COLLEXISM: COLLisional EXcitation of InterStellar Molecules: towards reactive systems

Towards non-LTE modelling of large interstellar cyclic species: the collisional excitation of cyclopentadiene

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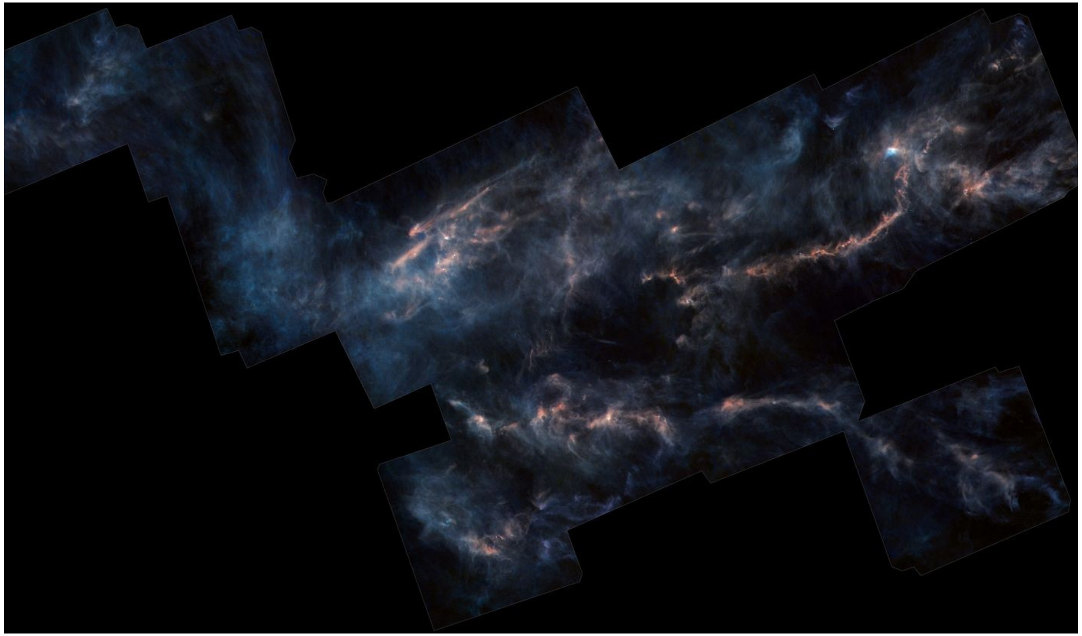
Motivation: interstellar molecular clouds

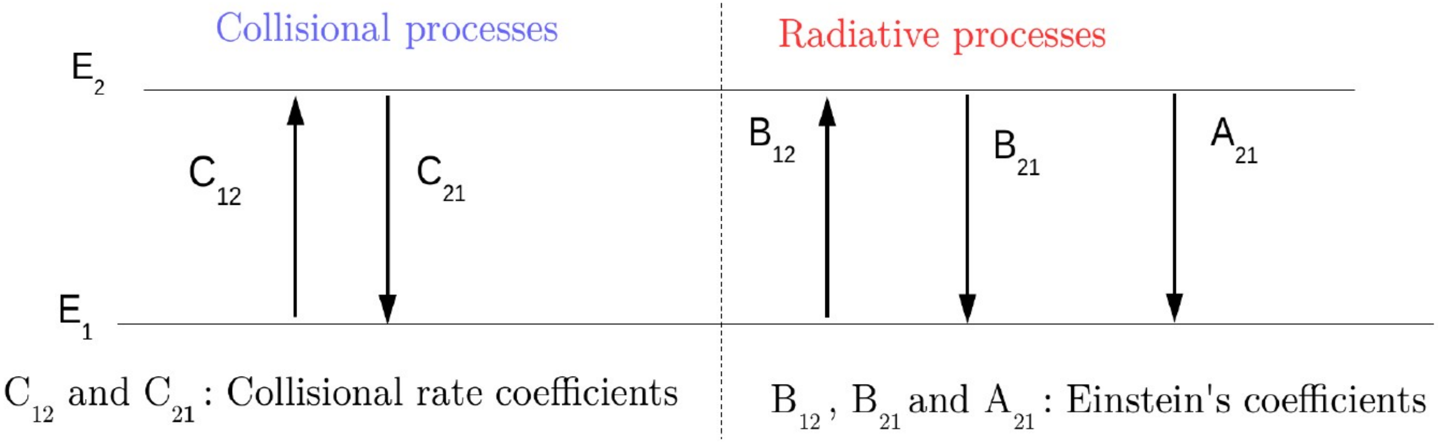
- **Molecular clouds** are active ***star-forming regions*** in the interstellar medium (**ISM**)
  - Consist of **gas and dust**, with typical **densities** between **10 to 10^8 cm^{-3}** and **temperatures** ranging from **a few K** up to **thousands of K.**
- **Cold molecular clouds** (like the *Taurus Molecular Cloud*, **TMC-1**) are relatively **dense** (**10^4 - 10^6 cm^{-3}**) regions of the ISM, with **low temperature (≤10 K)**
  - Extremely ***rich chemistry***, including long **cyanopolyyne chains** (**HC_nN** with $n = 3$-11) and large cyclic species, i.e. **prebiotic COMs** and **PAHs** such as c-C_5H_6, c-C_6H_5CN, c-C_5H_5CN, $C_{10}H_7CN$, C_9H_8, *etc.*



