Hyperfine Excitation of $HC^{17}O^+$ with p-H_2 Collisions [1]

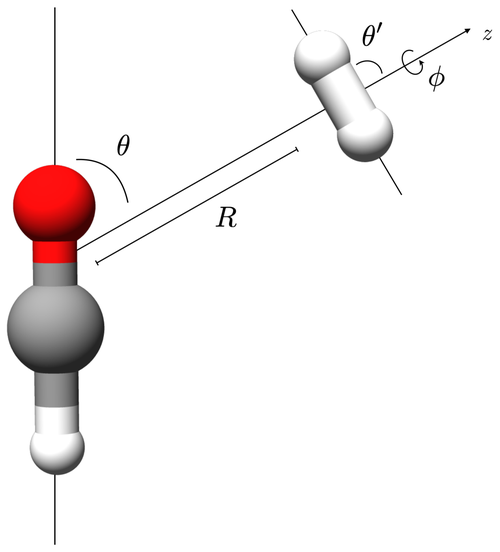
Francesca Tonolo[1,2], François Lique[3], Mattia Melosso[4], Cristina Puzzarini[2], Luca Bizzocchi[2]

[1]Scuola Normale Superiore, Pisa, Italy. [2]Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Bologna, Italy.
[3]Univ. Rennes, CNRS, IPR, Rennes, France. [4]Scuola Superiore Meridionale, Naples, Italy.

francesca.tonolo@sns.it

Introduction

When aiming at a deeper knowledge of the physical and chemical properties of star forming regions, the formyl cation (HCO^+) and its isotopic variants undoubtedly represent one of the most attracting systems. HCO^+ is the most abundant cation in dense molecular clouds and its chemistry is straightforward and well understood [2], thus making it an excellent candidate as a tracer of molecular ionized gas through the evolutionary stages of the interstellar medium (ISM) [3,4]. However, in spite of several spectroscopic studies and astrophysical detections, a thorough investigation of the collision physics of the $HC^{17}O^+$ and H_2 system has not been carried out yet. The presence of an hyperfine structure ($\mathbf{I = 5/2}$), moreover, could be useful to discriminate between opacity effects and excitation temperature effects in the determination of the column density.



Potential Energy Surface

Geometry

- HCO^+ fixed to its experimentally determined r_e geometry [5].
- $r(H_2)$ averaged over its ground-state vibrational wavefunction [6].

Level of theory

- Explicitly correlated **CCSD(T)-F12a** method in combination with **aug-cc-pVQZ** basis set[7].

Interaction energies

- Ab initio calculations over an irregular grid of 3375 points in the $\{R, \theta, \theta', \phi\}$ coordinates.
- Each energy has been corrected for the basis set superposition error (BSSE).

Scattering calculations

Full quantum close-coupling (CC) calculations on the interaction potential have been perfomed by employing the MOLSCAT program [8] at values of the kinetic energy ranging from **2 to 500 cm^{-1}**.

To take in account the splitting of the rotational levels given by the hyperfine structure of $HC^{17}O^+$ the spin wave-functions were decoupled from the rotational ones using the **recoupling method** described by [9].

$$\sigma^{\mathrm{REC}}_{jF\to j'F'} = \frac{\pi}{k^2_{jF}}(2F'+1)\sum_K \begin{Bmatrix} j & j' & K \\ F' & F & I \end{Bmatrix}^2 P^K(j\to j')$$

$HC^{17}O^+$ rotational basis

- Experimental rotational constants: $B_0 = 43528.92$ MHz, $D_0 = 78.96$ kHz [10].
- Energies of the hyperfine levels from Bizzocchi (2022).

