Rotational quenching study in isovalent H⁺ - CS and H⁺ - CO systems

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Outline

• Introduction
• Spectroscopy of stars
• H⁺ collision with CS and CO
• Results and discussion
• Ultracold Chemistry
• Conclusions
H is the most abundant element present in the interstellar medium (ISM) in the form of H, H₂, and H⁺

CO is the most abundant molecule after H₂ and more than 200 molecules have been detected till date

Abundance calculations of observed interstellar species require radiative and collisional rates

Studying chemistry of interstellar space under extreme conditions of low temperature
Spectroscopy

- UV and optical $\lambda \rightarrow$ electronic transition
- Infra Red $\lambda \rightarrow$ Vibrational within electronic states
- Submillimeter and far-IR $\lambda \rightarrow$ rotational transitions
- Many of the interstellar molecules are detected at mm $\lambda$, its high resolution results in high sensitivity to molecules of lower abundances
H$^+$ collision with CO and CS

- Cosmic rays initiates gas-phase chemistry after penetrating deeper into clouds resulting in ionization of small fraction of atomic and molecular hydrogen

- H$^+$ collision with interstellar species, CO and CS forms bound protonated species, HCO$^+$ and HCS$^+$, respectively

- CO an abundant species and CS first sulfur molecule in the ISM

- Both protonated species HCO$^+$ and HCS$^+$ observed in the interstellar clouds. Many species have their isomers stable and observed in the ISM
**Ab initio** potential energy surface

- Full three dimensional *ab initio* PES are generated at MRCI level using Dunning’s basis set for H$^+$ - CS using MOLPRO

- PES is generated using Jacobi’s coordinate

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H⁺ - CS

- Rotationless barrier between HSC⁺ and HCS⁺
- HSC⁺ unstable relative to its isomer HCS⁺
- HSC⁺ is still undetected in the space
H⁺ - CO

- Transition state exists between HOC⁺ and HCO⁺
- Both isomers are stable with minimum conformations
- HOC⁺ and HCO⁺ are observed in the space

Rigid rotor PES

- Rigid rotor PES for ground state of H\(^+\) - CO, with CO bond distance fixed at 2.138 a.u.

- Rigid rotor PES for ground state of H\(^+\) - CS, with CS bond distance fixed at 2.900 a.u.

Fitting of PES

\[ V(R, r_{eq}, \gamma) = \sum_{\lambda} V_\lambda(R) P_\lambda \cos \gamma \]

Potential is expanded in terms of Legendre Polynomials to get \((V_\lambda)\)
Asymptotic potential

- \( V_\lambda \) obtained from rigid rotor of interaction region are merged with long range multipole moments of CO and CS

\[
V_{as}(R, r; \gamma) \sim \frac{\mu(r)}{R^2} P_1(\cos \gamma) + \frac{Q(r)}{R^3} P_2(\cos \gamma) - \frac{\alpha_0(r)}{2R^4} - \frac{\alpha_2(r)}{2R^4} P_2(\cos \gamma) + O(P_3)
\]
Rotational quenching cross sections are obtained from $j = 4, 3, 2$ to lower $j'$ levels for H$^+$ - CO using MOLSCAT code.
Rotational quenching rate coefficients are obtained from $j = 4, 3, 2$ to lower $j'$ by averaging over Boltzmann distribution of kinetic energies.
Rotational quenching cross sections are obtained from $j = 5$ to $j' = 0,1,\ldots,4$ for H$^+$ - CS
Rotational quenching rate coefficients by averaging over Boltzmann distribution of kinetic energies from $j = 5$ to $j' = 0,1,\ldots,4$ for $H^+ - CS$
Ultracold collisional regime

- Cooling and trapping of molecules from cold (< 1 K) to ultracold regime (< 1 mK)

- Promising application towards precision spectroscopy

- For $\text{H}^+$ collision with CO and CS, both follows Wigners’ threshold laws in the region of $< 10^{-4}$ K

- Buffer gas cooling technique employed to unveil molecular properties at low temperature of molecular collisions

- $^{3,4}\text{He}$ collision with CS studied from ultracold to high temperature range
\[ \text{\(^3,^4\)He collision with CS} \]

- \textit{Ab initio} PES by Lique et al. at CCSD(T)/aug-cc-pVQZ level of theory
- He-CS data is available for astrophysical application from 10 K to 300 K.
- \(^4\)He collisional data with CS in the ultracold regime computed
- \(^3\)He collisional data with CS computed from ultracold to high temperature regime
- Inelastic cross sections are computed using close coupled equations from \(10^{-7}\) cm\(^{-1}\) to 5000 cm\(^{-1}\)

Cross section; $^3$He-CS

- Rotational quenching cross sections are obtained from $j = 1, 2, \ldots, 10$ to lower $j'$ levels

\[ j = 5 \rightarrow 0, 1, \ldots, 4 \quad \text{and} \quad j = 10 \rightarrow 0, 1, 2, \ldots, 9 \]
Rotational quenching rate coefficients are obtained from $j = 1, 2, \ldots, 10$ to lower $j'$. 

- $j = 5 \rightarrow 0, 1, \ldots, 4$
- $j = 10 \rightarrow 0, 1, 2, \ldots, 9$
Isotope effect

![Graph showing isotope effect](image)
Conclusions

- HCS$^+$ is linear and stable over bent HSC$^+$ ion
- HCO$^+$ and HOC$^+$ are both linear stable isomers
- Propensity of rotational transitions is $\Delta j = -1$ for $H^+$ collision with CS and CO, while $\Delta j = -2$ for $^3,^4$He-CS
- Wigners’ threshold law is obeyed below $10^{-2}$ cm$^{-1}$ for He-CS collision (neutral) while shifted to even lower $10^{-4}$ cm$^{-1}$ for $H^+$ collision with CS and CO (ionic)
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- ISMS for registration and accommodation
Thanks!
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