

Collisional excitation of radical molecules in the interstellar medium

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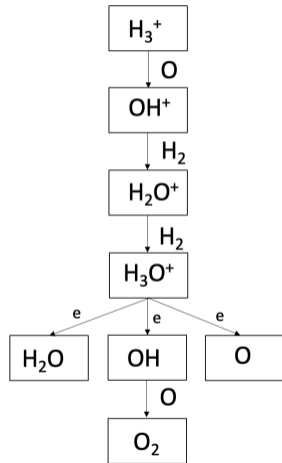


Figure: The oxygen chemistry in molecular clouds 2 / 16

Application to the $\text{NH}(^3\Sigma)-\text{H}_2(^1\Sigma)$ collisional system

Non-reactive collisions

The case of NH

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→ Nitrogen reservoirs are still in debate

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Isotopologue ND is also detected

→ Probe chemical pathways

→ Trace the $\frac{[ND]}{[NH]}$ ratio

→ Trace history of molecular cloud formation

Excitation mechanisms in the ISM

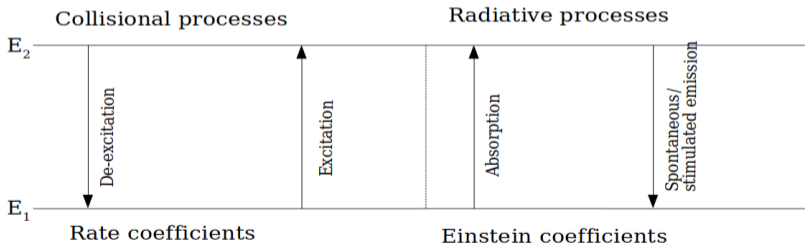
Characterization of physical and chemical conditions of the ISM:

- Interpretation of observational spectra
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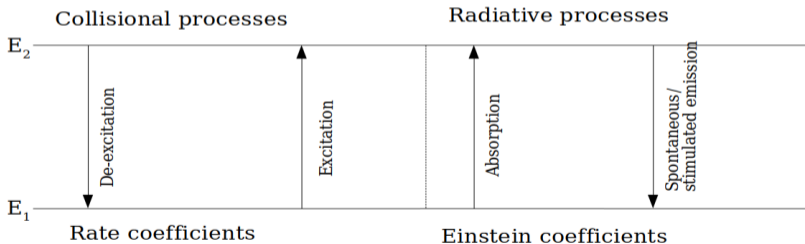
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Main colliders: e^- , H, He, $H_2(j_2)$

The non-LTE regime

Without rate coefficients: application of local thermodynamic equilibrium (LTE) models

⇒ generally not fulfilled

Lack of data for NH–H₂ and ND–H₂ collisional systems

¹A. Bacmann *et al.*, A&A 587, A26 (2016)

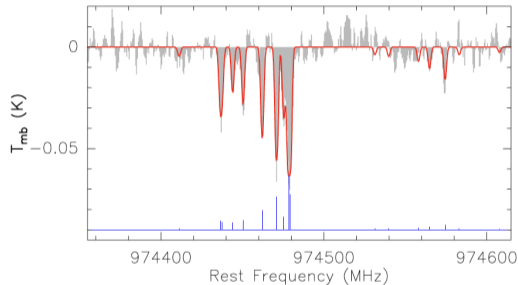


Figure: Observed spectrum of NH with a LTE model as red solid lines¹

Obtention of the rate coefficients

**Resolution of the Time-independent Schrödinger equation through
Born-Oppenheimer approximation**

Obtention of the rate coefficients

Resolution of the Time-independant Schrödinger equation through Born-Oppenheimer approximation

Determination of the potential energy surface (PES)

→ describe the electronic interaction between colliders

- *ab initio* calculations
- analytical representation of the potential $V(R, \alpha)$

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- cross sections $\sigma(E_{kin})$
- rate coefficients ($\sim \int_0^\infty \sigma(E_{kin}) dE_{kin}$)

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Most accurate approach ✓

Most expensive one ✗

Potential energy surface

- Linear rigid rotor approximation
- 4D PES¹
- RCCSD(T)-F12/aVTZ method
- Calculations are done with the MOLPRO code²
- The PES was expanded in bispherical harmonics

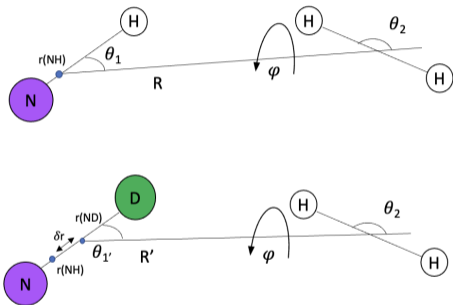


Figure: NH-H₂ representation in Jacobi coordinates

¹Pirlot Jankowiak *et al.*, J. Chem. Phys. 155, 134303 (2021)

