Chemistry of the Interstellar Medium

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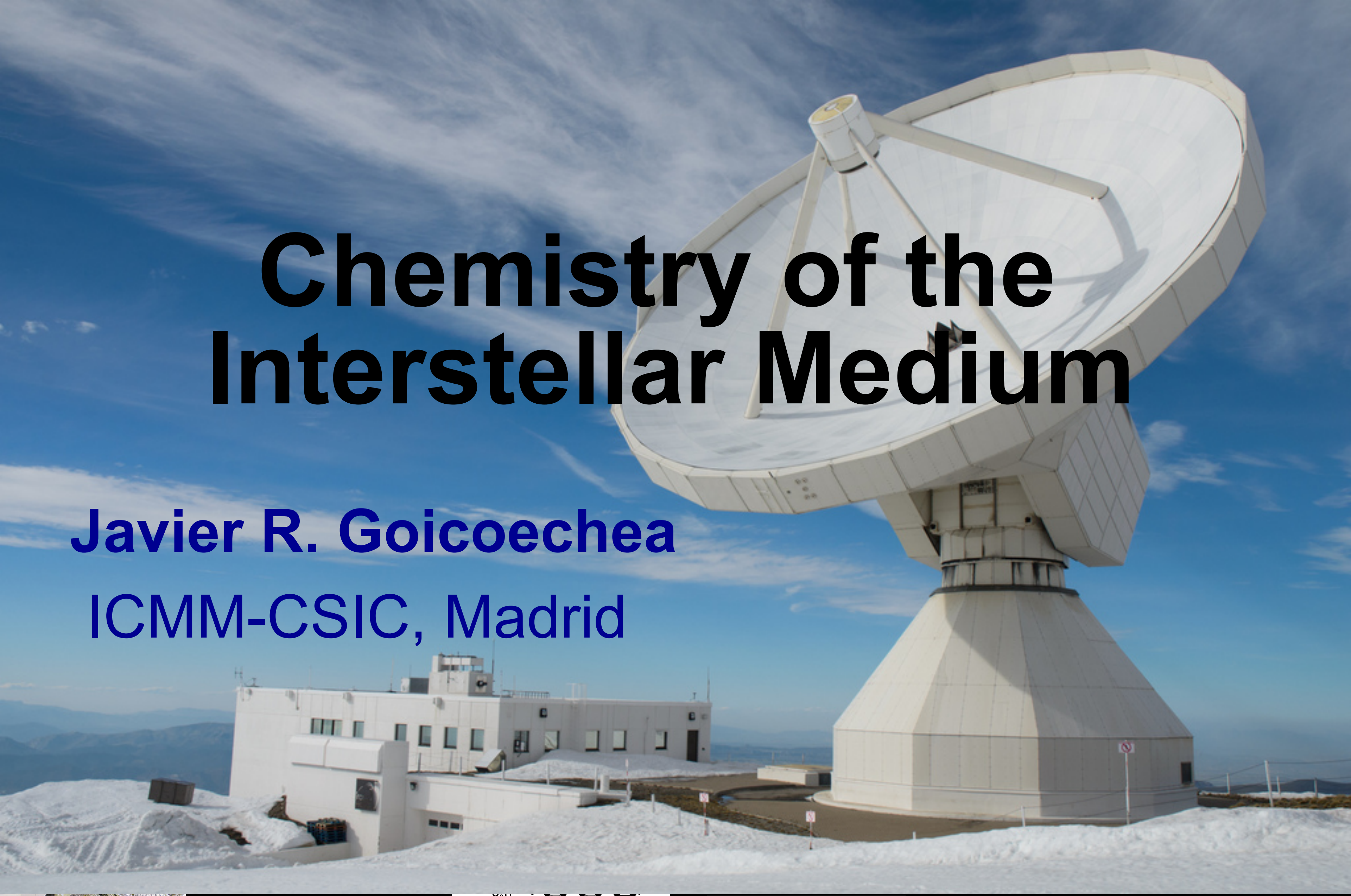

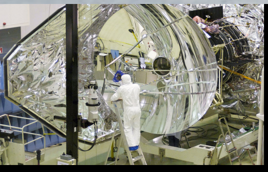

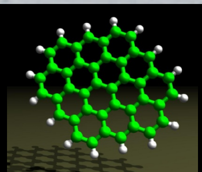

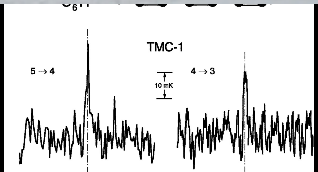

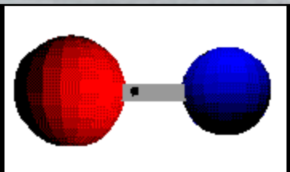

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OUTLINE

Chemistry of the ISM I:

- “The Molecular Universe”: Introduction and motivations
- Environments where we detect molecules.

Chemistry of the ISM II:

- Basic notions, basic formation and destruction mechanisms of gas-phase molecules in different environments.

- And now put all of this in computer models…

Bibliography on interstellar chemistry

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Molecules in the ISM? Typical Scales

"Size" of a diatomic molecule, $r \approx 2$ Å $= 2 \cdot 10^{-8}$ cm

Cross-section (surface) $\sigma = \pi r^2 \approx 10^{-15}\ cm^2$

Typical speeds $v \approx 0.1\ km\ s^{-1} = 10^4\ cm\ s^{-1}$

Collision rate $\Upsilon\ (cm^3\ s\text{-}1) = \sigma \cdot v = 10^{-11}\ cm^3\ s^{-1}$

H_2 density in dense clouds $n(H_2) \approx 10^5\ cm^{-3}$

Time between collisions $\mathbf{t\ (s) \approx 1 / (\Upsilon\ \mathit{n})} \approx$ 2 weeks !!

Distance between collisions $\mathbf{d = v\ t} \approx$ 100,000 km !!

SLOW chemistry, don't expect many molecules…

But… interstellar clouds contain a very rich molecular content !!

Molecules in Space

Where? Which? How? Do they provide any astrophysical information?

- More than 180 different molecules found in Space (55 outside our Galaxy)
- Ordinary species on Earth: H_2O, NH_3, H_2CO, alcohols (CH_3OH…)
- Exotic molecules: ions (HCO^+…), radicals (C_2H…), chains (HCCCCCN, …)

  (rare on Earth, e.g., very reactive, but very usual in space)

