Collisions moléculaires: théorie, expérience et observation

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Outline

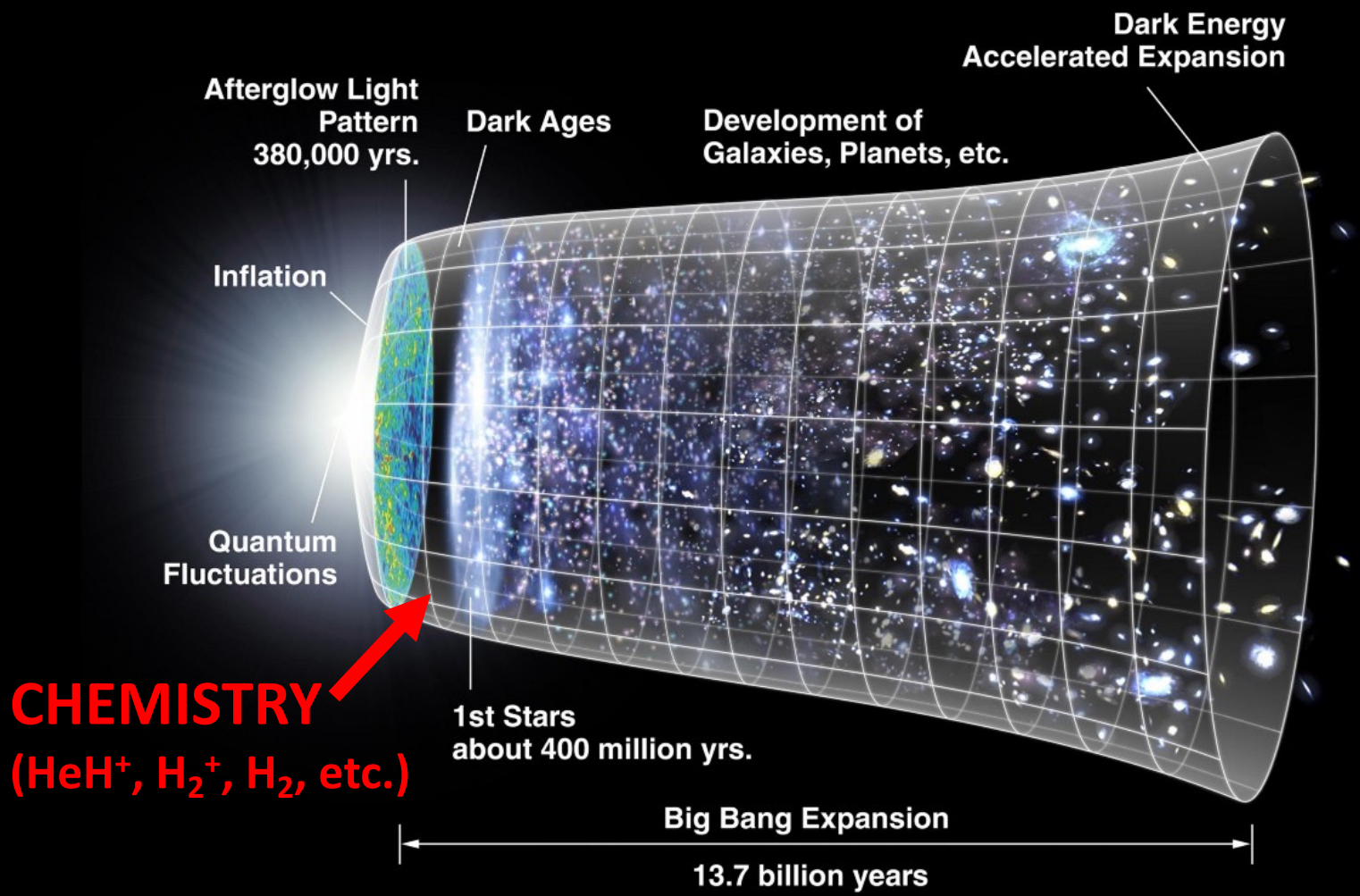
Introduction

I. Collisional excitation: theory vs experiment

II. Molecular diagnostics: CN, CH^+, CH_2NH

Conclusion

Chemistry starts at $z \simeq 1000$



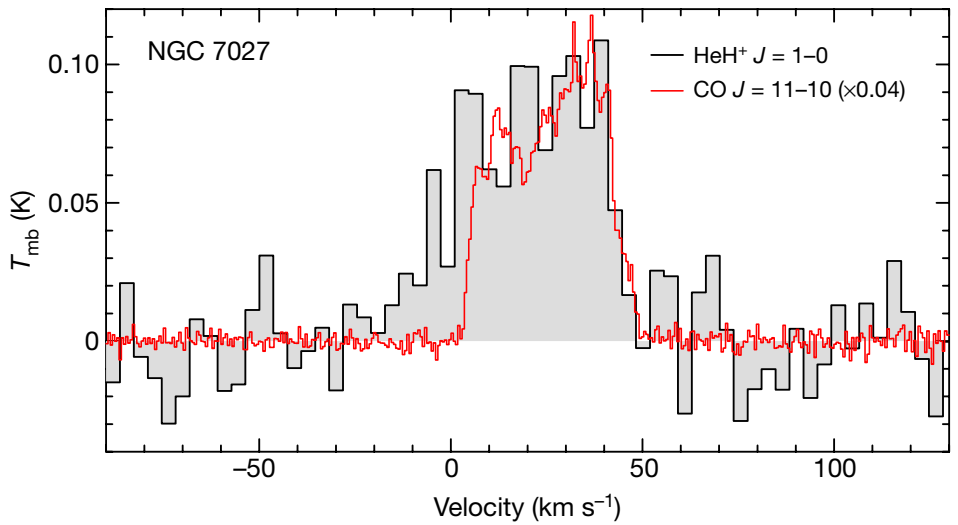
LETTER (April 2019)

https://doi.org/10.1038/s41586-019-1090-x

Astrophysical detection of the helium hydride ion HeH^+

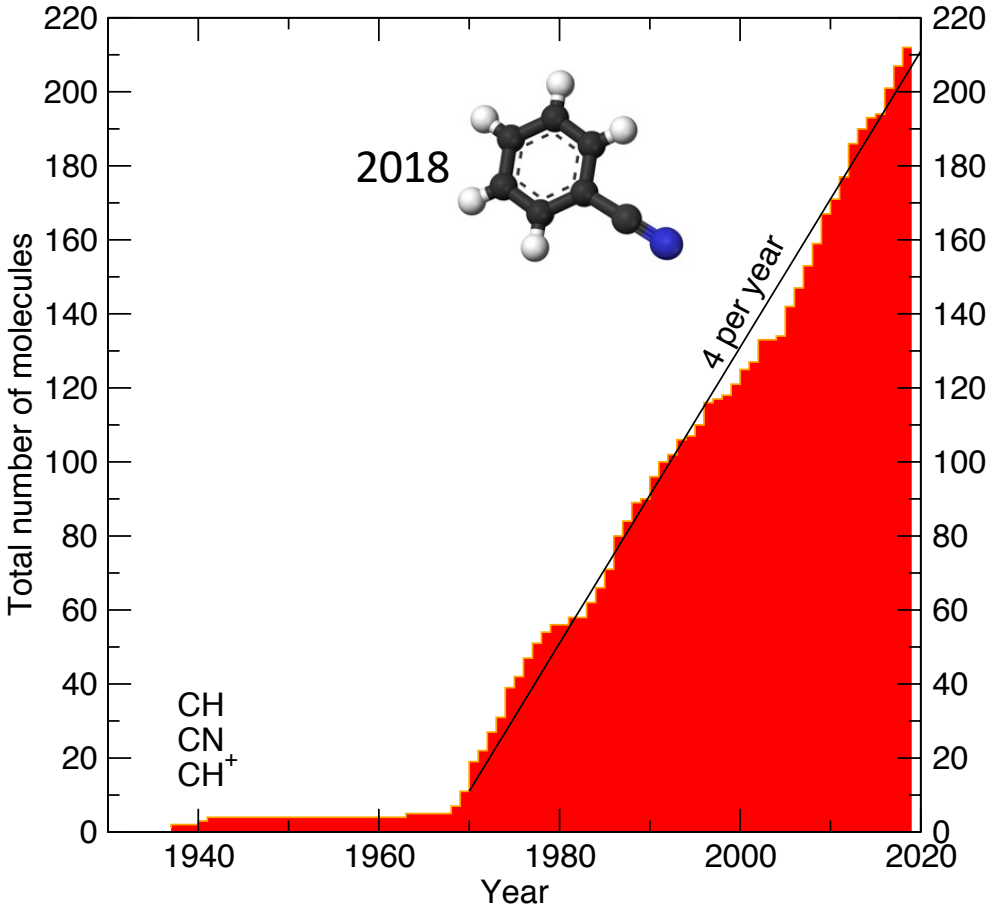
Rolf Güsten[1]*, Helmut Wiesemeyer[1], David Neufeld[2], Karl M. Menten[1], Urs U. Graf[3], Karl Jacobs[3], Bernd Klein[1,4], Oliver Ricken[1], Christophe Risacher[1,5] & Jürgen Stutzki[3]