²Werner, Molpro, a package of ab initio programs, version 2015.1, 2015

Energetic structure of $\text{NH}(^3\Sigma)$

Open-shell molecule $\rightarrow \mathbf{S} = 1$

$\rightarrow \mathbf{j}_1 = \mathbf{N} + \mathbf{S}$

Rotational levels $N \rightarrow$ Fine structure levels N_{j_1}

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NH and ND possess nonzero nuclear spins:

- $\mathbf{I}_{H/D} \rightarrow \mathbf{F}_1 = \mathbf{j}_1 + \mathbf{I}_{H/D}$
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Hyperfine structure levels $N_{j_1, F_1, F}$

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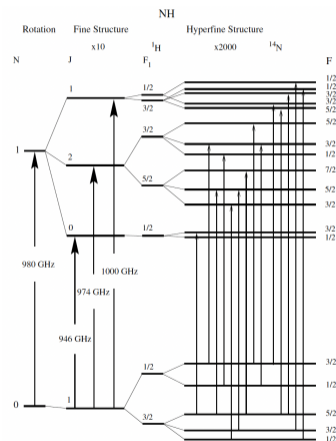
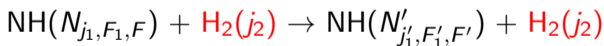
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Hyperfine structure levels $N_{j_1, F_1, F}$



¹ Klaus *et al.*, *Astron. Astrophys.* 322, L1–L4 (1997)

Figure: NH first hyperfine energy levels¹

Fine structure excitation of NH by H₂

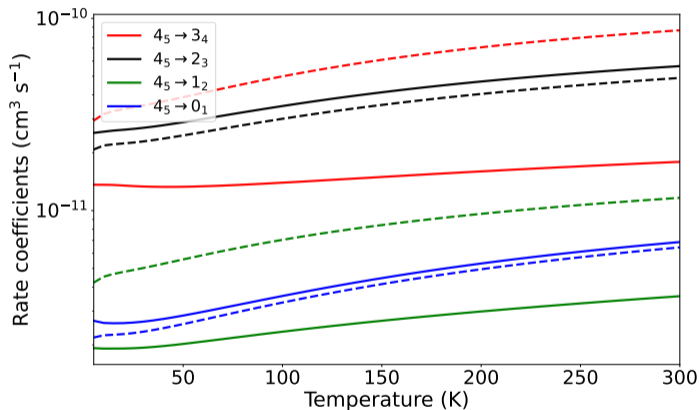


Figure: Temperature dependence of rate coefficients of NH with *para*- (solid) and *ortho*-H₂ (dashed) for $N_j \rightarrow N'_j$ transitions

- Resolution of the close-coupling equations
- Calculations have been done using HIBRIDON scattering code¹

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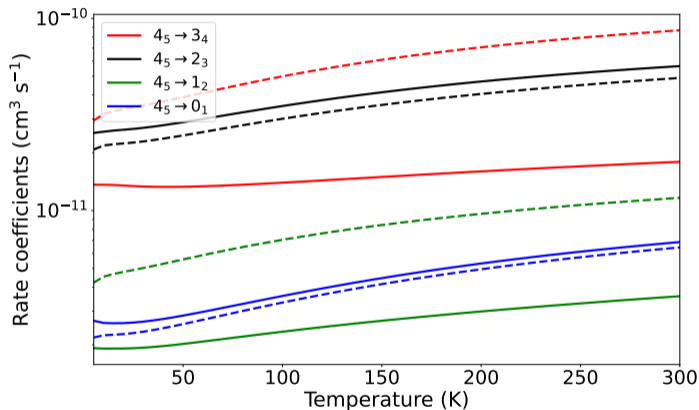


