# Réactivité unimoléculaire: cinétique et dynamique

Riccardo Spezia
riccardo.spezia@univ-evry.fr

CNRS – Université d'Evry-Val-d'Essonne

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# Outline

1. Unimolecular reaction dynamics

2. RRKM theory

# Unimolecular reaction dynamics

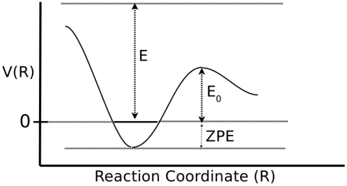
- Population decay of a species (simple kinetics)

$$-\frac{d}{dt}P_i = kP_i \tag{1}$$

$$P_i(t) = P_i(0)e^{-kt} \tag{2}$$

- $k$ is the rate constant that sets a uni-molecular kinetics
- $P_i$ is the fraction of a given species, that in the gas phase plays the same role as concentration in liquid phase

# Unimolecular reaction : activation



- Energy is given to a molecule in the gas phase (isolated) in order to induce reactivity
- Different ways to provide energy : collision, laser, electron . . .
- Energy is conserved (no coupling with a bath)
- To react the system has to pass the transition state (TST holds)
- Employing a statistical theory of reactivity and TST theory it is possible to obtain k(E) (micro canonical) from molecular information (i.e. from theoretical chemistry)

# IVR

- IVR = internal vibrational relaxation
- The energy absorbed by a mode can flow through the molecule via mode coupling
- A molecule as a set of independent harmonic oscillators

$$H = \frac{1}{2}\sum_i (p_i^2 + q_i^2) \tag{3}$$

- A mode coupling (anharmonicity, rotation, etc ...) allows energy flow/exchange between the modes

$$H' = \frac{1}{2}\sum_i (p_i^2 + q_i^2) + \sum_{i,j} G(q_i, q_j; p_i, p_j) \tag{4}$$

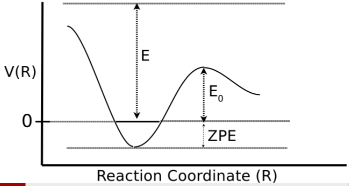
# IVR

- When a molecule gets energy, it is not in general localized so that to be available in reactivity the energy must flow to the reactive mode
- The energy flow time-scale is crucial!
- Putting together these concepts we obtain the well known Rice-Ramsperger-Kassel-Marcus (RRKM) theory

# RRKM theory : assumptions

- RRKM: IVR takes place + TST assumptions are valid
- the molecule populates all of phase space statistically throughout its dissociation so that the microcanonical ensemble is mantained
- all molecules which find them in the TS phase space region lead to products: no recrossing
- there is a special coordinate perpendicular to all other coordinates that can be separated
- the reaction rate will be given by the flux over the separation surface

$$Flux = \frac{d\mathbb{N}(q^{\ddagger}, p^{\ddagger})}{dt} \tag{5}$$



# RRKM theory : definitions

- Phase space: each atom has $(q, p)$, so for $m$ atoms, we have a phase space volume with dimension $2m$

$$PhaseSpaceVolume = \int_{H=0}^{H=E} \dots \int dp_1 \dots dp_m dq_1 \dots dq_m \tag{6}$$

- Sum of states: counting the number of states available to a particle to determine the available volume

$$N(E) = \frac{1}{h^m} \int_{H=0}^{H=E} \dots \int dp_1 \dots dp_m dq_1 \dots dq_m \tag{7}$$

according to Heisenberg principle the smallest unit in phase space is of the order of h

- N(E) represents the total number of states for a system corresponding to an energy less than or equal to a specified value, E.

