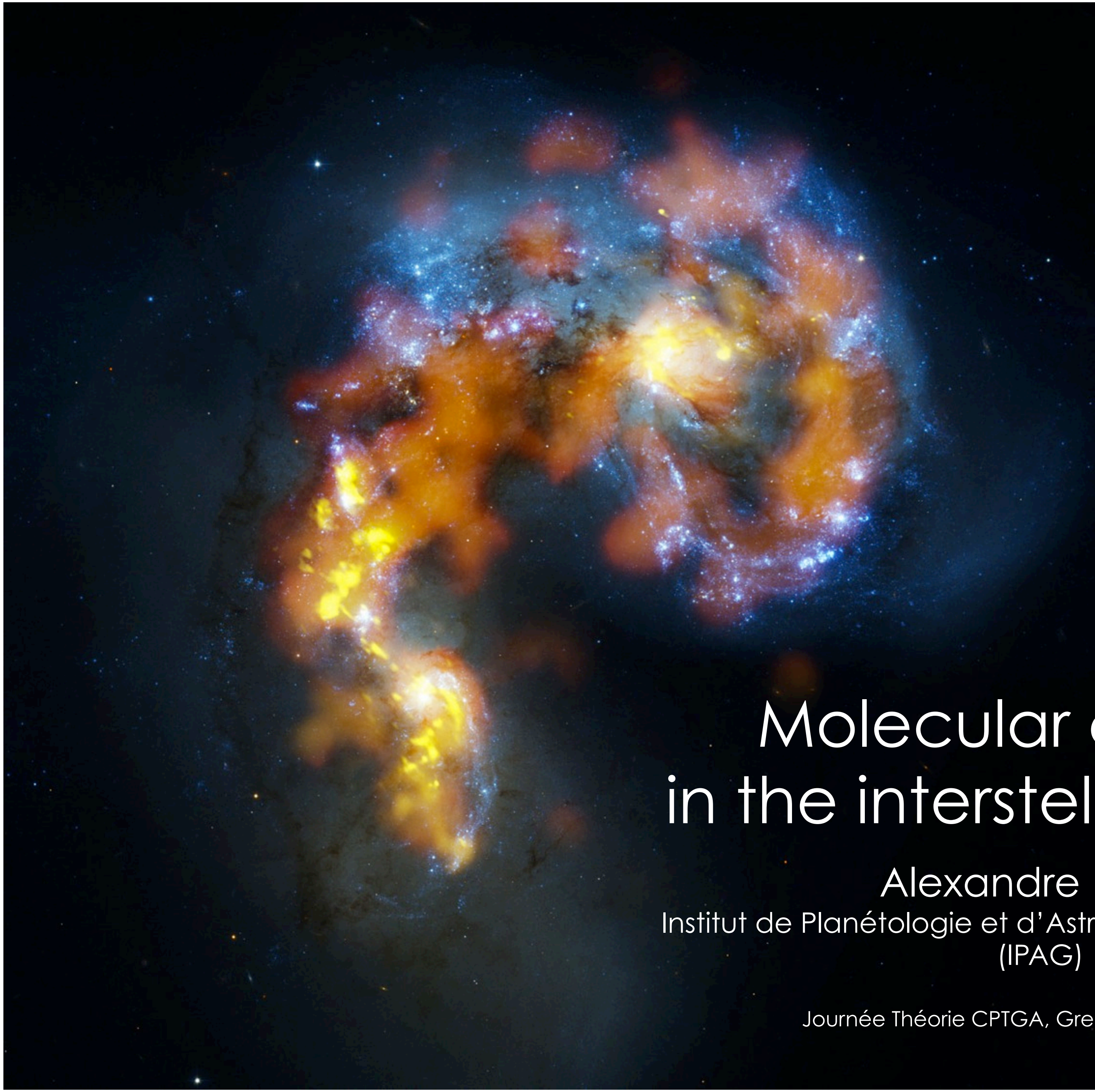

Molecular collisions in the interstellar medium

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Journée Théorie CPTGA, Grenoble, 7 april 2014

Outline

1. Interstellar molecules
2. Molecular excitation
3. Collisions out of equilibrium
4. Conclusions

1. Interstellar molecules

Molecular clouds
the early phase of star formation

- Ultra high-vacuum

  $n \sim 10^4$ cm^{-3}
  ($P \sim 10^{-13}$ mbar !)

