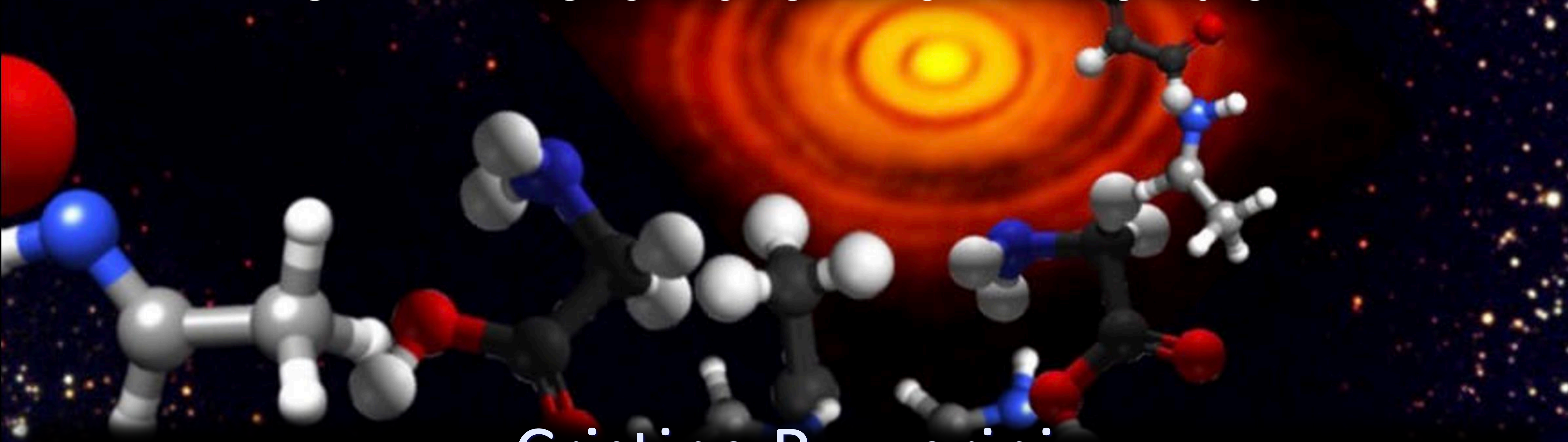
Il mistero della chimica dell'universo



Cristina Puzzarini

Dipartimento di Chimica "Giacomo Ciamician"

Università di Bologna

L’umanità osserva il cielo da millenni …

Se di notte, lontano dalle luci della città, guardiamo il cielo, lo vediamo ricco di stelle e sembra che non ci sia nulla tra una stella e l’altra: il cielo ci appare un grande spazio vuoto …

… In prima approssimazione quest’idea non è del tutto errata

… ma come spesso accade, una piccola quantità fa una grandissima differenza …

L’umanità osserva il cielo da millenni …

Se di notte, lontano dalle luci della città, guardiamo il cielo, lo vediamo ricco di stelle e sembra che non ci sia nulla tra una stella e l’altra: il cielo ci appare un grande spazio vuoto …

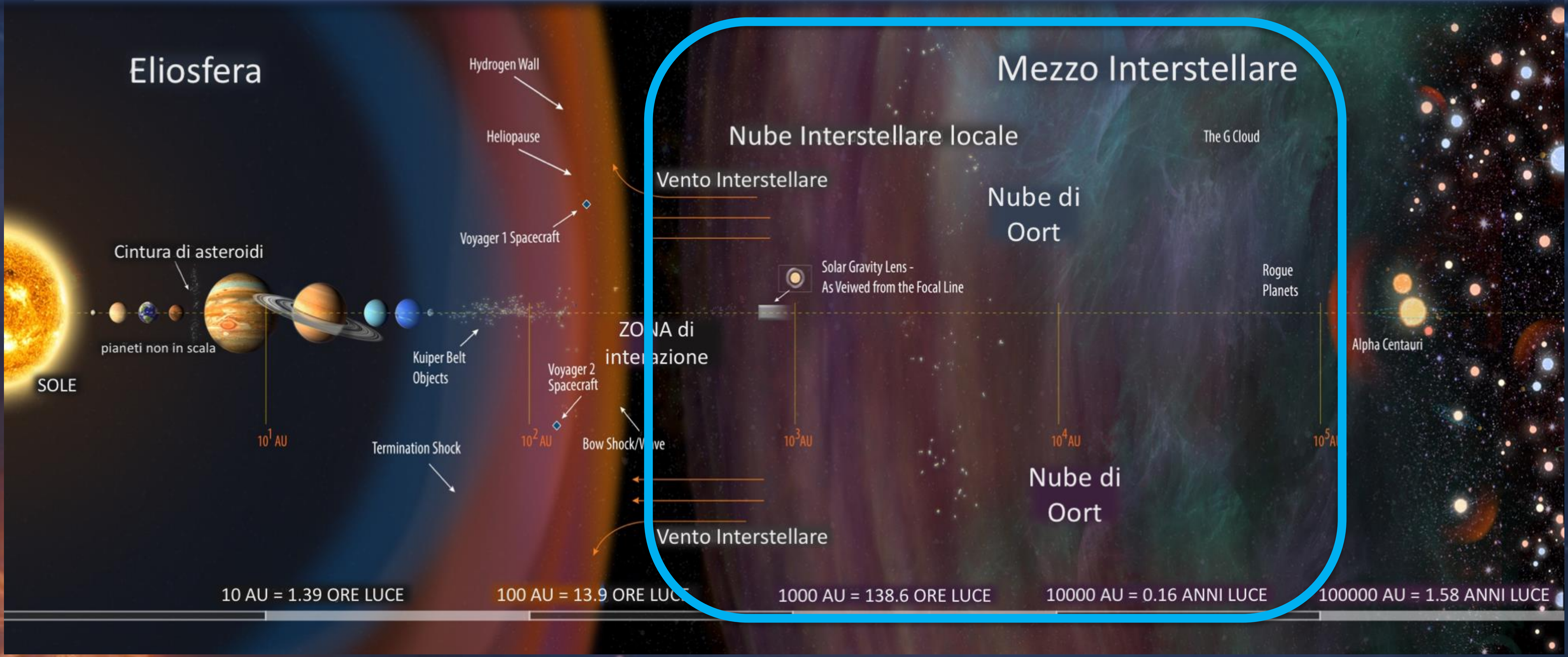
1904 (Hartmann):

Scoperta del gas interstellare …

1930 (Trumpler):

Scoperta della polvere interstellare …

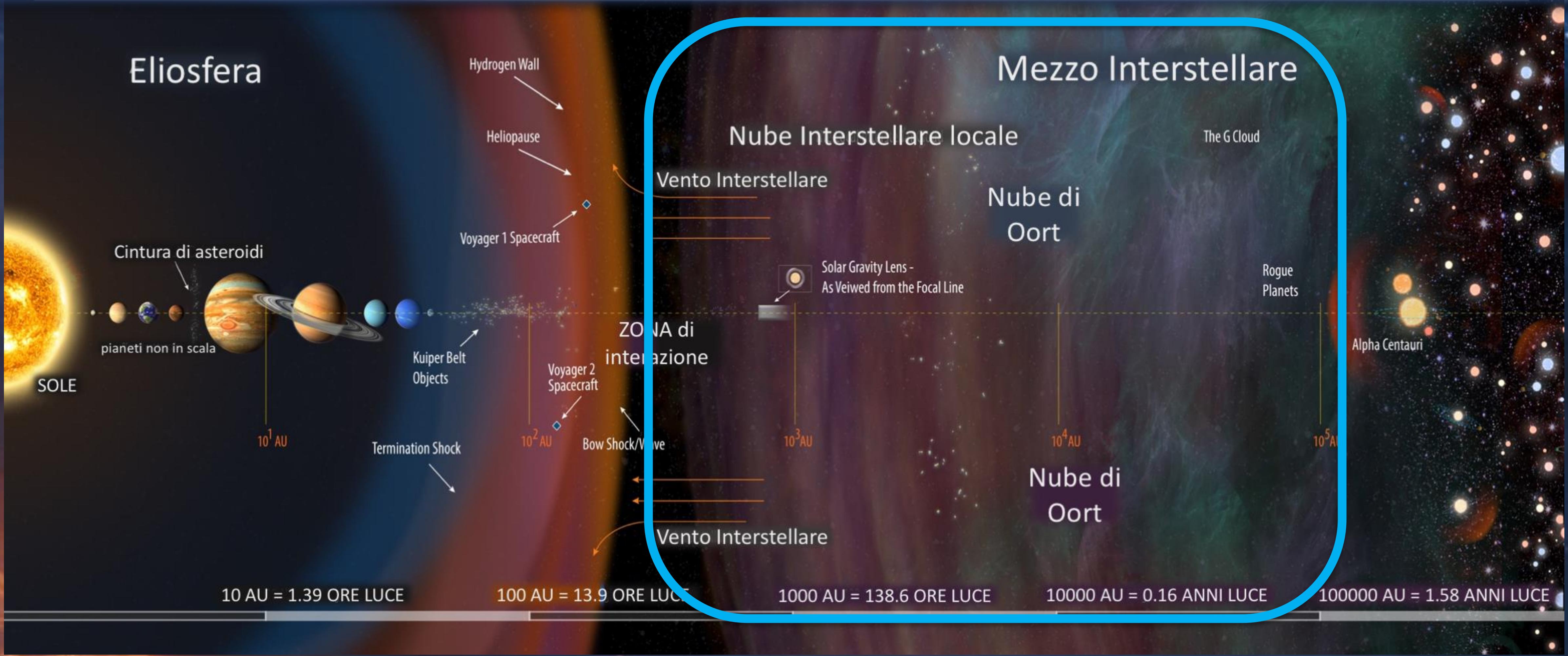
Che cos'è il mezzo interstellare?



~4%

Mezzo interstellare (ISM):
il materiale rarefatto costituito da gas e polvere che si trova tra i sistemi solari all'interno di una galassia

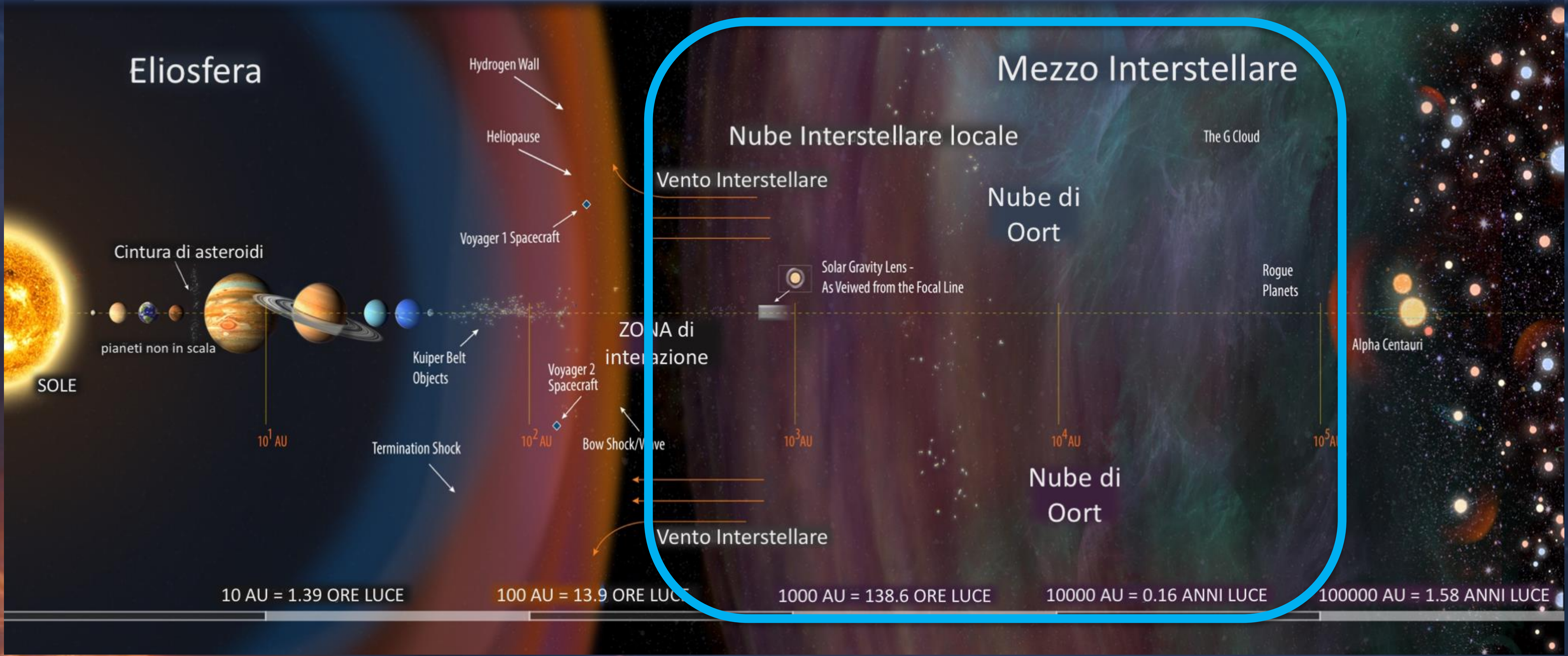
Che cos'è il mezzo interstellare?



Mezzo interstellare (ISM): ~99%

il materiale rarefatto costituito da gas e polvere che si trova tra i sistemi solari all'interno di una galassia ~1%

Che cos'è il mezzo interstellare?

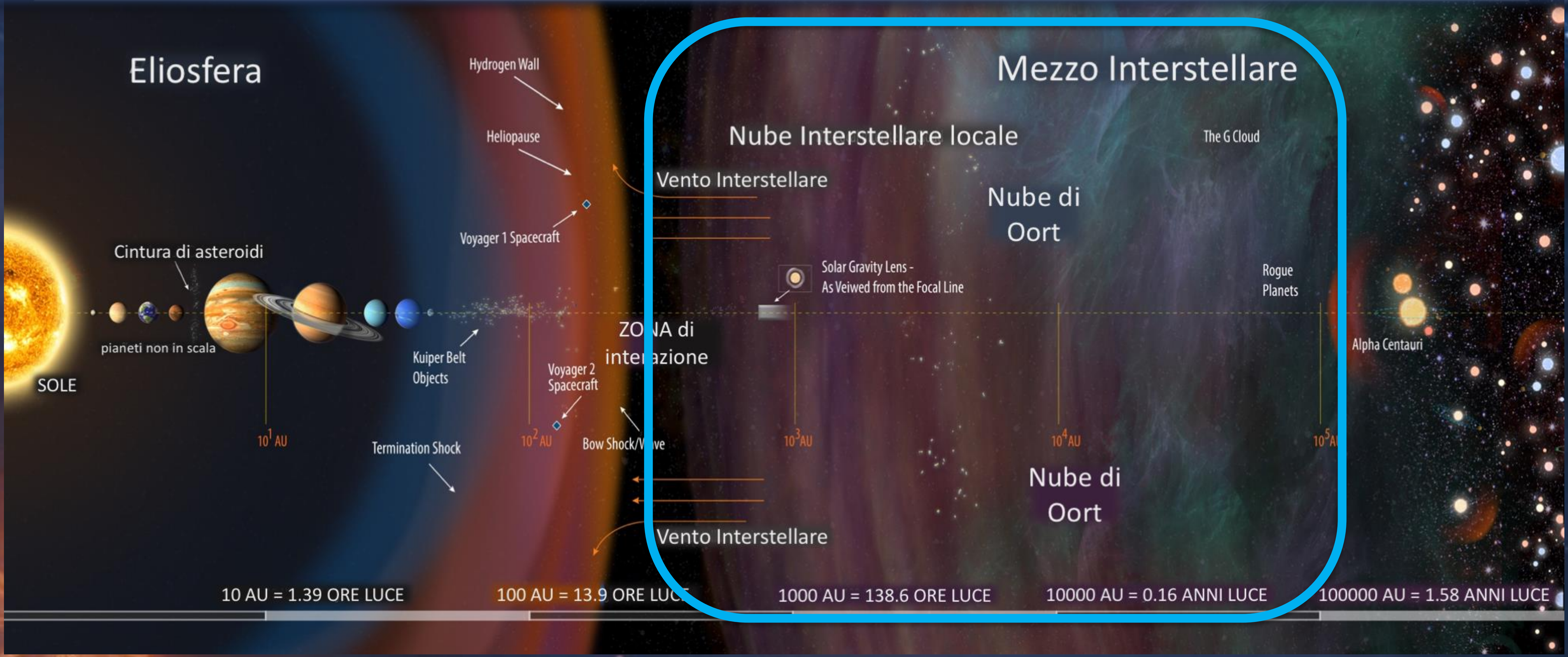


Mezzo interstellare (ISM):
il materiale rarefatto costituito da **GAS** e polvere che si trova tra i sistemi solari all'interno di una galassia

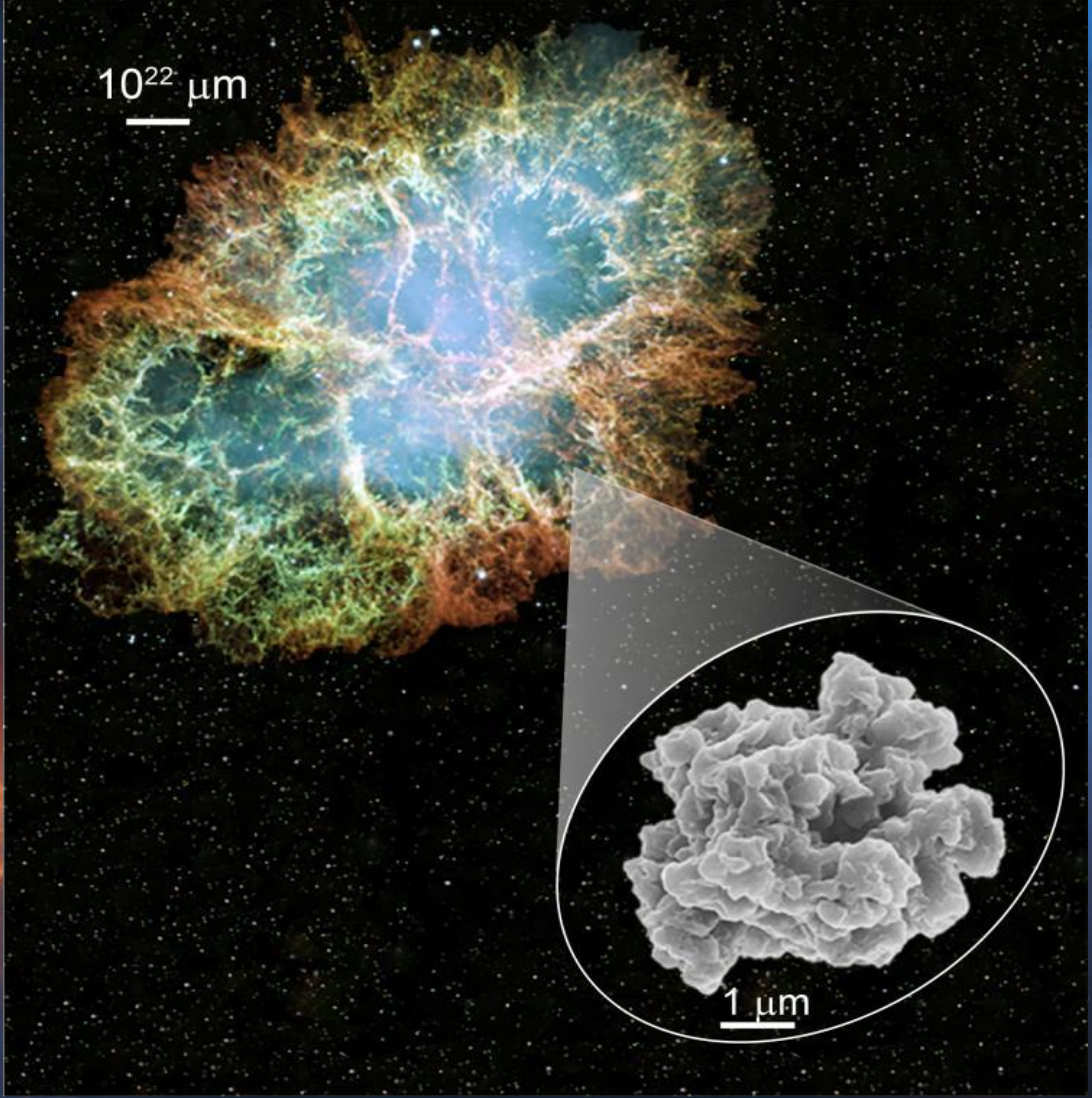
Tavola Periodica "astronomica"

I	1 **142** **H** 1.00794 Hydrogen																	2 He 4.002602 Helium
II	3 Li 6.941 Lithium	4 Be 9.012182 Beryllium											5 B 10.811 Boron	6 **156** **C** 12.0107 Carbon	7 **75** **N** 14.0067 Nitrogen	8 **66** **O** 15.9994 Oxygen	9 **3** **F** 18.9984032 Fluorine	10 Ne 20.1797 Neon
III	11 **2** **Na** 22.98976928 Sodium	12 **3** **Mg** 24.3050 Magnesium											13 **5** **Al** 26.9815386 Aluminum	14 **13** **Si** 28.0855 Silicon	15 **6** **P** 30.973762 Phosphorus	16 **23** **S** 32.065 Sulfur	17 **7** **Cl** 35.453 Chlorine	18 **1** **Ar** 39.948 Argon
IV	19 **2** **K** 39.0983 Potassium	20 Ca 40.078 Calcium	21 Sc 44.955912 Scandium	22 **2** **Ti** 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	25 Mn 54.938045 Manganese	26 **1** **Fe** 55.845 Iron	27 Co 58.933195 Cobalt	28 Ni 58.6934 Nickel	29 Cu 63.546 Copper	30 Zn 65.38 Zinc	31 Ga 69.723 Gallium	32 Ge 72.64 Germanium	33 As 74.92160 Arsenic	34 Se 78.96 Selenium	35 Br 79.904 Bromine	36 Kr 83.798 Krypton
V	37 Rb 85.4678 Rubidium	38 Sr 87.62 Strontium	39 Y 88.90585 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.90638 Niobium	42 Mo 95.96 Molybdenum	43 Tc [98] Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.90550 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.8682 Silver	48 Cd 112.411 Cadmium	49 In 114.818 Indium	50 Sn 118.710 Tin	51 Sb 121.760 Antimony	52 Te 127.60 Tellurium	53 I 126.90447 Iodine	54 Xe 131.293 Xenon
VI	55 Cs 132.9054519 Cesium	56 Ba 137.327 Barium	LA	72 Hf 178.49 Hafnium	73 Ta 180.94788 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium	77 Ir 192.217 Iridium	78 Pt 195.084 Platinum	79 Au 196.966569 Gold	80 Hg 200.59 Mercury	81 Tl 204.3833 Thallium	82 Pb 207.2 Lead	83 Bi 208.98040 Bismuth	84 Po [209] Polonium	85 At [210] Astatine	86 Rn [222] Radon
VII	87 Fr [223] Francium	88 Ra [226] Radium	AC	104 Rf [267] Rutherfordium	105 Db [268] Dubnium	106 Sg [271] Seaborgium	107 Bh [272] Bohrium	108 Hs [270] Hassium	109 Mt [276] Meitnerium	110 Ds [281] Darmstadtium	111 Rg [280] Roentgenium	112 Cn [285] Copernicium	113 Nh [284] Nihomium	114 Fl [289] Flerovium	115 Mc [288] Moscovium	116 Lv [293] Livermorium	117 Ts [294] Tennessine	118 Og [294] Oganesson
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18

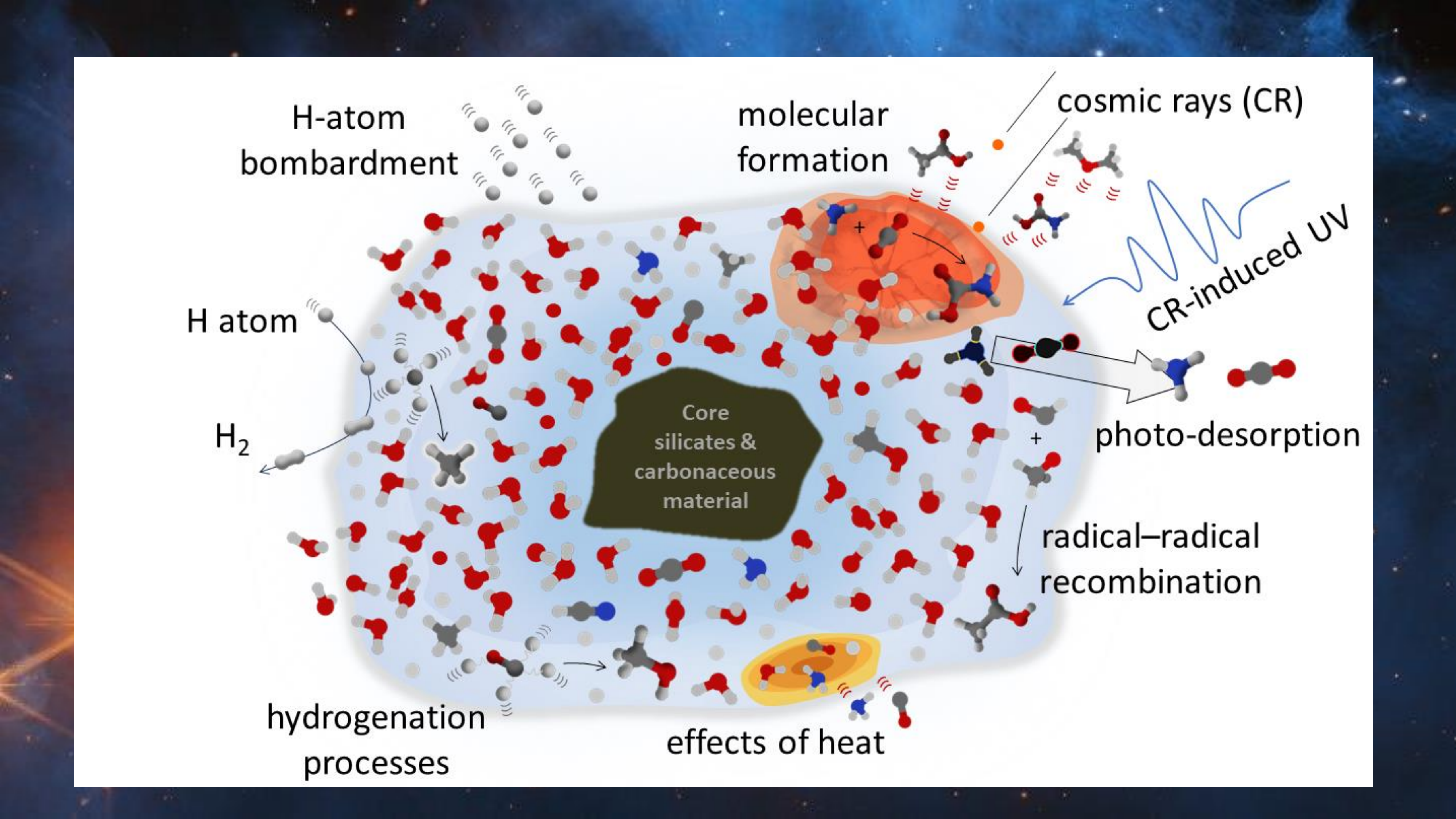
Che cos'è il mezzo interstellare?