HeH^+ @149.1 μm towards NGC 7027

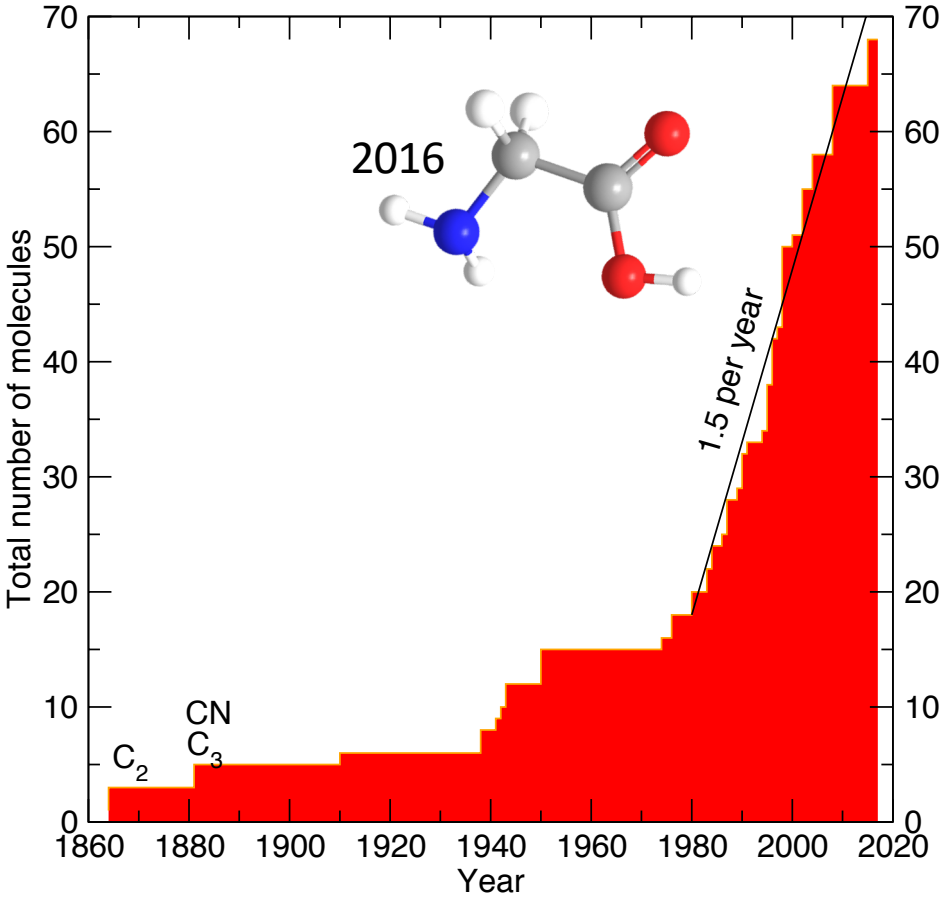


Astrochemistry: 50 years of discoveries

ISM



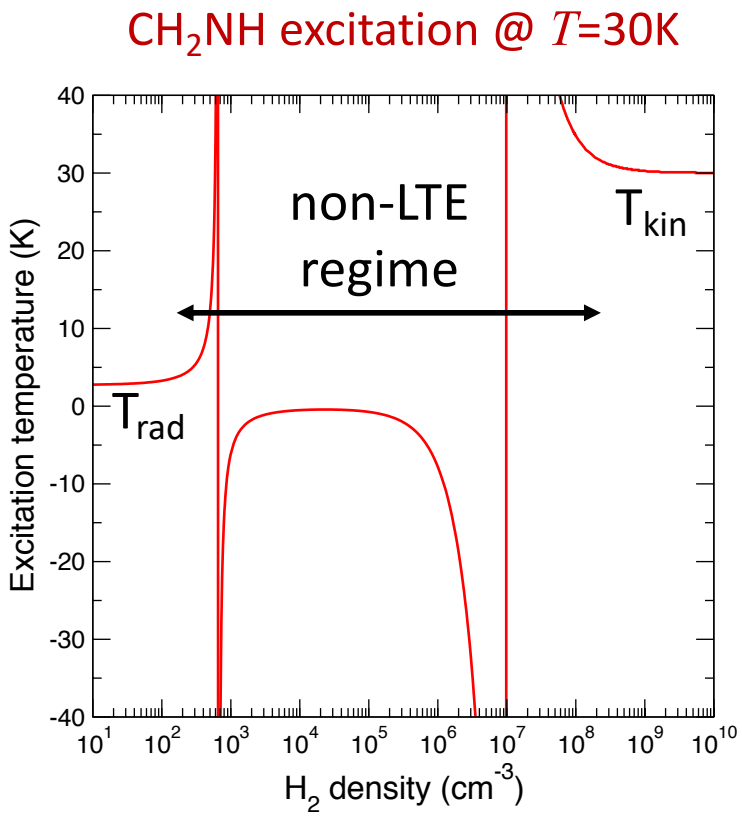
Comets



Source: http://www.astrochymist.org/

Non-local-thermodynamic-equilibrium (non-LTE)

- Pressure in the ISM are very low (< 10^{-10} mbar)
- Inelastic collisions are insufficient to maintain LTE
- Deviations from LTE, e.g. masers, are natural in space



Collisional data

- Interpreting a spectra requires to solve:
  - the radiative transfer
  - the statistical equilibrium

- Molecular data:
  - energies of levels
  - radiative rates (s^{-1})
  - collisional rate coefficients (cm^3s^{-1})

Colliding partners in the ISM

particle	$CO(j) + e^-$	$\rightarrow CO(j') + e^-$
atom	$CO(j) + H$	$\rightarrow CO(j') + H$
atom	$CO(j) + He$	$\rightarrow CO(j') + He$
molecule	$CO(j) + H_2(j_2)$	$\rightarrow CO(j') + H_2(j_2')$

Rotational energy transfer

- Cross sections and rate coefficients
  - heavy particles $\sigma \sim 10$ Å^2 $k \sim 3*10^{-11}$ cm^{3}s^{-1}
  - electrons $\sigma \sim 3000$ Å^2 $k \sim 10^{-6}$ cm^{3}s^{-1}

- Collision timescales (<< chemistry in general)
  - heavy particles t ~ 1 week (dense ISM)
  - electrons t ~ 1 year (diffuse ISM)

I. COLLISIONAL EXCITATION

Methods

- Scattering theory
  - Electronic Schrödinger equation (CCSD(T)/CBS)
  - Nuclei dynamics
    - Quantum close-coupling method
    - Classical, mixed quantum/classical or statistical methods
      - Loreau, Lique, Faure *ApJL* (2018)

- Experiment
  - Crossed molecular beams (relative cross sections)
  - Double resonance (absolute rate coefficients)
  - Raman spectroscopy
  - Pressure broadening

Experimental breakthrough

PRL **109,** 023201 (2012) PHYSICAL REVIEW LETTERS week ending 13 JULY 2012

Appearance of Low Energy Resonances in CO–*Para*-H_2 Inelastic Collisions

Simon Chefdeville,[1,2] Thierry Stoecklin,[1,2] Astrid Bergeat,[1,2] Kevin M. Hickson,[1,2] Christian Naulin,[1,2] and Michel Costes[1,2,*]

[1]*Université de Bordeaux, Institut des Sciences Moléculaires, F-33400 Talence, France*
[2]*CNRS, UMR 5255, F-33400 Talence, France*