The Herschel's view of the *Taurus Molecular Cloud* (TMC-1)
(*Credits*: SA/Herschel/NASA/JPL-Caltech)

Collisional data and radiative transfer *non-LTE* models

For the proper interpretation of the observational spectra, we also need state-resolved **collisional data**, in particular for **rotational (de)excitation** processes



- The **radiative** and **collisional processes** are in competition to populate the molecular levels when *Local Thermodynamic Equilibrium* (LTE) conditions are not fullfilled (*i.e.* under ***non-LTE conditions***)
- **State-to-state collisional rate coefficients** are needed for interactions with the *most abundant interstellar colliders* such as *H_2 and He* to correctly interpret the observations and derive the **physical conditions** and **molecular abundances** in interstellar clouds through **non-LTE radiative transfer models**

The state-of-the-art

State-to-state **collisional rate coefficients** are known **for** only ***~70 out of 320+*** **molecular species** detected in the ISM*

For **large cyclic** (nonlinear) **species**, the **studies are extremely limited:**

1) **C_6H_6 + He** was studied by a *mixed quantum-classical theory* (Mandal *et al.* 2022)[2]

2) **C_6H_5CN + He** was studied by the approximate *coupled-states (CS) quantum theory* by Ben Khalifa *et al.* (2023)[3]

List of molecules with collisional data available in the ***BASECOL database (2023 update)***[1]

ArH^+, ArD^+, AlO^+, CF^+, CH^+, CN^-, CO, CS
H_2, HD, HeH^+, HCl, HF, KCl, NaH, NeH^+, NO^+, NS^+, PN, SiH^+, SiO, SiS
CH ($X^2\Pi$), OH ($X^2\Pi$), OD ($X^2\Pi$), NO ($X^2\Pi$), SH ($X^2\Pi$), C_6H ($X^2\Pi$)
C_2^- ($X^2\Sigma_g^+$), CN ($X^2\Sigma^+$), ^{13}CN ($X^2\Sigma^+$), $C^{15}N$ ($X^2\Sigma^+$), CO^+ ($X^2\Sigma^+$)
C_4 ($X^3\Sigma_g^-$), H_2^+ ($X^2\Sigma_g^+$), NH ($X^3\Sigma^+$), O_2 ($X^3\Sigma_g^-$), SO ($X\,^3\Sigma^-$)
AlCN, AlNC, C_3, C_2H^-, CO_2, HCN, HNC, DCN, DNC, HCO^+, $HC^{17}O^+$, DCO^+,
HCP, HCS^+, N_2H^+, OCS
D_2O, HDO, H_2O, H_2S, SiC_2, SO_2
H_3^+, H_3O^+, NH_3, ND_3, CH_3CN, CH_3NC, CH_3OH polyatomic symmetric tops
CNCN, C_6H^-, HC_3N, HCCNC, HNCCC, HMgNC, $NCCNH^+$, C_3O, C_3S, C_4H^-, C_5, C_5O, C_5S
H_2CO, $HOCO^+$, C_3H_2, NH_2D, ND_2H polyatomic asymmetric tops

C_2H ($X^2\Sigma^+$), C_2D ($X^2\Sigma^+$), C_2N^- ($X^3\Sigma^-$), C_2O($X^3\Sigma^-$), MgCN ($X^2\Sigma^+$), MgNC ($X^2\Sigma^+$)

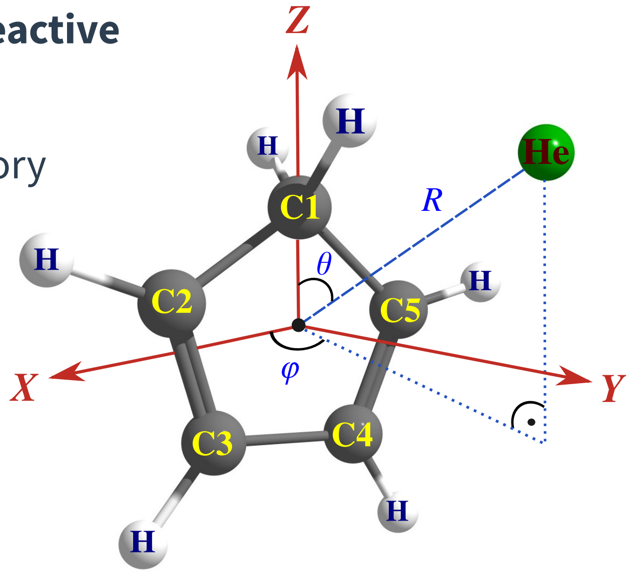
NH_2 (X^2B_1), CH_2 (X^3B_1), HCO

[1] M.L. Dubernet *et al.* « BASECOL2023 scientific content » , A&A 683, A40 (2024).
[2] B. Mandal, C. Joy, A. Semenov, and D. Babikov, *ACS Earth Space Chem*. **6**, 521 (2022).
[3] M. B. Khalifa and J. Loreau, *Mon. Not. Roy. Astron. Soc.* **527**, 846-854 (2023).

