

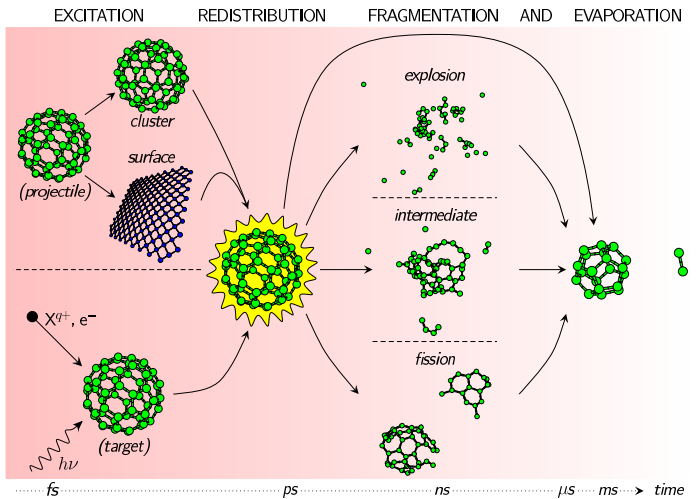
Intramolecular dynamics from statistical theories

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Introduction



Introduction

- Dynamics in the short time (sub-ps) is governed by non adiabatic couplings. **Dynamics in the excited states.**
- Following this electronic relaxation, the molecule can be found in the **fundamental electronic state.**
- In this course, we will focalize on the competition between different relaxation processes, may be sequential, of the system in this ground electronic state:
 - Dissociation
 - Isomerisation
 - IR Emission
- Following dynamics of a molecular system over a long time is really a challenge both for experimentalists and theoreticians.

Introduction

"Complex" molecular systems have some common properties:

- **P**otential Energy Surface (PES) is characterized by a large number of local minima (isomers) and extrema (saddle points).
- **A**nharmonicity of the PES
- **C**haracteristics times of different processes on different orders of magnitude [coexistence of **short time** (ps-ns) and **long time** (ms-s) dynamics].
- **M**olecular system with a large number of freedom. Difficult to follow the time evolution by solving Schrödinger equation.

Introduction

Born-Oppenheimer adiabatic approximation is generally used to compute electronic states.

- The molecular hamiltonian can be written as:

$$\mathcal{H} = \mathcal{T}(\mathbf{p}) + \mathcal{T}(\mathbf{P}) + \mathcal{U}(\mathbf{r}, \mathbf{R}) \quad (1)$$

- In this expression, \mathbf{r} is the set of the electronic coordinates, \mathbf{R} is the set of the nuclear coordinates. \mathbf{p} and \mathbf{P} are the momenta linked to \mathbf{r} and \mathbf{R} , respectively.

Introduction

- **As** the nuclei masses are larger of electrons, the electronic wavefunctions $\varphi_e^{(n)}(\mathbf{r}; \mathbf{R})$ can be computed by **fixing** molecular geometry (**adiabatic approximation**).
- **These** electronic wave functions depend parametrically on the nuclear positions. For each value of \mathbf{R} , the schrödinger equation is solved:

$$[\mathcal{T}(\mathbf{p}) + \mathcal{U}(\mathbf{r}, \mathbf{R})] \varphi_e^{(n)}(\mathbf{r}; \mathbf{R}) = V_n(\mathbf{R}) \varphi_e^{(n)}(\mathbf{r}; \mathbf{R}) \quad (2)$$

Introduction

- The function $V_n(\mathbf{R})$ corresponds to the electronic energy for the $n^{\text{ème}}$ adiabatic electronic state.
- For each electronic state, we will have a function of whole of the nuclear coordinates called **Potential Energy Surface** (PES).
- By the following, we will work on the ground PES $V(\mathbf{R})$.
- At the vicinity of a **local minimum** \mathbf{R}_e , the PES can be expressed as:

$$V(\mathbf{R}) = V(\mathbf{R}_e) + (\mathbf{R} - \mathbf{R}_e)^t H_h (\mathbf{R} - \mathbf{R}_e) + \dots$$

with H_h the Hessian matrix.

- On this PES, classical dynamics of the nuclei can be simulated.

Introduction

- Different methods can be used for the calculation of the PES $V(\vec{R}_1, \dots, \vec{R}_n)$:
 - 1 Atomistic model
 - *ab-initio* PES. Based on the calculation of the electronic wavefunction (or the electronic density).
 - Semi-empirical PES (TB, DFTB, ...)
 - **Non reactive** empirical PES (AMBER, CHARMM, ...)
 - **Reactive** empirical PES (AIREBO, REAX)
 - 2 Coarse grained model
- This choice will be mainly governed by:
 - The **size** and the **nature** of the molecular system
 - The **characteristics time** of the microscopic phenomena
 - The **quality of the PES sampling**

Introduction

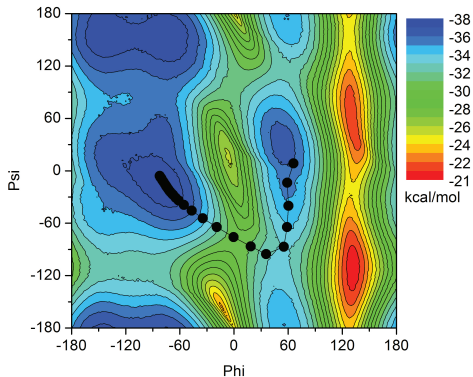


Figure: An example of Potential energy surface.