# RRKM theory : definitions

- Density of states: the number of states, $\rho(E)$, per energy unit

$$\begin{aligned} W(E) &= \frac{1}{h^m}\int_{H=E}^{H=E+dE}\dots\int dp_1\dots dp_m dq_1\dots dq_m && (8)\\ \rho(E) &= \frac{W(E)}{dE} && (9)\\ \rho(E) &= \frac{1}{h^m}\int_{H=E}\dots\int dp_1\dots dp_m dq_1\dots dq_m && (10)\end{aligned}$$

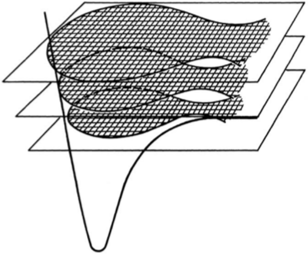
- the density of states is, by definition, the derivative of the sum of states with respect to energy

$$\rho(E) = dN(E)/dE \qquad (11)$$

# RRKM theory : definitions

Reaction coordinate with a saddle point

- energy conservation: $H = E$
- TS as a dividing surface: once the trajectory has reached it, it goes to products without coming back to reactants



# RRKM theory : derivation

- It is assumed that the phase space is statistically populated: the population density over the whole surface of the phase space is uniform.
- the ratio of molecules near the critical surface over the total number of molecule: the ration of phase space at the dividing surface over the total phase space

$$\frac{d\mathbb{N}(q^\ddagger, p^\ddagger)}{d\mathbb{N}} = \frac{dq^\ddagger dp^\ddagger \int \ldots \int_{E=E-\epsilon_t-E_0} \int dq_1^\ddagger \ldots dq_{n-1}^\ddagger dp_1^\ddagger \ldots dp_{n-1}^\ddagger}{\int_{H=E} \int dq_1 \ldots dq_n dp_1 \ldots dp_n} \tag{12}$$

- $\epsilon_t$ : translational energy
- $E_0$ : activation energy

# RRKM theory : derivation

Since it was assumed that the reaction coordinate is perpendicular to, and separable from, all other coordinates the time derivative involves only the $dq^{\ddagger}$ and $dp^{\ddagger}$ term. Thus we can write the flux as:

$$\frac{d\mathbb{N}(q^{\ddagger},p^{\ddagger})}{dt} = \frac{\mathbb{N}\frac{dq^{\ddagger}dp^{\ddagger}}{dt}\int_{H=E-\epsilon_t-E_0}\int dq_1^{\ddagger}\dots dq_{n-1}^{\ddagger}dp_1^{\ddagger}\dots dp_{n-1}^{\ddagger}}{\int_{H=E}\int dq_1\dots dq_n dp_1\dots dp_n} \tag{13}$$

This can be rearranged by noting that $dq^{\ddagger}/dt = p^{\ddagger}/\mu^{\ddagger}$, where $\mu^{\ddagger}$ is the reduced mass of the two separating fragments, such that we have

$$\frac{d\mathbb{N}(q^{\ddagger},p^{\ddagger})}{dt} = \frac{\mathbb{N}\frac{p^{\ddagger}dp^{\ddagger}}{\mu^{\ddagger}}\int_{H=E-\epsilon_t-E_0}\int dq_1^{\ddagger}\dots dq_{n-1}^{\ddagger}dp_1^{\ddagger}\dots dp_{n-1}^{\ddagger}}{\int_{H=E}\int dq_1\dots dq_n dp_1\dots dp_n} \tag{14}$$

# RRKM theory : derivation

The energy in the reaction coordinate is by definition

$$\epsilon_t = \frac{p^{\ddagger 2}}{2\mu^{\ddagger}} \tag{15}$$

and its derivative

$$d\epsilon_t = \frac{p^{\ddagger} dp^{\ddagger}}{\mu^{\ddagger}} \tag{16}$$

Now equation 14 reads

$$\frac{d\mathbb{N}(q^{\ddagger}, p^{\ddagger})}{dt} = \frac{\mathbb{N} d\epsilon_t^{\ddagger} \int_{H=E-\epsilon_t-E_0} \int dq_1^{\ddagger} \dots dq_{n-1}^{\ddagger} dp_1^{\ddagger} \dots dp_{n-1}^{\ddagger}}{\int_{H=E} \int dq_1 \dots dq_n dp_1 \dots dp_n} \tag{17}$$

