

Molecular collisions in the interstellar medium: successes and challenges

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Fonds Wetenschappelijk Onderzoek
Vlaanderen
Opening new horizons

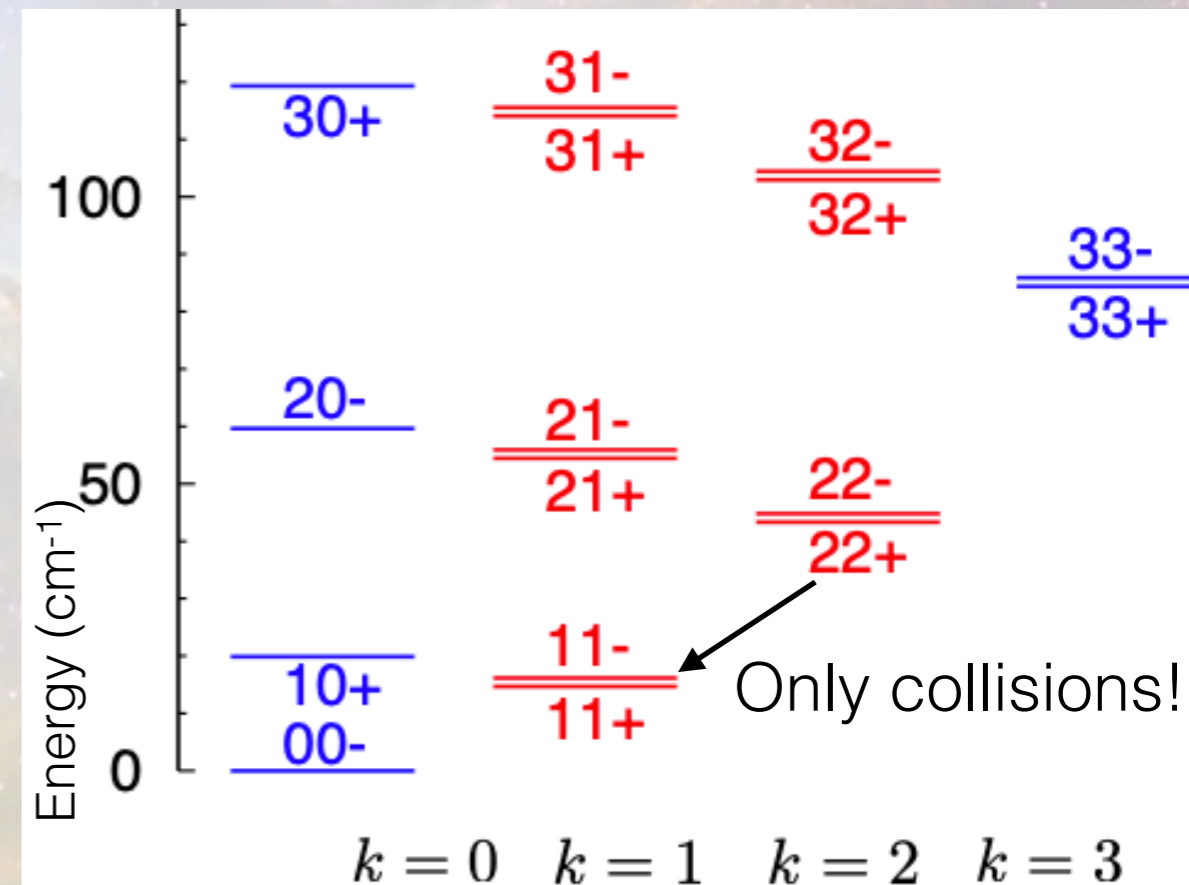
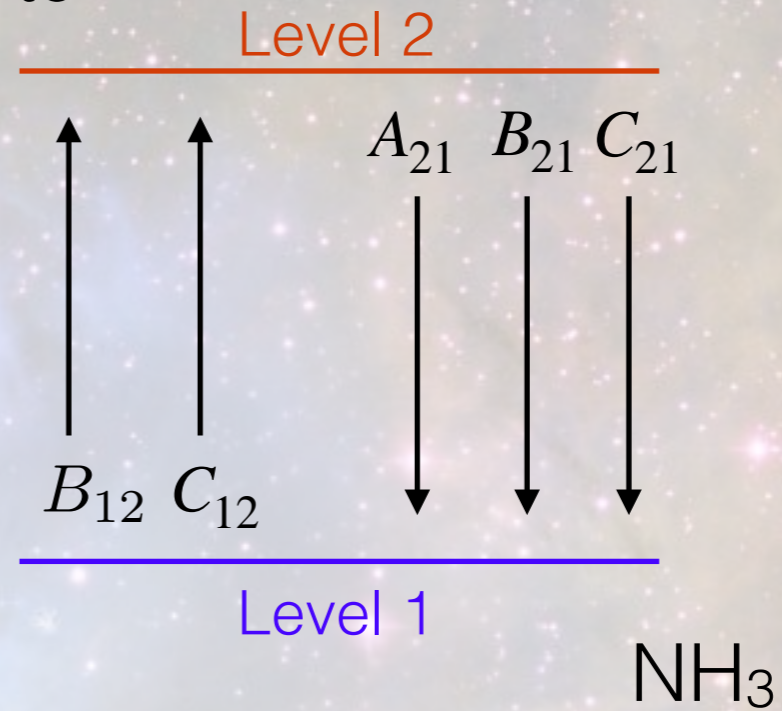
Introduction: Inelastic collisions in space

Inelastic collisions are crucial in environments where LTE is not achieved (molecular clouds, protostars, comets, etc) to

- Obtain accurate molecular abundances
- Put constraints on the chemistry (formation pathways)
- Probe local physical conditions such as temperature and density

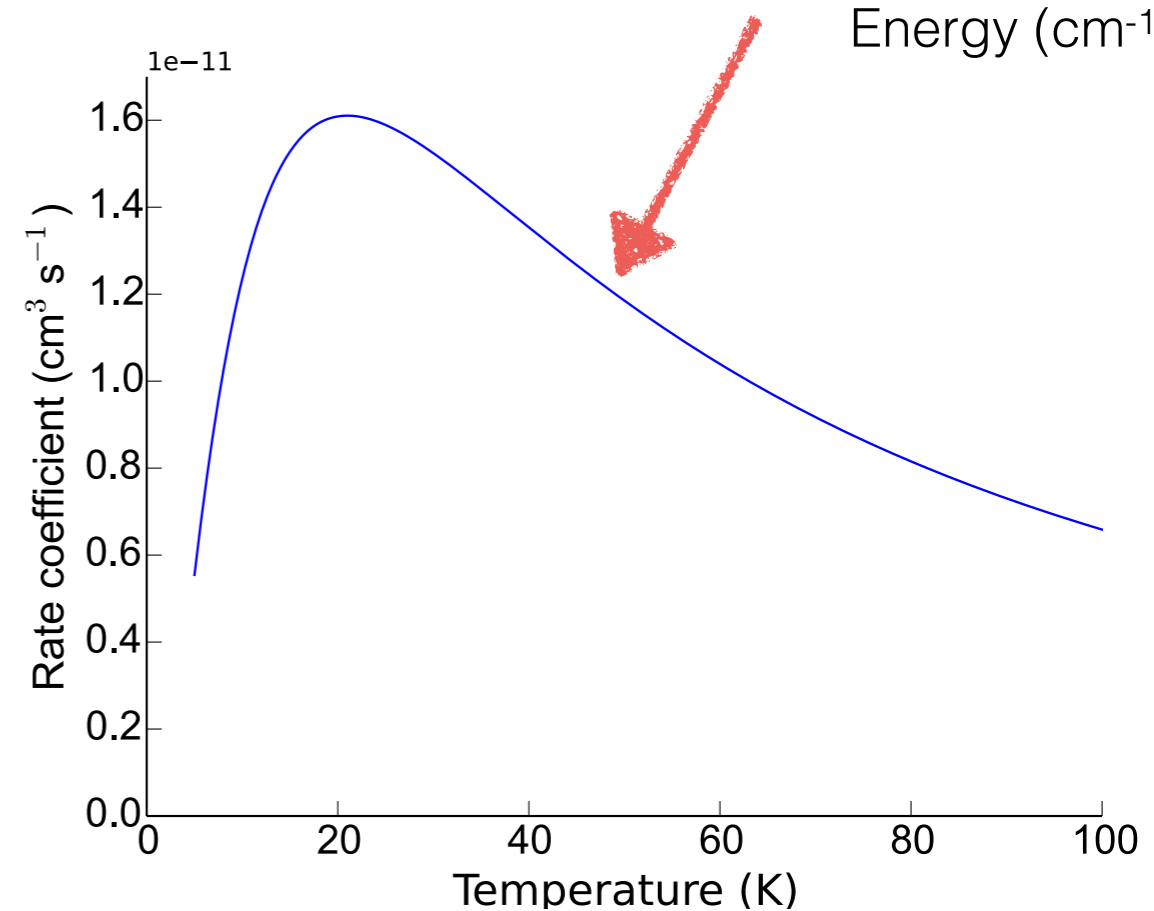
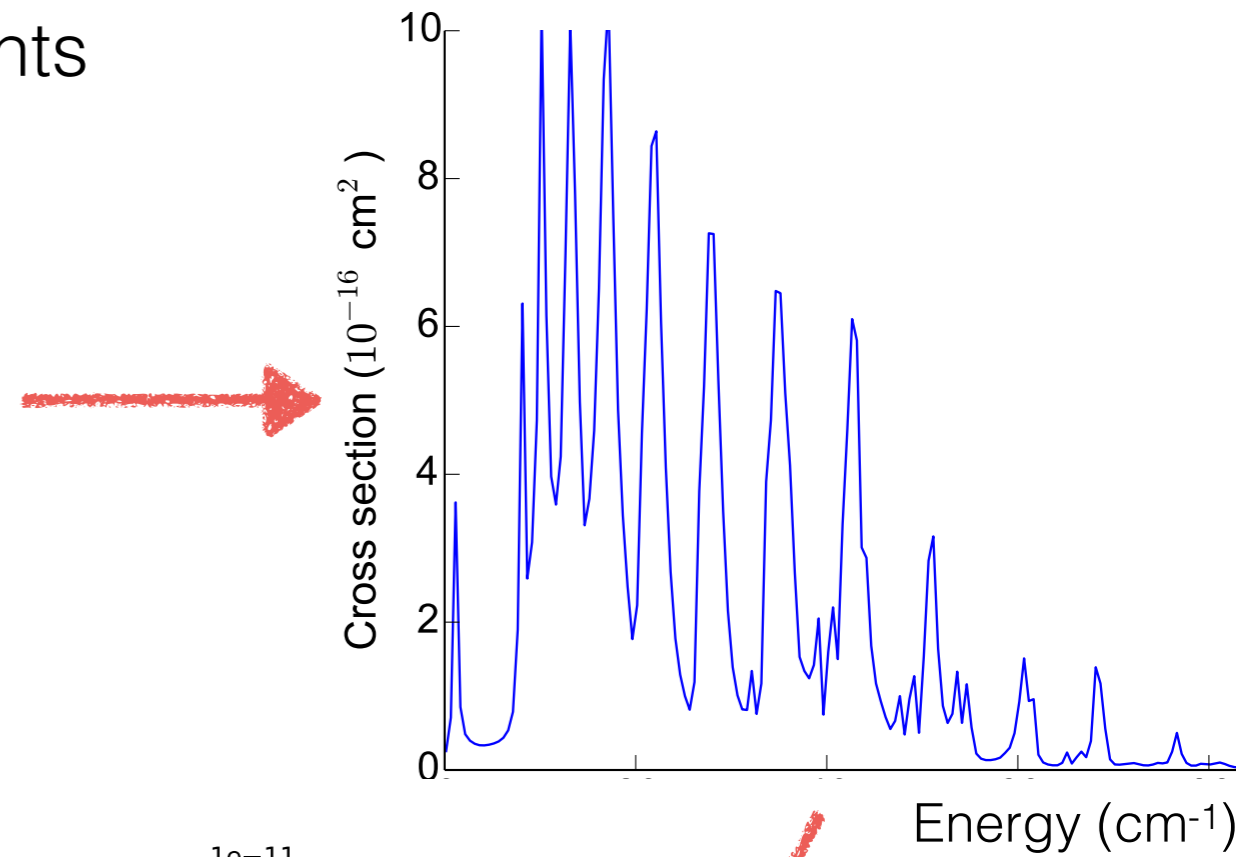
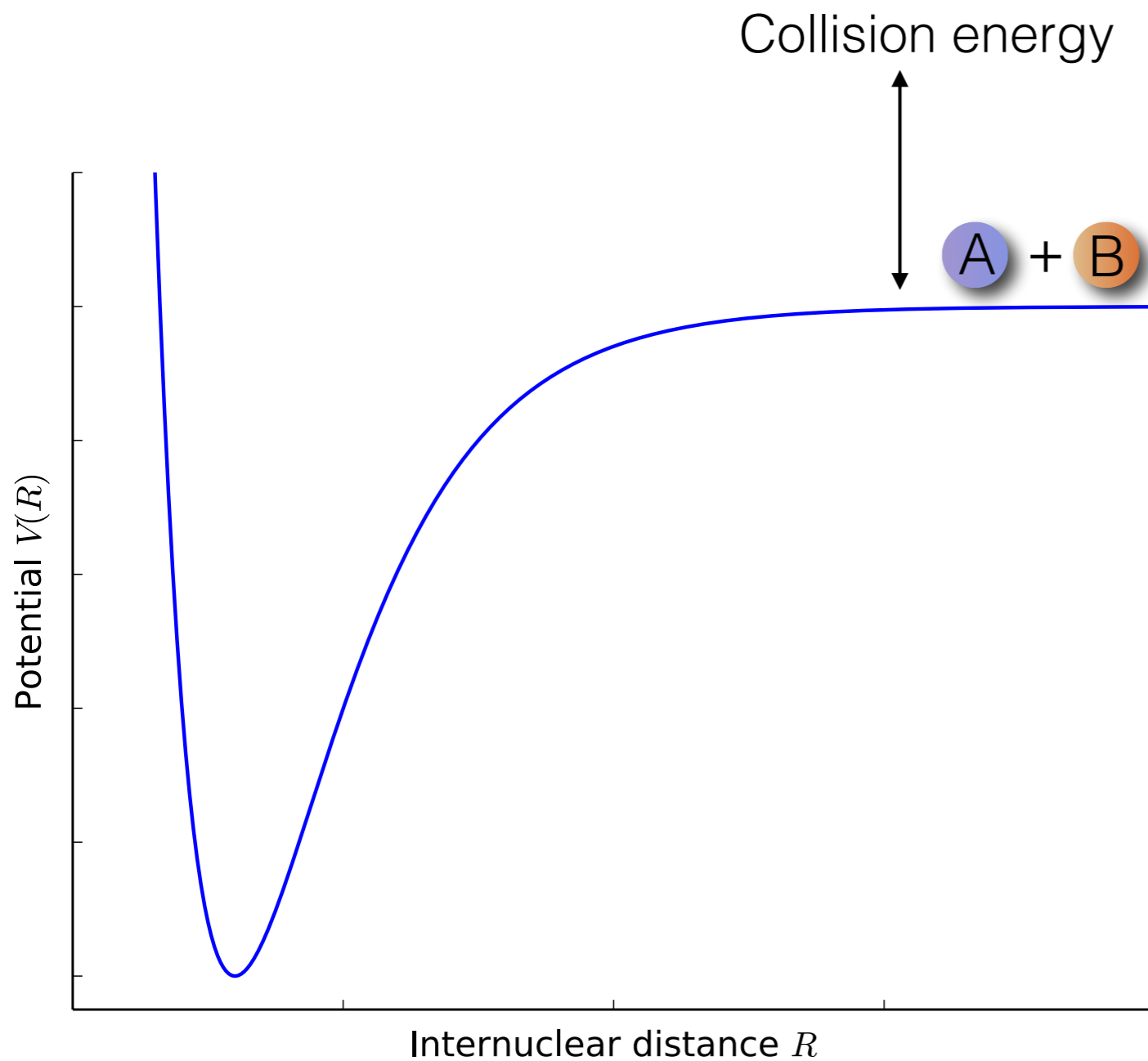
Ex: N_2H^+ , NH_3 , HCN/HNC ratio, CH_3CN

Non-LTE radiative transfer modelling requires collisional excitation and quenching cross sections and **rate coefficients** with main constituents of ISM (**He**, **H₂**, **H**) for $T \sim 5 - 500$ K



General methodology for inelastic collisions developed (starting in 1960s):

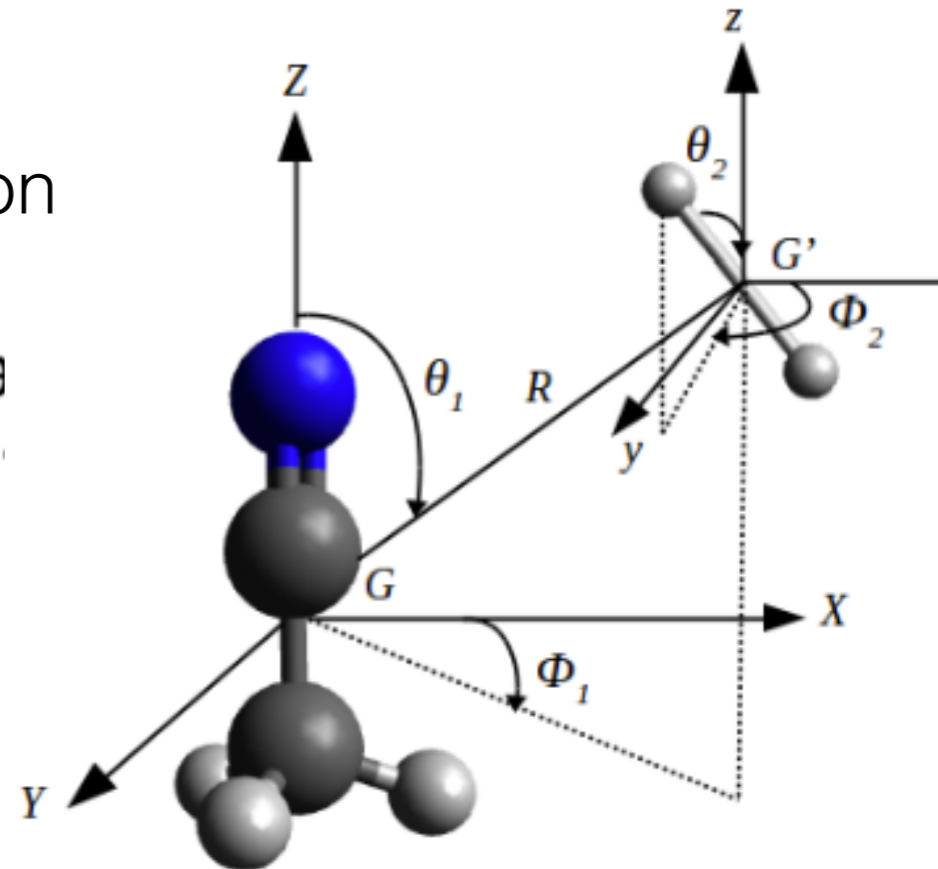
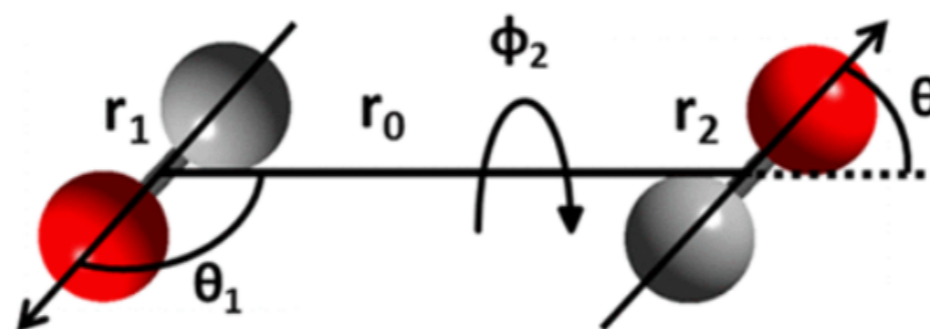
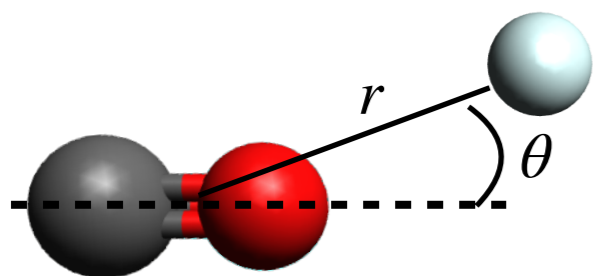
1. Construct the potential energy surface (PES) for molecule-He/H₂
2. Investigate the dynamics of the collision on the PES
3. Obtain cross sections and rate coefficients



$$k(T) = \left(\frac{2}{k_B T} \right)^{3/2} \frac{1}{\sqrt{\pi \mu}} \int_0^\infty E e^{-E/k_B T} \sigma(E) dE$$