Introduction

- **Why exploring** this PES ?
 - Important to find **local minima and extrema** which play a crucial role in the dynamics.
 - Following the time evolution of a given physical observable versus of E , T , ...
 - Understanding thermodynamics of the system ...
 - Understanding the reactional dynamics along a given path $\lambda(\mathbf{R})$.
- **How to properly explore** this PES ?
 - Exploration of the phase space. Dynamics in the (NVE), (NVT) statistical ensembles, ... **Time average** of physical observables.
 - Exploration of the configuration space in different statistical ensembles. **Ensemble average** of physical observables.
- Problem of ergodicity → **Numerical strategies to follow.**

Introduction

- **Molecular dynamics simulations in the (NVE) ensemble**

- ① Propagation of **Hamilton's equations**

$$(\mathbf{R}(t), \mathbf{P}(t))$$

- ② Perfectly adapted to follow the time evolution of **physical properties as a function of time**

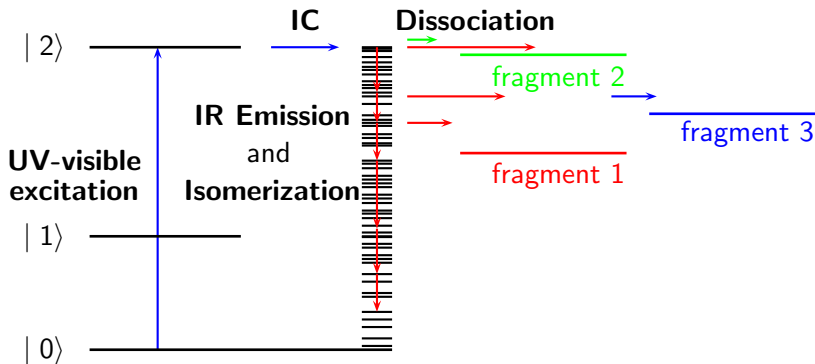
$$A(t) \equiv A(\mathbf{R}(t)) \text{ et } \langle A \rangle_t = \frac{1}{N} \sum_{i=1}^N A(t_i)$$

- ③ Allow to compute **rate constants** for different processes (isomerisation, dissociation, ...) from different initial conditions.

But ...

- **The gradient of the PES has to be computed.**
- **Difficult to extract information on rare events and/or for systems with $N \gg 1$. The accessible characteristics times depend on the complexity of the PES.**

Competition between isomerization, fragmentation and IR emission



Fragmentation

Introduction

- Following the non-adiabatic dynamics, the molecule can be found in the electronic ground state. A **statistical approach** could be used if $T_{\text{IVR}} \ll T_{\text{disso}}$.
- **T**he characteristics time of dissociation T_{disso} will depend on:
 - **I**nternal energy (or temperature)
 - **D**issociation energy
 - **T**he number of degrees of freedom
- **I**n the framework of statistical theories, the **density of states** will naturally play an important role.

RRK theory

- One simple model for a molecular dissociation of the parent X_n ($\rightarrow X_{n-1} + X$) is to consider X_n as a **set of harmonic oscillators**, following the idea of Rice, Ramsperger et Kassel. The molecule will be considered as dissociated when the localized energy on a given mode will be larger than the dissociation energy.
- We note $g = 3n - 6$ the number of degrees of freedom of the parent molecule. Let us computing the probability $P(E)$ for that E to be localized in **a dissociative mode**, will be larger than the dissociation energy D_n .
- The number of possibilities to distribute E over g oscillators is given by $E^{g-1}/(g-1)!$.

RRK theory

- The probability $P(E)$ is thus given by:

$$\begin{aligned} P(E) &= \frac{\int_0^{E-D_n} \epsilon^{g-2} d\epsilon / (g-2)!}{E^{g-1} / (g-1)!} \\ &= \left(\frac{E - D_n}{E} \right)^{g-1} \end{aligned} \quad (3)$$

- The **dissociation constant** $k_d^{(n)}(E)$ is proportional to this probability. We thus obtain:

$$k_d(E) = \nu_0 \left(\frac{E - D_n}{E} \right)^{g-1} \quad (4)$$

- The ν_0 prefactor is generally fitted to reproduce experimental results. Only the reactant is taken into account in this approach.
- Kassel has proposed a quantal version, much more adapted for small systems and/or at low energy.

RRKM Theory

- **Notion of transition state.**
 - Separation between nuclear and electronic degrees of freedom. Nuclear dynamics on a PES.
 - There is a **critical surface** which separates reactant and product.
 - Hypothesis of "non retour".
- In this approach, the dissociation rate is directly linked to the flux of trajectories through the critical surface. One of the major difficulty is to properly localize the transition state.
- **Also based on the quasi-equilibrium hypothesis:**
 - Energy redistribution much more rapid than the dissociation reaction.
 - Separability at the transition state: 1 dissociation coordinate + spectator modes.
 - Energy equipartition in the spectator modes at the transition state.

RRKM Theory

- **We** note D_n the energy of the transition state. We note v the derivative with respect time of the reaction coordinate at the TS. It thus simply corresponds to the velocity at the TS.
- **We** note E_t^\ddagger the kinetic energy along the reaction coordinate at the TS.
- **The** RRKM dissociation constant can be written:

$$k_d(E) \propto v \frac{\Omega^\ddagger(E^\ddagger)}{\Omega_n(E)} \quad (5)$$

with $E^\ddagger = E - D_n$ the energy available at the transition state.