# RRKM theory : derivation

Equation 19 express the flux (molecules per unit time) in terms of the number of molecules, $\mathbb{N}$, multiplied by the rate constant, $k(E, \epsilon_t)$:

$$\frac{d\mathbb{N}(q^\ddagger, p^\ddagger)}{dt} = \mathbb{N}k(E, \epsilon_t) \tag{18}$$

where the rate constant is the ration of the phase space areas

$$k(E, \epsilon_t) = \frac{d\epsilon_t^\ddagger \int_{H=E-\epsilon_t-E_0} \int dq_1^\ddagger \ldots dq_{n-1}^\ddagger dp_1^\ddagger \ldots dp_{n-1}^\ddagger}{\int_{H=E} \int dq_1 \ldots dq_n dp_1 \ldots dp_n} \tag{19}$$

The phase spaces can be converted into densities

$$k(E, \epsilon_t) = \frac{\rho(E - E_0 - \epsilon_t)h^{n-1}}{\rho(E)h^n} = \frac{\rho(E - E_0 - \epsilon_t)}{h\rho(E)} \tag{20}$$

# RRKM theory : derivation

Equation 20 is very important and expresses the rate constant in terms of total energy, $E$, and the translational energy of the departing fragments at the transition state, $\epsilon_t$. This equation is a state-to-state rate constant since there are many ways to partition the available energy, $E - E_0$.
To have the total dissociation rate, we must integrate over all the different translational energies in the transition state:

$$k(E) = \frac{\int_0^{E-E_0} \rho^{\ddagger}(E - E_0 - \epsilon_t) d\epsilon_t}{h\rho(E)} = \frac{N^{\ddagger}(E - E_0)}{h\rho(E)} \tag{21}$$

# RRKM theory : formula

The RRKM rate constant is simply obtained by

$$k(E) = \sigma \frac{N^{\ddagger}(E - E_0)}{h\rho(E)} \tag{22}$$

- $N^{\ddagger}(E - E_0)$ : sum of states at the transition state from 0 to $E - E_0$;
- $\rho(E)$: density of states of reactant;
- $\sigma$: the reaction symmetry

Note that this is the rotation free version.

# RRKM theory : formula

$$k(E) = \sigma \frac{N^{\ddagger}(E - E_0)}{h\rho(E)} \tag{23}$$

To obtain the $k(E)$ for a given unimolecular reaction we have to

1. locate the minimum and calculate the $3N - 6$ frequencies;
2. locate the (tight) TS and calculate the $3N - 7$ frequencies;
3. calculate the density and sum of states at the desired energies;
4. determine the reaction symmetry;
5. use equation 23 to easily get $k(E)$.

# Density of states I

There are different methods to obtain the density of states, $\rho(E)$, needed to solve Eq. 23 and get $k(E)$:

1. From inverse Laplace transform of the partition function. In fact, the partition function, $Q(\beta)$, can be written as

$$Q(\beta) = \int_0^{\infty} \rho(E) e^{-\beta E} dE = \mathcal{L}[\rho(E)] \tag{24}$$

so the density of states is just the inverse: $\rho(E) = \mathcal{L}^{-1}[Q(\beta)]$
In the case of $s$ classical harmonic oscillators, the partition function is

$$Q(\beta) = \prod_i^s [\beta h\nu_i]^{-1} = \beta^{-s} \prod_i^s (h\nu_i)^{-1} \tag{25}$$

# Density of states II

The Laplace transform of $\beta^{-s}$ is $E^{s-1}/\Gamma(s)$ and the gamma function of an integer $s$ is $(s-1)!$, so

$$\rho(E) = \prod_{i}^{s} (h\nu_i)^{-1} \frac{E^{s-1}}{(s-1)!} \tag{26}$$

# Density of states III

2. In the case of quantum oscillators the partition function

$$q_v(T) = \prod_{i-1}^{s}[1 - e^{-h\nu_i\beta}]^{-1} \tag{27}$$

and the inverse Laplace transform integral

$$\rho(E) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+\infty} Q(\beta)e^{\beta E}d\beta \tag{28}$$

can be solved numerically, for example via a steepest descent approximation. One problem is that it considers the $\rho(E)$ as a smooth function, even if it is a series of delta functions.