Mezzo interstellare (ISM):
il materiale rarefatto costituito da gas e **POLVERE** che si trova tra i sistemi solari all'interno di una galassia



Formazione della polvere interstellare in seguito alla morte di una stella

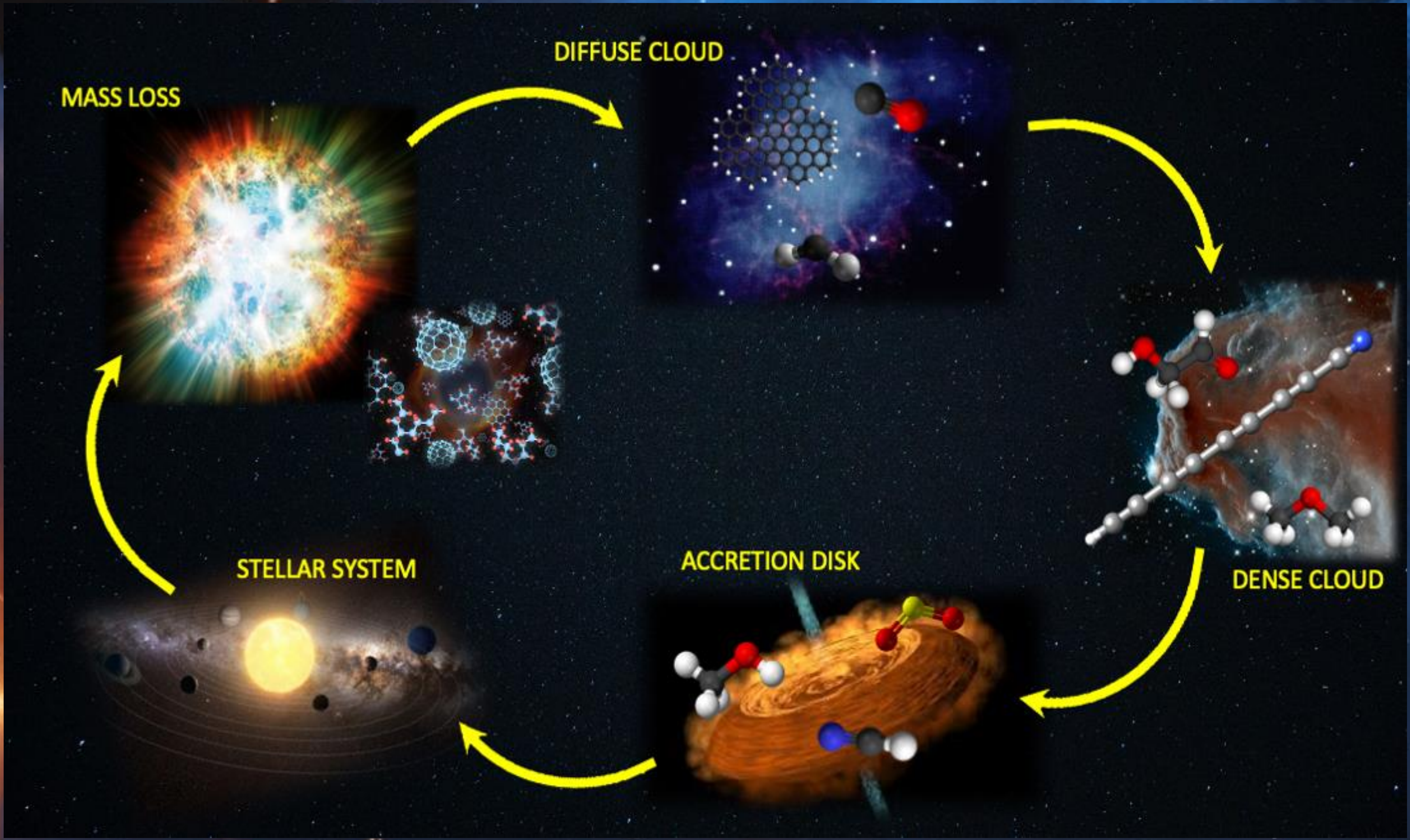

H-atom bombardment
molecular formation
cosmic rays (CR)
CR-induced UV
H atom
H_2
Core silicates & carbonaceous material
photo-desorption
radical–radical recombination
hydrogenation processes
effects of heat

Che cos'è il mezzo interstellare?

La distribuzione della massa nell'ISM non è omogenea

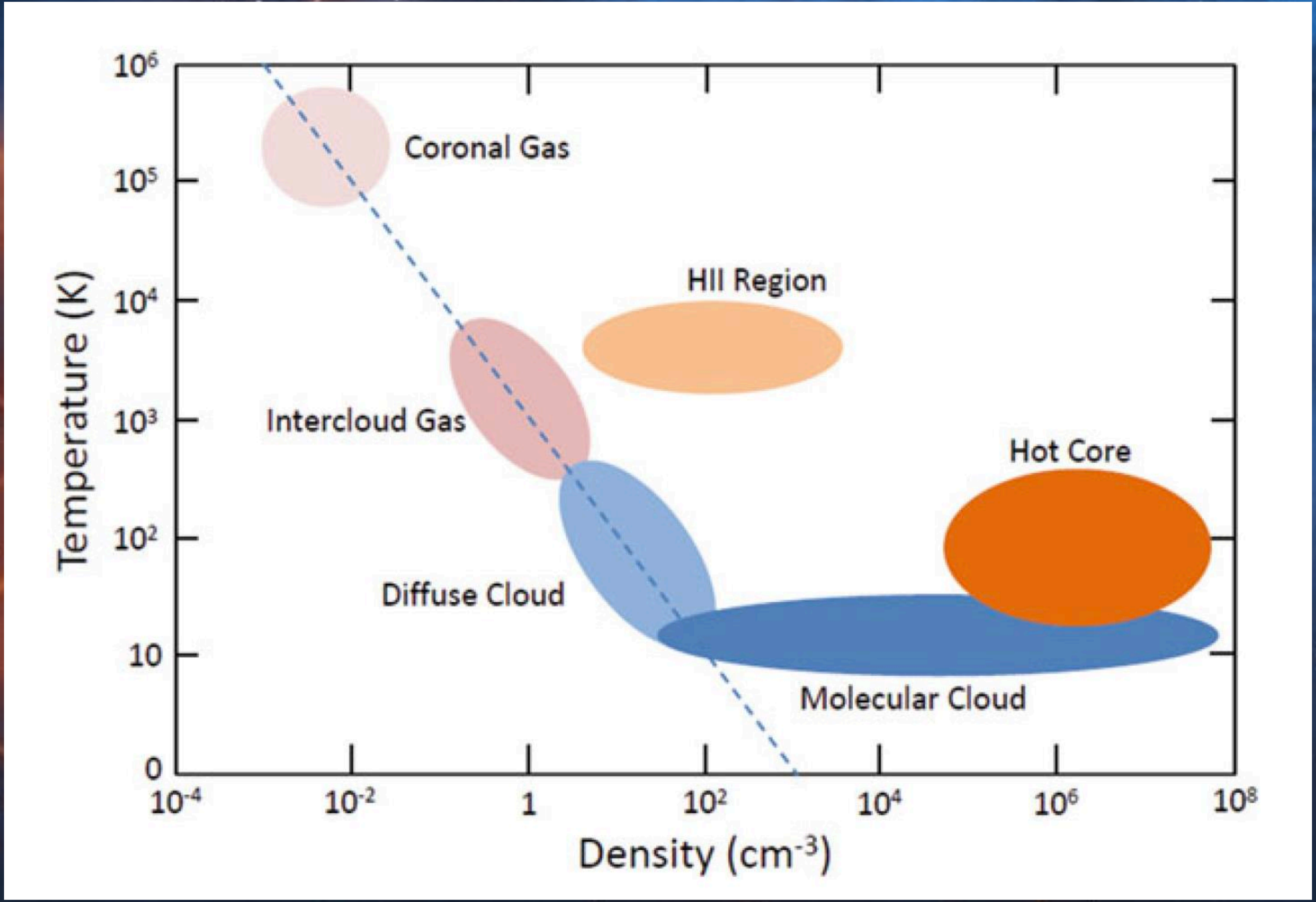
Che cos'è il mezzo interstellare?

I pilastri della creazione (Nebulosa dell'Aquila)



Ciclo di formazione di una stella e del suo sistema planetario

Il mezzo interstellare: le condizioni fisiche



L'umanità osserva il cielo da millenni …

L'universo è un luogo "ricco" di atomi …

Per molti anni il mezzo interstellare è stato considerato un ambiente troppo ostile* per le molecole …

Tuttavia, circa 90 anni fa osservazioni spettroscopiche nel visibile e nel vicino ultravioletto hanno iniziato a suggerire che al contrario …

*T molto bassa, p bassissima, radiazioni ionizzanti

Cos’è la spettroscopica astronomica?

Un po’ di storia … …

Galileo Galilei: 1609 primo telescopio

Al cospetto del Senato Veneziano, lo scienziato **Galileo Galilei** mostrò il funzionamento del primo *telescopio rifrattore* della storia.

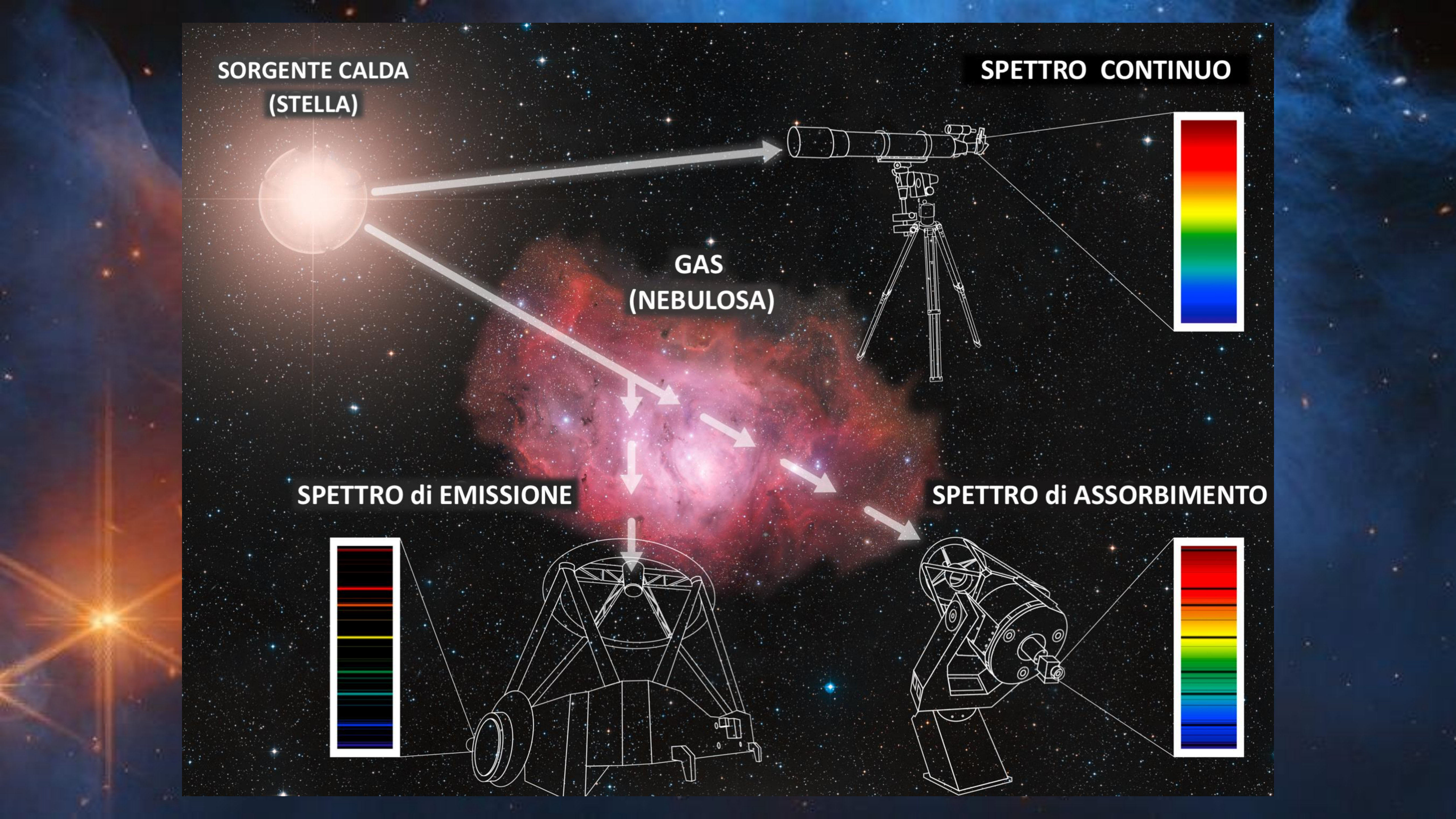
PRISMA: Nel **1671** Newton per primo usò il termine ***spettro*** (dal latino *spectrum*) descrivendo i suoi esperimenti di ottica. Newton divise lo spettro in sette diversi colori: rosso, arancione, giallo, verde, blue, indaco e violetto.

Newton: 1668 primo telescopio a specchio

Newton realizzò un piccolo *telescopio riflettore* capace di circa 35 ingrandimenti. Era composto da uno specchio concavo parabolico e uno specchietto piano.

La NASCITA della SPETTROSCOPIA ASTRONOMICA

Nel **1814**, **Fraunhofer** utilizzò un prisma di elevata qualità per diffrangere un raggio di sole filtrante dalle persiane su una parete bianca. Quello che scoprì, oltre i colori caratteristici dell'arcobaleno come ben noto dai tempi di Newton, furono molte righe scure che egli stesso catalogò. Queste sono ancora note come le "**righe di Fraunhofer**"


SORGENTE CALDA
(STELLA)
SPETTRO CONTINUO
GAS
(NEBULOSA)
SPETTRO di EMISSIONE
SPETTRO di ASSORBIMENTO

NOTES

CONSIDERATIONS REGARDING INTERSTELLAR MOLECULES

ABSTRACT

An attempt has been made to compute the numbers of certain molecules in interstellar space. The results obtained are unfavorable to Saha's identification of one of Merrill's interstellar lines with Na_2. A search for the bands of *CH*, *OH*, *NH*, *CN*, and C_2 would appear to be promising.

P. Swings and L. Rosenfeld, ApJ 86:483-486 (1937)

ζ Oph:

VIS lines at 3878.8, 3886.4, 3890.2, & 4300.3 Å

UV lines near 1271, 1368, 1369, 1370, 1549, & 1694 Å

PAPER 16

MICROWAVE AND RADIO-FREQUENCY RESONANCE LINES OF INTEREST TO RADIO ASTRONOMY

C. H. TOWNES

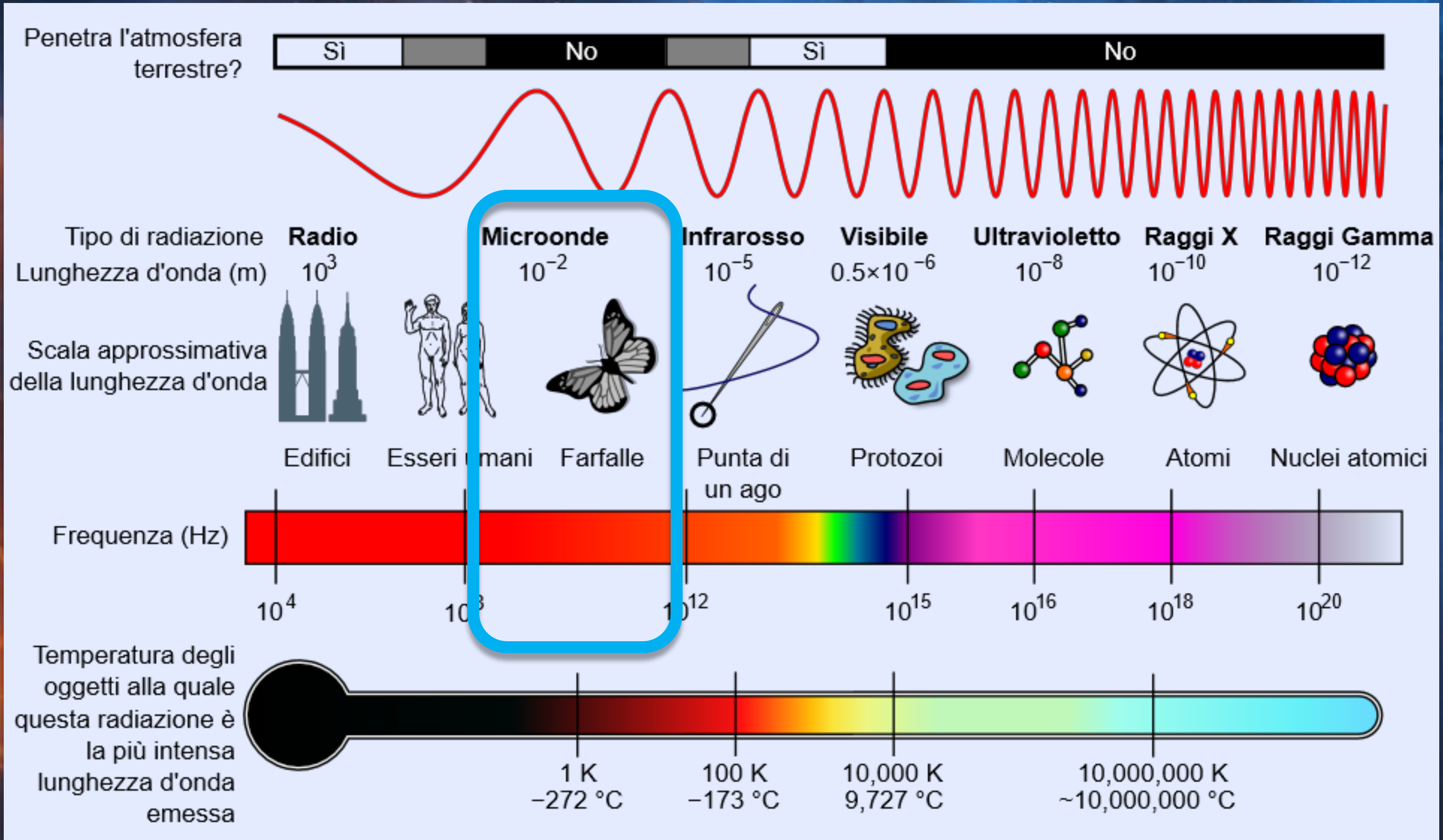
Physical Laboratory, Ecole Normale Supérieure, Paris

A review of microwave and radio-frequency spectral lines which might possibly be detected by the techniques of radio astronomy is attempted here. Brief discussions of this type have already been given by several authors [1, 2, 3, 4]. However, the present treatment is somewhat more complete than previously published material, and has the advantage of more recent information about certain transition frequencies. It includes a general discussion of types of spectra which might be found, expected intensities, and some characteristics and known frequencies of the lines which may be of interest in radio astronomy.

