How Rate Coefficients Contribute to Investigating the Chemistry of Sulfur in the ISM

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The ^{13}C-Anomaly in CCS

- **$C^{13}CS$ lines very intense** compared to **^{13}CCS** in TMC-1 (CP) (Sakai et al. 2007)
  - Due to the **chemistry** of CCS?
  - Due to **collisional effects**?
- Hyperfine structure resolved **collisional rate coefficients** provided by Godard Palluet & Lique (2023)

  → **Excellent agreement** between **^{13}CCS and $C^{13}CS$** rate coefficients
- **$C^{13}CS$ more abundant** than **^{13}CCS** due to **CCS chemistry**
- Abundance ratio **[$C^{13}CS$]/[^{13}CCS] = 4.2 ± 2.3** by Sakai et al. (2007)

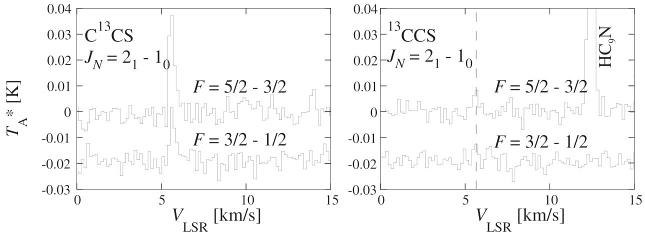


Figure 1: Observed hyperfine components of the $N_J = 1_2 - 0_1$ by Sakai et al. (2007) toward TMC-1 (CP).

Revision of the [$C^{13}CS$]/[^{13}CCS]

- **New observations** with QUIJOTE project (Cernicharo et al. 2022) toward TMC-1 (CP) (Fuentetaja et al. in prep.)
- **Non-LTE** modeling with **^{13}CCS and $C^{13}CS$ rate coefficients** of Godard Palluet & Lique (2023)
- Revised abundance ratio **[$C^{13}CS$]/[^{13}CCS] = 6.79 ± 0.7** from their column densities

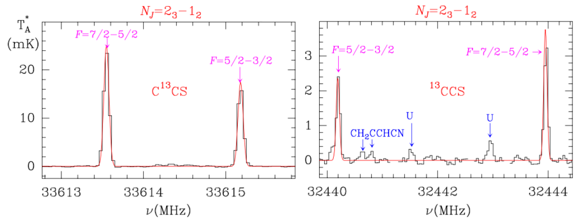


Figure 3: Observed hyperfine components of the $N_J = 2_3 - 1_2$ by Fuentetaja et al. (in prep) toward TMC-1 (CP).

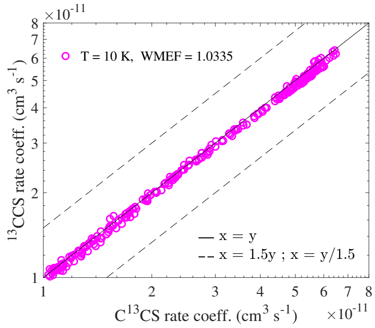


Figure 2: Hyperfine-structure resolved rate coefficients at 10 K of the ^{13}CCS (x-axis) and $C^{13}CS$ (y-axis) isotopologues. Taken from Godard Palluet (2023).

The Chemistry of CCS

- **Main formation paths** considered in the literature

  (1) $S^{(+)} + C_2H_2 \rightarrow CCS + H$ ✗

  (2) $CCH + S^{(+)} \rightarrow CCS + H$ ✗

  (3) $CH + CS \rightarrow CCS + H$ ✓
- Reaction (1) produce ^{13}CCS and $C^{13}CS$ in a **1:1 ratio**
- Reaction (2) **favors ^{13}CCS** over $C^{13}CS$ as [$C^{13}CH$]/[^{13}CCH] = 1.6 ± 0.4 (Sakai et al., 2010)
- Reaction (3) **requires [^{13}CH] << [^{13}CS]**

- **Exchange** reaction Furuya et al. (2011)

$$^{13}CCS + H \rightleftharpoons C^{13}CS + H + \Delta E$$

with ΔE = ZPE(^{13}CCS) - ZPE($C^{13}CS$) = 18.9 K
- **Consumes ^{13}CCS** into **$C^{13}CS$**
- Proceed **without** activation **barrier** (Talbi, 2018)
- **[$C^{13}CS$]/[^{13}CCS] = exp (ΔE/T) = 6.62**

→ **CCS chemistry** led by **thermodynamics**

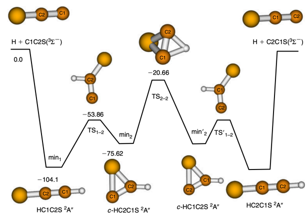
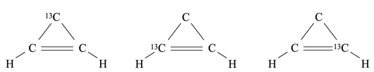


Figure 4: Energy profile of the H + CCS reaction calculated at the RCCSD(T)/aug-cc-pVQZ//M06-2X/aug-cc-pVTZ level of theory from Talbi (2018). The relative energies are given in kcal mol^{-1}.

^{13}C-Anomaly in Other Molecules?

- **CCH**, Sakai et al. (2010)
- **C_3S**, Sakai et al. (2010), Fuentetaja et al. (in prep.)
- **c-C_3H_2**, Agúndez et al. (2019)



- **Same excitation conditions** are assumed (except CCS)
- **No rate coefficients** for **C_3S** and **c-C_3H_2 isotopologues**

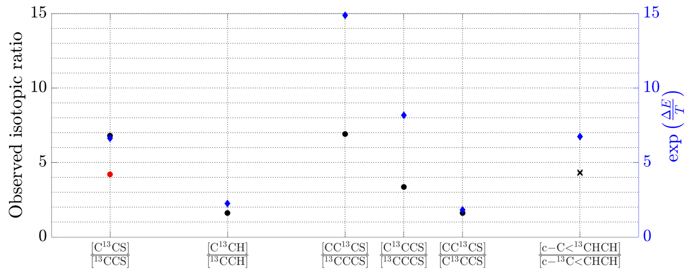


Figure 5: Abundance ratio of ^{13}C-based isotopologues of CCS, CCH, c-C_3H_2 based observations of TMC-1 (CP) (circles) and L483 (black crosses) and ZPE energy differences (blue diamonds). The red circle corresponds to the measurement of Sakai et al. (2007).

Conclusions

- **^{13}C-anomaly of CCS** explained by **interconversion of ^{13}CCS into $C^{13}CS$**
- **Revision of CCS formation path** in chemical models
- Other ^{13}C-anomaly:
  - Could be explained by **thermodynamics** for **CCH** and **c-C_3H_2**
  - **Uncertain** for **C_3S**, or at least **not for all isotopologues**
- **Other ^{13}C anomaly** should be investigated: **HC_nN** (n = 3, 5, 7), **C_4H**

→ **Need for accurate rate coefficients** to model these species and better **understand their chemistry.**

References

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