DYMCOM: Dynamic Methods for Cold Molecules, Orsay, 04 – 08 Novembre, 2019

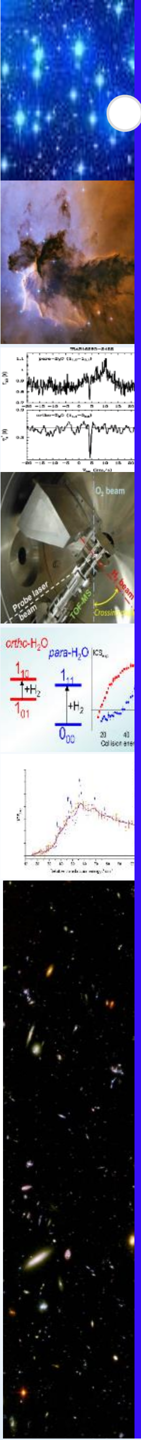
Low-energy inelastic and reactive collisions in crossed molecular beams

Astrid Bergeat, Sébastien Morales and Christian Naulin

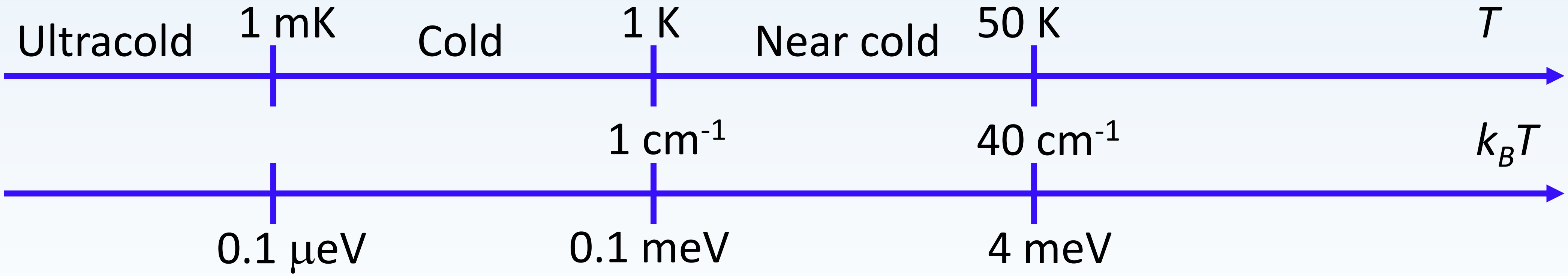
Groupe COMEX : COllisions en Milieux EXtrêmes
Institut des Sciences Moléculaires
UMR 5255, Université de Bordeaux / CNRS / INP



Bordeaux : 2007 World Heritage Site - UNESCO

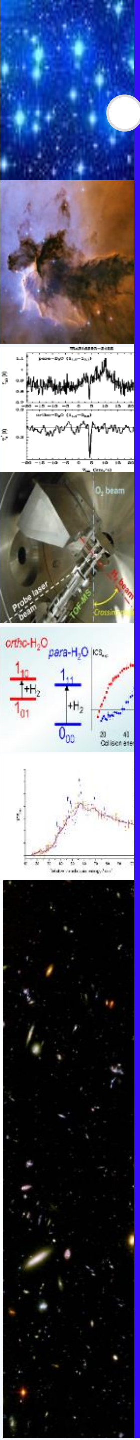


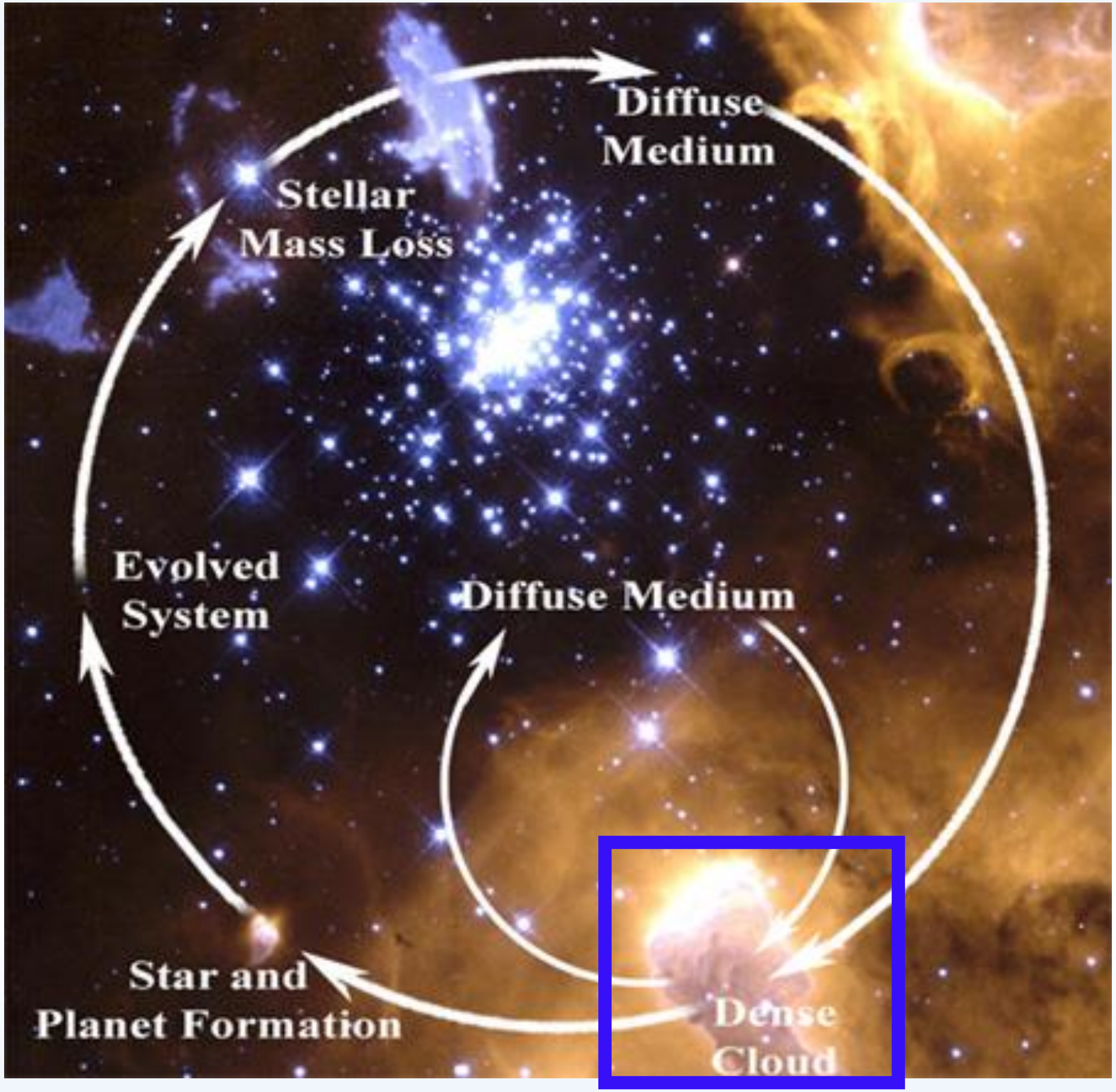
Cold Molecular Collisions

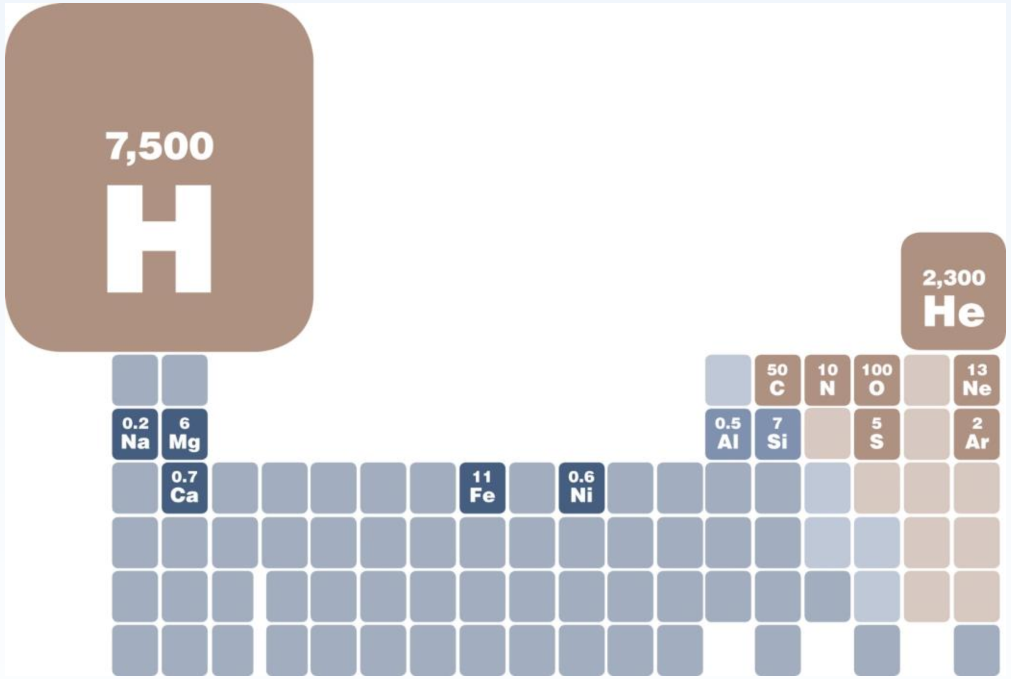


Near Cold Molecular Collisions

Astrophysics





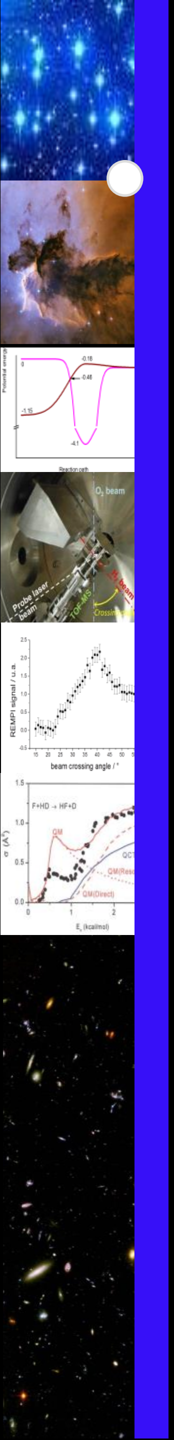


http://chandra.si.edu/resources/illustrations/chemistry_universe.html (Credit: NASA/CXC/M.Weiss)

Near cold molecular collisions

https://astrobiology.gsfc.nasa.gov/cycle.html

List of molecules and ions detected in the interstellar medium*

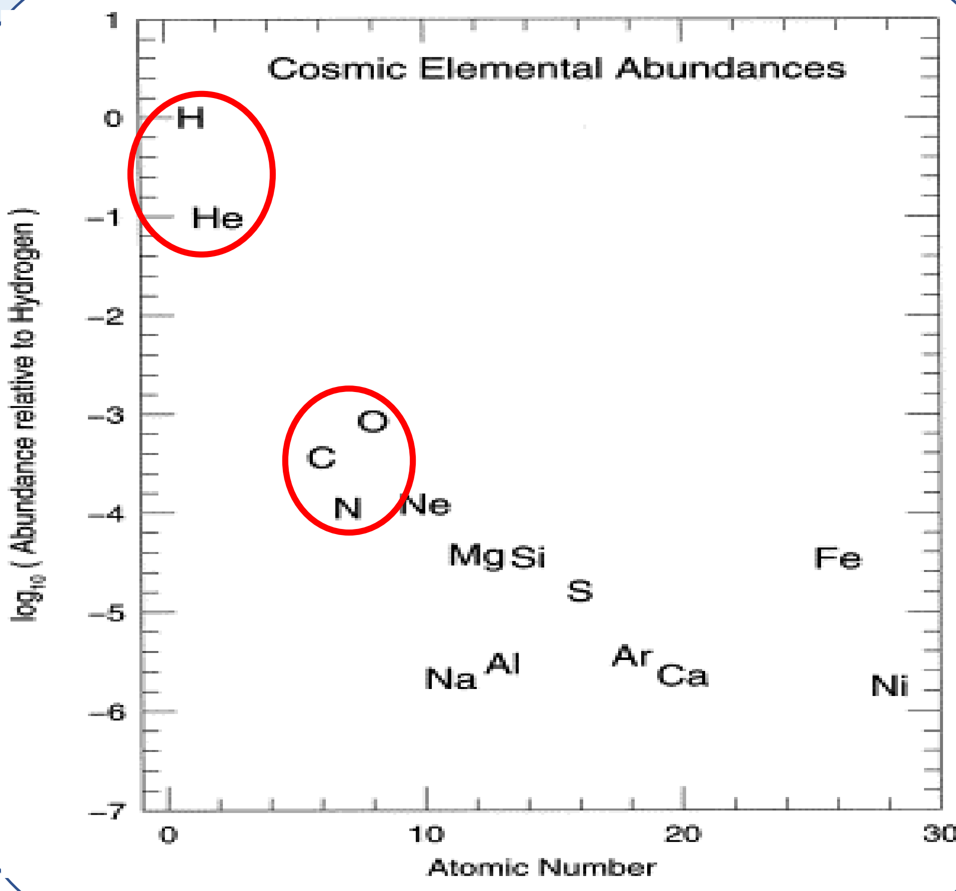


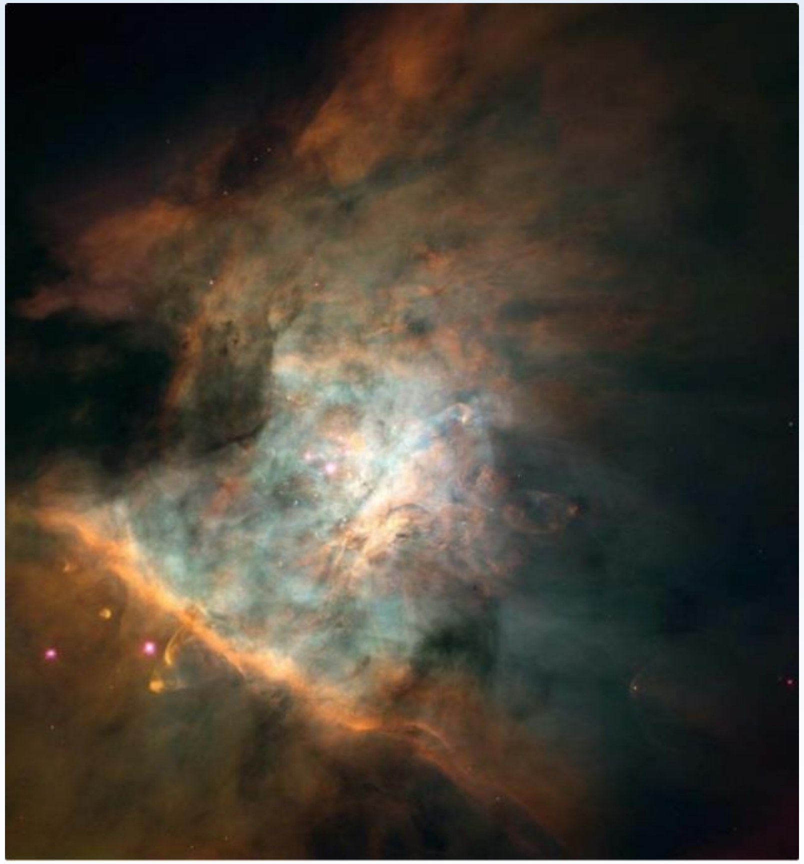
N =2	H2	CH	CH+	NH	OH	HF	C_2	CN	CO
	CS	CP	NO	NS	SO	HCl	NaCl	KCl	AlCl
	PN	SiN	SiO	SiS	CO^+	SO^+	PO	SH	AlF
	FeO	SiC	CF+	LiH	N_2	SiH	O_2	AlO	OH^+
	SH^+	*CN^-*							
N =3	H_3^+	CH_2	NH_2	H_2O	HO_2	H_2S	CCH	HCN	HNC
	HCO	HCO^+	HOC^+	HN_2^+	HNO	HCS^+	C_3	C_2O	C_2S
	OCS	MgCN	MgNC	NaCN	*KCN*	*FeCN*	*SO_2*	*N_2O*	*SiCN*
	CO_2	*c-SiC_2*	*SiNC*	[illegible]	[illegible]	*C_2P*	*AlOH*	*H_2O^+*	*HCl^+*
	H_2Cl^+								
N =4	CH_3	NH_3	H_3O^+	H_2CO	H_2CS	[illegible]	c-C_3H	HCCH	$HCNH^+$
	H_2CN	HCCN	[illegible]	[illegible]	[illegible]	[illegible]	HSCN	C_2CN	C_3O
	C_3S	SiC_3	C_3N^-	PH_3	HCO_2^+	*HOOH*			
N =5	CH_4	SiH_4	[illegible]	[illegible]	[illegible]	CH_2CN	H_2NCN	CH_2CO	HCOOH
	C_4H	HC_2CN	[illegible]	[illegible]	[illegible]	C_5	H_2COH^+	C_4H^-	CNCHO
N =6	CH_3OH	CH_3SH	C_2H_4	CH_3CN	CH_3NC	HC_2CHO	NH_2CHO	HC_3NH^+	H_2C_4
	C_5H	C_5N	HC_4H	HC_3CN	c-C3H2O	CH_2CNH	C_5N^-		
N =7	CH_3NH_2	CH_3CCH	CH_3CHO	c-CH_2OCH_2	CH_2CHCN	HC_4CN	C_6H	CH_2CHOH	C_6H^-
N = 8	$HCOOCH_3$	CH_3CCCN	HC_6H	C_7H	$HOCH_2CHO$	CH_3COOH	$H_2CCCHCN$	H_2C_6	
	CH_2CHCHO	CH_2CCHCN							
N =9	$(CH_3)_2O$	C_2H_5OH	C_2H_5CN	CH_3C_4H	C_8H	HC_6CN	CH_3CONH_2	C_8H^-	CH_3CHCH_2
N ≥ 10	$(CH_3)_2CO$	CH_3C_4CN	CH_3CH_2CHO	$(CH_2OH)_2$	$HCOOC_2H_5$	HC_8CN	CH_3C_6H	C_6H_6	C_3H_7CN
	$HC_{10}CN$	$C_2H_5OCH_3$	*C_{60}*	*C_{70}*	*$C_{14}H_{10}^+$*				

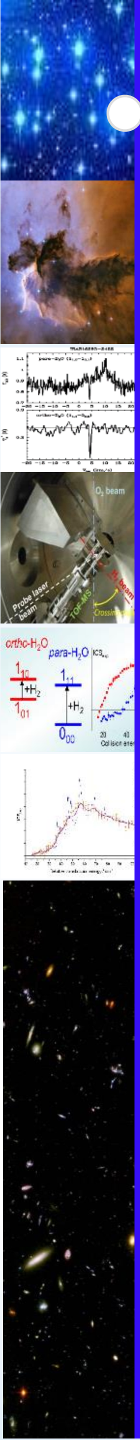
Nearly 200 molecules and ions detected**

*Wakelam *et al.*,*Space Sci. Rev.* **2010, 156, 13-72.** // ** ***http://astrochymist.org/***