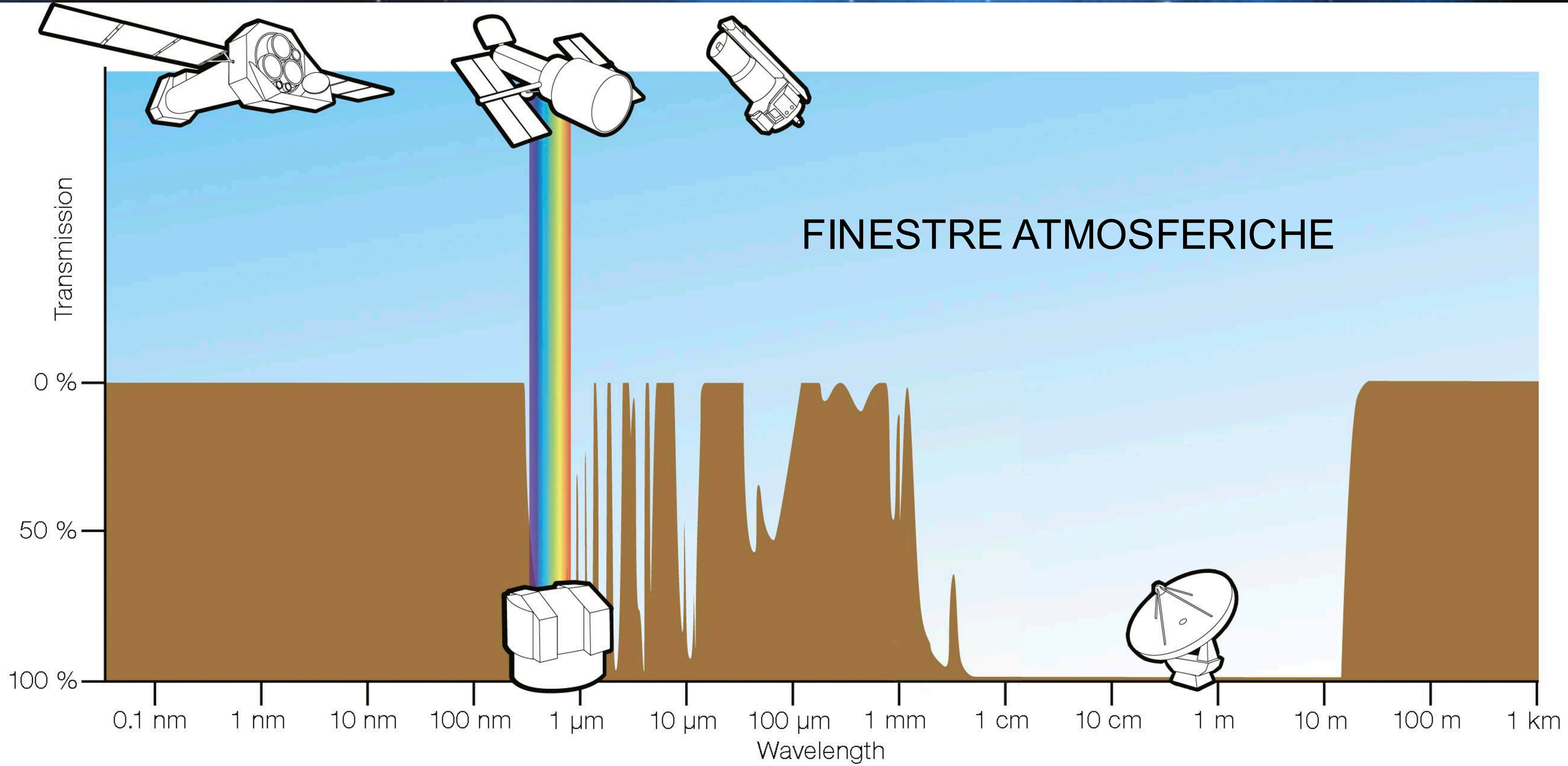
Transitions which lie in the microwave or radio-frequency region can be expected to come from atomic or molecular hyperfine structure, from atomic or molecular fine structure, and from molecular rotational frequencies. It is of course possible that some odd circumstance or chance

C.H. Townes, in "The Fourth International Astronomical Union Symposium", Manchester 1955

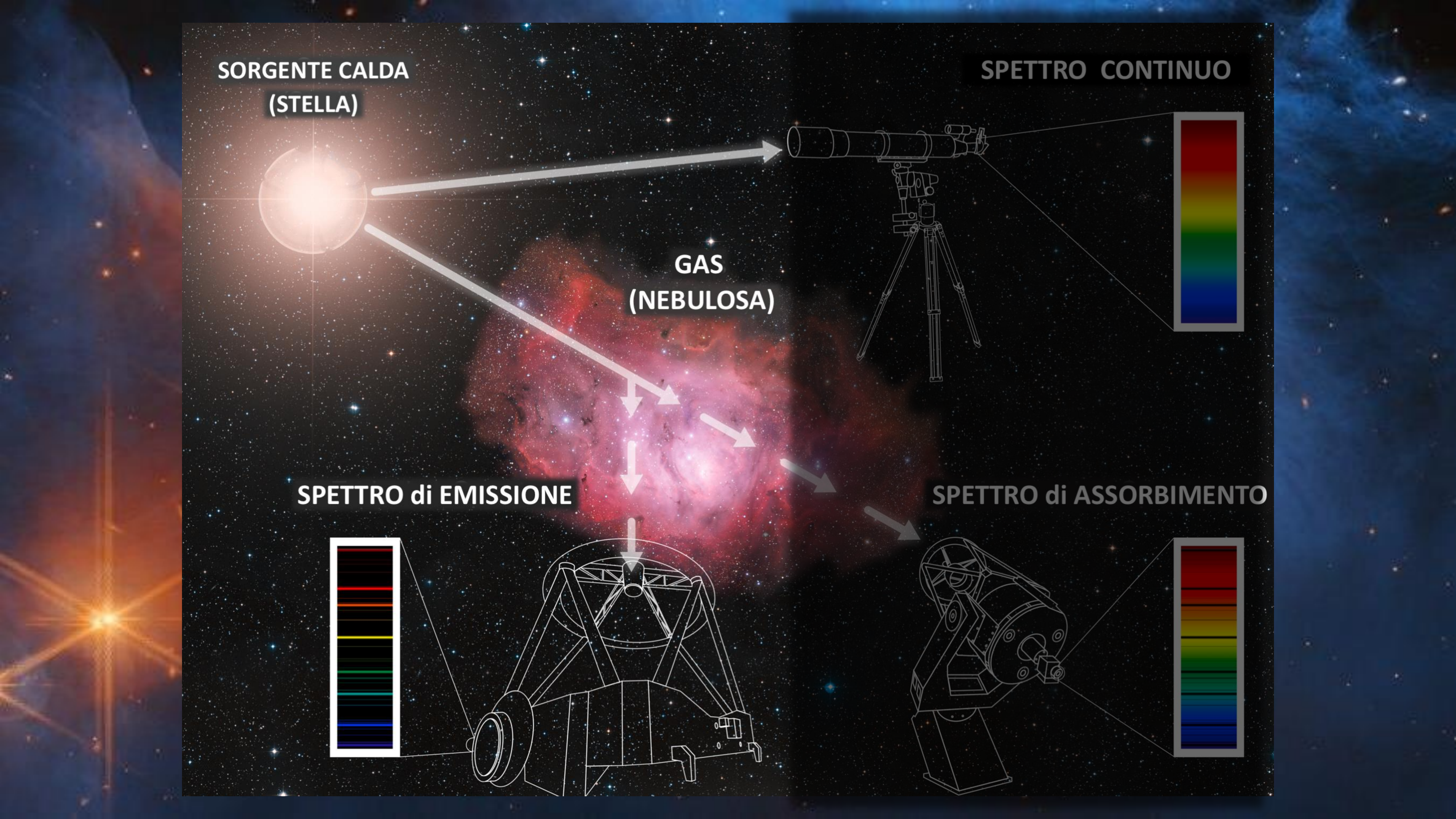
Cambridge University Press, Cambridge, 1957; paper 16



Perché proprio nelle microonde?



FINESTRE ATMOSFERICHE
Transmission
0 %
50 %
100 %
0.1 nm
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm
1 cm
10 cm
1 m
10 m
100 m
1 km
Wavelength

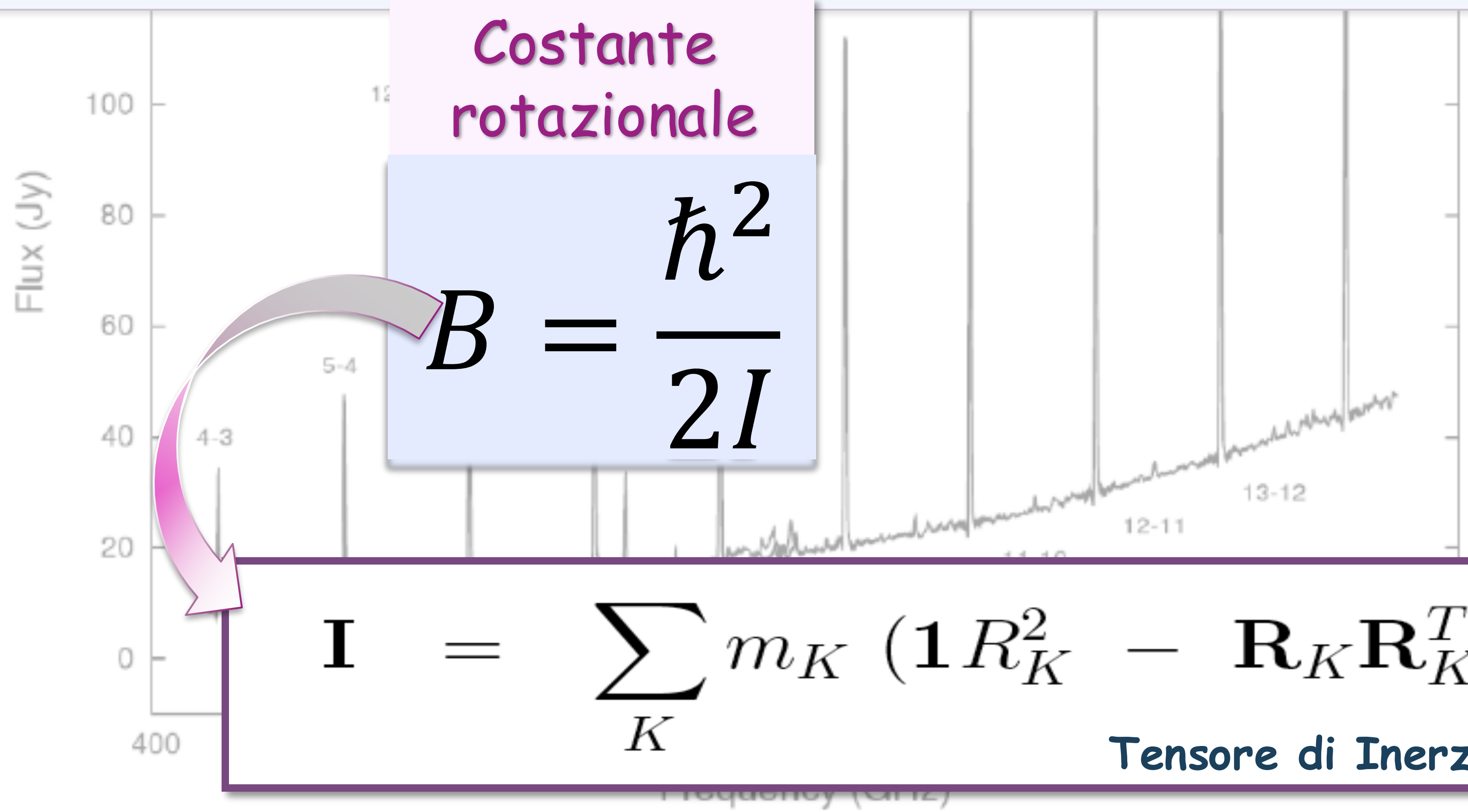

SORGENTE CALDA
(STELLA)
SPETTRO CONTINUO
GAS
(NEBULOSA)
SPETTRO di EMISSIONE
SPETTRO di ASSORBIMENTO

ALMA (Atacama Large Millimeter/submillimeter Array):
66 antennas - range: 84-950 GHz

$$\nu = 2B(J+1)$$

Costante rotazionale

$$B = \frac{\hbar^2}{2I}$$



$$\mathbf{I} = \sum_K m_K \left(\mathbf{1} R_K^2 - \mathbf{R}_K \mathbf{R}_K^T\right)$$

Tensore di Inerzia

Fig. 11.3 R… planetary neb-ula NGC 7027 using the using the SPIRE Fourier Transform Spectrometer on the Herschel Space Observ… 518, L144 (2010)].

Differente struttura (molecola)
= spettro rotazionale differente

From: J. Tennyson "Astronomical Spectroscopy", Imperial College Press

UNPUBLISHED PRELIMINARY DATA

(Submitted for publication in NATURE.)

Mass. Inst. of Tech.

NsG-419

11p.

N64 11379 *

CODE-1

NASA CR 52852

Radio Observations of OH in the Interstellar Medium

In this note we wish to report the detection of 18-cm absorption lines of the hydroxl (OH) radical in the radio absorption spectrum of Cassiopeia A, thereby providing positive evidence for the existence of OH in the interstellar medium. The microwave transitions of OH in the ground state, $^2\pi_{3/2}$, J = 3/2, arise from two Λ-type doublet levels, each of which is split by hyperfine interactions with the hydrogen nucleus, so that four transitions result. The two strongest lines have been previously measured in the laboratory at 1667.34 ± 0.03 Mc/sec (F = 2→2 and 1665.46 ± 0.10 Mc/sec (F = 1→1) with relative intensities of 9 and 5, respectively;[1] these results are in agreement with theory. The

S. Weinreb, A. H. Barrett, M. L. Meeks, J. C. Henry Nature 200:829-831 (1963)

DISCOVERY OF INTERSTELLAR METHYL FORMATE

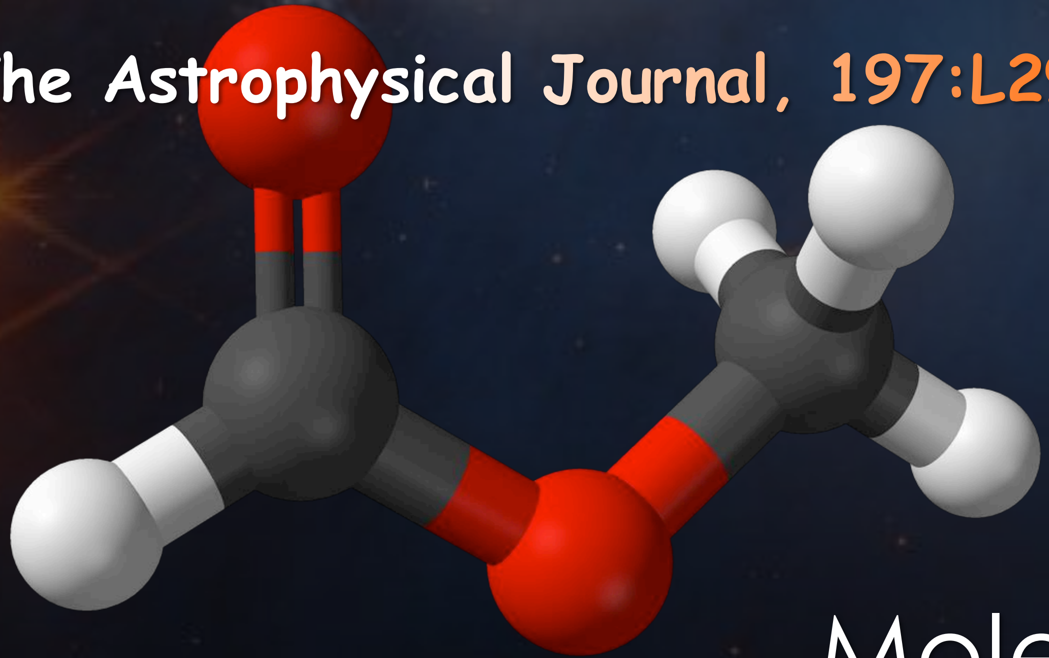
R. D. Brown,* J. G. Crofts,* F. F. Gardner,†
P. D. Godfrey,* B. J. Robinson,† and J. B. Whiteoak†

Received 1974 December 31

ABSTRACT

The 1_{10}–1_{11} A-state transition of methyl formate $HCOOCH_3$ has been detected in emission in the spectrum of Sgr B2. With a laboratory determination of 1610.249 MHz for the rest frequency of the transition, the radial velocity of the observed line is 53 ± 6 km s^{-1}. The nearby E-state transition at 1610.906 MHz may also have been detected. It is probable that the 1_{10} and 1_{11} levels are inverted and that the continuum emission of Sgr B2 is being amplified.

The Astrophysical Journal, 197:L29–L31, 1975



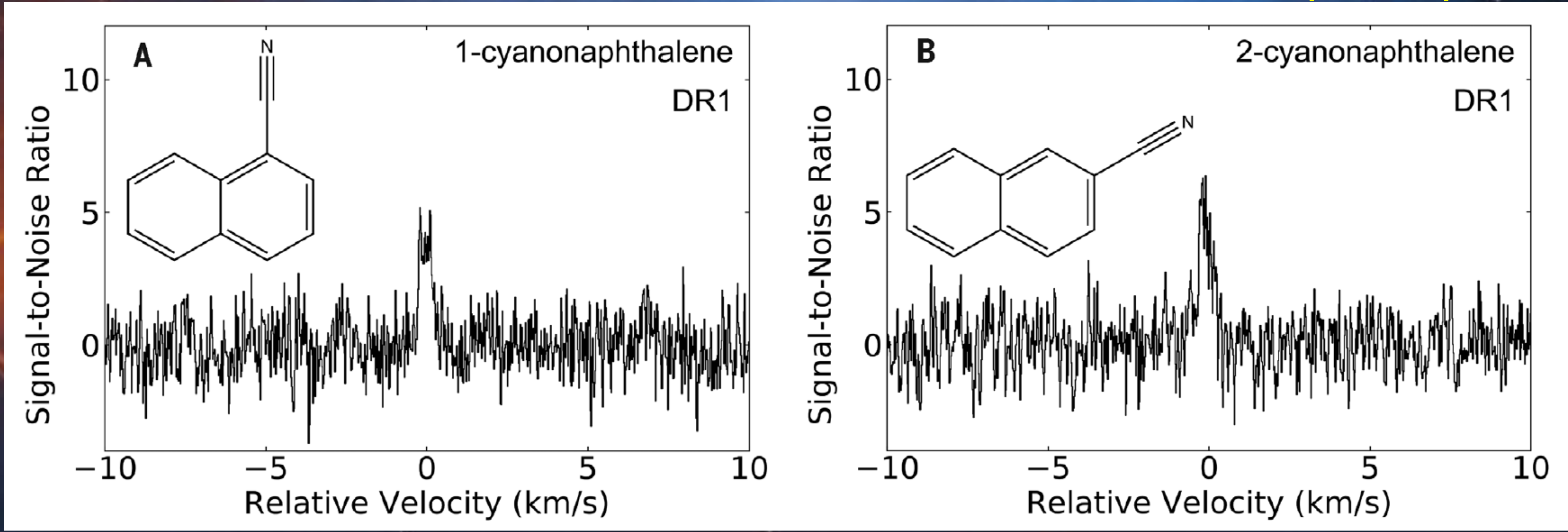
Molecole organiche "complesse"

ASTROCHEMISTRY

Detection of two interstellar polycyclic aromatic hydrocarbons via spectral matched filtering

Brett A. McGuire[1,2,3]*, Ryan A. Loomis[2]†, Andrew M. Burkhardt[3]†, Kin Long Kelvin Lee[1,3], Christopher N. Shingledecker[4,5,6], Steven B. Charnley[7], Ilsa R. Cooke[8], Martin A. Cordiner[7,9], Eric Herbst[10,11], Sergei Kalenskii[12], Mark A. Siebert[11], Eric R. Willis[10], Ci Xue[10], Anthony J. Remijan[2], Michael C. McCarthy[3]

Science **371**, 1265 (2021)



The Astrophysical Journal Letters, 984:L36 (19pp), 2025 May 1 https://doi.org/10.3847/2041-8213/adc911

Discovery of the Seven-ring Polycyclic Aromatic Hydrocarbon Cyanocoronene ($C_{24}H_{11}CN$) in GOTHAM Observations of TMC-1

Gabi Wenzel[1,2], Siyuan Gong[1], Ci Xue[1], P. Bryan Changala[3,4], Martin S. Holdren[1], Thomas H. Speak[5], D. Archie Stewart[1], Zachary T. P. Fried[1], Reace H. J. Willis[5], Edwin A. Bergin[6], Andrew M. Burkhardt[7], Alex N. Byrne[1], Steven B. Charnley[8], Andrew Lipnicky[9], Ryan A. Loomis[9], Christopher N. Shingledecker[10], Ilsa R. Cooke[5], Michael C. McCarthy[2], Anthony J. Remijan[9], Alison E. Wendlandt[1], and Brett A. McGuire[1,9]

1 Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA; gwenzel@mit.edu, br
2 Center for Astrophysics | Harvard & Smithsonian, Cambridge, MA 02138, USA
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5 Department of Chemistry, University of British Columbia, Vancouver, BC, Canada
6 Department of Astronomy, University of Michigan, Ann Arbor, MI 48109, USA
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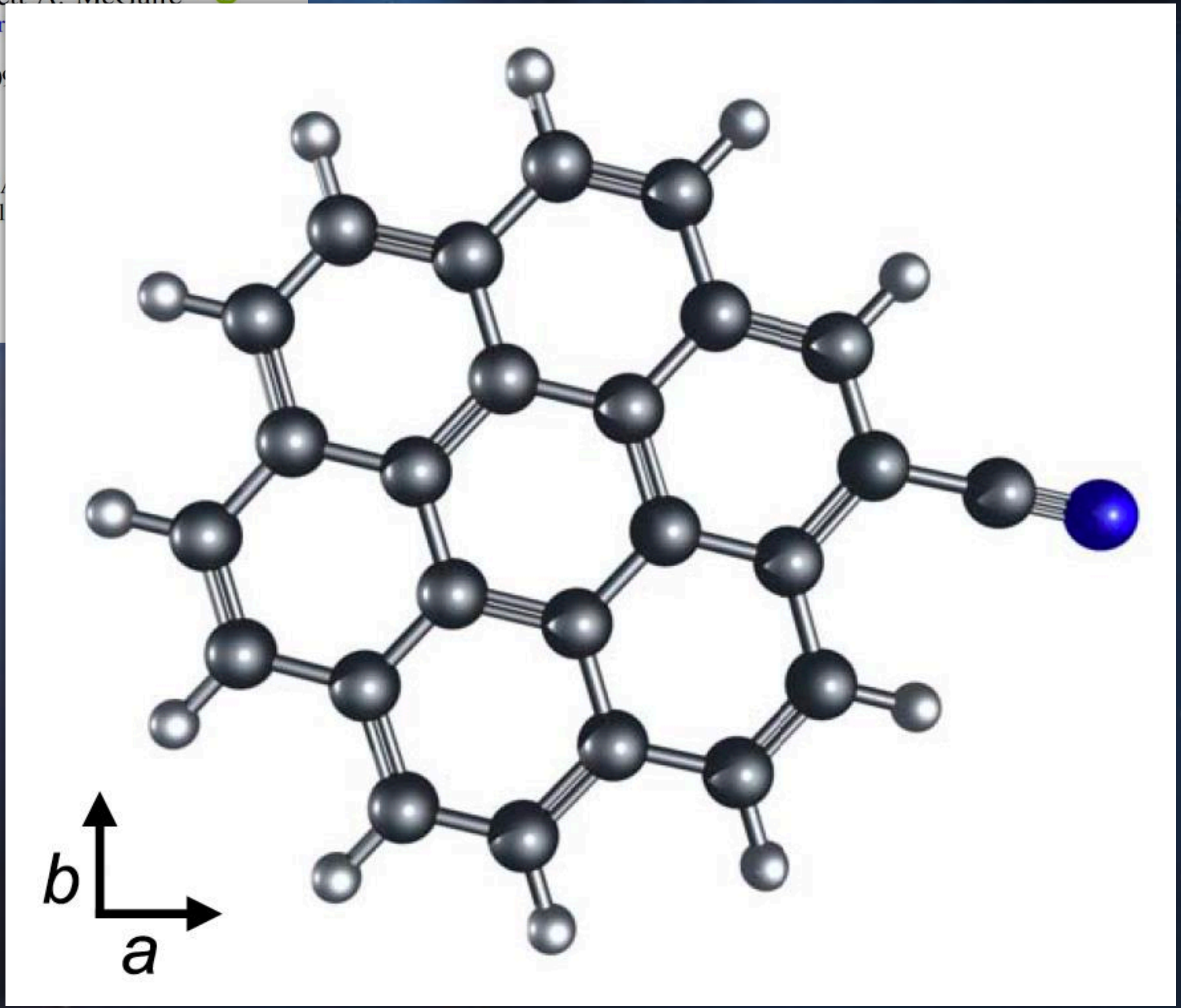
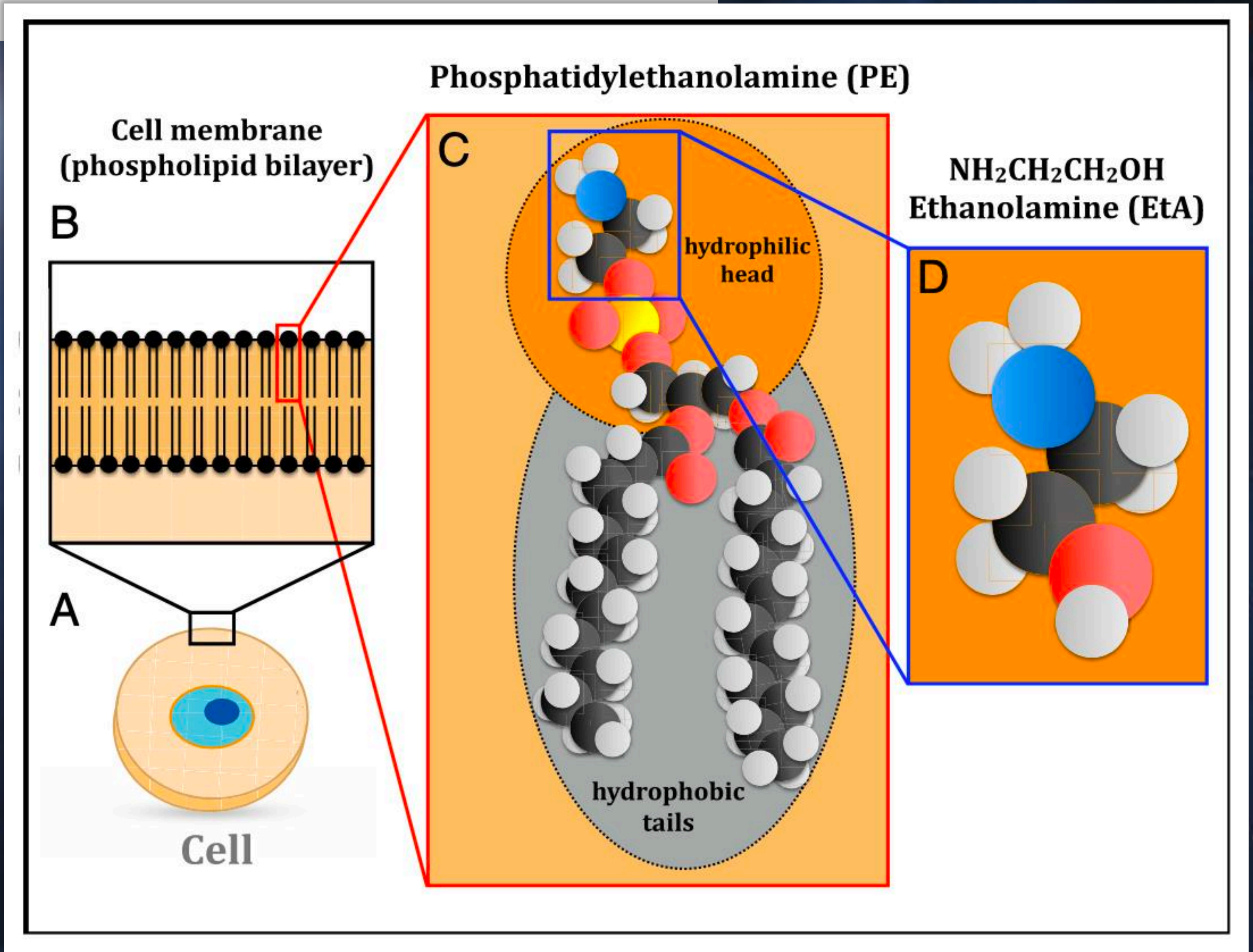
8 Astrochemistry Laboratory and the Goddard Center of Astrobiology, Solar System Exploration Division, NASA Goddard Space Fl
20771, USA
9 National Radio Astronomy Observatory, Charlottesville, VA 22903, USA
10 Department of Chemistry, Virginia Military Institute, Lexington, VA 24450, USA
Received 2025 March 8; revised 2025 March 30; accepted 2025 April 4; published 2025 April 30