Periodic Table of the Elements

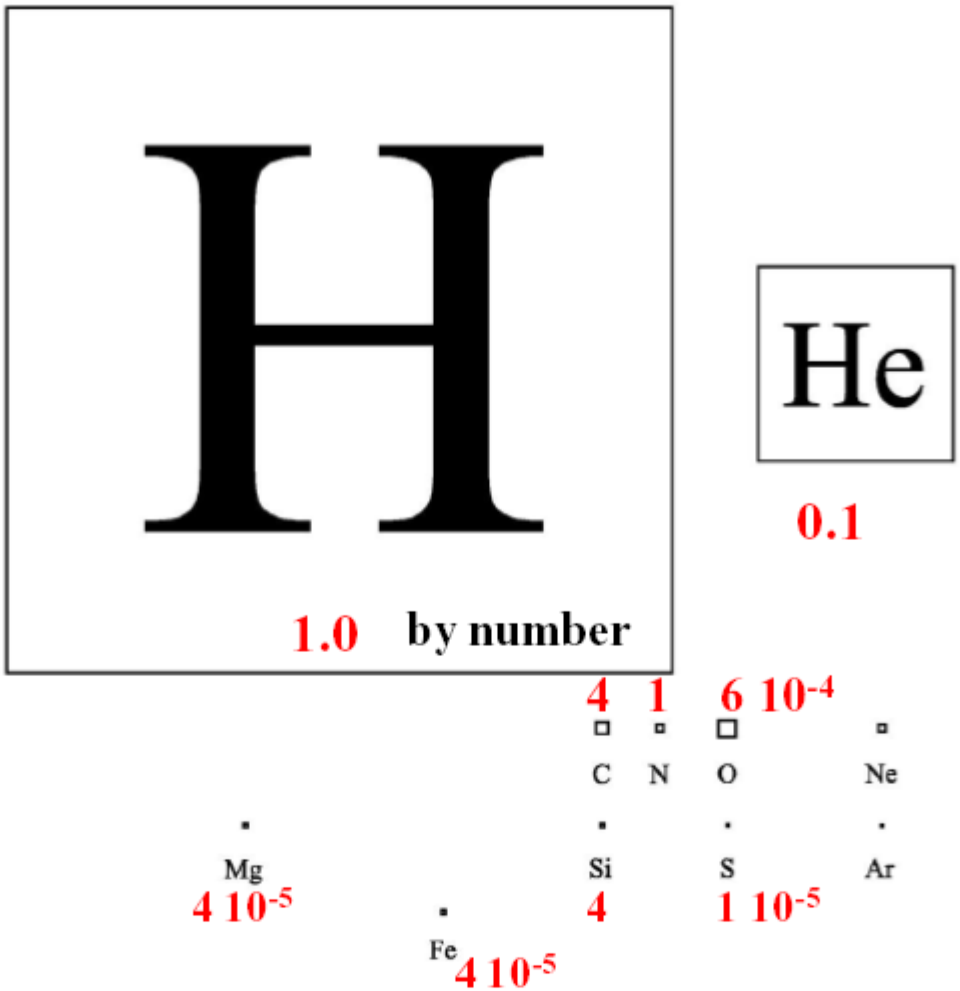
- hydrogen
- alkali metals
- alkali earth metals
- transition metals
- poor metals
- nonmetals
- noble gases
- rare earth metals

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The Astronomers' Periodic Table

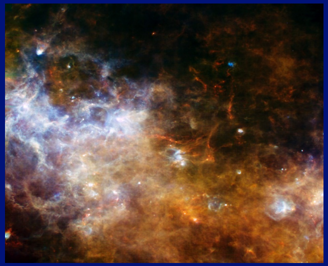
(Elemental abundances in Universe)



- **The number of C, N , O, S ... atoms represents < 0.1% of H atoms.**

B. McCall 2001

(H_2) Molecular clouds Typical Conditions



- Diffuse interstellar clouds (CNM): T_{kin}~100 K n~100 cm^{-3}
- Dense molecular clouds: T_{kin}~10-20 K n~10^3-10^5 cm^{-3}
- Star-forming: PDRs, Hot cores, outflows: T_{kin}~100-1000 K n~10^5-10^8 cm^{-3}

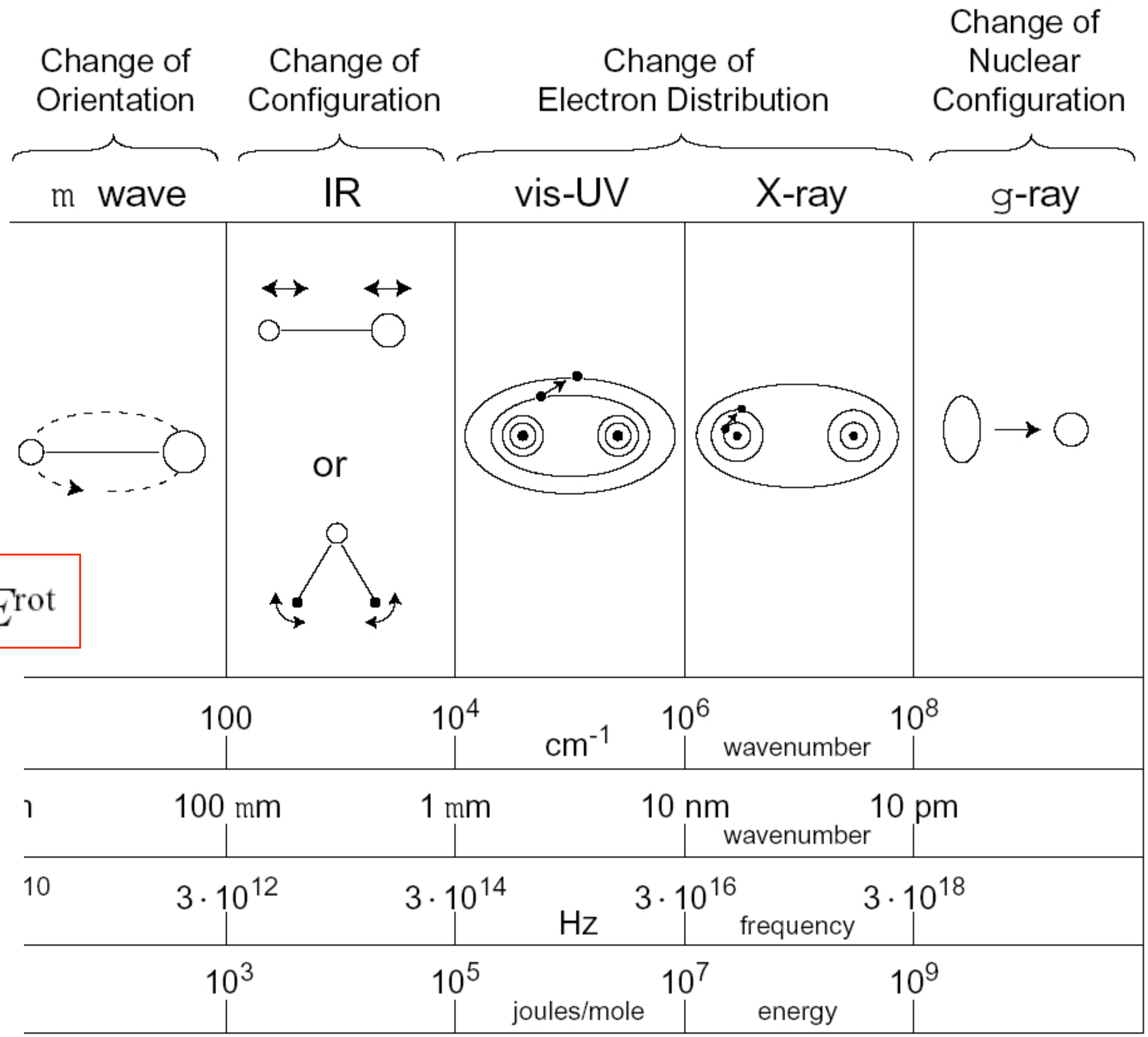
- Compare with this room: T_{kin}~300 K n~10^{19} cm^{-3} (!)
- Best laboratory ultra-vacuum chambers: P = $2.5 \cdot 10^{-11}$ mbar ≈ n~10^5 cm^{-3}

ISM = very low densities, often very low temperatures → conditions very different compared to Earth !!

+ chemistry affected by presence of UV-photons, X-rays, Cosmic Rays, turbulence, magnetic fields...