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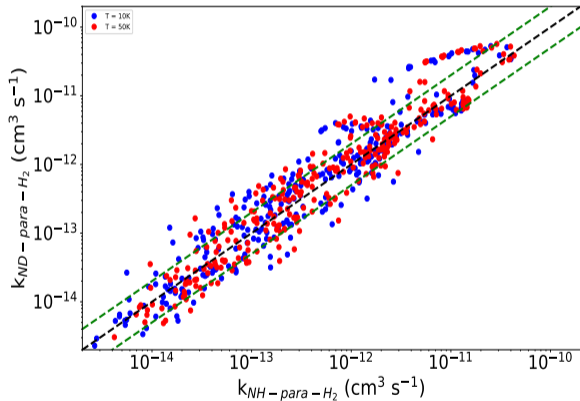
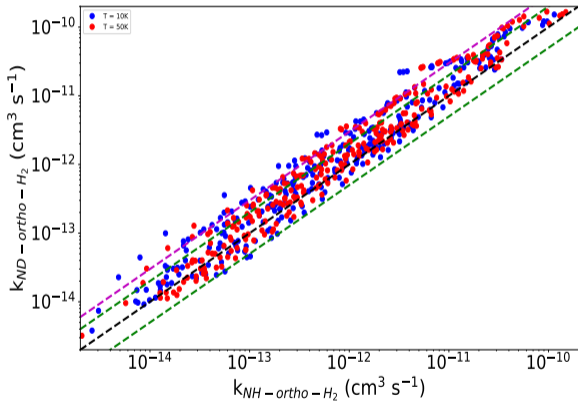
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→ Most of rate coefficients deviate within a factor of $\sim 2 - 3$ for NH-*ortho*-H₂ transitions

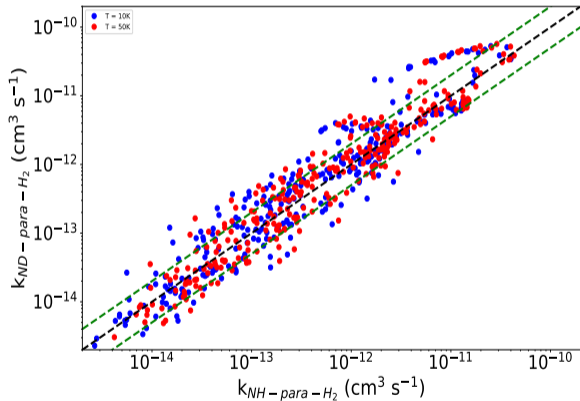
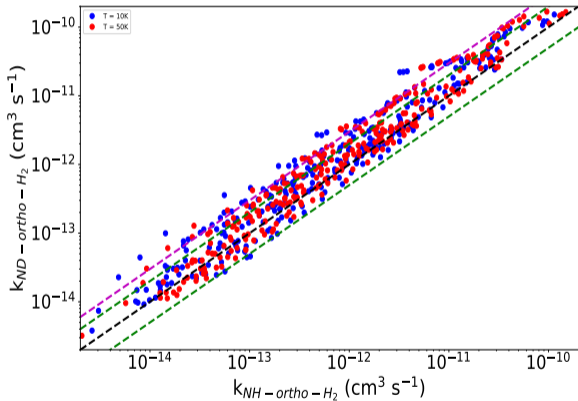
→ Some of the most dominant transitions ($> 4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$) are larger by a factor > 10 !

¹Alexander 2023

Fine structure excitation of ND by H₂



Fine structure excitation of ND by H₂



$\delta r = 0.11a_0 + \text{rotational structures} \rightarrow \text{deviation of the rate coefficients up to a factor of 3}$

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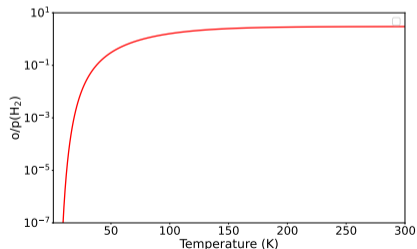
Type of interaction	Memory/task (Gb)	CPU time (hours)
Atom-Molecule ($I_1, I_2 \neq 0$)	≤ 7	> 1000000
Molecule-Molecule ($I_1 \neq 0$)	~ 10	~ 1000000
Molecule-Molecule ($I_1, I_2 \neq 0$)	~ 70	\times

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Table: Application of the recoupling approach



NH environments $\rightarrow T > 50$ K
The internal structure of H₂ **MUST** be taken into account for NH excitation