Astrophysics





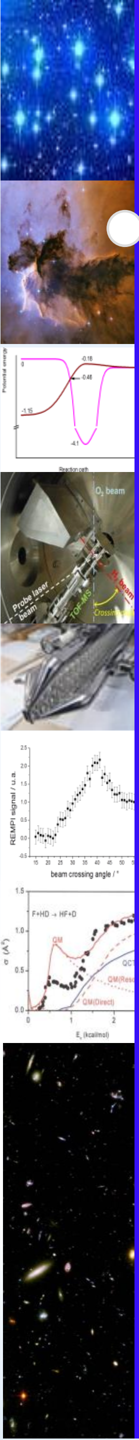


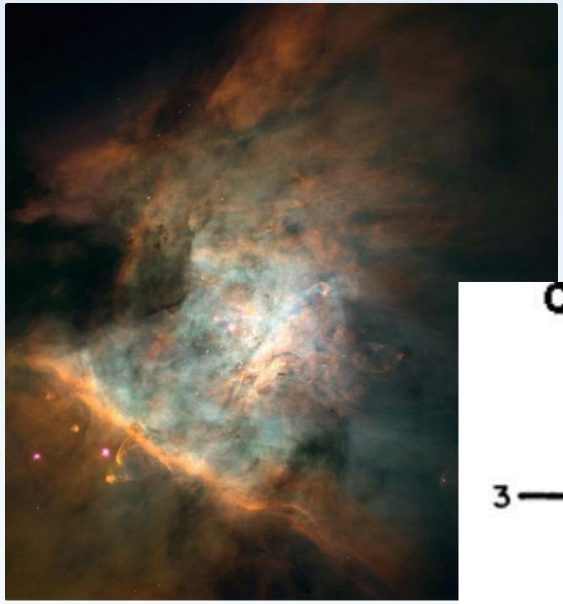
H_2 most abundant molecule in space

CO the second most abundant molecule in the ISM

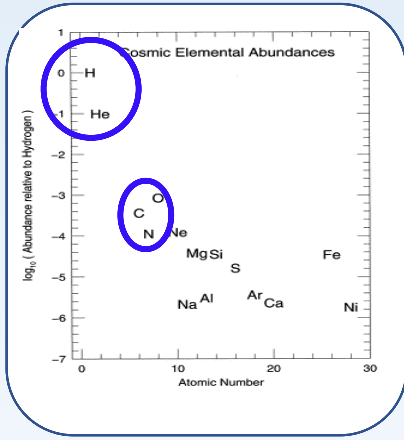
H_2O the third one

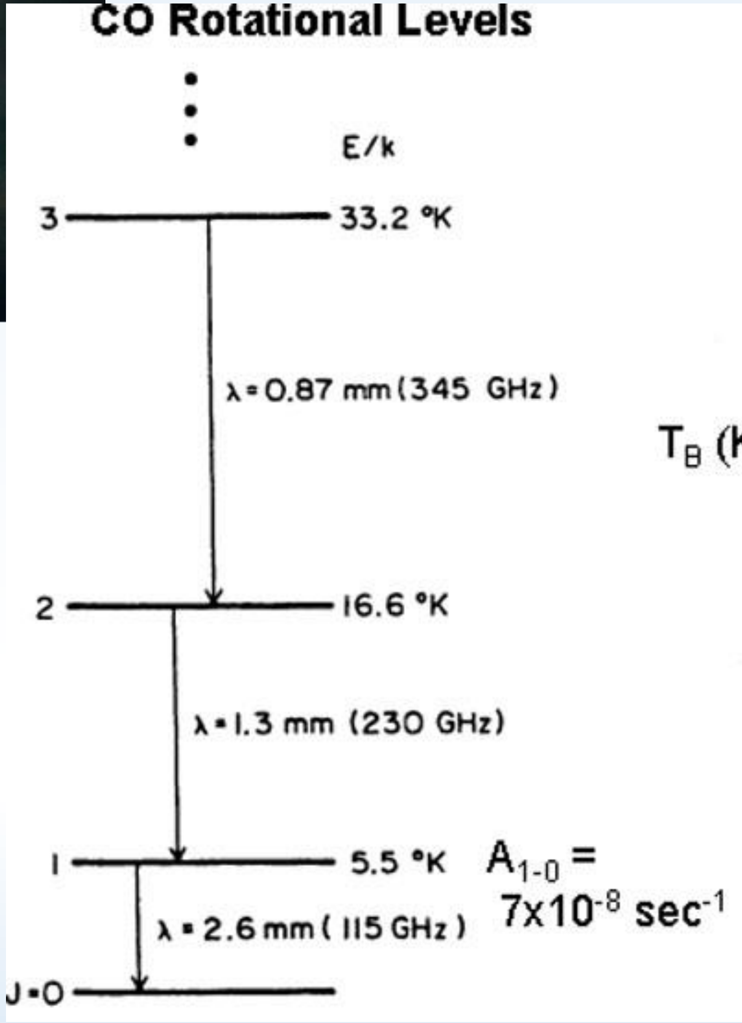
Why? Astrophysics

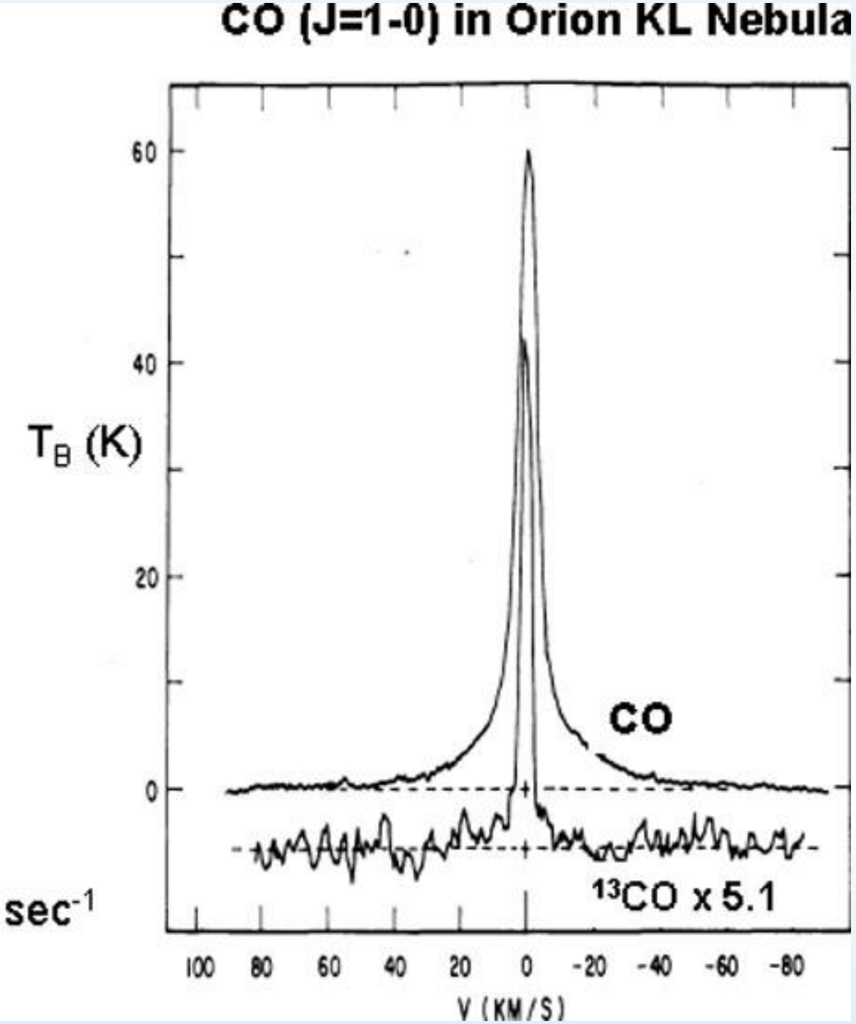




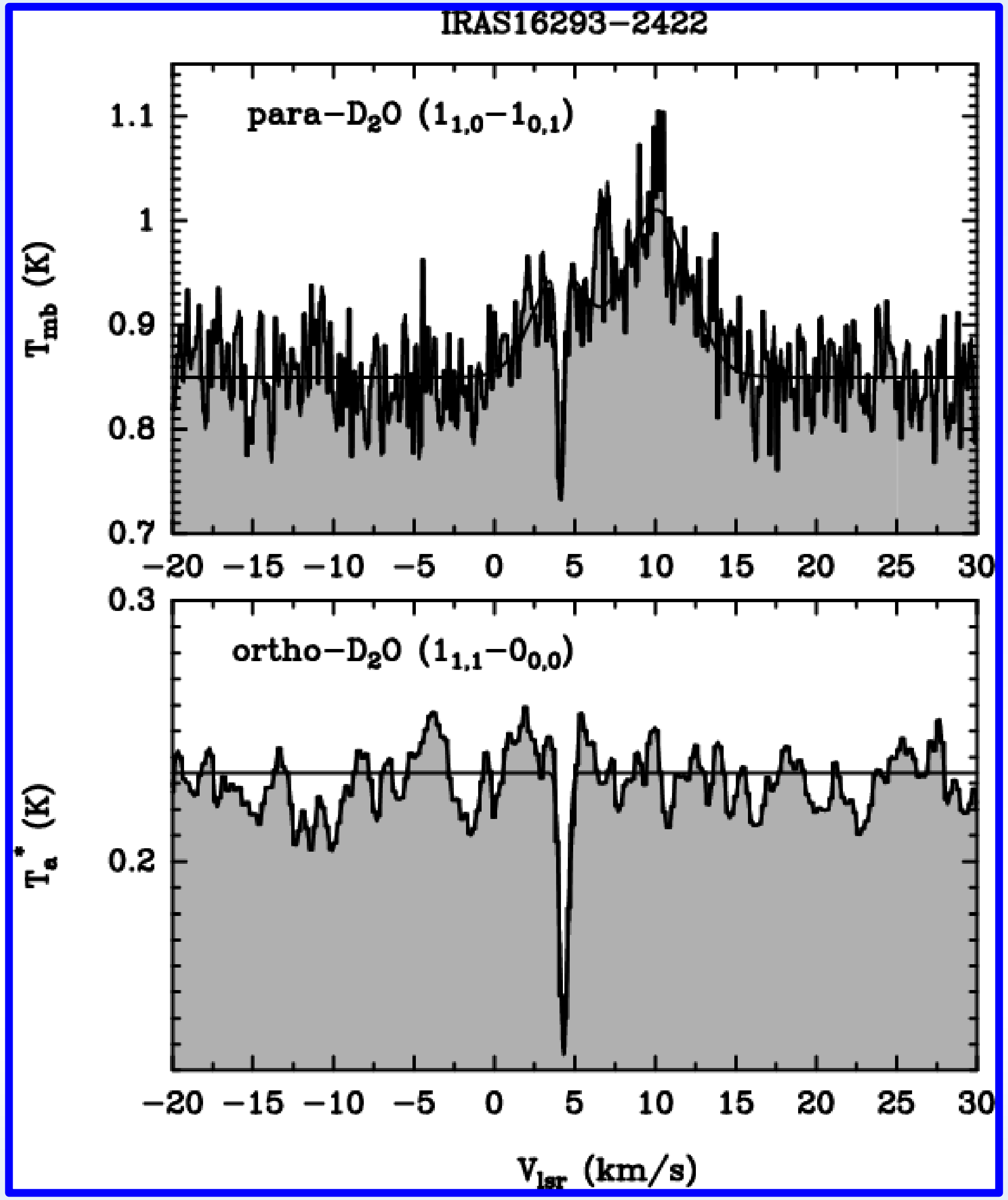
CO + H_2 or He







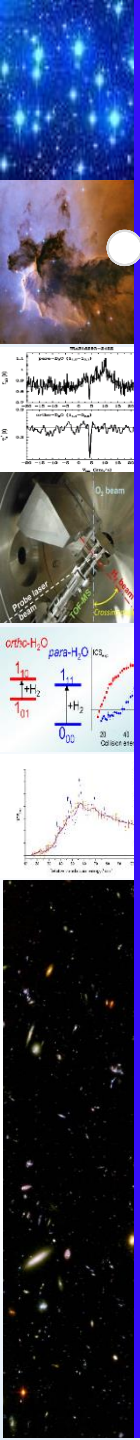
Astrophysics

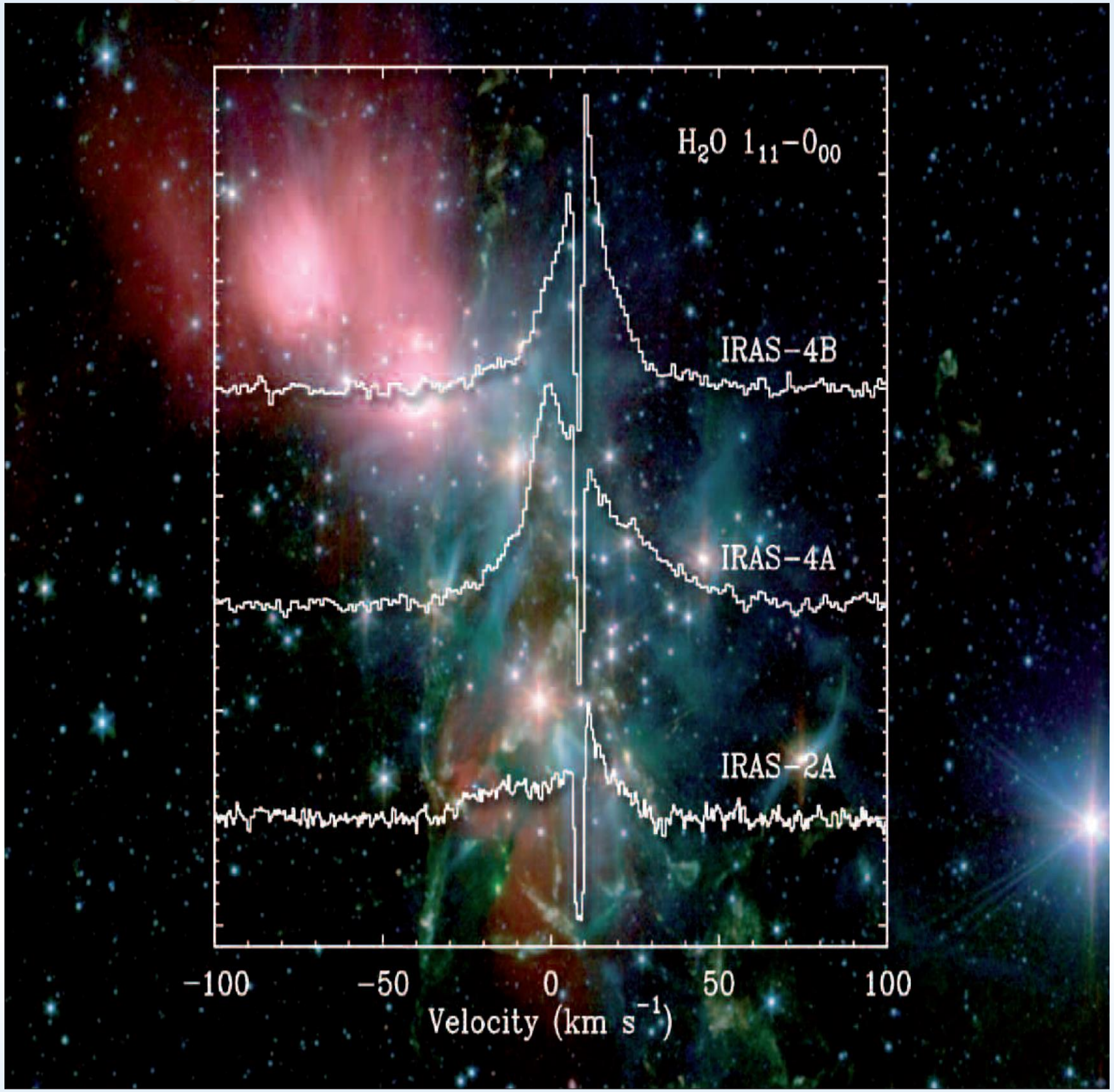


Profile of the *para*-D_2O (1_{10}–1_{01}) line (histogram) observed at JCMT (upper panel), and *ortho*-D_2O (1_{11}–1_{01}) line observed with HIFI (bottom panel). [Vastel et al . A&A 2010].

(Crédits : NASA, JPL-Caltech, WISE Team)

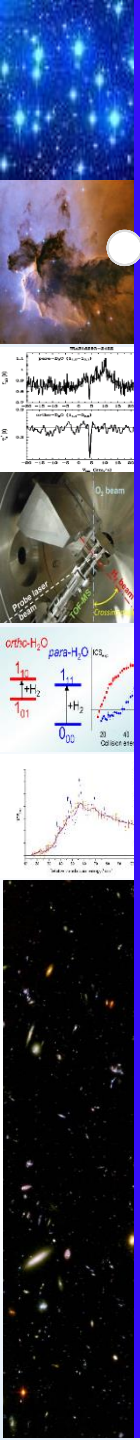
Astrophysics





Hifi spectra of the *p*-H_2O ground-state 1_{11}-0_{00} line at 1.1 tHz (270 μm) toward three lowmass protostars in the NgC 1333 star-forming region [L.E. Kristensen *et al.*, *Astron. Astrophys.* 521, L30 (2010)].

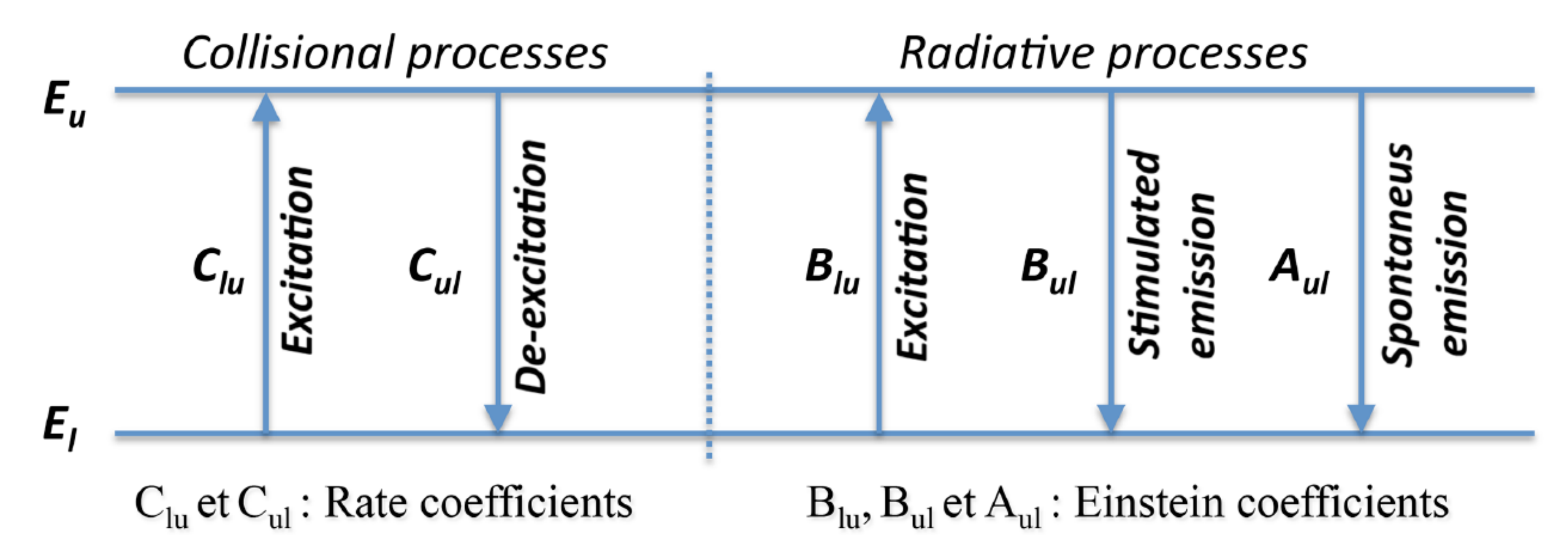
(Credit: Esa,wisH and the Hifi consortium; background spitzer image: Nasa/jPl-Caltech)

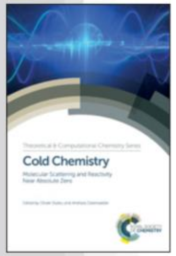


Astrophysics: state-to-state collisional rates

- *Density, temperature, metallicity, ortho/para ratio,* D_2O/H_2O, ……
- *Density in ISM can be so low that collisions cannot maintain Local Thermodynamic Equilibrium (non LTE):*

interpreting spectra and determining the physical and chemical conditions of molecular clouds ⇒ radiative transfer and statistical equilibrium equations