- The density of states Ω^\ddagger at the transition state is written as:

$$\Omega^\ddagger(E^\ddagger) = \sum N(E_v^\ddagger) \rho(E_t^\ddagger) \quad (6)$$

- As $\rho(E_t^\ddagger) \propto E_t^{\ddagger-1/2}$ and $v \propto \sqrt{E_t^\ddagger}$, we obtain:

$$k_d(E) \propto \frac{N^\ddagger(E)}{h \Omega_n(E)} \quad (7)$$

with $N^\ddagger(E) = \sum N(E_v^\ddagger)$ the number of vibrational states for the spectator modes which can be populated at the TS.

RRKM theory

- For a system with a large number of degrees of freedom, we can write:

$$N^\dagger(E) = \int_0^{E-D_n} \Omega^\dagger(E - D_n - \varepsilon) d\varepsilon \quad (8)$$

- The RRKM dissociation rate can be written as:

$$k_d(E) = \int_0^{E-D_n} \mathcal{R}(\varepsilon; E) d\varepsilon \quad (9)$$

with,

$$\mathcal{R}(\varepsilon; E) = \frac{\Omega^\dagger(E - D_n - \varepsilon)}{h \Omega_n(E)} \quad (10)$$

- $\mathcal{R}(\varepsilon; E)d\varepsilon$ corresponds to the dissociation rate for a given kinetic energy ε along the dissociative coordinate.

RRKM theory

- The probability density for the kinetic energy can be deduced:

$$f(\varepsilon; E) = \frac{\Omega^\dagger(E - D_n - \varepsilon)}{\int_0^{E-D_n} \Omega^\dagger(E - D_n - \varepsilon) d\varepsilon} \quad (11)$$

- In the harmonic limit of the RRK theory, we find:

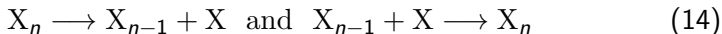
$$k_d(E) = \frac{\prod_{i=1}^{3n-6} \nu_i}{\prod_{i=1}^{3n-7} \nu_i^\dagger} \left(\frac{E - D_n}{E} \right)^{3n-7} \quad (12)$$

- The averaged kinetic energy is thus given by:

$$\begin{aligned} \langle \varepsilon \rangle &= \int_0^{E-D_n} \varepsilon f(\varepsilon) d\varepsilon \\ &= \frac{E - D_n}{3n - 6} \end{aligned} \quad (13)$$

Weisskopf theory

- The RRK(M) theories only consider the dissociation with respect to the "parent" molecule.
- The **Weisskopf theory** is based on the **microreversibility principle**. An equilibrium between the two inverse microscopic processes (dissociation and nucleation) is assumed:



- This theory has been first developed to describe the fragmentation of nuclei (nuclear physics).

Weisskopf theory

- **We** note k_d the dissociation rate for the reaction $X_n \longrightarrow X_{n-1} + X$.
- **We** note k_n the nucleation rate for the reaction $X_{n-1} + X \longrightarrow X_n$.
- **The** flux Φ_d linked to the dissociation is equal to $\Phi_d = k_d[X_n]$.
- **The** flux Φ_n linked to the nucleation is equal to $\Phi_n = k_n[X_{n-1}]$.
- **From** the microreversibility principle, we have $\Phi_d = \Phi_n$.
- **Let** us express Φ_d . We have:

$$\Phi_d = k_d(E) \Omega_n(E) \quad (15)$$

with Ω_n the vibrational density of states for the parent X_n .

Weisskopf theory

- Let us now express Φ_n . We have:

$$\Phi_n = \int_0^{E-D_n} k_n(\varepsilon) \rho(\varepsilon) \Omega_{n-1}(E - D_n - \varepsilon) d\varepsilon \quad (16)$$

- In this last equation, Ω_{n-1} is the vibrational states density of the **product** X_{n-1} . The relative kinetic energy of the fragments is noted ε . The nucleation rate $k_n(\varepsilon)$ is proportional to the **nucleation cross-section** $\sigma(\varepsilon)$ and to v , the relative velocity of the fragments. We thus obtain:

$$\begin{aligned} k_n(\varepsilon) &\propto v \sigma(\varepsilon) \\ &\propto \varepsilon^{1/2} \sigma(\varepsilon) \end{aligned} \quad (17)$$

- $\rho(\varepsilon)$ ($\propto \varepsilon^{1/2}$) is the density of translational states.

Weisskopf theory

- **We** thus obtain:

$$k_d(E) \propto \frac{\int_0^{E-D_n} \varepsilon \sigma(\varepsilon) \Omega_{n-1}(E - D_n - \varepsilon) d\varepsilon}{\Omega_n(E)} \quad (18)$$

- **The** kinetic energy (ε) probability density is written as:

$$f(\varepsilon; E) = \frac{\varepsilon \sigma(\varepsilon) \Omega_{n-1}(E - D_n - \varepsilon)}{\int_0^{E-D_n} \varepsilon \sigma(\varepsilon) \Omega_{n-1}(E - D_n - \varepsilon) d\varepsilon} \quad (19)$$

- **This** model is generally used in the approximation of a cross-section independent of the kinetic energy (hard sphere model).

Weisskopf theory

- In this case and considering harmonic vibrational density of states, we obtain:

$$k_d(E) \propto \frac{(E - D_n)^{3n-8}}{E^{3n-7}} \quad (20)$$

and,

$$f(\varepsilon; E) = (3n - 8)(3n - 9) \frac{\varepsilon(E - D_n - \varepsilon)^{3n-10}}{(E - D_n)^{3n-8}} \quad (21)$$

- We thus deduce the expression of the averaged released kinetic energy:

$$\langle \varepsilon \rangle = \frac{2(E - D_n)}{3n - 7} \quad (22)$$

Phase space theory

- The **Phase Space Theory** (PST) has been developed for the molecular physics by J. Light from the microreversibility principle.
- In the PST approach, **conservation of the angular momentum** is now taken into account:

$$\vec{J} = \vec{J}' + \vec{l} \quad (23)$$

- In the PST approach, the potential energy barrier along the dissociation coordinate is localized at the centrifugal barrier.