The case of cyclopentadiene c-C_5H_6

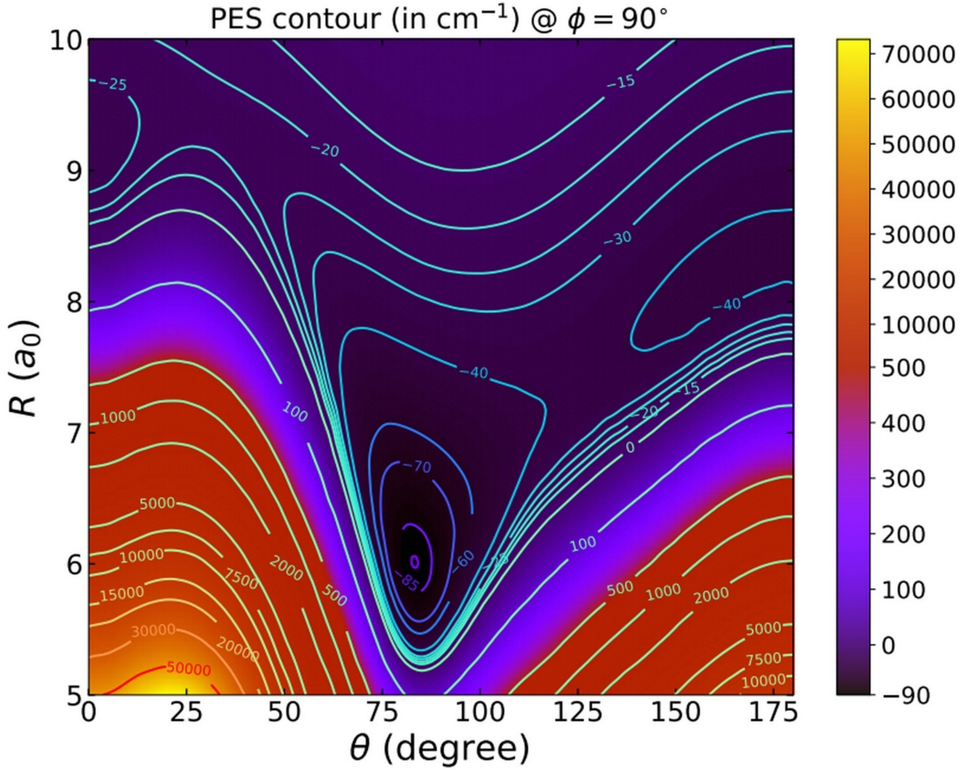
The **cyclopentadiene (c-C_5H_6)** molecule was **first detected in TMC-1** by Cernicharo *et al.* (2021)[1] and then detected again by Agúndez *et al.* (2023)[2] in other cold molecular clouds.

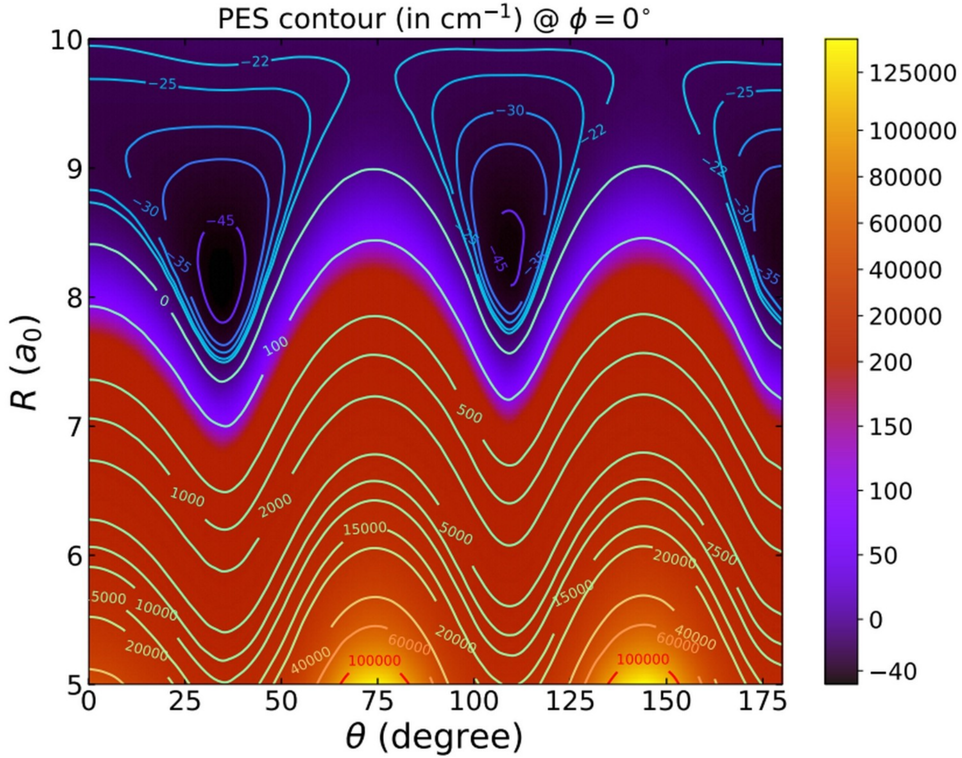
- **c-C_5H_6** is a closed-shell **asymmetric top molecule** (C_{2v} point group)
- *Collisions with helium*: the **[c-C_5H_6 – He] complex** is loosely bound and **not reactive**
- We need to calculate an accurate **potential energy surface (PES)**:
  We computed **12 540 points** using the **CCSD(T)-F12/AVTZ** *ab initio* theory
  - The 3-dimensional **PES is** expanded as **a product of radial and angular functions** (*81 terms in total*, high accuracy)
  - The **global minimum is ~90 cm^{-1}**, larger R (van der Waals complex)
  - **Several secondary minima** is observed **(~40-50 cm^{-1})**