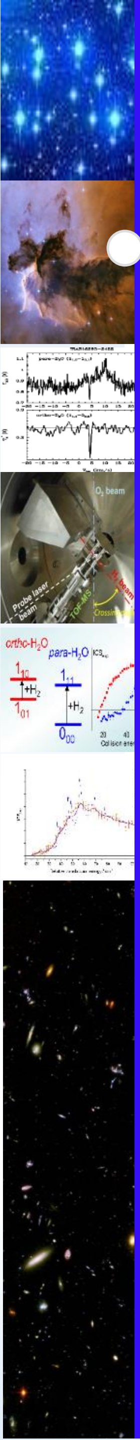


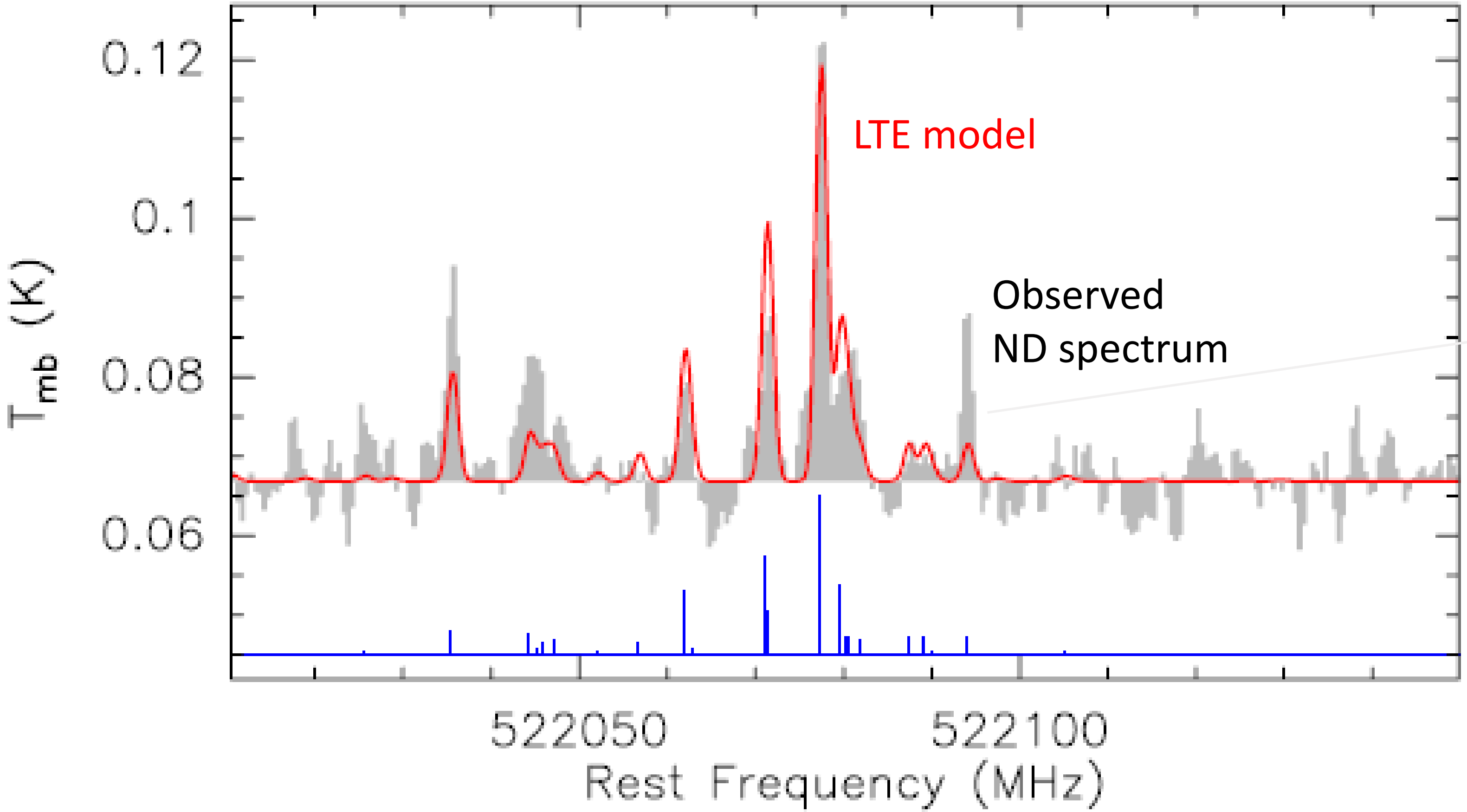
Cold Chemistry: Molecular Scattering and Reactivity Near Absolute Zero

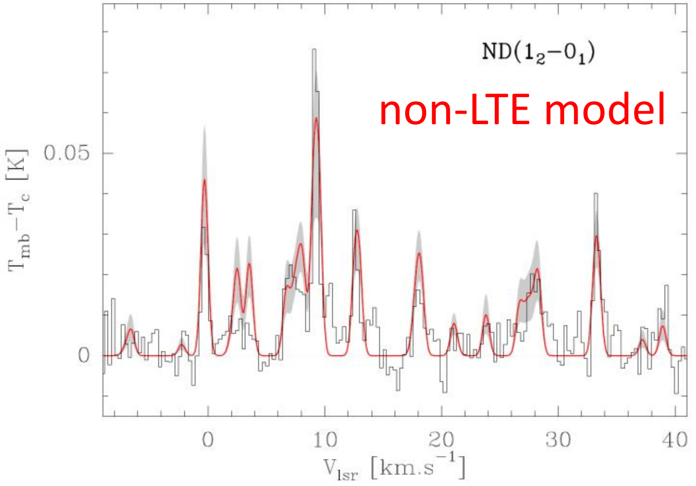
Editors: Olivier Dulieu, Andreas Osterwalder

Chap. 2: J. Klos & F. Lique

Astrophysics: state-to-state collisional rates



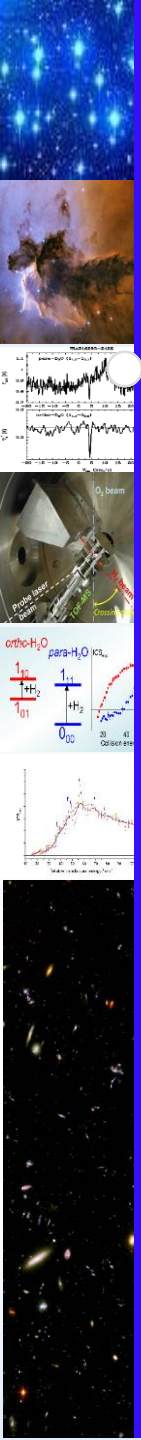




Stratified NH and ND emission in the prestellar core 16293E in L1689N★

A. Bacmann[1,2], F. Daniel[1,2], P. Caselli[3], C. Ceccarelli[1,2], D. Lis[4,5], C. Vastel[6,7], F. Dumouchel[8], F. Lique[8], and E. Caux[6,7]

A&A 587, A26 (2016)



Astrophysics: state-to-state collisional rates

- *ortho*-$H_2O(1_{01})$ + *p*-H_2 → *ortho*-$H_2O(1_{10})$ + *p*-H_2

k / $cm^3\ s^{-1}$	T = 20K
Phillips et al. (1996)	$3.06\ 10^{-12}$
Faure et al. (2007)	$3.4\ 10^{-11}$
Dubernet et al. (2009)	$3.3\ 10^{-11}$

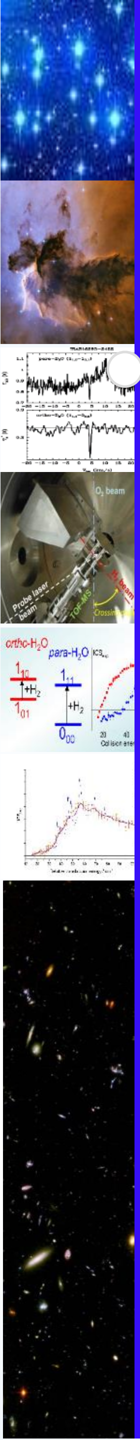
Database: Basecol (VAMDC)

Ewine F. van Dishoeck –
EuroPhysics News (EPN), **42/1,** 26 (2011)

Molecular physics and water

To use water as a physical and chemical probe of star-forming regions, many basic molecular processes need to be understood. Often, these astronomical needs drive further molecular physics studies, thus leading to a fruitful synergy between astronomy and physics. A prime example of this interaction are the cross sections for collisions of H_2O with the main collision partner in clouds, H_2, which are needed to translate the observed line intensities into abundances. Discrepancies between experiment and theory have recently been resolved thanks to intense discussions in the physics community, allowing astronomers to quantitatively analyze their data [8].

L. Wiesenfeld, and A. Faure, *Phys. Rev. A* 82, 40702 (2010)

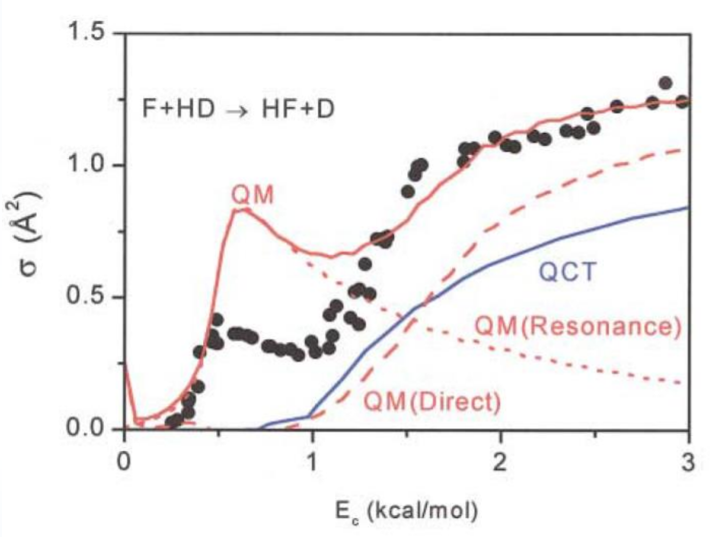


Fundamental Interest

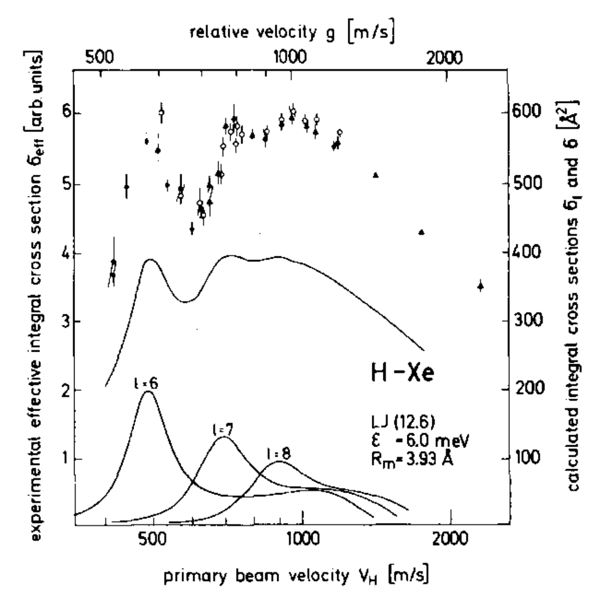
- *Theory predicts that the dynamics of many bimolecular collision processes (elastic, inelastic, reactive) are dominated by scattering resonances…*

- *Few experimental observations:*

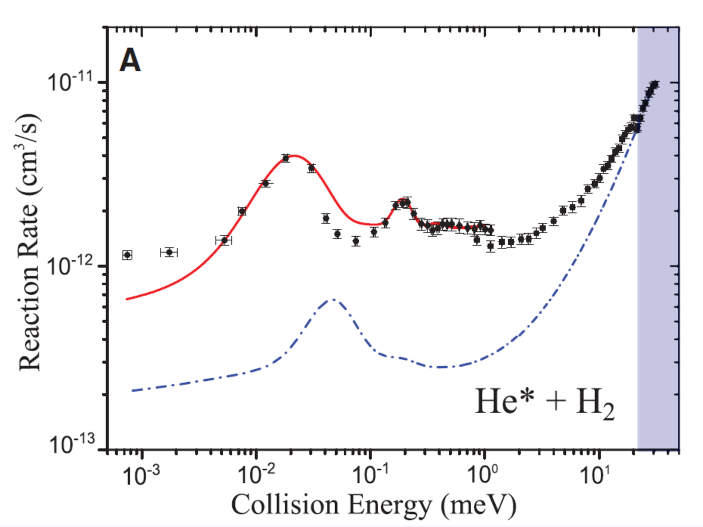
✓ Reactive collisions
$F + H_2/HD$
K. Liu, X. Yang (2000s)

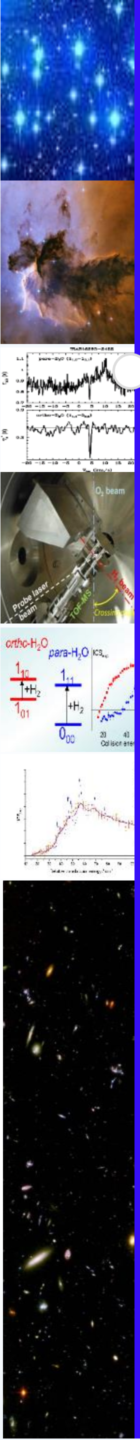


✓ Elastic collisions
H/H_2 + atom
G. Scoles, P. Toennies (1970s)



✓Penning ionisation
$He^* + H_2$
E. Narevicius (2012)



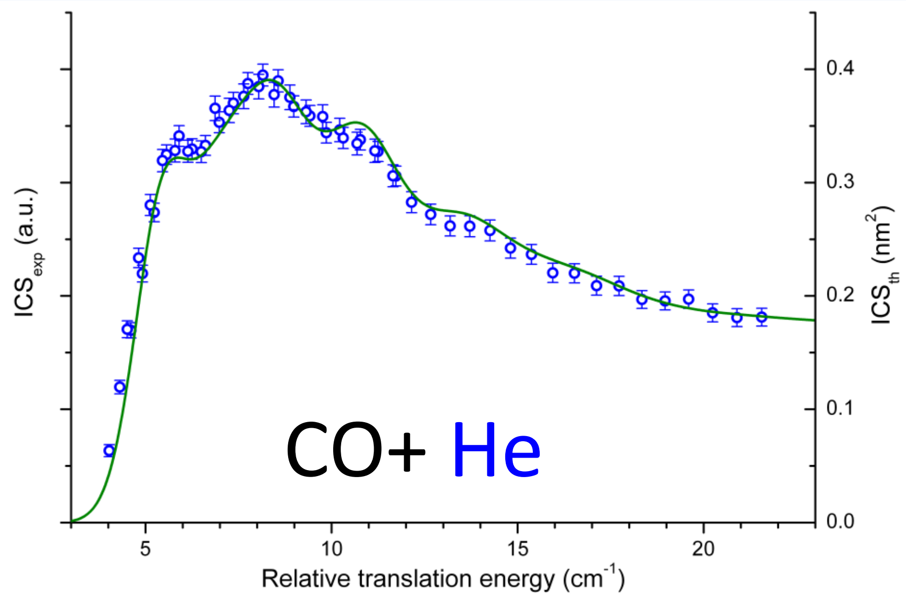


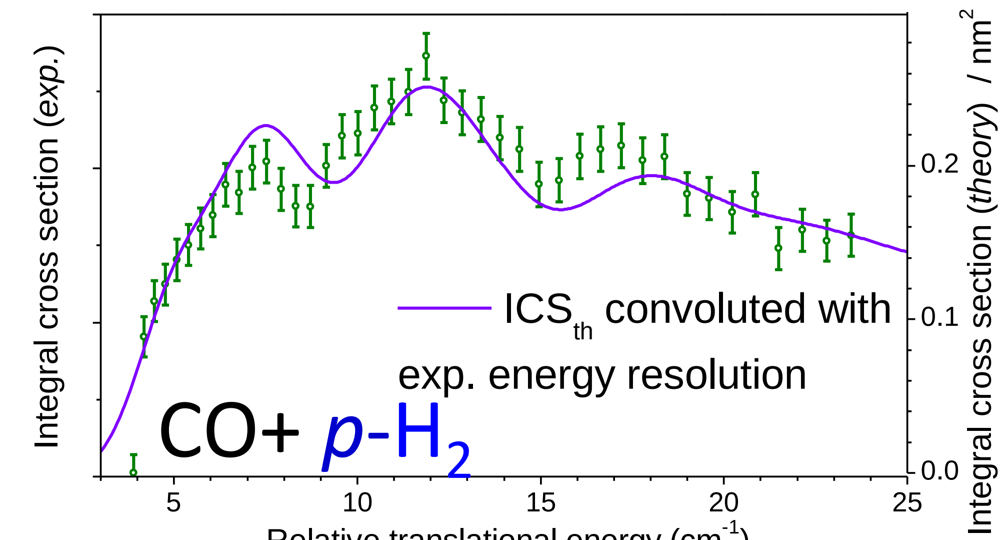
Fundamental Interest

$CO(j=0) + p/n\text{-}H_2/He \rightarrow CO(j=1) + H_2/He$

Rotational inelastic collisions

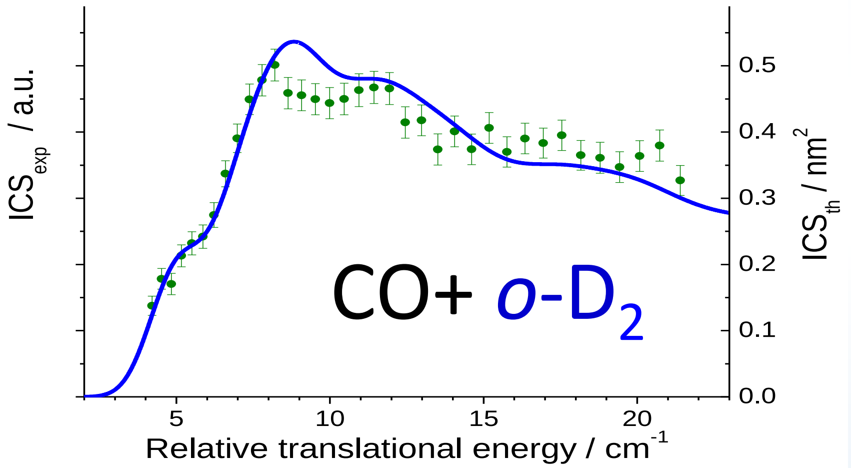
A. Bergeat, J. Onvlee, C. Naulin, A. van der Avoird, M. Costes, ***Nature Chem.* (2015)**



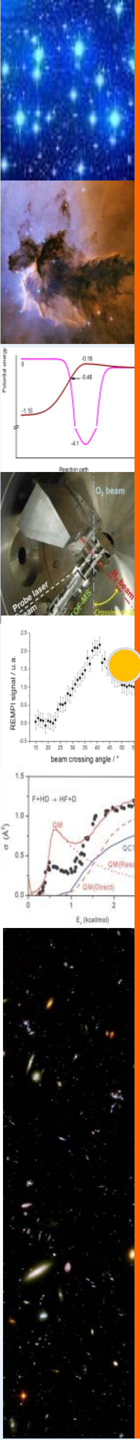


S. Chefdeville, T. Stoecklin, C. Naulin, P. Jankowski, K. Szalewicz, A. Faure, M. Costes, A. Bergeat, ***ApJ Lett.* (2015)**