Potential energy surface

Between 2 and 6 dimensions for rotational excitation

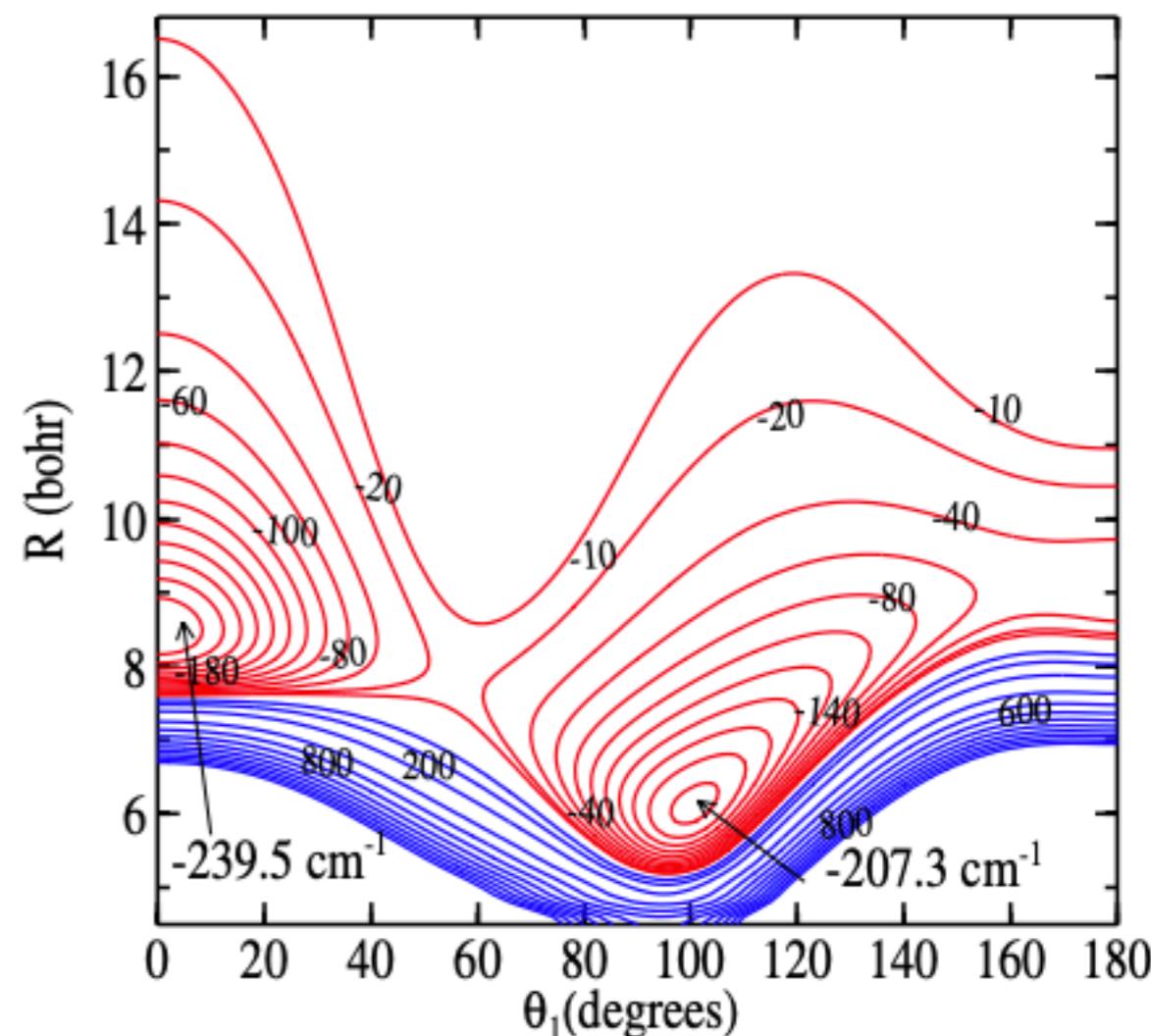


Calculation of the interaction energy for fixed nuclei on a grid of geometries

For Mol-He and Mol-H₂, typical well depth 20-500 cm⁻¹ : requires accurate quantum chemistry methods!

“Gold standard”

- CCSD(T) or CCSD(T)-F12a method
- Aug-cc-pVnZ basis sets on all atoms
- 10³ - 10⁵ points (geometries)
- Fitted using angular functions (spherical harmonics)



Collision dynamics

Many different methods to provide state-to-state collisional rate coefficients...

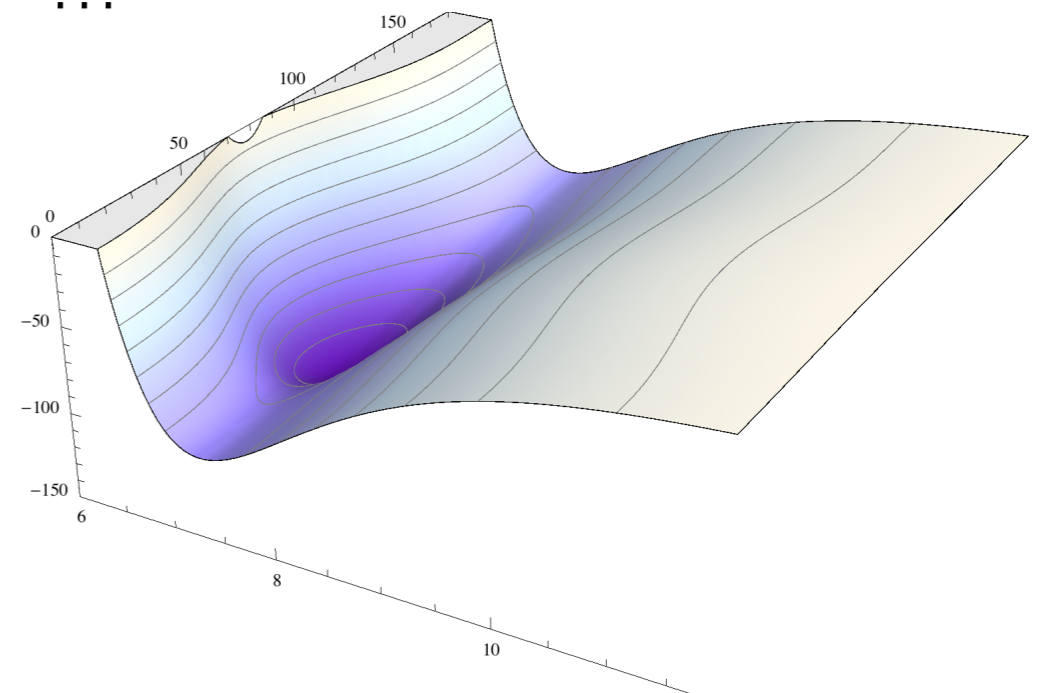
Non-reactive (inelastic)

- Close-coupling (CC) method (exact)
- Coupled states (decoupling)
- Infinite order sudden (IOS) approximation
- Mixed quantum/classical theory (MQCT)
- Quasi-classical trajectory (QCT)
- Statistical approaches (SACM+)
- ...

Reactive

- Time-independent QM (hyperspherical coordinates)
- Time-dependent QM (wave packet) methods
- QCT
- Statistical
- MCTDH
- ...

Common feature of all methods: need a PES



Close-coupling method: solve the time-independent Schrödinger equation

- Hamiltonian: $H = H_A + H_B - \frac{\hbar^2}{2\mu} \nabla^2 + V$ with $\mathbf{J} = \mathbf{j}_A + \mathbf{j}_B + \mathbf{L}$

- Total wave function : $\Psi = R^{-1} \sum_{\alpha} |\alpha\rangle \chi_{\alpha}(R)$
Radial functions
Angular functions

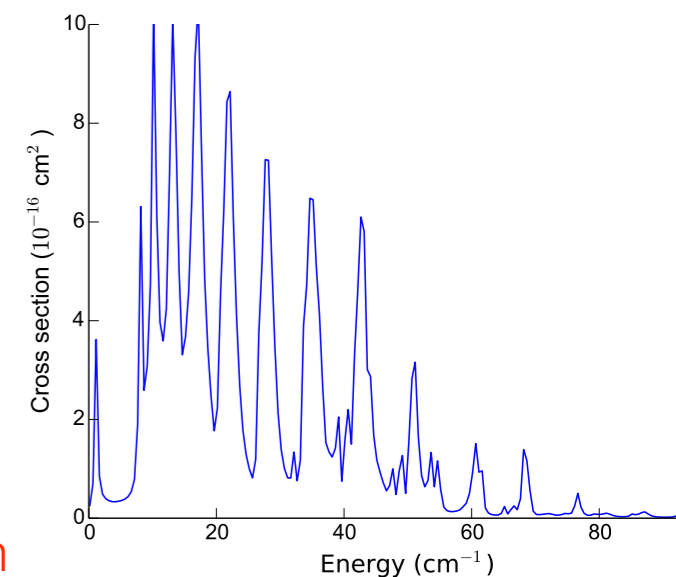
- Integration of Schrödinger equation over angles

- System of radial coupled equations (+ boundary conditions):

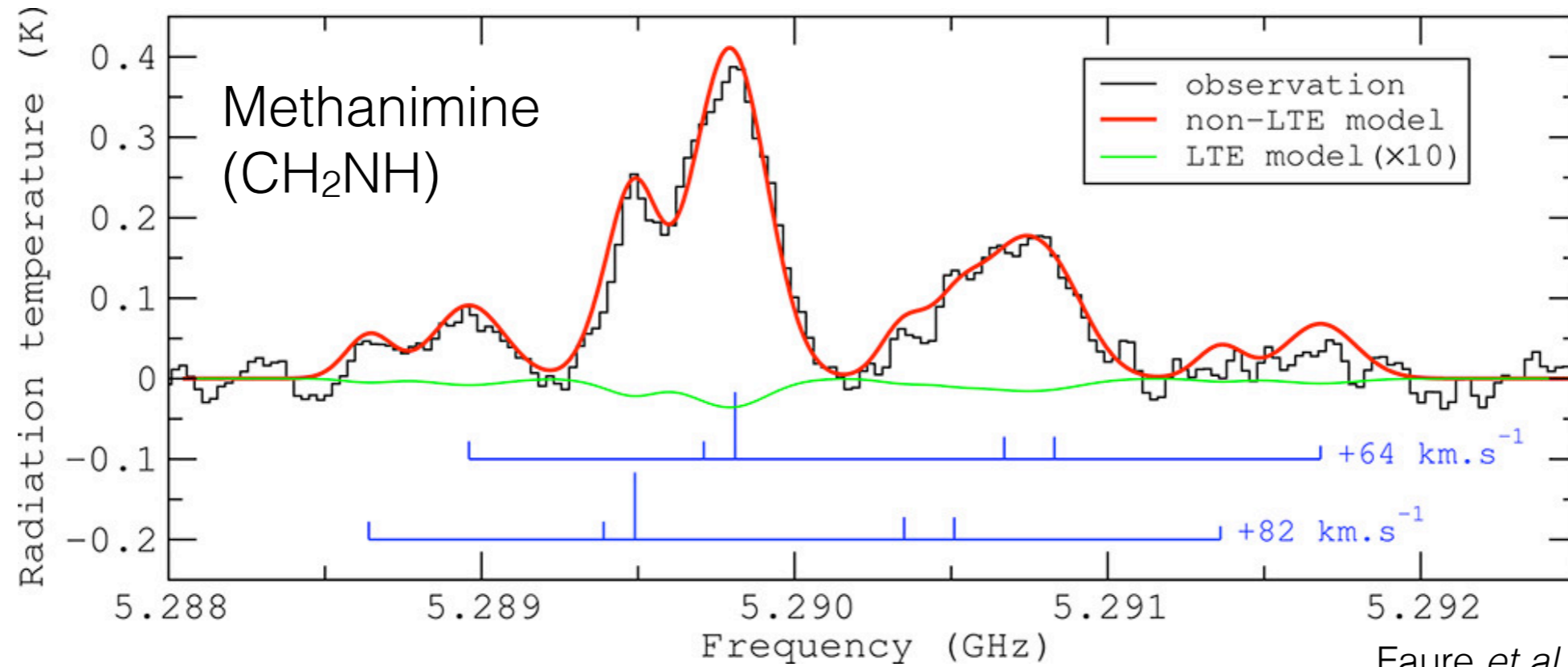
$$-\frac{\hbar^2}{2\mu} \frac{d^2 \chi_{\alpha}}{dR^2} + \sum_{\alpha'} \langle \alpha' | H_A + H_B + \underbrace{V}_{\text{PES}} + \frac{\mathbf{L}^2}{2\mu R^2} | \alpha \rangle \chi_{\alpha} = E \chi_{\alpha}$$

- Cross sections and rate coefficients:

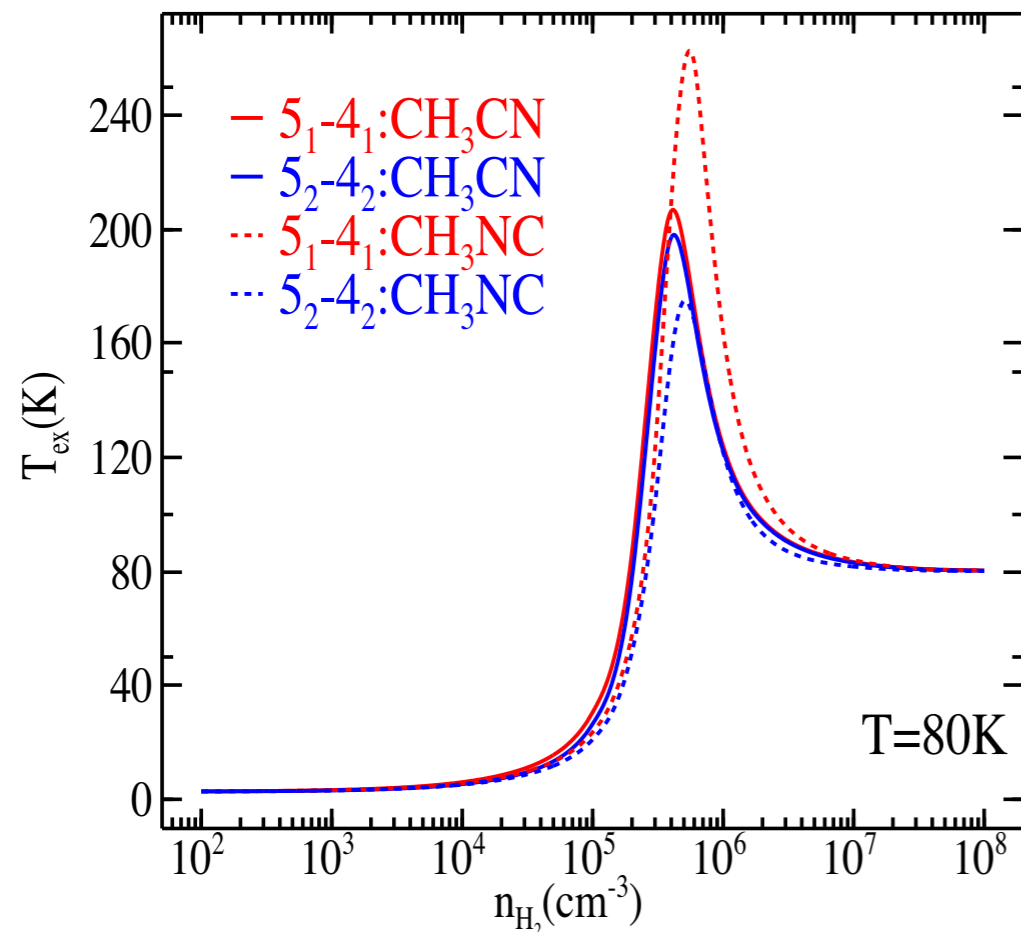
$$k_{vj \rightarrow v' j'}(T) = \sqrt{\frac{8}{\pi \mu (k_B T)^3}} \int_0^{\infty} \underbrace{E e^{-E/k_B T}}_{\text{Boltzmann distribution}} \underbrace{\sigma_{vj \rightarrow v' j'}(E)}_{\text{cross section}} dE$$



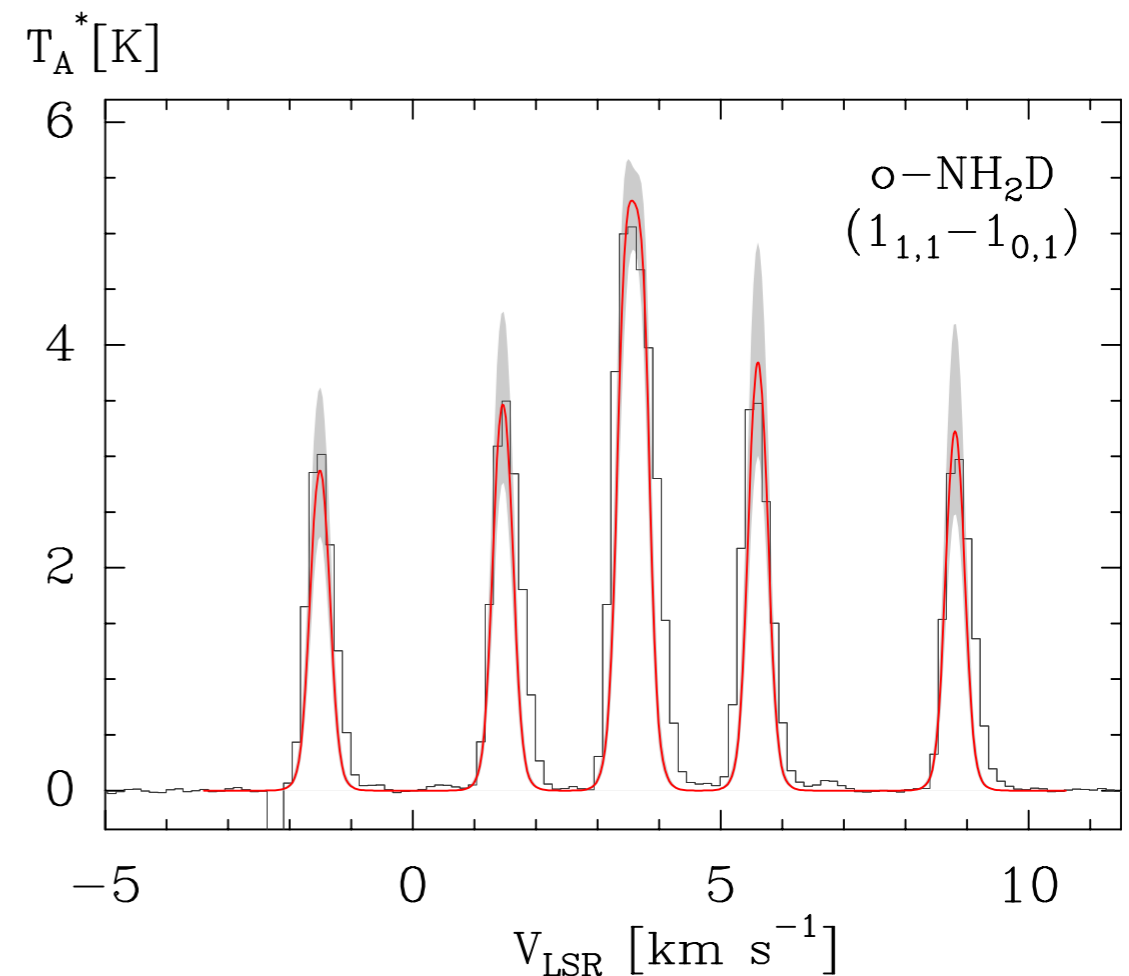
Use of rate coefficients in modelling



Faure *et al.*, JPCL 9 3199 2018



Ben Khalifa *et al.* *MNRAS* 523 2577 (2023)



Daniel *et al.*, *MNRAS* 457 1535 (2016)