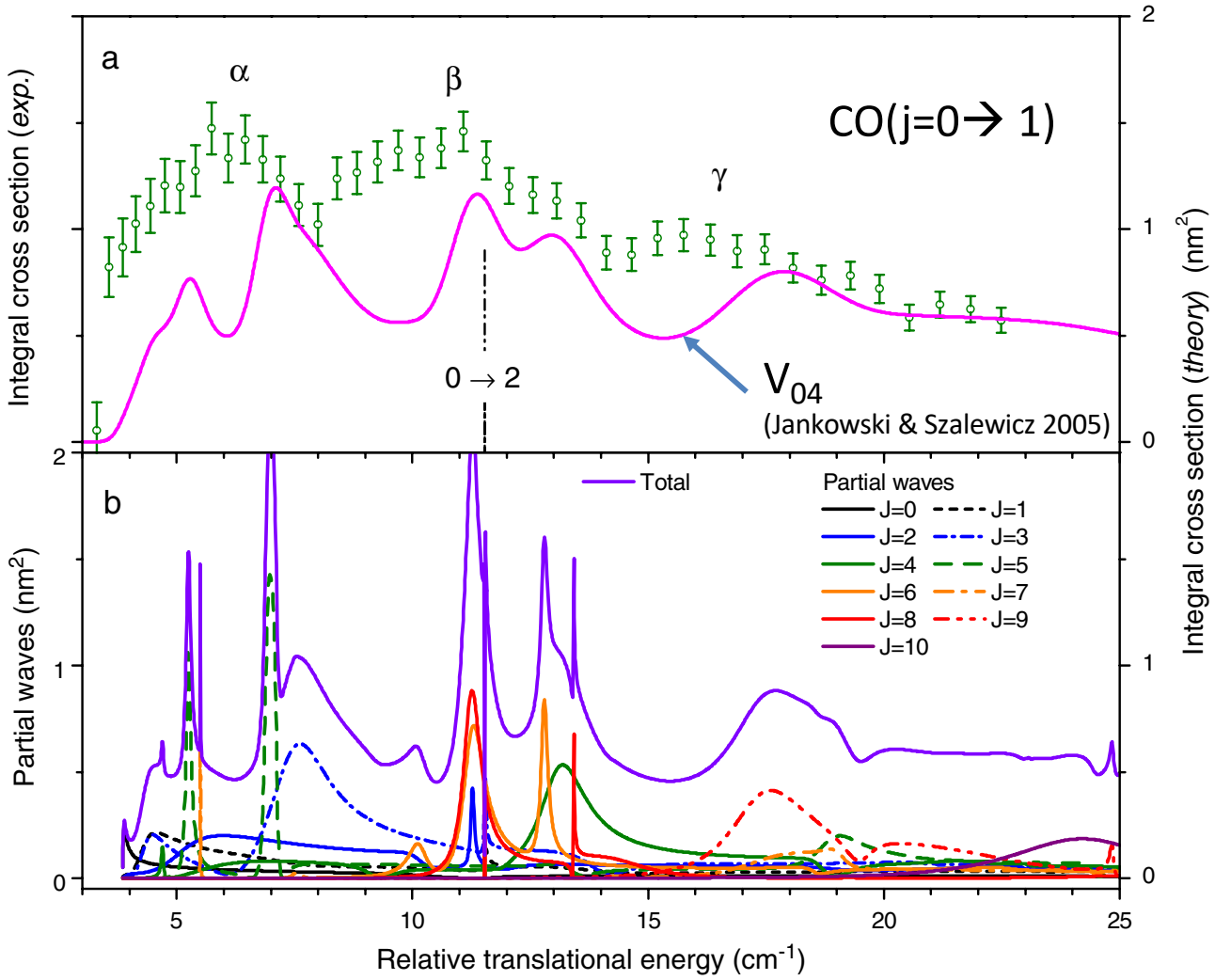
(Received 24 April 2012; published 11 July 2012)

We report on crossed-beam experiments and quantum-mechanical calculations performed on the $CO(j = 0) + H_2(j = 0) \rightarrow CO(j = 1) + H_2(j = 0)$ system. The experimental cross sections determined in the threshold region of the $CO(j = 0 \rightarrow j = 1)$ transition at 3.85 cm^{-1} show resonance structures in good qualitative agreement with the theoretical ones. These results suggest that the potential energy surface which describes the CO-H_2 van der Waals interaction should be reinvestigated for good quantitative agreement.

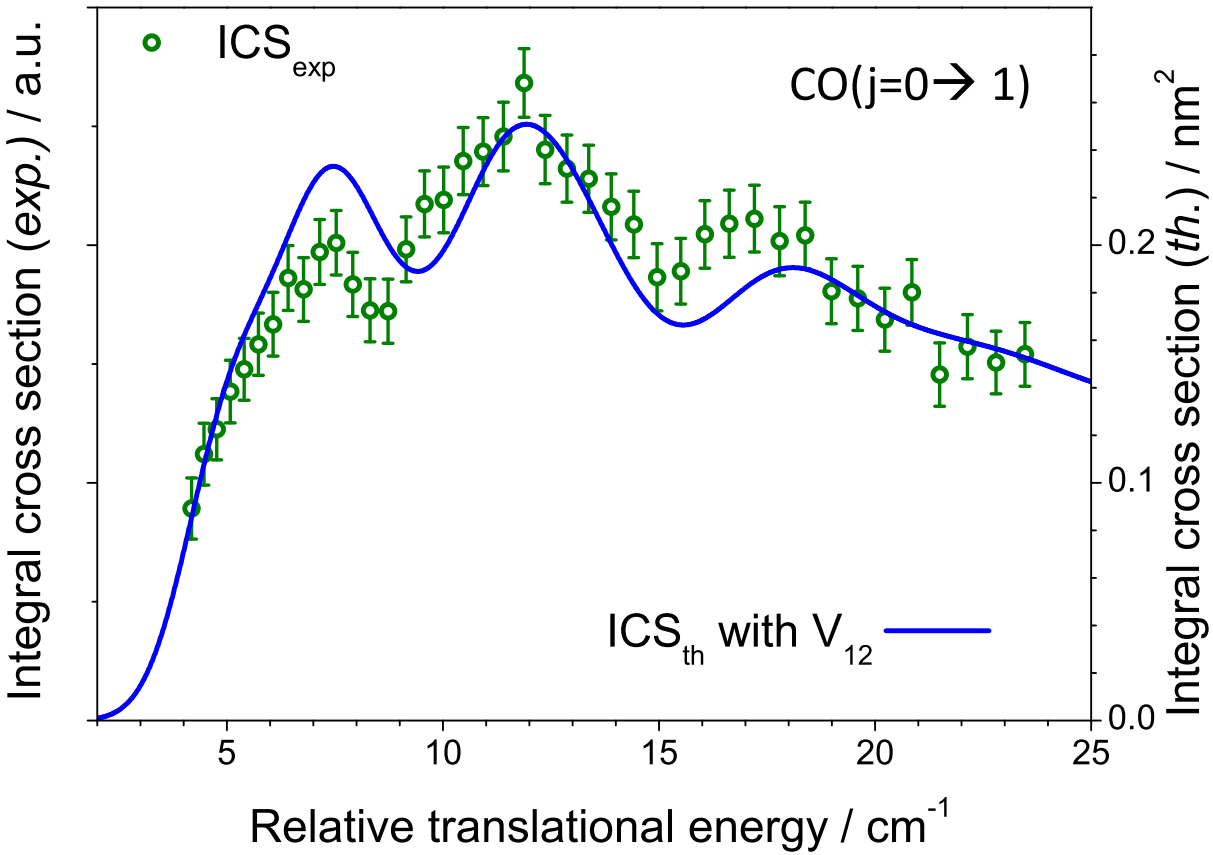
DOI: 10.1103/PhysRevLett.109.023201 PACS numbers: 34.50.Ez, 34.10.+x, 37.20.+j

‘The PES […] should be reinvestigated for good quantitative agreement’

Chefdeville et al. *PRL* (2012)



