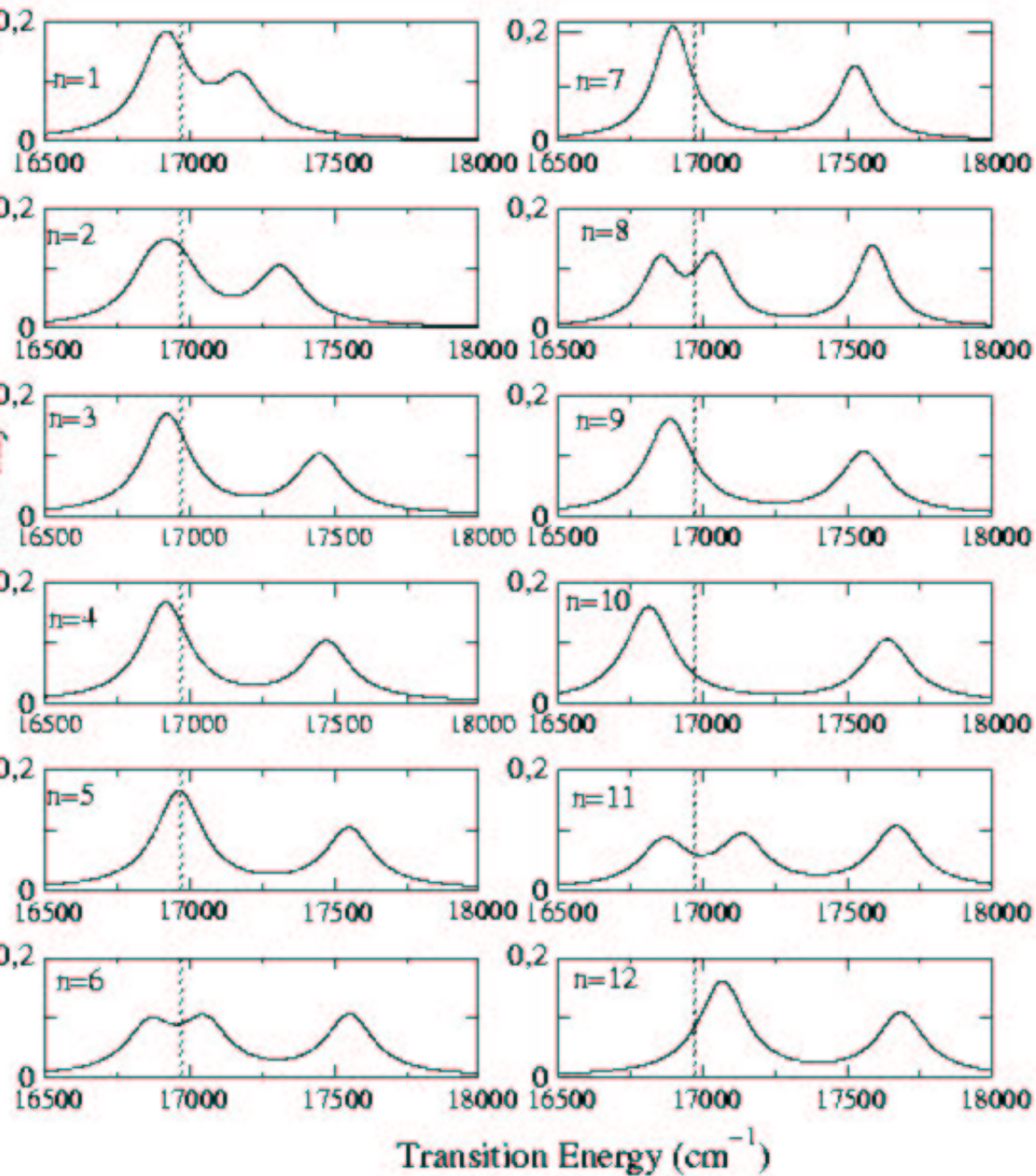
5px



5py

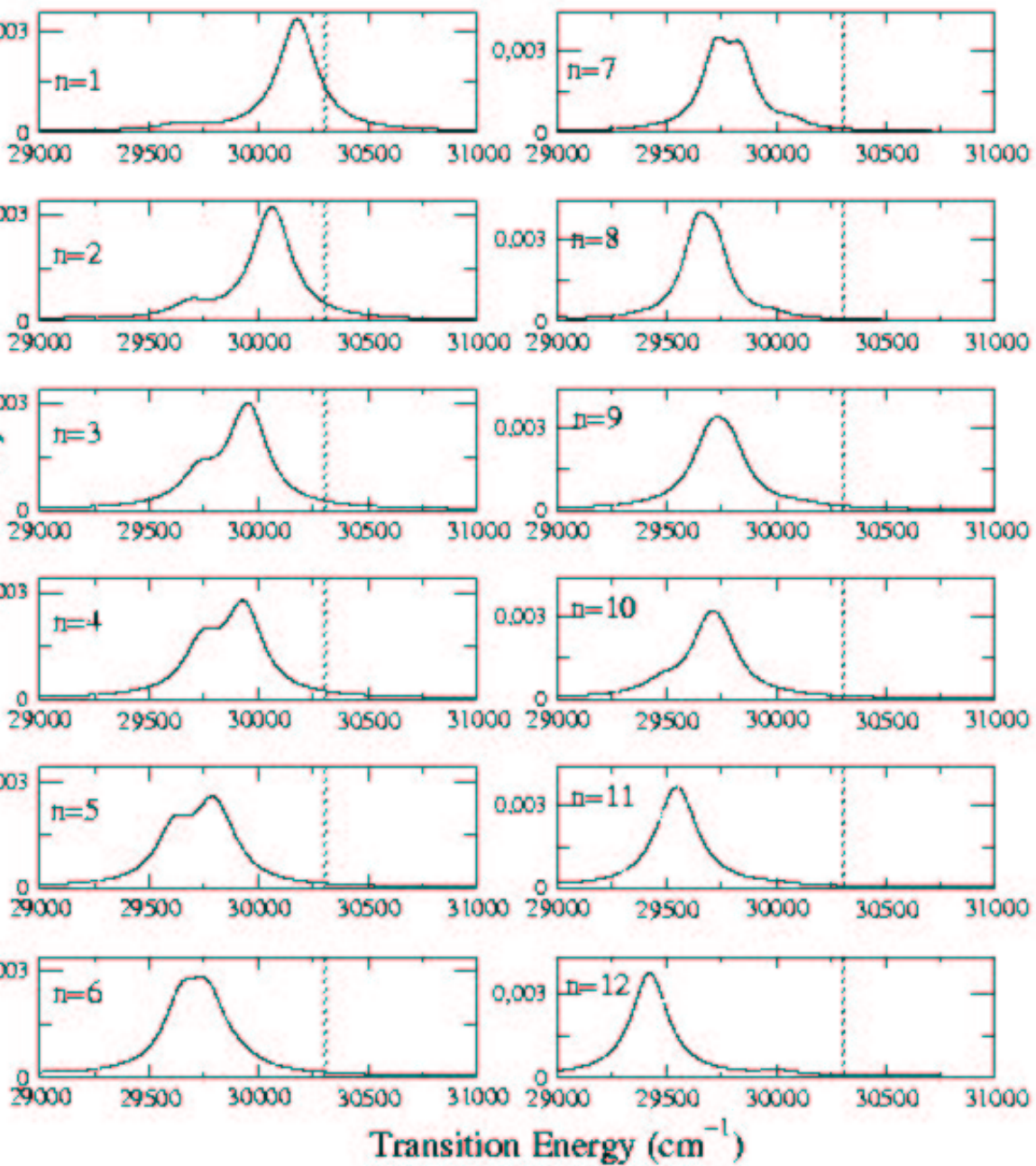


5pz



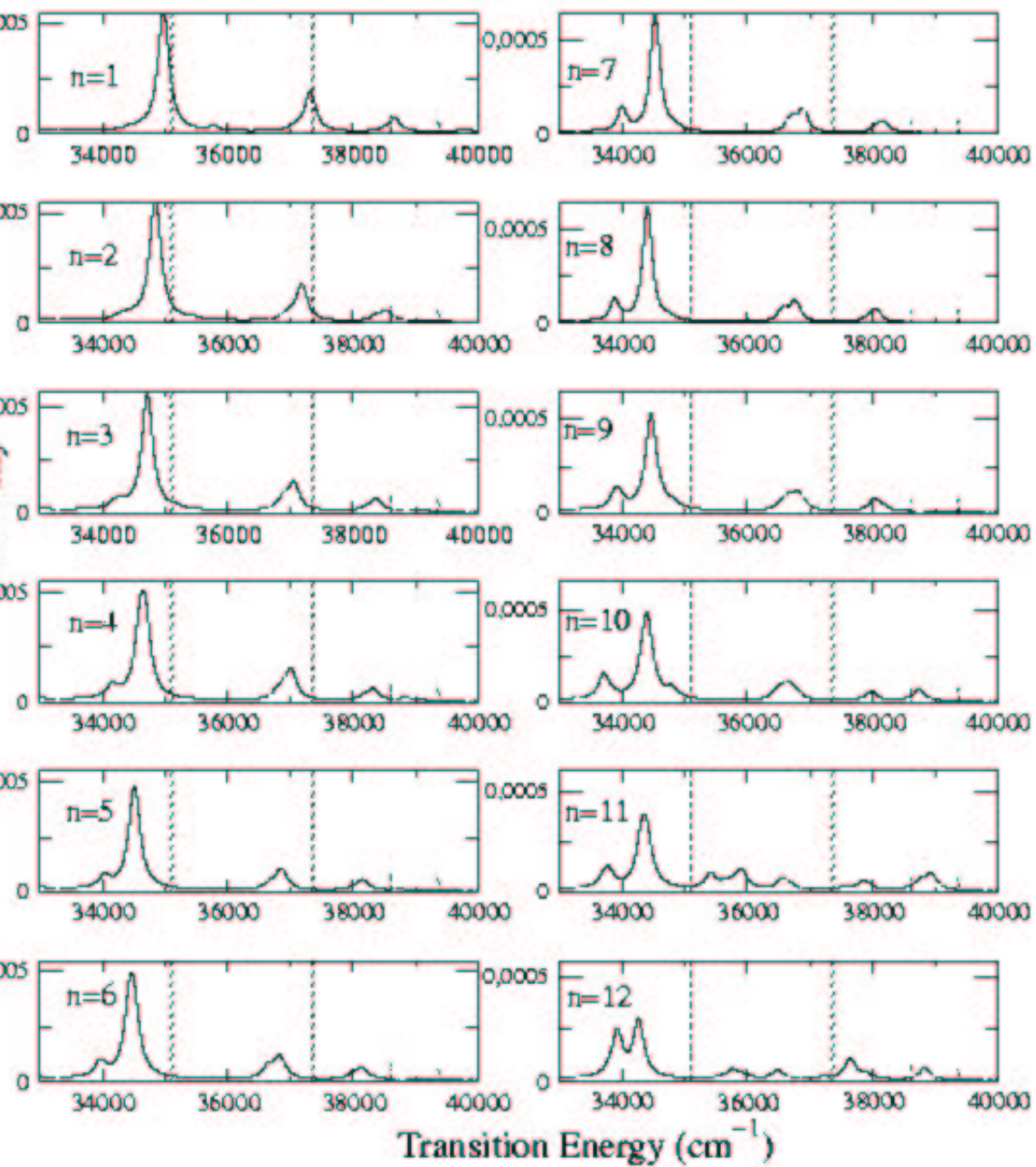
Absorption spectra of NaAr_n clusters

Atomic line 3s → 3p: 16968 cm⁻¹



Absorption spectra of NaAr_n clusters

Atomic line 3s → 4p: 30272 cm⁻¹

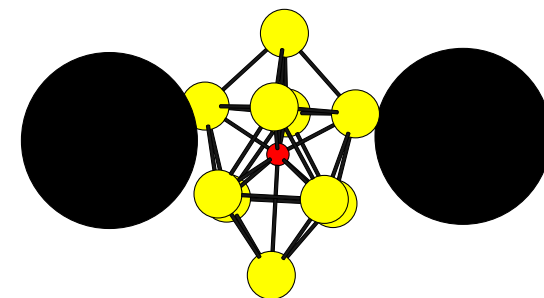
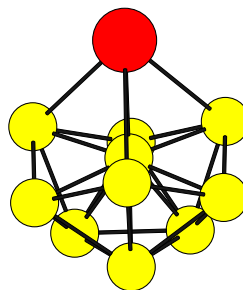
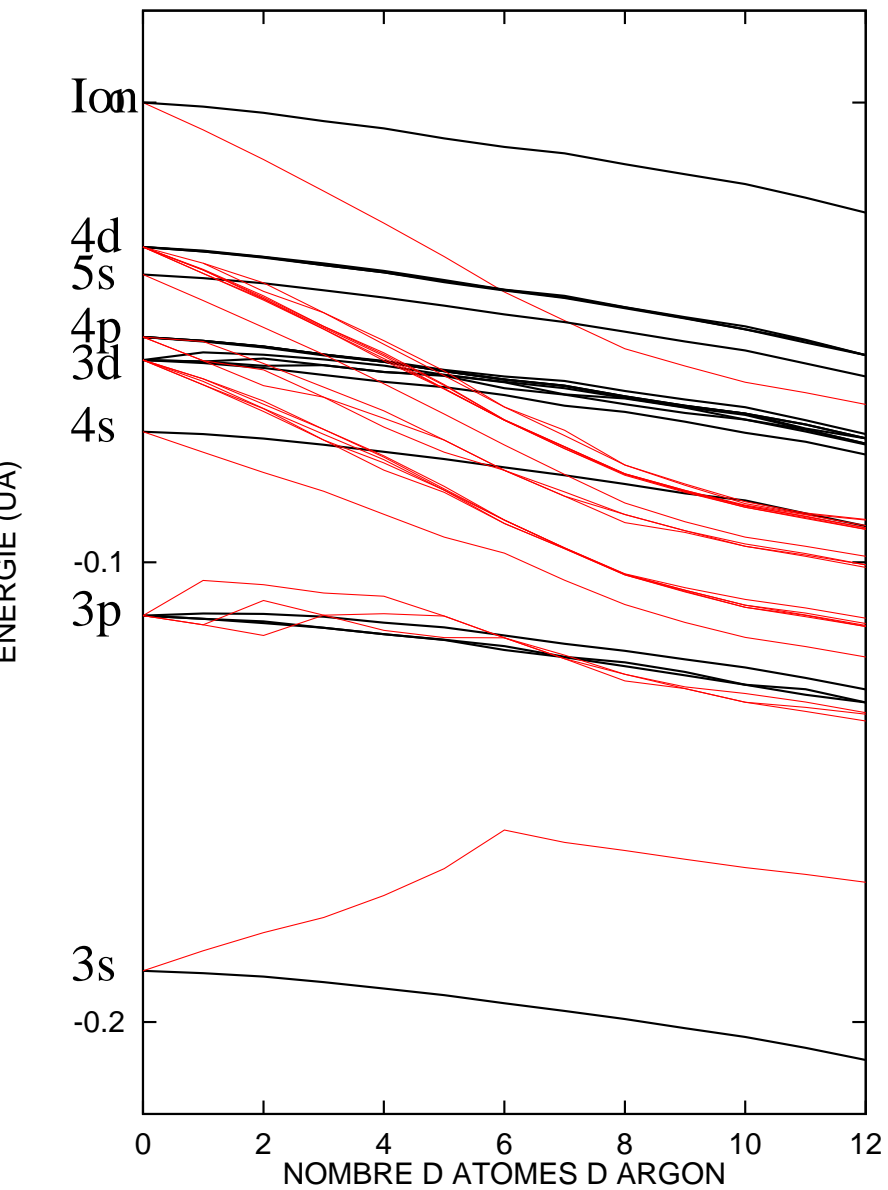


Absorption spectra of NaAr_n clusters

Atomic line 3s → 5p: 35041 cm⁻¹

Rydberg states of clusters: structural transition

ions geometry
neutrals geometry



Conclusion and outlook

Very small clusters

- detailed insight in excited states dynamics
- alternative: semi-classical treatment with surface hopping (cf. V. Bonacic-Koutecký)
- Up to which size can we observe or understand?

Spectroscopy, thermodynamics and long time processes in large systems

- The **superposition** method provides an alternative to direct MD: **isomerization** effects ; **quantal** effects approximated;
- The **gaussian theory** of Wadi and Pollack seems to work.
- Statistical relaxation towards equilibrium can be reached on timescales which are not accessible by MD. Quasiclassical quantum effects can be incorporated.
- Test should be performed in other cases: Neon
- Build such a theory for excited states and emission? more challenging and difficult.

Spectroscopic clues for izomerization and/or phase changes

Yes...

- At a given size, the cluster may show strong structural changes due to temperature (and sometimes also to quantum delocalization even at low T)
- The absorption sepctrum is sensitive to such changes and can detect the transition temperatures.
- The absorption spectrum can be even more affected than the thermodynamical functions themselves (see metal systems: H. Haberland et al.)

...but

- The spectroscopic signatures are strongly size-dependant

Other systems and high excited states may be interesting