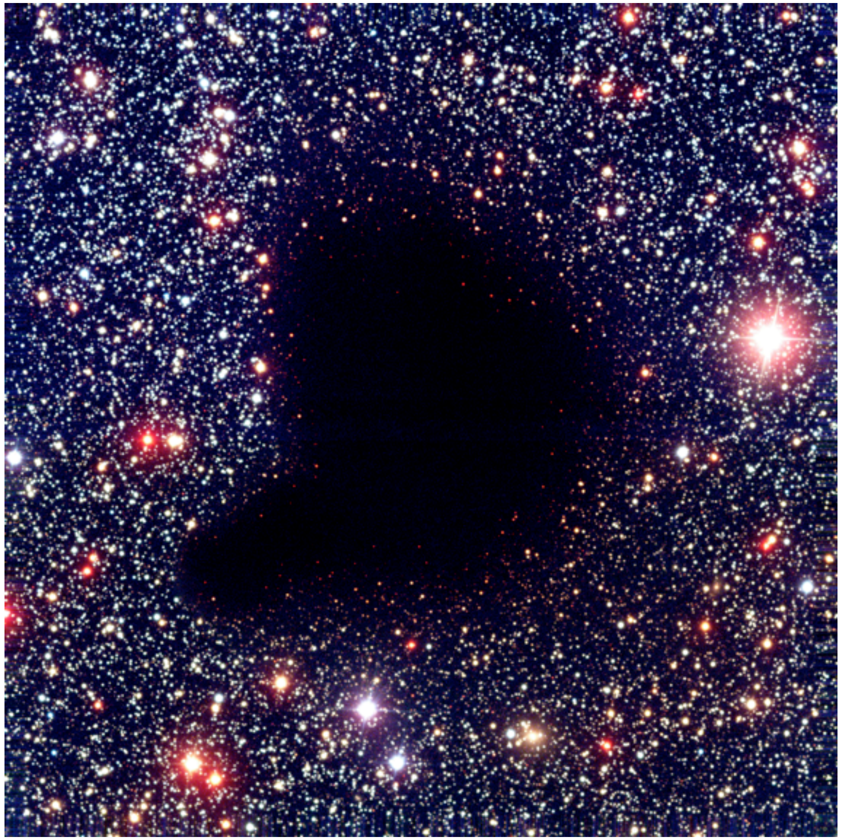
- Cold

  $T \sim 10$ K

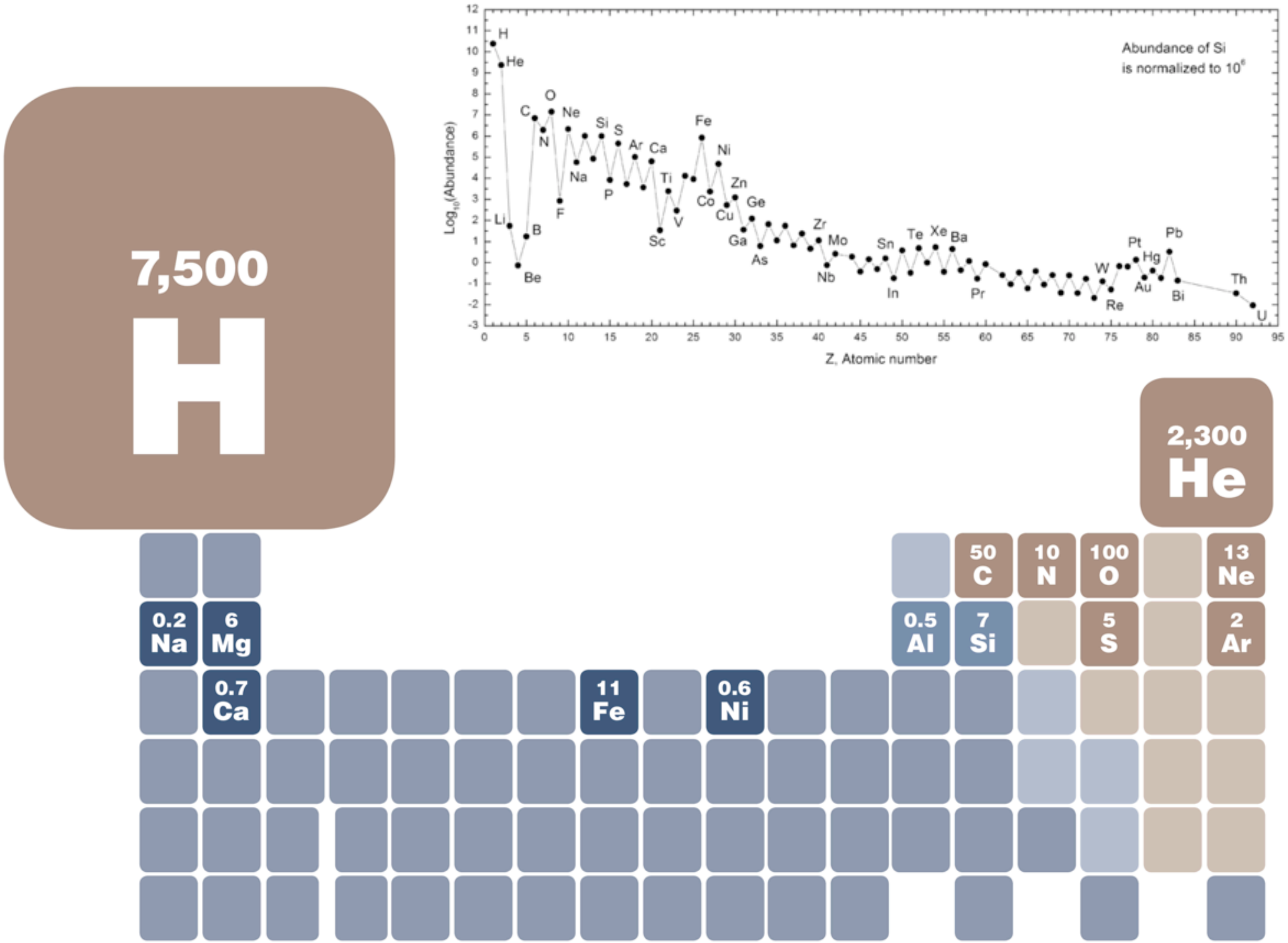
- Ionized

  $\xi(H_2) \sim 10^{-17}$ s^{-1}

  $x_e \sim 10^{-8}$



The periodic table for Astronomy



Interstellar chemistry in a nutshell

- $H + H + \text{grain} \rightarrow H_2 + \text{grain}$
- $CR + H_2 \rightarrow H_2^+ + CR'$
- $H_2^+ + H_2 \rightarrow H_3^+ + H$

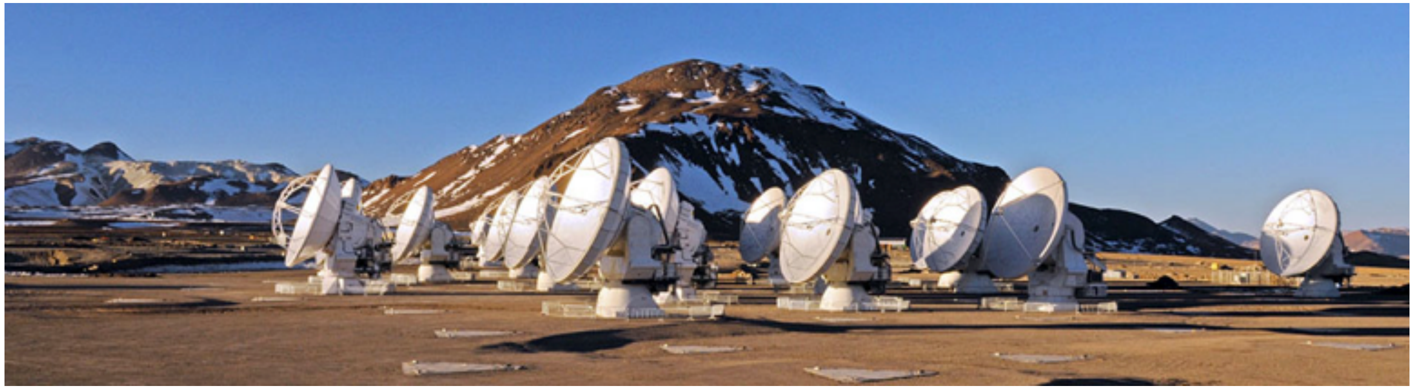
- $C + H_3^+ \rightarrow CH^+ + H_2 \rightarrow \dots e^-, H_2 \dots \rightarrow CH, CH_4$
- $O + H_3^+ \rightarrow OH^+ + H_2 \rightarrow \dots e^-, H_2 \dots \rightarrow OH, H_2O$
- $N^+ + H_2 \rightarrow NH^+ + H \rightarrow \dots e^-, H_2 \dots \rightarrow NH, NH_3$