# Density of states IV

3. The direct count method via the Bayer-Swinehart algorithm.

**Algorithm 1** Beyer-Swinehart density of vibrational states count

```
$\rho(I) = [1, 0, 0, \dots]$ (initialize the $\rho$ vector)
for $J = 1$ to $s$ do
    for $I = \omega(J)$ to $M$ do
        $\rho(I) = \rho(I) + \rho(I - \omega(J))$
    end for
end for
```

where M is the maximum energy bin of interest. The algorithm calculates $\rho(E)$ by dividing the energy scale into a series of cells and counting how many vibrational bands are in each cell.

# Density of states V

4. Whitten-Rabinovitch semi-classical approximation. The density of states is expressed as:

$$\rho(E) = \frac{(E + aE^{ZPE})^{s-1}}{(s-1)! \prod h\nu_i} \left[1 - \beta \frac{d\omega(\epsilon)}{d\epsilon}\right] \tag{29}$$

in which:

$$a = 1 - \beta\omega(\epsilon); \quad \beta = \tfrac{s-1}{s}\tfrac{\langle\nu^2\rangle}{\langle\nu\rangle^2} \tag{30}$$

$$\epsilon = E/E^{ZPE} \tag{31}$$

$$\omega(\epsilon) = [5\epsilon + 2.27\epsilon^{0.5} + 3.51]^{-1} \quad for 0.1 < \epsilon < 1 \tag{32}$$

$$\omega(\epsilon) = e^{[-2.419\epsilon^{0.25}]} \quad for 1.0 \leq \epsilon \tag{33}$$

# Sum of states I

The sum of states is, from the integration theorem

$$N(E) = \int_0^E \rho(E) = \mathcal{L}^{-1}[Q(\beta)/\beta] \tag{34}$$

1. For $s$ classical harmonic oscillators

$$N(E) = \prod (h\nu_i)^{-1} \mathcal{L}^{-1} (\beta)^{-(s+1)} = \prod_i^s (h\nu_i)^{-1} \frac{E^s}{s!} \tag{35}$$

2. In the Whitten-Rabinovich approximation

$$N(E) = \frac{(E + aE^{ZPE})^s}{s! \prod h\nu_i} \tag{36}$$

# Sum of states II

3. The direct count method. This is the most accurate procedure and the most used scheme is the Bayer-Swinehart algorithm.

**Algorithm 2** Beyer-Swinehart sum of vibrational states count

```
N(I) = [1, 1, 1, ...]
for J = 1 to s do
    for I = ω(J) to M do
        N(I) = N(I) + N(I − ω(J))
    end for
end for
```

# Convolution properties

Laplace transform is an integral transform (like Fourier transform) an the convolution theorem holds. Given two partition functions $Q_1(\beta)$ and $Q_2(\beta)$, their product is the Laplace transform of the convolution between $\rho_1$ and $\rho_2$:

$$Q_1 Q_2 = \mathcal{L}[\rho_1 * \rho_2] \tag{37}$$

and thus

$$\rho_{12} = \mathcal{L}^{-1}[Q_1 Q_2] = \rho_1 * \rho_2 \tag{38}$$

For the sum of states we thus have

$$\begin{aligned} N_{12}(E) = \int_0^E \rho_{12}(x) dx = \int \mathcal{L}^{-1} Q_1 Q_2 dx = \mathcal{L}^{-1}[Q_1 Q_2/\beta] \\ = N_1 * \rho_2 = \rho_1 * N_2 \end{aligned} \tag{39}$$

# RRK equation

In the classical limit, the vibrational density of states for $s$ oscillators and the sum of states for the $s-1$ oscillators at the transition state are:

$$\rho(E) = \frac{E^{s-1}}{(s-1)! \prod_{i=1}^{s} h\nu_i}; N^{\ddagger}(E-E_0) = \frac{(E-E_0)^{s-1}}{(s-1)! \prod_{i=1}^{s-1} h\nu_i^{\ddagger}} \tag{40}$$

Using these expressions in Eq. 23 we obtain the classical RRKM rate constant

$$k_{cl}(E) = \left(\frac{E-E_0}{E}\right)^{s-1} \frac{\prod_{i=1}^{s} \nu_i}{\prod_{i=1}^{s-1} \nu_i^{\ddagger}} \tag{41}$$