→ ISM is NEVER in thermochemical equilibrium
(reaction kinetics needed)

Detecting molecules in Space: Spectroscopy



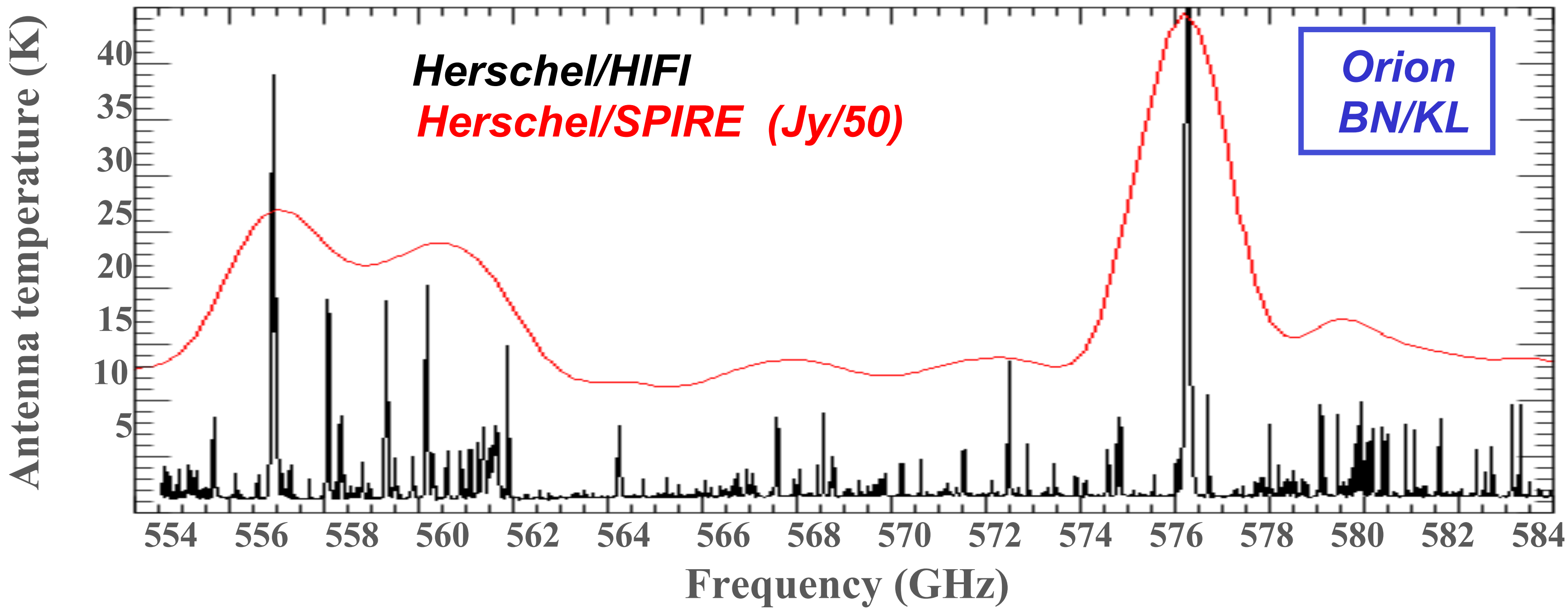
$$E = E^{\mathrm{el}} + E^{\mathrm{vib}} + E^{\mathrm{rot}}$$

Rotation-Vibration-Electronic transtions

High-resolution spectroscopy

- “Unresolved spectroscopy” → line blending in (spectrally) crowed regions
  integrated line intensities conserved but…

- High resolution → line profiles are “resolved” → accurate frequencies, shape, width, etc.

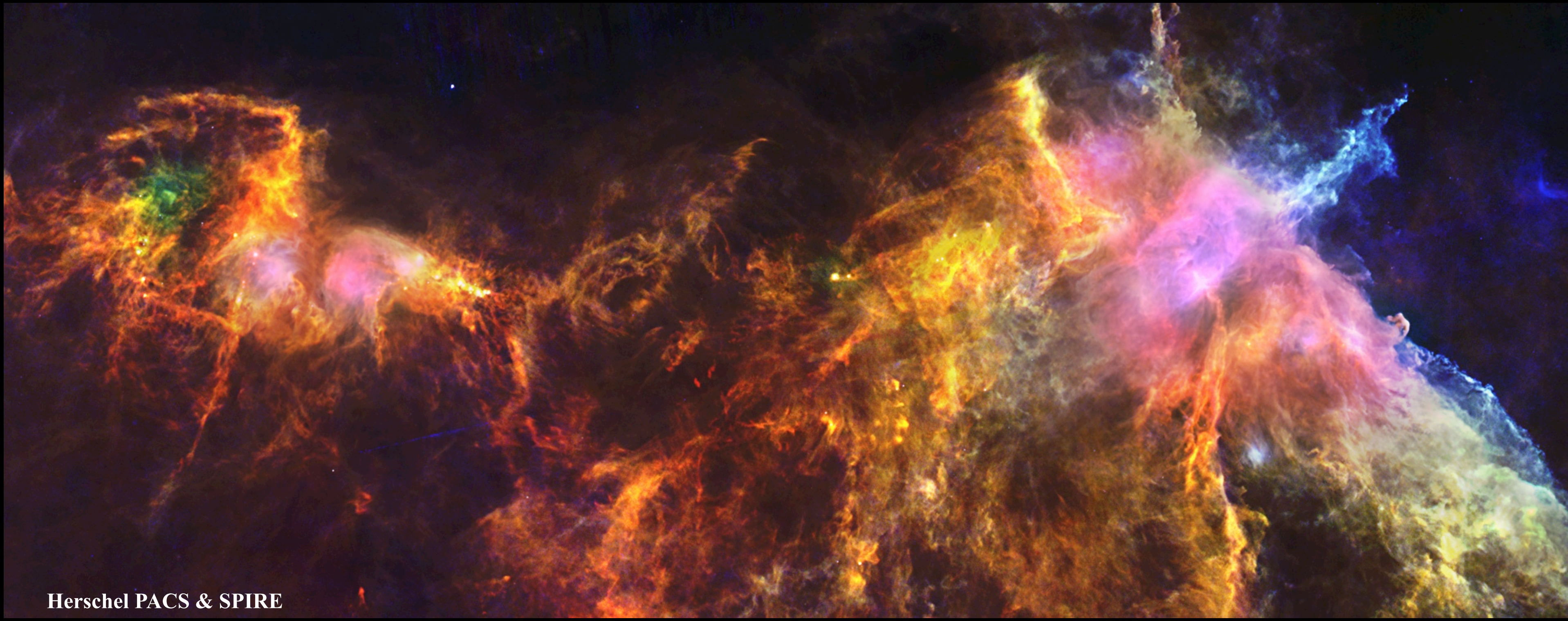


HIFI (heterodyne) and SPIRE (FTS) spectral scans of Orion star-forming region (on board ESA’s *Herschel Space Observatory*)

INTERSTELLAR CLOUDS are COMPLEX

- The structure of molecular clouds is complex with strong gradients (T_k, n_H, UV field, …) between different regions…

.. we don't have exact *laws* to determine $T_k\,(x,y,z,t)$, $n\,(x,y,z,t)$..

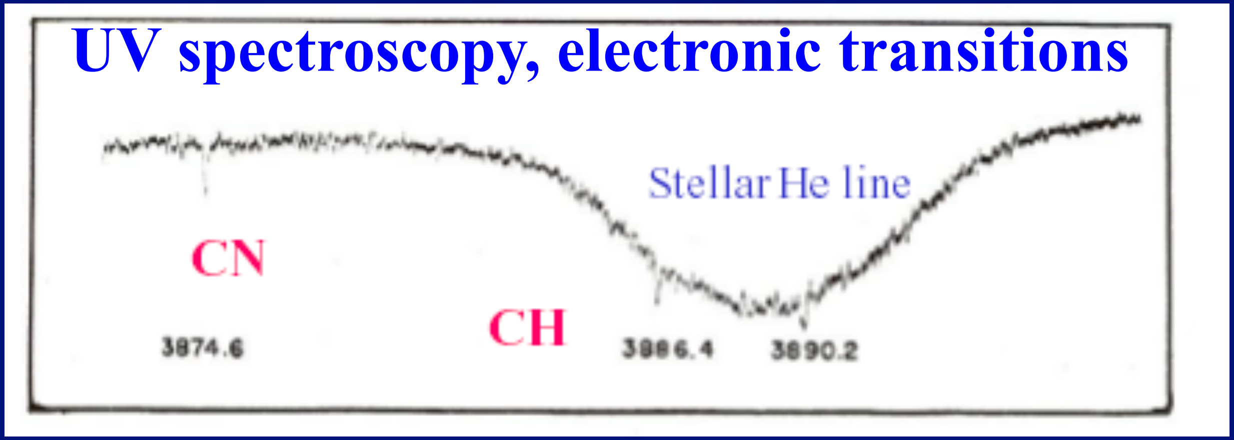


(SHORT) HISTORY OF ASTROCHEMSITRY

* 1926 – A. Eddington

Existence and survival of molecules in the harsh conditions of the ISM is controversial…

* In 1930-1940 <u>three</u> molecules were observed in the line-of-sight towards slightly reddened stars in the <u>VISIBLE</u>: CN, CH and CH^+.