Scattering experiments

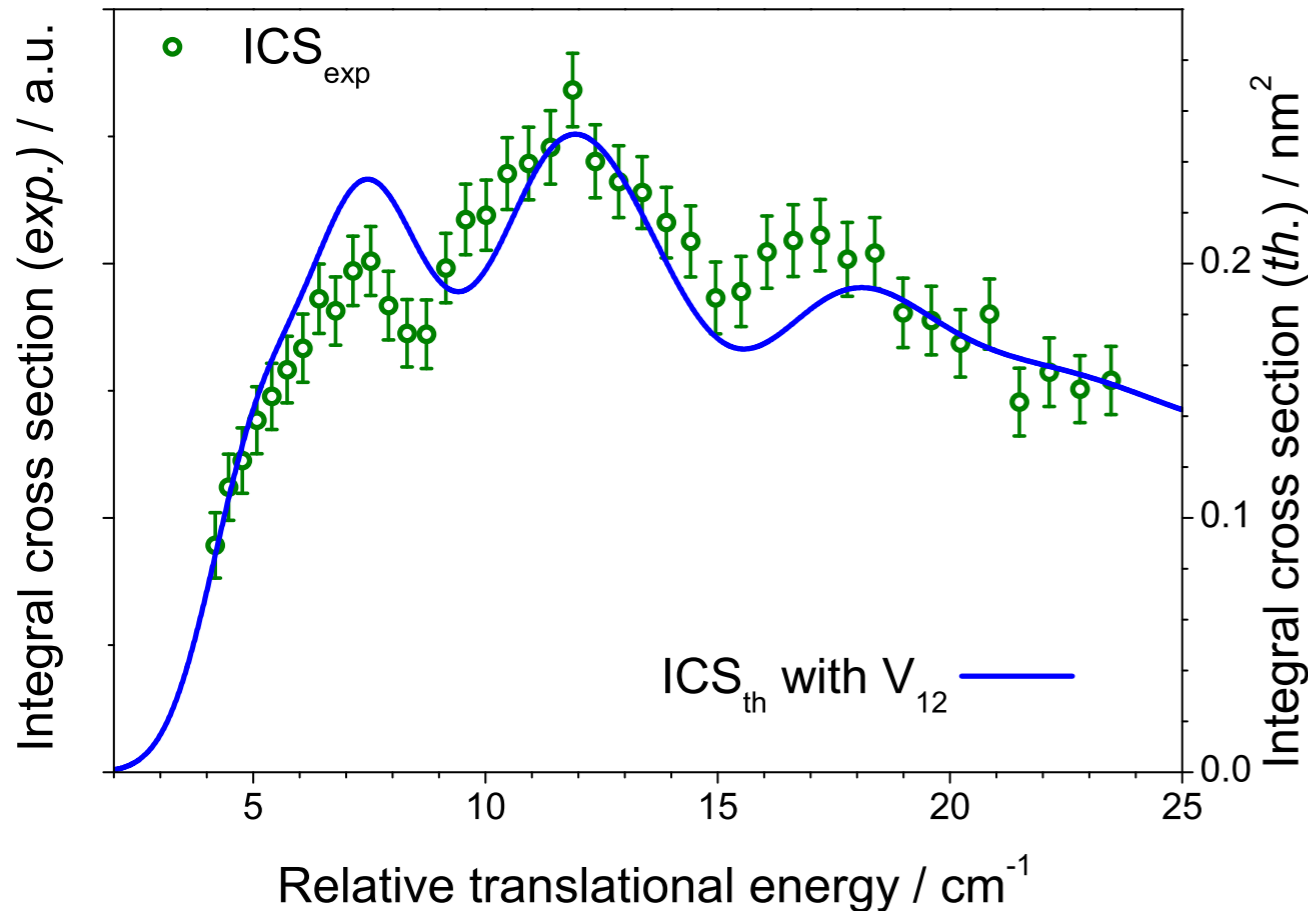
Allows to probe quantum chemistry + quantum dynamics methods.

In the last 20y, huge progress in measuring accurate cross sections and/or rate coefficients for inelastic collisions at low temperature.

Theory has been validated at low temperatures...

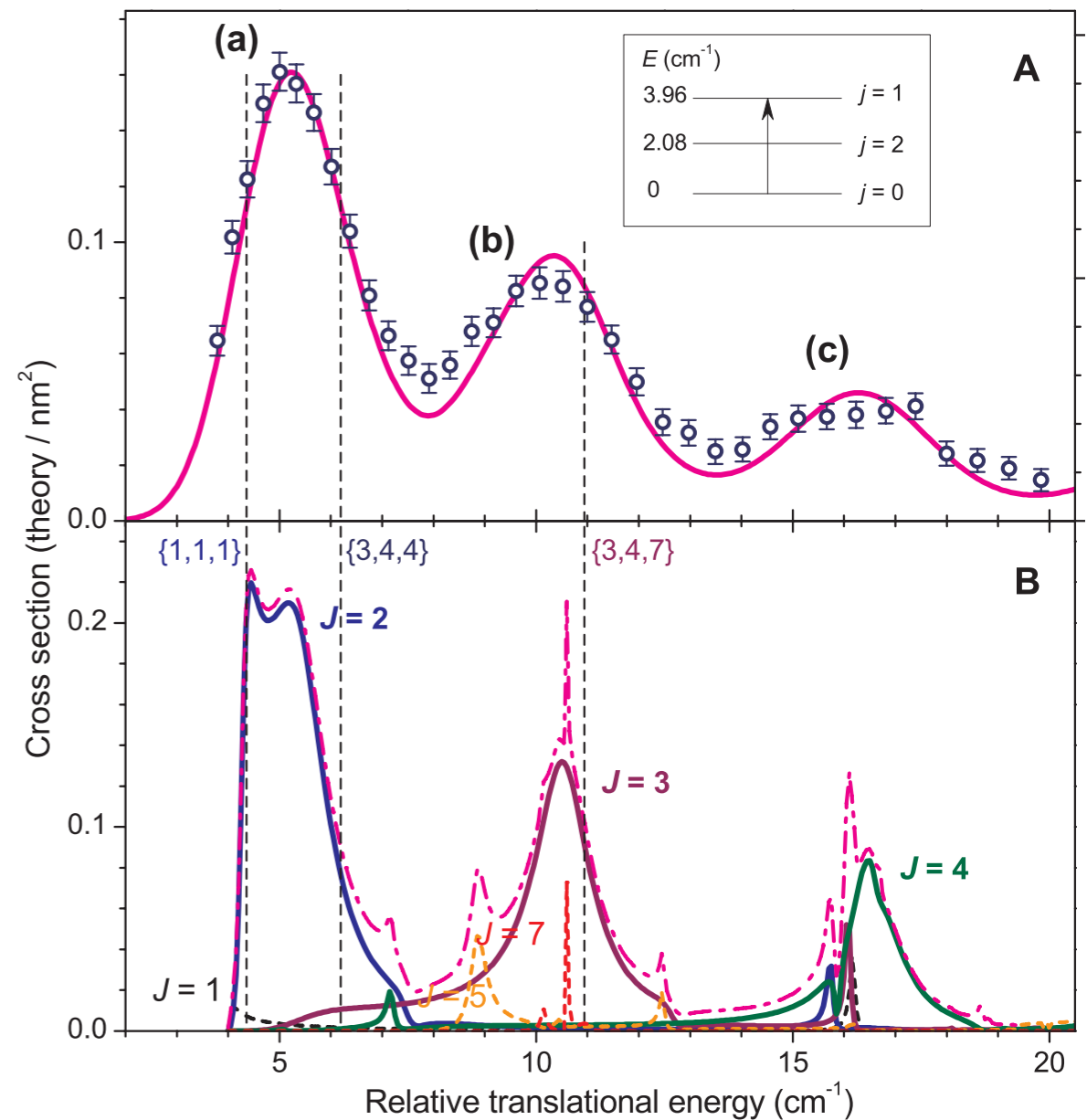
Ex: Bergeat/Costes/Naulin (Bordeaux)

CO($j=0$) + H₂



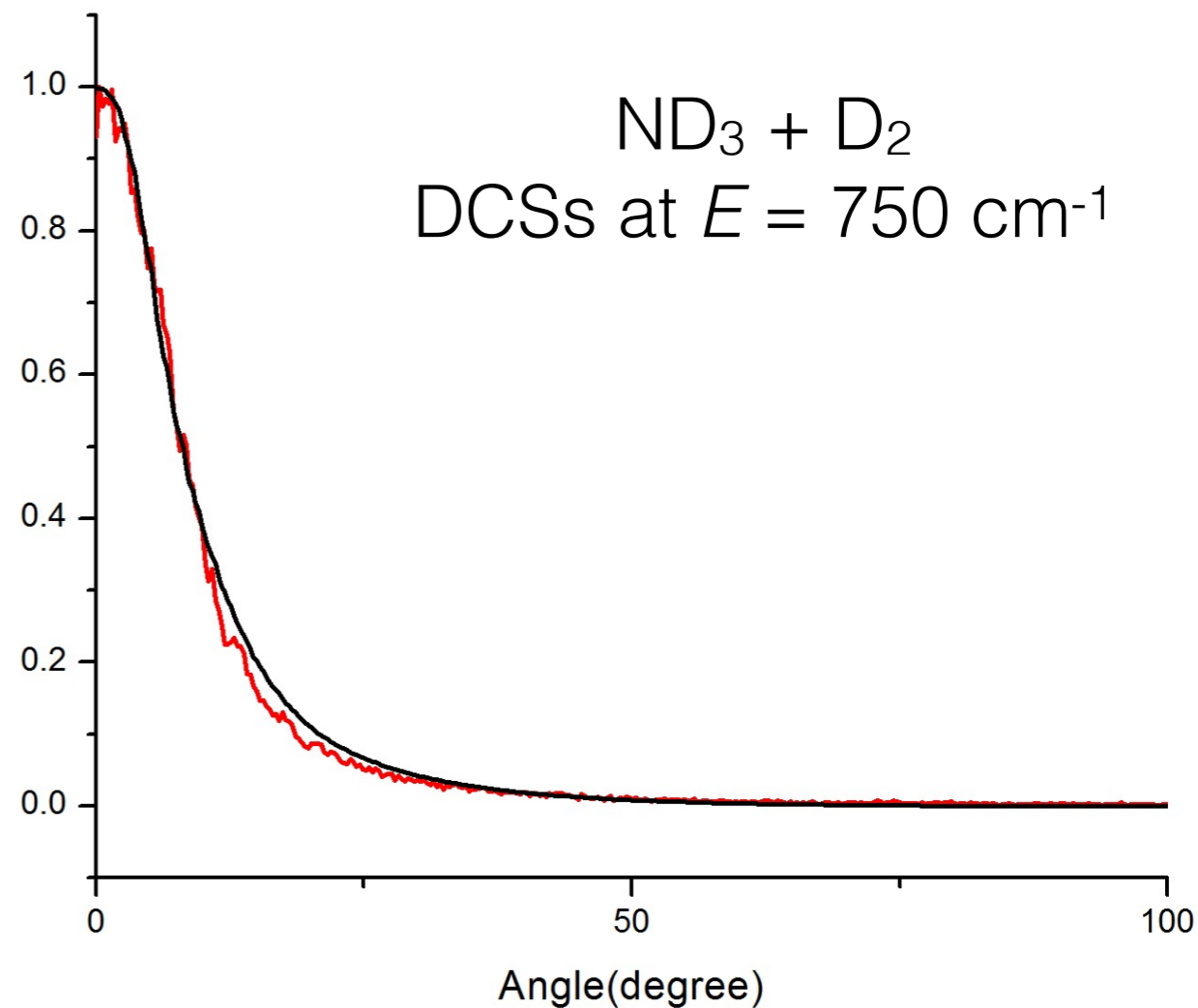
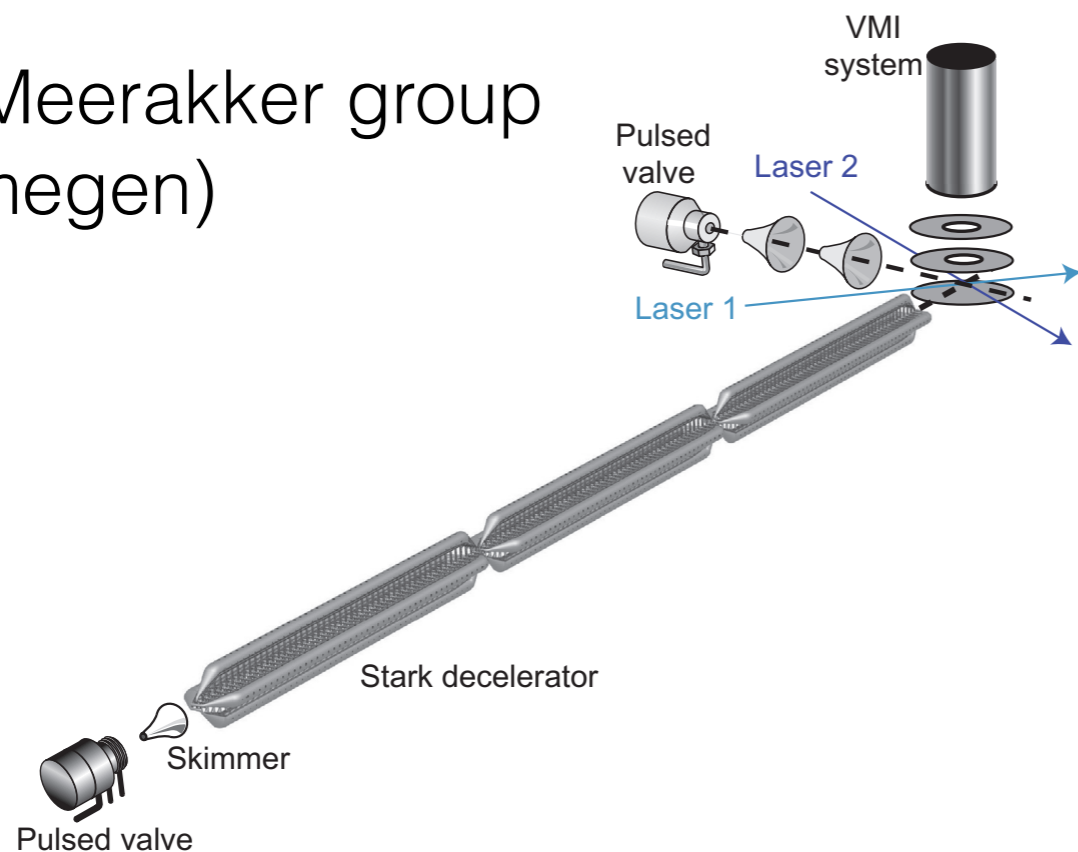
Chefdeville *et al.*, *ApJ* 799 L9 (2015)

O₂($j=0$) + H₂

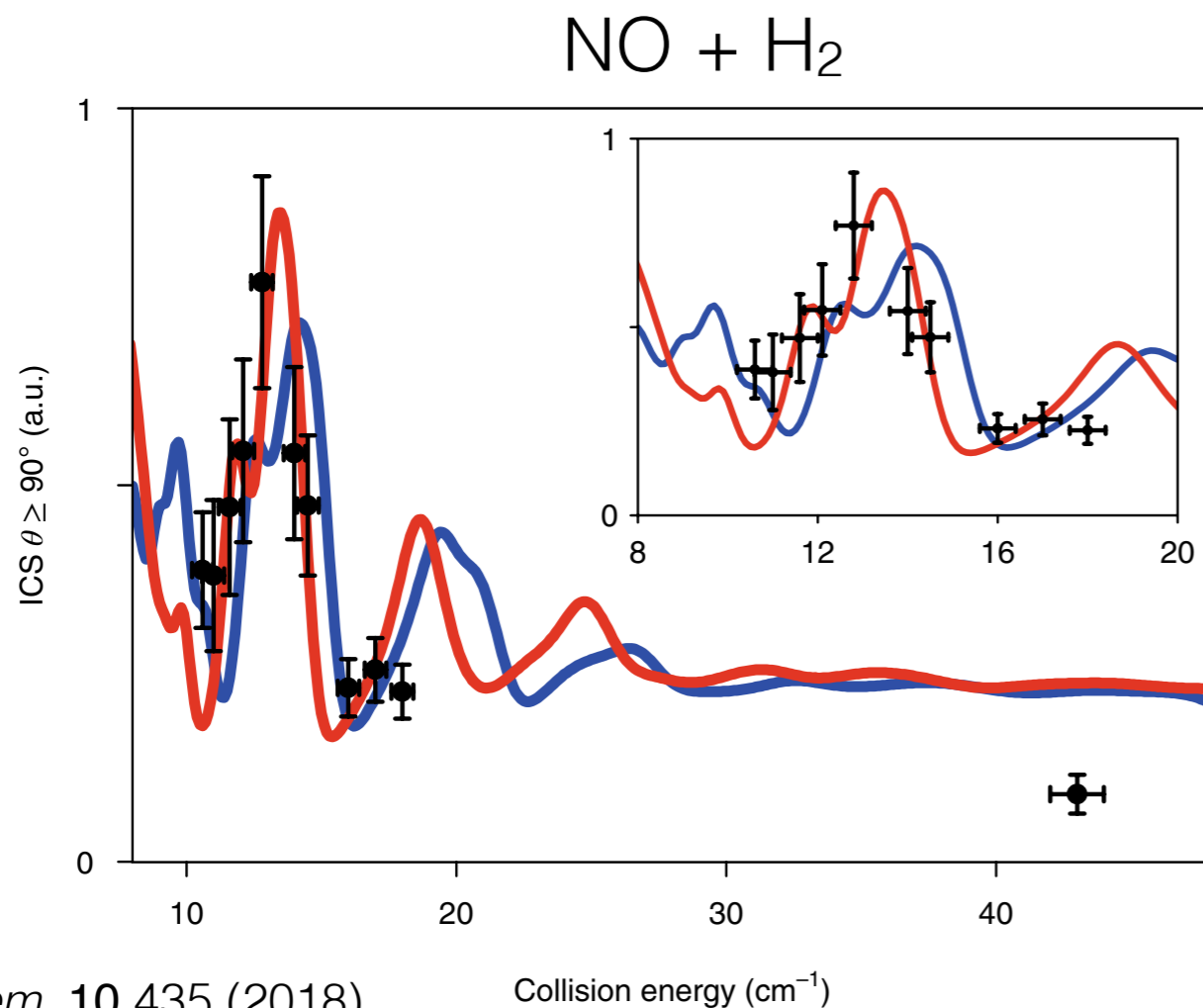


Chefdeville *et al.*, *Science* 341 1094 (2013)

Ex: Meerakker group
(Nijmegen)



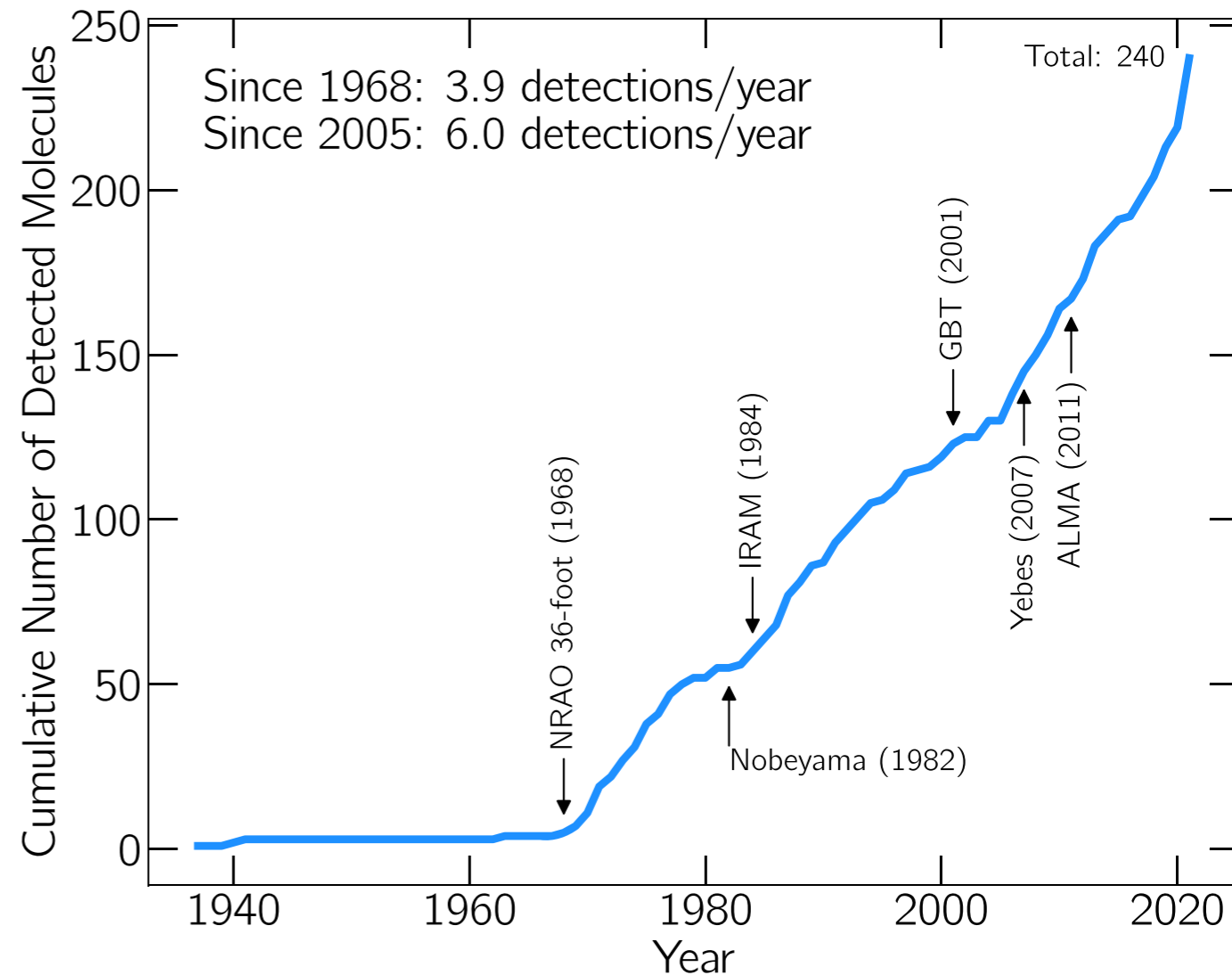
Gao et al., PCCP 21 14033 (2019)



Theory has passed
experimental tests so far!
But only for specific (small)
systems...