Astrophys. J. Lett. **984**, L36 (2025)

Discovery in space of ethanolamine, the simplest phospholipid head group

Víctor M. Rivilla[a,b,1], Izaskun Jiménez-Serra[a], Jesús Martín-Pintado[a], Carlos Briones[a], Lucas F. Rodríguez-Almeida[a], Fernando Rico-Villas[a], Belén Tercero[c], Shaoshan Zeng[d], Laura Colzi[a,b], Pablo de Vicente[c], Sergio Martín[e,f], and Miguel A. Requena-Torres[g,h]



PNAS **118**, e2101314118 (2021)

Molecules in the Interstellar Medium or Circumstellar Shells (as of 08/2025)

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
CH^+	C_3^*	c-C_3H	C_5^*	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	c-$C_6H_6^*$	C_{60}^*
CH	C_2H	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HC(O)OCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	n-C_3H_7CN	C_{70}^*
CN	C_2O	C_3N	C_4Si	$C_2H_4^*$	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$	C_2H_5OCHO	i-C_3H_7CN	C_{60}^{+*}
OH	C_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO	$CH_3OC(O)CH_3$	$C_2H_5OCH_3$	c-C_6H_5CN
CO	CH_2	C_3S	c-C_3H_2	CH_3NC	CH_3CHO	C_6H_2	HC_7N	CH_3CHCH_2O	$CH_3C(O)CH_2OH$	1-c-C_5H_5CN	$HC_{11}N$
H_2	HCN	$C_2H_2^*$	H_2CCN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H	CH_3OCH_2OH	c-C_5H_6	2-c-C_5H_5CN	1-$C_{10}H_7CN$
SiO	HCO	NH_3	CH_4^*	CH_3SH	c-C_2H_4O	l-HC_6H^*	$CH_3C(O)NH_2$	c-C_6H_4	$HOCH_2CH_2NH_2$	CH_3C_7N (?)	2-$C_{10}H_7CN$
CS	HCO^+	$HCCN$	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO	C_8H^-	H_2CCCHC_3N	H_2CCCHC_4H	n-C_3H_7OH	c-C_9H_8
SO	HCS^+	$HCNH^+$	$HCCNC$	$HCCCHO$	C_6H^-	CH_2CCHCN	C_3H_6	C_2H_5NCO	$C_{10}H^-$	i-C_3H_7OH	1-c-C_5H_5CCH
SiS	HOC^+	$HNCO$	$HCOOH$	NH_2CHO	CH_3NCO	H_2NCH_2CN	CH_3CH_2SH	$C_2H_5NH_2$ (?)	$H_2C(CH)_3CN$?	$(CH_3)_2C{=}CH_2$	2-c-C_5H_5CCH
NS	H_2O	$HNCS$	H_2CNH	C_5N	HC_5O	CH_3CHNH	CH_3NHCHO	HC_7NH^+			c-$C_5H_4CCH_2$
C_2^{**}	H_2S	$HOCO^+$	H_2C_2O	l-HC_4H^*	$HOCH_2CN$	CH_3SiH_3	HC_7O	E-$CH_3CHCHCN$			2-C_9H_7CN
NO	HNC	H_2CO	H_2NCN	l-HC_4N	$HCCCHNH$	$H_2NC(O)NH_2$	$HCCCHCHCN$	Z-$CH_3CHCHCN$			C_6H_5CCH
HCl	HNO	H_2CN	HNC_3	c-H_2C_3O	HC_4NC	$HCCCH_2CN$	H_2CCHC_3N	$CH_3C(CN)CH_2$			$CH_3OCH_2CH_2OH$ (2024)
$NaCl$	$MgCN$	H_2CS	SiH_4^*	H_2CCNH	c-C_3HCCH	HC_5NH^+	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
KCl	$MgNC$	H_3O^+	H_2COH^+	C_5N^-	l-H_2C_5	CH_2CHCCH	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
$AlCl$	N_2H^+	c-SiC_3	C_4H^-	$HNCHCN$	MgC_5N	MgC_6H	HC_7N^+ (2024)	CH_3CH_2CCH (2024)			1-$C_{16}H_9CN$ (2024)
AlF	N_2O	CH_3^*	$HC(O)CN$	SiH_3CN	CH_2C_3N	$C_2H_3NH_2$	$CH_2(CCH)_2$ (2024				2-$C_{16}H_9CN$ (2025)
PN	$NaCN$	C_3N^-	$HNCNH$	C_5S	NC_4NH^+	$(CHOH)_2$	$(CH_3)_2S$ (2025)				4-$C_{16}H_9CN$ (2025)
SiC	OCS	PH_3	CH_3O	MgC_4H	MgC_5N^+	$HC_2(H)C_4$					$C_{24}H_{11}CN$ (2025)
CP	SO_2	$HCNO$	NH_4^+	CH_3CO^+	HC_5N^+ (2024)	C_7N^-					
NH	c-SiC_2	$HOCN$	H_2NCO^+	C_3H_3	HNC_5 (2024)	CH_3CHCO					
SiN	CO_2^*	$HSCN$	$NCCNH^+$	H_2C_3S	$CH_2(CN)_2$ (2024	MgC_6H^+					

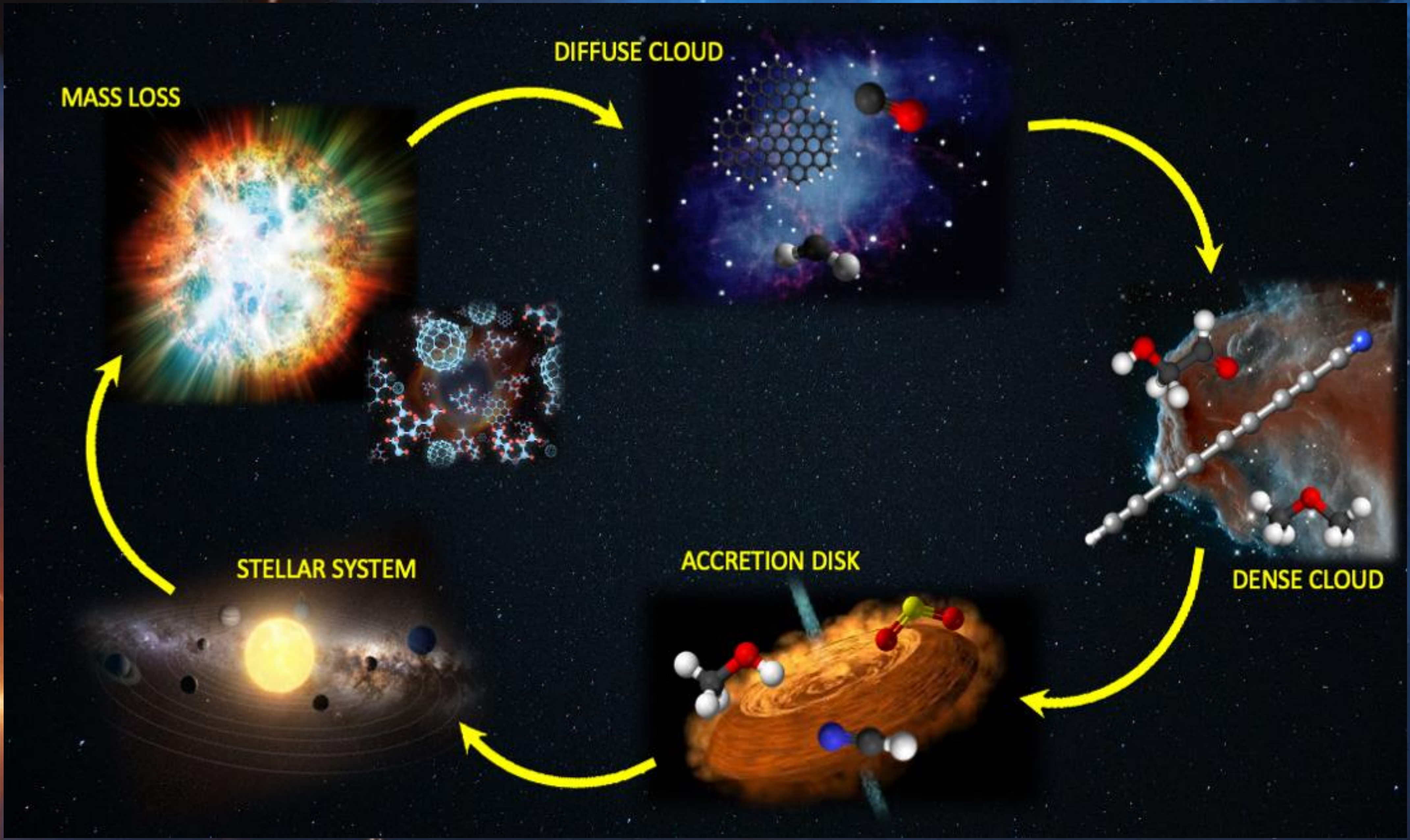
>90% RADIOASTRONOMIA

CIRCA 330
MOLECULE
SCOPERTE NELLO SPAZIO

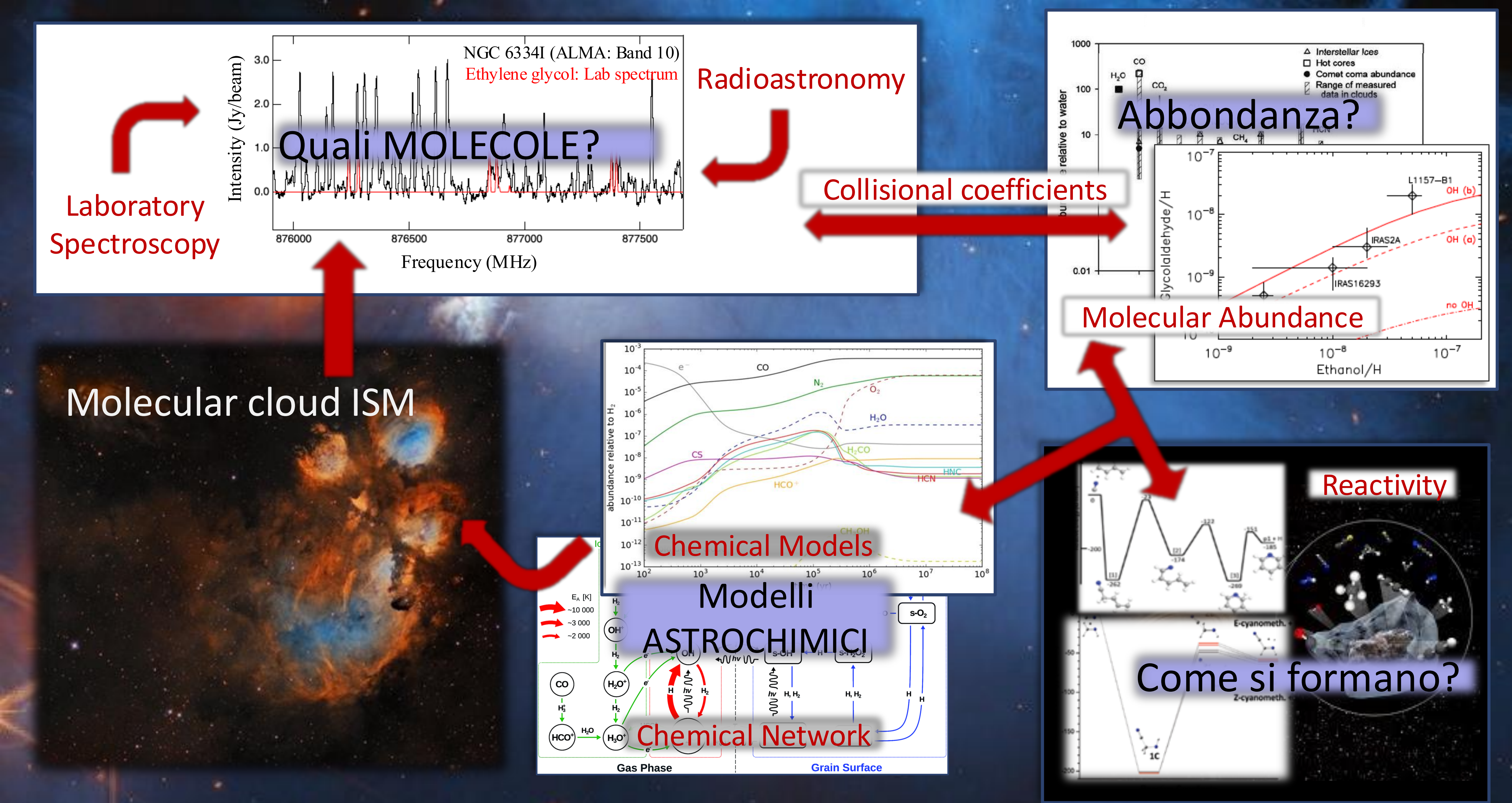
https://cdms.astro.uni-

Con l'osservazione che le molecole pervadono lo spazio interstellare è nato il desiderio di comprenderne quali e quante molecule ci sono e la loro origine… Dunque, come si sono formate queste molecole?

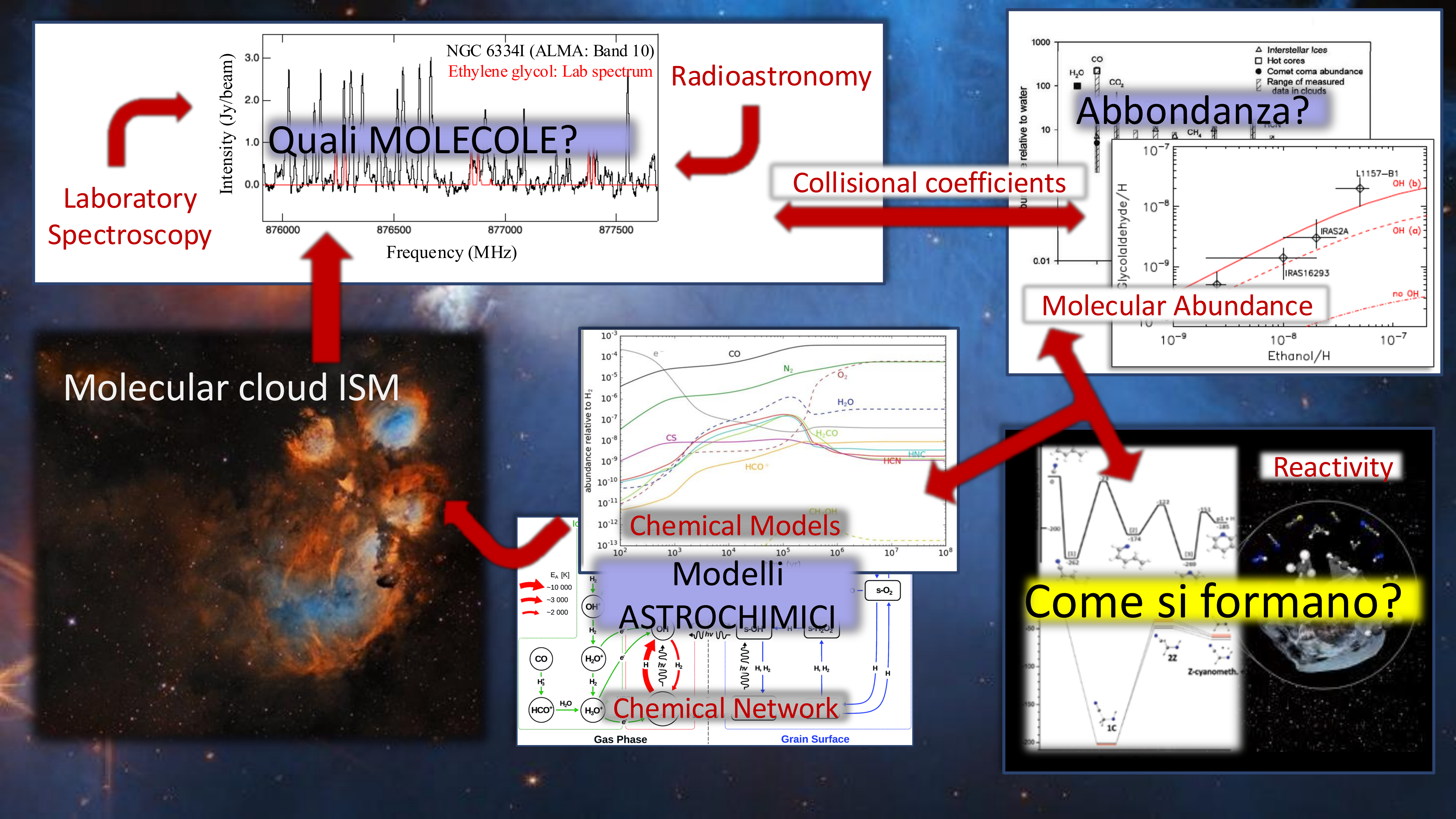
La scienza dell'ASTROCHIMICA è nata dal tentativo di rispondere a queste domande…