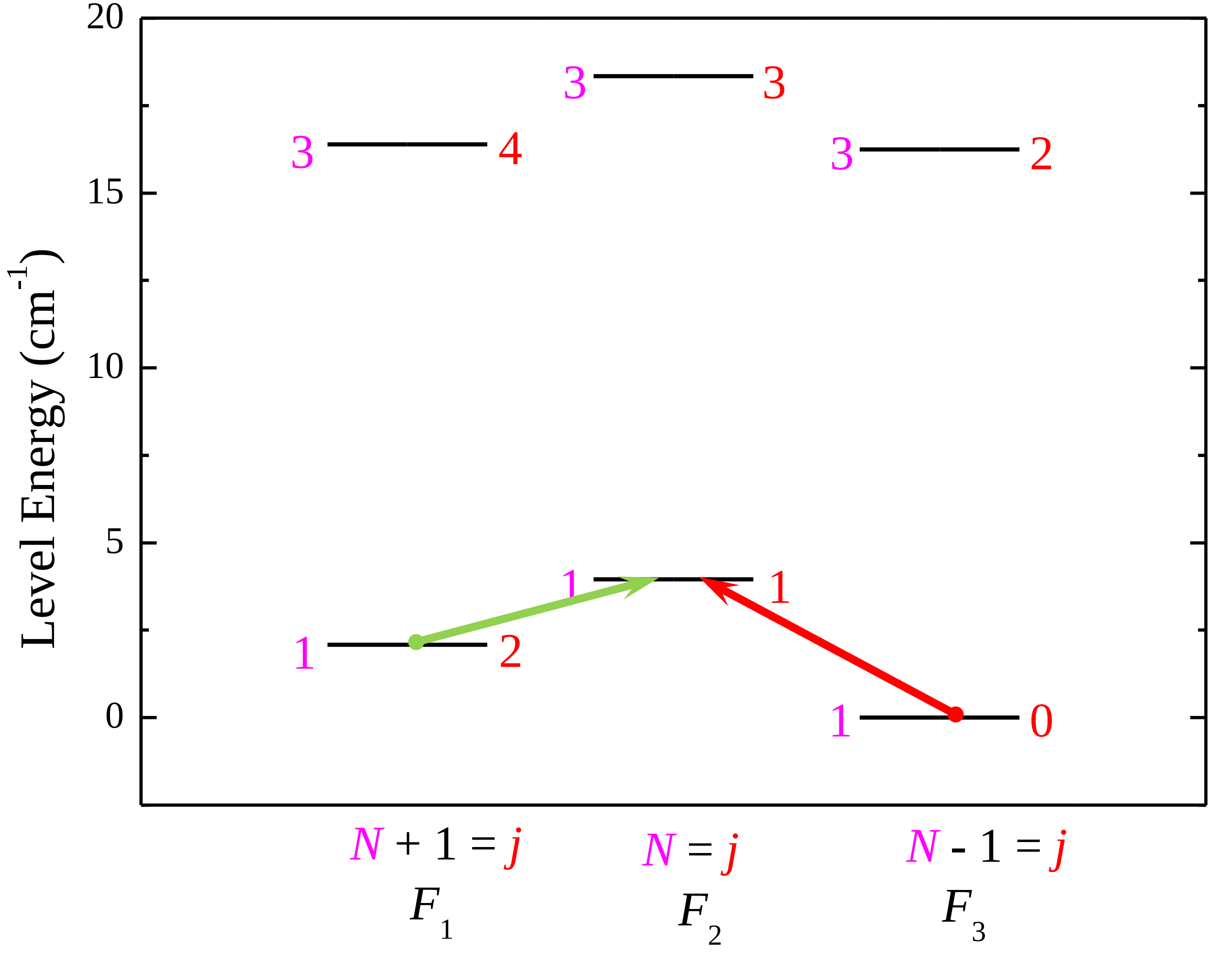
T. Stoecklin, et al., ***PCCP* (2017)**



$O_2(N=1, j=0) + p\text{-}H_2 \rightarrow O_2(N=1, j=1) + p\text{-}H_2$



Energy level diagram of $O_2(X^3\Sigma_g^-)$



O_2 (0.3 % in He, 100 K)

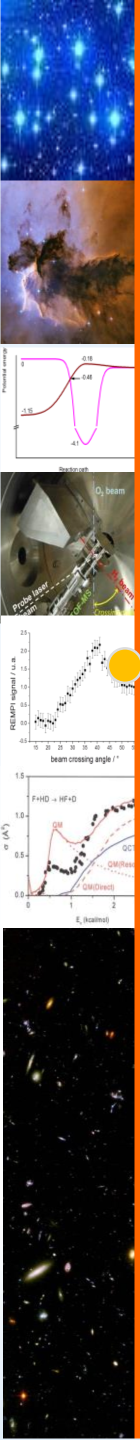
< 15 %   < 0.5 %   > 85 %

Propensity rules in rotationally inelastic collisions of molecules in $^3\Sigma$ electronic states (*):

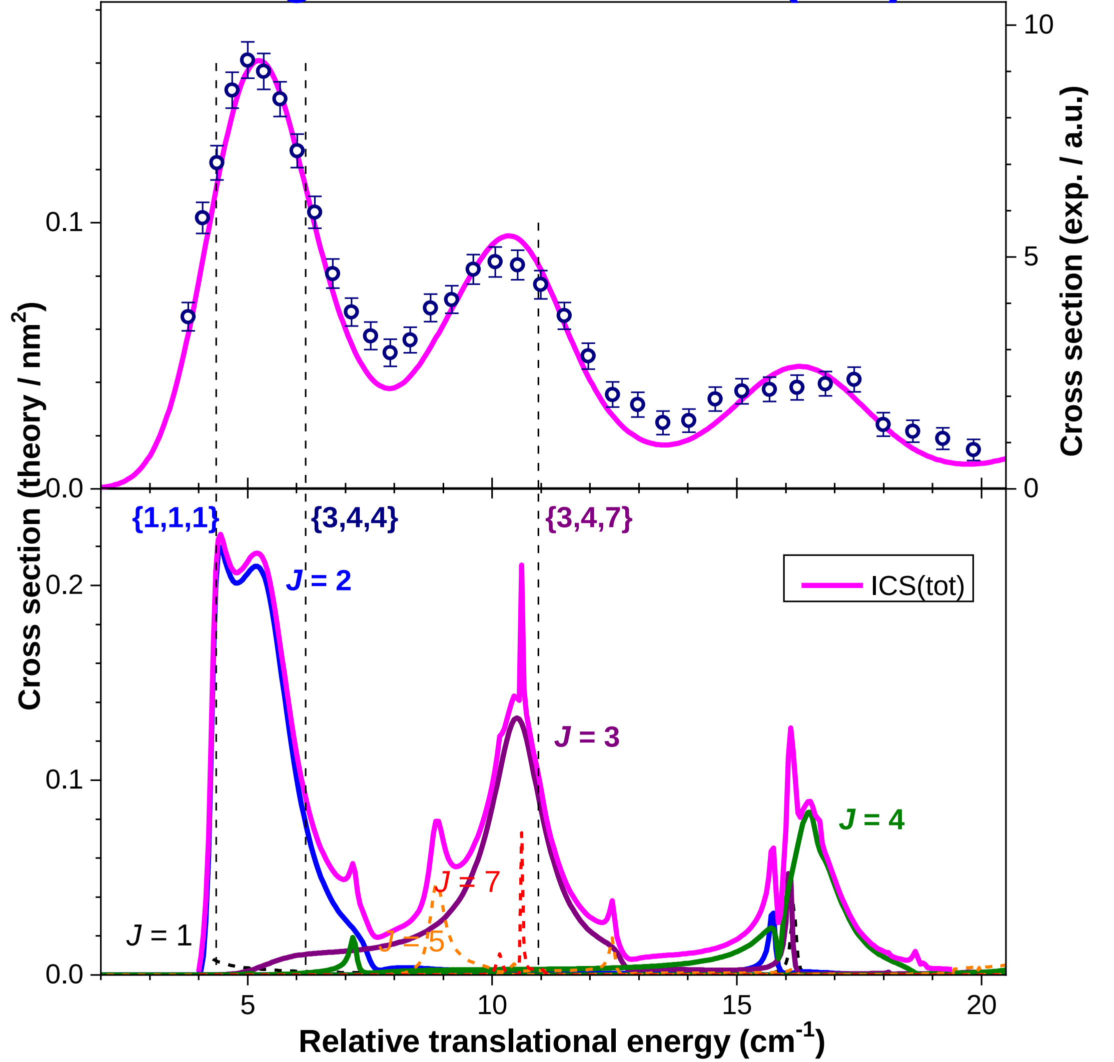
Transitions from the unique *j* = 0 state to any F_2 level will be forbidden!

(*) M. H. Alexander & P. J. Dagdigian, *JCP* **1983,** 79, 302.

$O_2(N=1, j=0) + p\text{-}H_2 \rightarrow O_2(N=1, j=1) + p\text{-}H_2$



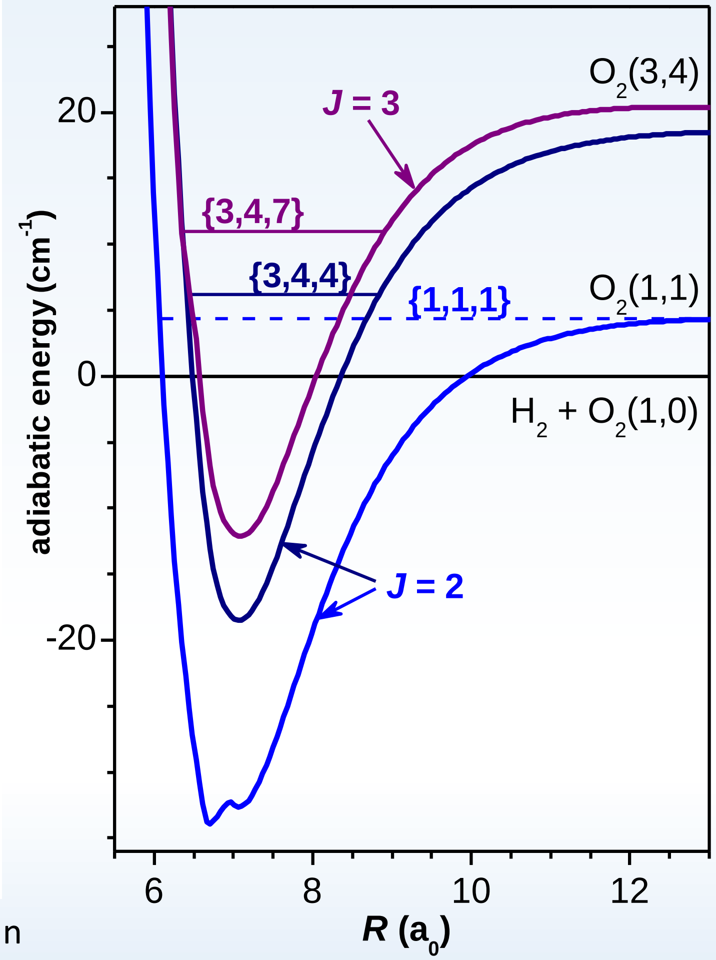
Integral cross sections (ICS)



Adiabatic bender curves

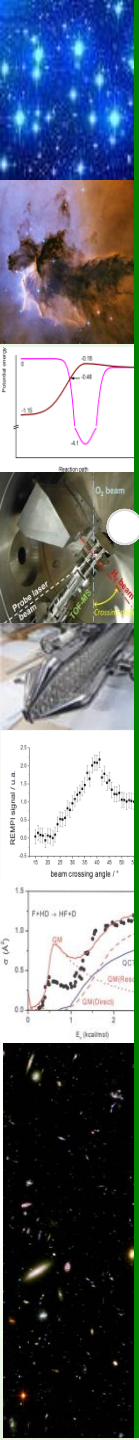
(for *J* = 2 and 3 peaks)

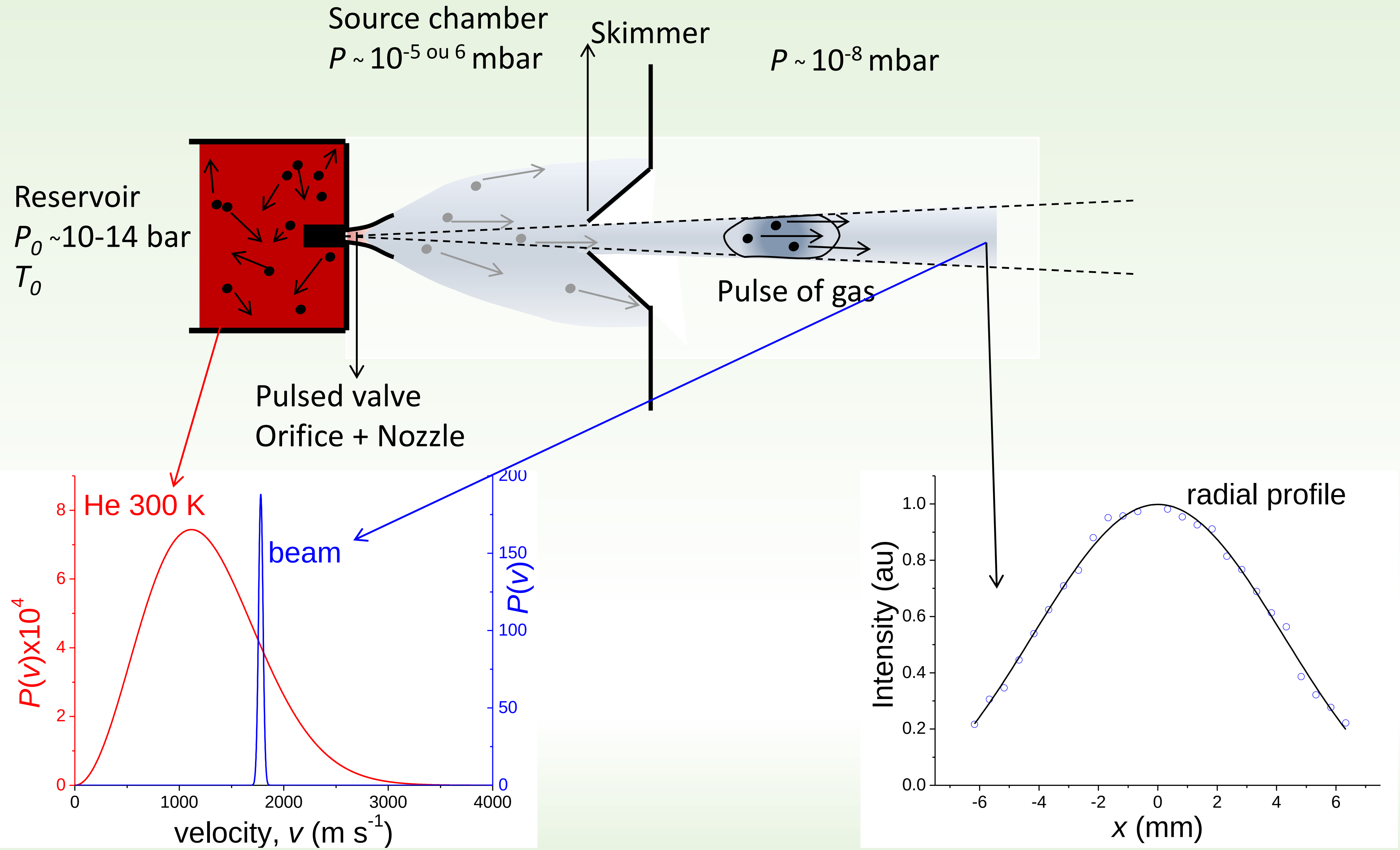
Quasi-bound states labeled as {N, j, l}



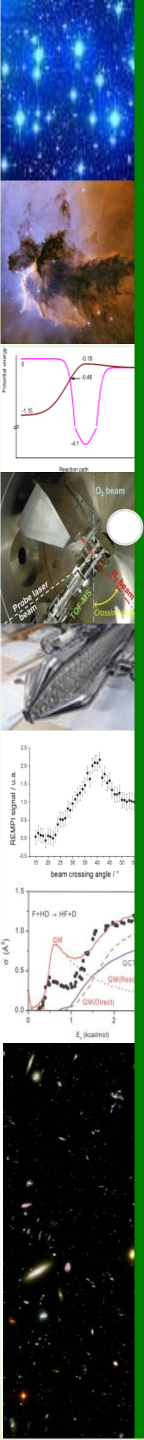
Simon Chefdeville, Yulia Kalugina, Sebastiaan Y. T. van de Meerakker, Christian Naulin, François Lique, Michel Costes, ***Science, 341, 1094 (2013)***