Some history:

- Development of radio astronomy
  - H I 21 cm: Ewen & Purcell 1951; Oort & Muller 1951
  - OH 18 cm: Weinreb et al. 1963
  - NH_3 1 cm: Cheung, Townes et al. 1968
    - First polyatomic molecule!
  - H_2O 1 cm (22 GHz): Cheung et al. 1969
- Development of UV astronomy
  - 1970: H_2
- Development of millimeter astronomy
  - 1970: CO
  - >1970: flood of new molecules

(many with the IRAM-30m telescope!!)

- Development of IR astronomy
  - 1983: ***IRAS***
    - First full-sky survey at 12, 25, 60 and 100 μm
    - Cirrus clouds and dust properties
    - Presence of very small dust particles (10-100 Å), large molecules (PAH
  - 1995 – 98: ***Infrared Space Observatory (ISO)***
    - First complete 2-200 μm spectra
    - Nature and composition of grains (silicates, ices) and PAHs
    - H_2O, OH, [O I] far-IR lines
    - Symmetric molecules: C_6H_6, CH_3, C_2H_4, CO_2,…
    - H_2 lines as probe of shocks and PDRs
  - 2003-2009: ***Spitzer Space Telescope***
    - High sensitivity imaging and mapping; limited spectroscopy
    - Ices and silicates toward low mass protostars and disks
  - 1980's – now: ***Ground*** and ***airborne*** IR instruments

Last years: ***Herschel*** & ***ALMA***

Interesting detections in Space

- H_2 most abundant species, but actually <u>not detected until 70's</u>
- H_3^+, H_2D^+, D_2H^+ key species ion-molecule chemistry
- OH^+, H_2O^+, CH^+ simple hydrides, first steps of ISM chemistry
- C_3, C_4, … HC_3N, HC_5N … linear carbon chains
- C_6H_6 benzene, simplest aromatic unit and C_{60}, C^+_{60} (fullerenes)
- D_2CO, ND_3, CD_3OH doubly and triply deuterated molecules
- NaCl, AlCN, TiO … metal-containing molecules
- $HCOCH_2OH$ glycolaldehyde, simplest sugar
- NH_2CH_2COOH glycine?, simplest aminoacid, but not detected!

N=2		N=3		N=4	N = 5	N = 6	N = 7	N = 8	N = 9	N = 10
H_2	AlCl	CH_2	C_2S	NH_3	CH_4	CH_3OH	CH_3NH_2	$HCOOCH_3$	$(CH_3)_2O$	$(CH_3)_2CO$
CH	PN	H_2S	OCS	H_2CO	SiH_4	CH_3SH	CH_3CCH	CH_3C_2CN	C_2H_5OH	CH_3C_4CN
NH	SiN	NH_2	MgCN	H_2CS	CH_2NH	C_2H_4	CH_3CHO	HC_6H	C_2H_5CN	CH_3CH_2CHO
OH	SiO	H_2O	MgNC	H_2CN	C_5	H_2C_4	c-CH_2OCH_2	C_7H	CH_3C_4H	$(CH_2OH)_2$
O_2(?)	SiS	HNO	NaCN	*l*-C_3H	*l*-C_3H_2	CH_3CN	CH_2CHCN	$HOCH_2CHO$	C_8H	
HF	PO	C_2H	SO_2	c-C_3H	c-C_3H_2	CH_3NC	HC_4CN	CH_3COOH	HC_6CN	
C_2	SH	HCN	N_2O	HCCH	H_2CCN	NH_2CHO	C_6H	H_2CCHCN	CH_3CONH_2	N = 11
CN	AlF	HNC	SiCN	HNCO	H_2NCN	H_2CCHO	H_2CCHOH	H_2C_6	CH_2CHCH_3	HC_8CN
CO	FeO	HCO	SiNC	HNCS	CH_2CO	C_5H		CH_2CHCHO		CH_3C_6H
CS	SiC	c-SiC_2		HCCN	HCOOH	C_5N		C_2H_6		
CP		MgCN		C_2CN	C_4H	HC_4N				
NO		MgNC		C_3O	HC_2CN	C_5S(?)				N = 12
NS		AlNC		C_3S	HC_2NC	HC_4H				C_6H_6
SO		HCP	H_3^+	c-SiC_3	C_4Si	CH_2CNH				
HCl	CH^+	C_3	HCO^+	C_3N^-	HNCCC	HC_2CHO				
NaCl	CO^+	C_2O	HOC^+	H_3O^+		c-C_3H_2O				N = 13
KCl	SO^+	CO_2	N_2H^+	$HCNH^+$	H_2COH^+					$HC_{10}CN$
N_2(?)	CF^+		HCS^+	$HOCO^+$	C_4H^-	HC_3NH^+	C_6H^-		C_8H^-	

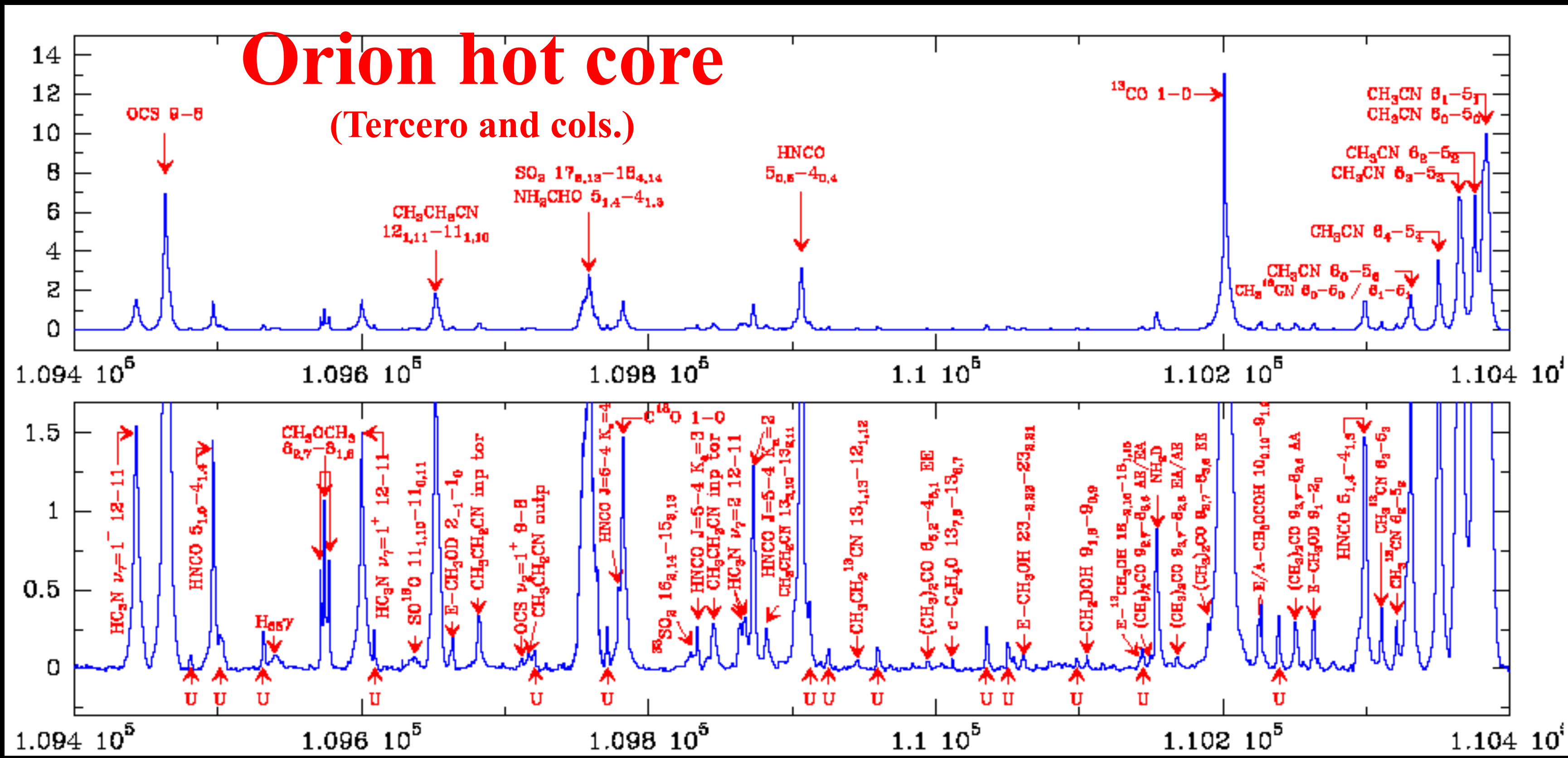
- List not complete
- Some identifications challenged
- About 3 new species/yr for last 30 years!