Ciclo di formazione di una stella e del suo sistema planetario

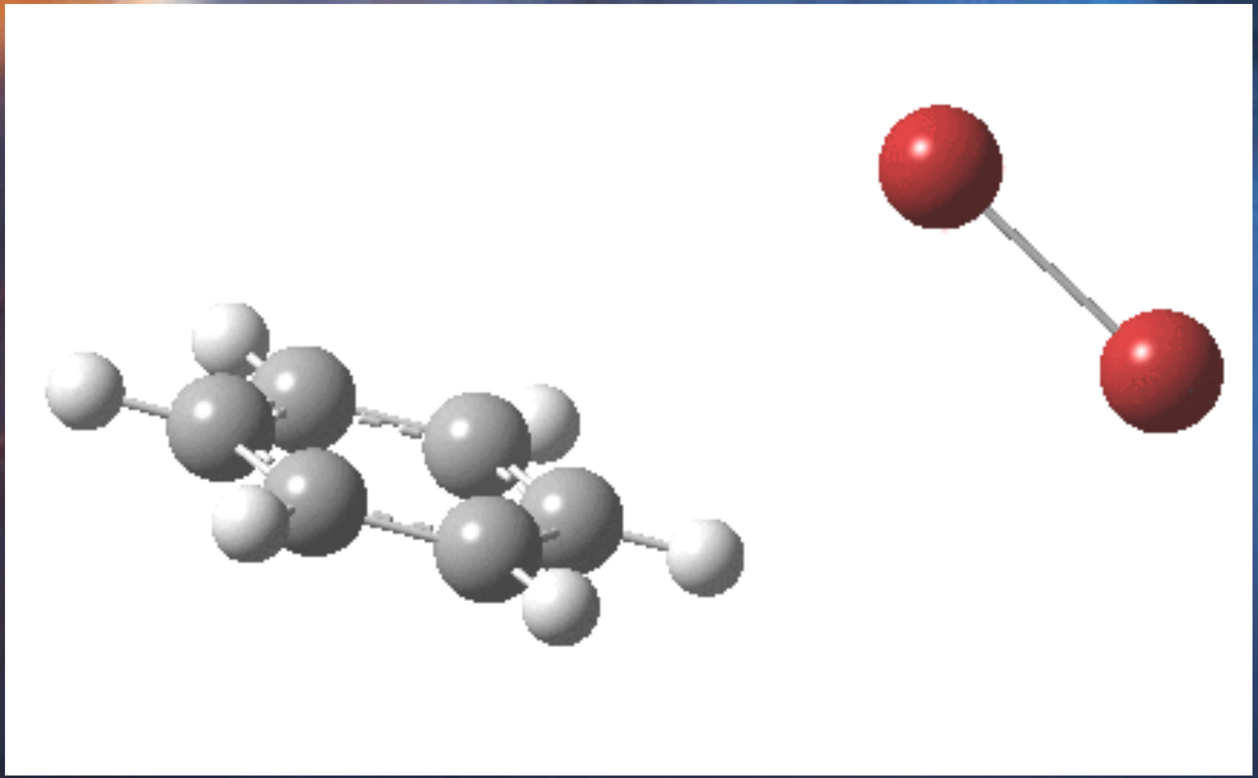


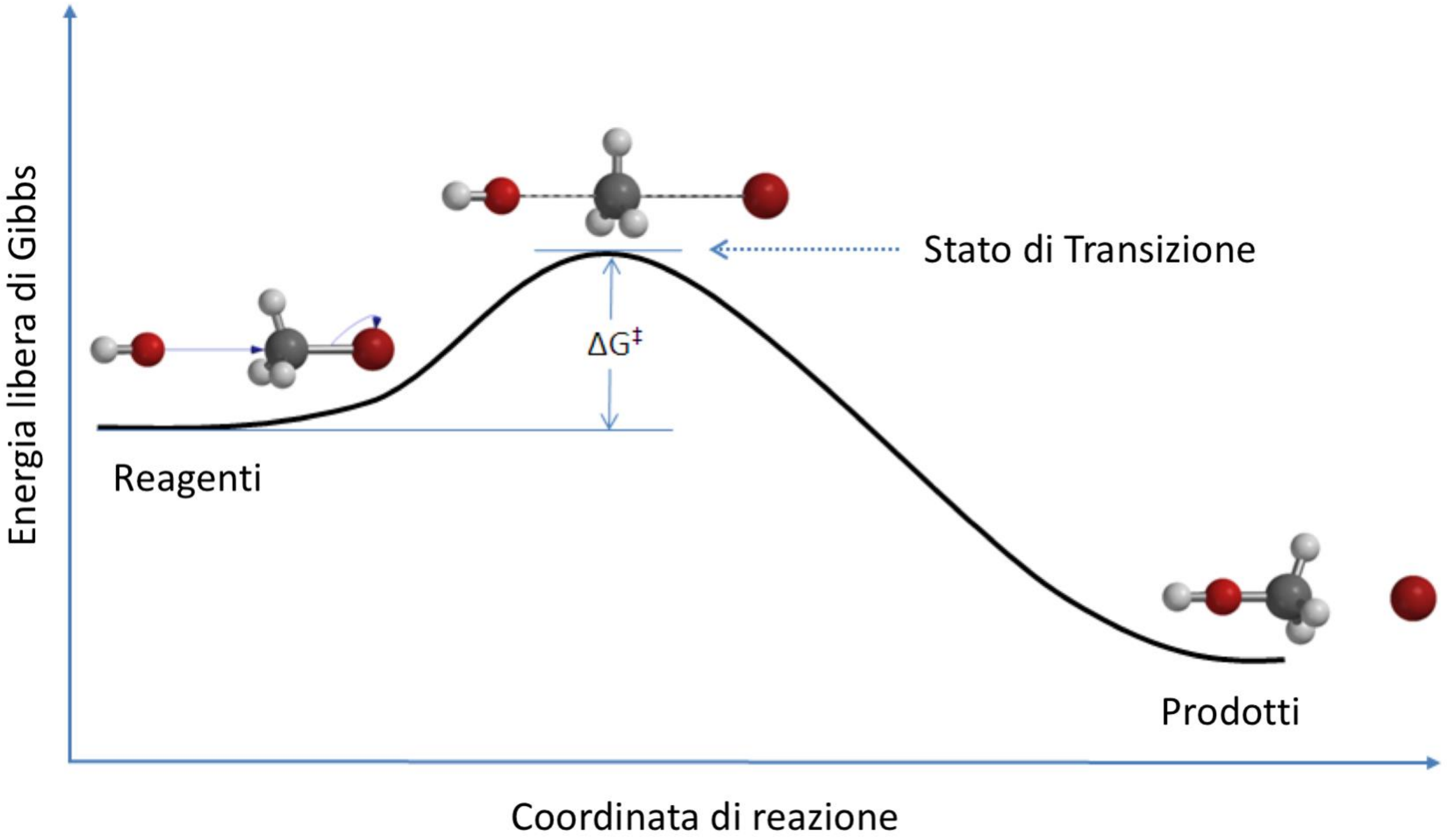
C. Puzzarini "Grand Challenges in Astrochemistry" Front. Astron. Space Sci. 7, 19 (2020)



NGC 6334I (ALMA: Band 10)
Ethylene glycol: Lab spectrum
Intensity (Jy/beam)
Frequency (MHz)
876000
876500
877000
877500
Quali MOLECOLE?
Radioastronomy
Laboratory Spectroscopy
Abbondanza?
Interstellar Ices
Hot cores
Comet coma abundance
Range of measured data in clouds
Collisional coefficients
Glycolaldehyde/H
Ethanol/H
L1157–B1
IRAS2A
IRAS16293
OH (b)
OH (a)
no OH
Molecular Abundance
Molecular cloud ISM
abundance relative to H2
CO
N2
O2
H2O
CS
H2CO
HNC
HCN
HCO+
Chemical Models
Modelli ASTROCHIMICI
Chemical Network
Gas Phase
Grain Surface
Reactivity
Come si formano?
Z-cyanometh.

Come avviene una reazione chimica?





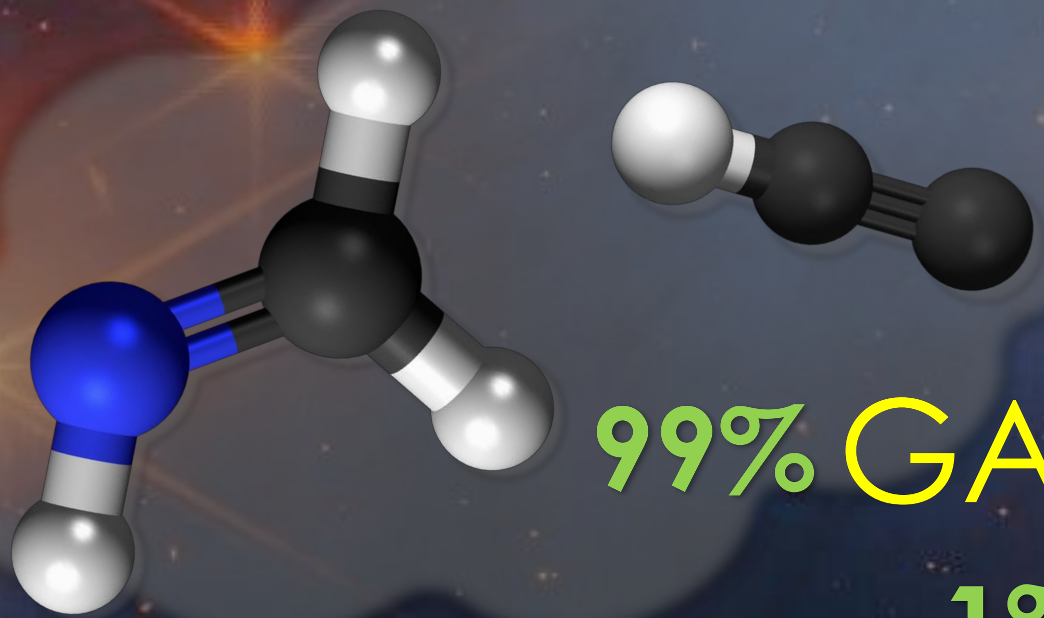
Reazione: $HO^{-} + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^{\ddagger} \rightarrow CH_3OH + Br^{-}$

CONDIZIONI ESTREME:

Bassa Temperatura (10-200 K)

Bassa Densità (1-10^8 molec. cm^{-3})

Radiazioni ionizzanti



99% GAS

1% POLVERE

Le condizioni del mezzo interstellare

Temperatura: 10K – 200 K

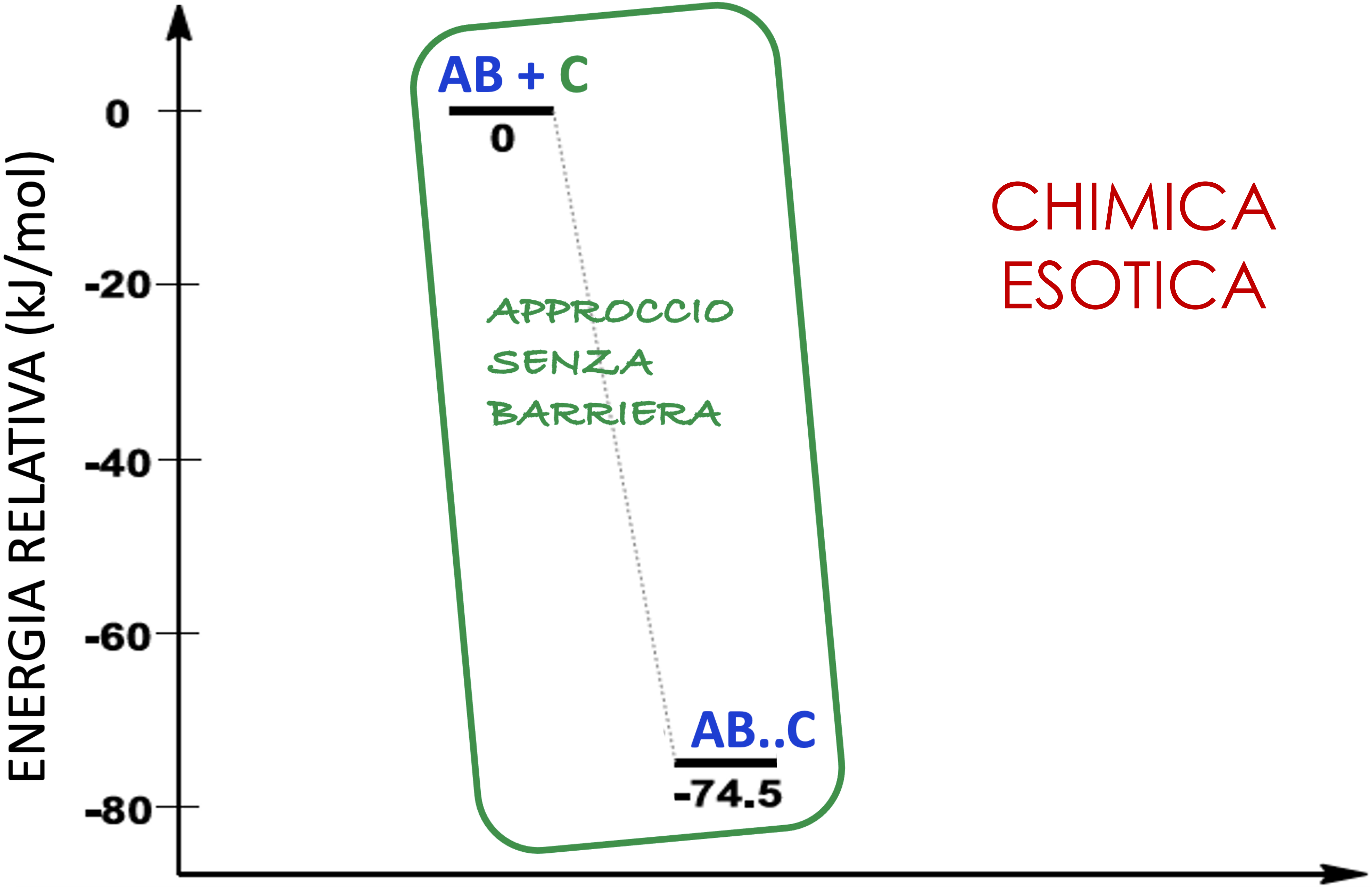
Densità: 1 - 10^8 particelle/cm^3

Bassa P: pochissime collisioni
no stabilizzazione

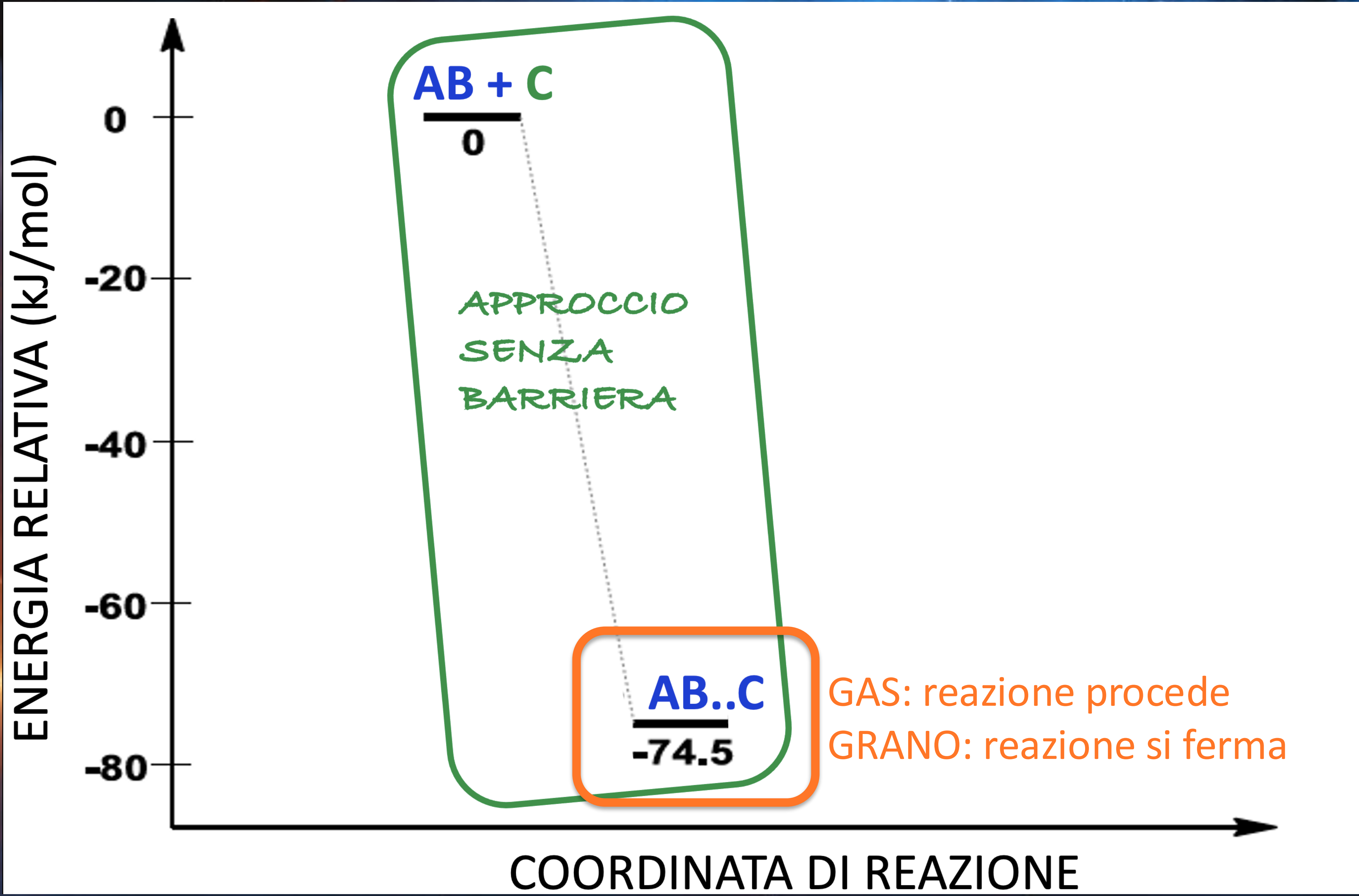
Bassa T: Reazioni Esotermiche
Nessuna barriera

densità di 10^4 part/cm^3 = pressione di 3.8×10^{-10} Pa ($\sim 3.8 \times 10^{-15}$ atm)

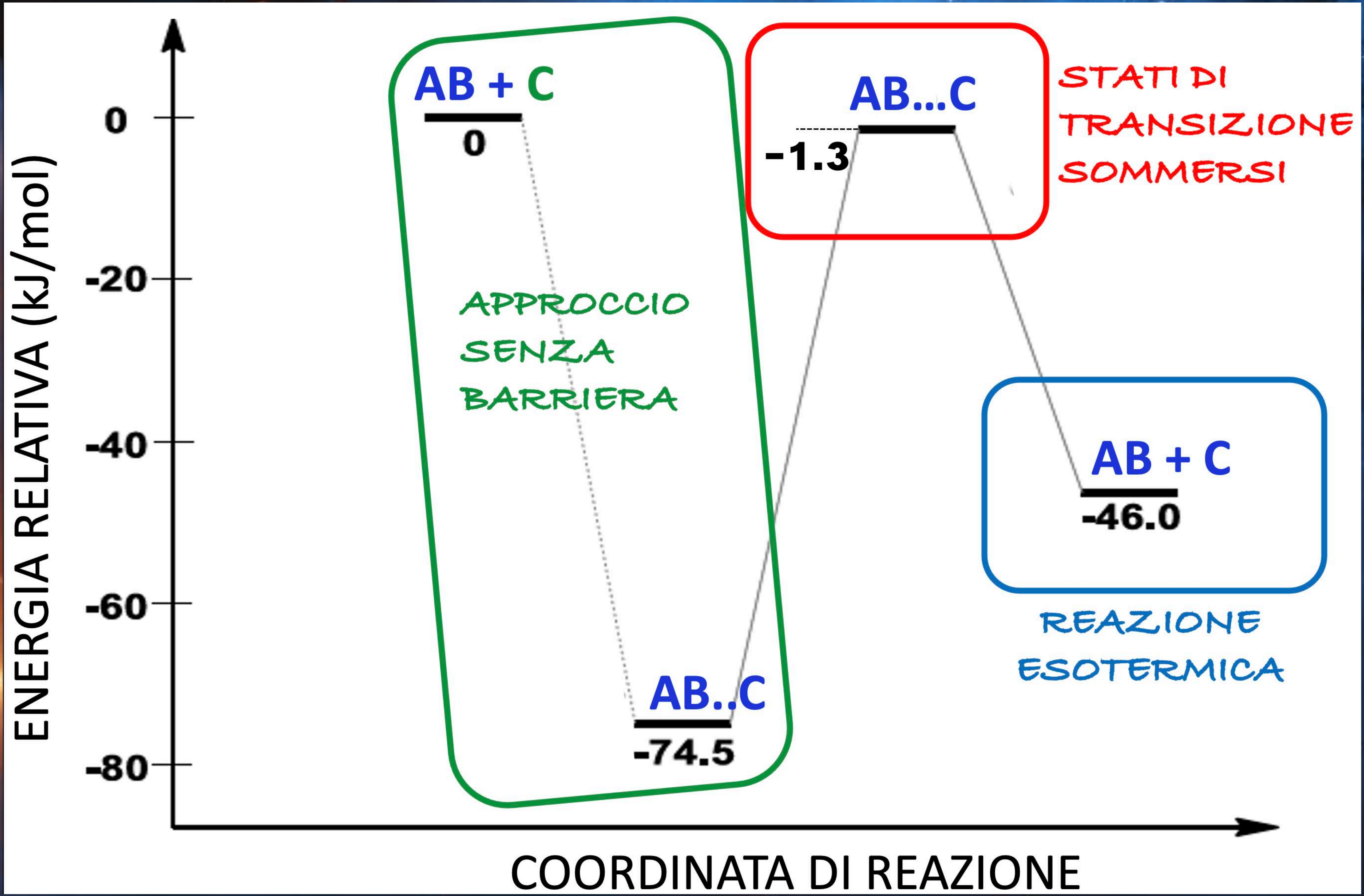
CHIMICA ESOTICA



C deve essere una specie molto reattiva: IONE o RADICALE



AB + C
0
APPROCCIO
SENZA
BARRIERA
AB..C
-74.5
GAS: reazione procede
GRANO: reazione si ferma
0
-20
-40
-60
-80
ENERGIA RELATIVA (kJ/mol)
COORDINATA DI REAZIONE



AB + C
0
0
AB...C
-1.3
STATI DI
TRANSIZIONE
SOMMERSI
-20
APPROCCIO
SENZA
BARRIERA
-40
AB + C
-46.0
-60
REAZIONE
ESOTERMICA
AB..C
-74.5
-80
ENERGIA RELATIVA (kJ/mol)
COORDINATA DI REAZIONE

Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY

Royal Astronomical Society

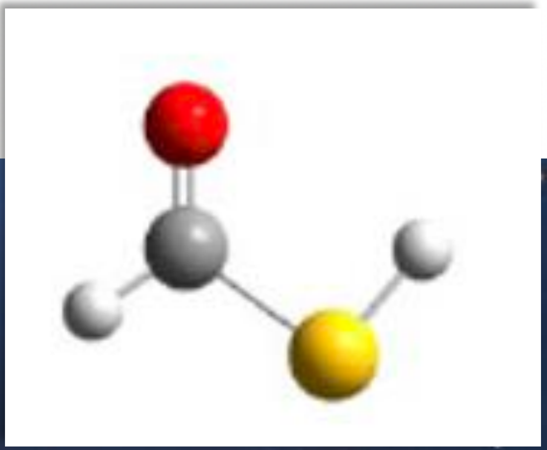
MNRAS **525,** 1158–1166 (2023)
Advance Access publication 2023 July 26

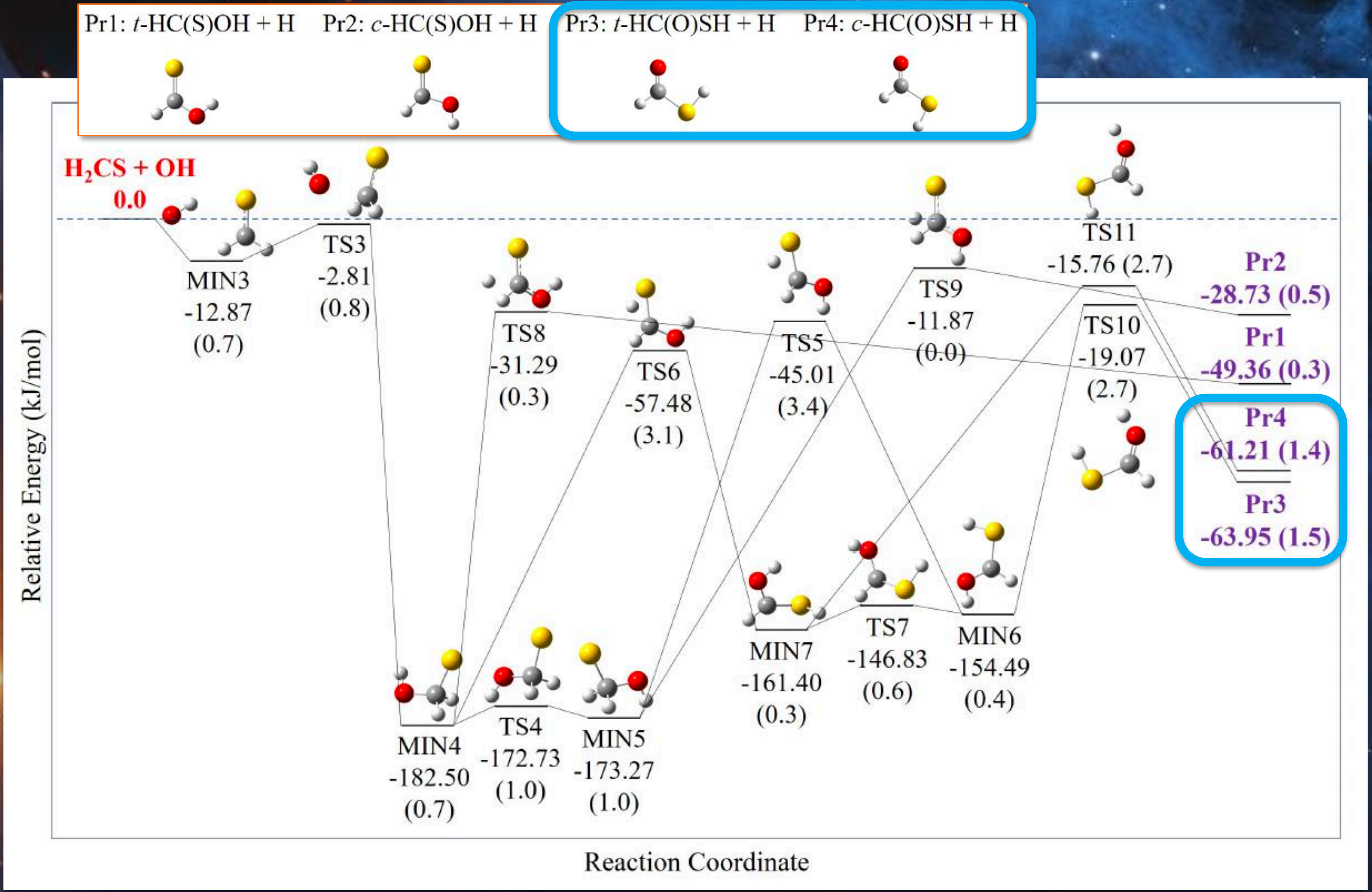
https://doi.org/10.1093/mnras/stad2253

Gas-phase formation route for *trans*-HC(O)SH and its isomers under interstellar conditions: a state-of-the-art quantum-chemical study