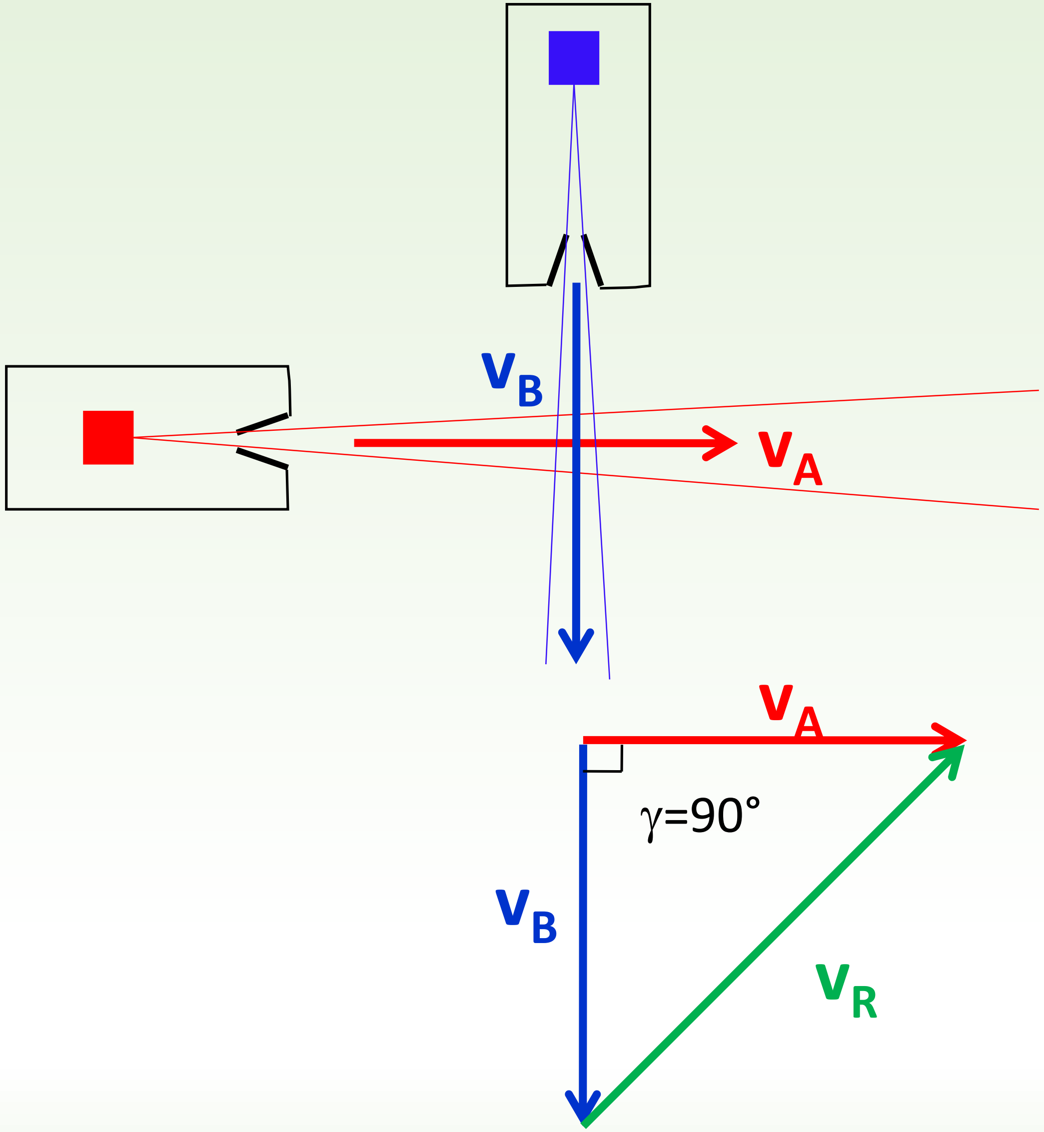
The Quest for cold collisions



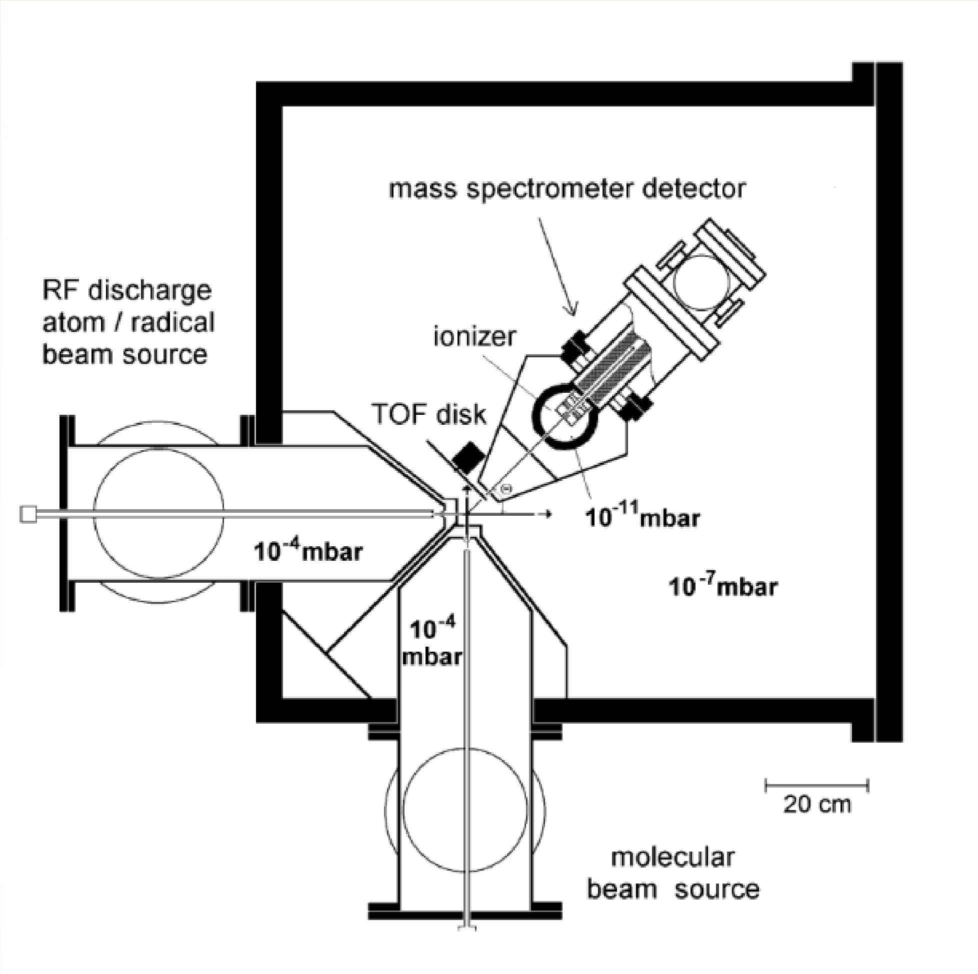


The Quest for cold collisions

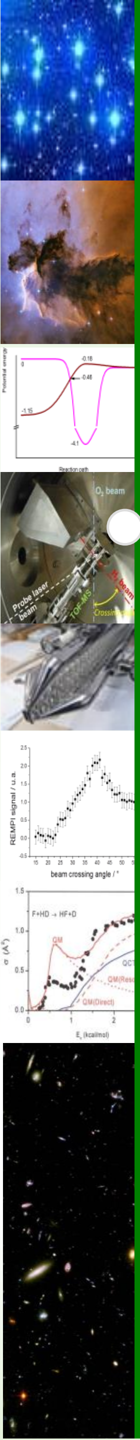




$$E_T = \tfrac{1}{2}\,\mu V_R^2 = \tfrac{1}{2}\,\mu\,(v_A^2 + v_B^2 - 2\,v_A\,v_B\cos\gamma)$$



P. Casavecchia et al., Univ. Perugia, It

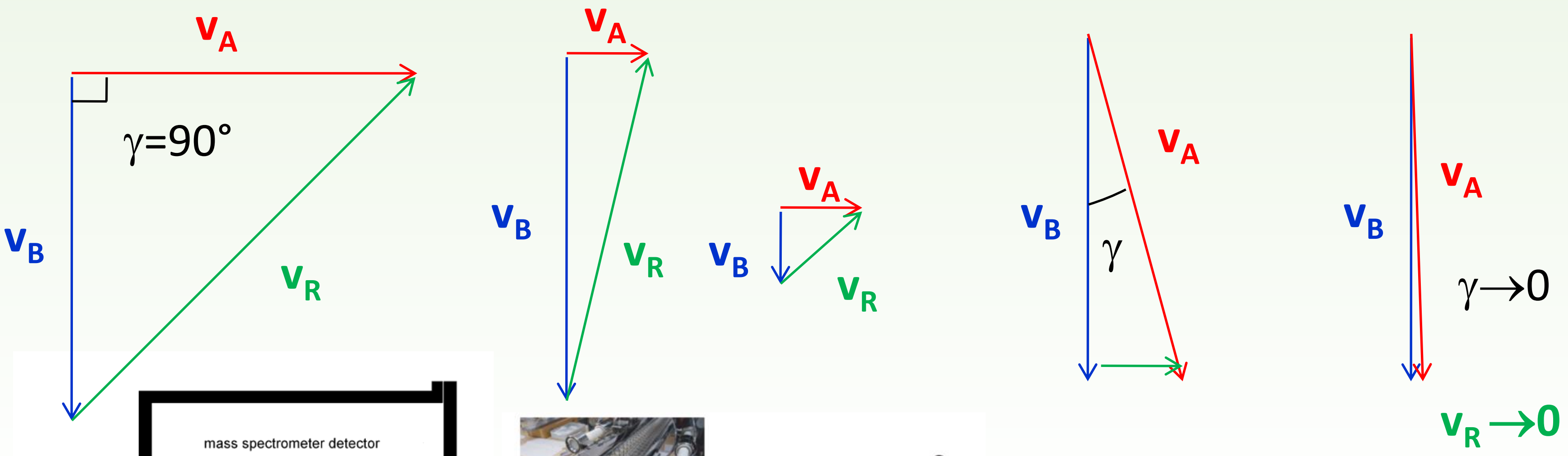


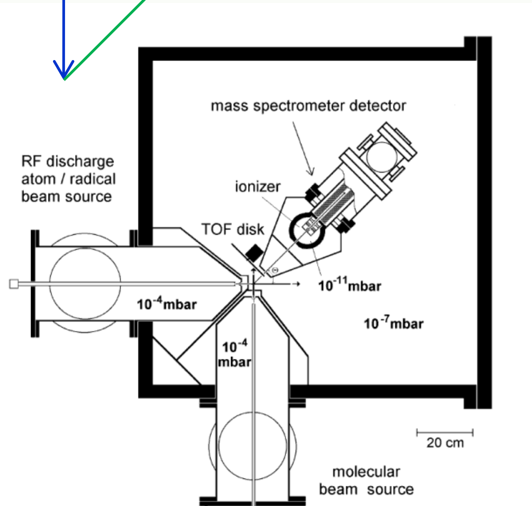
The Quest for cold collisions

Very cold collisions: HOW?

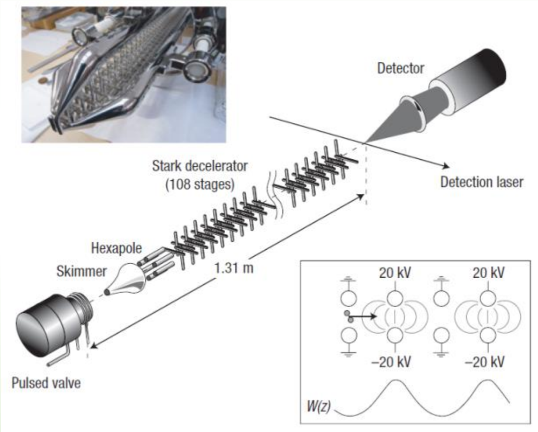
$$E_T = \tfrac{1}{2}\,\mu V_R^2 = \tfrac{1}{2}\,\mu\,(V_A^2 + V_B^2 - 2\,V_A\,V_B\cos\gamma)$$

$v_A \approx v_B$, ***matched velocity vectors absolutely needed!***

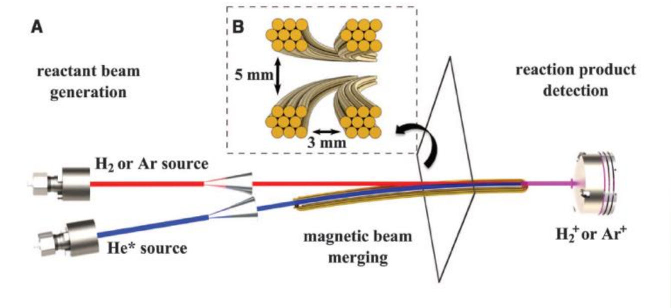




P. Casavecchia

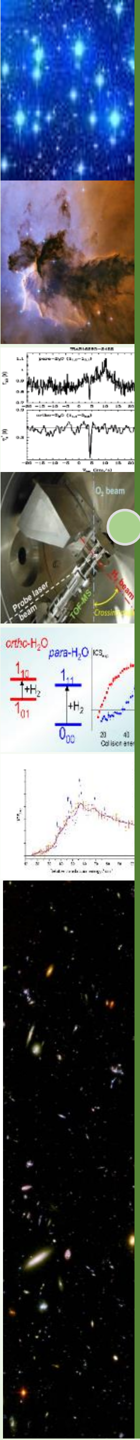


S. van de Meerakker

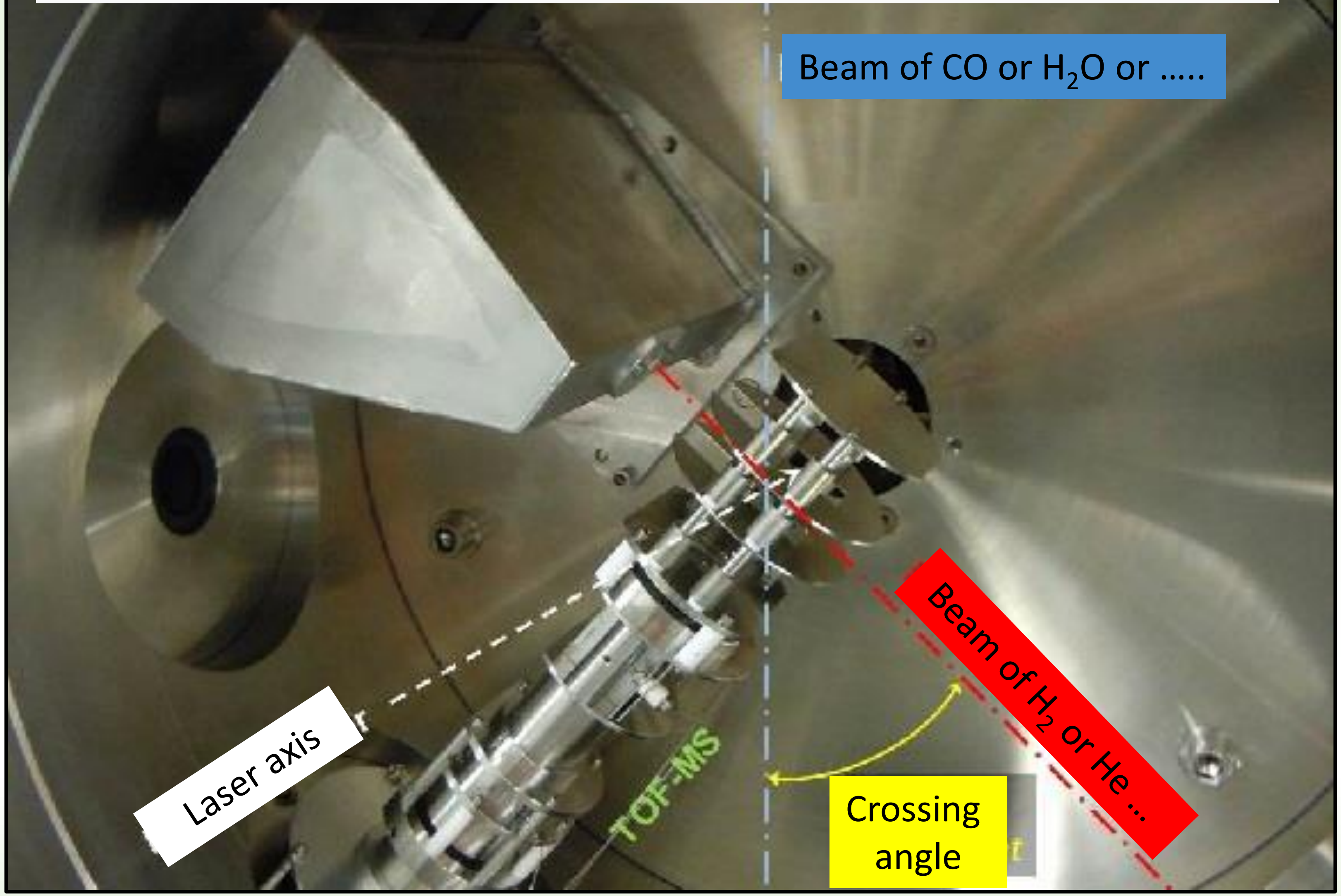


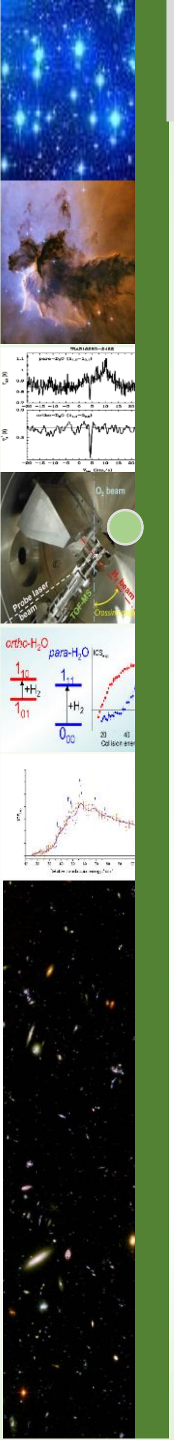
E. Narevicius

CMB in Bordeaux



CMB = crossed-molecular beams



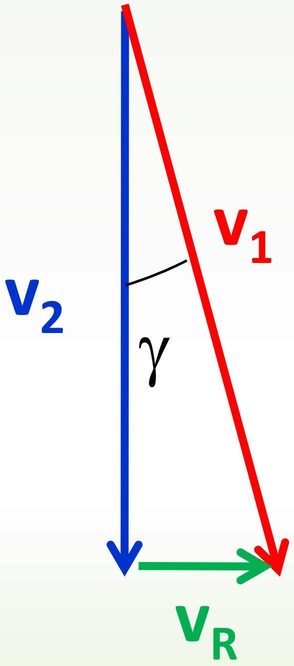


CMB in Bordeaux

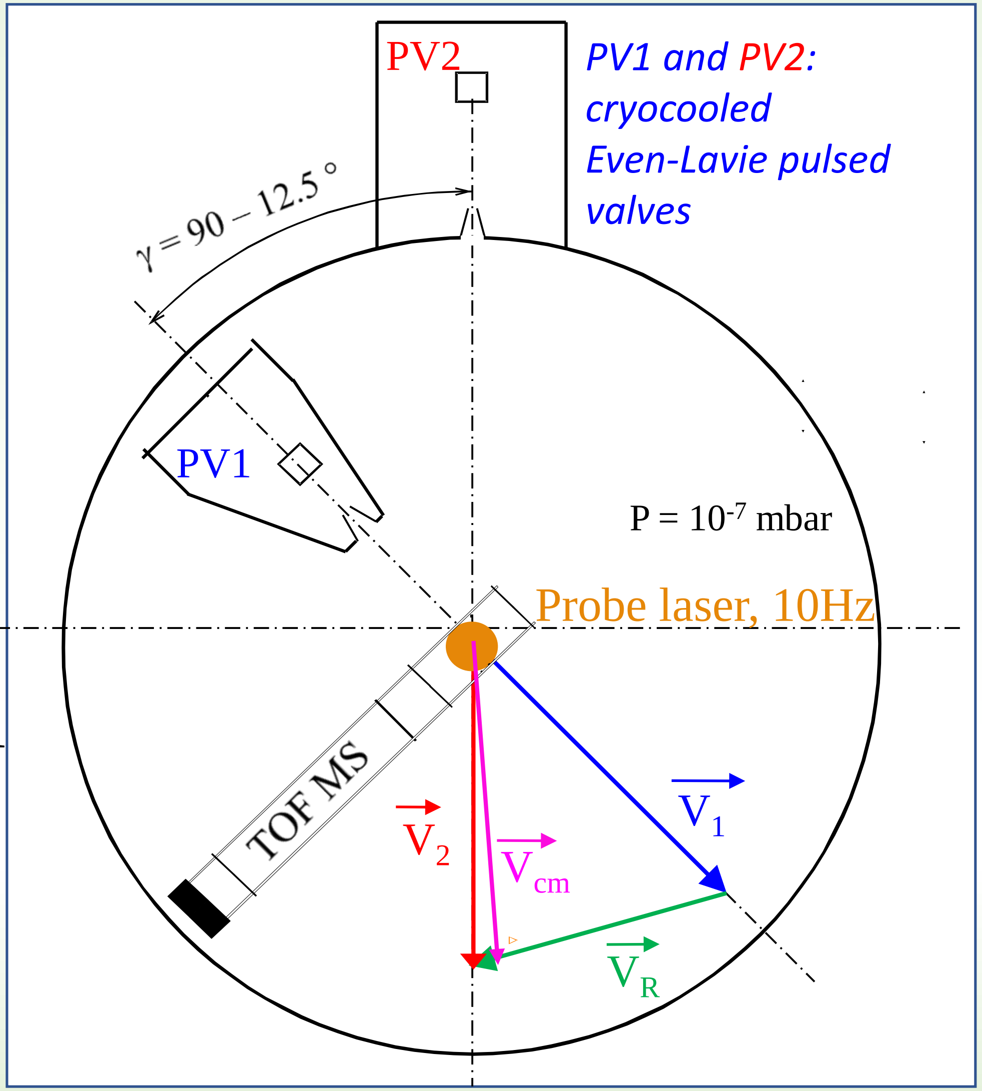
Very cold collisions: HOW?

$$E_T = \frac{1}{2}\,\mu\,v_R^2 = \frac{1}{2}\,\mu\,(v_1^{\,2} + v_2^{\,2} - 2\,v_1\,v_2\cos\chi)$$

$v_1 \approx v_2$, matched velocity vectors absolutely needed!