E. Herbst.

Interesting competition…

(e.g. http://www.astrochymist.org)

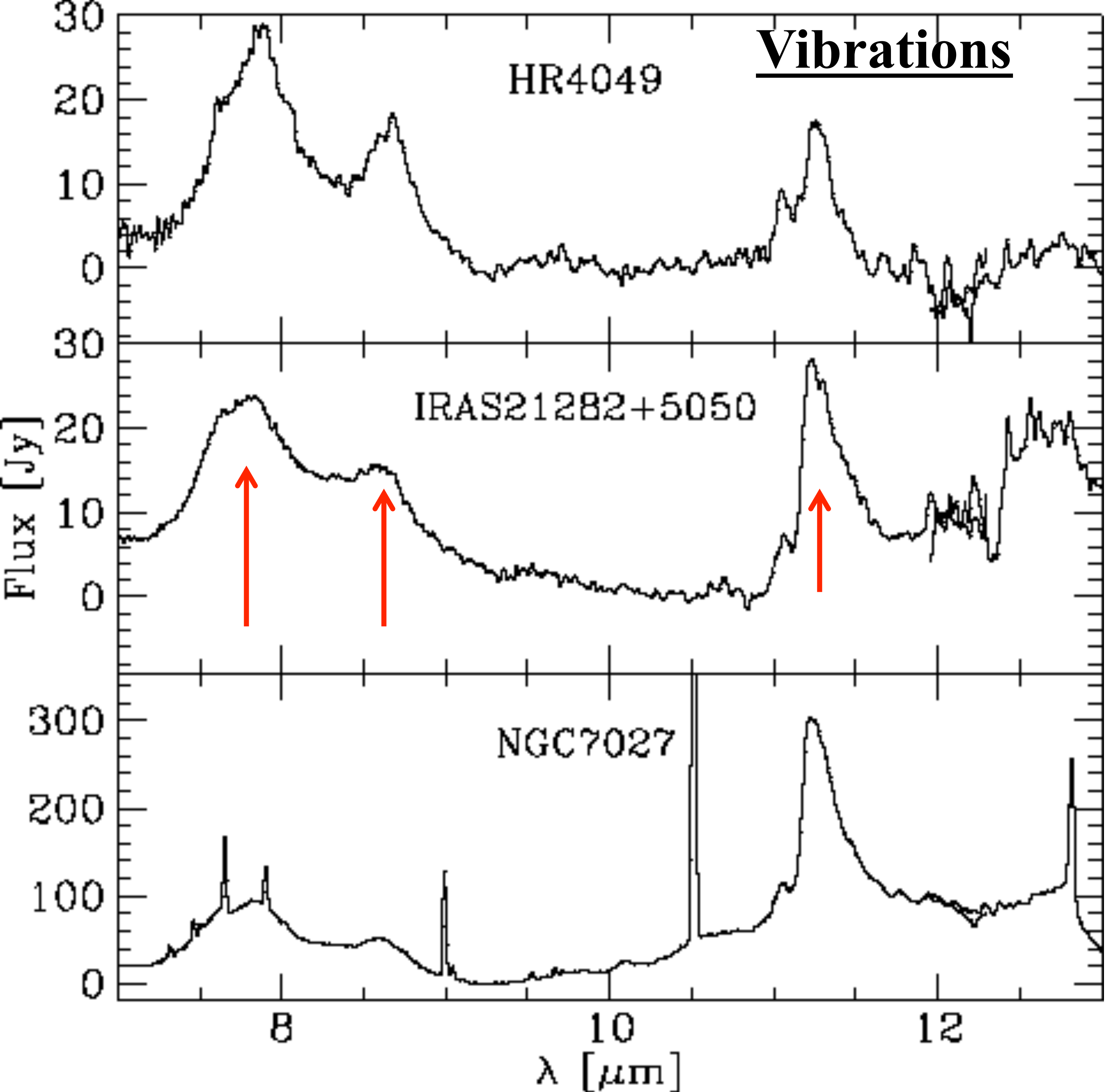
Chemical complexity (high-mass protostars)



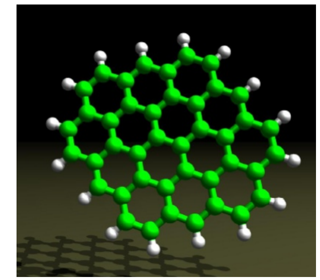
MHz

Rotational spectroscopy in the mm and submm domain

Vibrations



Unidentified infrared bands due to PAHs



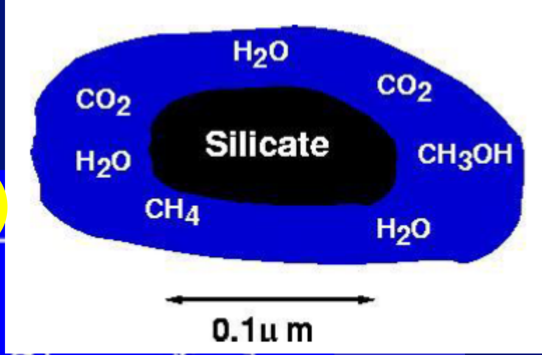
Seen everywhere where UV photons are present