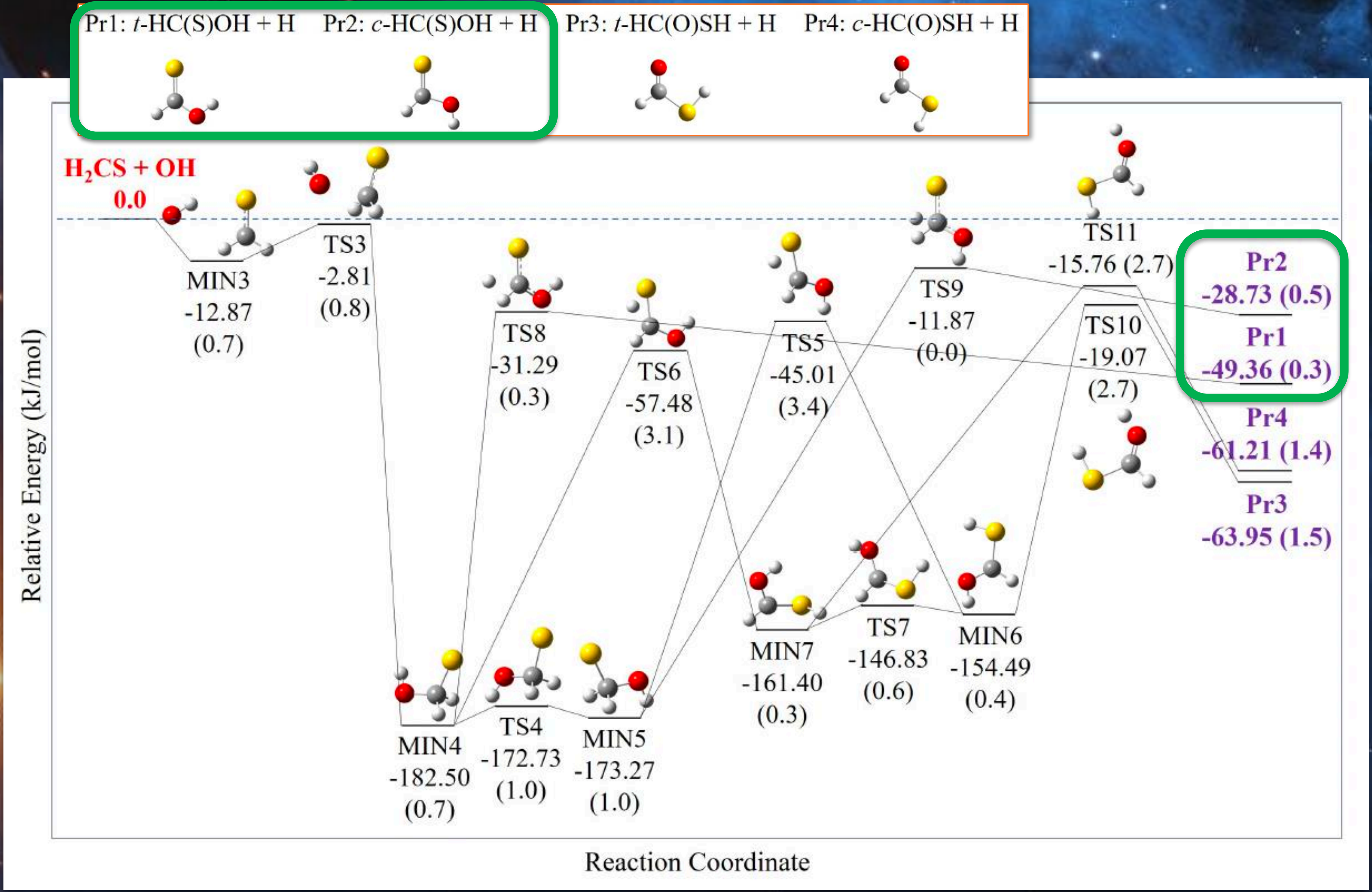
Hexu Ye, Silvia Alessandrini ★ and Cristina Puzzarini ★

Dipartimento di Chimica 'Giacomo Ciamician', Università di Bologna, Via F. Selmi 2, I-40126 Bologna, Italy





Pr1: t-HC(S)OH + H
Pr2: c-HC(S)OH + H
Pr3: t-HC(O)SH + H
Pr4: c-HC(O)SH + H
H2CS + OH
0.0
MIN3
-12.87
(0.7)
TS3
-2.81
(0.8)
TS8
-31.29
(0.3)
TS6
-57.48
(3.1)
TS5
-45.01
(3.4)
TS9
-11.87
(0.0)
TS11
-15.76 (2.7)
TS10
-19.07
(2.7)
Pr2
-28.73 (0.5)
Pr1
-49.36 (0.3)
Pr4
-61.21 (1.4)
Pr3
-63.95 (1.5)
MIN4
-182.50
(0.7)
TS4
-172.73
(1.0)
MIN5
-173.27
(1.0)
MIN7
-161.40
(0.3)
TS7
-146.83
(0.6)
MIN6
-154.49
(0.4)
Relative Energy (kJ/mol)
Reaction Coordinate



Pr1: t-HC(S)OH + H
Pr2: c-HC(S)OH + H
Pr3: t-HC(O)SH + H
Pr4: c-HC(O)SH + H
H2CS + OH
0.0
MIN3
-12.87
(0.7)
TS3
-2.81
(0.8)
TS8
-31.29
(0.3)
TS6
-57.48
(3.1)
TS5
-45.01
(3.4)
TS9
-11.87
(0.0)
TS11
-15.76 (2.7)
TS10
-19.07
(2.7)
Pr2
-28.73 (0.5)
Pr1
-49.36 (0.3)
Pr4
-61.21 (1.4)
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MIN4
-182.50
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-172.73
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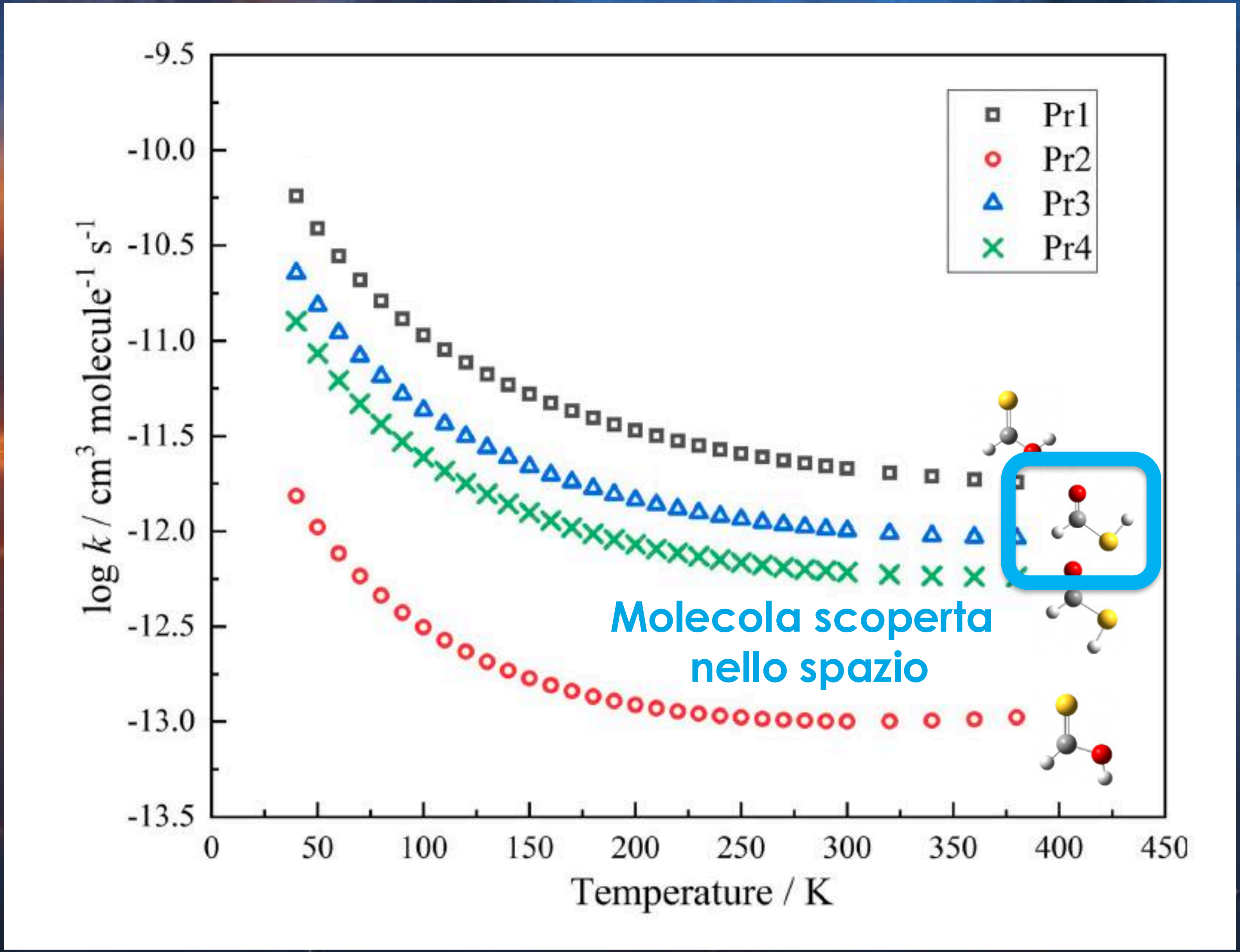
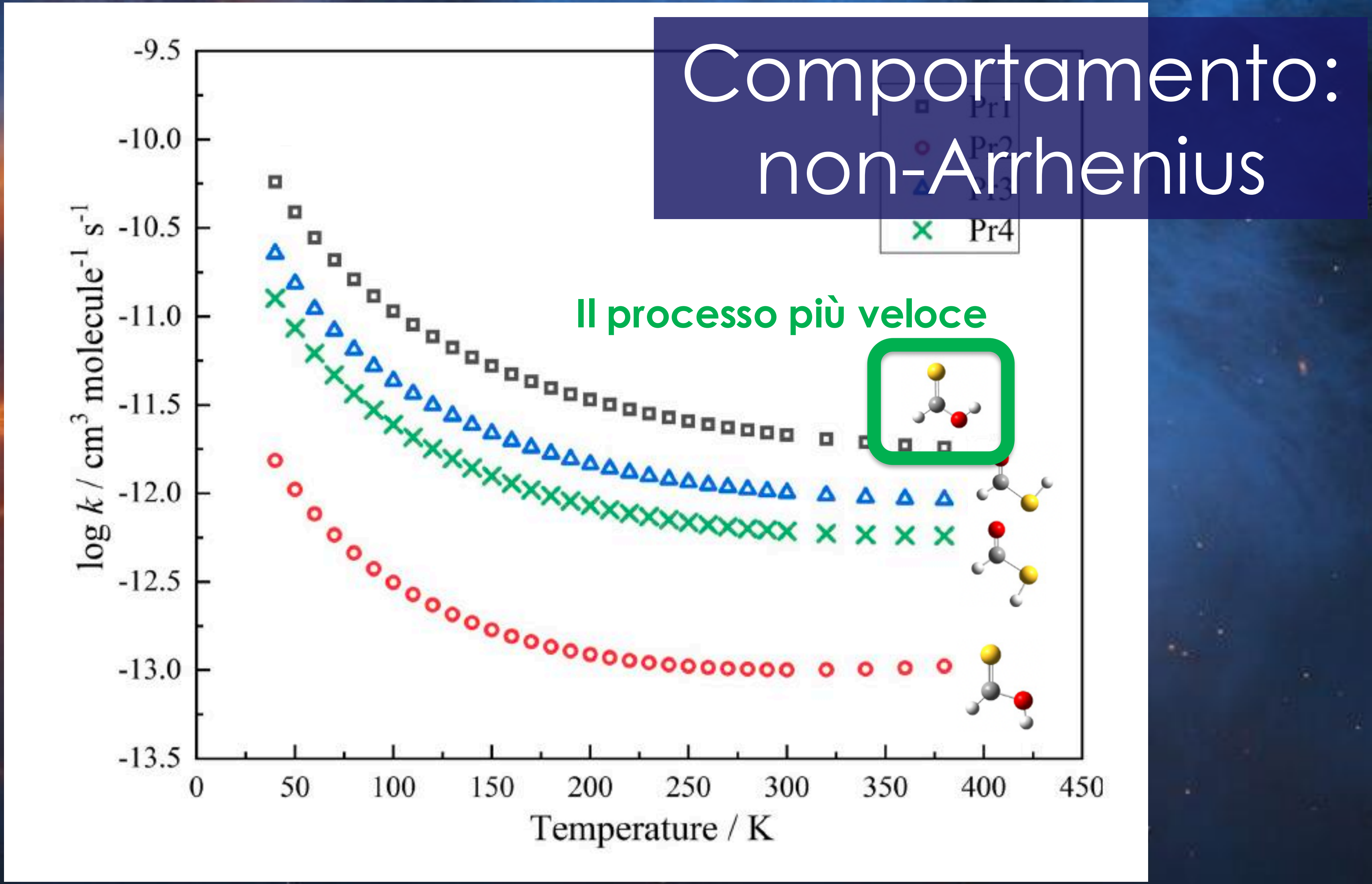
MIN5
-173.27
(1.0)
MIN7
-161.40
(0.3)
TS7
-146.83
(0.6)
MIN6
-154.49
(0.4)
Relative Energy (kJ/mol)
Reaction Coordinate

Cosa dice la CINETICA?



Cosa dice la CINETICA?

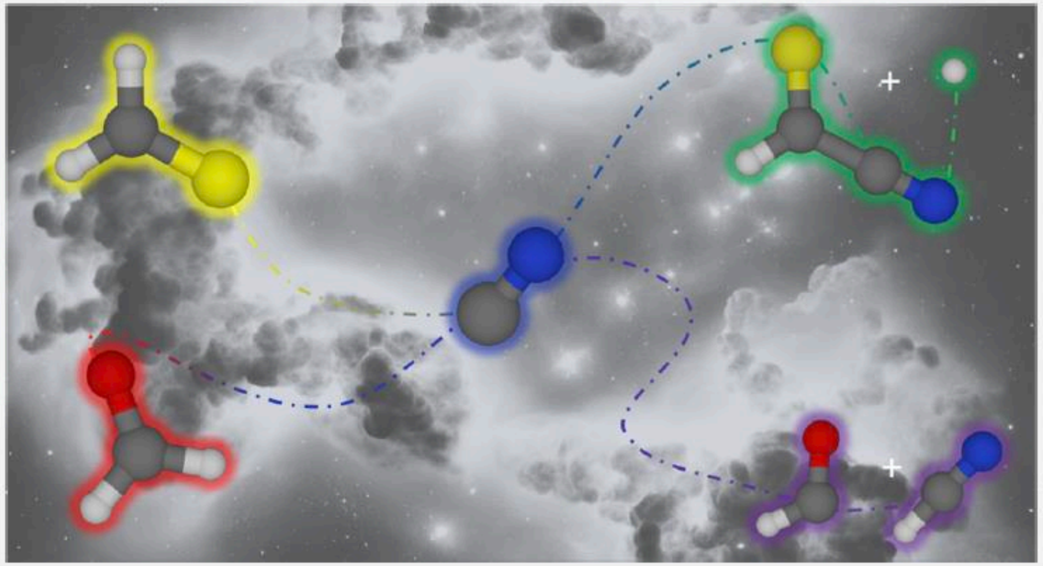


Gas-Phase Reactions of H_2CS and H_2CO with CN: Similarities and Differences from a Computational Study

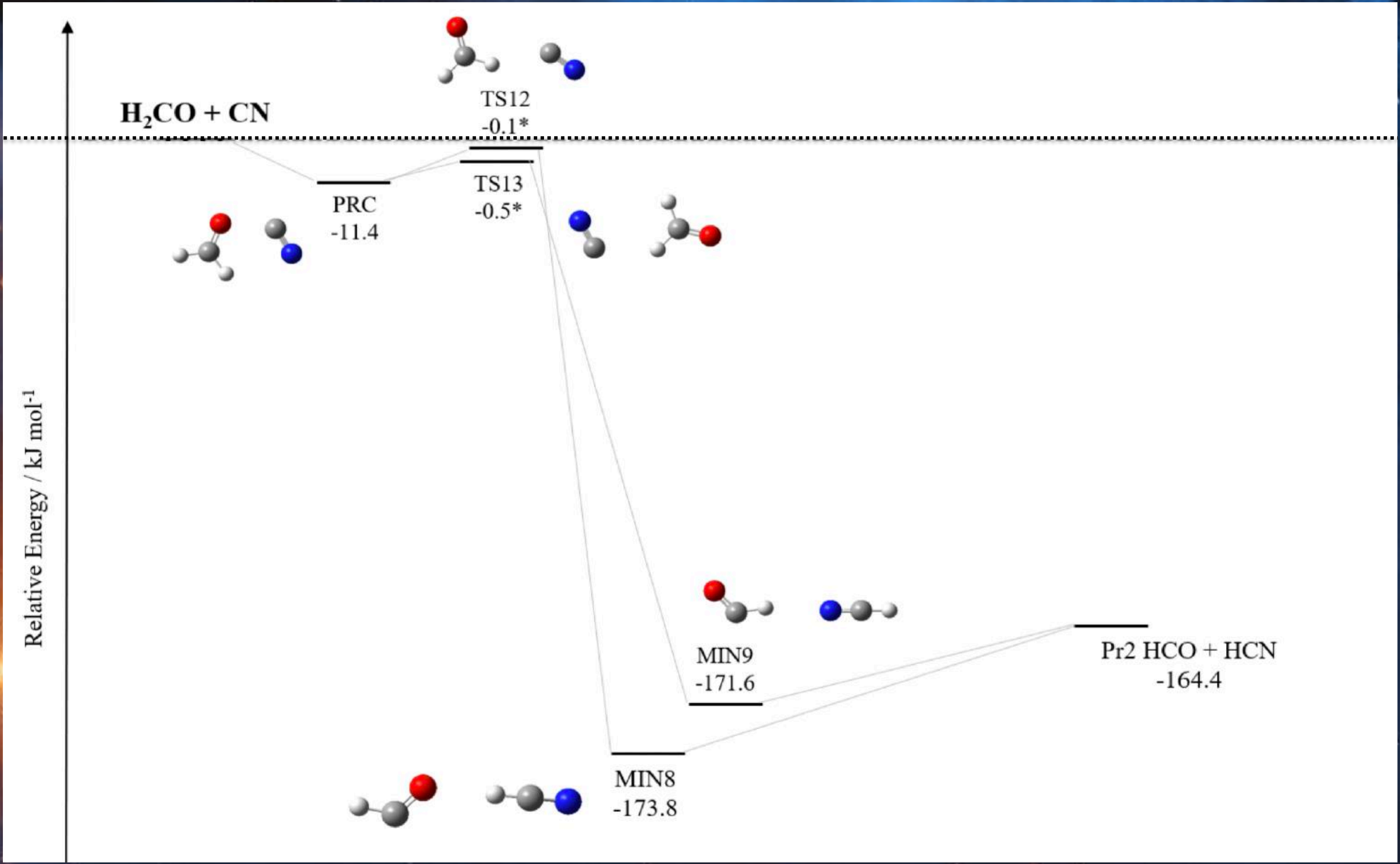
Published as part of ACS Earth and Space Chemistry special issue "Harold Linnartz Festschrift".

Silvia Alessandrini,* Hexu Ye, and Cristina Puzzarini*

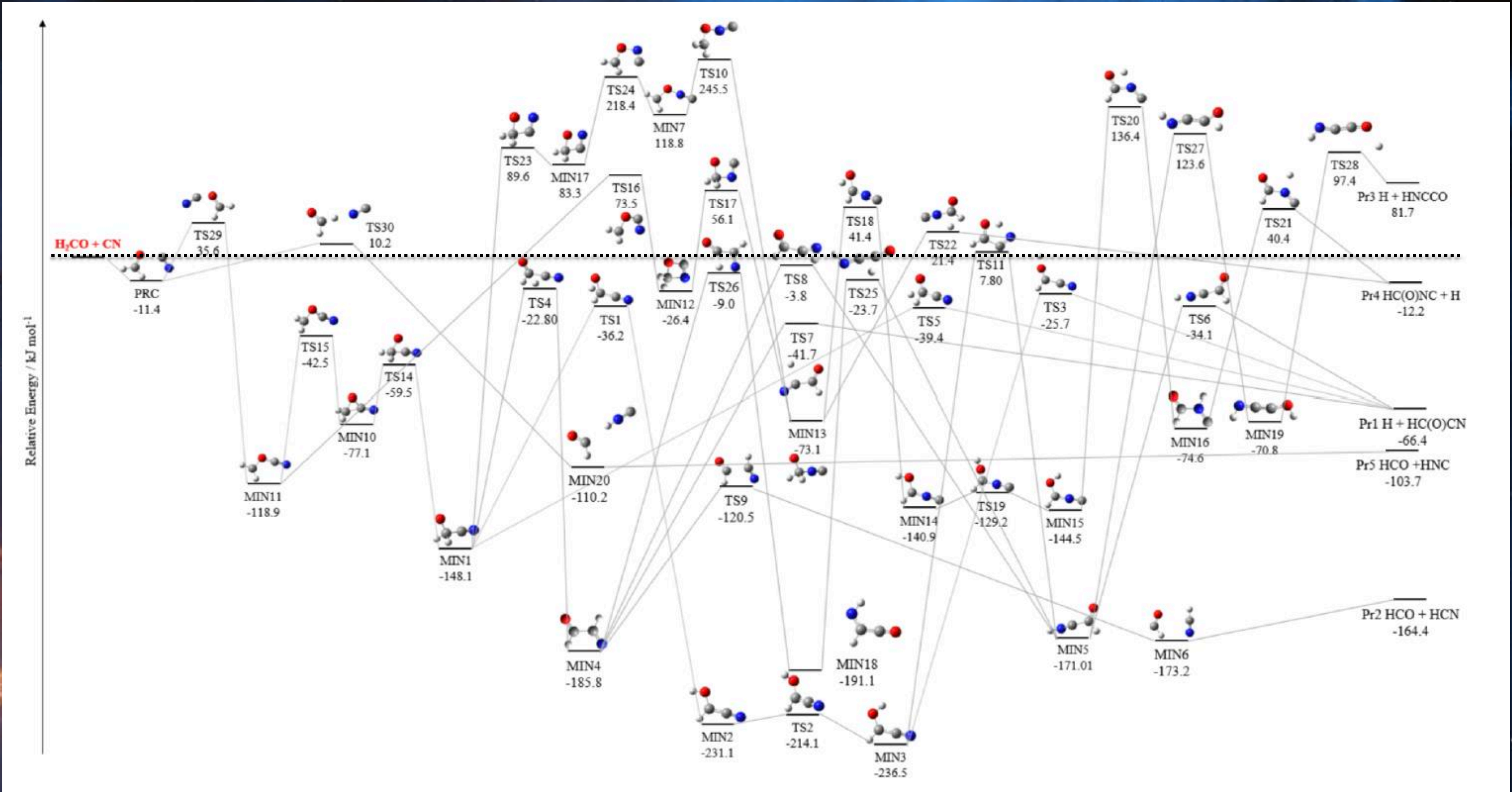
Cite This: *ACS Earth Space Chem.* 2025, 9, 1217−1226