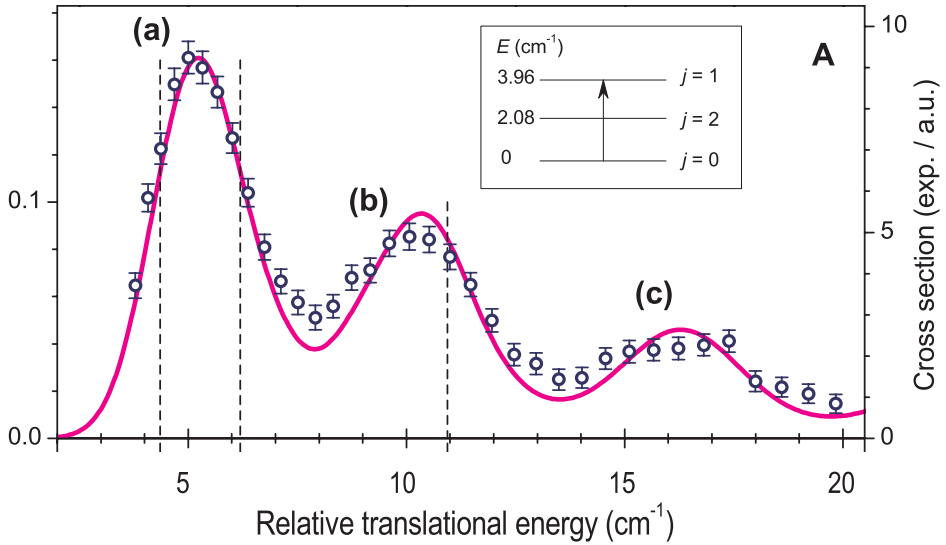
Revised results (2015)



Chefdeville et al. *ApJL* (2015)

Other results: oxygen and water

O_2 ($1_0 \rightarrow 1_1$) by pH_2



Chefdeville et al., *Science* (2013)

D_2O ($0_{00} \rightarrow 2_{02}$) by pH_2

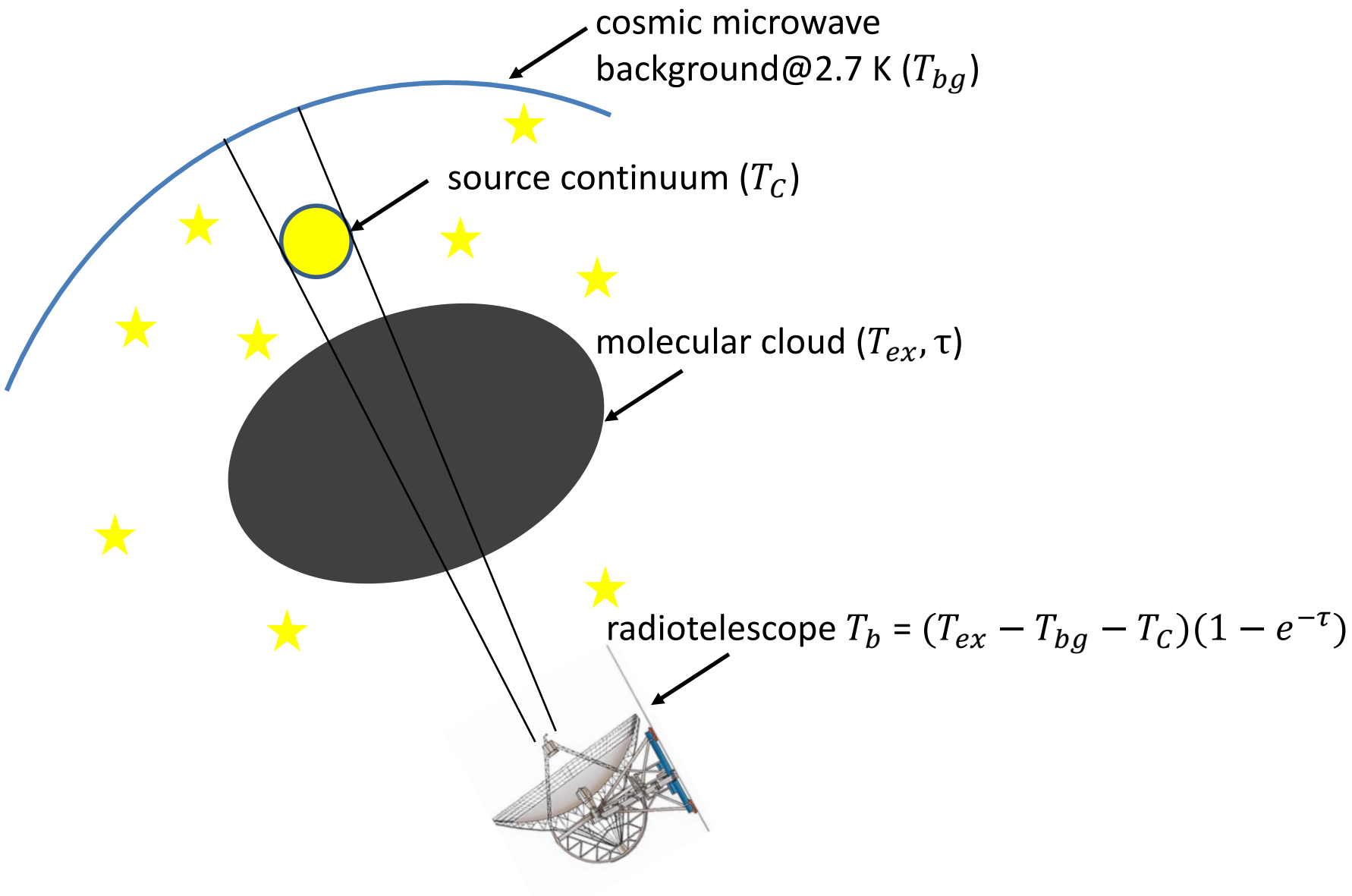
Bergeat et al., in prep.

CO-H_2 @ CRESU (5-20 K)

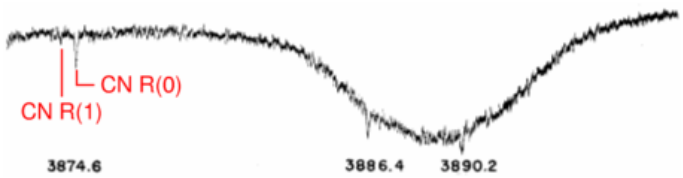
Labiad et al., in preparation

II. MOLECULAR DIAGNOSTICS

Molecules as probes



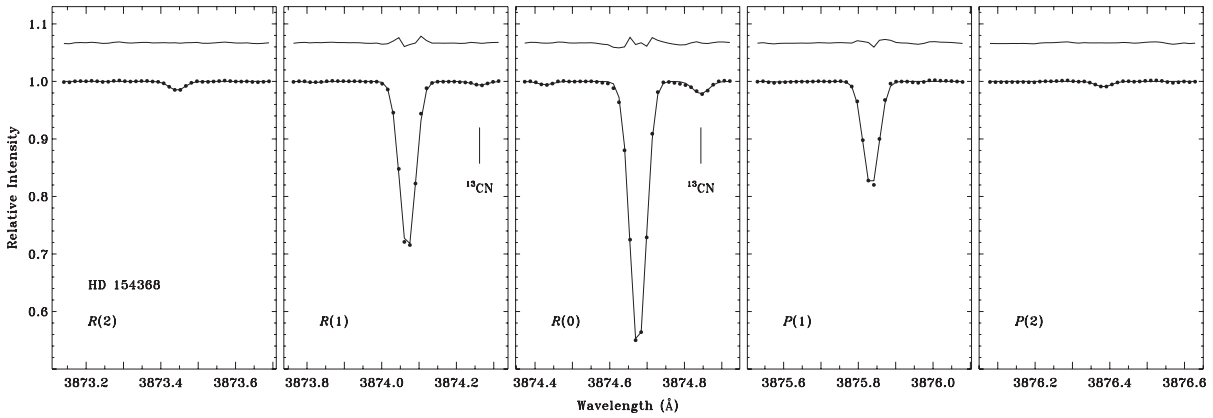
CN absorption in diffuse clouds



MWO, McKellar (1940)