[1]J. Cernicharo, M. Agúndez, C. Cabezas *et al.* *A&A*, **649** L15 (2021)
[2]M. Agúndez, N. Marcelino, B. Tercero, and J. Cernicharo, *A&A* **677**, L13 (2023).

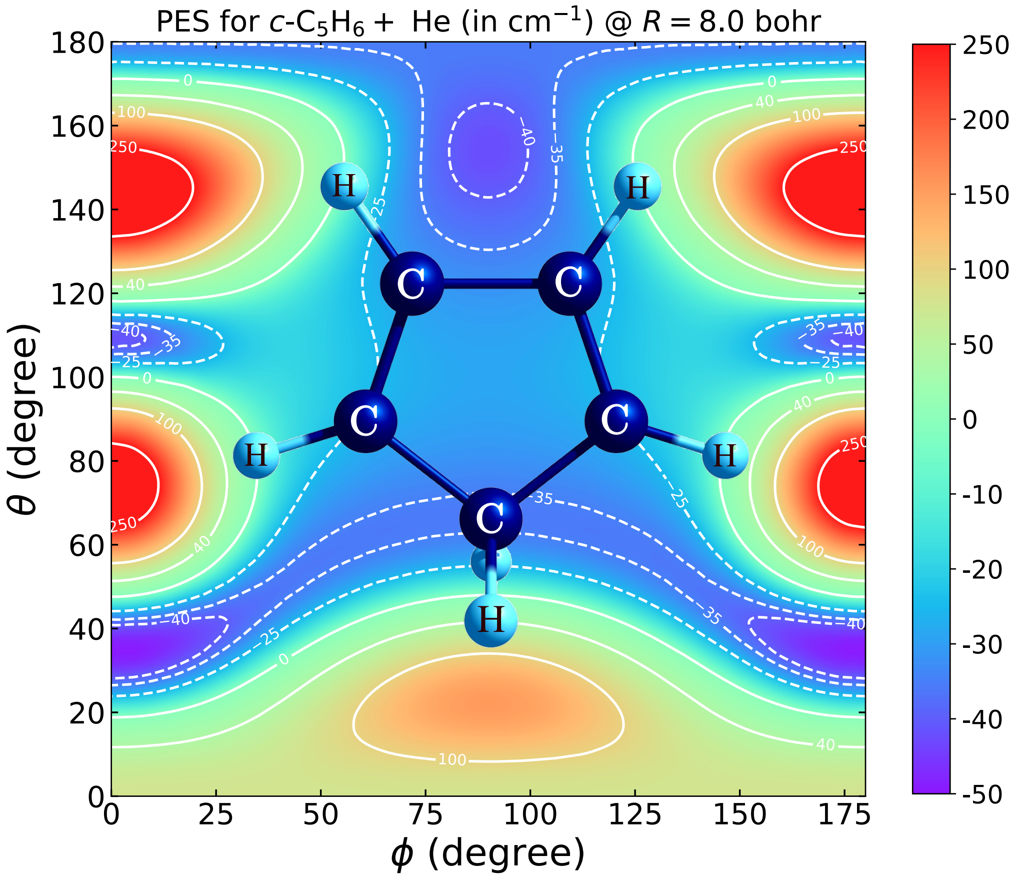
Contour plots of the 3D PES





R vs. θ dependence of the PES at different azimuthal angles $\phi = 90^\circ$ (left) and $\phi = 0^\circ$ (right)