Successes:

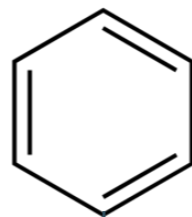
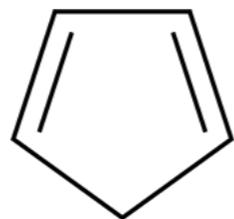
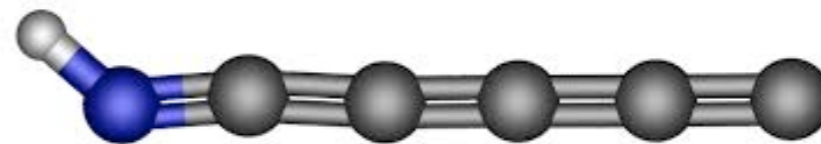
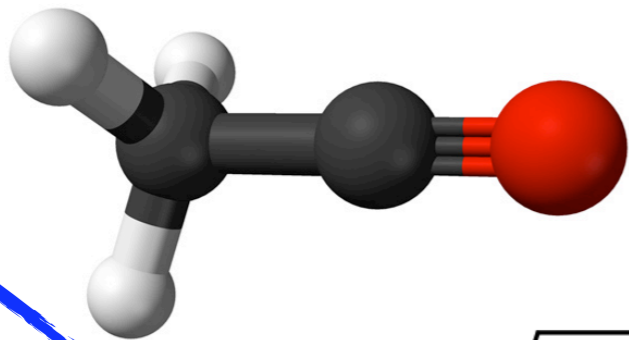
- Clear methodology for rotational excitation of molecules
- Validated by experiments
- Extensions to fine/hyperfine excitation
- New approximate approaches available
- Data (rate coefficients) available for about 70 molecules (with He and/or H₂)
- Databases of rate coefficients for the community (EMAA, Basecol, LAMDA)
- Interactions between the Astro and Chemical Physics communities



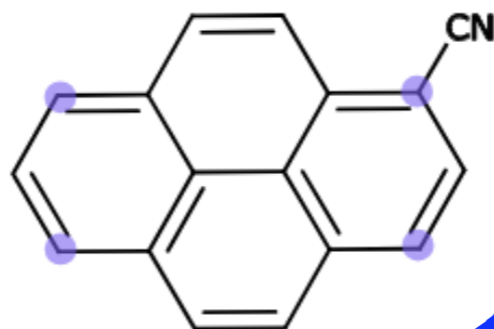
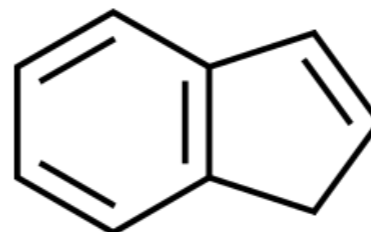


Challenges

Increase in size

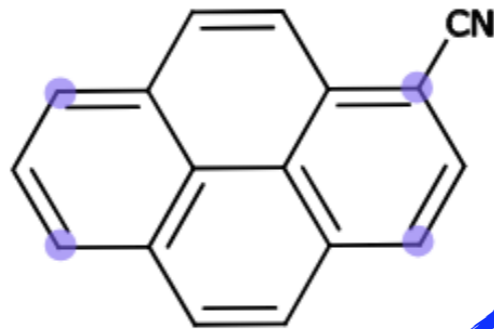
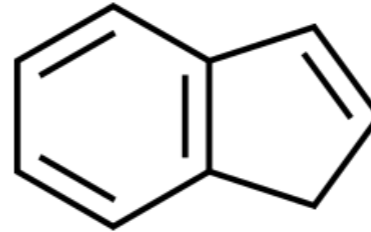
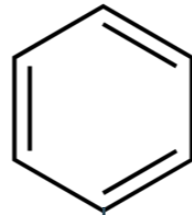
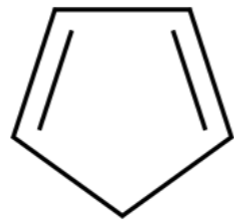
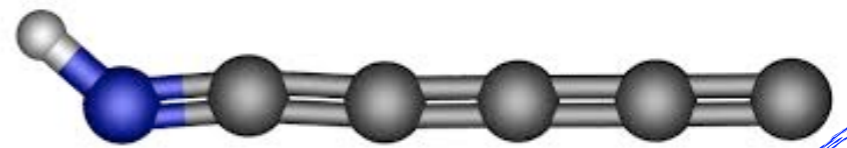
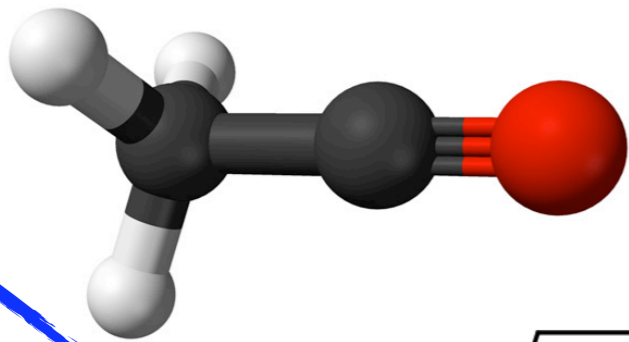


CN

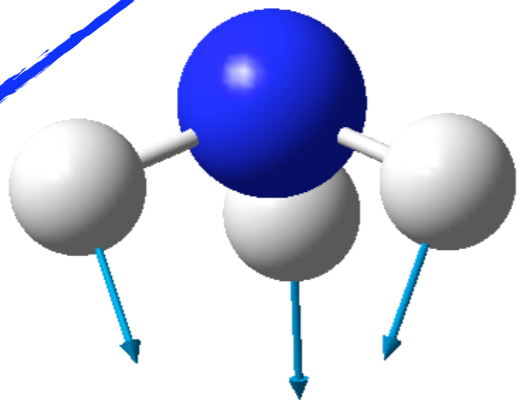
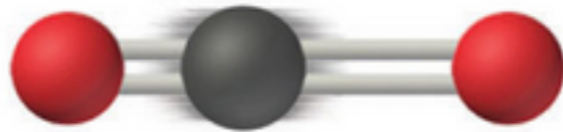


Challenges

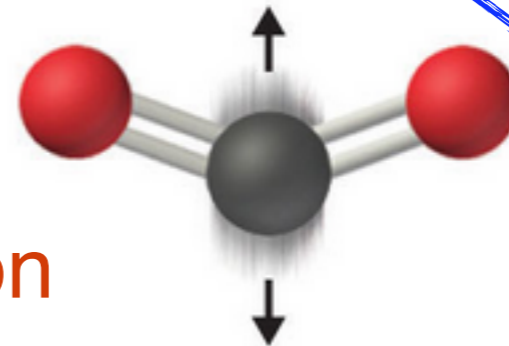
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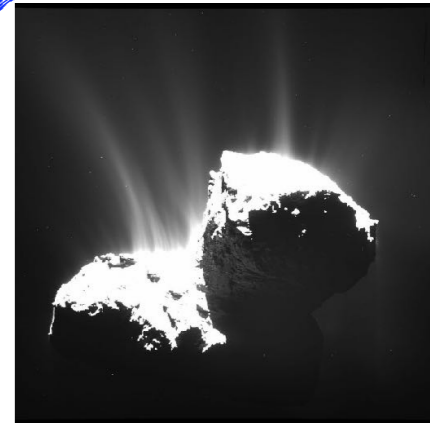
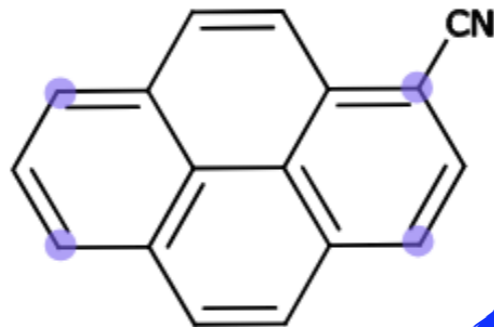
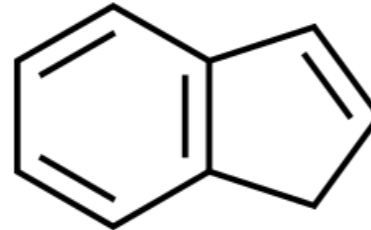
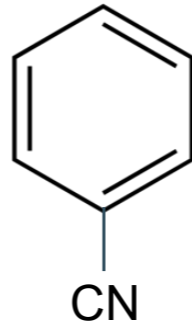
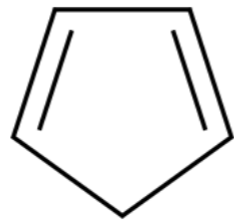
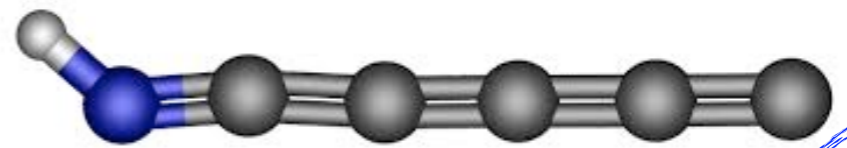
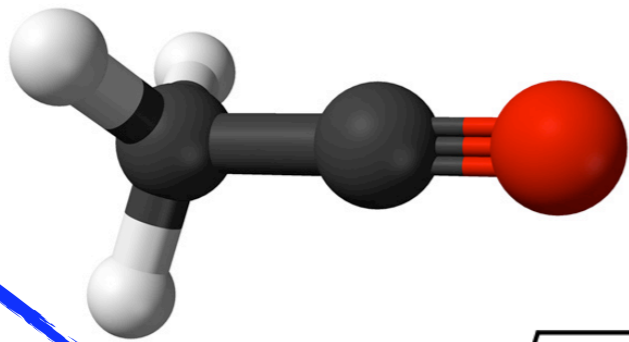
Challenges



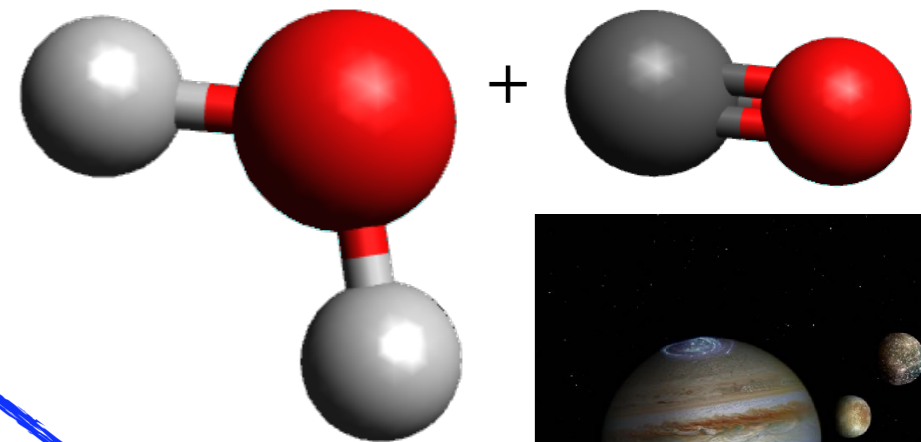
Vibrational excitation



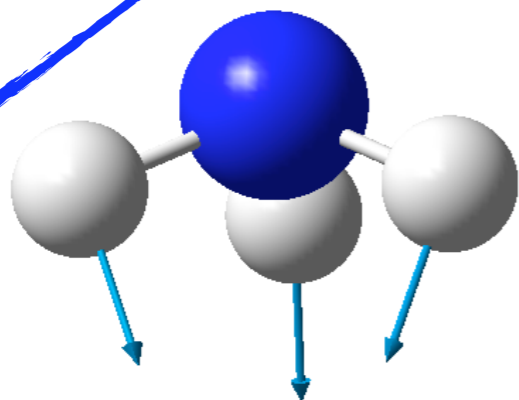
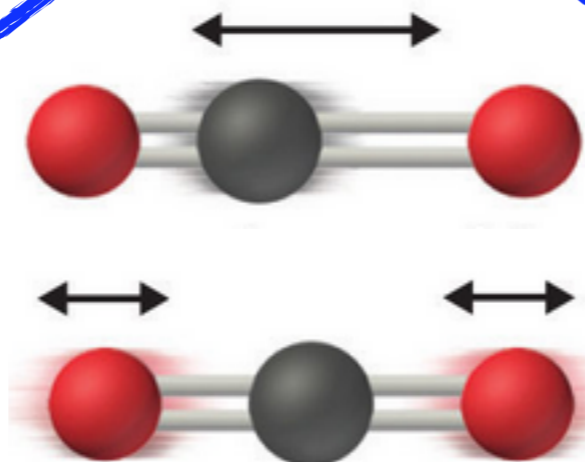
Increase in size



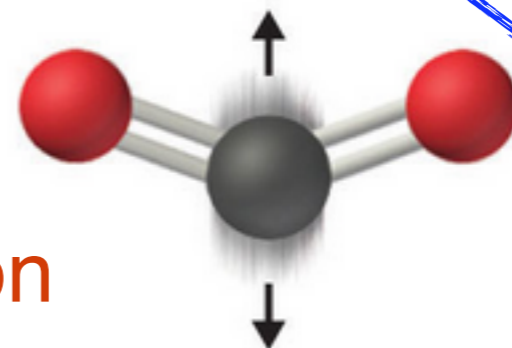
Heavy colliders



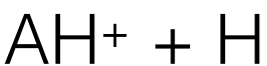
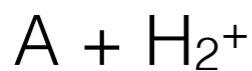
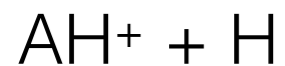
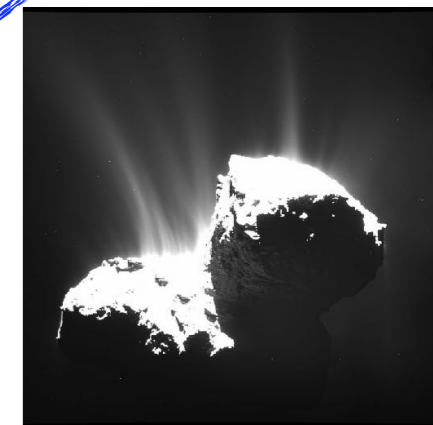
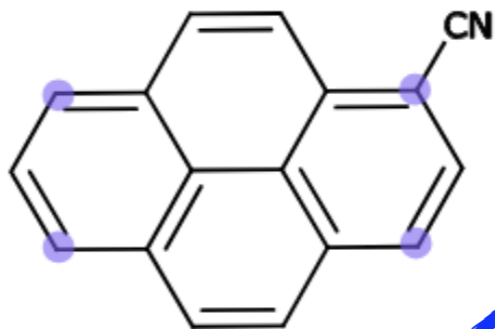
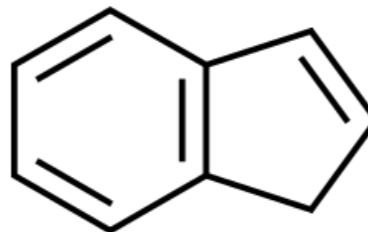
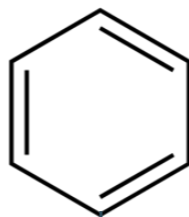
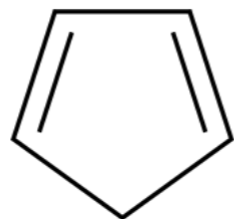
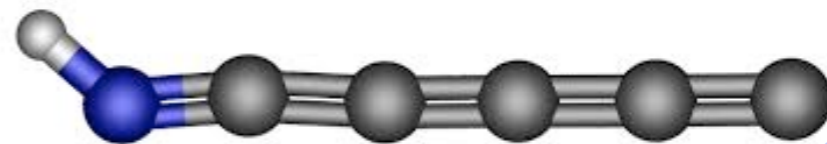
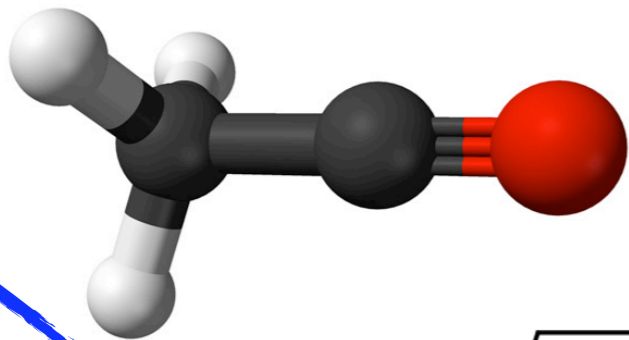
Challenges



Vibrational excitation



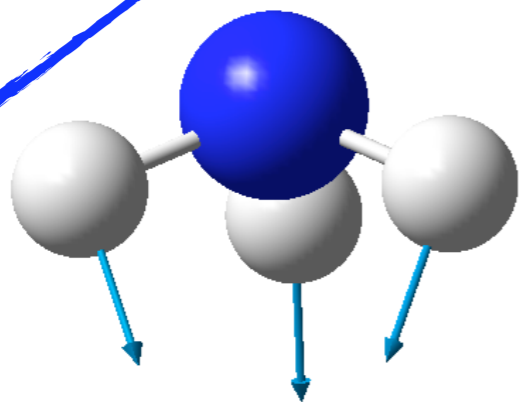
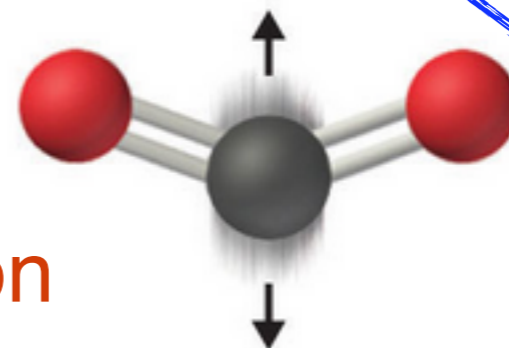
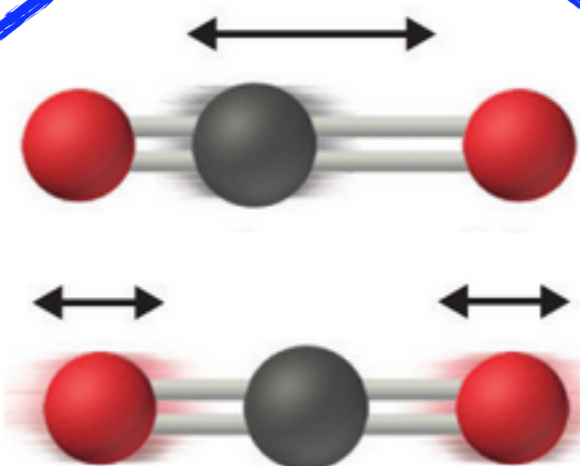
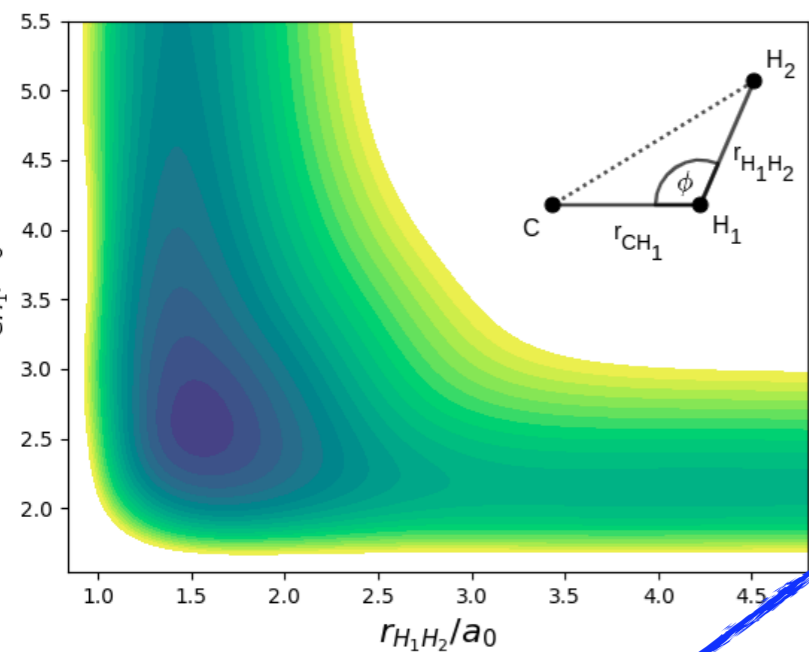
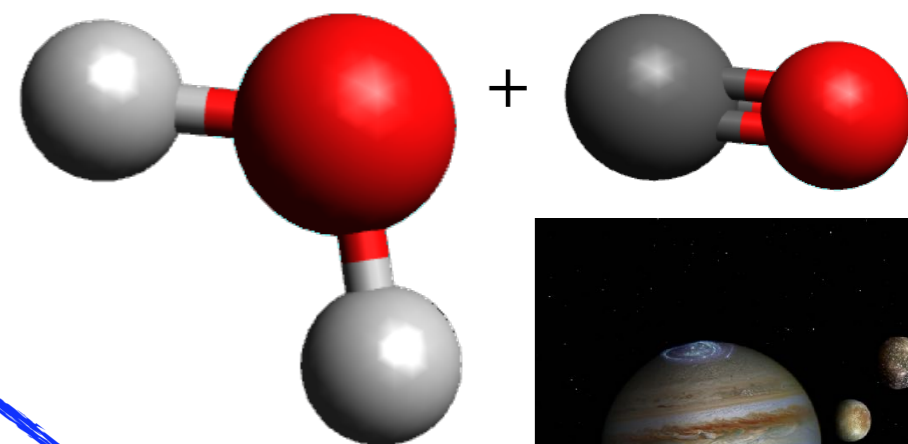
Increase in size