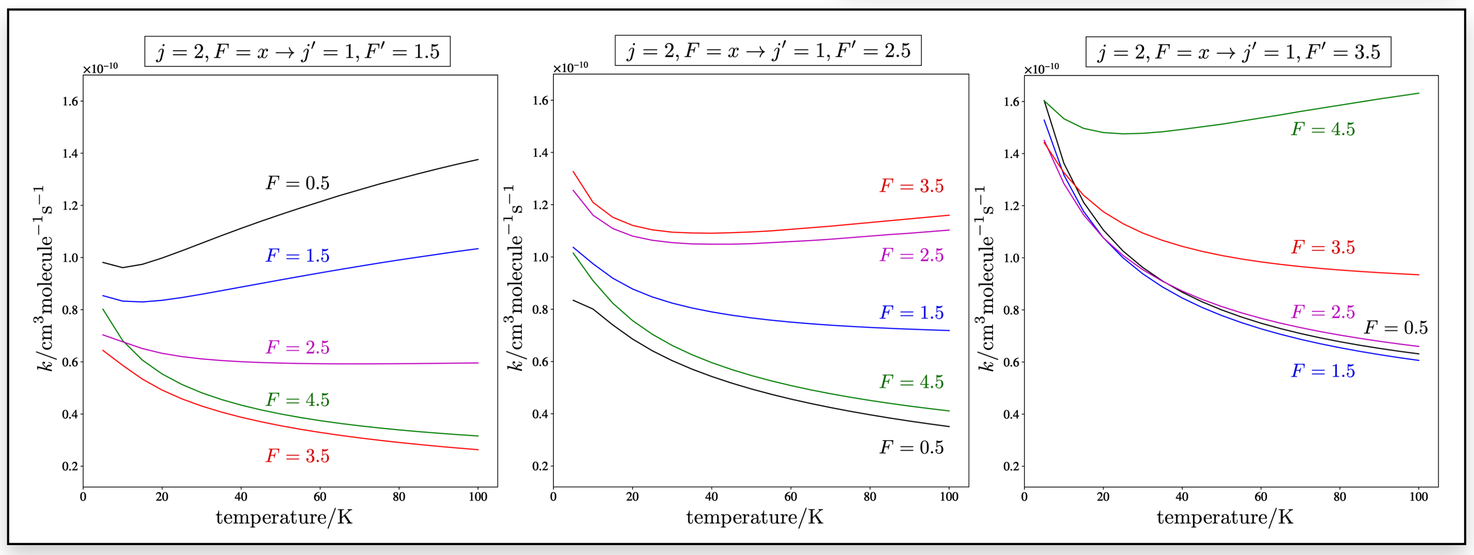
Finally, the **hyperfine resolved (de-)excitation rate coefficients** for the lowest six rotational levels in the **5—100 K** range have been straightforwardly derived.

$$k^{\mathrm{REC}}_{jF\to j'F'}(T) = \left(\frac{8}{\pi\mu k_B^3 T^3}\right)^{1/2}\int_0^\infty \sigma^{\mathrm{REC}}_{jF\to j'F'}\; E_c\; \mathrm{e}^{-E_c/k_BT}\; \mathrm{d}E_c$$

Isotopic effect

The comparison of the cross section at 50 cm^{-1} of HCO^+ and $HC^{17}O^+$ showed significant differences and different patterns.

$j \to j'$	Cross sections / Å^2		% Error
	$HC^{17}O^+$	HCO^+	
$1 \to 0$	53.41	64.96	21.62
$2 \to 0$	50.31	55.34	10.00
$3 \to 0$	44.00	47.18	7.24
$4 \to 0$	30.28	41.16	35.90
$5 \to 0$	15.74	20.49	30.20
$2 \to 1$	60.87	60.25	−1.03
$3 \to 1$	53.18	49.24	−7.40
$4 \to 1$	35.19	40.20	14.22
$5 \to 1$	18.77	18.88	0.59
$3 \to 2$	52.95	64.27	21.39
$4 \to 2$	41.75	51.14	22.47
$5 \to 2$	21.02	23.86	13.47
$4 \to 3$	51.02	61.93	21.38
$5 \to 3$	23.19	37.58	62.02
$5 \to 4$	35.63	47.33	32.85
Average absolute % error			20.12