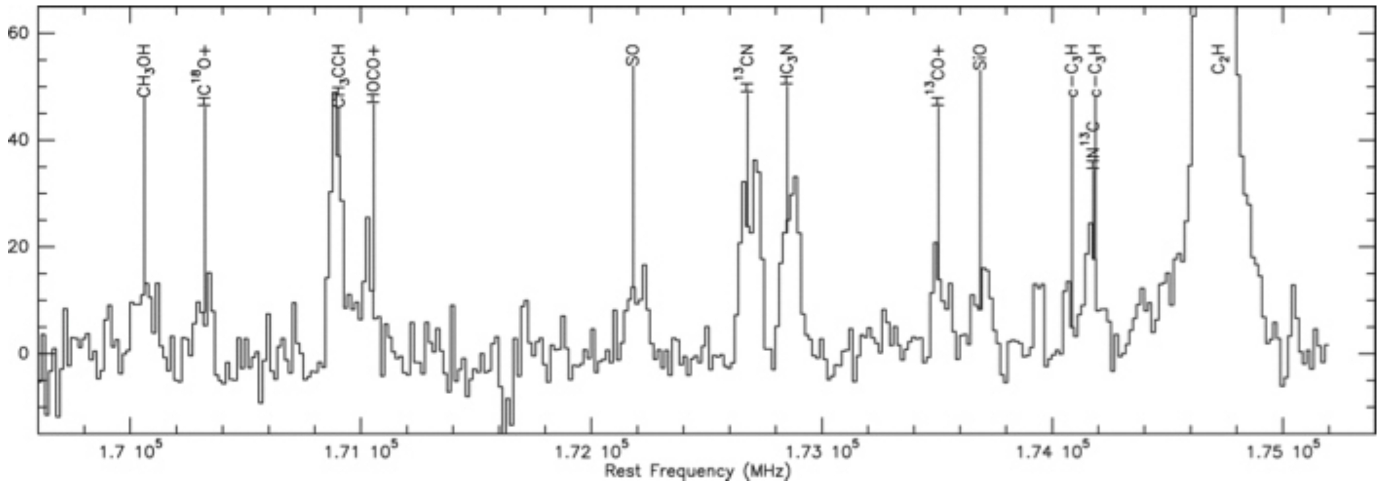
Interstellar molecules

2 atoms		3 atoms		4 atoms	5 atoms	6 atoms	7 atoms	8 atoms
H_2	CP	H_3^+	MgCN	CH_3	NH_3D^+	C_2H_4	CH_3NH_2	CH_3CHNH
LiH ?	AlO	CH_2	NaCN	NH_3	CH_4	CH_3OH	CH_3C_2H	CH_2CHCHO
CH	CS	NH_2	C_2S	H_3O^+	CH_2NH	CH_3CN	CH_3CHO	NH_2CH_2CN
CH^+	SiO	H_2O	OCS	C_2H_2	SiH_4	CH_3NC ?	*c*-C_2H_4O	CH_3COOH
NH	PN	H_2O^+	SO_2	H_2CN	CH_3O	CH_2CNH	CH_2CHOH	CH_2OHCHO
OH	NS	C_2H	*c*-SiC_2	$HCNH^+$	H_2COH^+	NHCHCN	CH_2CHCN	$HCOOCH_3$
OH^+	AlF	HCN	SiCN	H_2CO	*c*-C_3H_2	NH_2CHO	C_6H	CH_3C_3N
HF	PO	HNC	SiNC	H_2O_2	H_2C_3	CH_3SH	C_6H^-	CH_2CCHCN
C_2	SO	HCO	C_2P	PH_3 ?	CH_2CN	C_4H_2	HC_5N	C_6H_2
CN	SO^+	HCO^+	AlNC	C_3H	HNCNH	H_2C_4		H_2C_6
CN^-	NaCl	HOC^+	KCN	*c*-C_3H	H_2C_2O	HC_4N	**9 atoms**	C_7H
CO	SiS	N_2H^+	TiO_2	C_3H^+	NH_2CN	HC_3NH^+	CH_2CHCH_3	**10 atoms**
CO^+	AlCl	HNO	FeCN	HC_2N	HCOOH	HC_2CHO	CH_3OCH_3	CH_3COCH_3
N_2	TiO	HO_2		HNCO	C_4H	*c*-H_2C_3O	CH_3CH_2OH	$OHCH_2CH_2OH$
NO	FeO ?	H_2S		HCNO	C_4H^-	C_5H	CH_3CH_2CN	CH_3CH_2CHO
CF^+	KCl	H_2Cl^+		HOCN	HC_3N	C_5N	CH_3CONH_2	CH_3C_5N
SiH ?		HCP		HCO_2^+	HC_2NC	C_5N^-	CH_3C_4H	**11 atoms**
O_2		N_2O		H_2CS	HNC_3		C_8H	C_2H_5OCHO
SH		AlOH		C_3N	CNCHO		C_8H^-	CH_3COOCH_3
SH^+		CO_2		C_3N^-	C_5		HC_7N	CH_3C_6H
HCl		HCS^+		C_3O		**>12 atoms**		HC_9N
HCl^+		C_2O		HNCS		$HC_{11}N$		**12 atoms**
SiC		C_3		HSCN		$C_{14}H_{10}^+$?		$C_2H_5OCH_3$?
SiN		MgNC		*c*-SiC_3		C_{60}		C_3H_7CN
				C_3S		C_{60}^+		C_6H_6
						C_{70}		

Credit: Agundez & Wakelam,Chem. Rev. 2013

Microwave observations





Credit: ESO, ALMA

Radiative transfer

- RT equation $$\frac{dI_\nu}{ds} = -\alpha_\nu(\vec{r})I_\nu + j_\nu(\vec{r})$$
- Statistical equilibrium $$\begin{cases} \frac{dn_1}{dt} = -n_1(B_{12}\bar{J} + C_{12}) + n_2(A_{21} + B_{21}\bar{J} + C_{21}) \\ \frac{dn_2}{dt} = n_1(B_{12}\bar{J} + C_{12}) - n_2(A_{21} + B_{21}\bar{J} + C_{21}), \end{cases}$$
- Excitation temperature $$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\frac{h\nu}{kT_{\mathrm{ex}}}}$$
- Antenna temperature $$\Delta T_a^* = [J_\nu(T_{ex}) - J_\nu(T_{cmb}) - T_c](1 - e^{-\tau})$$

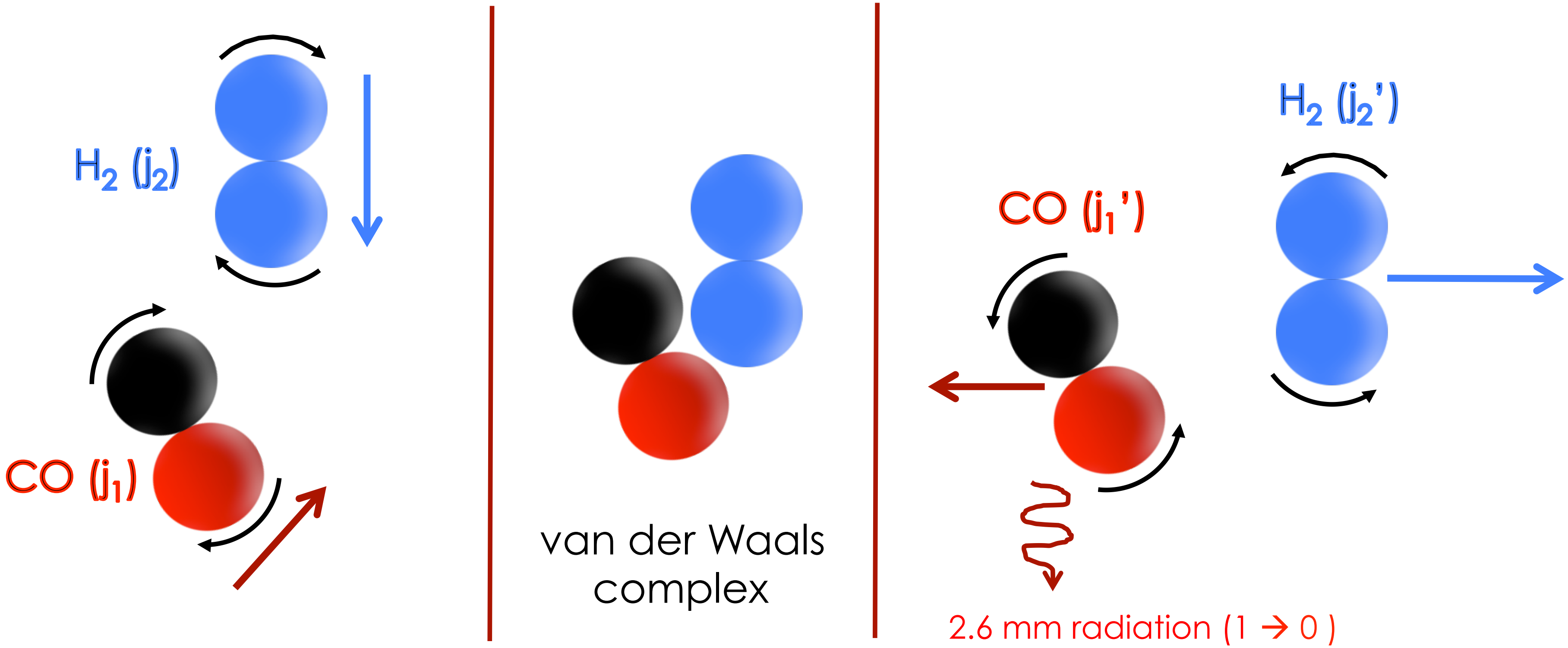
  with $J_\nu(T) = (h\nu/k_B)/(e^{h\nu/k_B T} - 1)$.