Reactive ions

Heavy colliders

Challenges



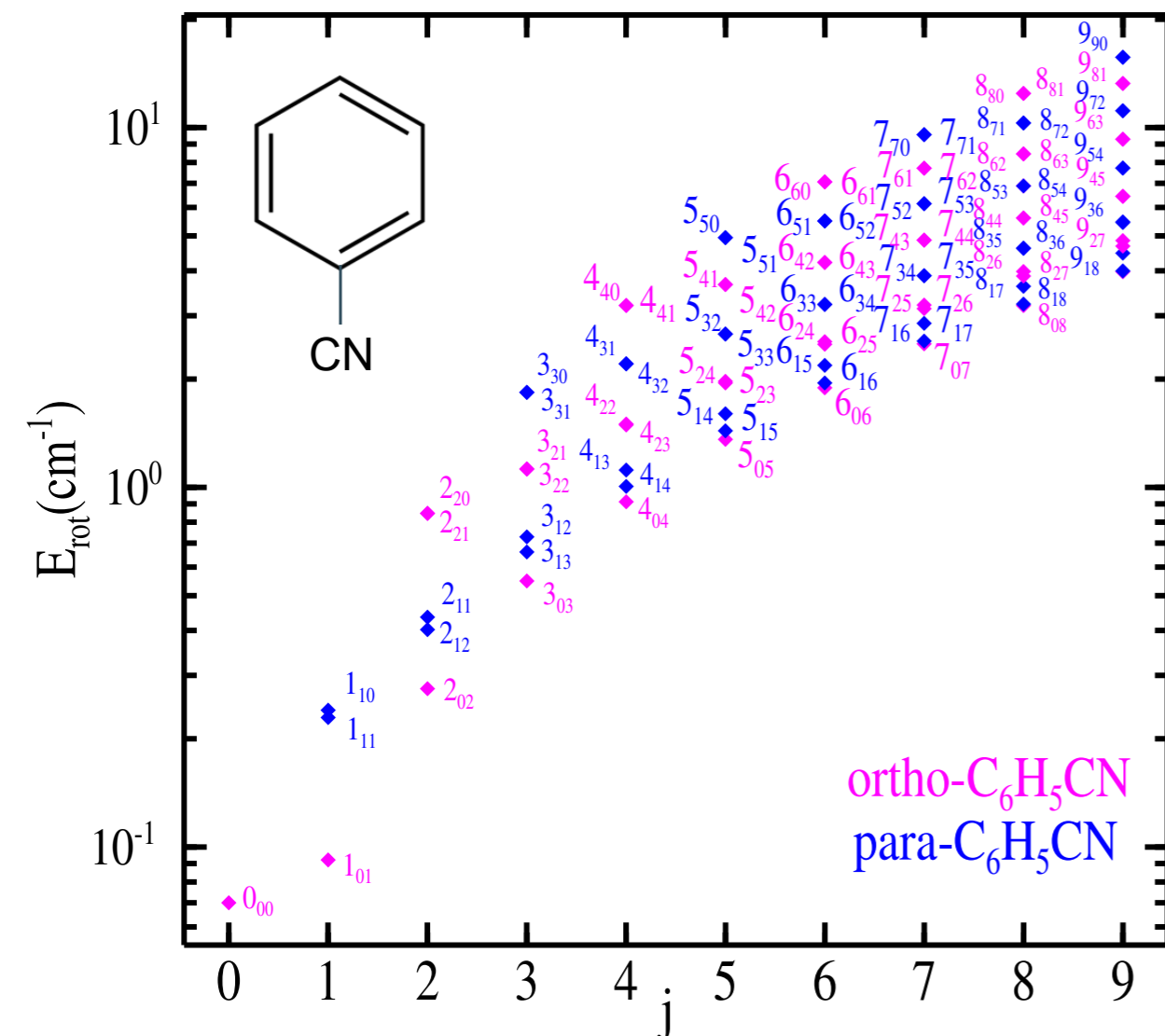
Vibrational excitation

Increase in size

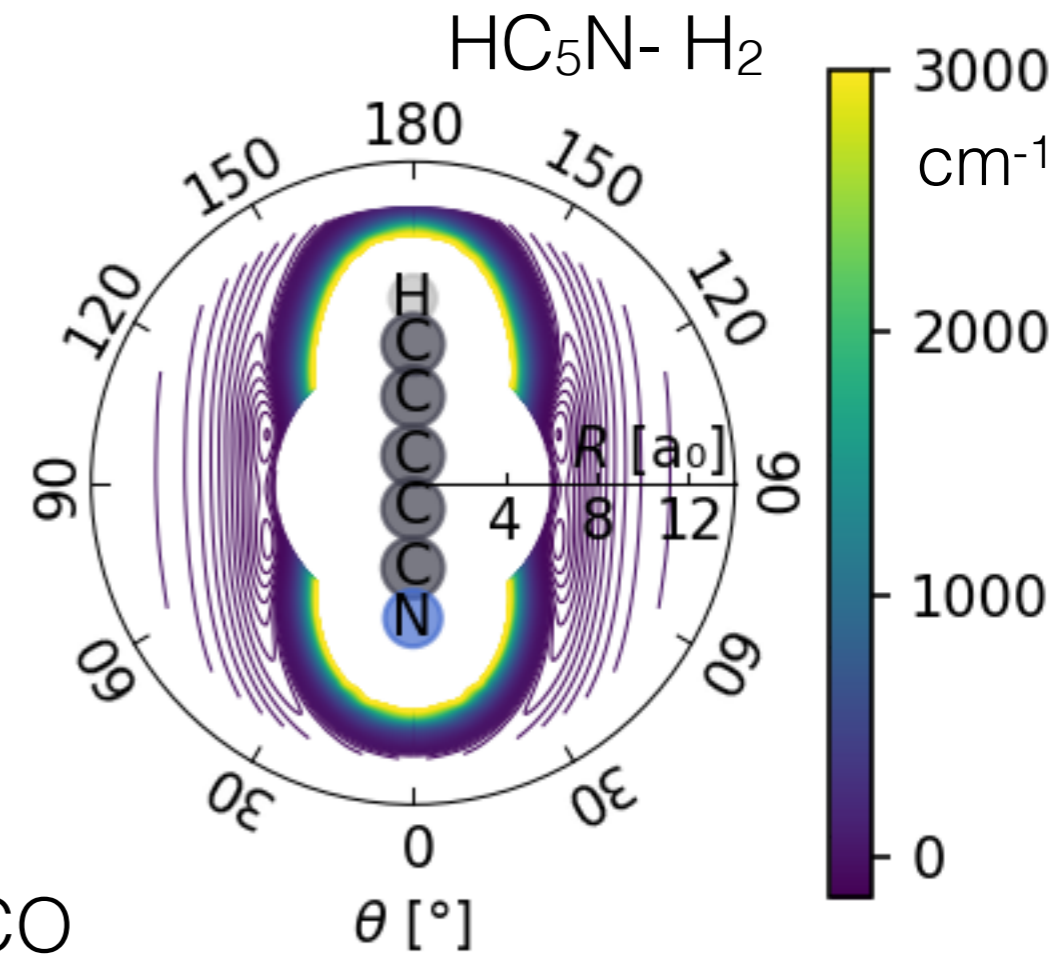
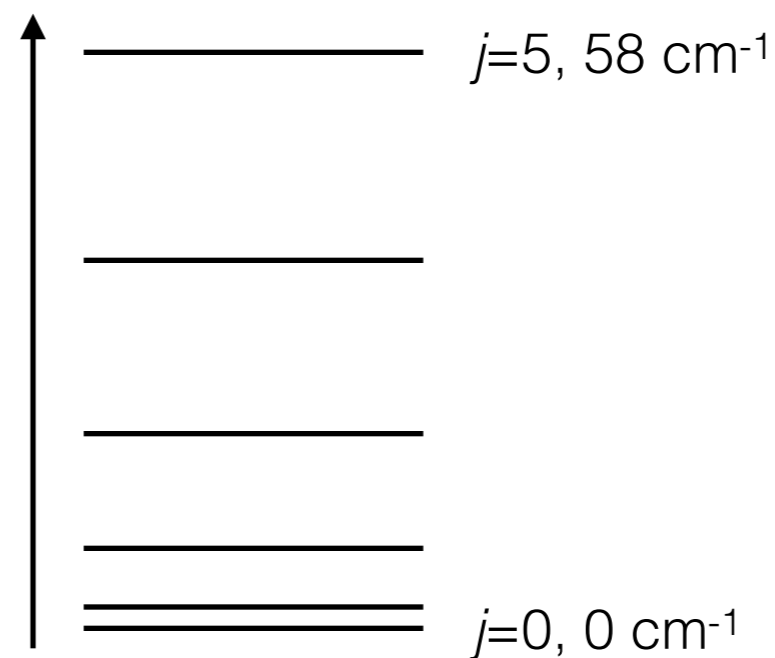
Challenges are mostly numerical...

- Highly anisotropic PESs
- Number of rotational states is huge even at low T due to small rotational constants

C_6H_5CN



CO

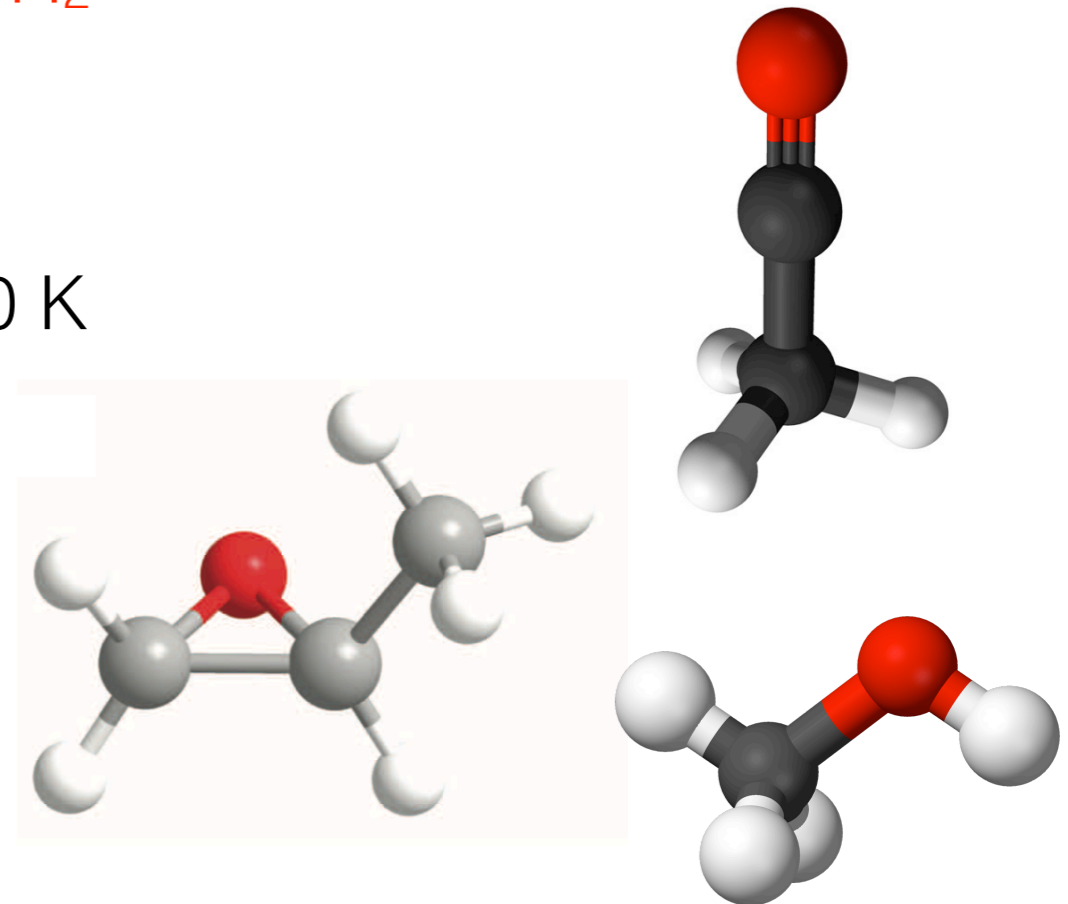


Recent progresses for COMs excitation: rate coefficients computed for some...

Linear molecules: HC_5N , C_6H , C_6H^- ,... + He/H_2

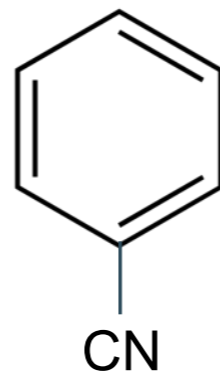
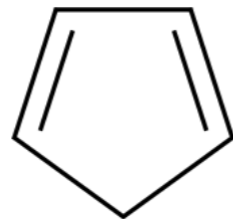
Non-linear molecules

- CH_3CN , CH_3NC , CH_3CCH - He up to 100 K
- CH_2CHCN - He up to 20 K
- $\text{CH}_3\text{CHCH}_2\text{O}$ - He up to 30 K
- CH_3OH - H_2
- CH_3CN - H_2



Cyclic molecules

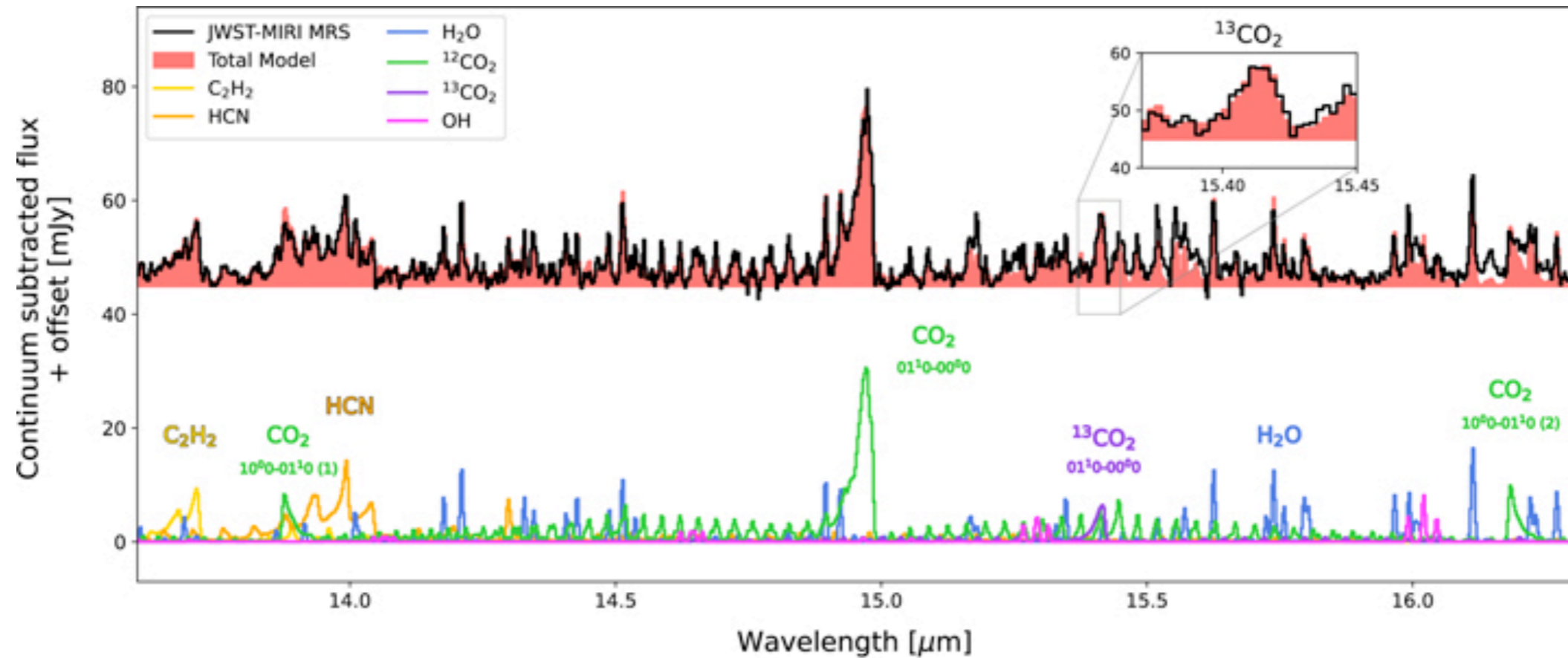
- C_5H_6 - He
- $\text{C}_5\text{H}_5\text{CN}$ - He
- $\text{C}_6\text{H}_5\text{CN}$ - He up to 40 K



Note: lowest vibrational modes:

- CH_3CN : 363 cm^{-1}
- $\text{CH}_3\text{CHCH}_2\text{O}$: 200 cm^{-1}
- $\text{C}_6\text{H}_5\text{CN}$: 141 cm^{-1}
- HC_7N : 64 cm^{-1} (92 K)

Vibrational excitation



Previous works on collisional vibrational excitation of molecules with **QM methods** is limited:

- Diatomic molecules + He, H₂ (ex: CO, CN, HCl, H₂)
- Linear molecules + He, H₂ (HCN, C₃, ... , Stoecklin et al.)
- H₂O + H₂ (Stoecklin et al.; Wiesenfeld)
- CH₃OH + He (Pottage et al.)
- CO₂ + He (Selim et al.)
- CH₃ + He (Ma et al.)
- NH₃ + He (Loreau and van der Avoird)

Challenges:

- Construction of the PES (increased dimensionality)
- Increased number of coupled equations (more internal states available)

$$\Psi = R^{-1} \sum_{\alpha} |\alpha\rangle \chi_{\alpha}(R)$$
$$-\frac{\hbar^2}{2\mu} \frac{d^2 \chi_{\alpha}}{dR^2} + \sum_{\alpha'} \langle \alpha' | H_A + H_B + V + \frac{\mathbf{L}^2}{2\mu R^2} | \alpha \rangle \chi_{\alpha} = E \chi_{\alpha}$$

- Rovibrational excitation of molecules by H₂ is expected to be very different than by He
- At high temperatures data for collision with *ortho*-H₂ is needed

Need new methods...