Phase space theory

- Let us consider the dissociation of a molecule with an internal energy E and an angular momentum J .
- The microreversibility principle equalises the outgoing flux $\Phi(E, J)$ and $\Phi'(E, J)$ fluxes of dissociation and nucleation processes, respectively.
- The dissociation flux Φ is equal to the product of the dissociation rate k_d by the vibrational density of states Ω_n for the "parent" molecule. S_{rot} is added for the rotational degeneracy of the "parent" molecule:

$$\Phi(E, J) = k(E, J) S_{\text{rot}} \Omega_n(E - E_{\text{rot}}) \quad (24)$$

- In the spherical top approximation, the rotational energy of the "parent" molecule is given by $E_{\text{rot}} = B J^2$, with B the rotational constant.

Phase space theory

- Consider now the nucleation process. The flux Φ' depends on translational and rotational energies:

$$\begin{aligned}\Phi'(E - D_n, J) &= S'_{\text{rot}} \iint k'(\varepsilon_r, \varepsilon_t; J) \rho_t(\varepsilon_t) d\varepsilon_t \\ &\times \Omega_{n-1}(E - D_n - \varepsilon_t - \varepsilon_r) d\varepsilon_r\end{aligned}\quad (25)$$

- In this expression, S'_{rot} corresponds to the rotational degeneracy for the dissociation products. $\rho_t(\varepsilon_t)$ is the translational density of states. $k'(\varepsilon_r, \varepsilon_t; J)$ is the differential rate for that collision forms a cluster with an angular momentum J with kinetic energies ε_r and ε_t .

Phase space theory

- We obtain the expression of the differential rate of dissociation as a function of the total released kinetic energy $\varepsilon_{\text{tr}} = \varepsilon_{\text{t}} + \varepsilon_{\text{r}}$:

$$\mathcal{R}(\varepsilon_{\text{tr}}; E, J) = \frac{S'_{\text{rot}}}{S_{\text{rot}}} \frac{\Omega_{n-1}(E - D_n - \varepsilon_{\text{tr}}) \Gamma_{\text{rot}}(\varepsilon_{\text{tr}}, J)}{\Omega_n(E - E_{\text{rot}})}. \quad (26)$$

- In this equation, **the rotational density of states** Γ_{rot} corresponds to the number of available rotational states for given values of J and ε_{tr} .

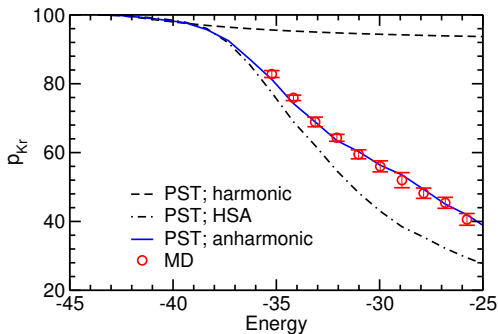
Phase space theory

- We can deduce the expression of the probability density for ε_{tr} as:

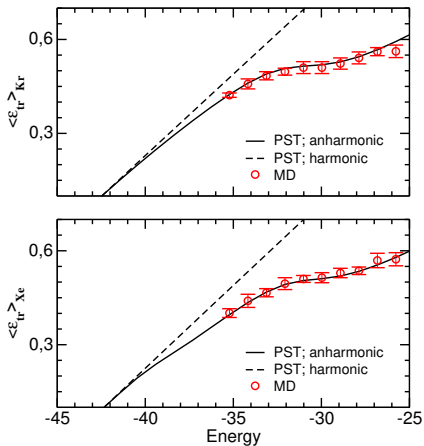
$$\begin{aligned} f(\varepsilon_{\text{tr}}; E, J) &= \frac{\mathcal{R}(\varepsilon_{\text{tr}}; E, J)}{\int_{\varepsilon_{\text{tr}}^{(\min)}}^{E-D_n} \mathcal{R}(\varepsilon_{\text{tr}}; E, J) d\varepsilon_{\text{tr}}} \\ &= \frac{\Omega_{n-1}(E - D_n - \varepsilon_{\text{tr}}) \Gamma_{\text{rot}}(\varepsilon_{\text{tr}}, J)}{\int_{\varepsilon_{\text{tr}}^{(\min)}}^{E-D_n} \Omega_{n-1}(E - D_n - \varepsilon_{\text{tr}}) \Gamma_{\text{rot}}(\varepsilon_{\text{tr}}, J) d\varepsilon_{\text{tr}}} \quad (27) \end{aligned}$$

- We have to compute $\Gamma_{\text{rot}}(\varepsilon_{\text{tr}}, J)$ and $\varepsilon_{\text{tr}}^{(\min)}$ by taking into account **constraints linked to energy and angular momentum**.
- In the PST approach, we can also obtain the distributions $f(\varepsilon_t; E, J)$ and $f(J_r; E, J)$.

mixtes Lennard-Jones
cluster KrXe_{12}
Competition entre
ejection of Kr and Xe



Mixed Lennard-Jones KrXe₁₂ clusters



Isomerization

Transition state theory

- The isomerization rate constant from isomer i towards isomer j , noted $k_{i \rightarrow j}^{(t_{ij})}$, depends on the statistical properties of isomer i and of the saddle point which connects both isomers.
- This **isomerization rate constant** can be written as:

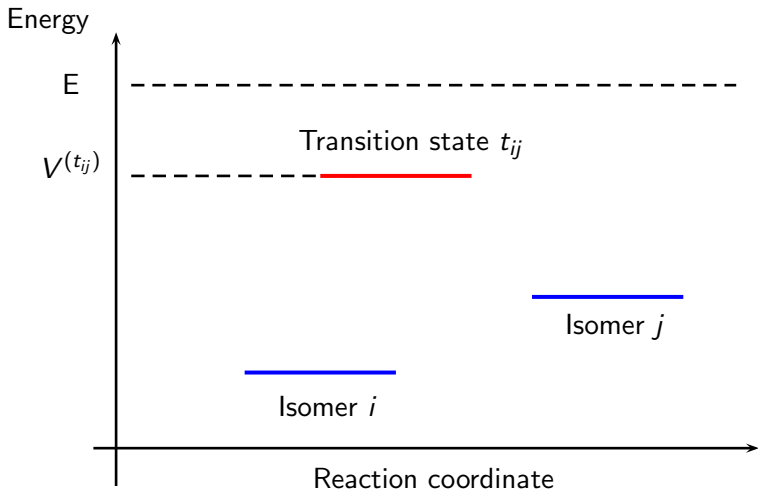
$$k_{i \rightarrow j}^{(t_{ij})}(E) = \frac{1}{h} \frac{N^{(t_{ij})}(E)}{\Omega_i(E)} \quad (28)$$

In this expression, $N^{(t_{ij})}(E)$ corresponds to the number of available states at energy E for the transition state. $N^{(t_{ij})}$ is given by:

$$N^{(t_{ij})}(E) = \int_{V^{(t_{ij})}}^E \Omega^{(t_{ij})}(\epsilon) d\epsilon \quad (29)$$

with $V^{(t_{ij})}$ the potential energy of the saddle point and $\Omega^{(t_{ij})}(\epsilon)$ the density of states for the transition state at the energy ϵ .

Transition state theory



Transition state theory

- **The** isomerization rate from isomer j towards isomer i , noted $k_{j \rightarrow i}^{(t_{ij})}$, is written as:

$$k_{j \rightarrow i}^{(t_{ij})}(E) = \frac{1}{h} \frac{N^{(t_{ij})}(E)}{\Omega_j(E)} \quad (30)$$

- **The** equilibrium between these two isomers can be easily deduced. The population ratio, for a **microcanonical energy** E , is given by:

$$\frac{N_i}{N_j} = \frac{k_{j \rightarrow i}^{(t_{ij})}(E)}{k_{i \rightarrow j}^{(t_{ij})}(E)} = \frac{\Omega_i(E)}{\Omega_j(E)} \quad (31)$$

- **This** ratio is independent of the transition state.

Transition state theory

- The transition state linked to two isomers will be a **saddle point** of the PES.
- We note $\{Q^{(e)}\}$ the molecular geometry at the saddle point. In the vicinity of this saddle point, we can express the potential energy as:

$$V(\{Q\}) = V(\{Q^{(e)}\}) + \frac{1}{2!} \sum_i \lambda_i (Q_i - Q_i^{(e)})^2 \quad (32)$$

- We will have $(g-1)$ positive eigenvalues and one negative, noted λ_α . We note \vec{u}_α the eigenvector associated to the negative eigenvalue.
- Parallel and anti-parallel displacements to this eigenvector and we minimize the PES to find the two local minima locaux linked to this saddle point.

Transition state theory

- In the harmonic limit, $\Omega_i(E)$ is given by:

$$\Omega_i(E) = \frac{E^{g-1}}{(g-1)!(h\bar{\nu}^{(i)})^g} \quad (33)$$

with $\bar{\nu}^{(i)}$ the geometrical average of the vibrational frequencies for isomer i , defined as $h\bar{\nu}^{(i)} = \left\{ \prod_{k=1}^g h\nu_k^{(i)} \right\}^{1/g}$.

- For the transition state, $N^{(t_{ij})}(E)$ is given by:

$$N^{t_{ij}}(E) = \int_{\nu^{(t_{ij})}}^E \frac{\epsilon^{g-2}}{(g-2)!(h\bar{\nu}^{(t_{ij})})^{g-1}} d\epsilon \quad (34)$$

- As different transition states can connect two same isomers, we have:

$$W_{ij}(E) = \sum_{t_{ij}} k_{ij}^{(t_{ij})}(E) \quad (35)$$

Isomerization dynamics

- From the \tilde{W} matrix, we can easily build the master equations allowing to describe isomerization for a large molecular system with a large number of isomers and saddle points.
- We note $P_i(t; E)$ the probability for the system to be in isomer i at t . The equations of evolution for the system can be written as:

$$\frac{dP_i(t; E)}{dt} = \sum_{j=1}^{N_{\text{iso}}} \omega_{ij}(E) P_j(t; E) \quad (36)$$

with $\omega_{ij}(E) = W_{ij}(E) - \delta_{ij} \sum_{k \neq j} W_{kj}(E)$. The total number of isomers is noted N_{iso} .

- By numerically solving this system of coupled equations, it allows to obtain **time evolution** of populations $P_i(t; E)$.