Contour plots of the 3D PES



Angular dependence of the PES at $R = 8.0\ a_0$ radial distance

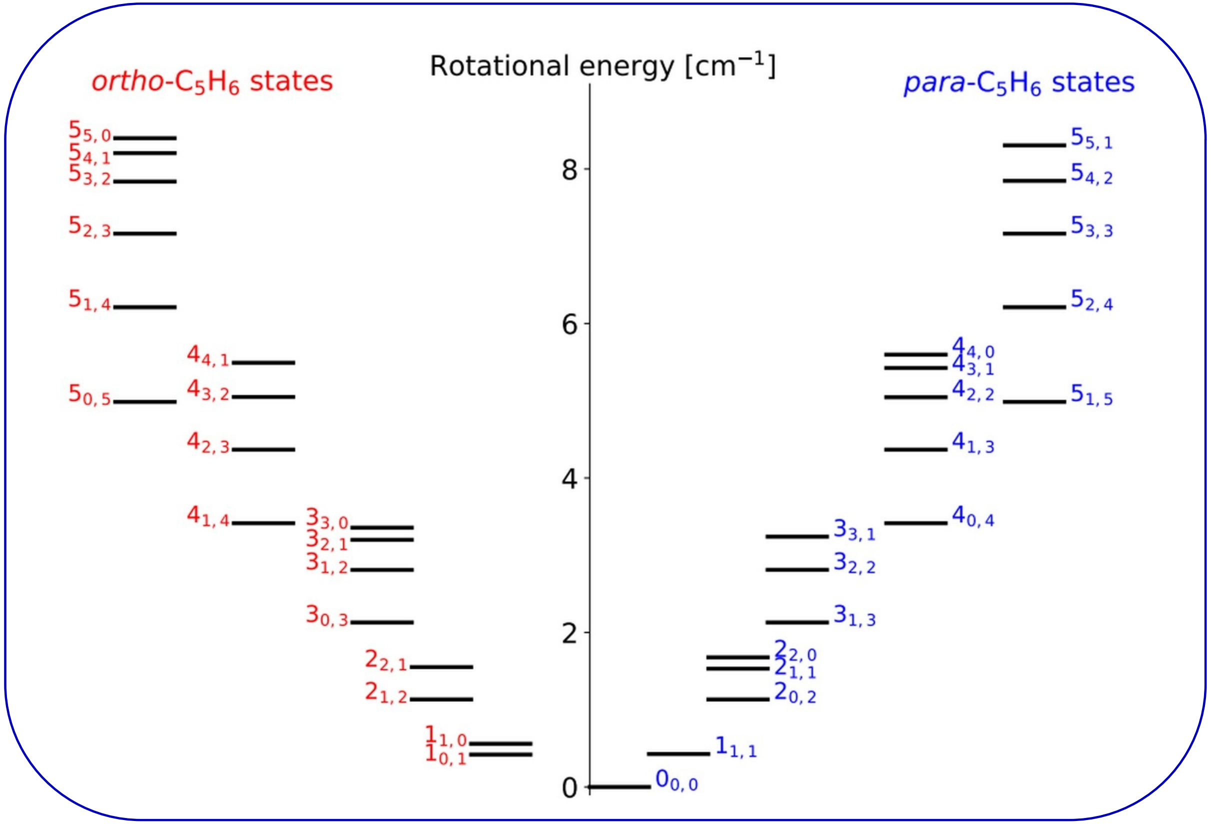
Scattering calculations

- We calculated **rotational (de-)excitation cross sections** for collision of both ***ortho/para*-C_5H_6** with **He** from the **coupled channel (CC)** quantum scattering method. The **CS method** is also used.
- The total **energy range** considered is E_{tot} **< 500 cm^{-1}**
- **Rate coefficients** are calculated **up to 50 K** kinetic temperatures as:

$$k(T) = \frac{1}{k_B T}\sqrt{\frac{8}{\pi \mu_R k_B T}} \int e^{-E_c/k_B T} \sigma(E_c) E_c dE_c$$

  - By CC, the **lowest <u>55 rotational states</u>** were targeted, both for ***para*-C_5H_6** and ***ortho*-C_5H_6**:
    - **up to 25 cm^{-1}** (~36 K) **internal energies**, involving ***all levels with <u>j = 9</u>***, and ***some with <u>j ≤ 12</u>***
  - **Extending** the calculation range **to levels up to 100 cm^{-1}** (~141 K) **internal energies**, involving states ***with <u>j ≤ 25</u>*** (but only using the CS theory)

The rotational structure of *c*-C_5H_6



The **dipole moment** (**0.416 D**) **and rotational constants** of cyclopentadiene **are very low**,* inducing an extremely dense rotational structure