- Fully QM (close-coupling, CC)
- QM + decoupling (coupled states, CS)
- Multichannel distorted-wave Born approximation
- QCT
- **Need to benchmark approximations!**

Example: ro-vibrational relaxation of the umbrella mode of NH₃ by He atoms

- Typical rotational excitation rate coefficients are $\sim 10^{-11}$ cm³s⁻¹
- Strong temperature dependence

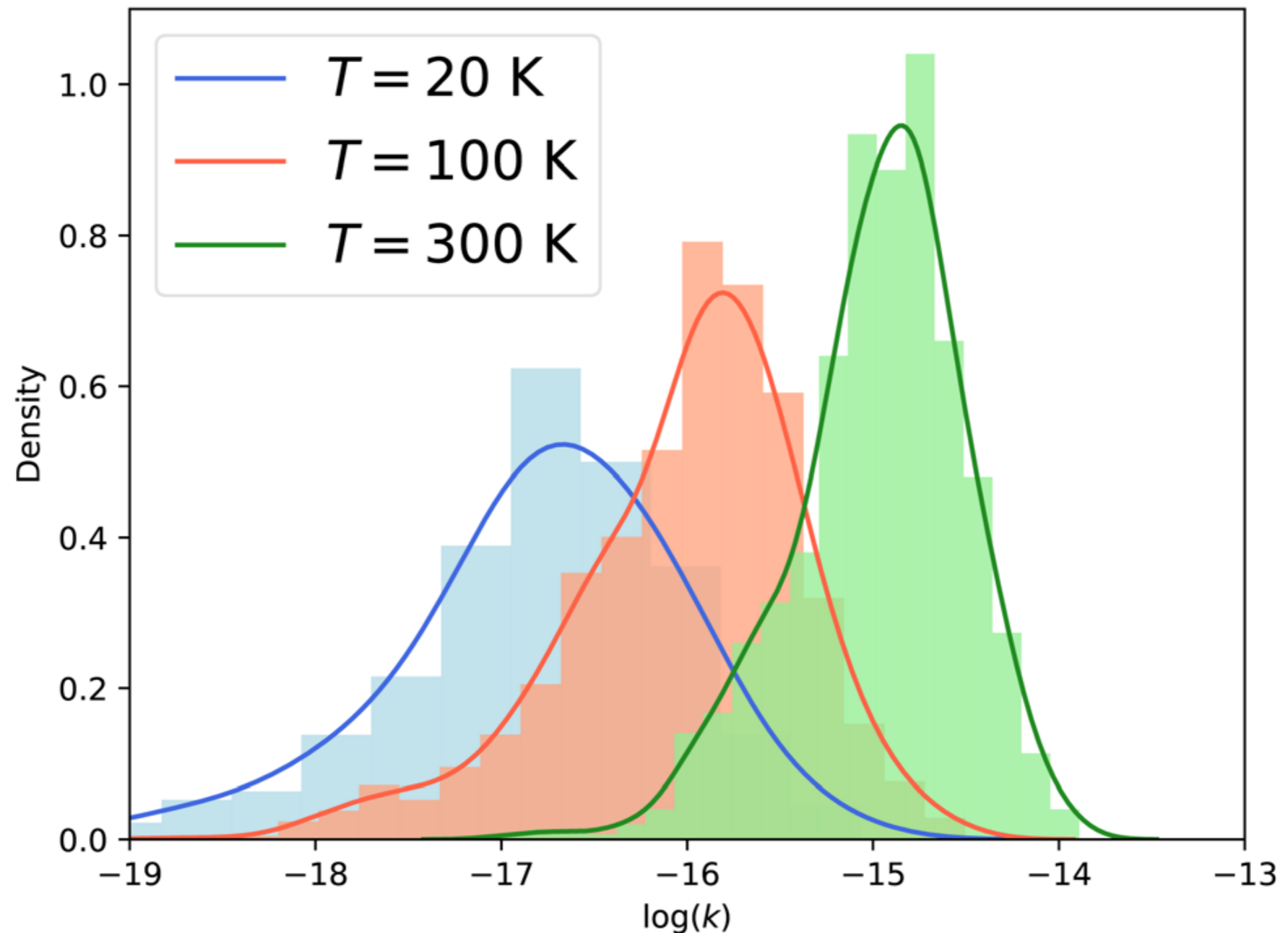
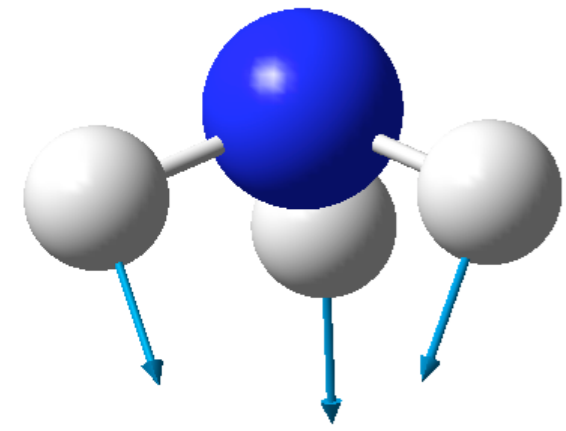


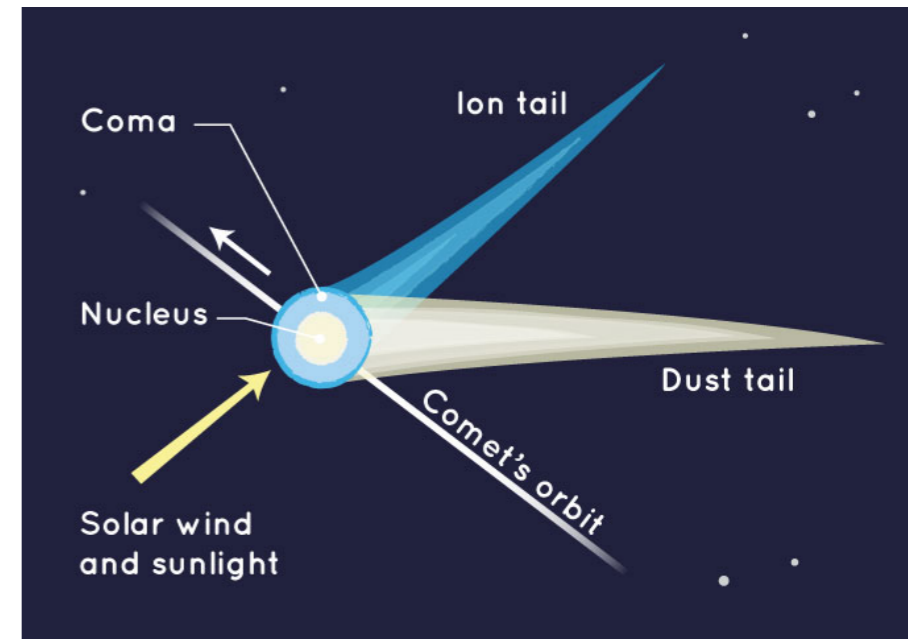
Fig. 7 Distribution of the logarithm base 10 of the vibrational relaxation rate coefficients $\nu_2 = 1 \rightarrow 0$ at three temperatures for all initial states $j = 0-3$ of *ortho*- and *para*-NH₃ and all final states $j' = 0-10$ (964 transitions). The lines represent kernel density estimates.

Collisions involving heavy partners

When the two colliders are “heavy” (= heavier than H_2) the calculations become intractable...

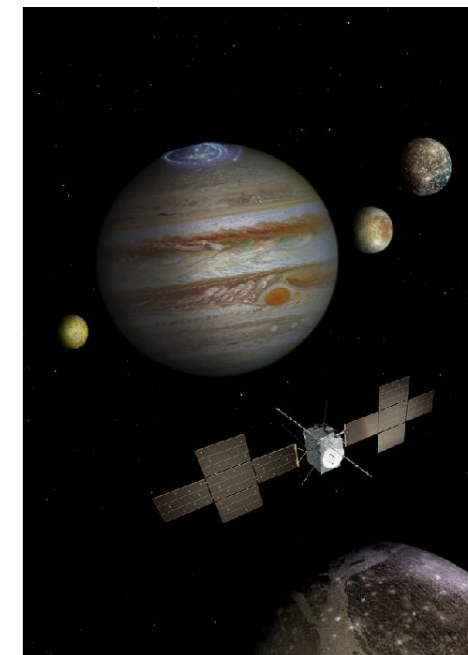
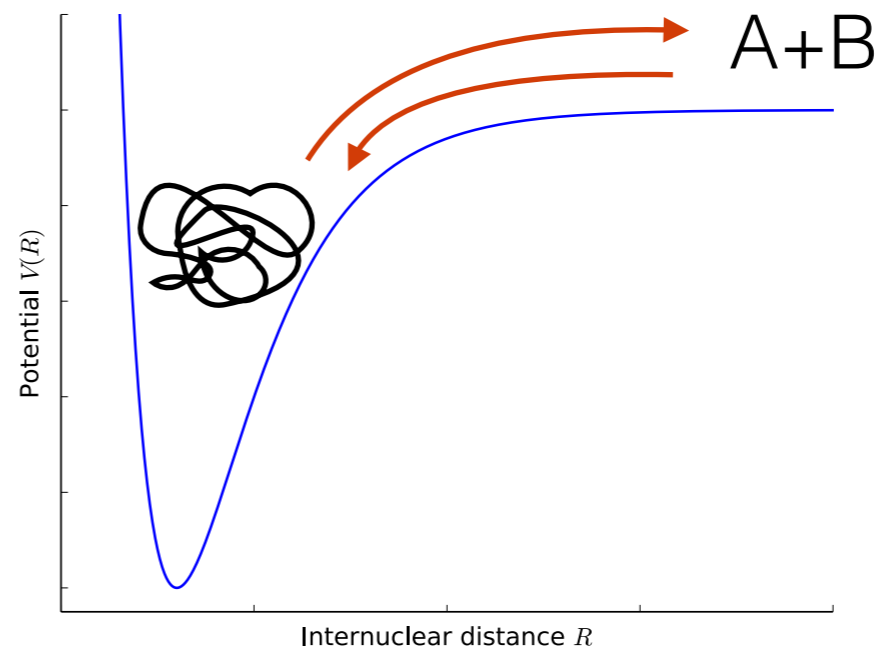
Ex: The coma of a comet is composed mainly of H_2O , CO and CO_2 . The composition of the coma changes with the distance to the Sun!

→ need collisional data for excitation by these molecules...



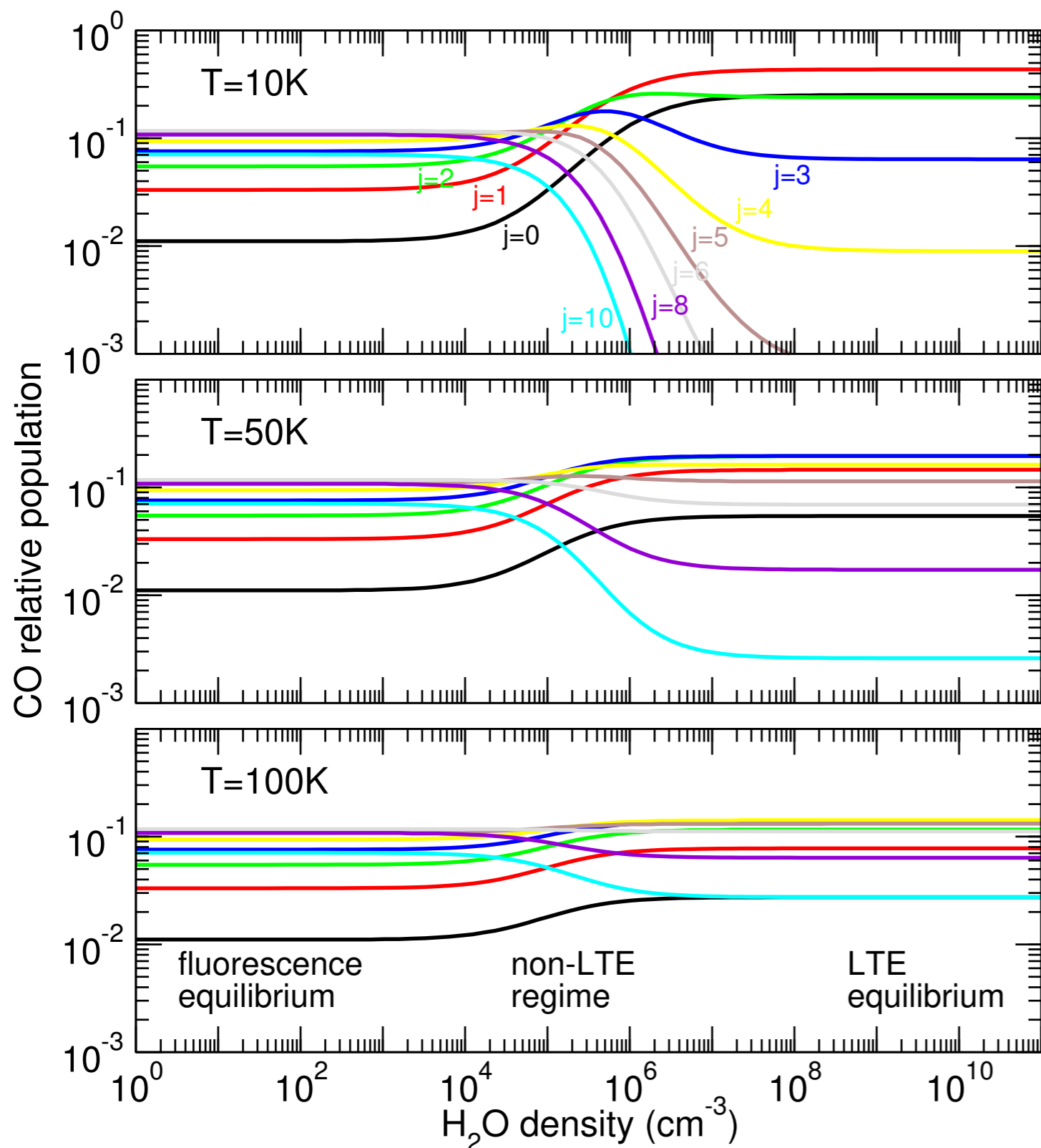
If the PES is attractive (no barrier), and the well is deep enough, the collision is mostly determined by the long-range potential.

At **low temperature** we can introduce a statistical approximation: equal probability among open channels. Complementary to other approximate methods at high T !



Ex: rate coefficients for H₂O-CO collisions.

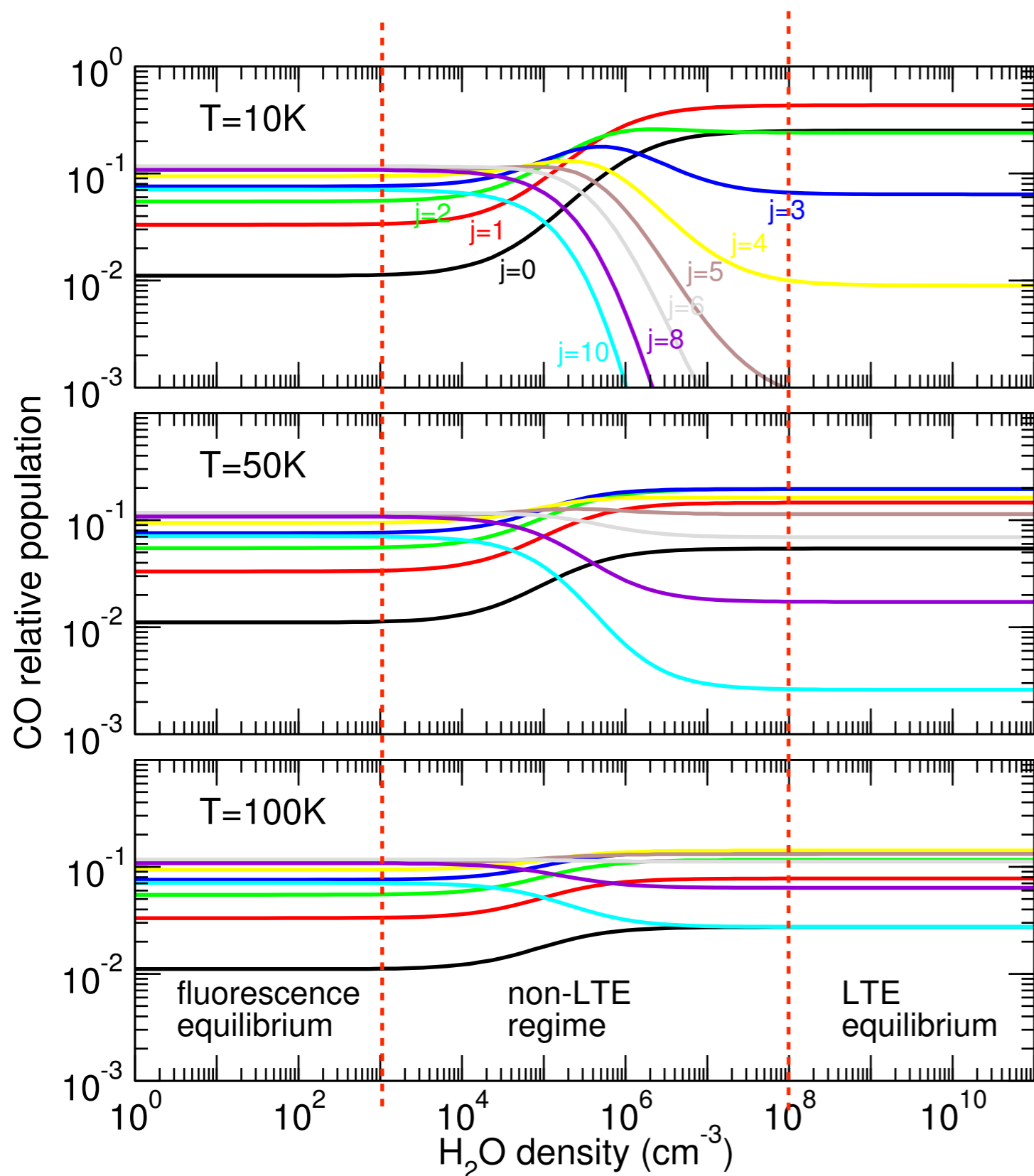
Level populations of CO as functions of H₂O density for kinetic temperatures of 10, 50 and 100 K:



Data for H₂O-H₂O, HF-H₂O, HCN-H₂O, CO-CO, now available

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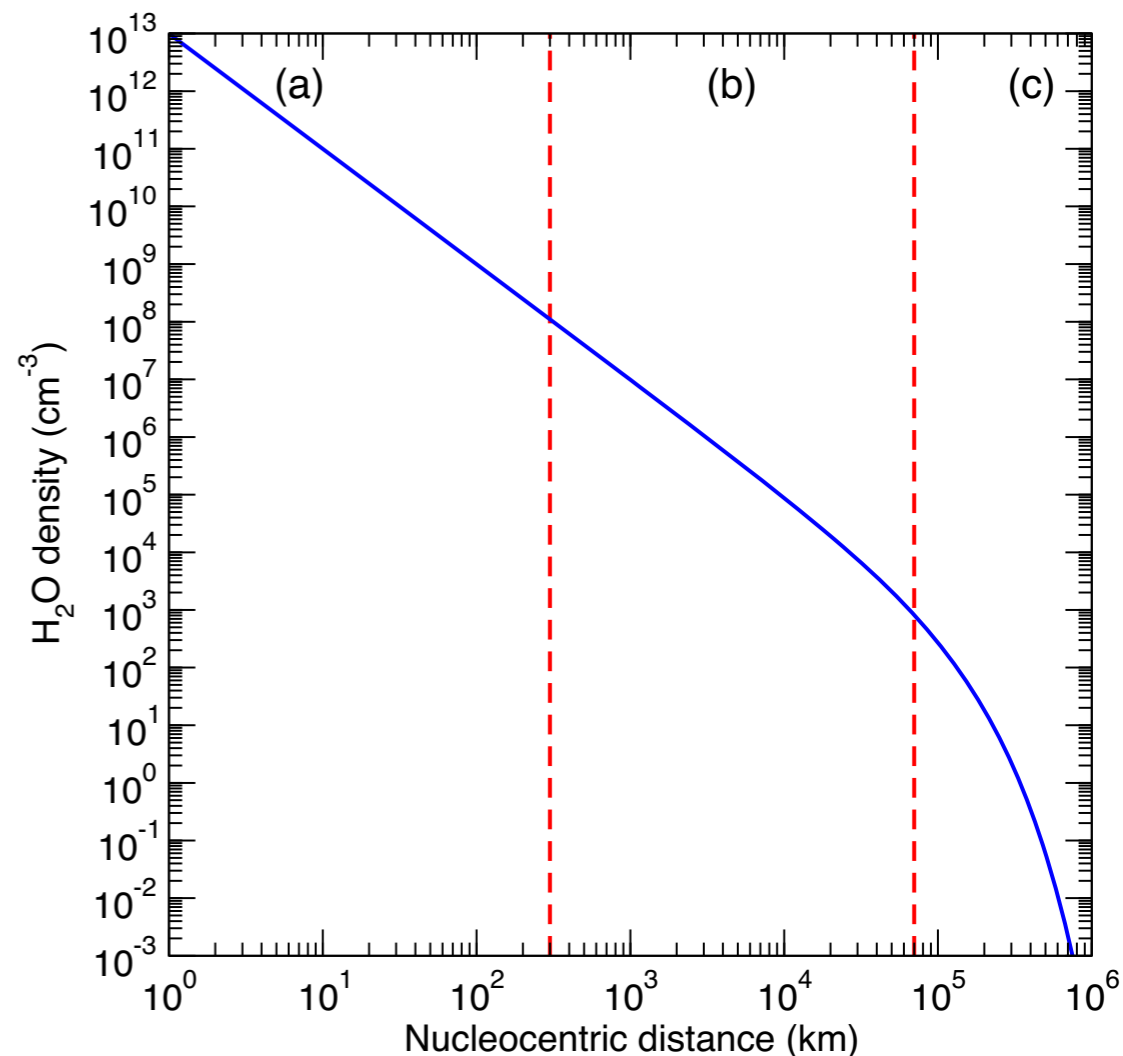
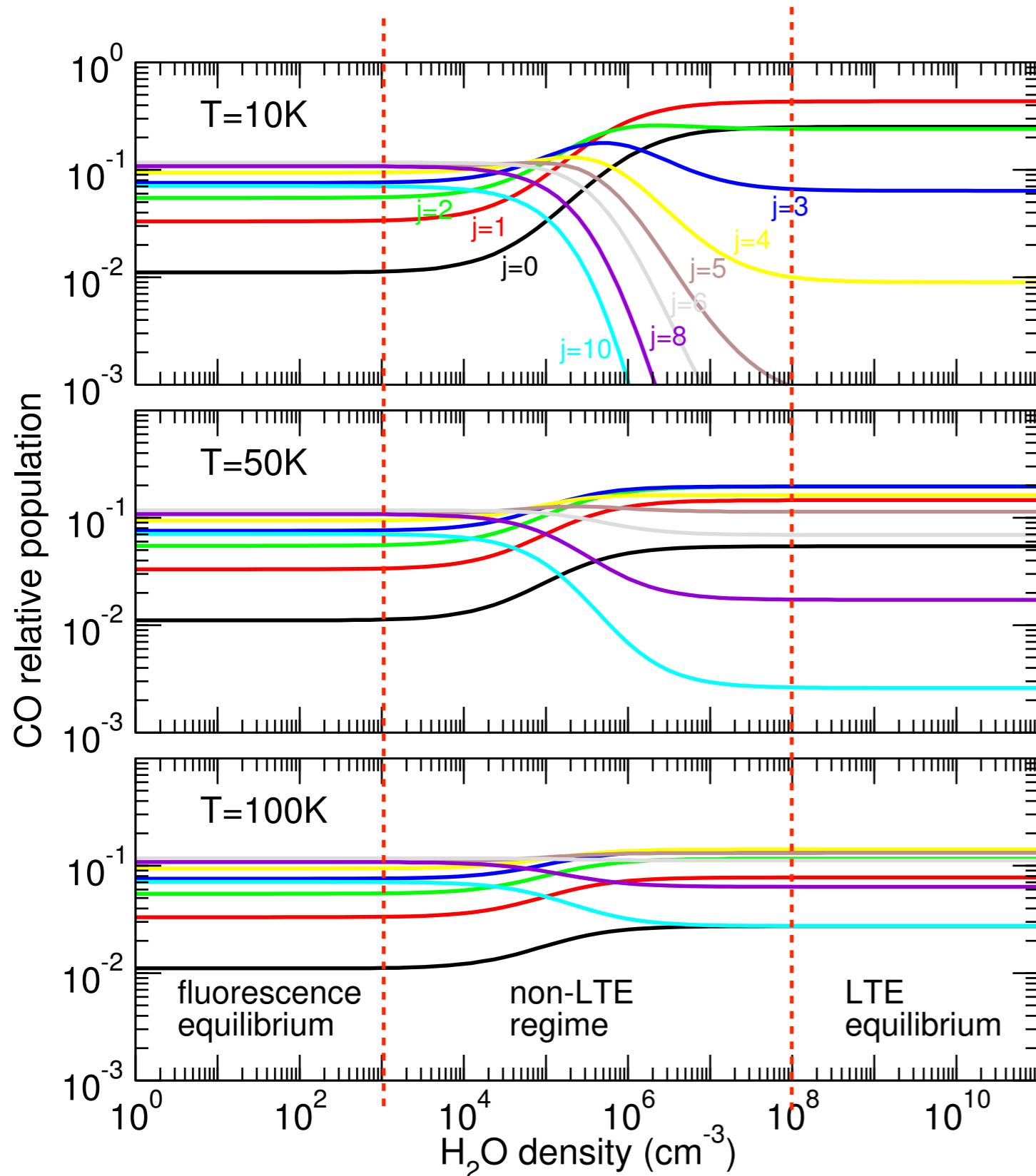
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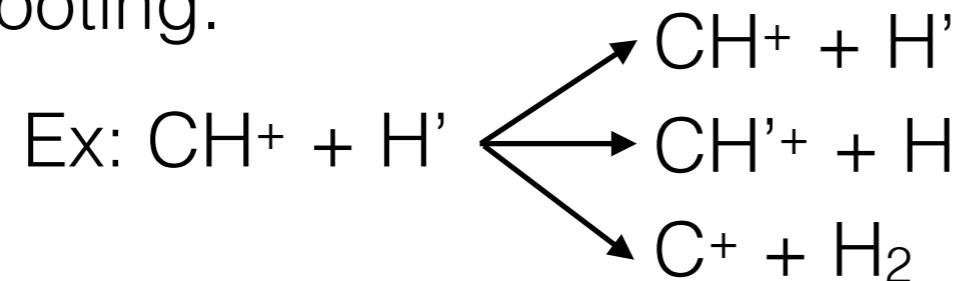
The non-LTE regime extends typically from 300 to 70 000 km

Data for H₂O-H₂O, HF-H₂O, HCN-H₂O, CO-CO, now available

Collisions involving reactive ions

Challenges:

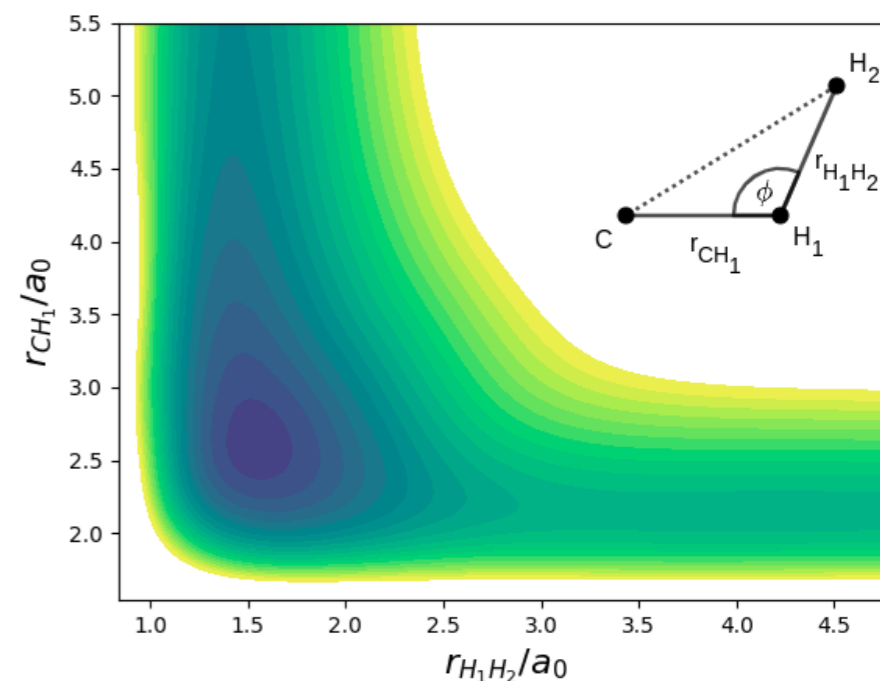
- Competition between reactive and inelastic processes - must be treated on the same footing.



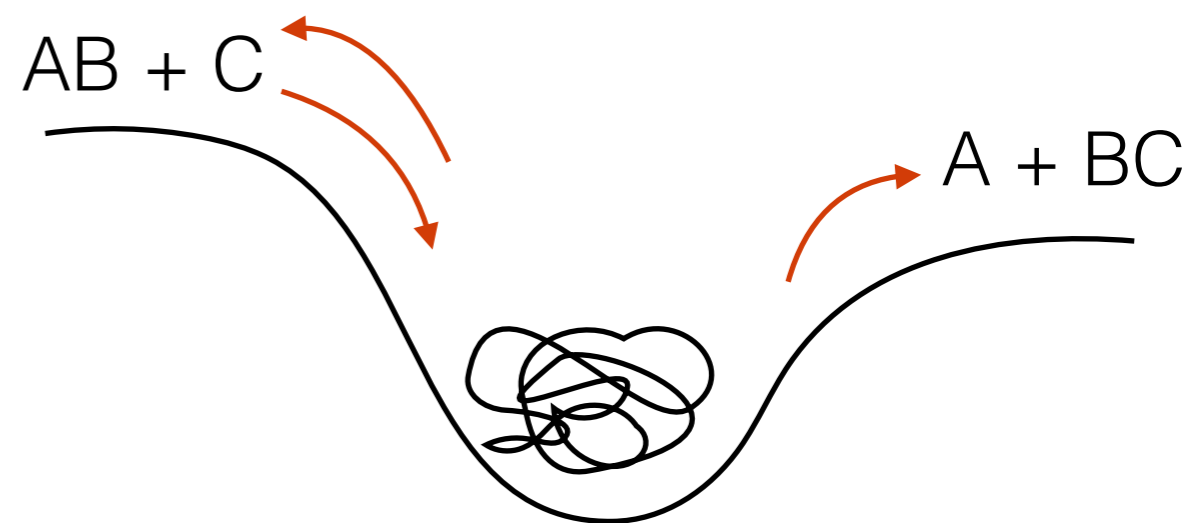
- Need state-to-state $k(T): (v, j) \longrightarrow (v', j')$

- Often deep well on the PES - many quantum states can be involved...

Ex: $\text{CH}^+ + \text{H}$: well of 4.8 eV!

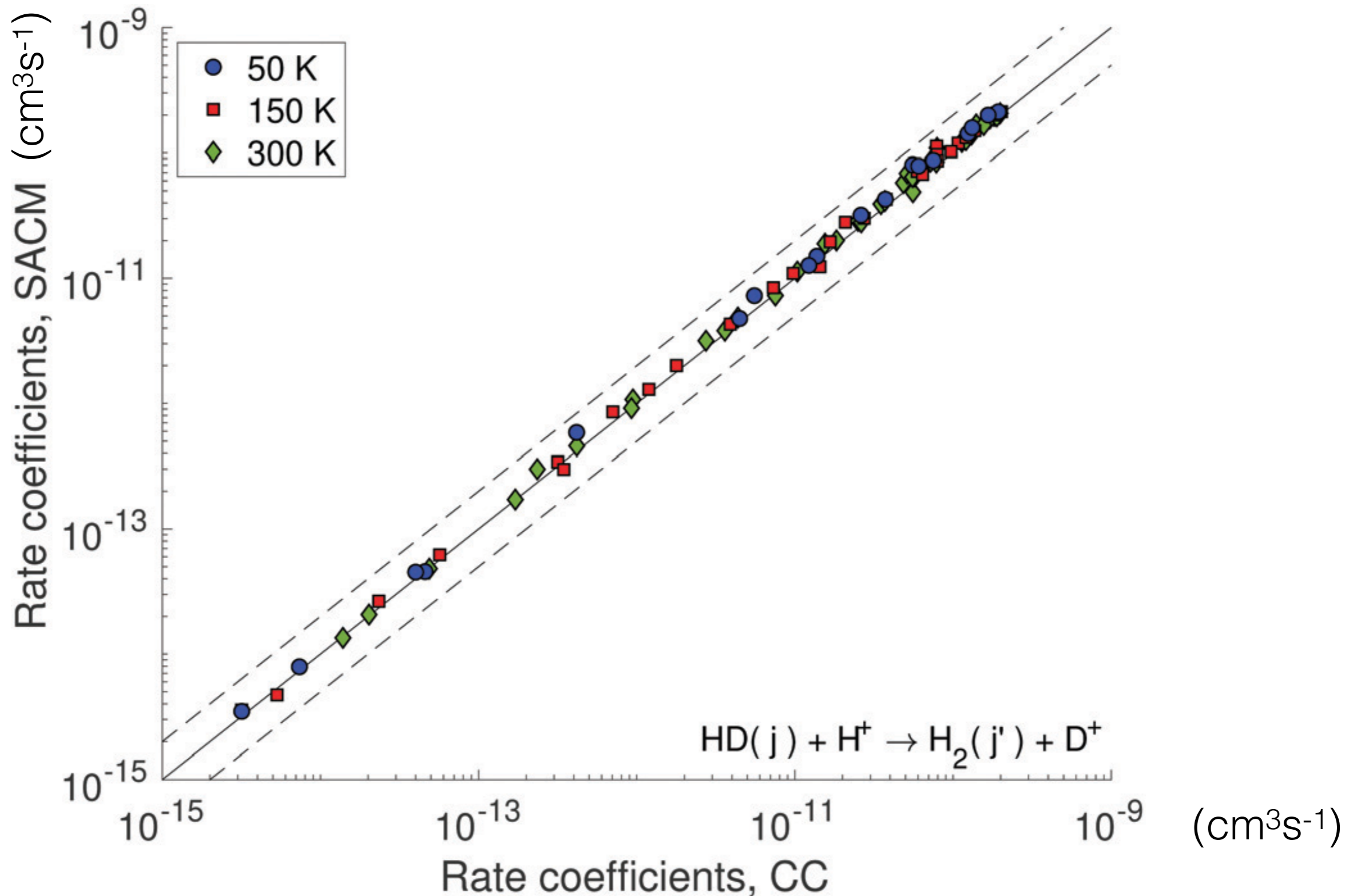
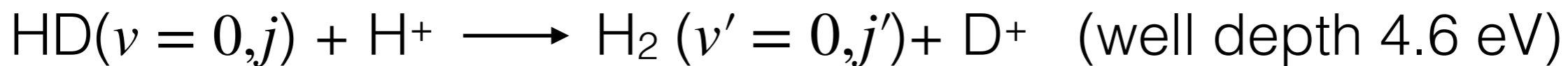


Statistical adiabatic channel model assumes that collision proceeds through formation of a **long-lived complex**.

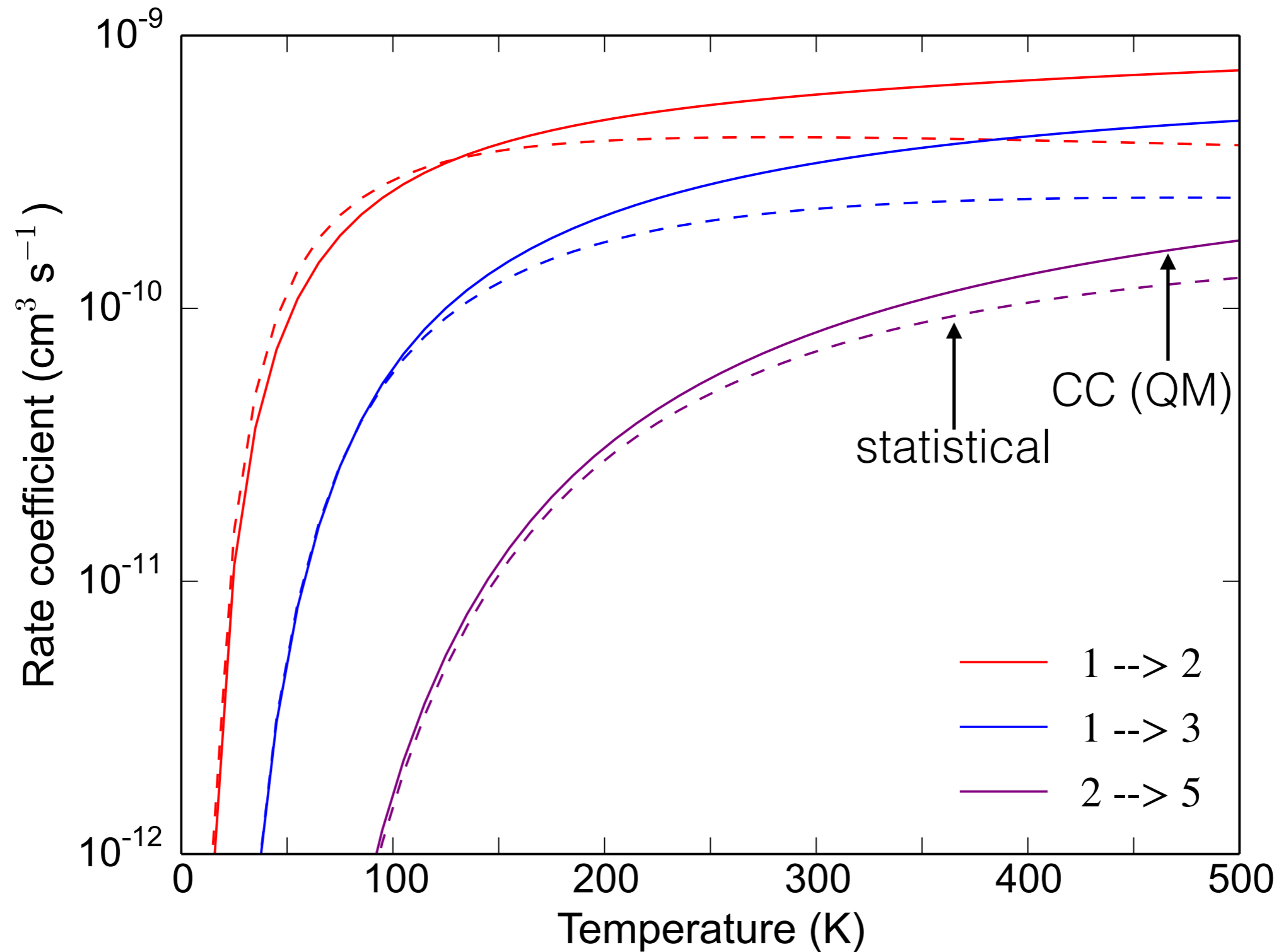
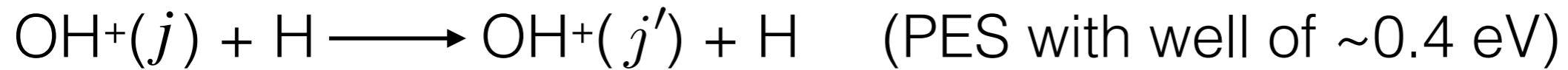


Benchmarked on some systems for which accurate QM data are available:
 $\text{H}_2 + \text{H}^+$, $\text{CH}^+ + \text{H}$, $\text{SH}^+ + \text{H}$, $\text{OH}^+ + \text{H}$, $\text{H}_2^+ + \text{Ar}$, etc

Example: Rate coefficients for insertion reaction



Example: Rate coefficients for **inelastic** collisions



Outlook

Successes:

- Methodology tested vs experiments for small systems
- Sets of rate coefficients for rotational excitation in molecule + He/H₂ collisions are available for a large number of molecules, including iCOMs

Challenges:

- In many cases collisions with He are not sufficient, data with H₂ is needed
- Rate coefficients at higher temperatures
- Rate coefficients for more rotational states
- Rate coefficients for *ortho*-H₂ ($j=1$)
- Deuterated molecules
- Fine/hyperfine structure
- Isomers

Need to develop and benchmark approximate methods!