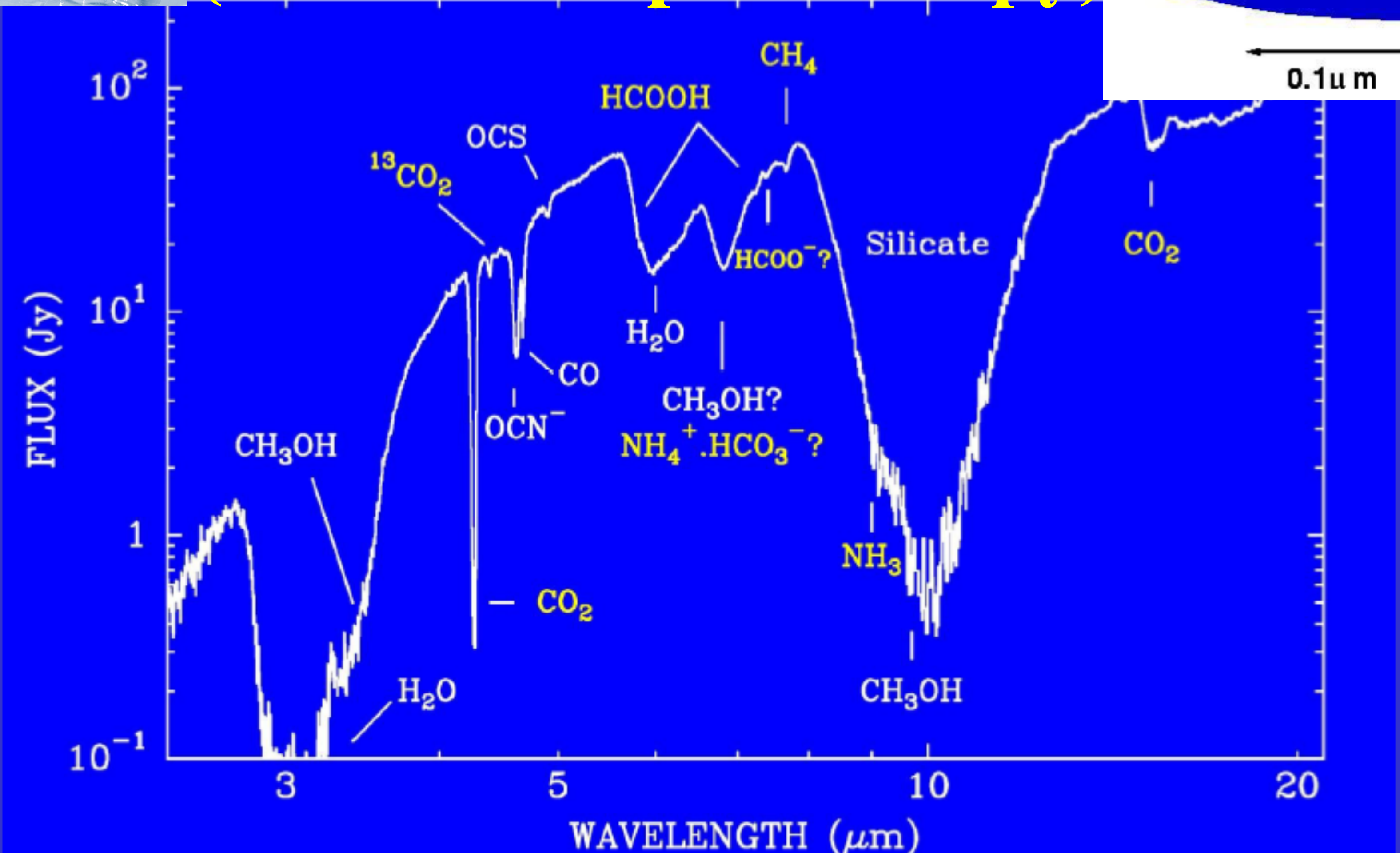
(star formation tracers!)

Puget, Leger…

Allamandola, Tielens…

Ice grain mantles
(solid-state spectroscopy)





- **Grain surface chemistry:** **formation of complex molecules**

  e.g. $CO \rightarrow HCO \rightarrow H_2CO \rightarrow CH_3O \rightarrow CH_3OH$

Gibb et al. 2000

Where do we see these molecules?