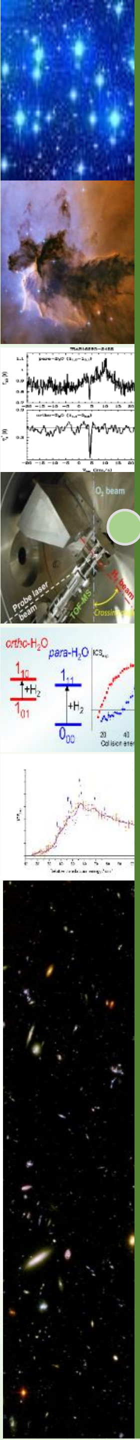


Lowest E_T = 87 J mol^{-1}
for C(^{3}P) + He
$T \approx 10.4$ K



Bergeat et al., Nat. Chem., 10, 519 (2018) (C+He)

$C(^3P_0)$ + He → $C(^3P_1)$ + He

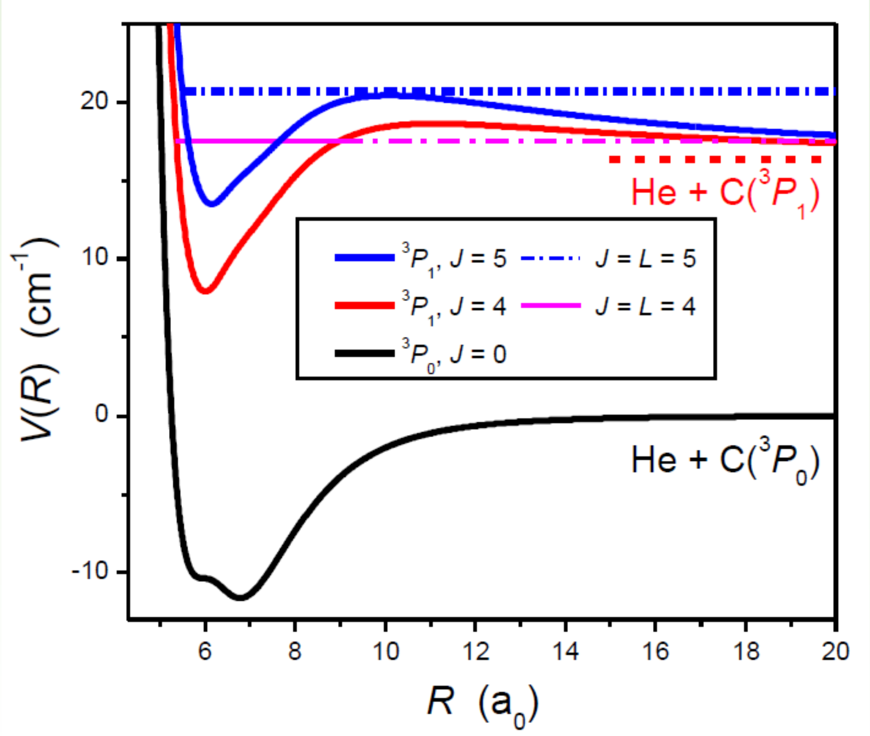


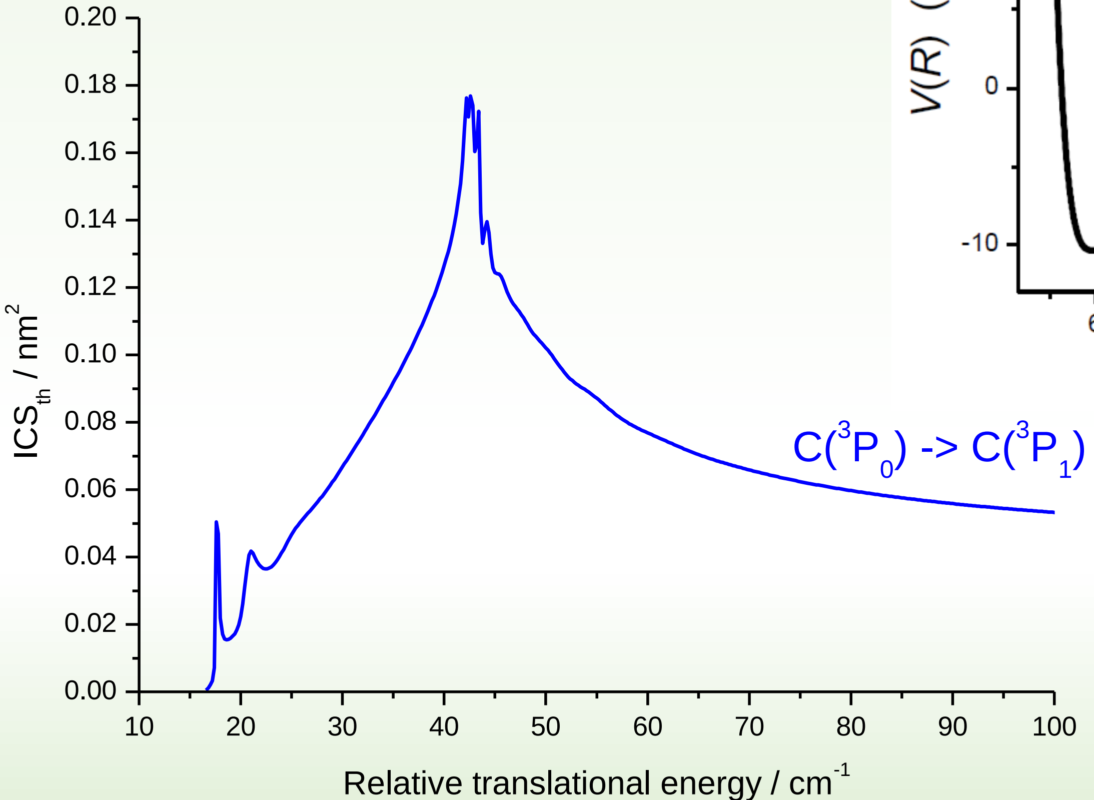
Partial wave analysis of the scattering resonances:

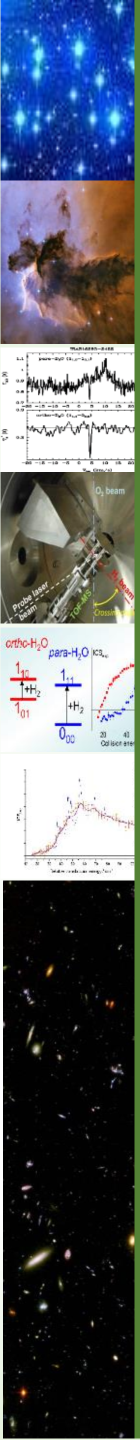
J. Kłos (*Univ. of Maryland)* and François Lique (*Univ. LeHavre*)

Adiabatic bender model :

- *First peak (J=4) at* 16.5 cm^{-1}*:*
  Shape resonances
- *Second peak (J=5) at* 20.5 cm^{-1}*:*
  Continuum state resonance



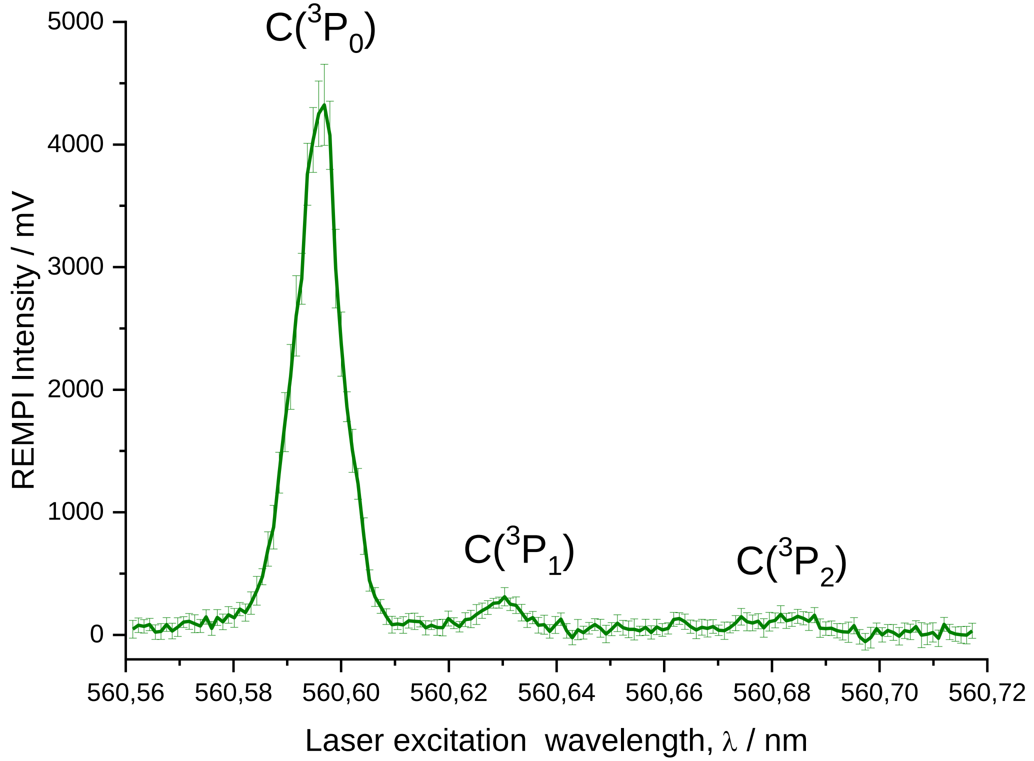


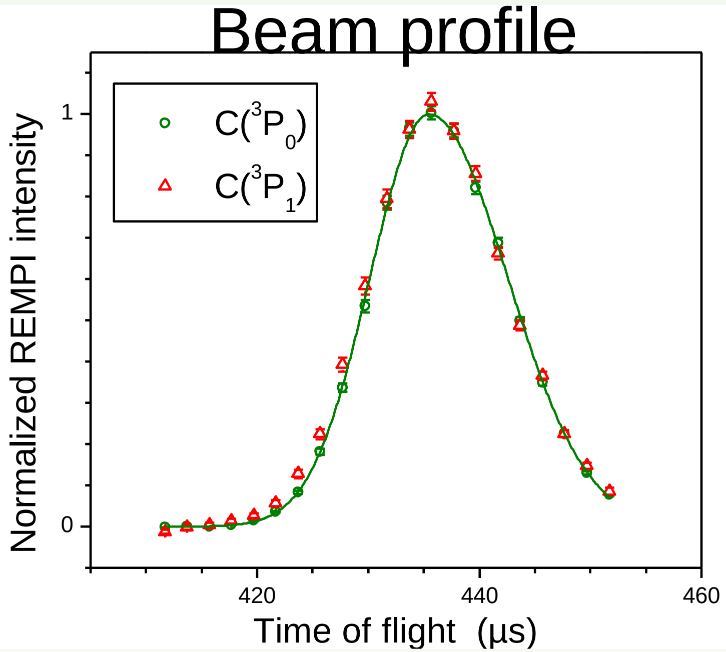


$C(^3P_0)$ + He → $C(^3P_1)$ + He

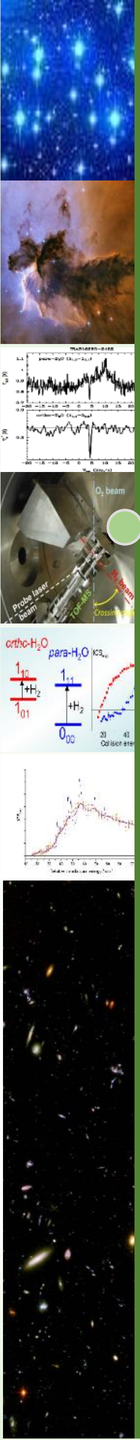
Gas	***T* / K**	**ν /m s⁻¹**	**δν /m s⁻¹**	***S*=ν/δν**	**Angular spread**
0.3% CO:Ne + discharge = C	300	814	12.1	>65	0.94°
He	45	864	11.5	>65	1.46°

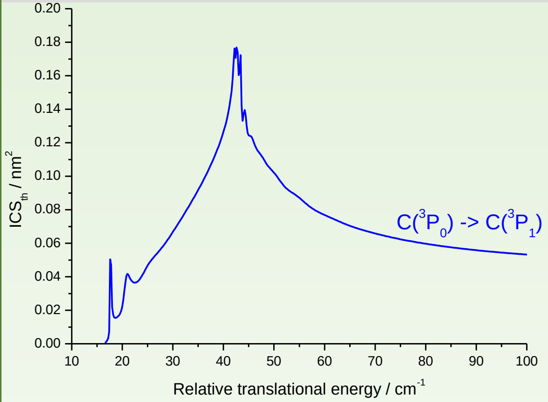
- less than 10% $C(^3P_1)$, corresponding to an equilibrium distribution at T < 8 K.

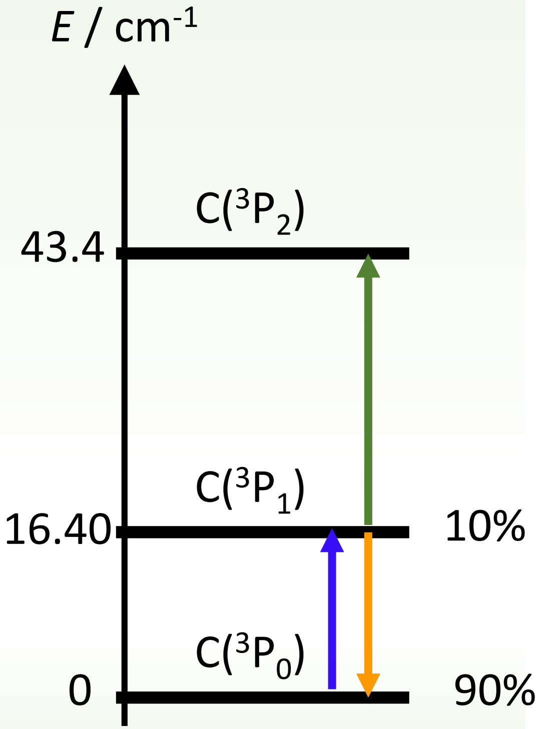




$C(^3P_0)$ + He → $C(^3P_1)$ + He



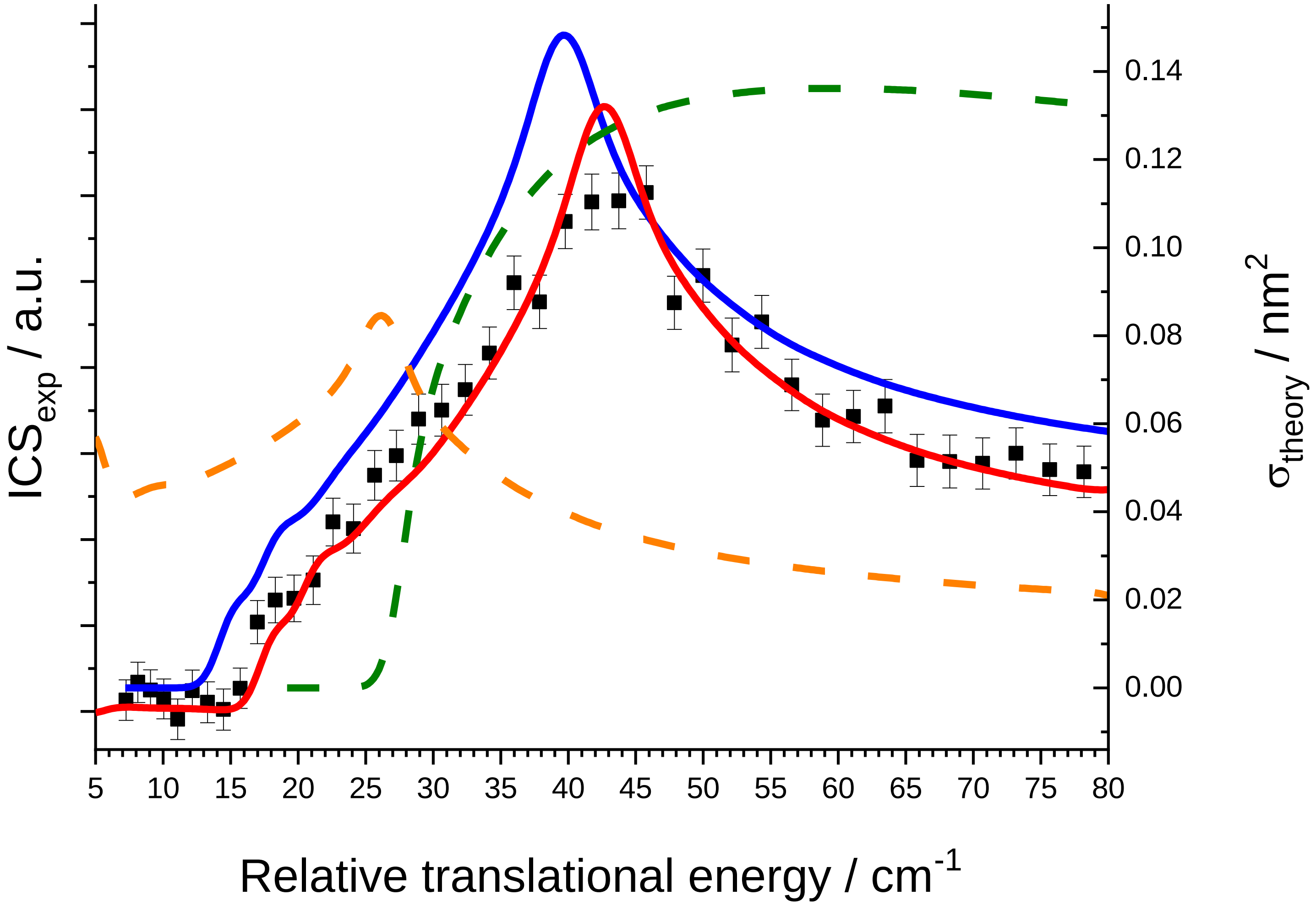




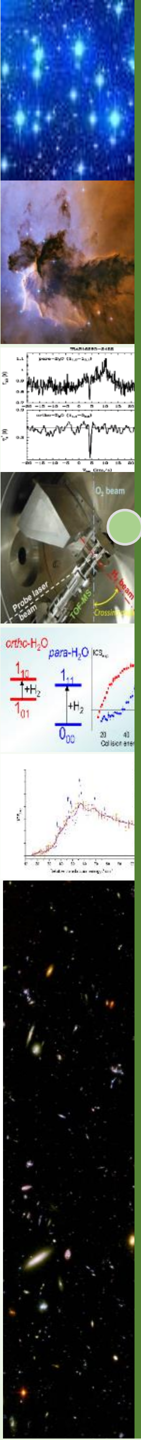
convoluted theory:

- $C(^3P_0)$ + He → $C(^3P_1)$ + He
- $C(^3P_1)$ + He → $C(^3P_2)$ + He
- $C(^3P_1)$ + He → $C(^3P_0)$ + He
- Total $(\sigma_{0\rightarrow1})$ - 0.1 $(\sigma_{1\rightarrow2} + \sigma_{1\rightarrow0})$

A. Bergeat, S. Chefdeville, M. Costes, S.B. Morales, Christian Naulin, U. Even, J. Klos, François Lique,
***Nat. Chem.*, <u>10</u>, 519 (2018)**