Acknowledgments

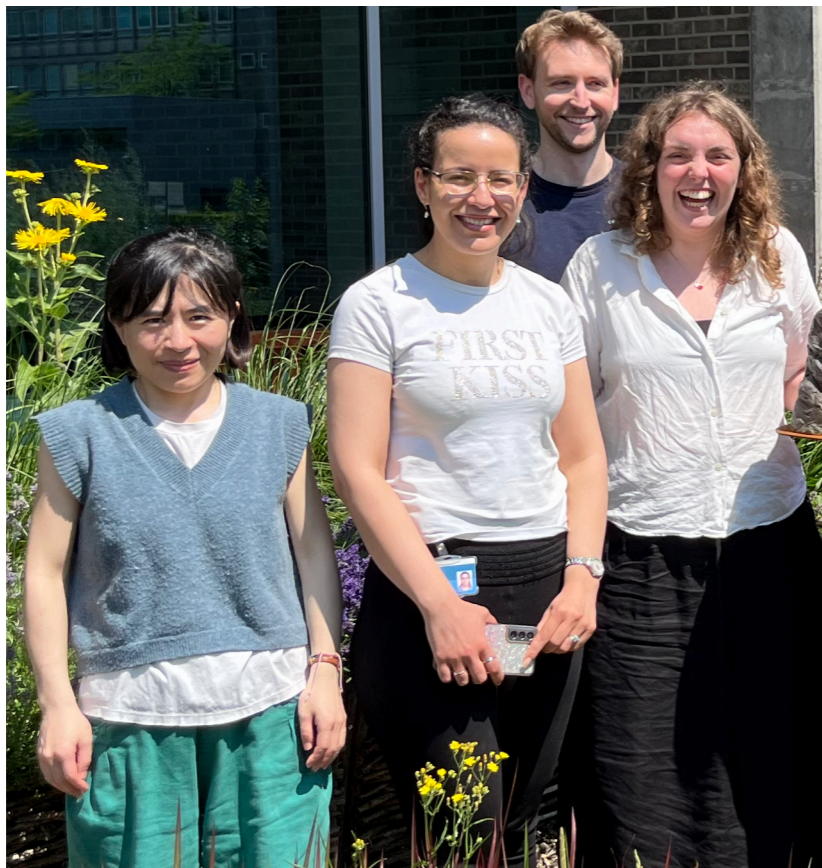
Molecular collisions @ KU Leuven

Malek Ben Khalifa

Maarten Konings

Karina Sogomonyan

Shan Gao



Collaborators

François Lique (Rennes)

Alex Faure (Grenoble)

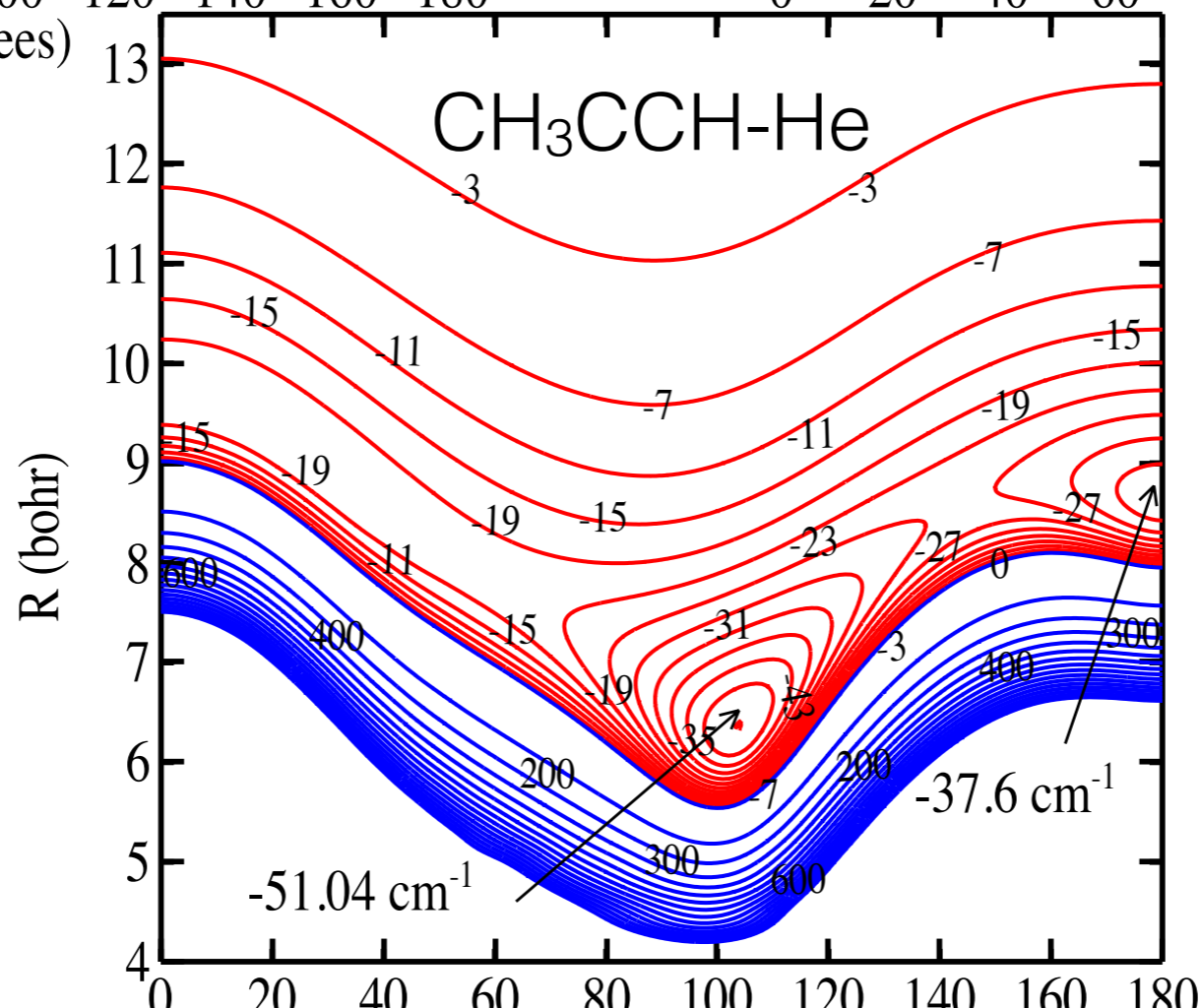
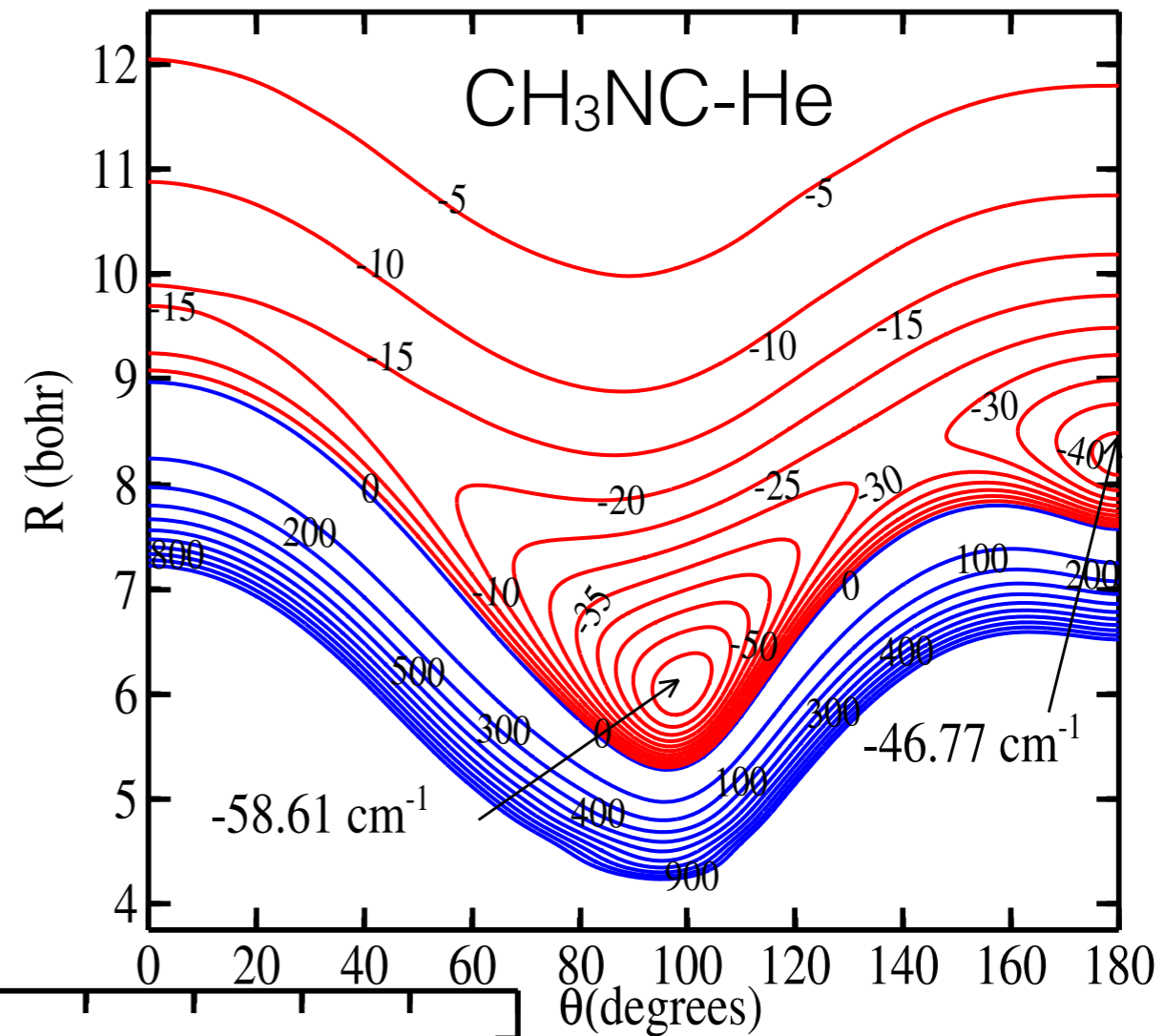
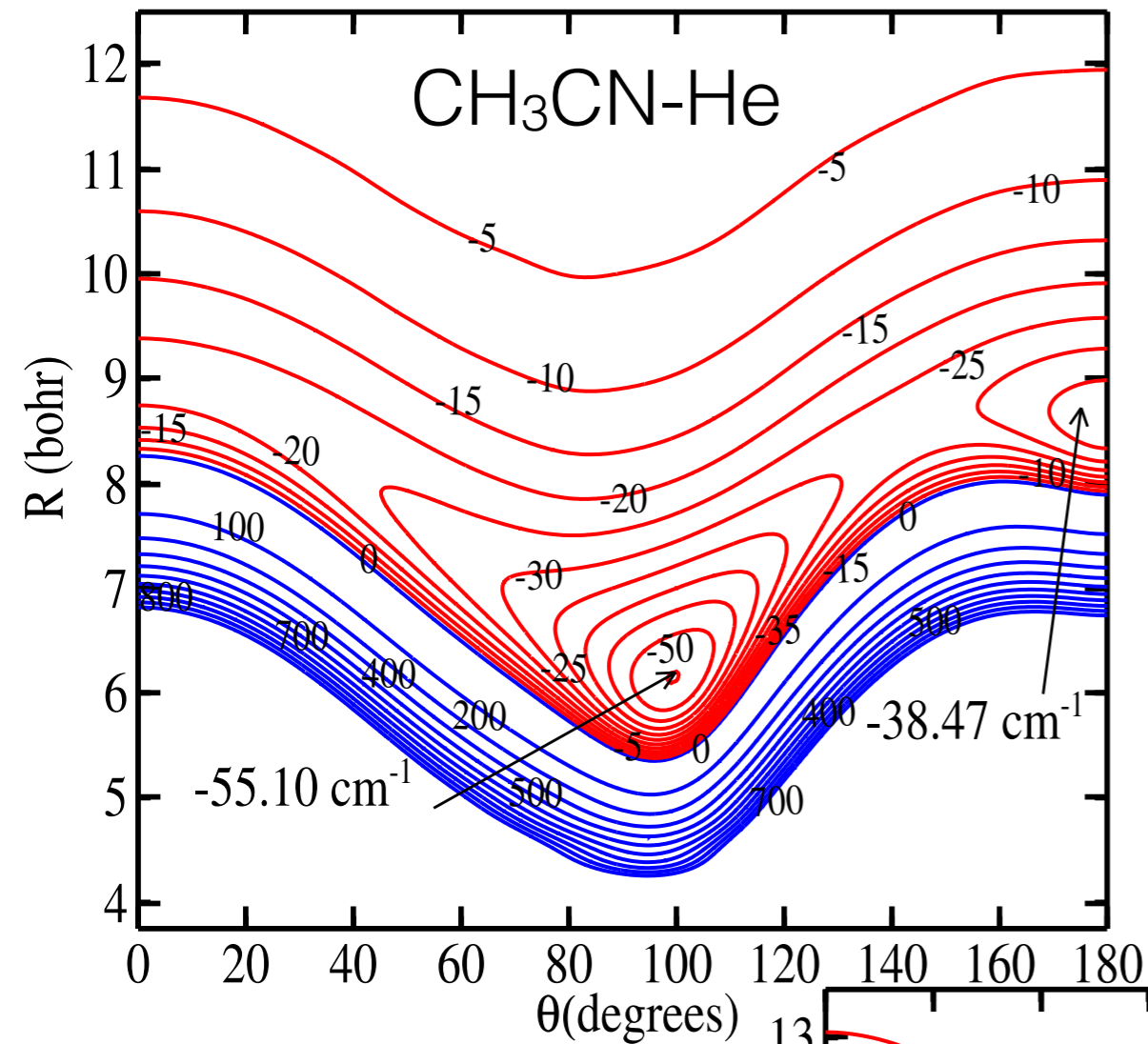
Ad van der Avoird (Nijmegen)

Michal Zoltowski (Rennes)

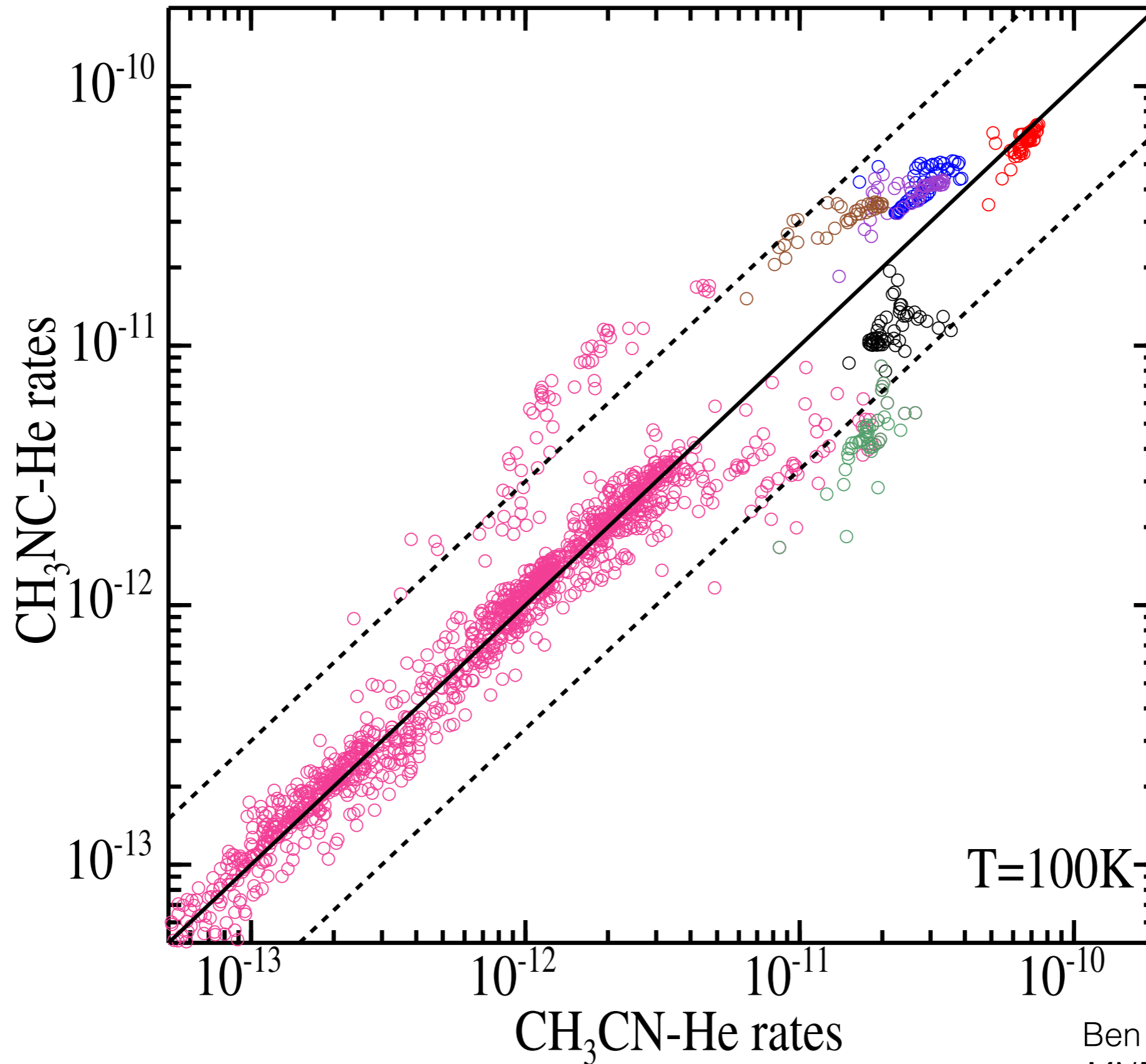
Laurent Wiesenfeld (Orsay)



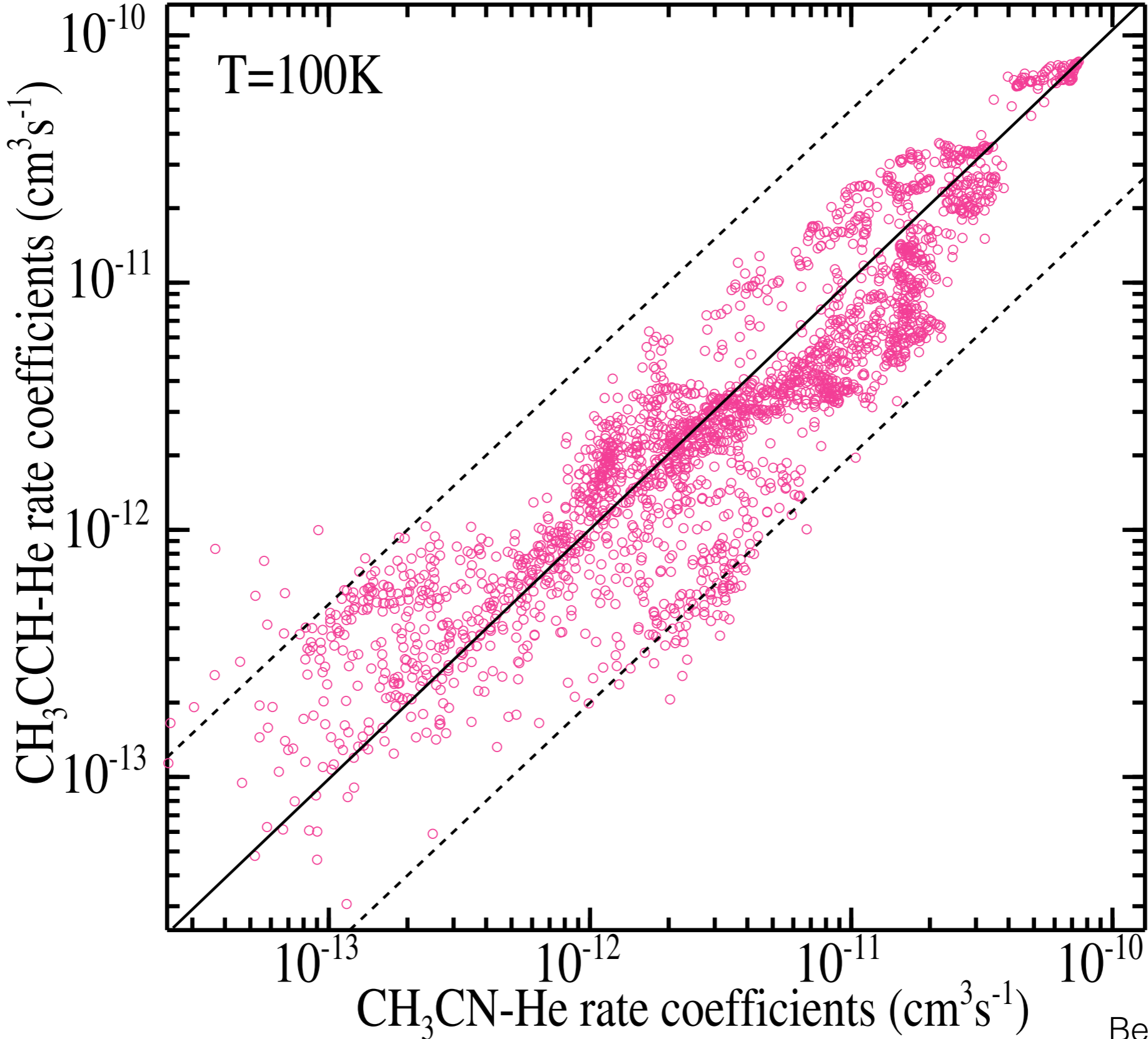
Thank you for your attention!



Ortho-CH₃CN-He vs. CH₃NC-He : rate coefficients at 100 K



CH₃CN-He vs. CH₃CCH-He : rate coefficients at 100 K



Non-LTE modelling

Excitation temperature of
CH₃CN and CH₃NC:

- RADEX: uniform, homogeneous medium
- Critical densities $< 10^4 \text{ cm}^{-3}$ at 50 K
- LTE only achieved at $n(\text{H}_2) > 10^6 \text{ cm}^{-3}$
- Differences between CH₃CN and CH₃NC
- Similar observations for CH₃CCH, but for smaller densities