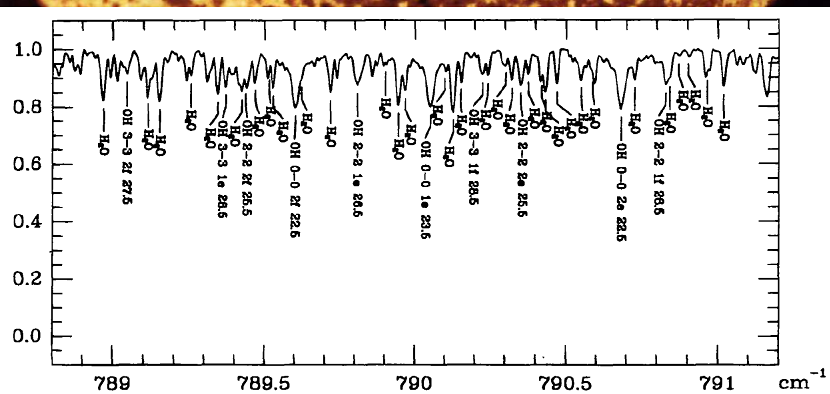
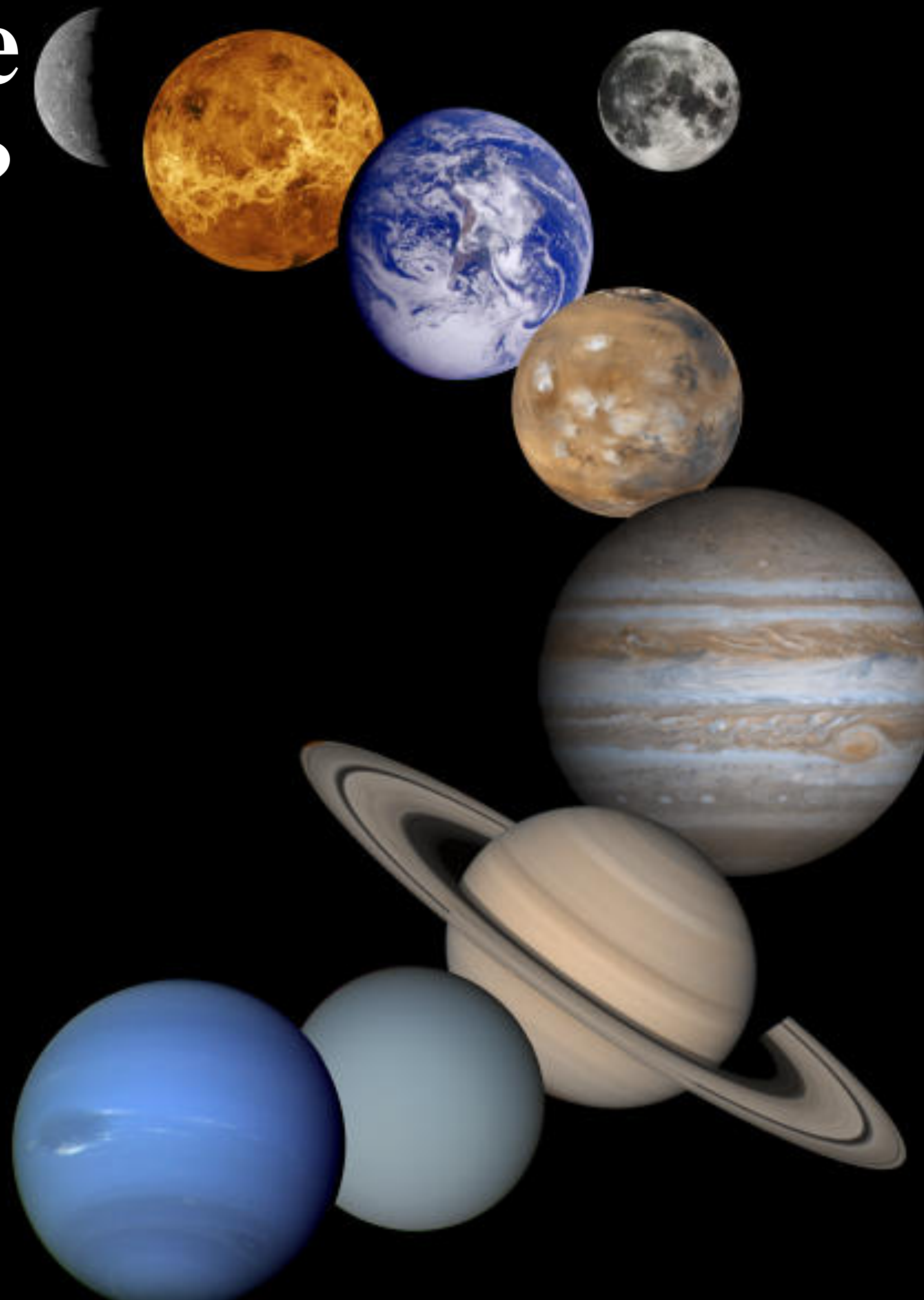
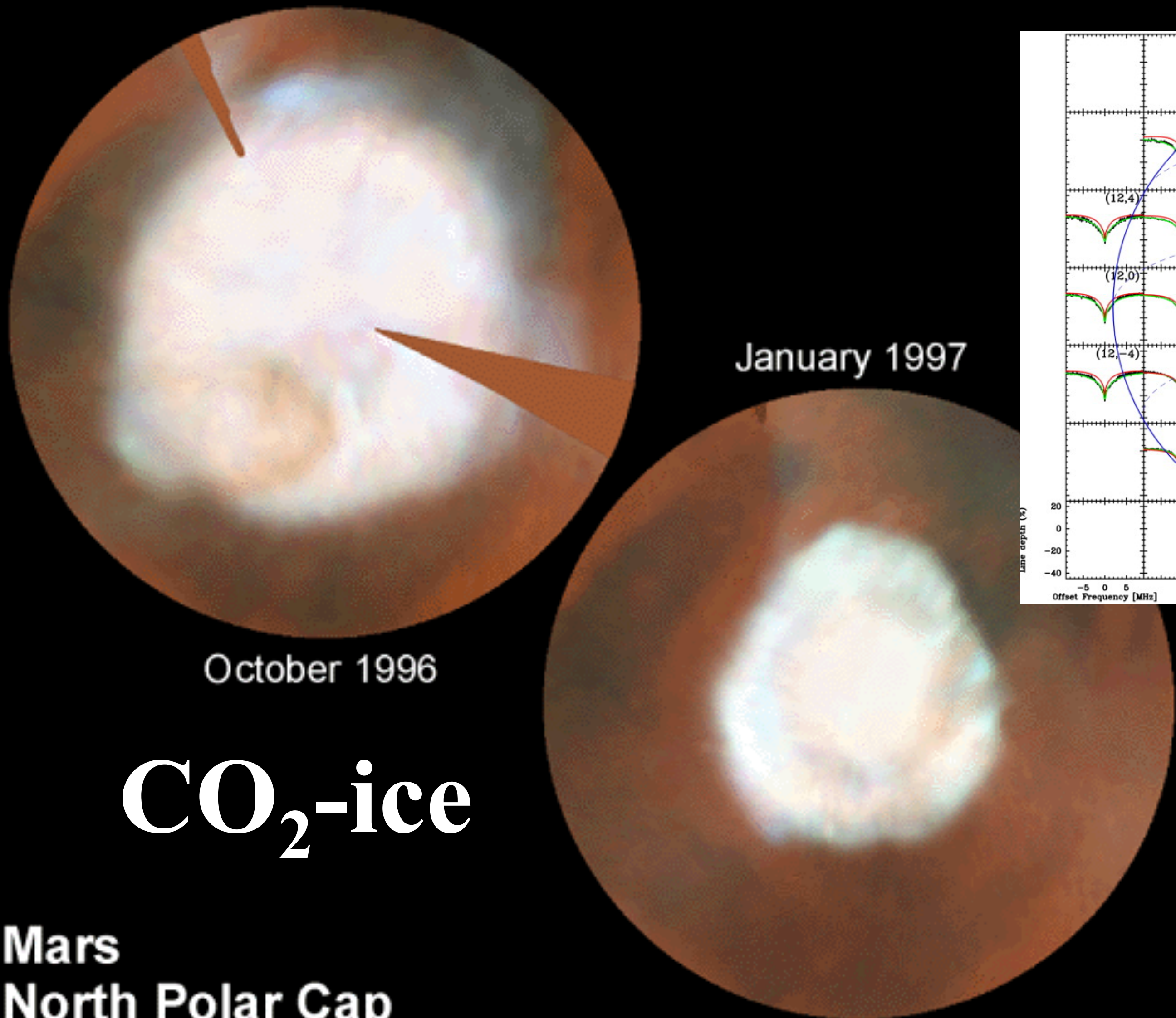
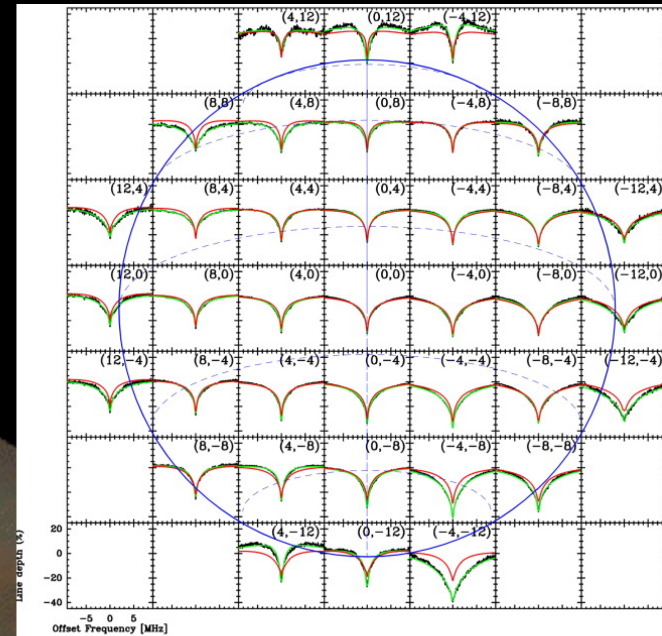


FIG. 3.—A section of the umbral spectrum from 12.636 to 12.674 μm from atlas 4. The unidentified lines in this region are probably H_2O. The telluric lines were divided out with a penumbral reference spectrum similar to a photospheric spectrum.