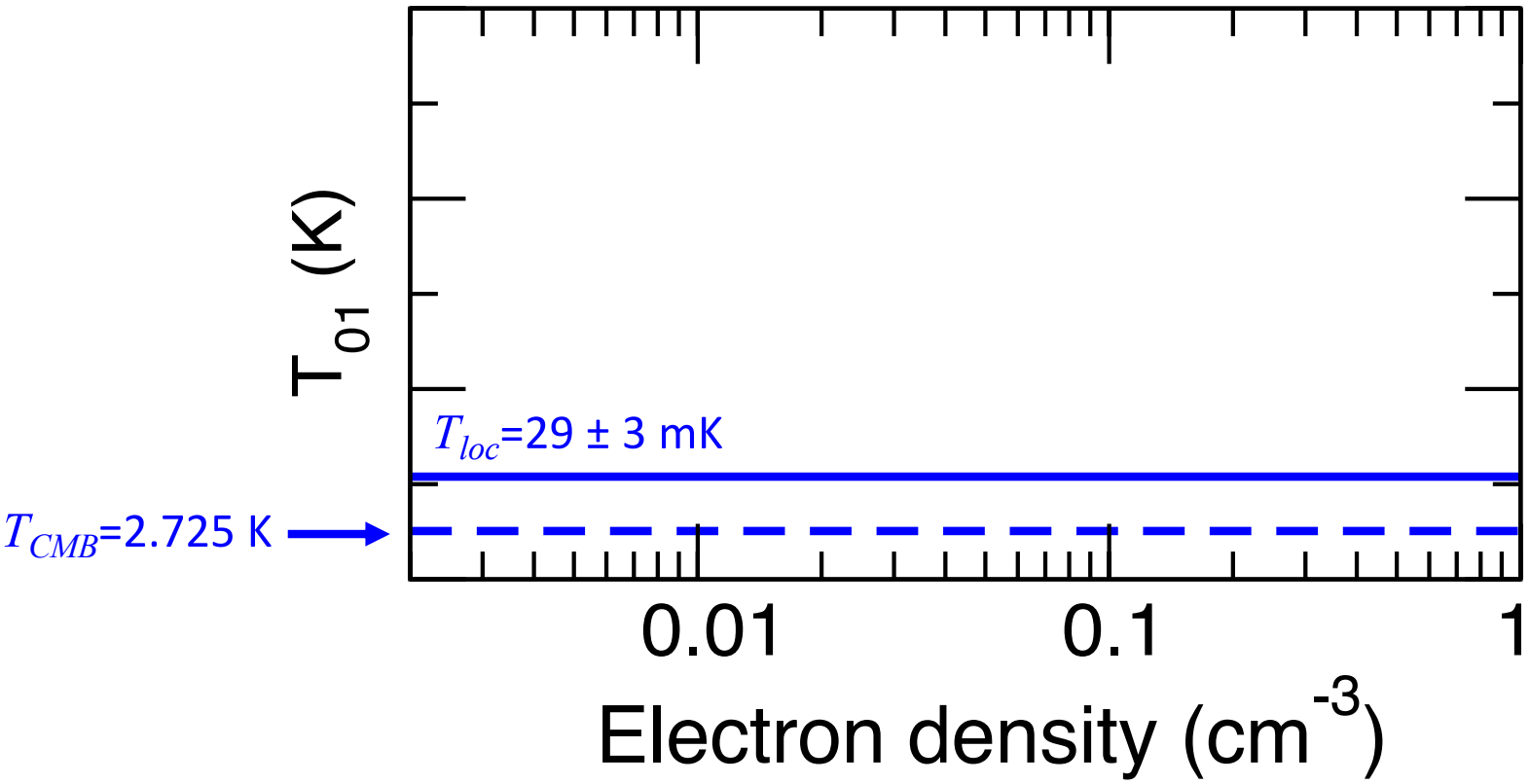
'From the intensity of the lines [of CN] a rotational temperature of 2.3K follows, which has of course only a restricted meaning.'

G. Herzberg (1950)

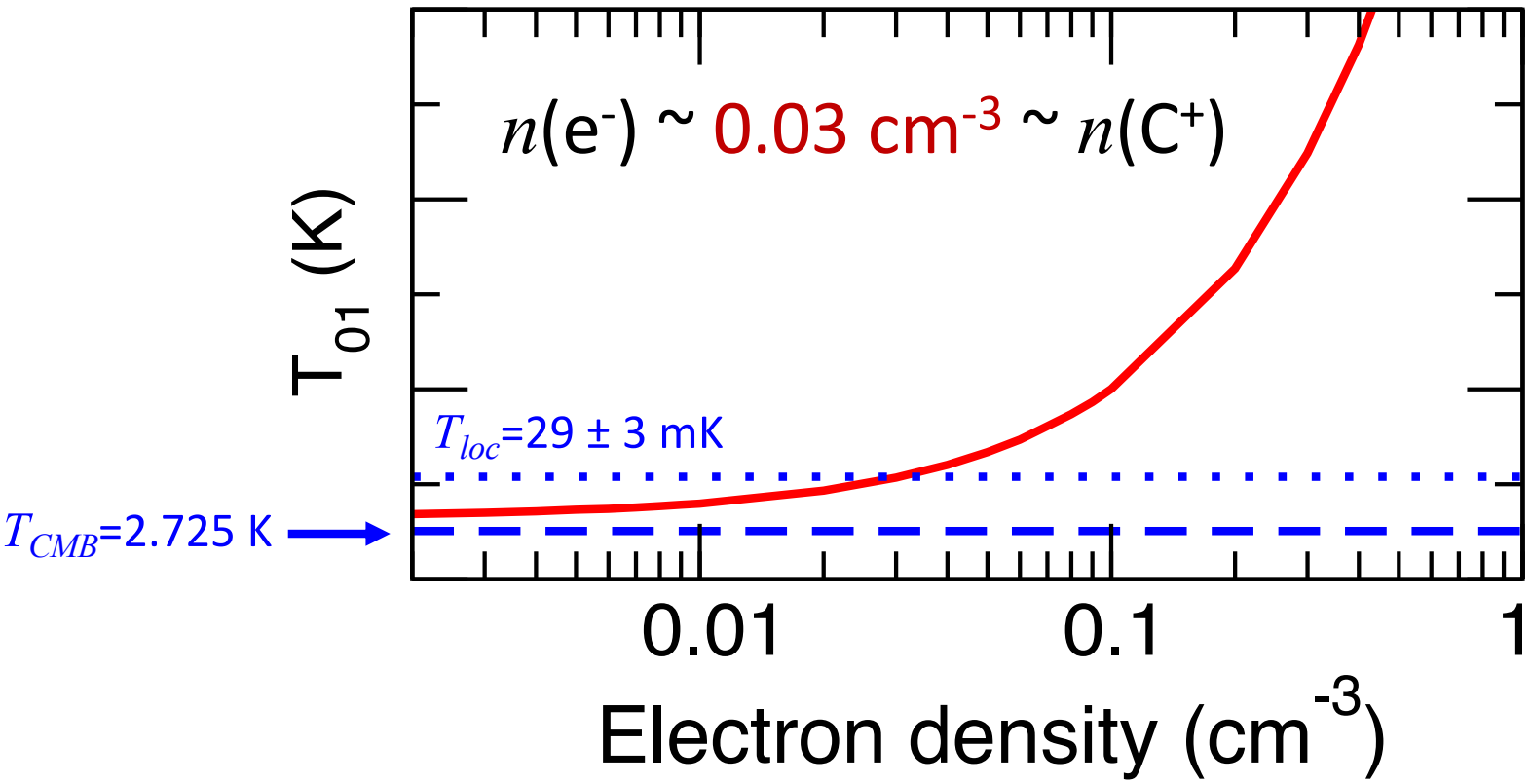


VLT, Ritchey et al. (2011)

CN as a probe of electron density



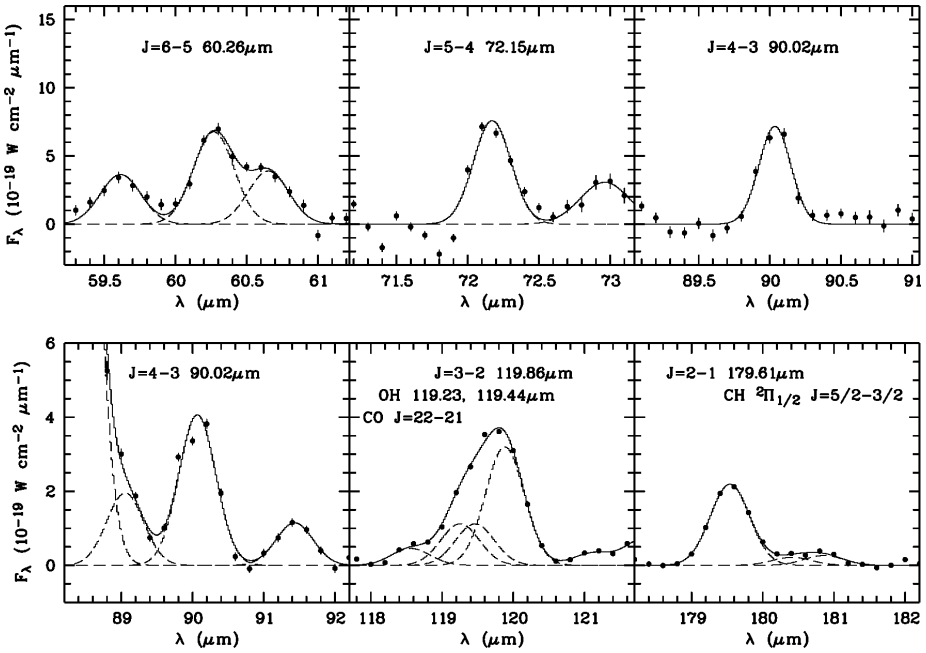
CN as a probe of electron density



Harrison, Faure & Tennyson *MNRAS* (2013)