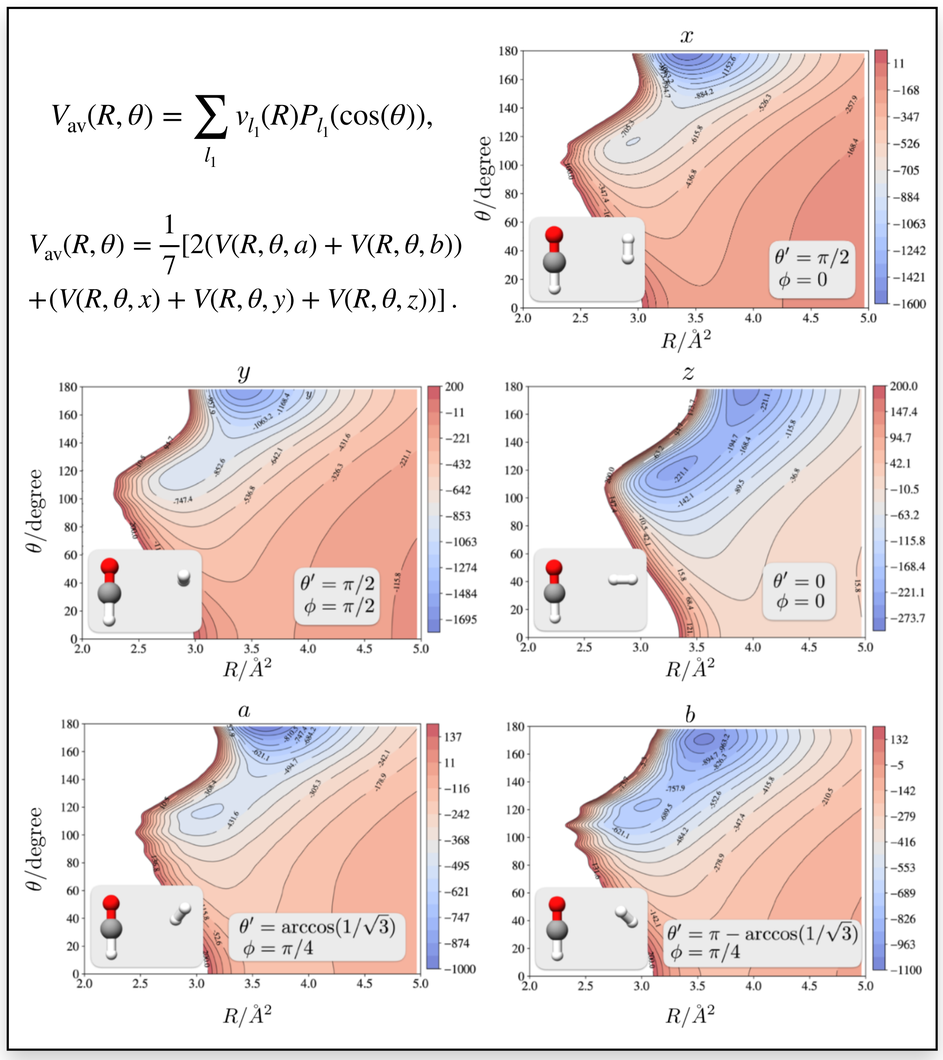


Fitting procedure

Having assessed the negligible coupling effect with the j(H_2) > 0 rotational levels of H_2, a **spherical average** of the potential with respect to five orientations of **H_2** has been performed.