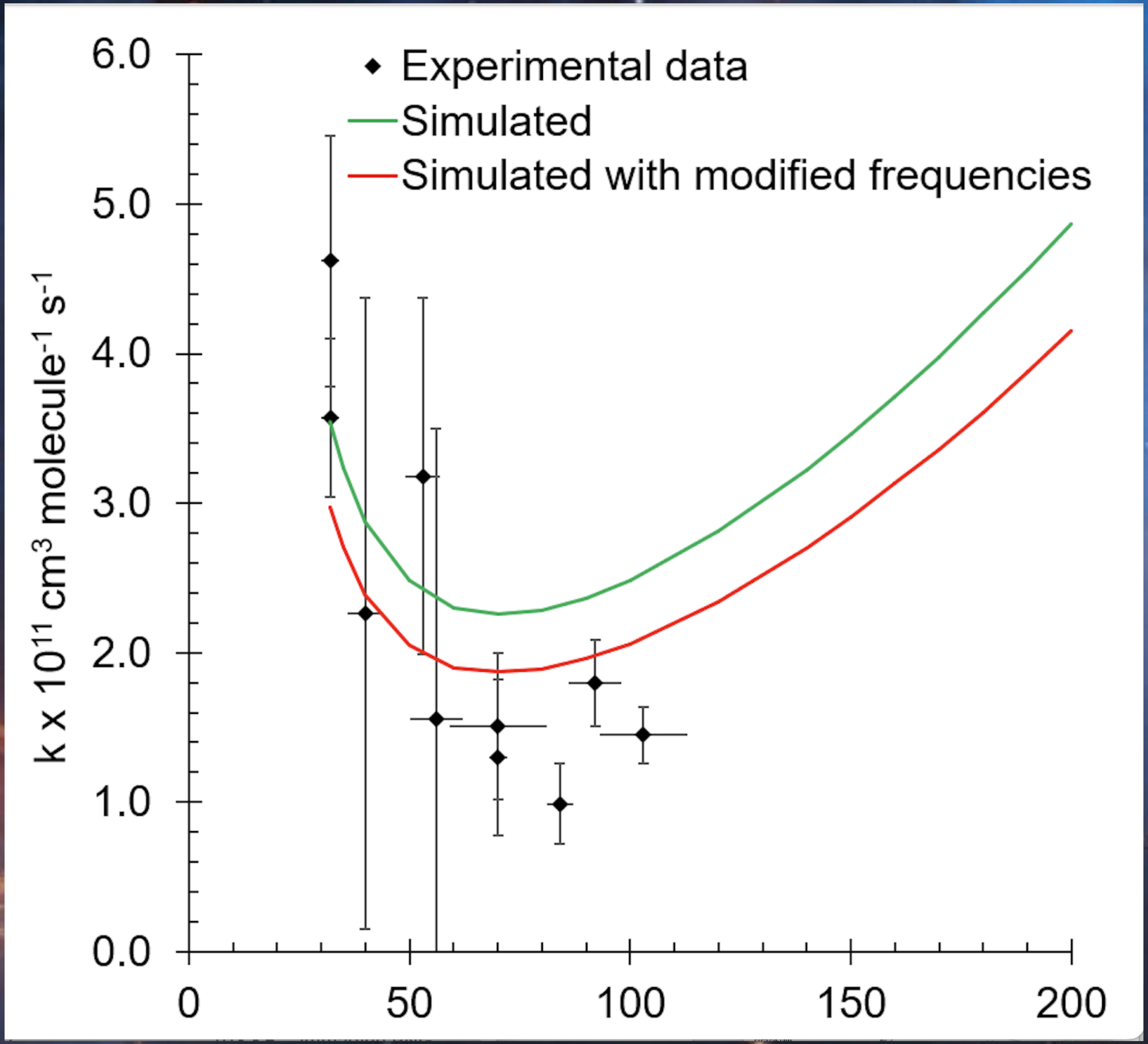
ABSTRACT: The gas-phase reaction of H_2CS with the CN radical has been investigated with the aim of understanding its evolution in the interstellar medium (ISM). After the detection of thioformyl cyanide in TMC-1, this process has been incorporated into astrochemical models because it is considered the most efficient (if not the only) gas-phase formation route for such a molecule in dark molecular clouds. However, neither experimental nor theoretical studies have been reported in the literature regarding its feasibility in the typical conditions of the ISM. In this work, the corresponding reactive potential energy surface has been accurately investigated and complemented by ab initio transition state theory calculations to derive global rate coefficients. In view of the potential similarities between the H_2CS + CN and H_2CO + CN reactions, this latter process has also been reinvestigated. The availability of experimental data for the H_2CO + CN reaction has been exploited to derive the accuracy of the computed rate constants for the sulfur-bearing counterpart.



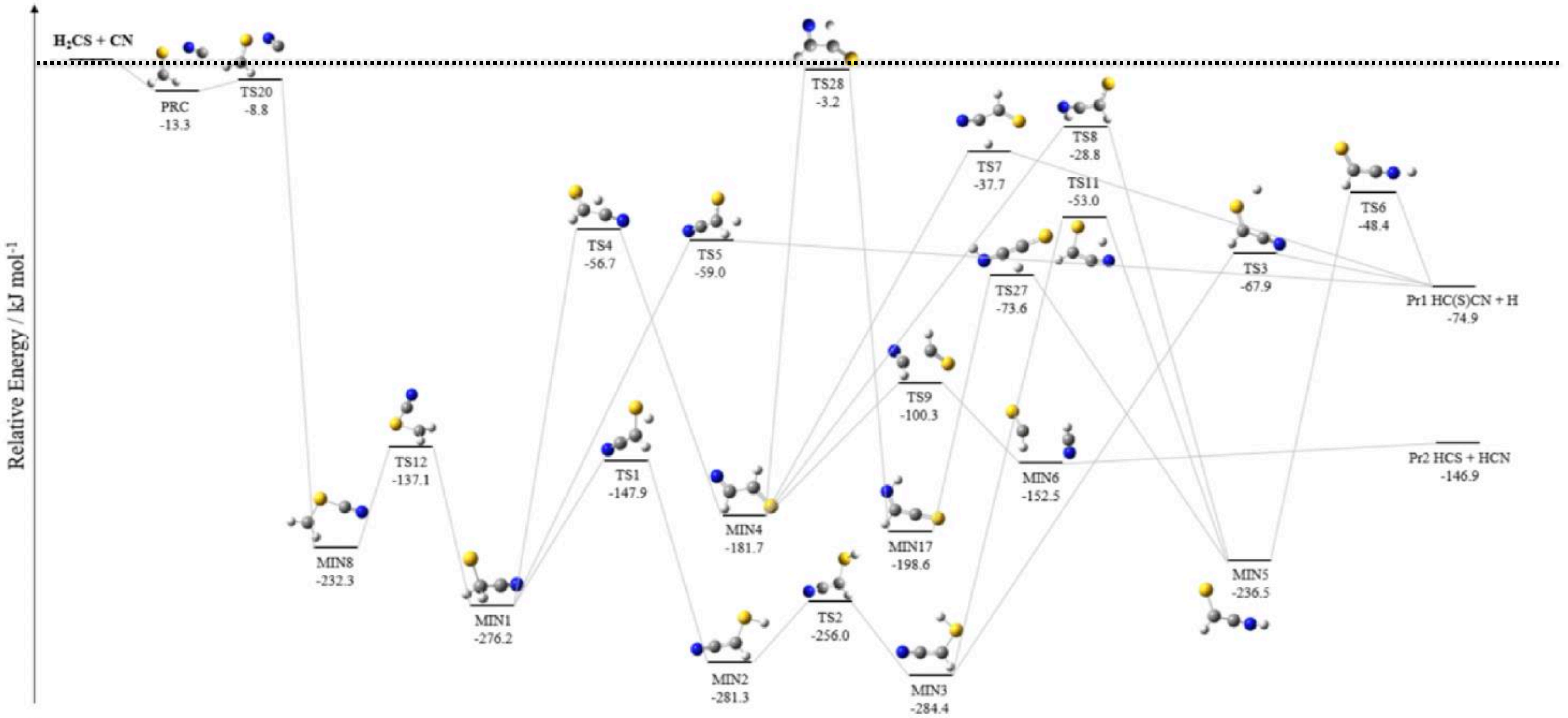
$H_2CO + CN$
TS12
-0.1*
TS13
-0.5*
PRC
-11.4
MIN9
-171.6
MIN8
-173.8
Pr2 HCO + HCN
-164.4
Relative Energy / kJ mol^{-1}



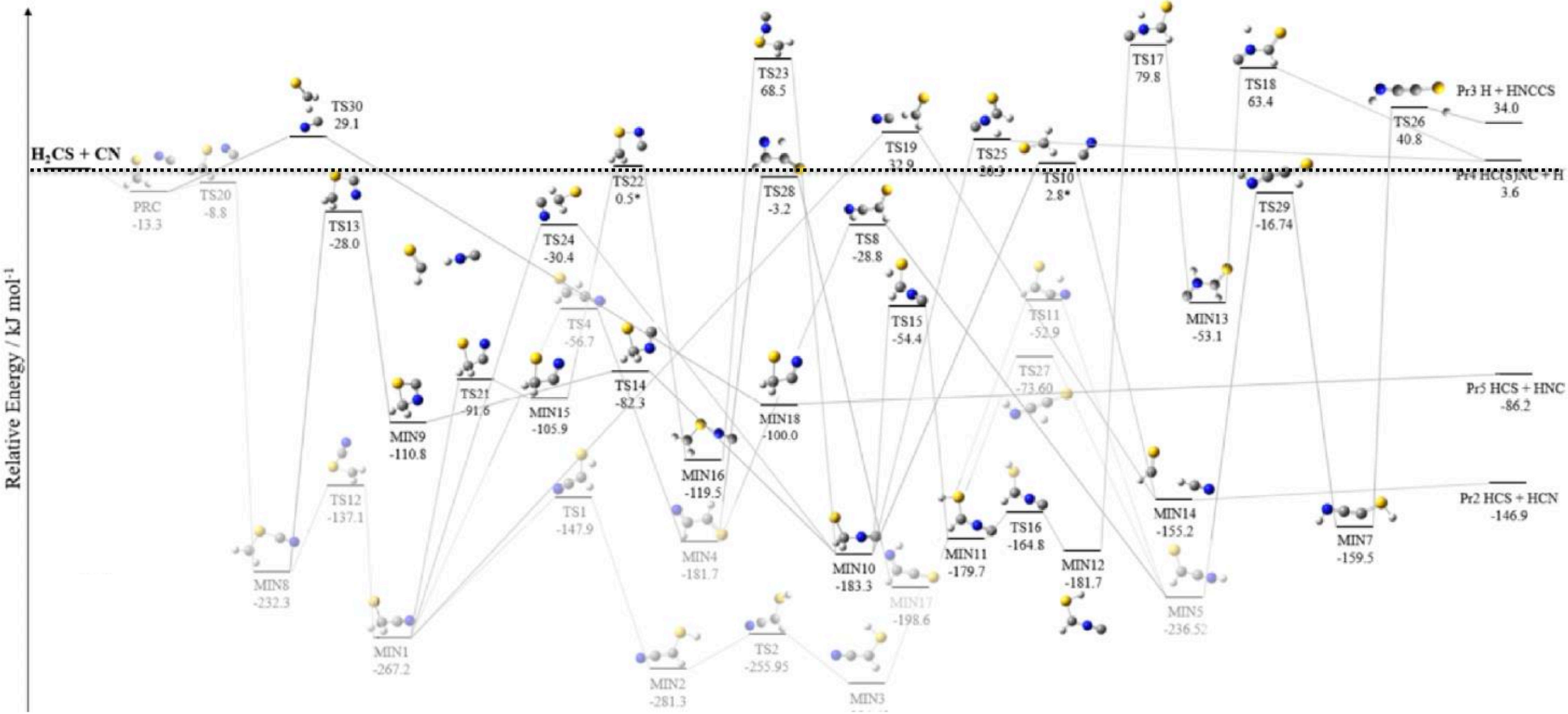
Relative Energy / kJ mol^{-1}
$H_2CO + CN$
PRC -11.4
TS29 35.6
TS30 10.2
MIN11 -118.9
TS15 -42.5
MIN10 -77.1
TS14 -59.5
MIN1 -148.1
TS23 89.6
MIN17 83.3
TS4 -22.80
TS24 218.4
TS16 73.5
TS1 -36.2
MIN20 -110.2
MIN4 -185.8
MIN7 118.8
TS10 245.5
MIN12 -26.4
TS17 56.1
TS26 -9.0
TS9 -120.5
MIN2 -231.1
TS8 -3.8
TS7 -41.7
MIN13 -73.1
TS2 -214.1
TS18 41.4
TS25 -23.7
MIN18 -191.1
MIN3 -236.5
MIN14 -140.9
TS22 21.4
TS5 -39.4
TS11 7.80
TS19 -129.2
TS3 -25.7
MIN15 -144.5
MIN5 -171.01
TS20 136.4
TS27 123.6
TS6 -34.1
MIN16 -74.6
MIN6 -173.2
TS21 40.4
MIN19 -70.8
TS28 97.4
Pr3 H + HNCCO 81.7
Pr4 HC(O)NC + H -12.2
Pr1 H + HC(O)CN -66.4
Pr5 HCO +HNC -103.7
Pr2 HCO + HCN -164.4



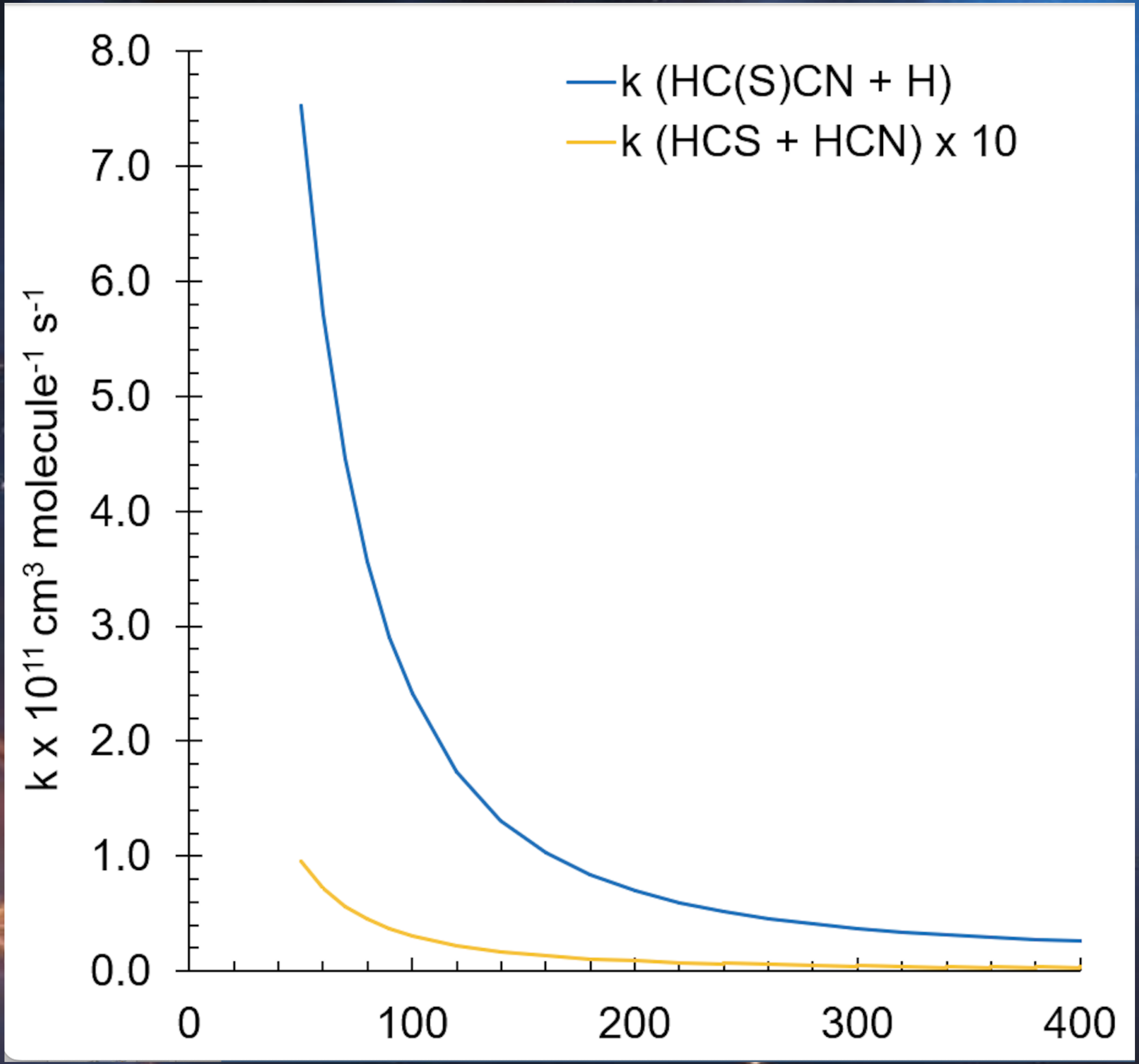
La reazione che avviene è:
$H_2CO + CN \rightarrow HCO + HCN$



Relative Energy / kJ mol-1
H2CS + CN
PRC
-13.3
TS20
-8.8
TS28
-3.2
TS7
-37.7
TS8
-28.8
TS11
-53.0
TS6
-48.4
TS4
-56.7
TS5
-59.0
TS27
-73.6
TS3
-67.9
Pr1 HC(S)CN + H
-74.9
TS9
-100.3
TS12
-137.1
TS1
-147.9
MIN6
-152.5
Pr2 HCS + HCN
-146.9
MIN4
-181.7
MIN17
-198.6
MIN8
-232.3
MIN5
-236.5
MIN1
-276.2
TS2
-256.0
MIN2
-281.3
MIN3
-284.4



Relative Energy / kJ mol-1
H2CS + CN
PRC -13.3
TS20 -8.8
TS30 29.1
TS13 -28.0
MIN8 -232.3
TS12 -137.1
MIN1 -267.2
MIN9 -110.8
TS21 -91.6
MIN15 -105.9
TS24 -30.4
TS4 -56.7
TS1 -147.9
TS22 0.5*
TS14 -82.3
MIN2 -281.3
MIN16 -119.5
MIN4 -181.7
TS23 68.5
TS28 -3.2
MIN18 -100.0
TS2 -255.95
MIN3
TS19 32.9
TS8 -28.8
TS15 -54.4
MIN10 -183.3
MIN17 -198.6
TS25
MIN11 -179.7
TS16 -164.8
TS11 -52.9
TS27 -73.60
TS10 2.8*
MIN12 -181.7
TS17 79.8
MIN14 -155.2
MIN5 -236.52
MIN13 -53.1
TS18 63.4
TS29 -16.74
MIN7 -159.5
TS26 40.8
Pr3 H + HNCCS 34.0
Pr4 HC(S)NC + H 3.6
Pr5 HCS + HNC -86.2
Pr2 HCS + HCN -146.9



Le reazioni che avvengono sono:

$H_2CS + CN \rightarrow HC(S)CN + H$ (blu)

$H_2CS + CN \rightarrow HCS + HCN$ (giallo)

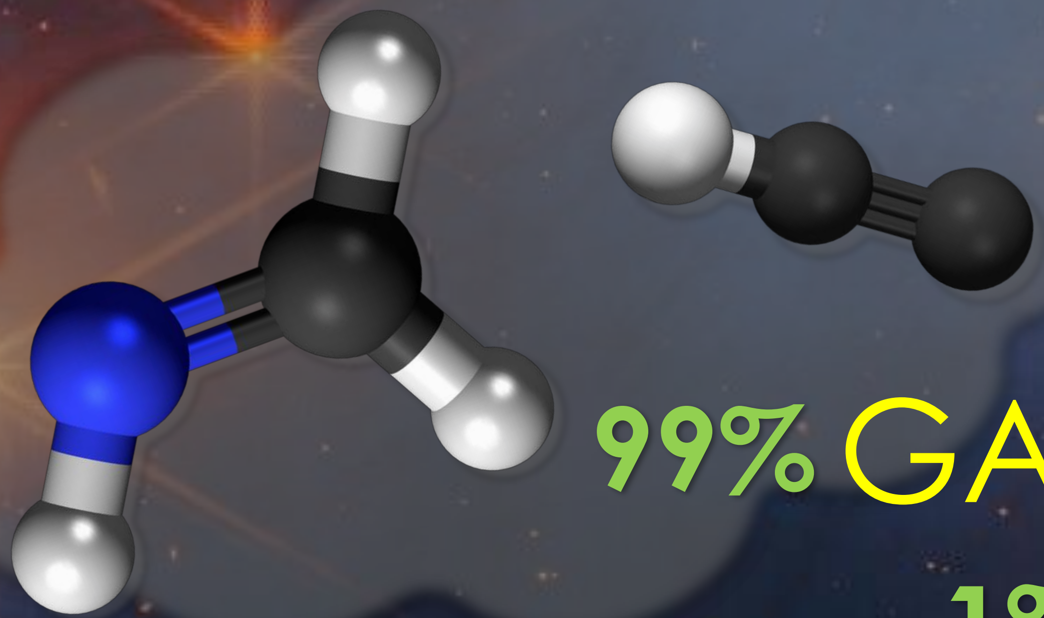
ma la seconda è molto lenta

CONDIZIONI ESTREME:

Bassa Temperatura (10-200 K)

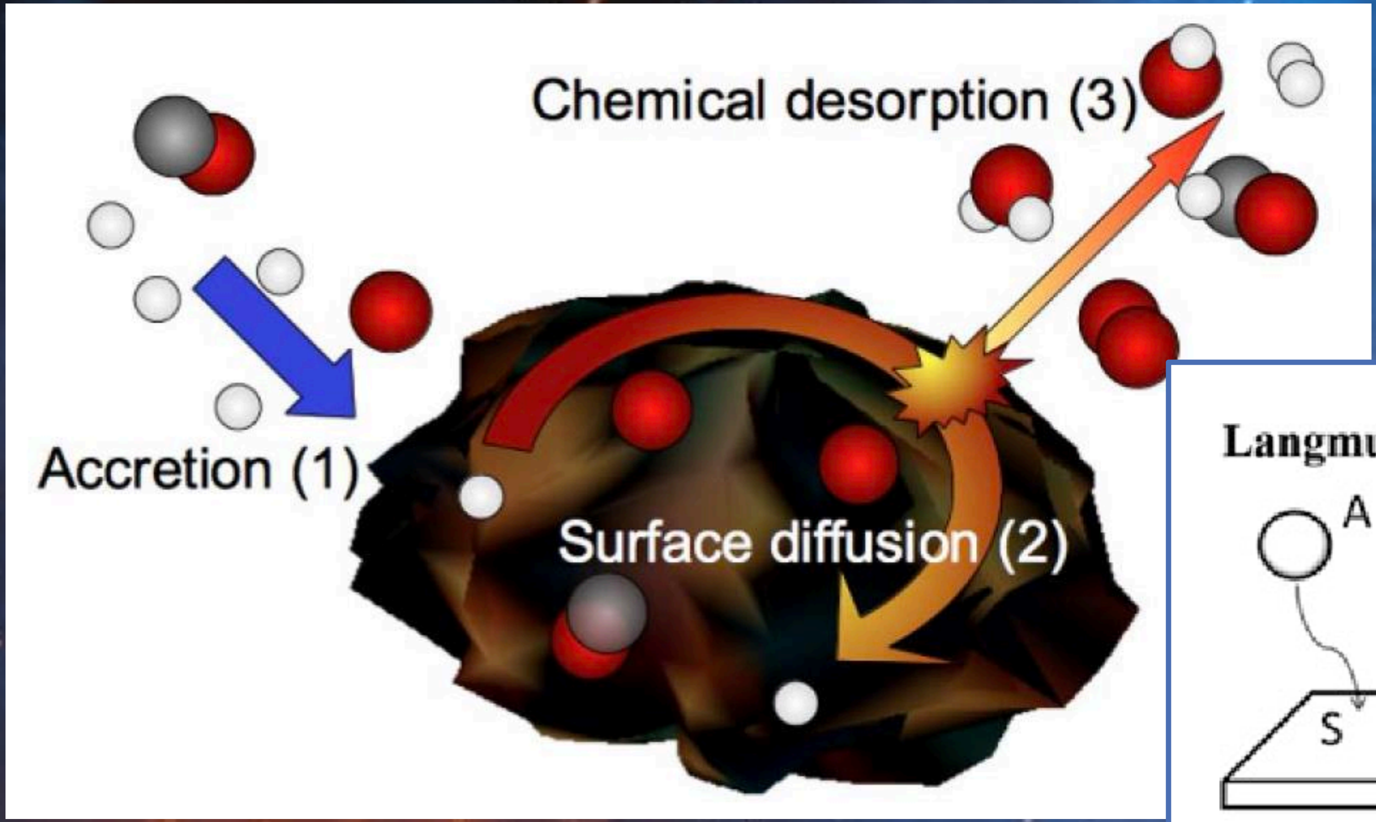
Bassa Densità (1-10^8 molec. cm^{-3})