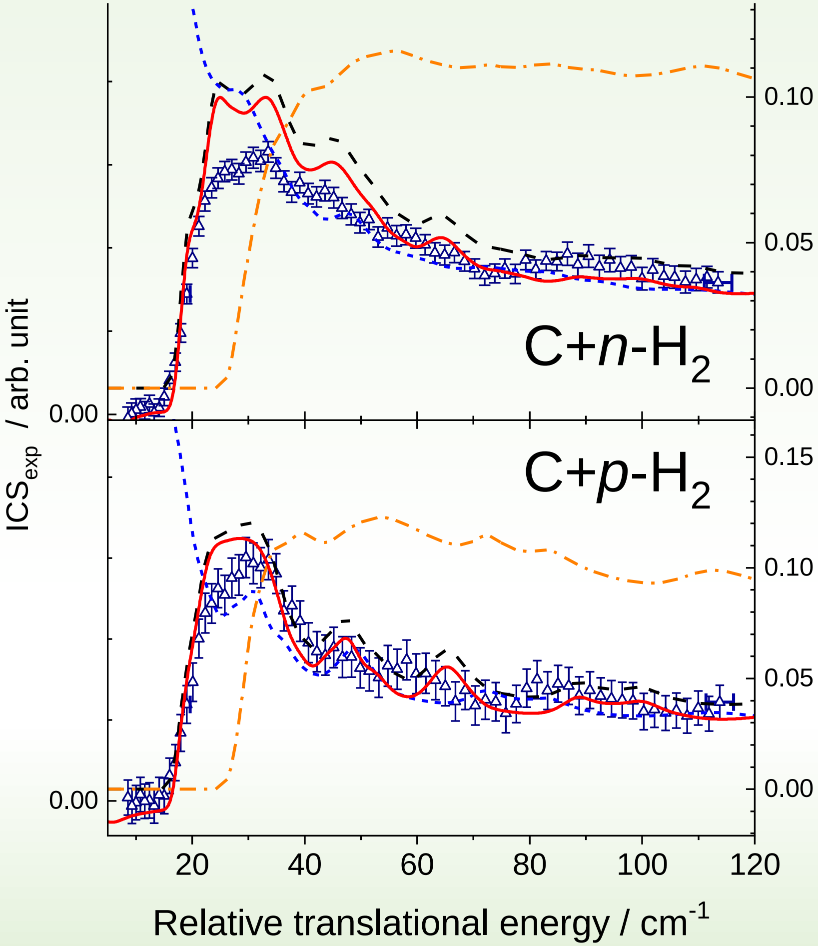


$C(^3P_0) + H_2 / D_2 \rightarrow C(^3P_1) + H_2 / D_2$

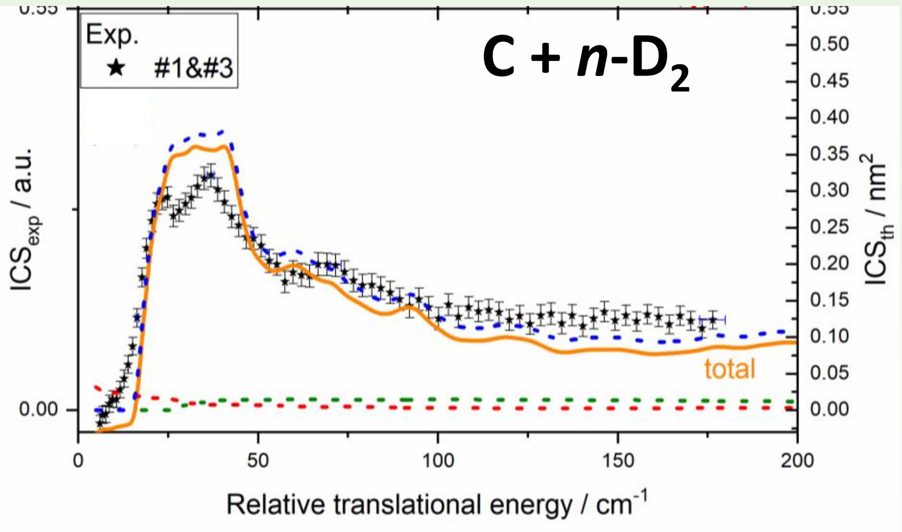


convoluted theory:

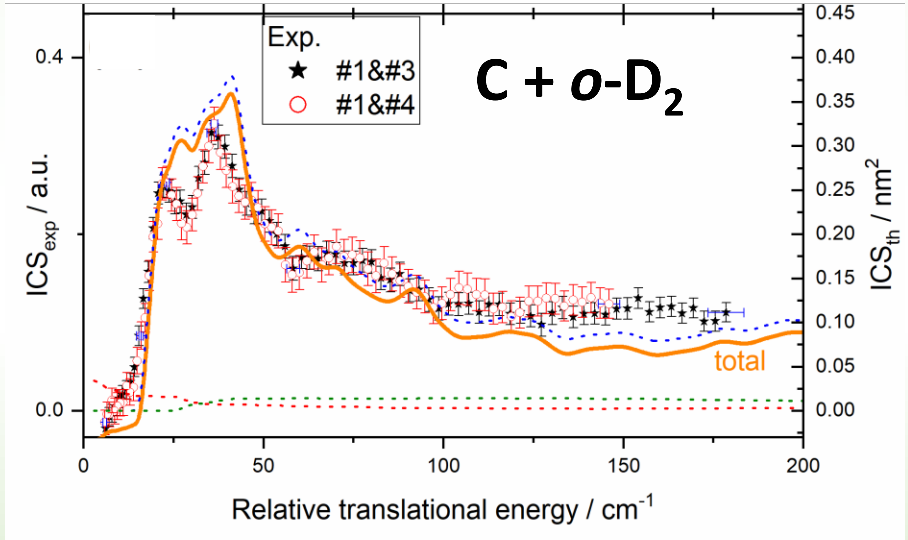
- $C(^3P_0) + H_2 \rightarrow C(^3P_1) + H_2$
- $C(^3P_1) + H_2 \rightarrow C(^3P_2) + H_2$
- $C(^3P_1) + H_2 \rightarrow C(^3P_0) + H_2$
- Total

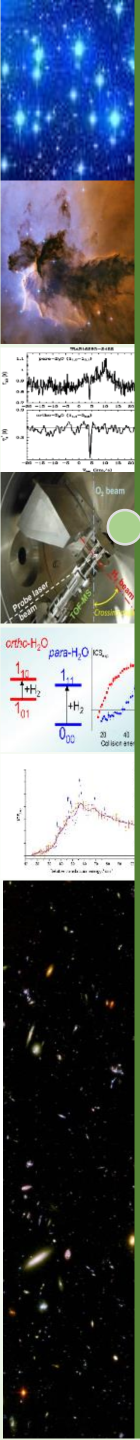


- *para*-H_2: 100% j=0
- *normal*-H_2: 25% j=0 and 75% j=1



- *ortho*-D_2: 100% j=0
- *normal*-D_2: 66% j=0 and 33% j=1

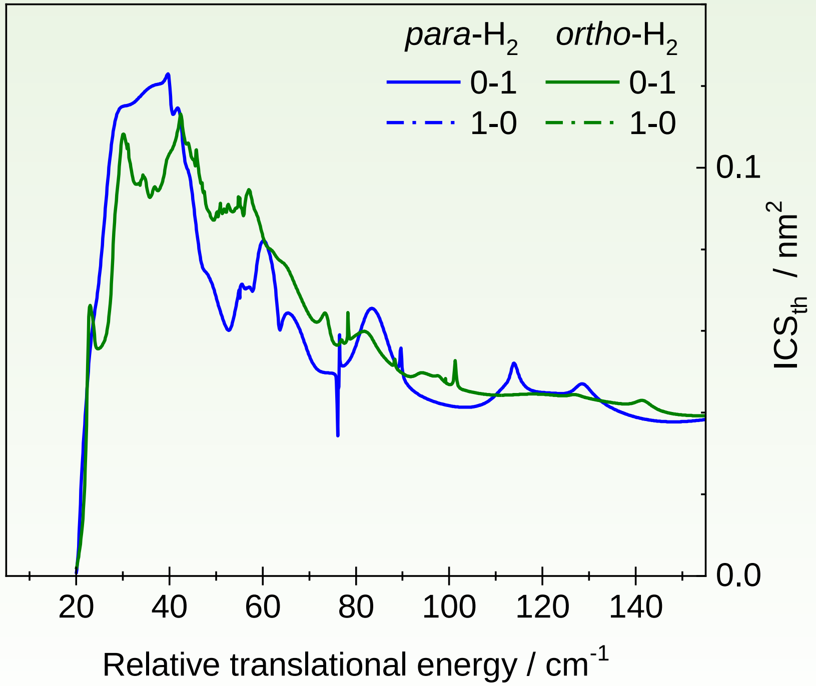


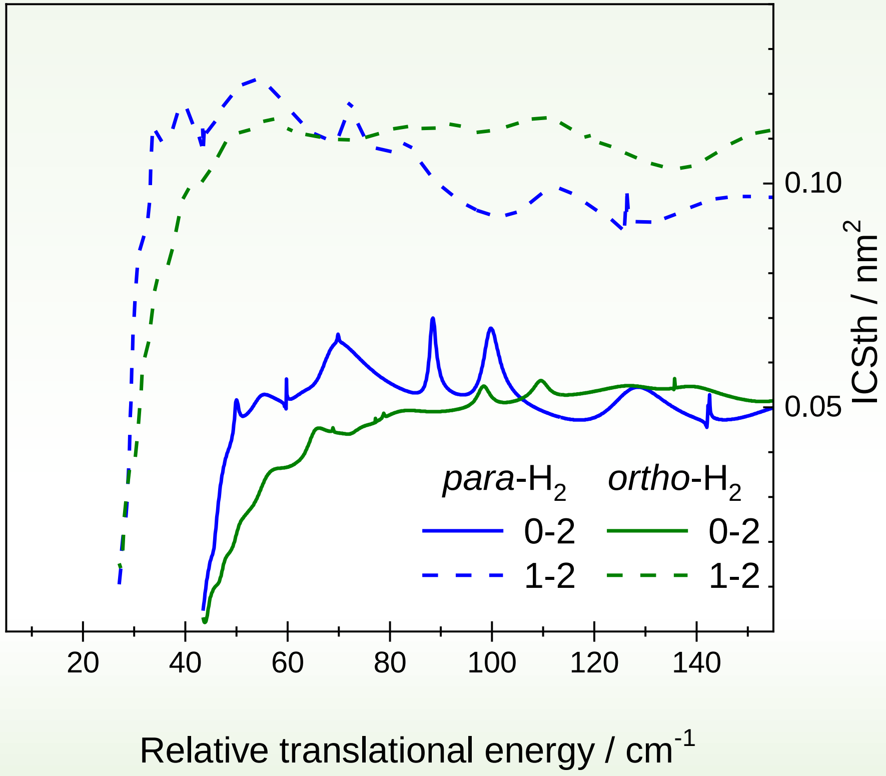


$C(^3P_0) + H_2 \rightarrow C(^3P_{1,2}) + H_2$

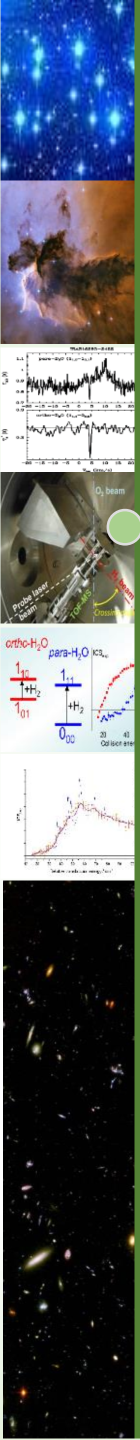
Calculated ICSs:

J. Kłos (*Univ. of Maryland)* and François Lique (*Univ. LeHavre*)





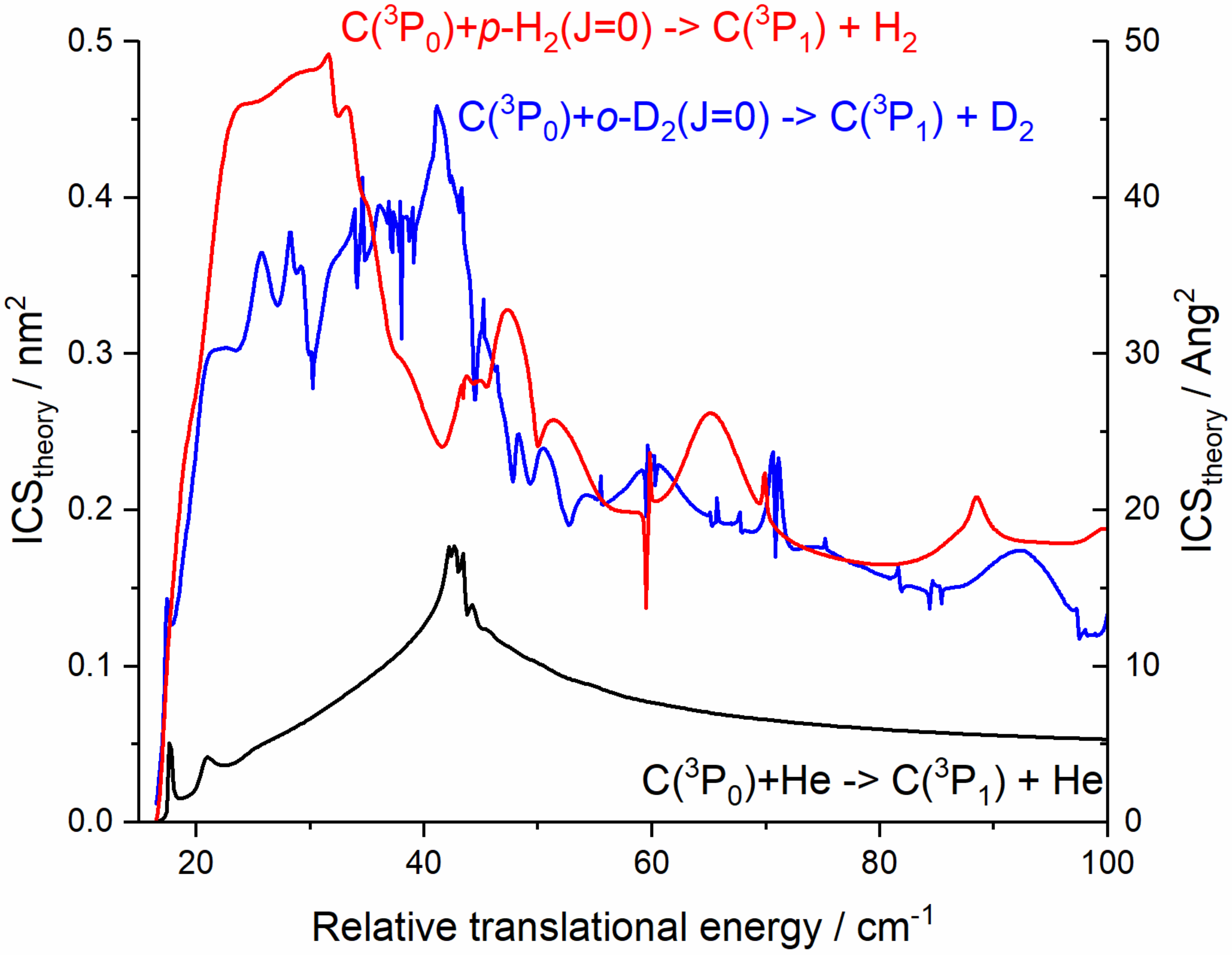
J. Klos, A. Bergeat, G. Vanuzzo, S.B. Morales, Christian Naulin, François Lique,
J. Phys. Chem. Lett., 9, 6496 (2018)



$C(^3P_0)$ + He / H_2 / D_2 → $C(^3P_1)$ + He / H_2 / D_2

Calculated ICSs:

J. Kłos (*Univ. of Maryland)* and François Lique (*Univ. LeHavre*)



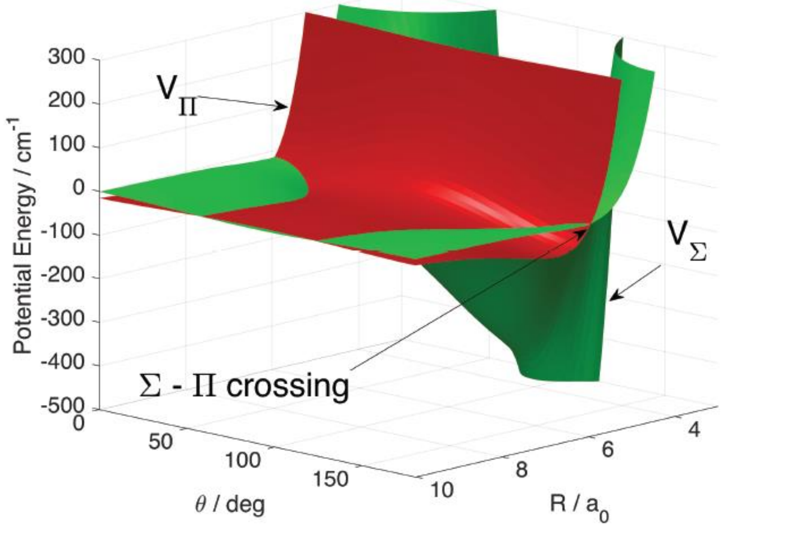


Figure 2: Surface plot of the V_Σ (green) and V_Π diabatic PESs. The crossing between collinear Σ and Π states is indicated with the arrow.

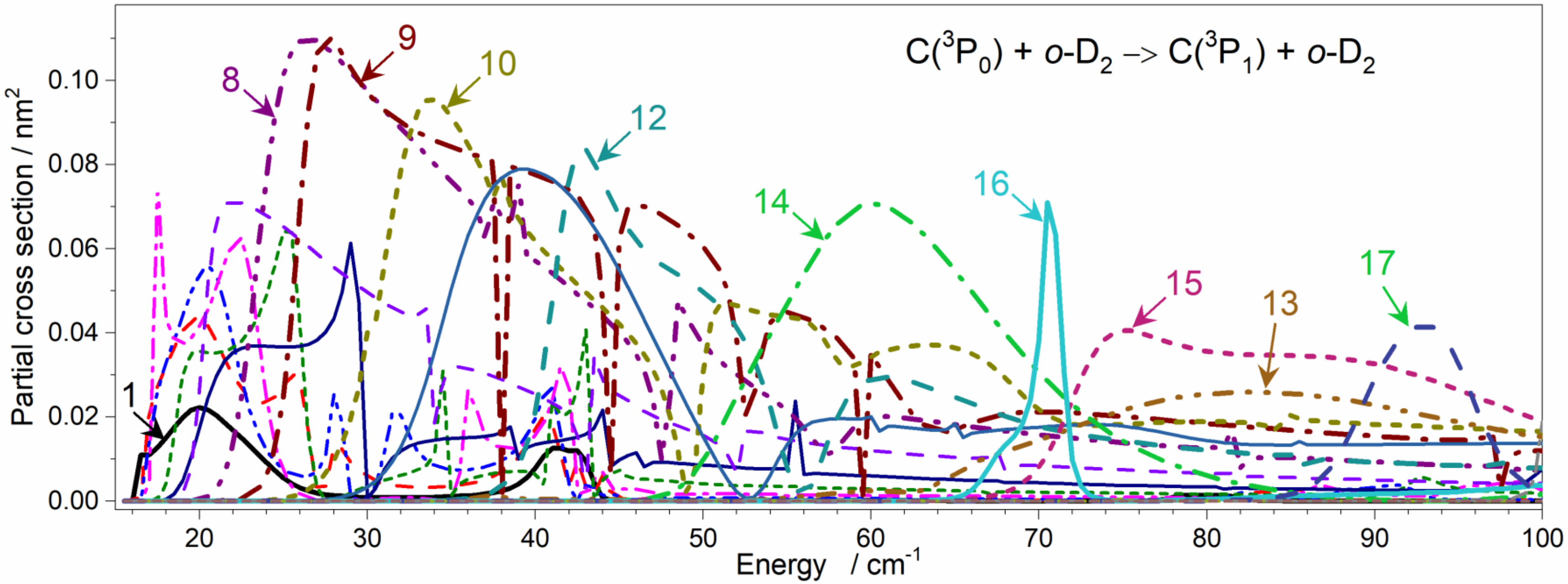
New highly correlated $C(^3P)$-H_2 PESs were computed at multireference configuration interaction method with large atomic basis set.