The numerator has only one additional frequency, that can be identified with the reaction coordinate. We thus obtain the original RRK equation

$$k_{RRK}(E) = \nu \left(\frac{E-E_0}{E}\right)^{s-1} \tag{42}$$

# Canonical rate constant

To obtain an expression of the rate constant at constant temperature (canonical ensemble) we need to average over the internal energy distributions at a given temperature, $T$. Given the distribution function ($\beta = 1/k_B T$)

$$P(E,\beta) = \frac{\rho(E)e^{-\beta E}}{\int_0^\infty \rho(E)e^{-\beta E}dE} = \frac{\rho(E)e^{-\beta E}}{Q(\beta)} \tag{43}$$

so for the rate constant

$$k(T) = \int_0^\infty k(E)P(E,\beta)dE = \int_0^\infty \frac{N^\ddagger(E-E0)\rho(E)}{h\rho(E)Q(\beta)}e^{-\beta E}dE \tag{44}$$

# Canonical rate constant

We note that $N^{\ddagger}$ is different from zero only for $E > E_0$ , so

$$k(T) = \frac{1}{hQ(\beta)} \int_{E_0}^{\infty} N^{\ddagger}(E - E_0) e^{-\beta E} dE = \frac{e^{-\beta E_0}}{hQ(\beta)} \int_0^{\infty} N^{\ddagger}(E) e^{-\beta E} dE \tag{45}$$

the last integral is the Laplace transform of the sum of states can be expressed as (following integration theorem)

$$\mathcal{L}[N^{\ddagger}(E)] = \mathcal{L}\left[\int_0^E \rho^{\ddagger}(E) dE\right] = \frac{\mathcal{L}[\rho^{\ddagger}(E)]}{\beta} = \frac{Q^{\ddagger}(\beta)}{\beta} \tag{46}$$

and thus the rate constant that is expressed as from canonical TST

$$k(\beta) = \frac{Q^{\ddagger}(\beta)}{h\beta Q(\beta)} e^{-\beta E_0} \tag{47}$$

# Tunneling

To include tunneling the rate constant is

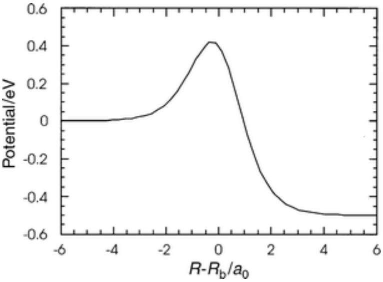
$$\begin{aligned} k(E) &= \int_{-E_0}^{E-E_0} \kappa(\epsilon_t) k(E, \epsilon_t) d\epsilon_t \\ &= \frac{1}{h\rho(E)} \int_{-E_0}^{E-E_0} \kappa(\epsilon_t) \rho^{\ddagger}(E - E_0 - \epsilon_t) d\epsilon_t \end{aligned} \tag{48}$$

where $\kappa(\epsilon_t)$ is the tunneling probability function of the translation energy, $\epsilon_t$.

# Tunneling

For an Eckart barrier, the transmission coefficient is

$$\kappa(\epsilon_t) = \frac{\sinh(a)\sinh(b)}{\sinh^2[(a+b)/2] + \cosh^2(c)} \qquad (49)$$



# Tunneling

The three coefficient are function of the three parameters of the Eckart barrier, $V_0$, $V_1$ and $\nu_c$, the curvature at the barrier.

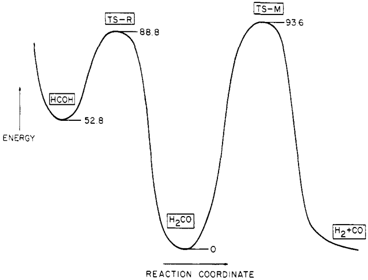
$$a = \frac{4\pi}{h\nu_c}\sqrt{\epsilon_t + V_0}\frac{1}{V_0^{-1/2} + V_1^{-1/2}} \qquad (50)$$

$$b = \frac{4\pi}{h\nu_c}\sqrt{\epsilon_t + V_1}\frac{1}{V_0^{-1/2} + V_1^{-1/2}} \qquad (51)$$