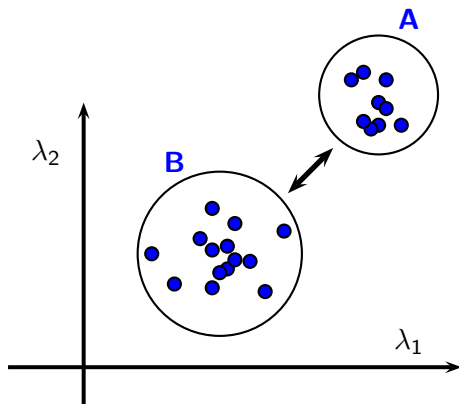
Isomerization dynamics

- In these molecular systems, the number of isomers can become very huge. It is thus much more useful to follow the time evolution of isomers groups.
- These isomers have to be classified in these groups following different geometrical criteria (order parameters).
- Notons A et B two isomers groups with N_A and N_B their respective populations.
- We note K_{eq} the equilibrium between these two groups. We have:

$$K_{\text{eq}} = \frac{k_{B \rightarrow A}}{k_{A \rightarrow B}} = \frac{N_A(\infty)}{N_B(\infty)} \quad (37)$$

with $k_{A \rightarrow B}$ the isomerization rate from A towards B and $k_{B \rightarrow A}$ from B towards A .

Isomerization dynamics



- The configurational parameters $\lambda_i(\{Q\})$ have to be chosen to well separate the isomers bassins.

Isomerization dynamics

- Let us calculate the isomerization constant $k_{A \rightarrow B}$.
- We have:

$$\frac{dN_A}{dt} = -k_{A \rightarrow B} N_A + k_{B \rightarrow A} N_B \quad (38)$$

- Let us note $N = N_A + N_B$. We deduce:

$$\frac{dN_A}{dt} = -(1 + K_{\text{eq}}) k_{A \rightarrow B} N_A + K_{\text{eq}} k_{A \rightarrow B} N \quad (39)$$

- We note $k = (1 + K_{\text{eq}}) k_{A \rightarrow B}$ and we obtain:

$$\frac{N_A(t)}{N} = \left[\frac{N_A(t=0)}{N} - \frac{K_{\text{eq}}}{1 + K_{\text{eq}}} \right] e^{-kt} + \frac{K_{\text{eq}}}{1 + K_{\text{eq}}} \quad (40)$$

- In this expression, K_{eq} is given by the ratio of vibrational states for the two basins A and B .

Isomerization dynamics

- By solving the master equation, we obtain $P_i(t) = \frac{N_i(t)}{N}$ for $i=1$, N_{iso} and we thus obtain:

$$\frac{N_A(t)}{N} = \sum_{i=1}^{N_{\text{iso}}^{(A)}} P_i(t) \quad (41)$$

in which $N_{\text{iso}}^{(A)}$ correspond to the number of isomers in the bassin A .

- The rate constant $k [(1 + K_{\text{eq}}) k_{A \rightarrow B}]$ can be thus deduced from a simple comparison of the two last expressions.

Isomerization dynamics

- **A**s an example, we can analyse theoretical results on $\text{Mg}^+\text{-Ar}_{12}$.
- **Q**uestion: where is localized the Mg^+ ion (surface or volume) ?
Analysis as a function of internal energy.
- 83 local minima and 137 saddle points have been considered in this work.
- **S**eparation between the two isomer groups A (ion in volume) and B (ion at the surface) is based on the value of distance between the ion and the center of mass of the system for each isomer.
- **W**e note d_α this distance for isomer α . If $d_\alpha < R_{\text{crit}}$, the isomer α is considered in the group A .

Isomerization dynamics

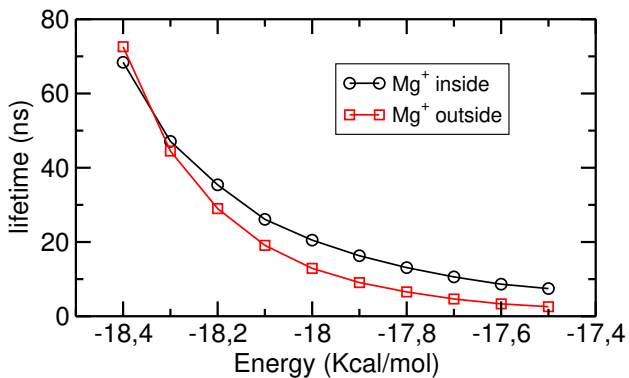


Figure:

Isomerization dynamics - Canonical ensemble

- In the transition state theory, the rate constant from isomer i to isomer j , at a given inverse temperature β , can be deduced from a Laplace transformation:

$$\begin{aligned}k_{i \rightarrow j}^{(t_{ij})}(\beta) &= \frac{1}{Z_i(\beta)} \int_0^\infty \Omega_i(E) k_{i \rightarrow j}^{(t_{ij})}(E) e^{-\beta E} dE \\&= \frac{1}{Z_i(\beta)} \frac{1}{h} \int_0^\infty \Omega_i(E) \frac{N^{(t_{ij})}(E)}{\Omega_i(E)} e^{-\beta E} dE \\&= \frac{1}{h} \frac{\int_0^\infty N^{(t_{ij})}(E) e^{-\beta E} dE}{Z_i(\beta)}\end{aligned}\tag{42}$$

Isomerization dynamics - Canonical ensemble

- As $N^{(t_{ij})}(E) = 0$ when $E \leq V^{t_{ij}}$, we obtain:

$$k_{i \rightarrow j}^{(t_{ij})}(\beta) = \frac{1}{h} \frac{\int_{V^{(t_{ij})}}^{\infty} N^{(t_{ij})}(E) e^{-\beta E} dE}{Z_i(\beta)} \quad (43)$$