A. Bergeat, S.B. Morales, Christian Naulin, J. Klos, François Lique,
***Front. Chem.**, **7**, 164 (2019)*

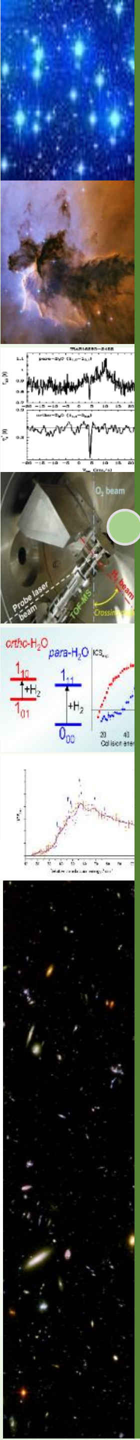
$C(^3P_0) + D_2 \rightarrow C(^3P_1) + D_2$

Calculated ICSs:

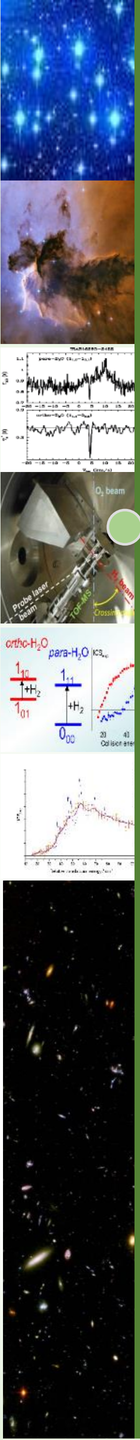
J. Kłos (*Univ. of Maryland)* and François Lique (*Univ. LeHavre*)

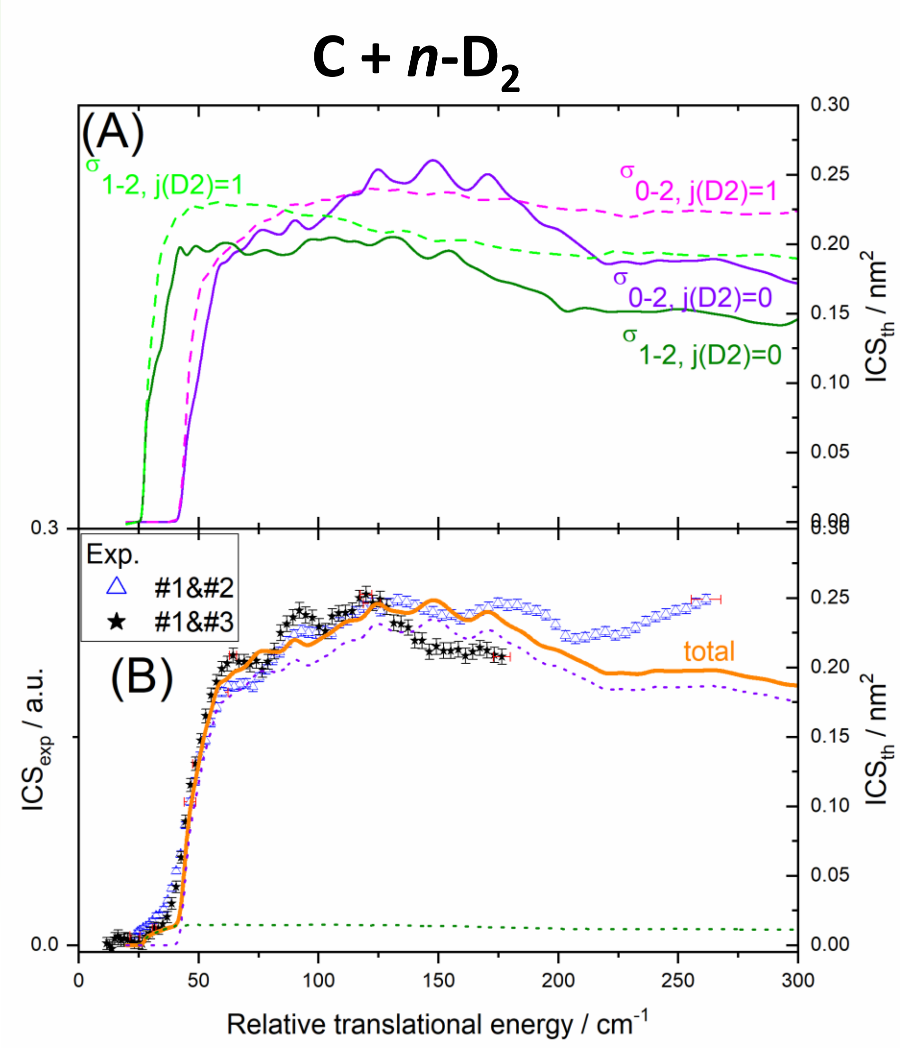


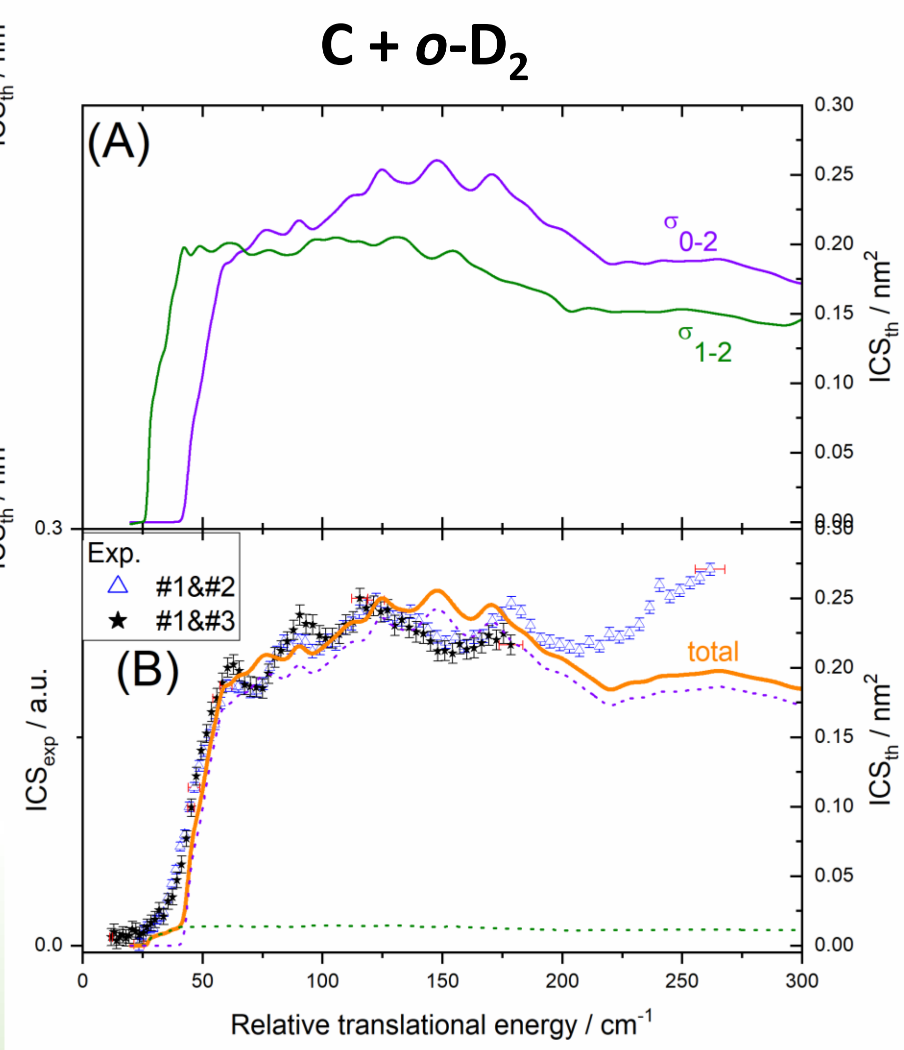
A. Bergeat, S.B. Morales, Christian Naulin, J. Klos, François Lique,
***Front. Chem.**, 7, 164 (2019)*

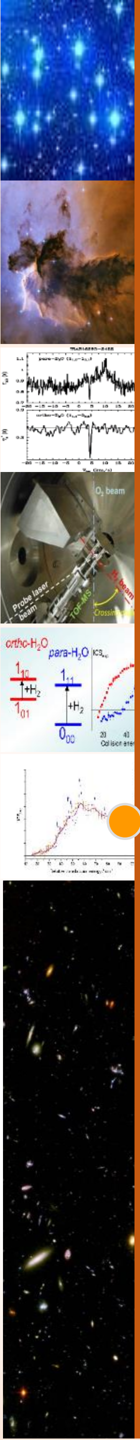


$C(^3P_1) + D_2 \rightarrow C(^3P_2) + D_2$

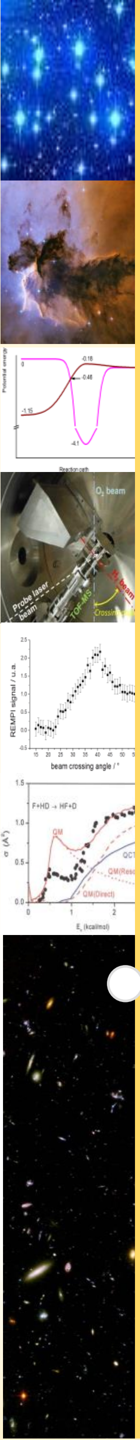








Results: $D_2O + H_2$



Ozone in the stratosphere

- *Free radical O_3:* Mass Independent Fractionation

MEASUREMENT OF HEAVY OZONE IN THE STRATOSPHERE

Konrad Mauersberger

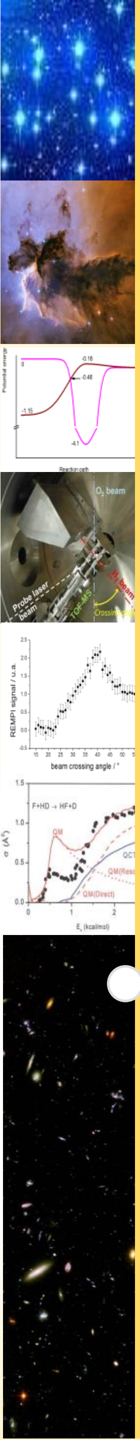
School of Physics and Astronomy, University of Minnesota, Minneapolis, MN 55455

Geophys. Res. Lett. 1981, *8*, 935.

Abstract. The distribution of heavy ozone (molecular mass 50) has been measured for the first time in the stratosphere with a mass spectrometer system. During a balloon descent after midnight on Sept. 4, 1980, a pronounced enhancement of heavy ozone was found. The maximum in the isotopic ratio, $^{18}O^{16}O_2/^{16}O_3$, occurred at 32 km where the enhancement of heavy ozone was over 40%. The ratio decreased toward higher and lower altitudes, and reached the standard value below 24 km. These measurements confirm an earlier prediction that there exists a preferred production mechanism for heavy ozone in the stratosphere.

- $O + O_2 \rightarrow O_3^*$
- $O_3^* + M \rightarrow O_3 + M$

- $^{18}O + O_2 \rightarrow {}^{16}O + {}^{18}O^{16}O$ ΔH°_0= -0.26 kJ/mol
- $^{16}O + {}^{18}O_2 \rightarrow {}^{18}O + {}^{18}O^{16}O$ ΔH°_0= 0.28 kJ/mol



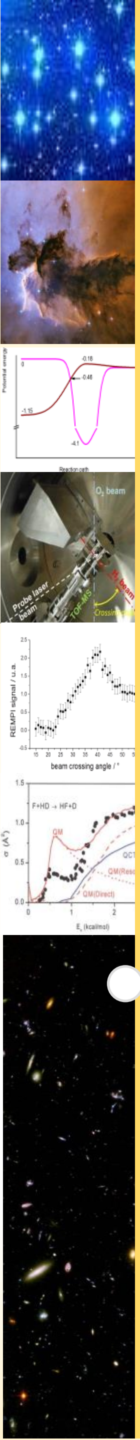
Astrophysics: fractionation

- *Fractionation in the ISM: C, N, H some theoretical works and experiments. O ?*

Table 4: Observed $^{32}S^{16}O/^{32}S^{18}O$, $^{32}S^{16}O/^{34}S^{16}O$, and $^{34}S^{16}O/^{32}S^{18}O$ column density ratios.

	$N(H_2)$ in cm^{-2}	$^{32}S^{16}O/^{32}S^{18}O$	$^{32}S^{16}O/^{34}S^{16}O$	$^{34}S^{16}O/^{32}S^{18}O$
TMC1 (this work)	1.0×10^{22}	115 ± 13	19.5 ± 2.2	5.9 ± 1.4
L483 (this work)	3.0×10^{22}	158 ± 47	31 ± 9	5.1 ± 1.5
B1-b (this work)	7.6×10^{22}	–	–	5.2 ± 1.4
L1689B (this work)	1.4×10^{23}	70 ± 20	23 ± 7	3.3 ± 1.1
Horsehead nebula (dense cloud) (this work)	3.0×10^{22}	170 ± 20	27.3 ± 1.2	6.1 ± 0.7
L1544 (Vastel et al. 2018)	4.5×10^{22}	–	–	4.7 ± 1.0
		$^{16}O/^{18}O$	$^{32}S/^{34}S$	$(^{16}O \times ^{34}S)/(^{18}O \times ^{32}S)$
Local ISM (Wilson 1999)		557 ± 30	≈ 22	25
Solar system (Lodders 2003)		500	22.5	22.2

JC Loison et al. MNRAS (2019)



$O + O_2$

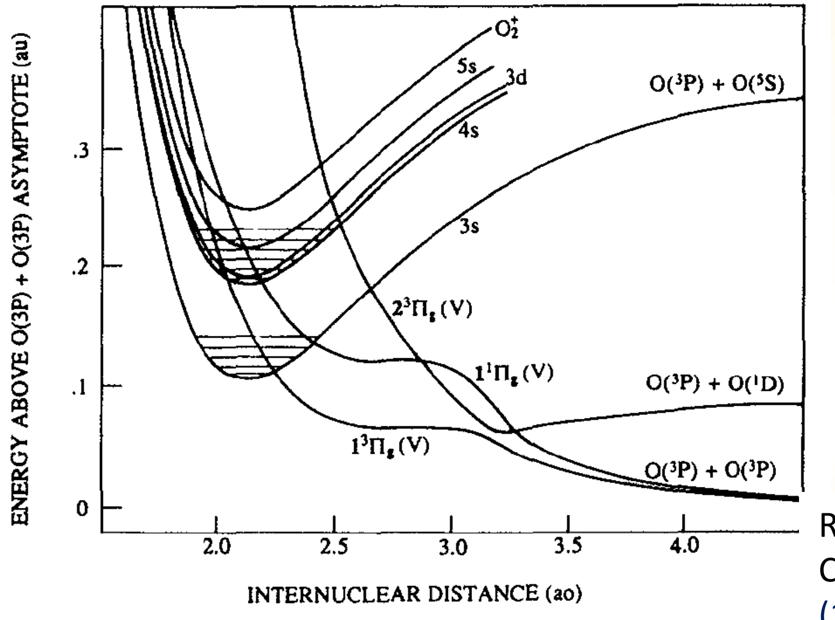
Detection of the $^{16}O_2$ beam:

Detection: 2+1 REMPI transitions at ~ 225 nm

($^3\Sigma_0^-$,v=2 ← $X^3\Sigma_g^-$,*v*=0) and

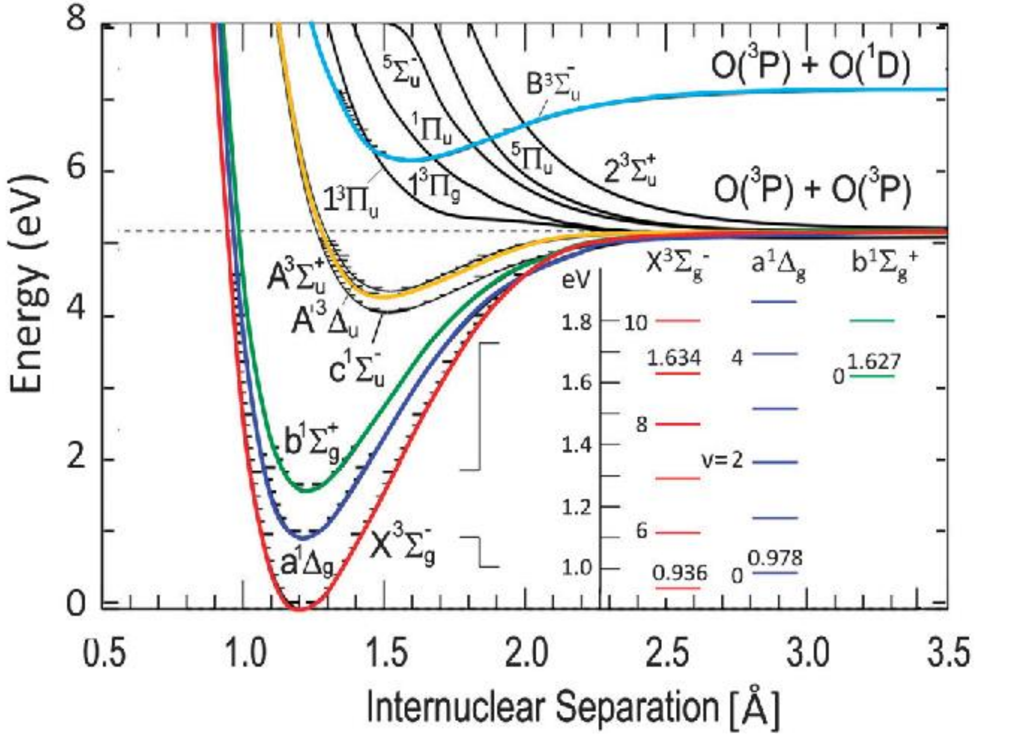
($^3\Sigma_1^-$,*v*=2 ← $X^3\Sigma_g^-$,*v*=0)

Rydberg states



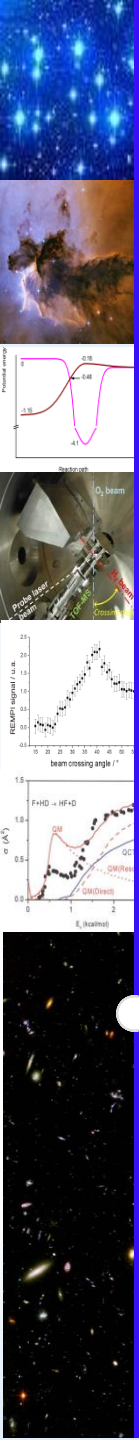
R.J. Yokelson, R.J. Lipert, W. A. Chupka, *J Chem Phys* 97, 6153 (1992)

O_2: Multiple states, products



Z Farooq, D Chestakov, B Yan, GC Groenenboom, W van der Zande, DH Parker PCCP (2014)

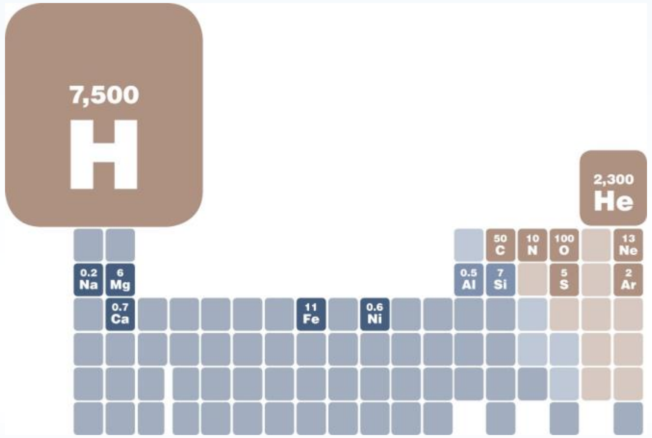
Conclusion: Atomic and molecular collisions

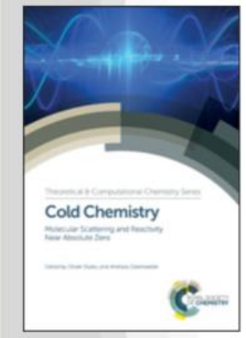


✓ first experimental observations of partial wave resonances for an inelastic collision processes studied under collision conditions approaching the cold energy regime

✓ sensitive probe of a PESs under such conditions (reactive and inelastic collisions)

✓ validation of the PESs allowing for rate calculations valuable for astrophysics models





Cold Chemistry: Molecular Scattering and Reactivity Near Absolute Zero

Editors: Olivier Dulieu, Andreas Osterwalder

Chap. 3

C. Naulin & A. Bergeat, ***Low-energy Scattering in Crossed Molecular Beams (2018)***

CMB Group's members:
Astrid Bergeat
Sébastien Morales
Christian Naulin
Chloé Miossec (Master 1)

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Université de Bordeaux and CNRS

BORDEAUX

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CUB 727 256 Inhabitant (rank 3) 1 255 hab./km²