CH^+ emission in Photon Dominated Regions

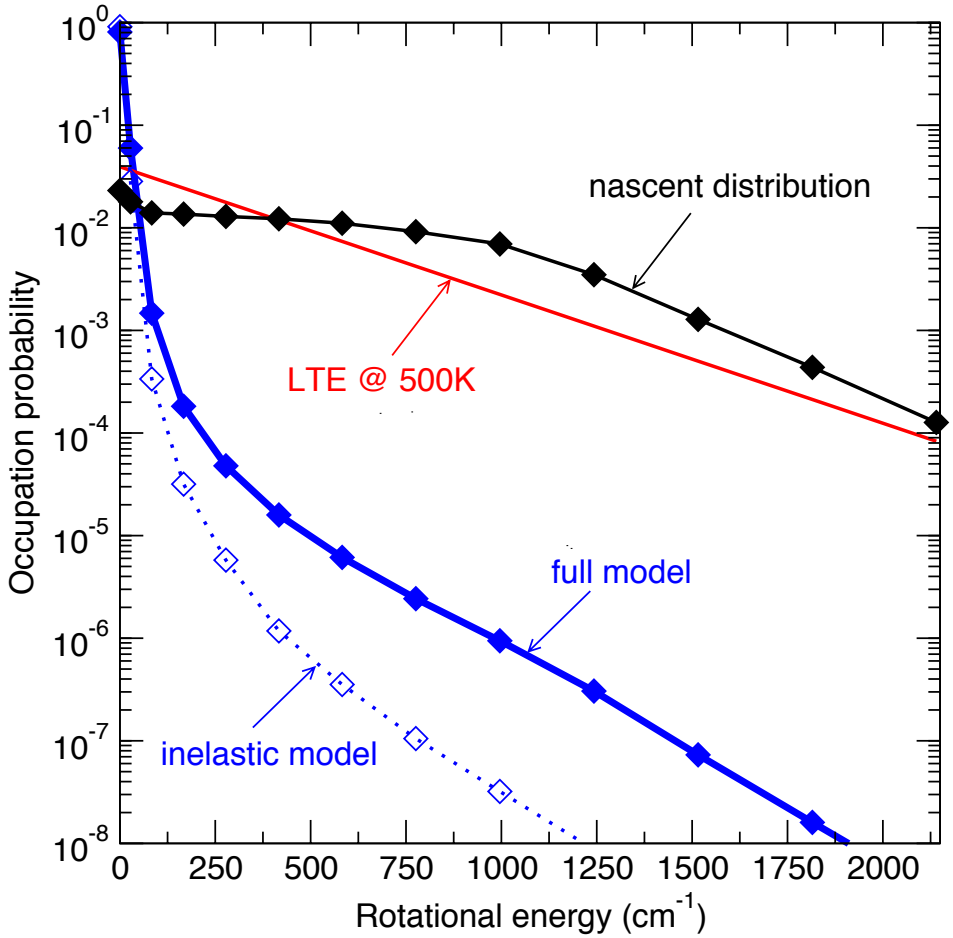
- CH^+ ubiquity is an enigma:
  - $C^+ + H_2$ endothermic (4620 K)
  - CH^+ is destroyed by H, H_2, e^-
- In PDR, the UV field can provide a reservoir of rovibrationally excited H_2



Cernicharo et al. *ApJ* (1997)
[here toward NGC 7027]

Need for state-to-state chemistry

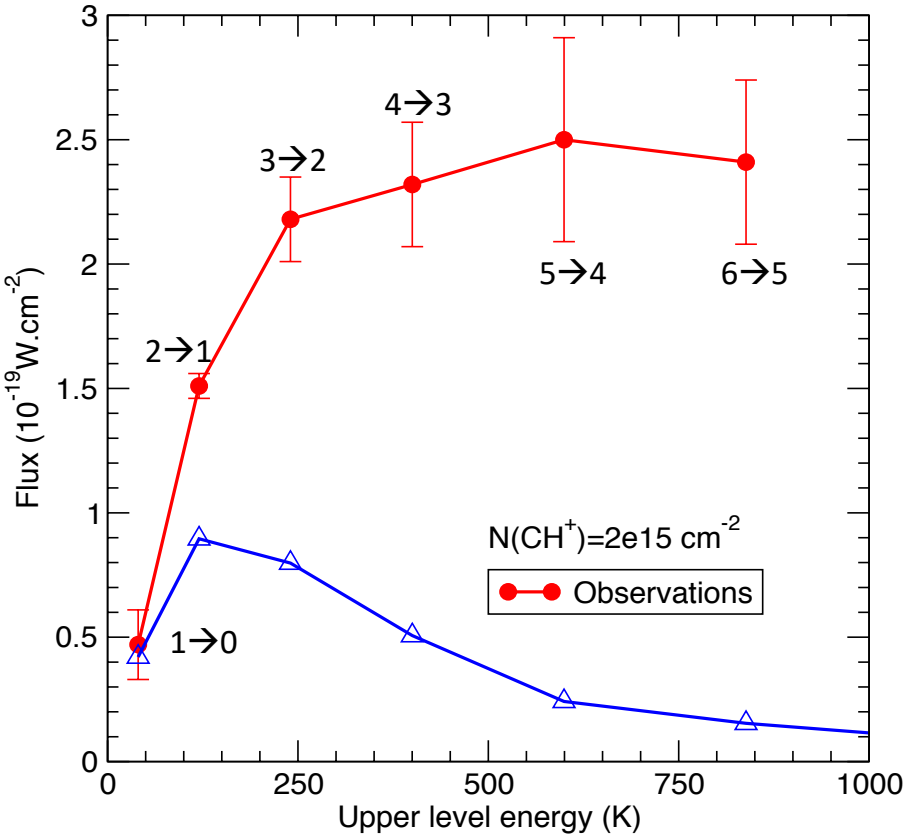
- « Chemical » pumping is crucial for short-lived i.e. reactive species
- State-resolved data from quantum and quasi-classical calculations



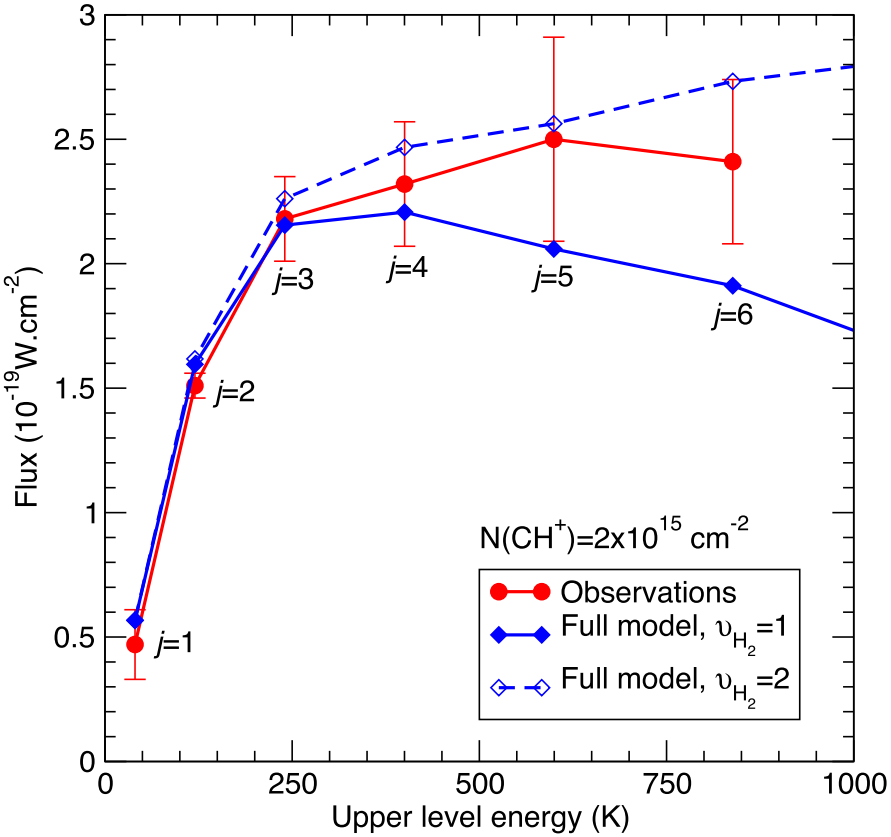
Faure et al. *MNRAS (2017)*

CH^+ as a tracer of $H_2(v>0)$

Inelastic model



Reactive model



Faure et al. *MNRAS* (2017)