Excitation temperature

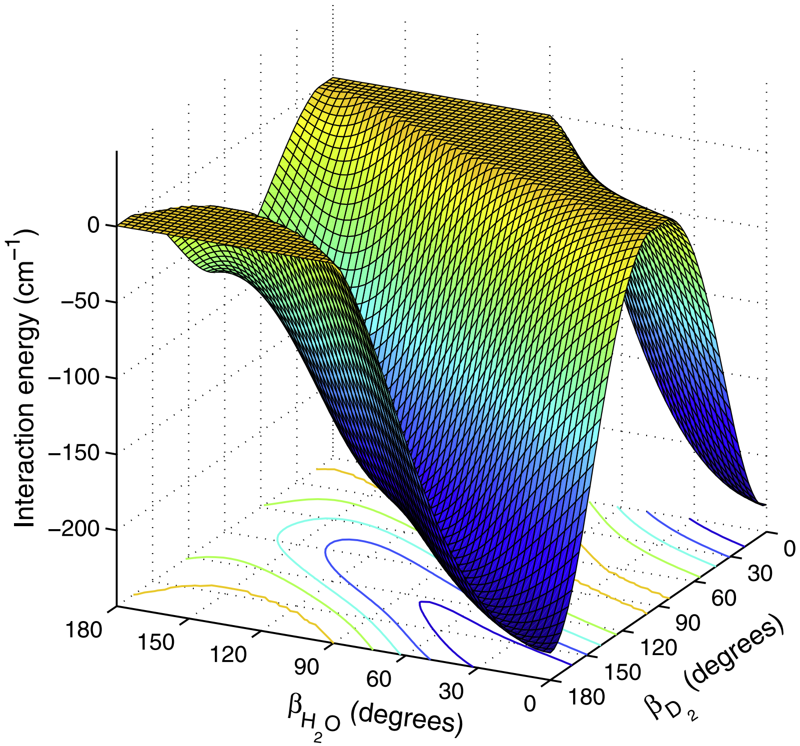
- $T_{ex} = T_{kin}$ Local thermodynamical equilibrium
- $T_{ex} = T_{rad}$ Radiative equilibrium
- $T_{ex} < T_{kin}$ sub-thermal excitation
- $T_{ex} < 0$ population inversion (maser)
- $T_{ex} < T_{rad}$ anti-inversion (cooling)

2. Molecular excitation

Molecular energy transfer at low energy (E_C <100 cm^{-1})



Theoretical framework: Born-Oppenheimer approximation



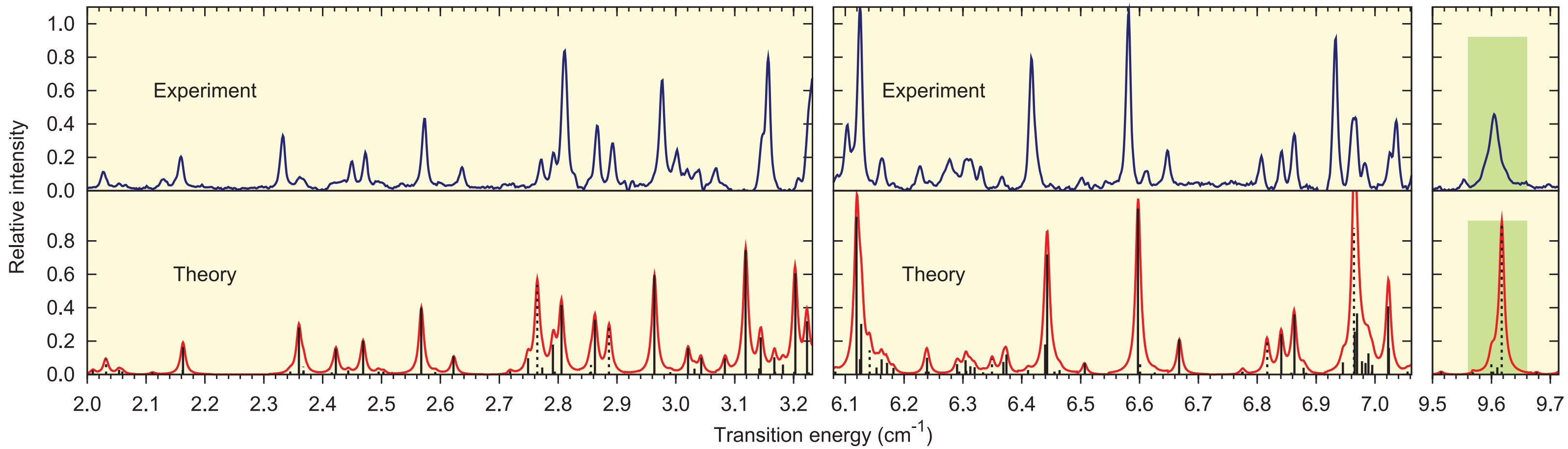
Credit: van der Avoird et al. Chem. Phys. 2010

- Solve the « electronic » Schrödinger equation
  - CCSD(T)
  - Quadruple zeta basis set
  - BSSE correction
- Solve the nuclear motion
  - Close-coupling expansion
  - S-matrix
  - Cross sections, rate coefficients

When theory untangles experiment

Science AAAS

Theory Untangles the High-Resolution Infrared Spectrum of the *ortho* -H_2-CO van der Waals Complex
Piotr Jankowski *et al.*
Science **336**, 1147 (2012);
DOI: 10.1126/science.1221000