- From an integration by parts, we obtain:

$$\begin{aligned} k_{i \rightarrow j}^{(t_{ij})}(\beta) &= \frac{-1}{h\beta} \frac{[N^{(t_{ij})}(E) e^{-\beta E}]_{V^{t_{ij}}}^{\infty} - \int_{V^{t_{ij}}}^{\infty} \frac{dN^{(t_{ij})}(E)}{dE} e^{-\beta E} dE}{Z_i(\beta)} \\ &= \frac{1}{h\beta} \frac{\int_{V^{(t_{ij})}}^{\infty} \frac{dN^{(t_{ij})}(E)}{dE} e^{-\beta E} dE}{Z_i(\beta)} \end{aligned} \quad (44)$$

Isomerization dynamics - Canonical ensemble

- By definition, $\frac{dN^{(t_{ij})}(E)}{dE} = \Omega^{(t_{ij})}(E)$. We deduce:

$$\begin{aligned}k_{i \rightarrow j}^{(t_{ij})}(\beta) &= \frac{1}{h\beta} \frac{\int_{V^{(t_{ij})}}^{\infty} \Omega^{(t_{ij})}(E) e^{-\beta E} dE}{Z_i(\beta)} \\ &= \frac{1}{h\beta} \frac{Z^{(t_{ij})}(\beta)}{Z_i(\beta)}\end{aligned}\tag{45}$$

with $Z^{(t_{ij})}(\beta)$ the partition function for the saddle point at β .

- In this last expression, the zero of energy is taken for the isomer i .

IR Emission

Absorption cross-section for an oscillator

- In the case of E1 transitions, the **radiative transition probability** between two vibrational states $|n\rangle$ et $|n'\rangle$ is proportional to the transition moment $|\langle n | \mu | n'\rangle|^2$.
- The dipole moment μ depends on the normal coordinate Q and can be expressed as:

$$\mu(Q) = \mu(Q = 0) + \sum_k \frac{1}{k!} \frac{\partial^k \mu}{\partial Q^k} Q^k \quad (46)$$

- In the harmonic approximation, the vibrational wavefunction functions are the Hermite polynômes . By only considering the first term in the expression of the dipole moment, we obtain:

$$|\langle n | \mu | n + 1 \rangle|^2 = (n + 1) |\langle 0 | \mu | 1 \rangle|^2 \quad (47)$$

Microcanonical distribution $\mathcal{P}(n_i; E)$

- Let us calculate the probability $\mathcal{P}(n_i; E)$ to have n_i vibrational quanta in the $i^{\text{ème}}$ mode at energy E .
- The energy $E - n_i\hbar\omega_i$ has to be shared on the $(g - 1)$ other vibrational modes.
- We note $\Omega'_i(E)$ the vibrational density of states for these $(g-1)$ harmonic oscillators. The number of vibrational modes between E and $E+dE$ is equal to $\Omega'_i(E)dE$.
- The probability $\mathcal{P}(n_i; E)$ is thus given by:

$$\mathcal{P}(n_i; E) = \frac{\Omega'_i(E - n_i\hbar\omega_i)}{\Omega(E)} \quad (48)$$

- For a given energy, the probability $\mathcal{P}(n_i; E)$ is monotonically decreasing when n_i increases.

IR Absorption in the canonical ensemble

- Consider the case of a set of harmonic oscillators. $\{n\}$ is the collection of vibrational quantum numbers.
- We note $\mathcal{P}(\{n\}; T)$ the probability to obtain a given set of vibrational quantum numbers at temperature T . We have:

$$\mathcal{P}(\{n\}; T) = \prod_{i=1}^g e^{-\beta n_i \hbar \omega_i} [1 - e^{-\beta \hbar \omega_i}] \quad (49)$$

- The **absorption cross-section**, at a fixed temperature β is:

$$\mathcal{S}^{(a)}(\omega, T) = \sum_{i=1}^g \sum_{n_i=0}^{\infty} \sigma_{n_i \rightarrow n_i+1}(\omega_i) \mathcal{P}(\{n\}; T) \delta(\omega - \omega_i) \quad (50)$$

- In the **harmonic approximation**, the rate of IR radiative desexcitation by spontaneous emission for an oscillator of pulsation ω_i from a vibrational state $|n\rangle$ towards $|n-1\rangle$, noted $A_i^{(n \rightarrow n-1)}$, satisfy $A_i^{(n \rightarrow n-1)} = n A_i^{(1 \rightarrow 0)}$.
- In the **canonical ensemble**, for each vibrational mode, we can calculate the radiative desexcitation rate of this mode as:

$$\begin{aligned} k_i(T) &= \sum_{n=1}^{\infty} P(n) n A_i^{(1 \rightarrow 0)} \\ &= A_i^{(1 \rightarrow 0)} \sum_{n=1}^{\infty} n e^{-\beta n \hbar \omega_i} [1 - e^{-\beta \hbar \omega_i}] \\ &= \frac{A_i^{(1 \rightarrow 0)}}{e^{\beta \hbar \omega_i} - 1} \end{aligned} \tag{51}$$

- Initial excitation of the molecular system at an energy E_{init} . From the heat capacity $C_V(T)$, we associate an initial temperature T_{init} such as $E_{\text{init}} = \int_0^{T_{\text{init}}} C_V(T') dT'$ (thermal approximation).
- In the harmonic approximation, the heat capacity is analytical and given by:

$$C_V(T) = k_B \sum_{i=1}^g \frac{e^{-\beta\hbar\omega_i}}{(1 - e^{-\beta\hbar\omega_i})^2} (\beta\hbar\omega_i)^2 \quad (52)$$

- We want to analyse the IR emission of the molecule down to final temperature T_{final} . Along the cooling, temperature is discretized. We note $\Delta T = \frac{(T_{\text{init}} - T_{\text{final}})}{N}$. We have $T_k = T_{\text{init}} - k\Delta T$ (avec $k=0, 1, \dots, N$).