Methanimine (CH_2NH) in the galactic center

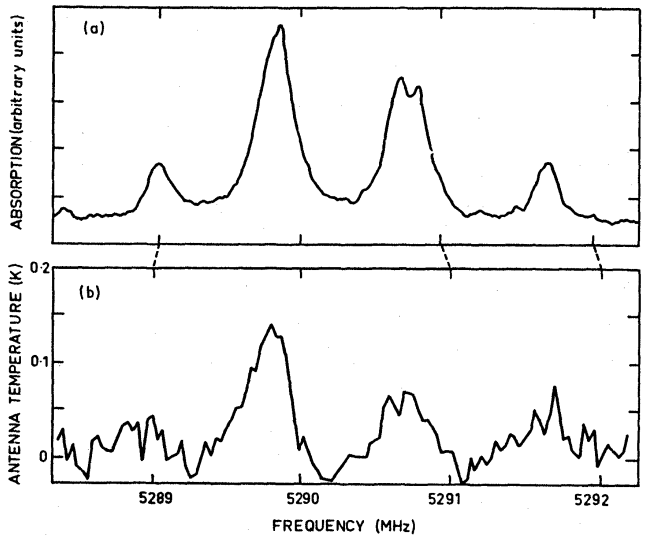
Astrophysical Letters, 1973, Vol. 13, pp. 119–121

Discovery of Interstellar Methanimine (Formaldimine†)

P. D. GODFREY and R. D. BROWN *Department of Chemistry, Monash University, Melbourne, Australia*

B. J. ROBINSON and M. W. SINCLAIR *Division of Radiophysics, CSIRO, Sydney, Australia*

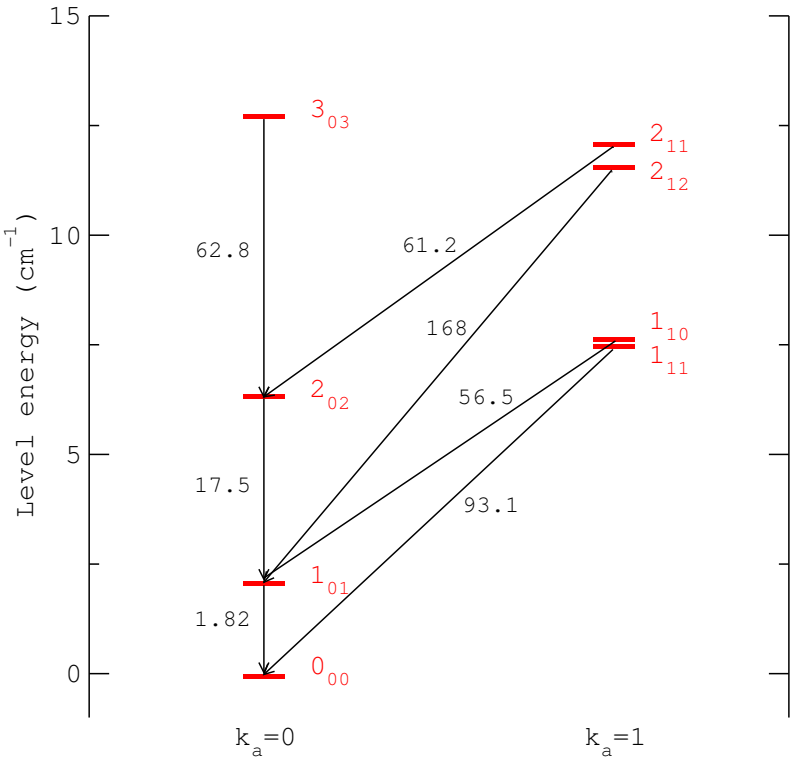
The 1_{10}–1_{11} transition of methanimine $H_2C{=}NH$ has been detected in emission in the spectrum of Sagittarius B2 with the Parkes 64-m telescope. The frequencies of the observed multiplet, near 5.290 GHz, agree well with the multiplet detected in the laboratory, if a radial velocity of 63 ± 2 km sec^{-1} is adopted for the Sgr B2 emission.