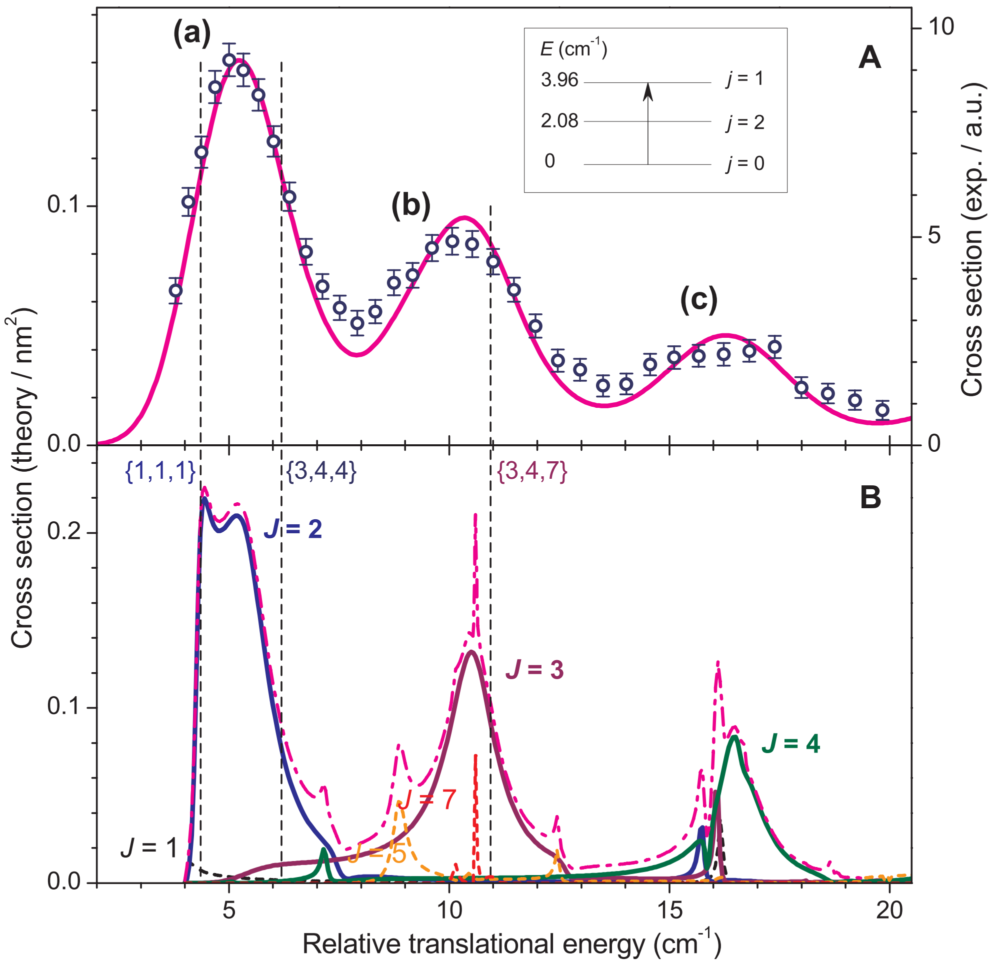


Science AAAS

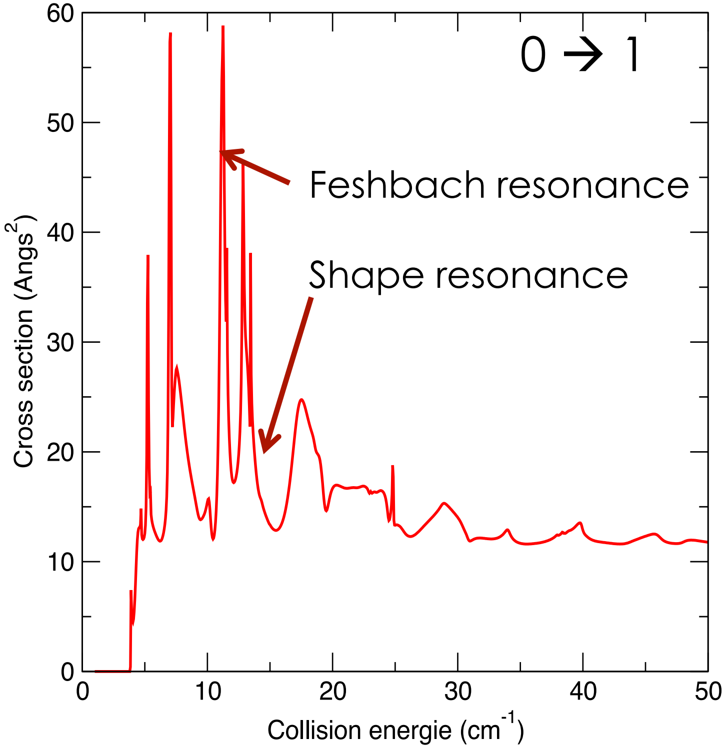
Observation of Partial Wave Resonances in Low-Energy O_2–H_2 Inelastic Collisions

Simon Chefdeville *et al.*

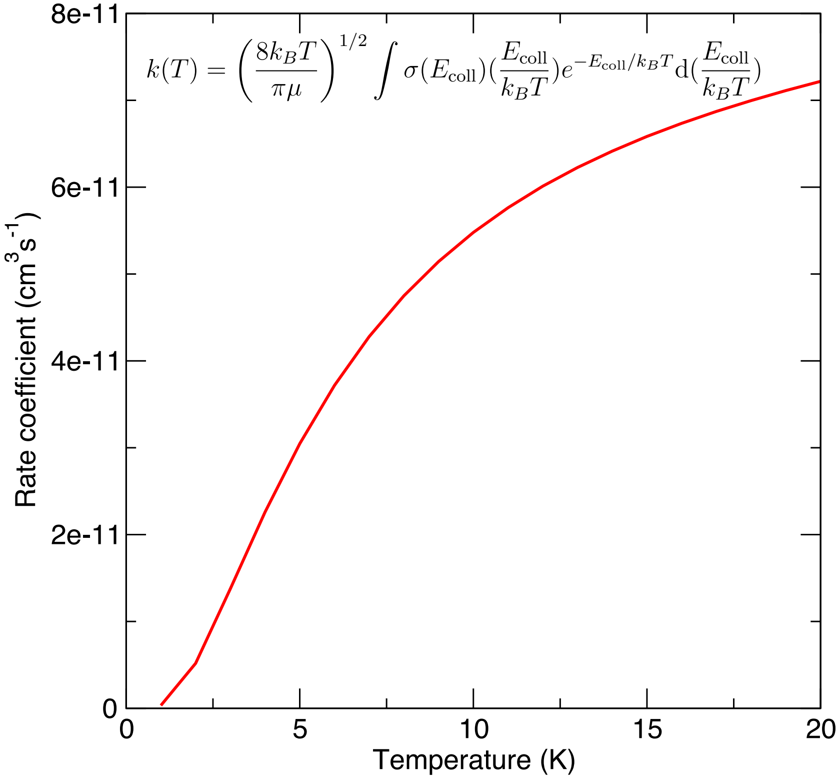
Science **341**, 1094 (2013);
DOI: 10.1126/science.1241395