Infinite Order Sudden approximation

- neglect rotation during collision
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$$k_{i \rightarrow f}^{IOS} \propto \sum_l H_l(i, f) k_{1,0 \rightarrow l+1,l}^{CC}$$

$$WMEF = \frac{\sum_i k_i^{rec} r_i}{\sum_i k_i^{rec}}$$

$$r_i = \max(k_i^{rec} / k_i^{NG}, k_i^{NG} / k_i^{rec})$$

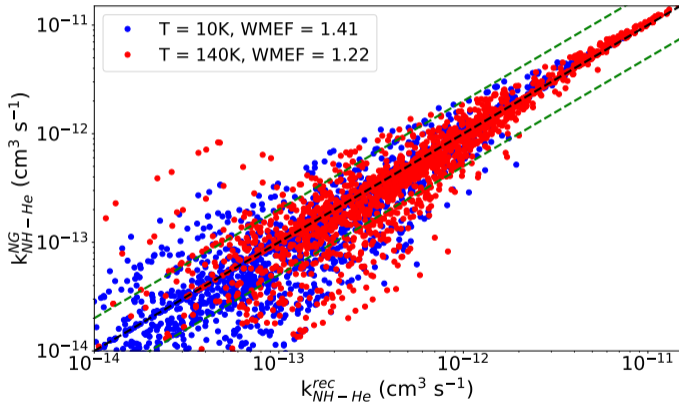


Figure: Systematic comparison of NH-He rate coefficients with recoupling ones¹

¹Dumouchel *et al.*, J. Chem. Phys. 137, 114306 (2012)

Conclusion

Collisional excitation of open-shell molecules with molecular hydrogen is a true theoretical and numerical challenge

- First fine structure resolved rate coefficients for NH-H_2 and ND-H_2 collisional systems (5 - 300 K)
- Hyperfine structure treatment still needs improvement

→ The internal structure of H_2 is not negligible

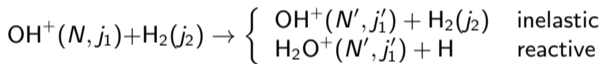
→ The isotopic substitution has an impact on the order of magnitude of rate coefficients

Perspectives: The $\text{OH}^+(\text{}^3\Sigma) - \text{H}_2$ collisional system

OH^+ is a very reactive molecule

→ rapidly destroyed after its formation

Competition between reactive and inelastic collisions



→ **Both inelastic and reactive channels will be taken into account with a statistical approach**

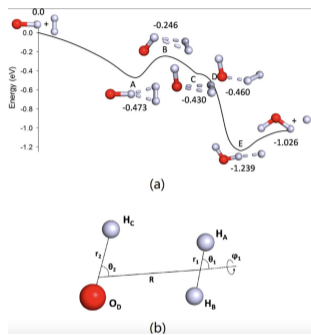


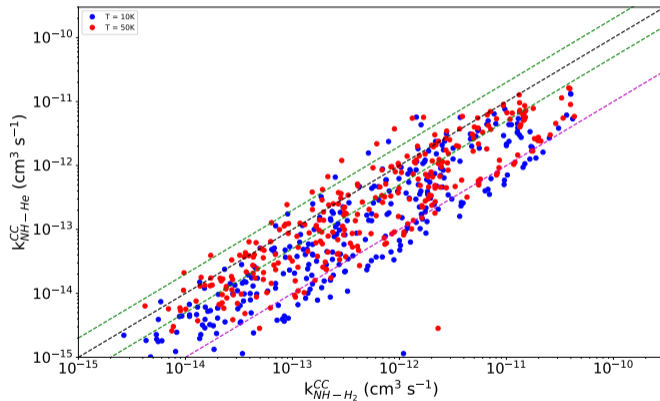
Figure: Reaction path of the $\text{OH}^+ - \text{H}_2$ collisional system (a) and the representation of the complex in Jacobi coordinates (b)¹

¹ Song *et al.*, J. Phys. Chem. A 2016, 120, 4742-4748

Acknowledgments



Comparison of NH-H₂ with NH-He



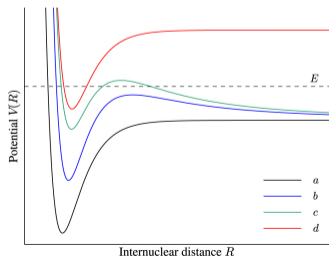
$$k_{\text{H}_2} = 1.3335 \times k_{\text{He}}$$

The Statistical Adiabatic Channels Model (SACM)

In the time-independent Close-Coupling equations:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 F(\alpha)}{dR^2} + \sum_{\alpha'} \langle \alpha' | H_{int} + V + \frac{L^2}{2\mu R^2} | \alpha \rangle F(\alpha) = EF(\alpha)$$

- The kinetic term is removed
- Calculations are independent of collisional energy \rightarrow Adiabatic curves¹



$$|S_{ij}(E, j)|^2 = \begin{cases} \frac{1}{N(E, j)} & \text{open channels} \\ 0 & \text{closed channels} \end{cases}$$

¹ Loreau, Lique, and Faure, ApJL, 853 L5 (2018)