IR emission Cascade / Thermal approximation

- **A**t a temperature T_k , a variation of temperature ΔT will induce a variation of internal energy ΔU_k .
- **T**he energy fraction in the i th mode is simply given by:

$$\Delta E_k^{(i)} = \frac{k_i(T_k)}{\sum_j k_j(T_k)} \Delta U_k \quad (53)$$

- **A**long the radiative emission cascade, the total energy emitted in the i th mode is written as:

$$\Delta E^{(i)} = \sum_{k=0}^N \Delta E_k^{(i)} \quad (54)$$

- **I**n these **thermal** et **harmonic** approximations, the emission spectrum will be given by:

$$\mathcal{I}^{(e)}(\omega) \propto \sum_{i=1}^g \frac{\Delta E^{(i)}}{\hbar \omega_i} \delta(\omega - \omega_i) \quad (55)$$

dt' (55)

IR emission cascade / Time evolution

- Can be solved by discretization of the time and by calculating the energy at $t + \Delta t$ from $\mathcal{P}(n_j; E(t; E_{\text{init}}))$ at t .
- For each vibrational mode and for each new energy E , the microcanonical probability $\mathcal{P}(n_j, E)$ has to be computed.
- To simplify, we can use here the thermal approximation ($\mathcal{P}(n_j, T)$ with T for which $E = \int_0^T C_V(T') dT'$).
- From the time evolution of the internal molecular energy $[E(t; E_{\text{init}})]$, we can obtain the time resolved IR emission spectrum.
- The number of emitted IR photons, per initially excited molecule, in the j th vibrational mode during T is written as:

$$\mathcal{N}_j(T) = A_j^{(1 \rightarrow 0)} \int_0^T \sum_{n_j=1}^{\infty} n_j \mathcal{P}(n_j; E(t'; E_{\text{init}})) dt' \quad (56)$$

- Experimentally, the emission spectra are obtained in a given time windows (10^0 - 10^1 μ s). We note T_{exp} this experimental time.
- In the harmonic approximation, the emission spectrum, integrated over T_{exp} , is written as:

$$\begin{aligned} \mathcal{I}(\omega; E_{\text{init}}, T_{\text{exp}}) &= \sum_{j=1}^g \delta(\omega - \omega_j) A_j^{(1 \rightarrow 0)} \\ &\times \left[\int_0^{T_{\text{exp}}} \left\{ \sum_{n_j=1}^{\infty} n_j \mathcal{P}(n_j; E(t'); E_{\text{init}}) \right\} dt' \right] \quad (57) \end{aligned}$$

- This emission spectrum depends parametrically of E_{init} and T_{exp} .
- In a ns laser experiment, E_{init} is perfectly defined if the initial thermal energy is perfectly known.

- For a given internal energy of the molecule, we can define for the j th oscillator:

$$\begin{aligned}
 A_j(E) &= \sum_{n_j=1}^{N_{\max}^{(j)}} \mathcal{P}(n_j; E) A_j^{(n_j \rightarrow n_j-1)} \\
 &= A_j^{(1 \rightarrow 0)} \sum_{n_j=1}^{N_{\max}^{(j)}} n_j \mathcal{P}(n_j; E)
 \end{aligned} \tag{58}$$

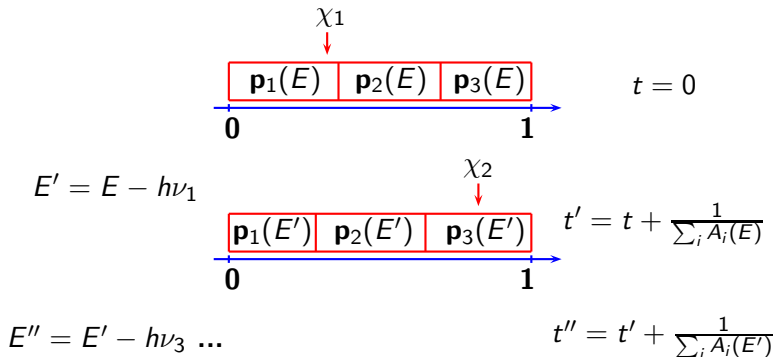
with $N_{\max}^{(j)} = \frac{E}{\hbar\omega_j}$.

- For this molecule, there are g channels of radiative desexcitation. The probability to loose one vibrational quantum in the j th vibrational mode is given by:

$$\mathcal{P}_j(E) = \frac{A_j(E)}{\sum_{k=1}^g A_k(E)} \tag{59}$$

Kinetic Monte-Carlo

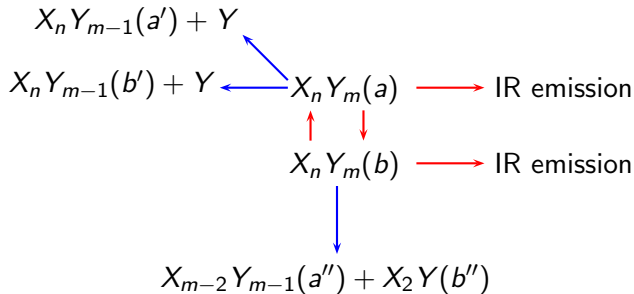
- The previous simulation approach, for a non linear triatomic molecule, can be summarized as:



- Possible to take into account anharmonicity

Kinetic Monte-Carlo

- Obvious extension for the IR Emission IR/Dissociation/Isomerization competition



$$p_i(E) = \frac{k_i(E)}{\sum_j k_j(E)}$$

Thank you for your attention !