CO rotational excitation

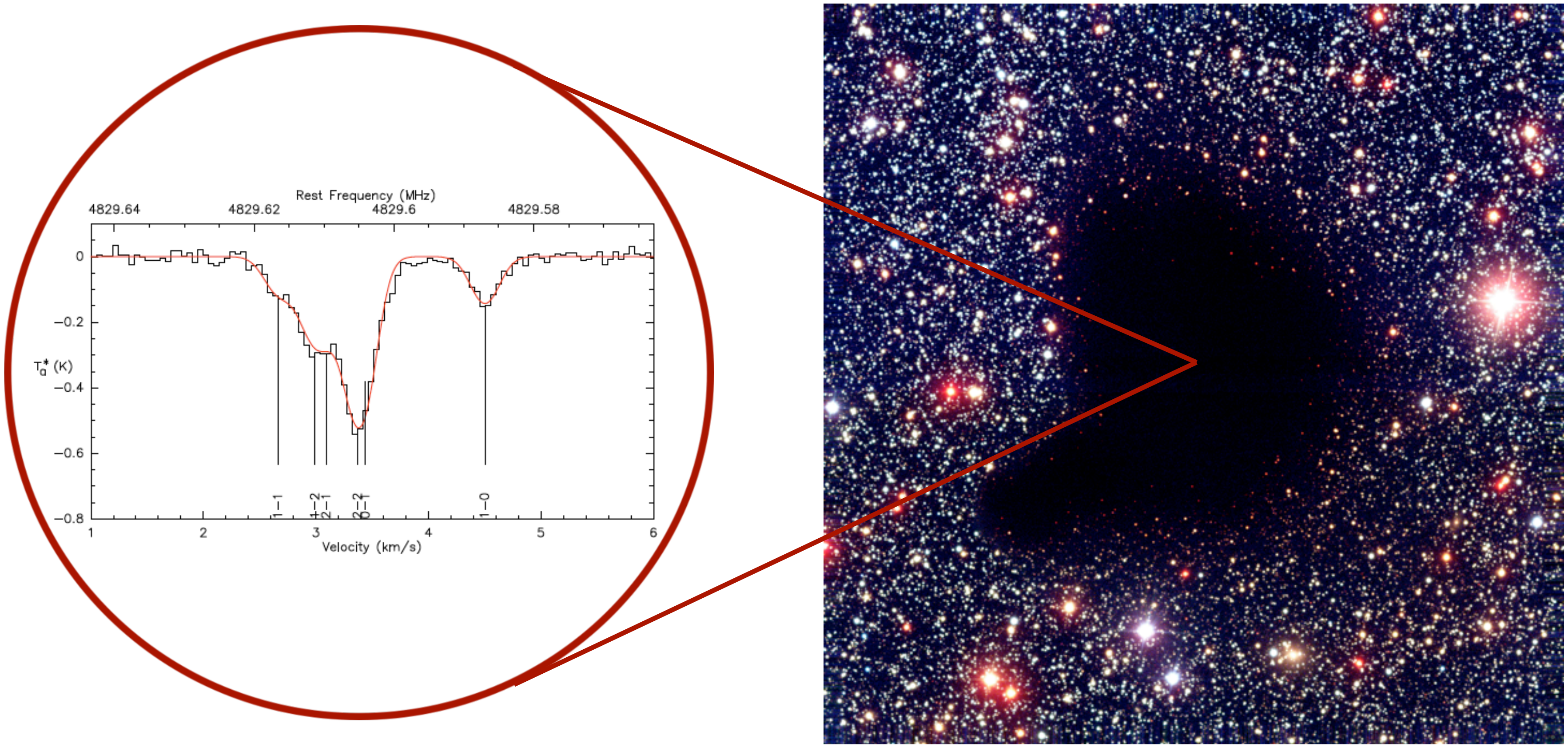


Maxwell-Boltzmann averaging



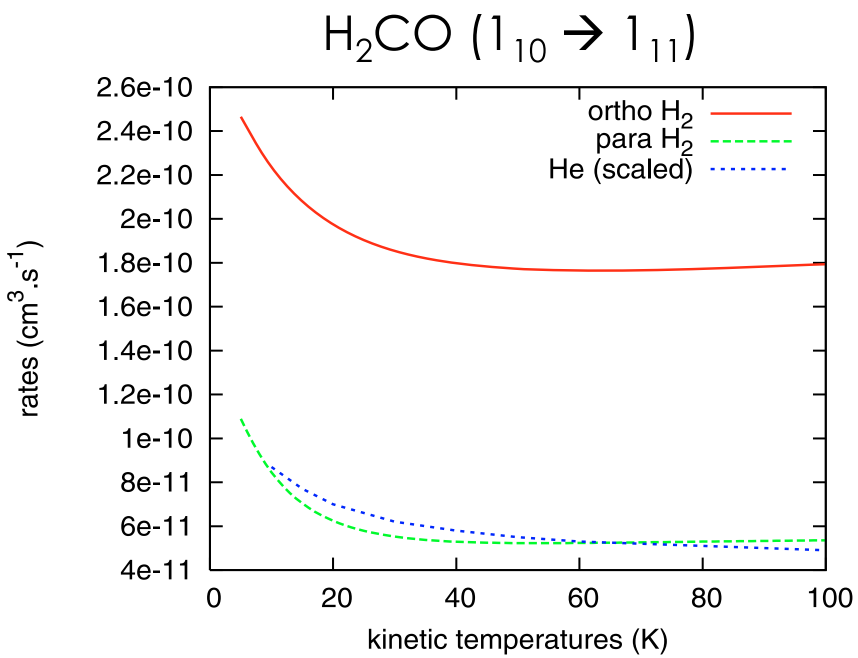
3. Collisions out of equilibrium

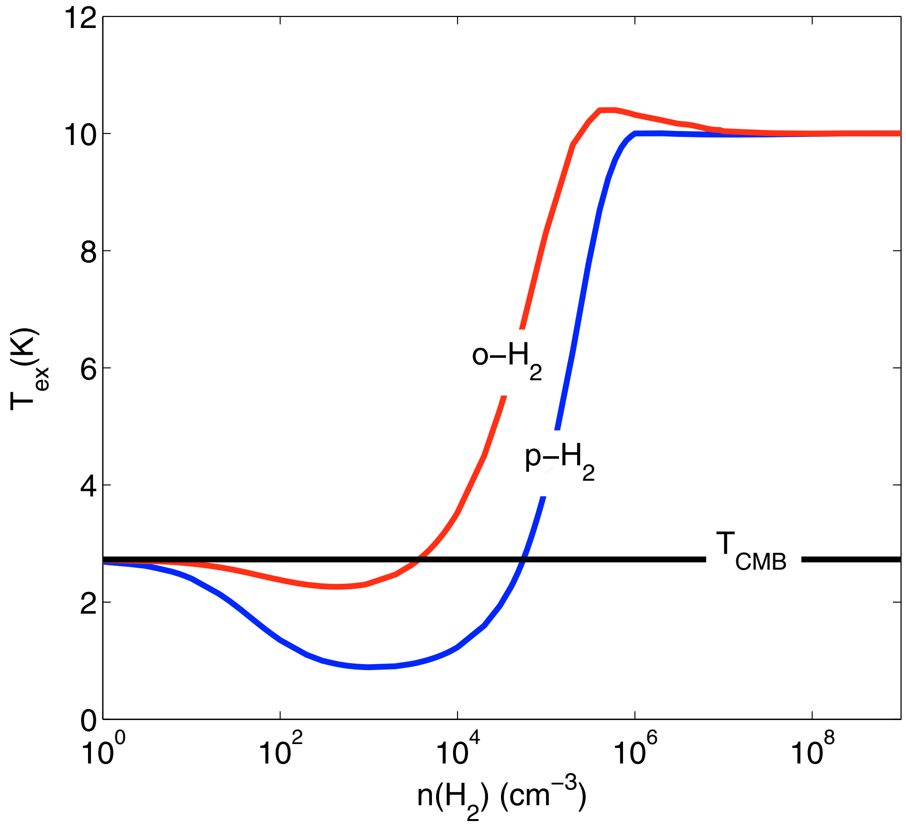
« Anomalous » H_2CO absorption (λ = 6cm)



Credit: Troscompt et al. A&A (2009b)