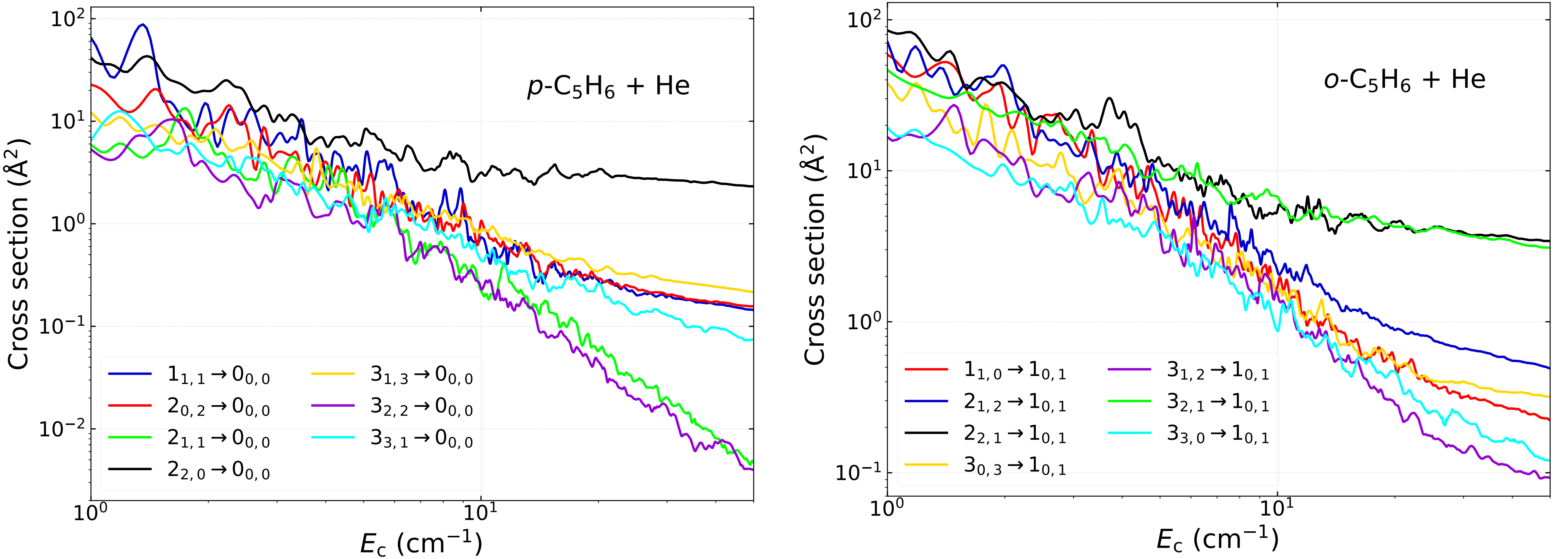
A = **8.426** [GHz] = **0.281** [cm^{-1}]

B = **8.226** [GHz] = **0.274** [cm^{-1}]

C = **4.271** [GHz] = **0.142** [cm^{-1}]

* Bogey *et al.*, *J. Mol. Spectrosc.*, **132**, 277 (1988)