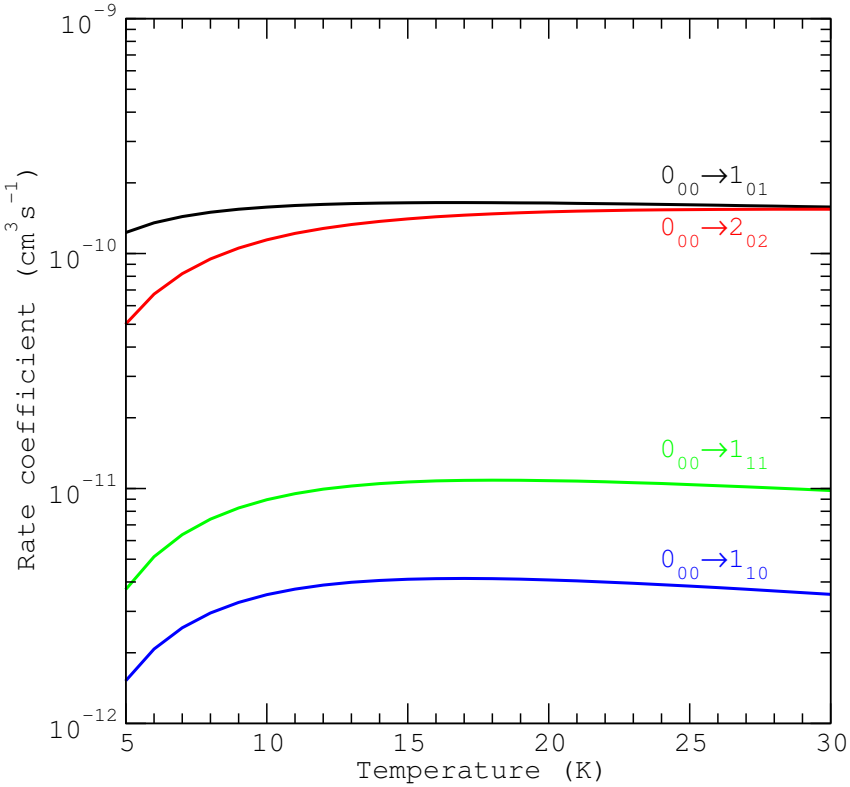


Laboratory

Observation

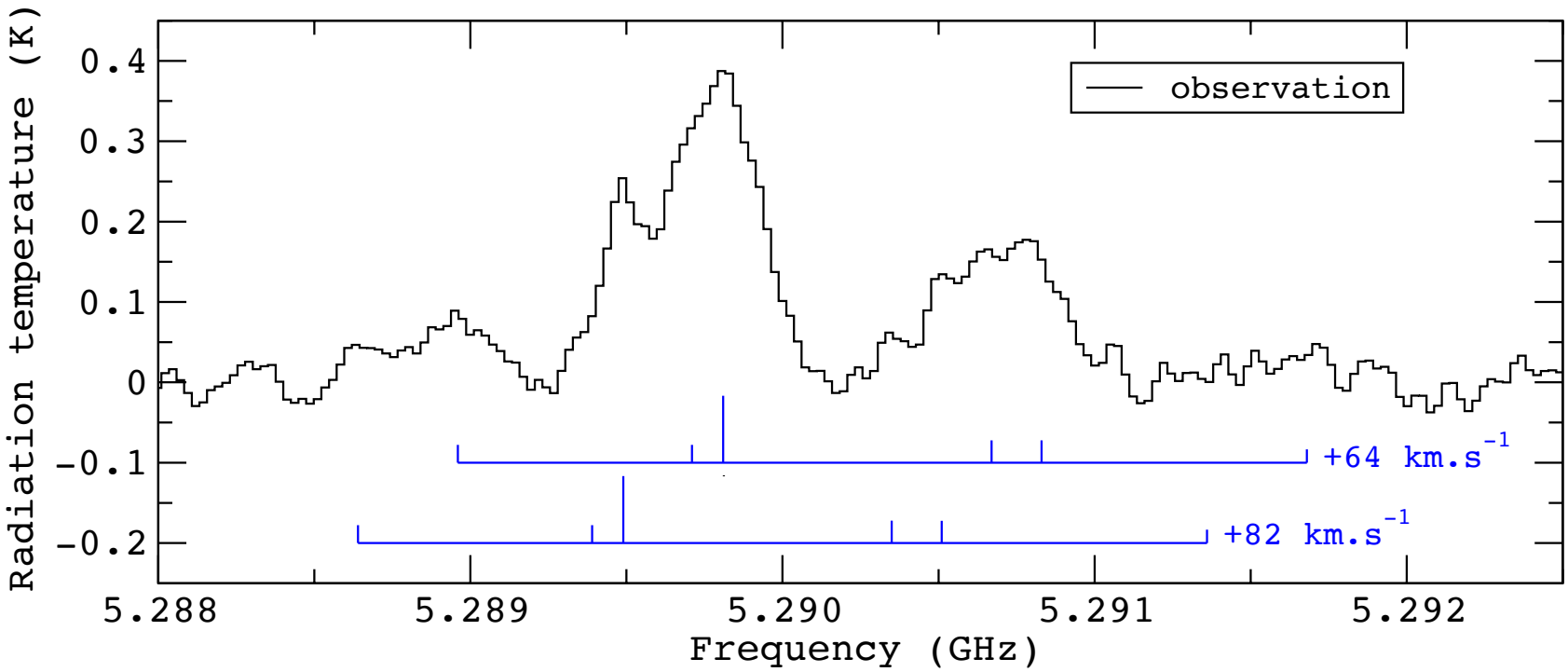
CH_2NH selection / propensity rules





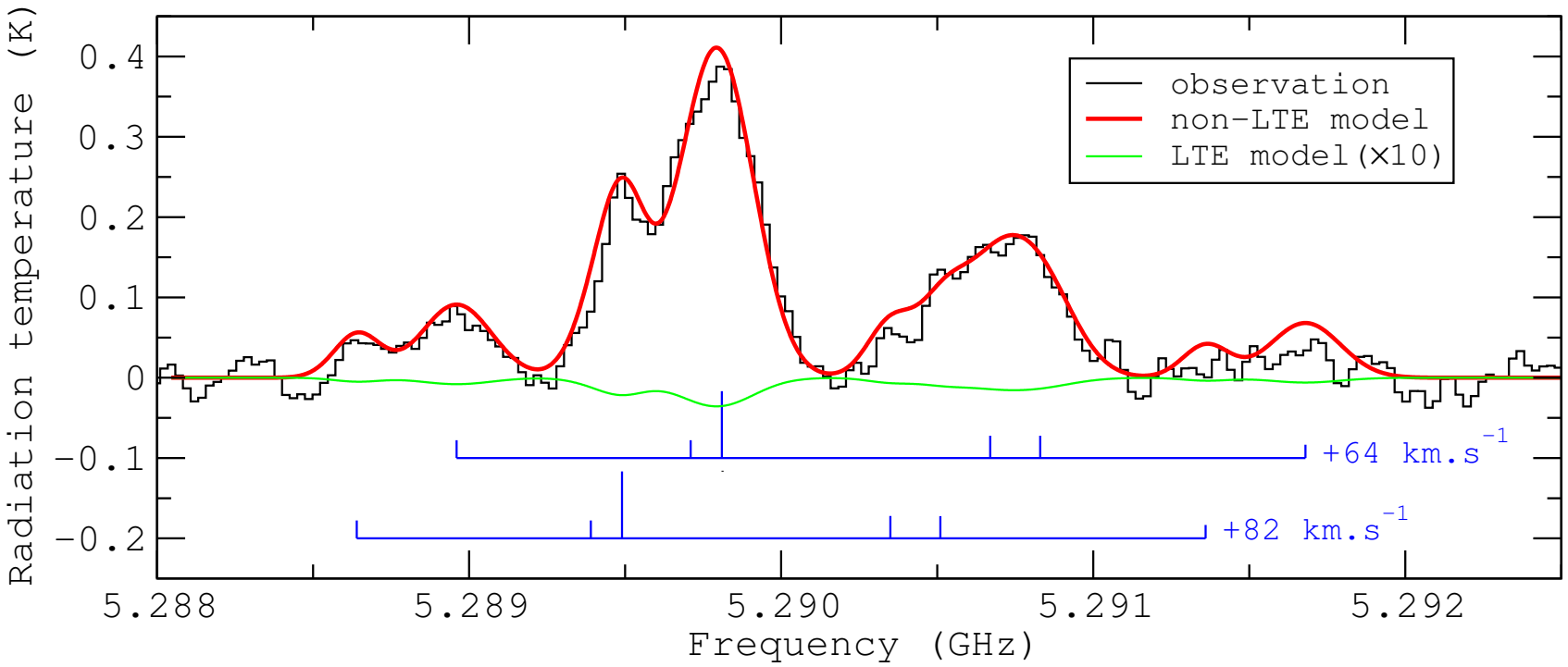
Faure et al. *J. Phys. Chem. Lett.* (2018)

New GBT observations



Faure et al. *J. Phys. Chem. Lett.* (2018)

CH_2NH probes a cold dilute gas (T ~ 30K, n ~ 10^4 cm^{-3})



Faure et al. *J. Phys. Chem. Lett.* (2018)

CONCLUSIONS

Conclusions

- Interaction potentials have now reached a high level of refinement
- Collision data are no longer a limiting factor in the modelling of non-LTE spectra
- Strongly non-LTE situations offer new diagnostics, e.g. masers → SKA

Current / future works

(April 2019)

ACS EARTH AND SPACE CHEMISTRY

Article

Cite This: *ACS Earth Space Chem.* XXXX, XXX, XXX–XXX

http://pubs.acs.org/journal/aesccq

Interaction of Chiral Propylene Oxide (CH_3CHCH_2O) with Helium: Potential Energy Surface and Scattering Calculations

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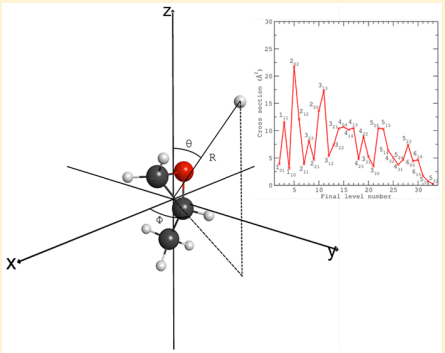
Supporting Information

ABSTRACT: The first chiral interstellar organic molecule, propylene oxide (CH_3CHCH_2O), was detected recently toward the galactic center. Accurate determination of its abundance relies on the knowledge of collisional cross sections. We investigate here the rotational excitation of propylene oxide induced by collisions with helium. The calculations are based on a three-dimensional CH_3CHCH_2O−He potential energy surface computed using the explicitly correlated coupled-cluster theory extended to the complete basis set limit [CCSD(T)-F12b/CBS]. The interaction energies are fitted using an interpolating moving least squares method, and this potential is refitted using a partial wave expansion based on spherical harmonics. Rotational cross sections are obtained at the quantum close-coupling level for a collision energy of 10 cm^{-1}. Convergence issues and collisional propensity rules are discussed.



KEYWORDS: *astrochemistry, organic molecules, chirality, energy transfer, quantum scattering*

Current / future works

- Organics
  - Nitriles, HC_2NC, HC_5N, C_6H_5CN
  - Ro-vibration (HCN, HC_3N) → JWST
- Reactive ions
  - OH^+, SH^+, H_2O^+ (ERC COLLEXISM PI Lique)
- H_2O-molecule
  - H_2O-CO, see Loreau et al. *J Chem Phys* (2018)

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- F. Lique, I. Schneider — Le Havre
- J. Tennyson — London
- O. Roncero, A. Zanchet — Madrid
- K. Szalewicz — Newark
- L. Wiesenfeld — Orsay
- H. Labiad, S. Le Picard, I. Sims — Rennes
- P. Jankowski — Torun

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