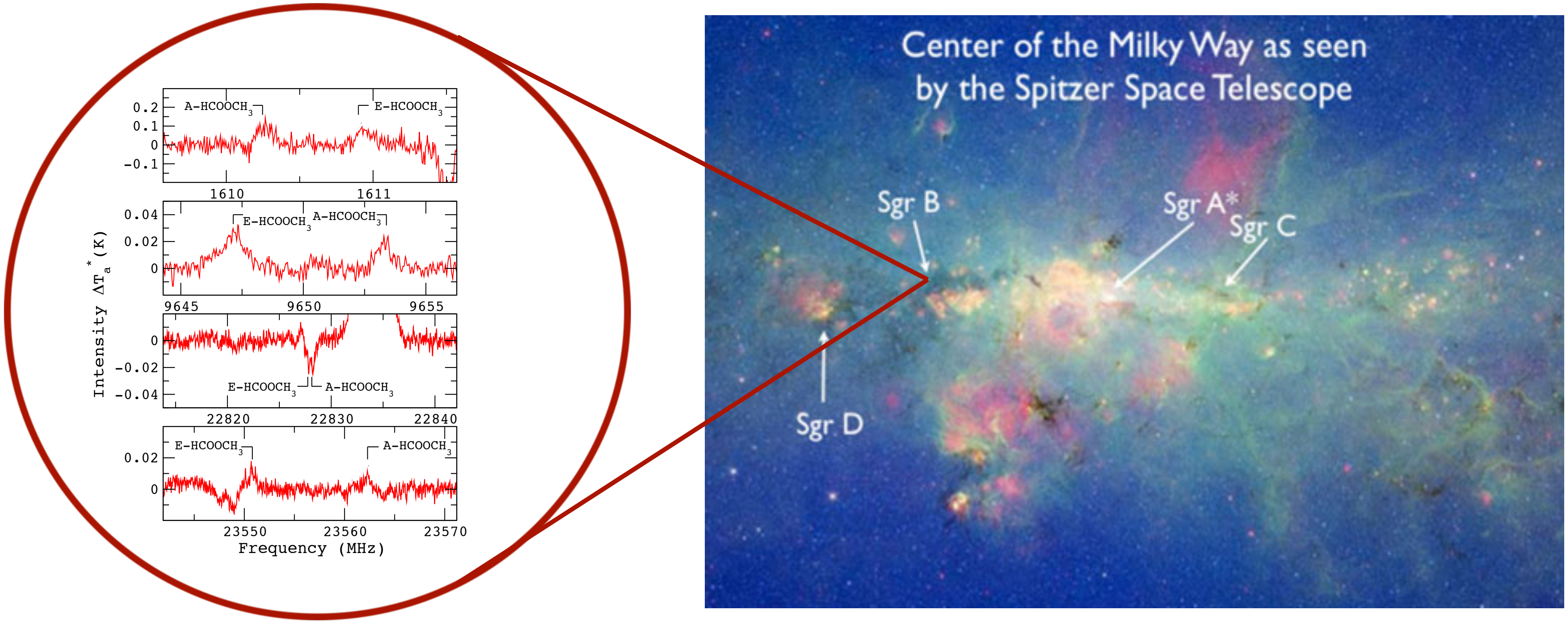
Indirect probe of *para*-H_2
$T_{ex} < 2.725$ K





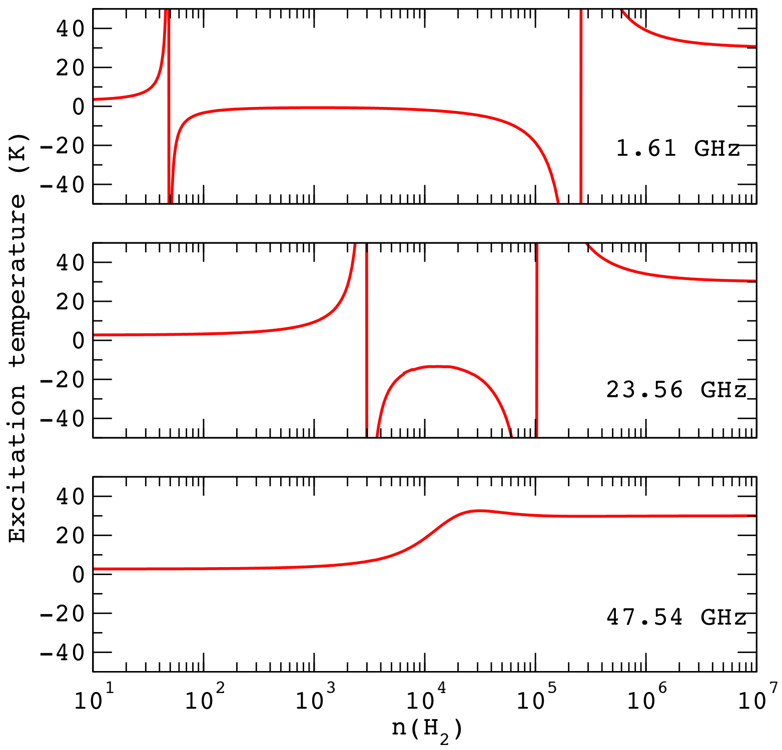
Credit: Troscompt et al. A&A (2009a, 2009b)