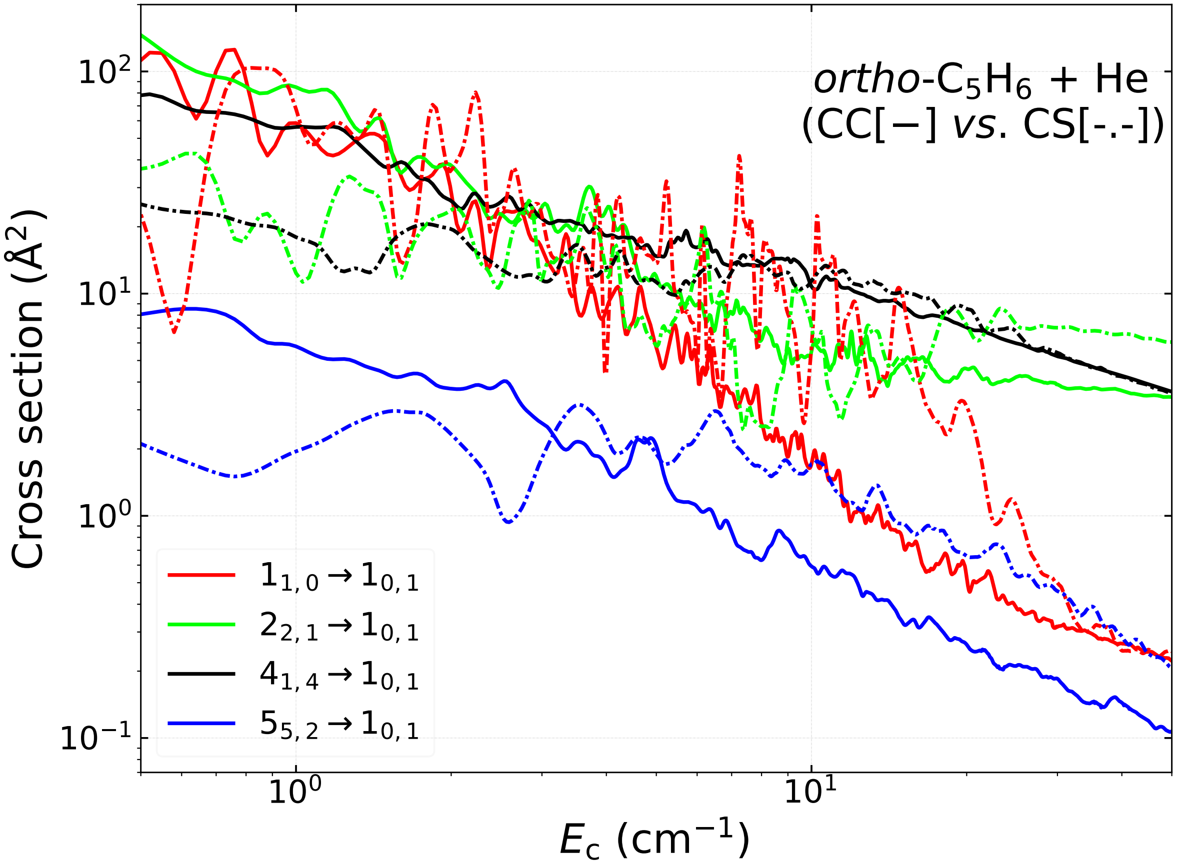
Results: cross sections



Collision-energy dependence of the **rotational de-excitation cross sections** for transitions to the lowest ***para*-C_5H_6 ($0_{0,0}$, *left*)** and ***ortho*-C_5H_6 ($1_{0,1}$, *right*)** states due to **collision with He** *(from the close coupling theory)*

More details at: S. Demes *et al. Phys. Chem. Chem. Phys.* **26**, 16829 (2024)

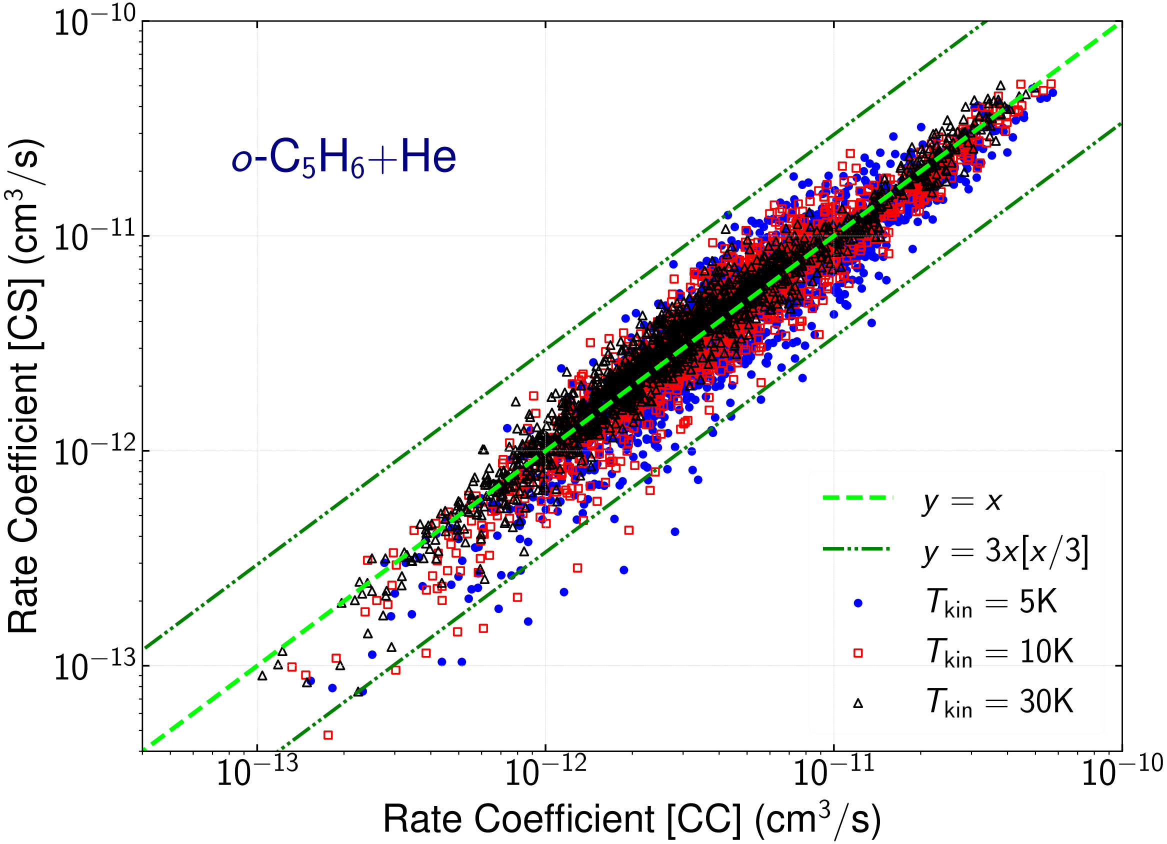
Results: cross sections from CC *vs.* CS



Rotational de-excitation cross sections for the *ortho*−C_5H_6 + He collision: ***close coupling*** (CC) *vs*. ***coupled states*** (CS) scattering theory

- The CC **cross sections strongly deviate** from the CS at lower energies (especially due to intensive false resonances)
- Some **deviations are found also at higher energies**, but not for all transitions
- **Differences up to a factor of 2** are found, even in the case of the most **dominant k_c-conserving transitions**

Results: rate coefficients from CC *vs.* CS



Comparison of the ***state-to-state rotational de-excitation rate coefficients*** for the *ortho*−C_5H_6 + He collision from the ***exact CC*** *vs.* ***approximate CS*** scattering methods.