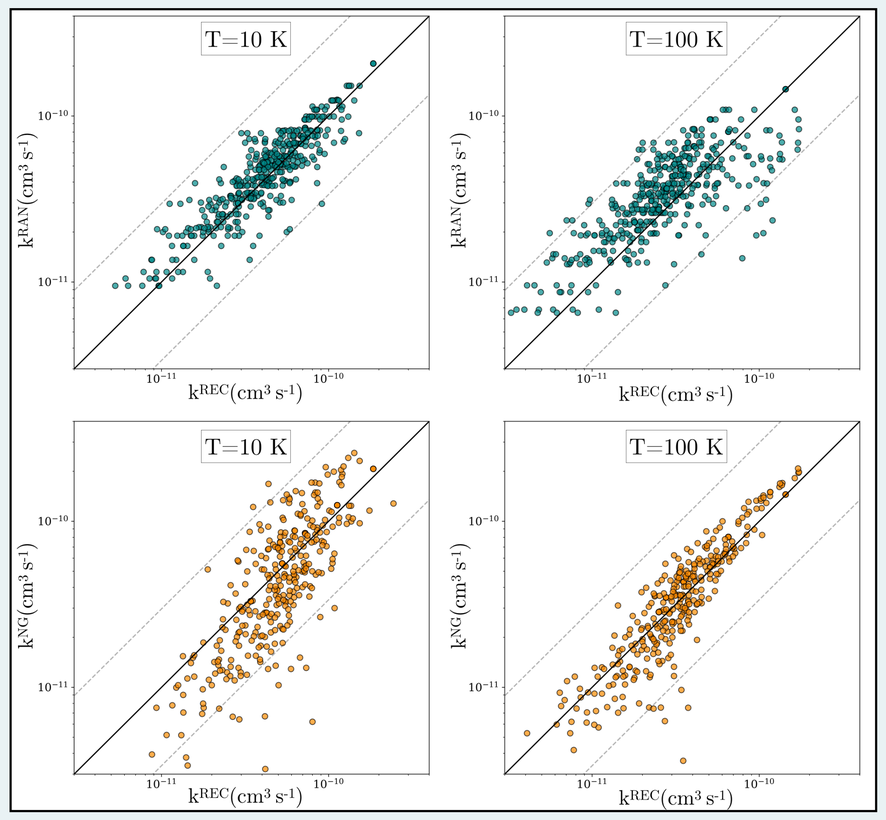
$$V_{\mathrm{av}}(R,\theta) = \sum_{l_1} v_{l_1}(R) P_{l_1}(\cos(\theta)),$$

$$V_{\mathrm{av}}(R,\theta) = \frac{1}{7}[2(V(R,\theta,a) + V(R,\theta,b)) + (V(R,\theta,x) + V(R,\theta,y) + V(R,\theta,z))]\,.$$



Comparison with approximate methods

We have compared the hyperfine rate coefficients obtained with the full quantum CC plus recoupling approach with those derived from the corresponding rotational collision data employing the **NG and RAN approximations** [11] at 10 and 100 K.



Concluding remarks

Here are presented the first computed rate coefficients for the hyperfine (de-)excitation of $HC^{17}O^+$ by collisions with $H_2(j = 0)$, in the $10 - 100$ K temperature range. The importance of these data is highlighted by the significant difference between the values of the collision cross sections computed for HCO^+ and $HC^{17}O^+$ targets. Finally, the comparison with the commonly adopted RAN and NG approximations indicated that the recoupling approach represents the most reliable methodology to compute hyperfine resolved inelastic rate coefficients for astrophysically interesting systems.

Rotational and Computational Spectroscopy Group

SCUOLA NORMALE SUPERIORE

References

[1] F. Tonolo, F. Lique, M. Melosso *et al.* (2022), *MNRAS*, **516/2**, 2653. [2] E. Herbst, W. Klemperer (1973), *ApJ*, **185**, 505. [3] J. K. Jørgensen, F. L. Schöier, E. F. Van Dishoeck. (2004), *A&A*, **416/2**, 603. [4] M. Guélin, W. Langer, R. Wilson (1982), *A&A*, **107**, 107. [5] L. Dore, S. Beninati, C. Puzzarini *et al.* (2003), *JCP*, **118**, 7857. [6] P. Jankowski, K. Szalewicz (1998), *JCP,* **108**, 3554. [7] F. Lique, J. Kłos, M. Hochlaf (2010), *PCCP,* **12**, 15672. [8] J. M. Hutson, S. Green (1994), MOLSCAT version 14, distributed by Collaborative Computational Project No. 6 of Engineering and Physical Sciences Research Council (UK). [9] M. H. Alexander, P. J. Dagdigian (1985), *JCP.*, **83**, 2191. [10] L. Dore, G. Cazzoli, P. Caselli (2001), *A&A*, **368**, 71. [11] A. Faure, F. Lique (2012), *MNRAS*, **425**, 740.