$$c = 2\pi\sqrt{\frac{V_0 V_1}{(h\nu_c)^2} - \frac{1}{16}} \qquad (52)$$

# Tunneling: an example

Unimolecular decomposition of formaldehyde.[1]
Potential energy surface



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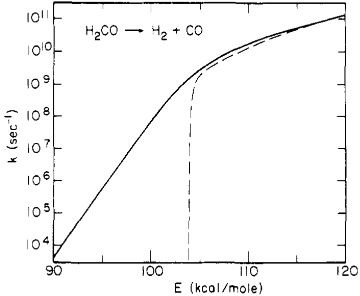
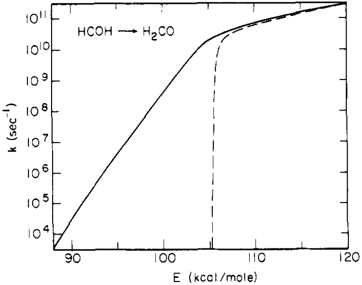
[1] W.H.Miller. J. Am. Chem. Soc. 101, 6810 (1979)

# Tunneling: an example

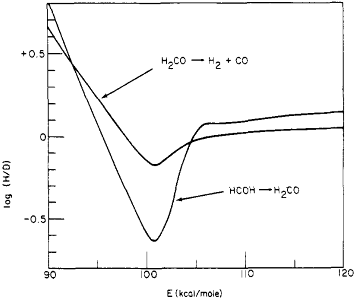
Unimolecular decomposition of formaldehyde
Reactivity





# Tunneling: an example

Unimolecular decomposition of formaldehyde
Isotopic effect



# Loose TS

A TS is generally obtained as a saddle point on the potential energy surface. But in some reactions (e.g. dissociations) this topological point can not be present. A loose TS is defined when:

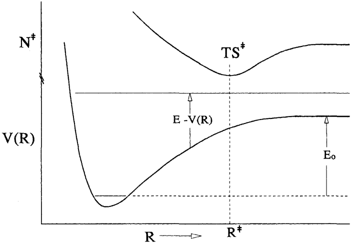
- $\Delta S^{\ddagger} < 0$
- Reactions with no reverse activation energies

In this case we use the more general definition of TS to locate it: the point corresponding to the minimum in the sum of states along the reaction coordinate. This is called Variational Transition State Theory

# Variational Transition State Theory I

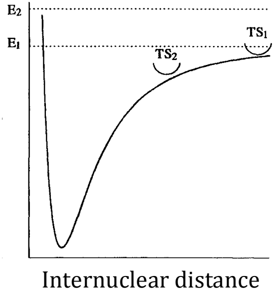
The TS is obtained by locating the minimum flux setting to zero the derivative of the sum of states and solving for $R^{\ddagger}$

$$\frac{dN^{\ddagger}(E,R)}{dR} = 0 \tag{53}$$



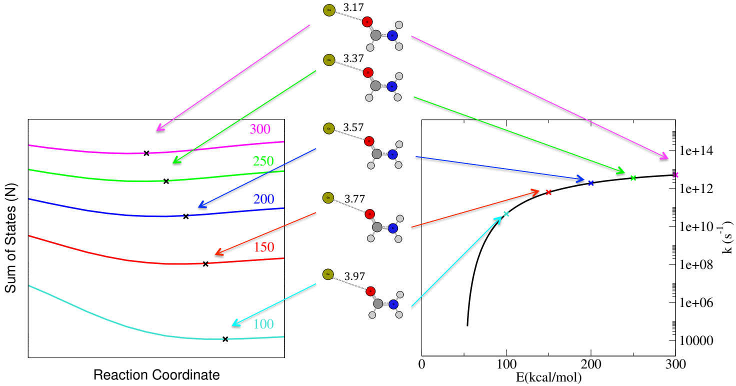
# Variational Transition State Theory II

Note that the position of the TS will depend on the energy !



# Variational Transition State Theory: an example[2]

Given the reaction: $[Ca - NH_2CHO]^{2+} \rightarrow Ca^{2+} + NH_2CHO$



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[2] A.Martin-Somer et al. Phys. Chem. Chem. Phys. 16, 14813 (2014).

