Fine and hyperfine excitation of CCS isotopologues induced by collisions with He

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Context

- **Physical conditions** in **astrophysical media** are derived from **spectral line** analysis
  → Requires the **population** of molecular energy levels
- Local thermodynamic equilibrium conditions rarely fulfilled
  → Need of **radiative** and **collisional** molecular data
- **Rate coefficients**, which **characterize transitions** induced by **collisions**, are obtained in 2 steps:
  1. **Interaction potential** between the colliders
     → Potential energy surface (PES)
  2. **Scattering calculations** based on the PES
     → Inelastic cross sections and **rate coefficients**

CCS - He collisional system

- CCS detected in several **molecular clouds** and in **IRC+10216**[1,2]
- **CC^{34}S**, **^{13}CCS** and **C^{13}CS** also detected in **several astronomical sources**
- **He** is one of the **dominant collider** and a **proxy** for **H_2**

Objectives

- **First PES** for the CCS-He system
- First accurate **fine structure** resolved **rate coefficients** for the **CCS** and **CC^{34}S** isotopologues
- First **hyperfine structure** resolved **rate coefficients** for the **^{13}CCS** and **C^{13}CS** isotopologues

Potential energy surface

- UCCSD(T)/aVQZ level of theory using MOLPRO[4]
- Legendre polynomial expansion based on 1351 geometries

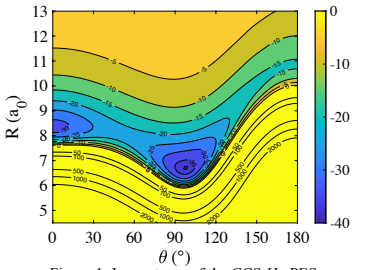

Figure 1: Isocontours of the CCS-He PES.

- Highly anisotropic
- Shallow minima ~ 35 cm^{-1}

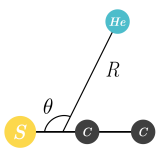

Figure 2: CCS-He collisional system in Jacobi coordinates.

CCS($^3\Sigma^-$) fine structure

- $\boldsymbol{S} = 1 \rightarrow \boldsymbol{j} = |\boldsymbol{N} - 1|\ ;\ \boldsymbol{N}\ ;\ \boldsymbol{N}+1$

Electronic angular momentum $\boldsymbol{S}$
Nuclear rotational momentum $\boldsymbol{N}$
Total angular momentum $\boldsymbol{j} = \boldsymbol{N} + \boldsymbol{S}$

1 rotational level $\boldsymbol{N}$
→ **3 fine structure** levels $\boldsymbol{N_j}$

- Large spin-splitting
  → Energy levels **mixed up** up to $\boldsymbol{N_j} = 10_j$

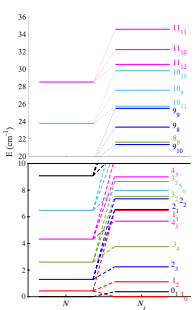

Figure 3: Energy levels of the CCS radical.

Rate coefficients

- Close-coupling approach using a modified version of MOLSCAT[5]
- Thermal averaging of the cross sections

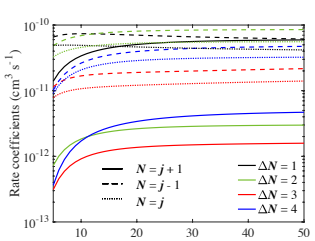

Figure 4: Fine structure resolved rate coefficients from $N_j = 1_j$ for $\Delta N = \Delta j$ transitions.

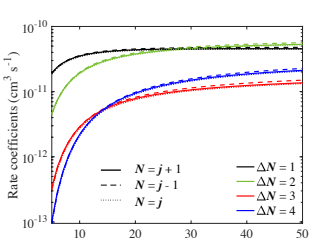

Figure 5: Fine structure resolved rate coefficients from $N_j = 10_j$ for $\Delta N = \Delta j$ transitions.

Fine structure:

- Must be **accurately** taken into account for **low N_j levels**
- Could be **approximatively** taken into account for **high N_j**

Effect of the isotopic substitution

Fine structure rate coefficients:

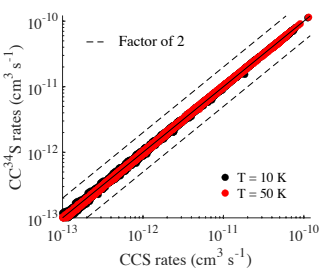

Figure 6: Systematic comparison of the rate coefficients of CCS and CC^{34}S isotopologues.

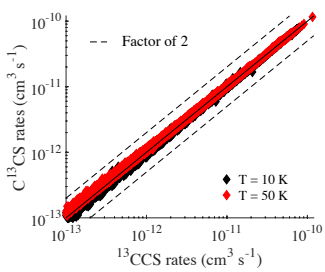

Figure 7: Systematic comparison of the rate coefficients of ^{13}CCS and C^{13}CS isotopologues.

→ Rate coefficients for **one isotopologues** can be use to infer the ones of all **4 isotopologues**

Hyperfine structure rate coefficients:

- $\boldsymbol{I} = 1/2 \rightarrow \boldsymbol{F} = |\boldsymbol{j} - 1/2|\ ;\ \boldsymbol{j} + 1/2$

Nuclear angular momentum $\boldsymbol{I}$
Total angular momentum $\boldsymbol{F} = \boldsymbol{j} + \boldsymbol{I}$

1 fine structure level $\boldsymbol{N_j}$
→ **2 hyperfine structure** levels $\boldsymbol{N_j}$, $\boldsymbol{F}$

- Recoupling method[6]

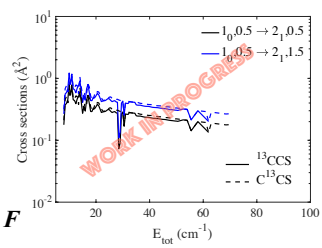

Figure 8: Hyperfine excitation cross sections of ^{13}C-based isotopologues.

Conclusions and Perspectives

- ✓ CCS-He PES at the **UCCSD(T)/aVQZ** level of theory
- ✓ First **accurate** set of rate coefficients for the **5 - 50 K** temperature range
- ✓ **Isotopic substitution** has **no** significant **effect**

- **Hyperfine** structure resolved rate coefficients for **^{13}C-based isotopologues**
- Modelisation of observation:
  1. Observation of CCS
  2. Determination of ^{13}C-based isotopologues **abundances**

→ Investigation of the **chemical processes** leading to the **formation of CCS isotopologues**

References

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