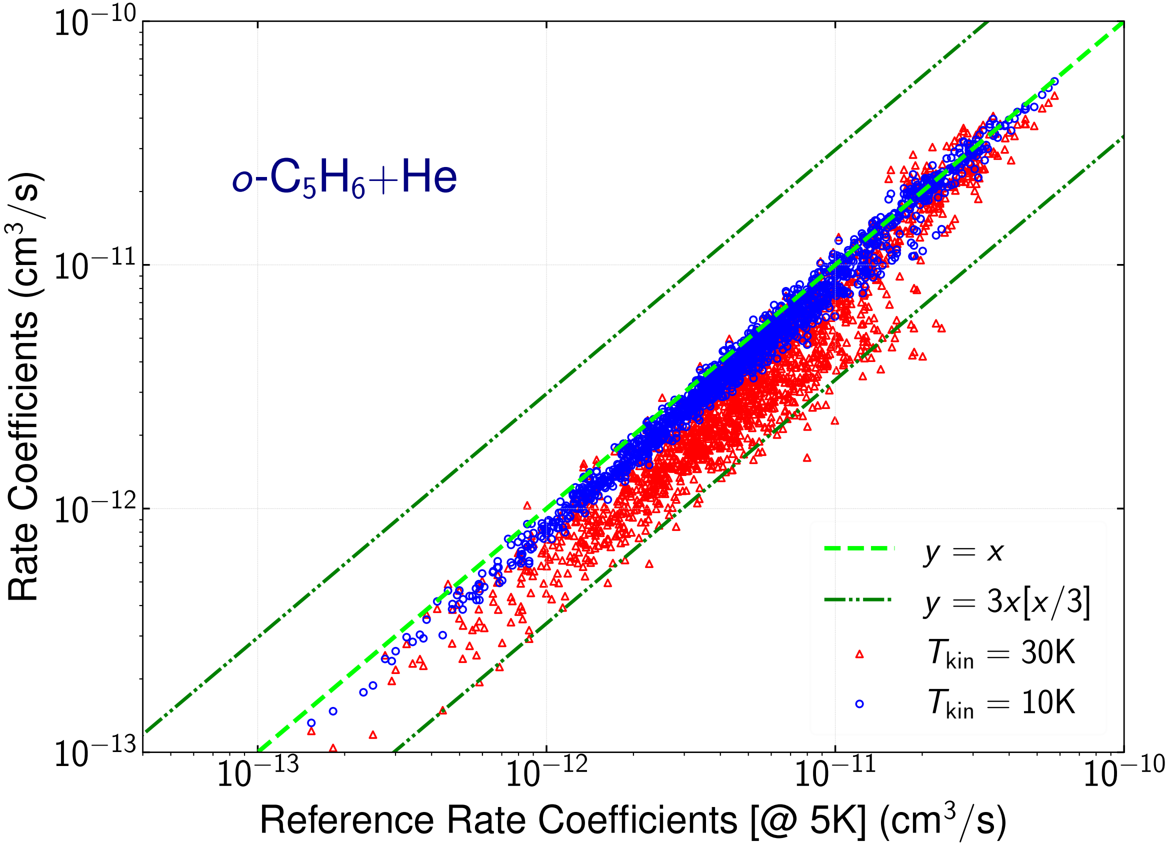
- Most of the dominant transitions are in **quantitatively good agreement**
- **For less dominant transitions**, differences up to more than a **factor of 3** are found
- The **agreement is better with increasing T**:

  MAE (5K) = 27.5% *vs.* **MAE (10K) = 22.4%**

  vs. **MAE (50K) = 17.5%**

Preliminary results!

Results: rate coefficients temperature dependence



Comparison of the **rotational de-excitation rate coefficients** for the *ortho*–C_5H_6 + He collision at various kinetic temperatures **with respect to the data at T_{kin} = 5K**

- Rather **strong temperature dependence:**
  - **at 10K**, the changes are weaker (**<50%**)
  - **at 30K**, the changes are up to **a factor of 3**

Preliminary results!

Take home messages

- The **number of large, complex species observed in the ISM is intensively growing**
- Apart from spectroscopy and laboratory measurements, there is also **a need for accurate** theoretical **data for** state-to-state **collisional excitation**
- We studied the **rotational excitation of a large cyclic molecule** (cyclopentadiene, C_5H_6) **for the first time** calculated **from the exact CC** quantum scattering **method**
- **A full set of rate coefficients along with radiative transfer calculations are coming soon**, allowing a possible re-interpretation of earlier observations and using them for new detections!
  - → *Covering a **range of kinetic temperatures up to 50 K***
  - → *Including **rotational levels with $j \leq 25$** (with $E_{rot} \leq 100$ cm^{-1})*

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Molecular Dynamics in the GAS phase

Thank you for your attention!