# Rotational energy

Reactants and products have also rotational energy that can vary during the reaction.
If modes can freely exchange the energy they are active: this holds generally for all vibrational modes in RRKM theory.
For rotational energy this is not always the case.
Given a non-linear symmetric topi rotors ($I_x = I_y$) the rotational energy is

$$E_r(J,K) = BJ(J+1) + (A-B)K^2 \tag{54}$$

where $J$ and $K$ are the two quantum numbers: $J = 0, 1, 2, \dots$ and $K = 0, \pm1, \pm2, \dots, \pm J$. $A$ and $B$ are defined in terms of moments of inertia

$$\begin{aligned} A &= \hbar^2/2I_z & (55) \\ B &= \hbar^2/2I_x & (56) \end{aligned}$$

# Rotational energy

The $z$-axis is the symmetry axis, thus $J$ is a constant of the motion and always active.
$K$ can be:

- adiabatic: it is conserved
- active rotor: it allows energy exchange between vibration and rotation

# Rotations in RRKM

For adiabatic K, the rate constant is

$$k(E, J, K) = \frac{N^{\ddagger}[E - E_0 - E_r^{\ddagger}(J, K)]}{h\rho[E - E_r(J, K)]} \tag{57}$$

We have to consider three cases in which rotational energy can be shared

1. All the rotational energy is in the $(x - y)$ plane, so $K = 0$ and $J = (-1 + \sqrt{1 + 4E_{rot}/B})$ where $E_{rot}$ is the rotational energy got, for example, after a collision.
2. The rotational energy is equally distributed among the three axes.
3. All the rotational energy is added along the $z$-axis such that $K = \sqrt{E_{rot}/[3(A - B)]}$

# Rotations in RRKM

For active-K two ways of obtaining the rate constant are possible:

1. By summing over contributions from all possible values of $K$ to give

$$k(E,J) = \frac{\sum_{K=-J}^{K=+J} N^{\ddagger}[E - E_0 - E_r^{\ddagger}(J,K)]}{h \sum_{K=-J}^{K=+J} \rho(E,J,K)} \tag{58}$$

2. Considering $\rho$ and $N^{\ddagger}$ as convolutions between the densities and sum of states for the internal degrees of freedom and the active external rotation

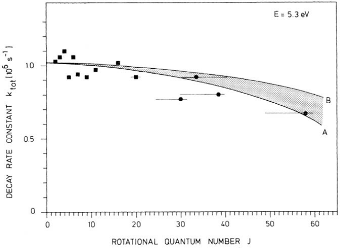
$$\rho(E_v) = \int_0^{E_v} \rho_v(E)\rho_r(E_v - E)dE \tag{59}$$

$$N^{\ddagger}(E,J) = \int_0^{E^{\ddagger}} N_v(E)\rho_r(E^{\ddagger} - E)dE \tag{60}$$

where $E_T = E_v + E_r(J)$

# Example 1. Benzene decomposition[3]

$C_6H_6 \rightarrow C_6H_5 + H$



The effect of J at a constant total energy: $E_{vib} + E_{rot} = 5.3$ eV. Numerical results from an RRKM calculation in which the rotational constant of the H loss transition state was assumed to be identical to that of the benzene ion;

- Curve A: K-mixing
- Curve B: no K-mixing

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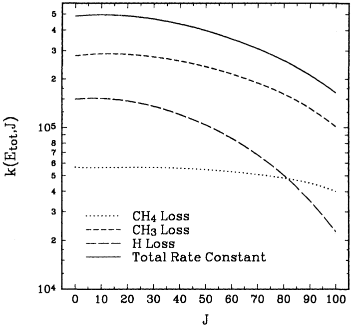
[3] A. Kiermeier et al. . J. Chem. Phys. 88, 6182 (1988).

# Example 2. Butene ion decomposition[4]

$C_4H_8^+ \rightarrow$



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[4] J.A.Booze et al.. J. Chem. Phys. 99, 4441 (1993).

# Non-RRKM behaviors