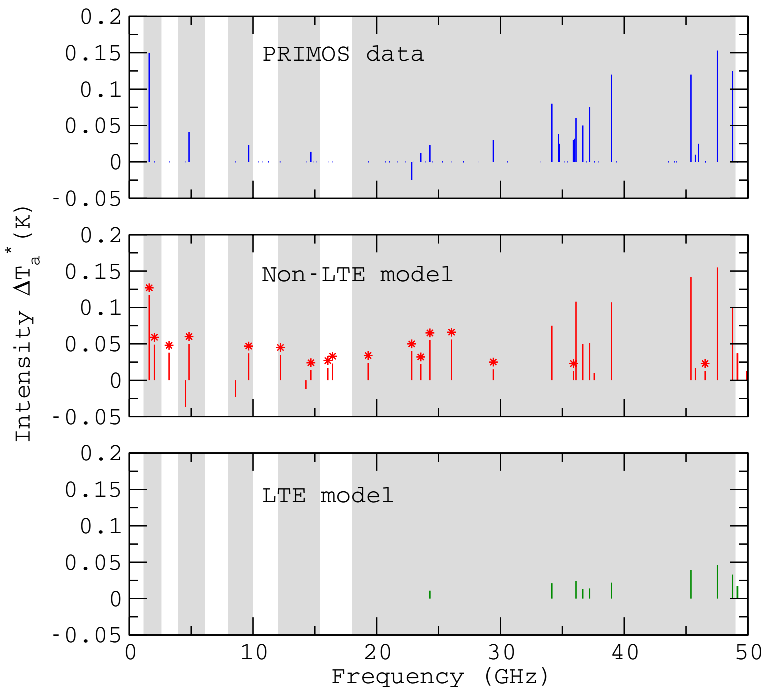
Methyl formate ($HCOOCH_3$) emission



Credit: NASA JPL/Caltech/Univ. of Wisconsin

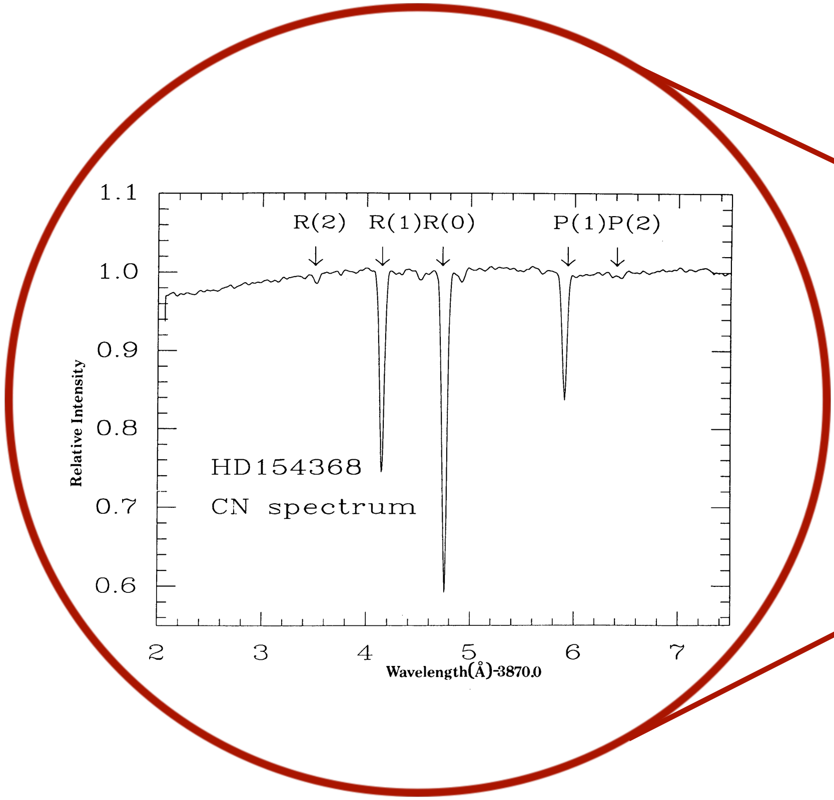
Weak masers below 30 GHz
$T_{ex} < 0$



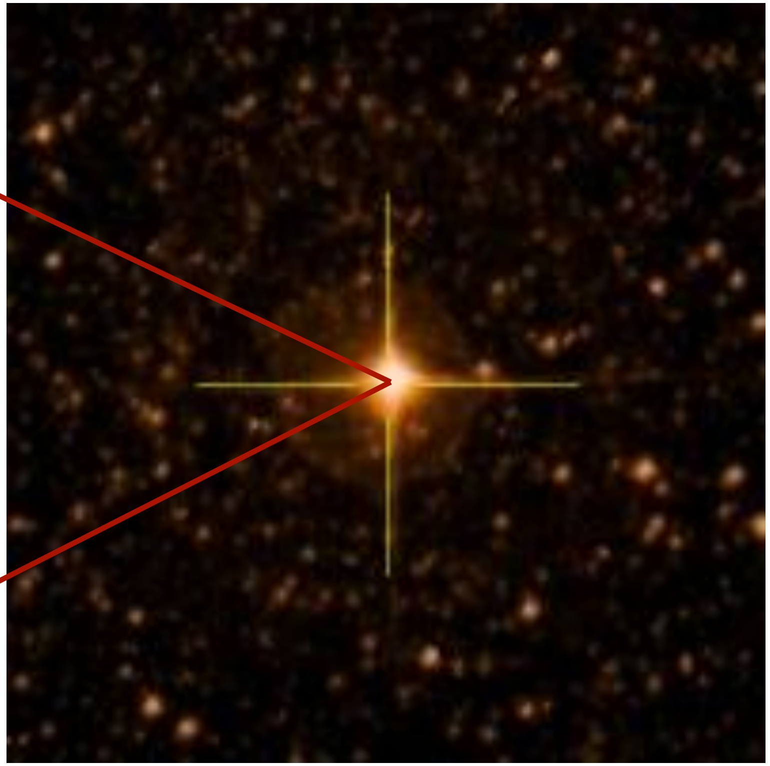


Credit: Faure et al. J. Chem. Phys. (2011)
Faure et al. ApJ (2014)

CN as a measure of the cosmic microwave background

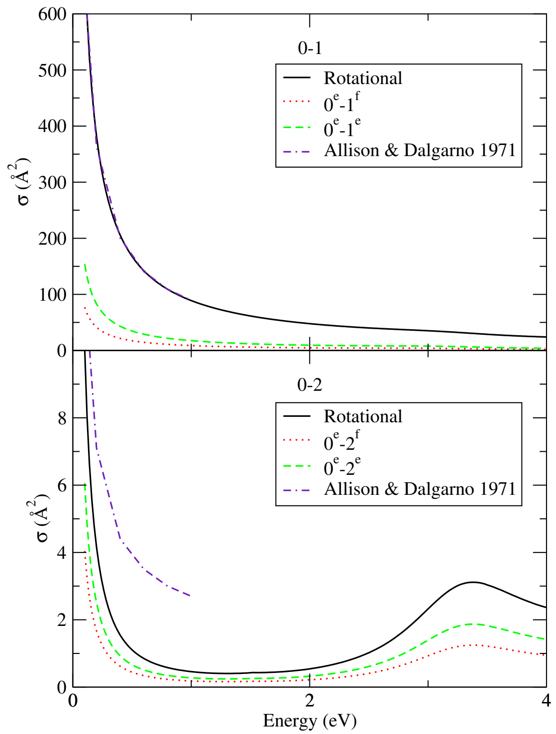


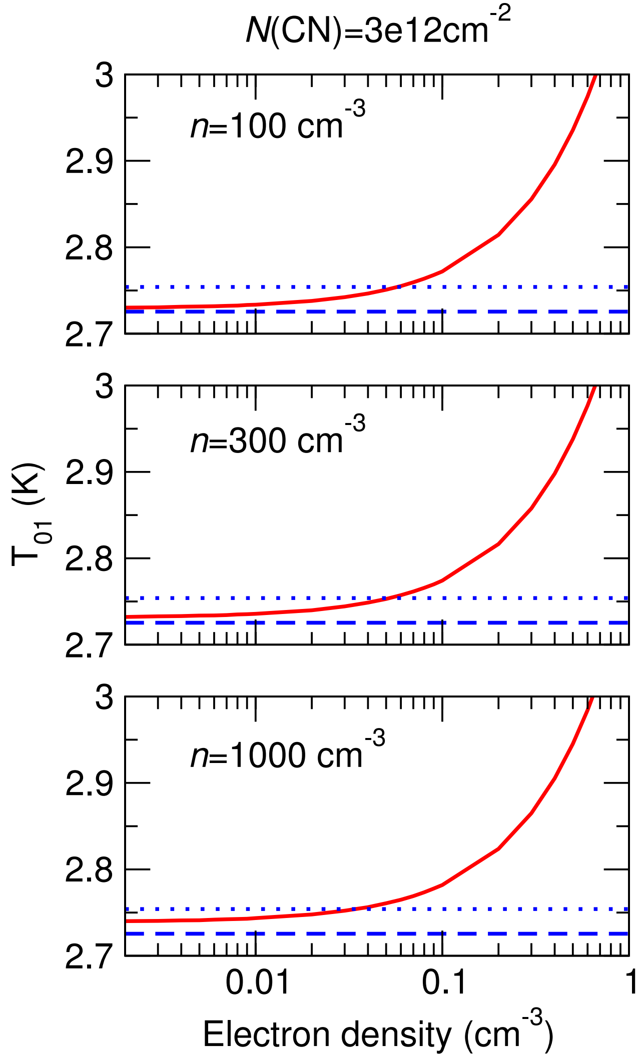
Credit: Palazzi et al. ApJ (1990)



Credit: SIMBAD (HD154368)

Measure of electron density
T_{ex} = 2.725 + 0.029 K





Credit: Harrison et al. J. Phys. B (2012)
Harrison et al. MNRAS (2013)

5. Conclusion

The interstellar medium: « molecules in Wonderland »

- The interstellar medium is a unique laboratory to study state-to-state molecular dynamics
- Non-equilibrium processes are common in space: non-LTE populations, masers, etc.
- State-of-the-art molecular physics is required