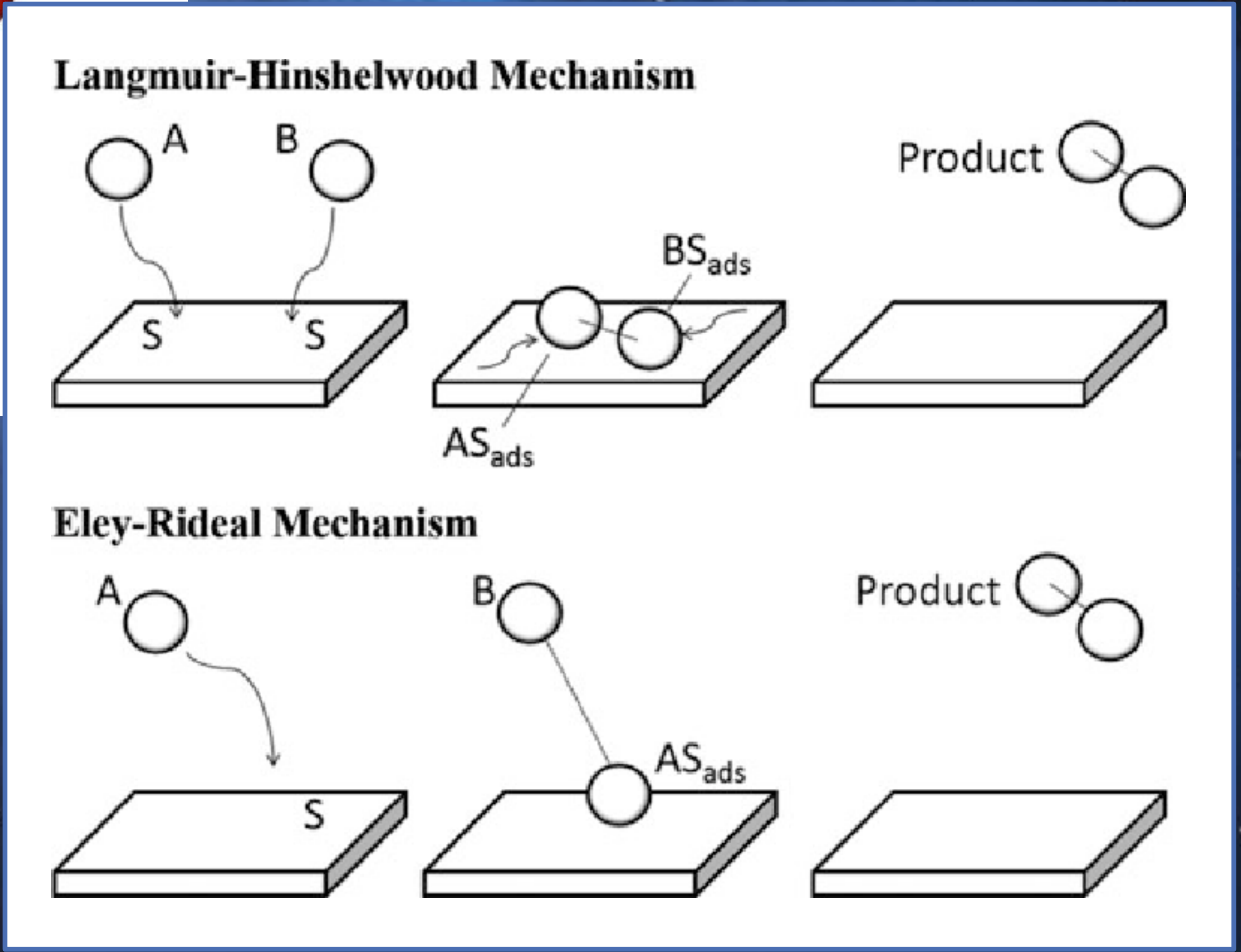
Radiazioni ionizzanti



99% GAS

1% POLVERE


Chemical desorption (3)
Accretion (1)
Surface diffusion (2)


Langmuir-Hinshelwood Mechanism
A
B
Product
S
S
BS_{ads}
AS_{ads}
Eley-Rideal Mechanism
A
B
Product
S
AS_{ads}

A&A, 698, A51 (2025)
https://doi.org/10.1051/0004-6361/202554330

Astronomy & Astrophysics

Formation of the glycine isomer glycolamide ($NH_2C(O)CH_2OH$) on the surfaces of interstellar ice grains: Insights from atomistic simulations

J. Perrero[1,2,3,⋆], S. Alessandrini[4,⋆], H. Ye[4], C. Puzzarini[4], and A. Rimola[1]

Reazione in 2 step:

$$H_2CO + NH_2CO^\bullet \rightarrow NH_2C(O)CH_2O^\bullet \qquad (1)$$

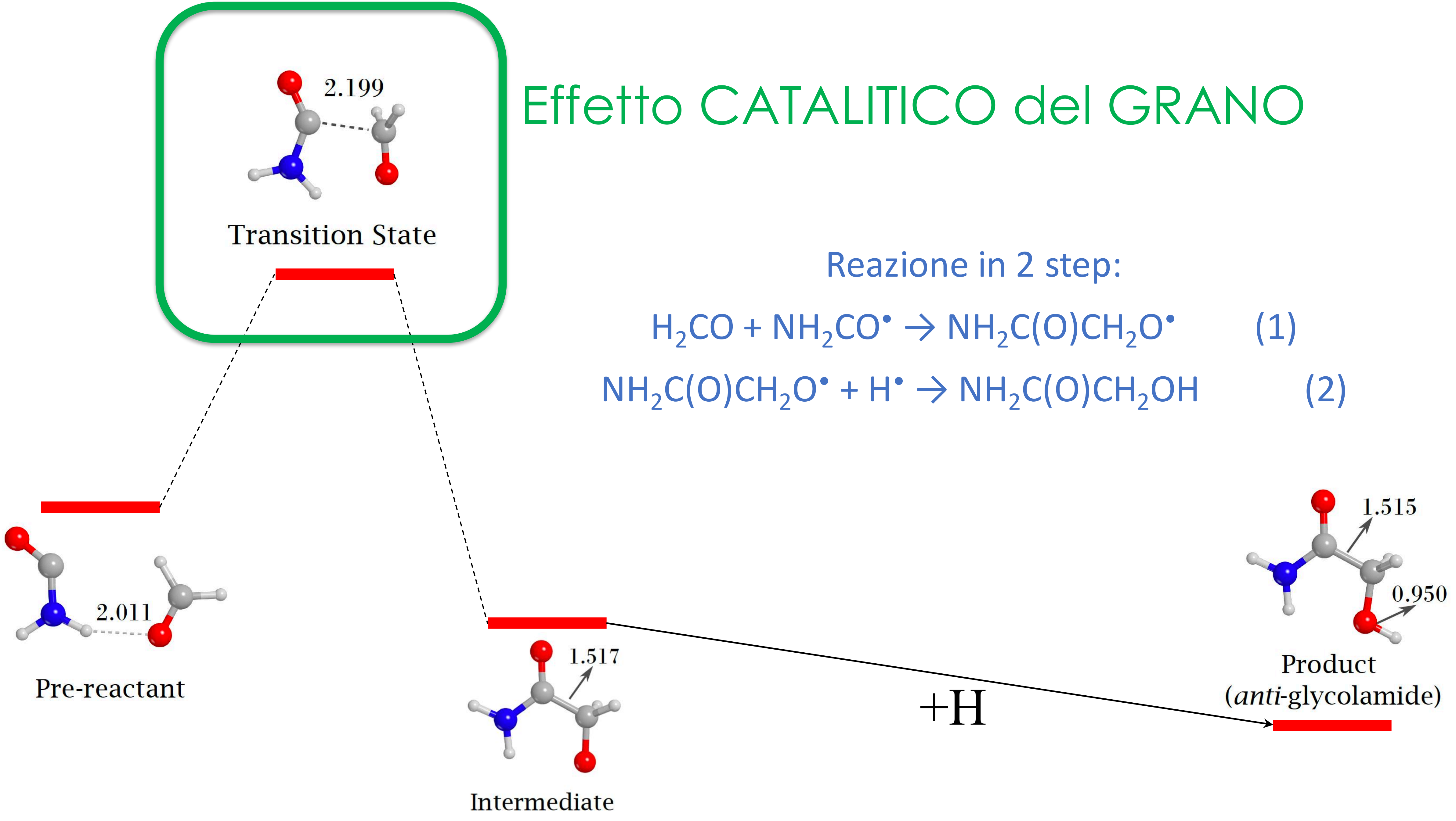
$$NH_2C(O)CH_2O^\bullet + H^\bullet \rightarrow NH_2C(O)CH_2OH \qquad (2)$$

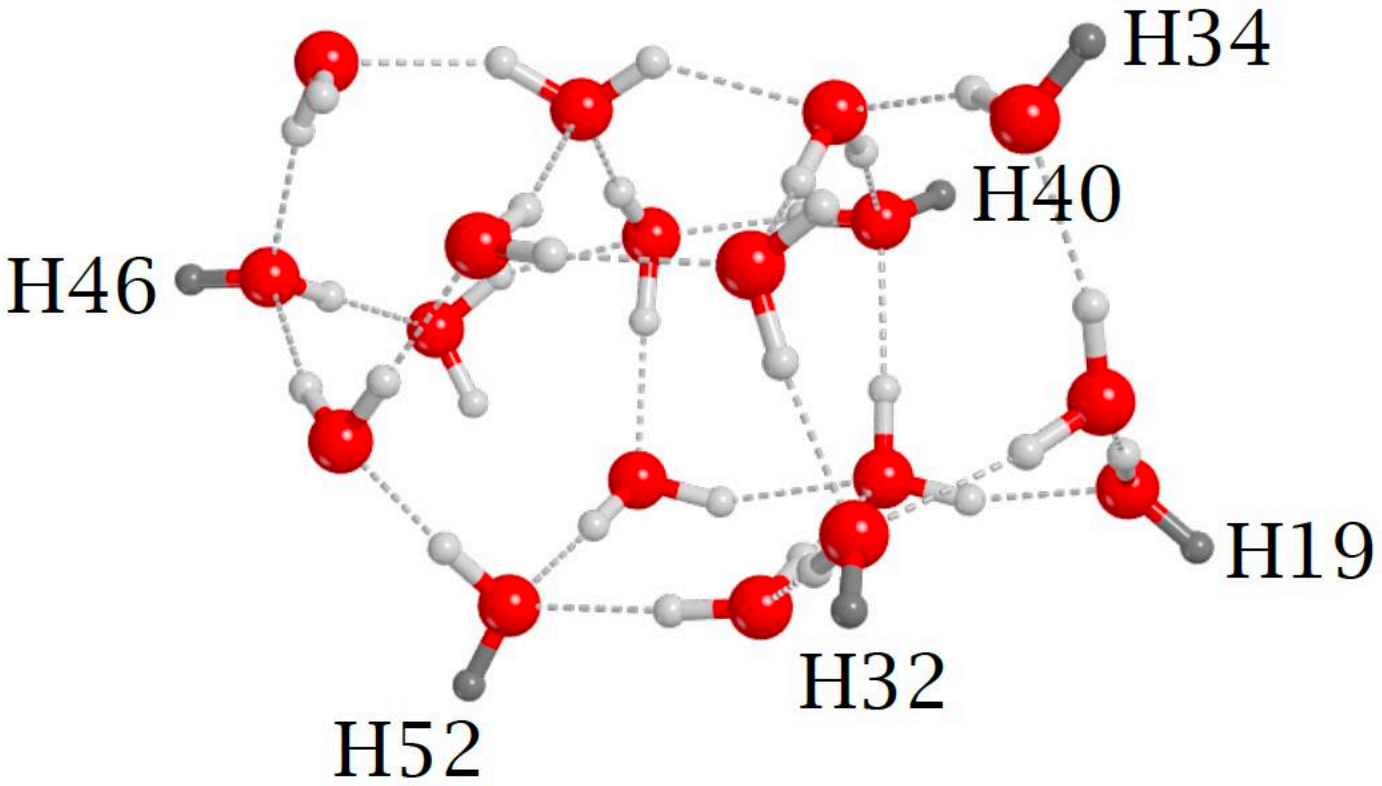
Effetto CATALITICO del GRANO

Reazione in 2 step:

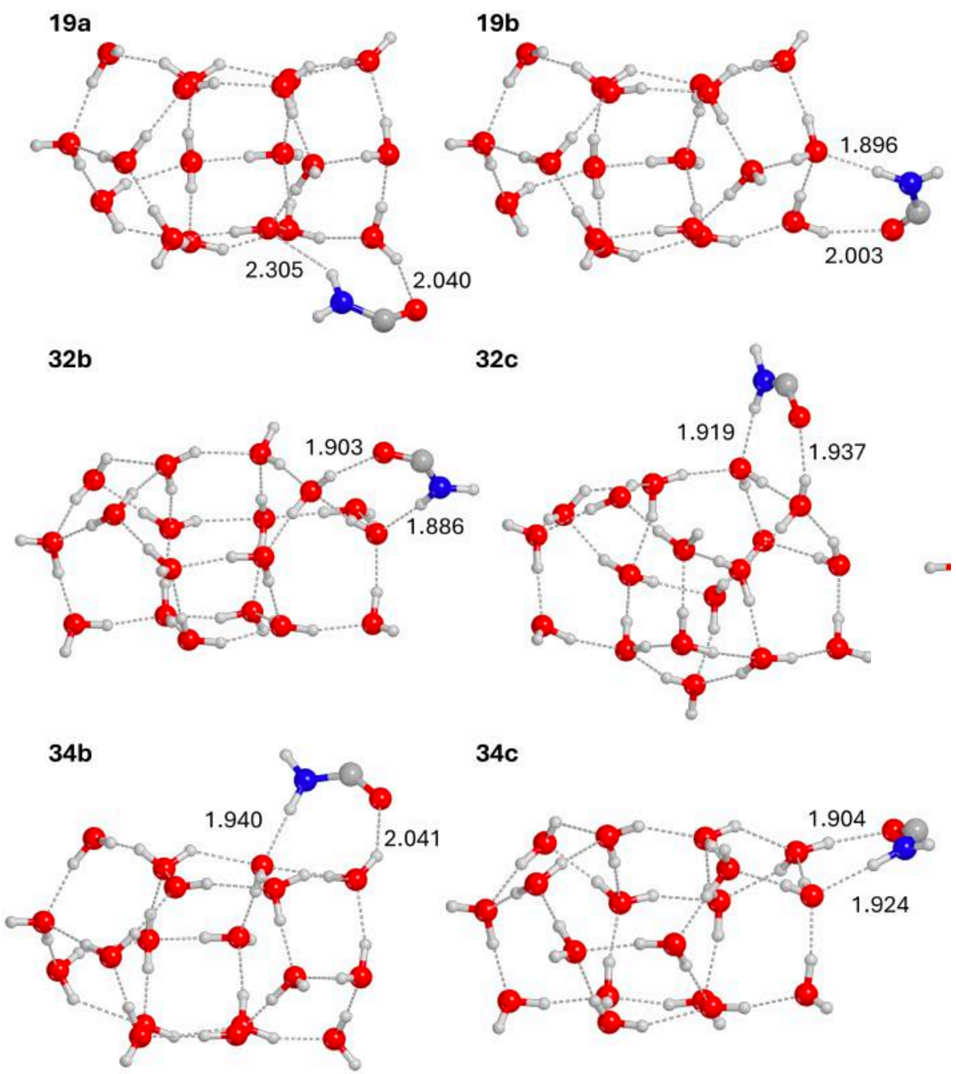
$$H_2CO + NH_2CO^{\bullet} \rightarrow NH_2C(O)CH_2O^{\bullet} \qquad (1)$$

$$NH_2C(O)CH_2O^{\bullet} + H^{\bullet} \rightarrow NH_2C(O)CH_2OH \qquad (2)$$

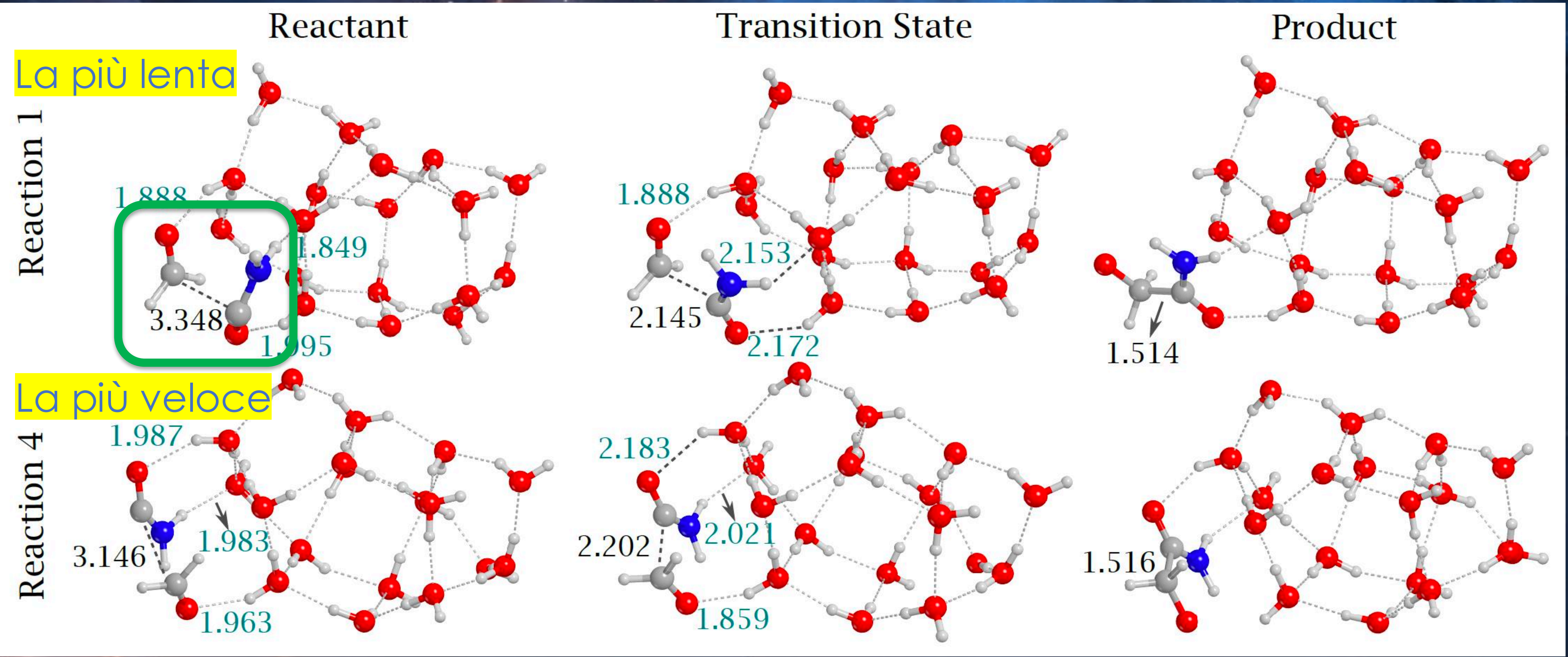


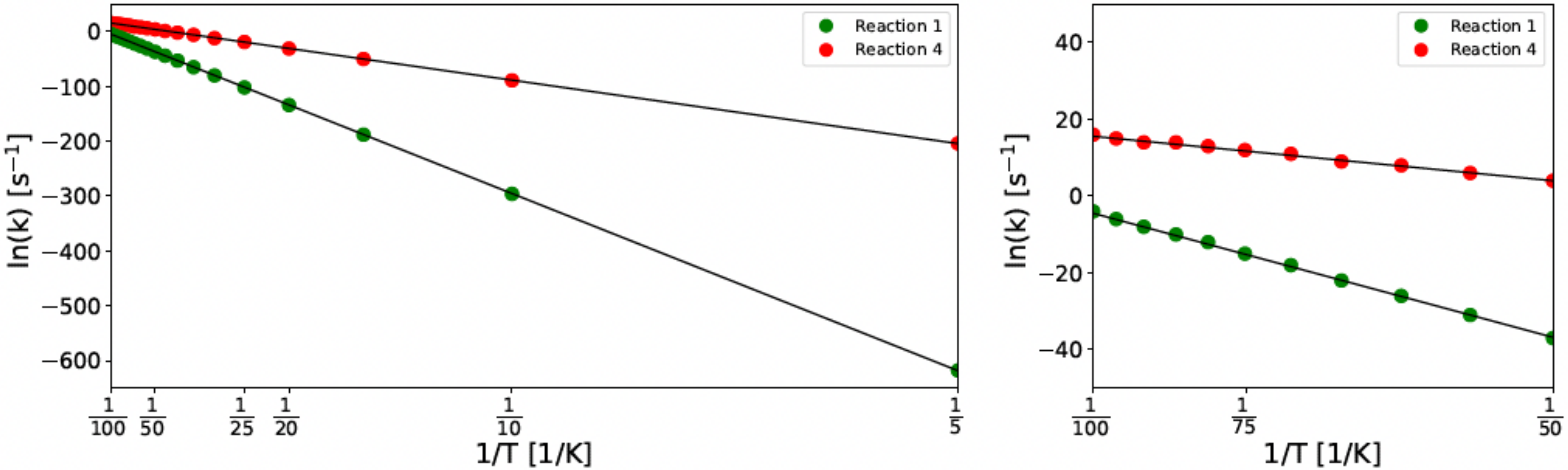


Cluster of 18 molecole d'acqua (W18) per simulare la superficie di ghiaccio sul grano.
In grigio: gli idrogeni dove i reagenti (H_2CO e $NH_2CO^{\bullet}$) si attaccano.



Esempi di reagente adsorbito


Reactant
Transition State
Product
La più lenta
Reaction 1
1.888
1.849
3.348
1.995
1.888
2.153
2.145
2.172
1.514
La più veloce
Reaction 4
1.987
1.983
3.146
1.963
2.183
2.021
2.202
1.859
1.516



Arrhenius plots for Reactions 1 and 4

$$k(T) = \kappa \times \frac{k_B T}{h} \times exp(-\Delta G^{\ddagger}/RT)$$

Cinetica:
equazione semi-classica di Eyring

L’umanità osserva il cielo da millenni …

L’universo è un luogo “ricco” di atomi …

Per molti anni il mezzo interstellare è stato considerato un ambiente troppo ostile per le molecole …

Abbiamo scoperto molto, ma è solo la punta dell’iceberg … una cosa però è certa: spetta alla CINETICA l’ultima parola su una reazione che può avvenire o meno, essere efficiente o meno, nello spazio.


GRAZIE
per la
vostra
ATTENZIONE