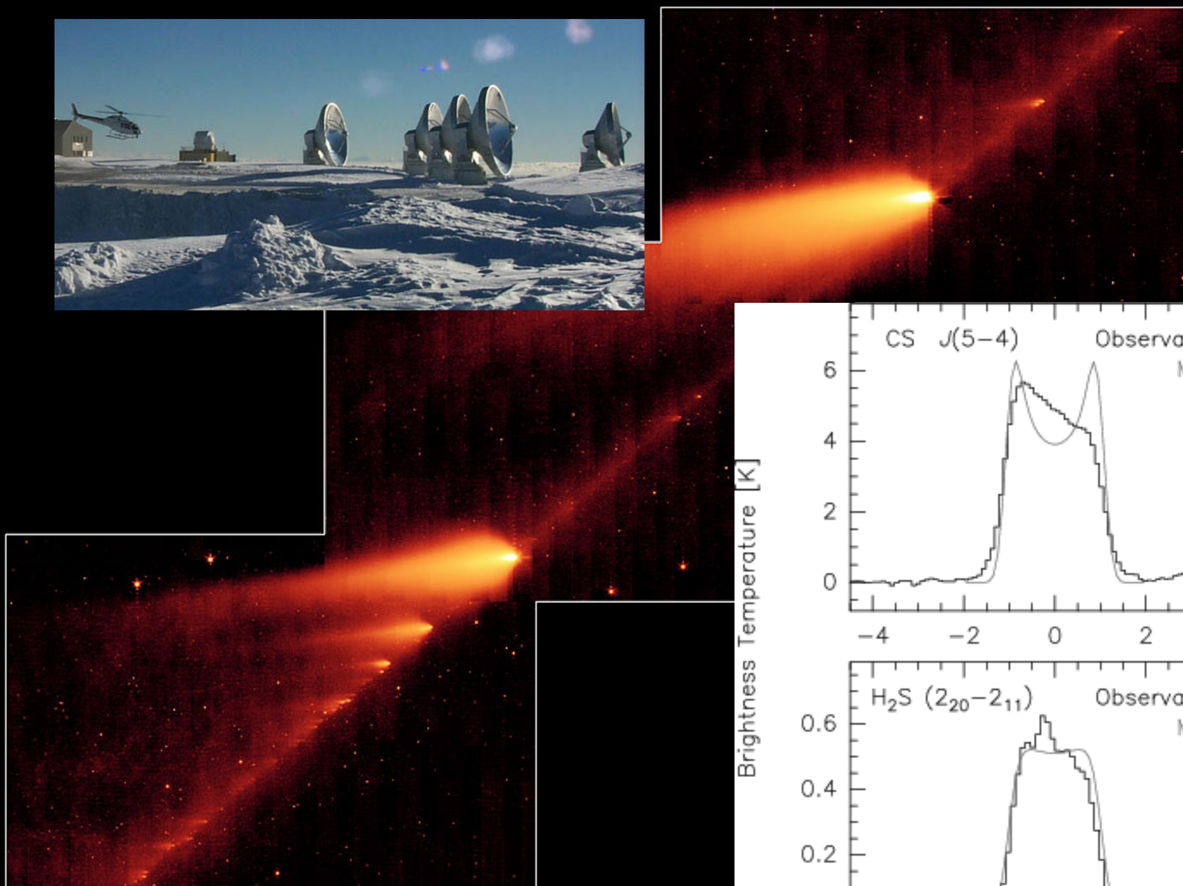
CO_2-ice

CO gas

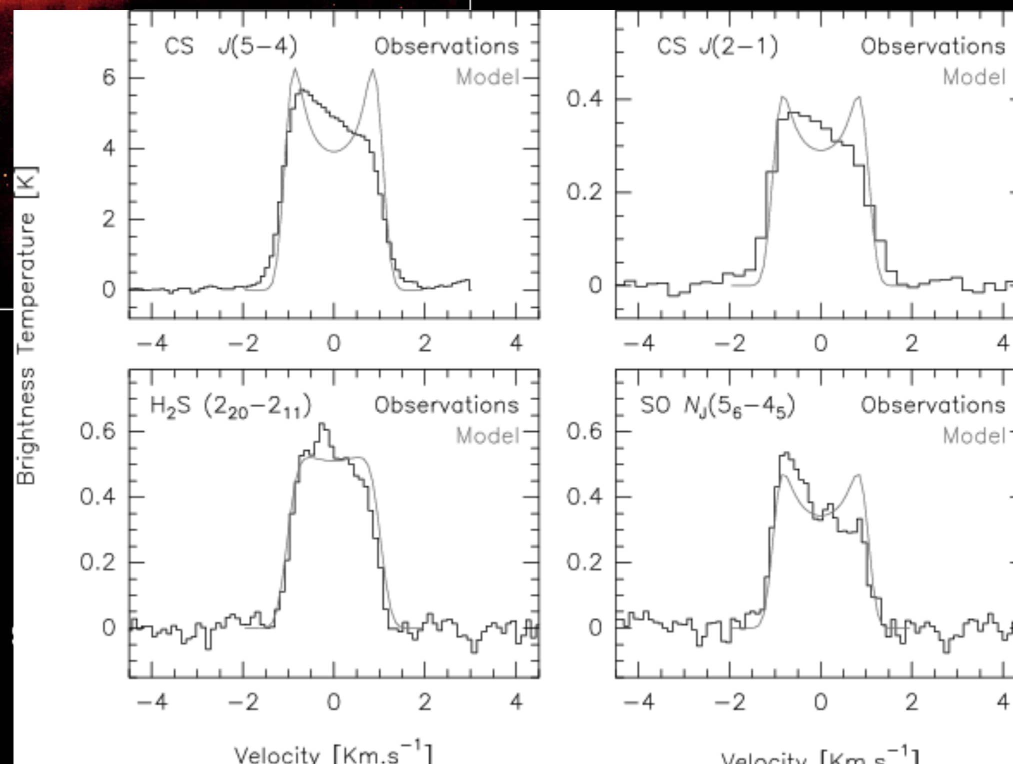
Mars
North Polar Cap

PRC97-15b • ST ScI OPO • May 20, 1997
P. James (Univ. Toledo), T. Clancy (Space Science Inst.), S. Lee (Univ

In Comets ...

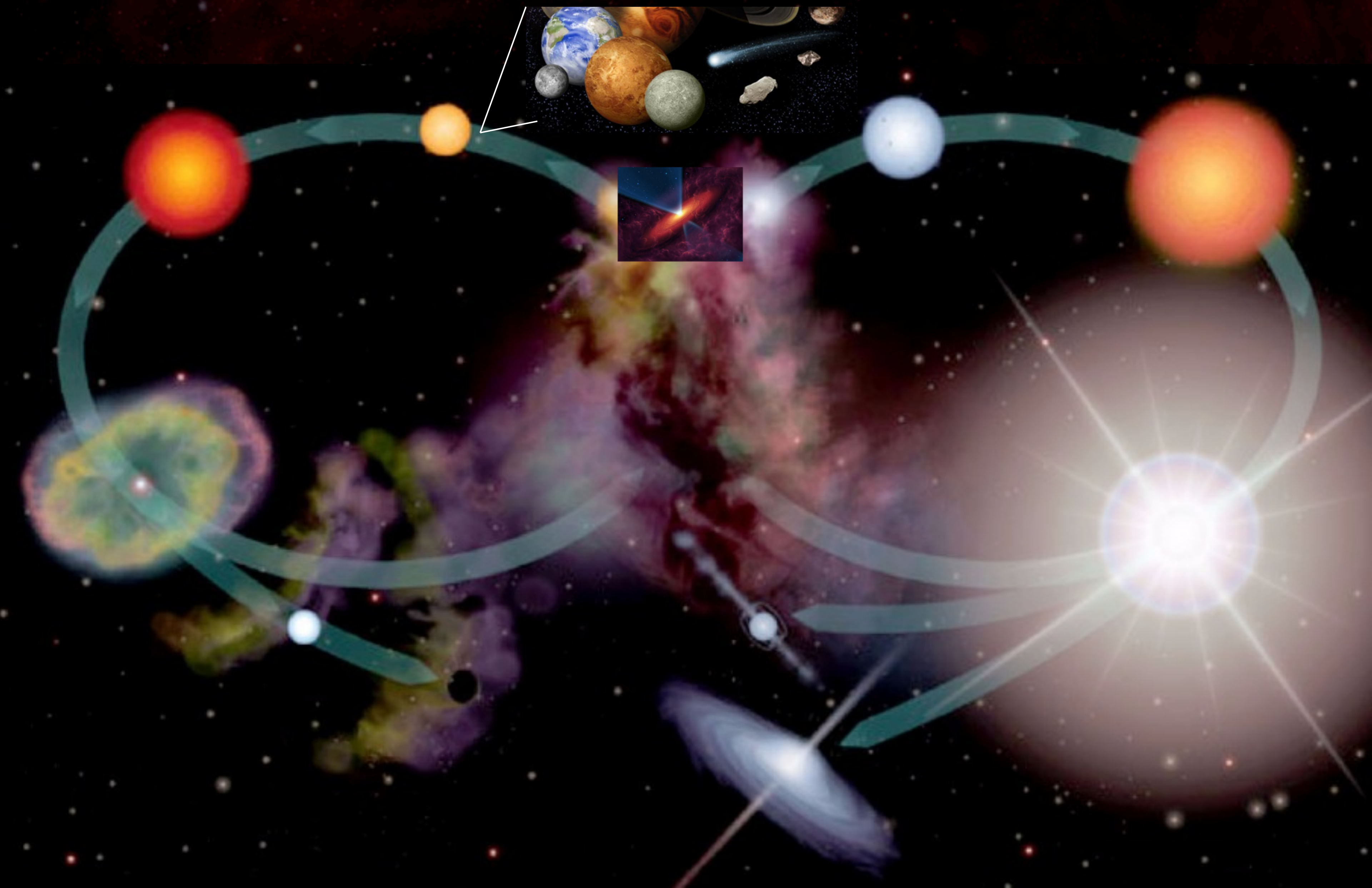


Comet 73P/Schwassmann-Wachmann 3
NASA / JPL-Caltech / W. Reach (SSC/Caltech)



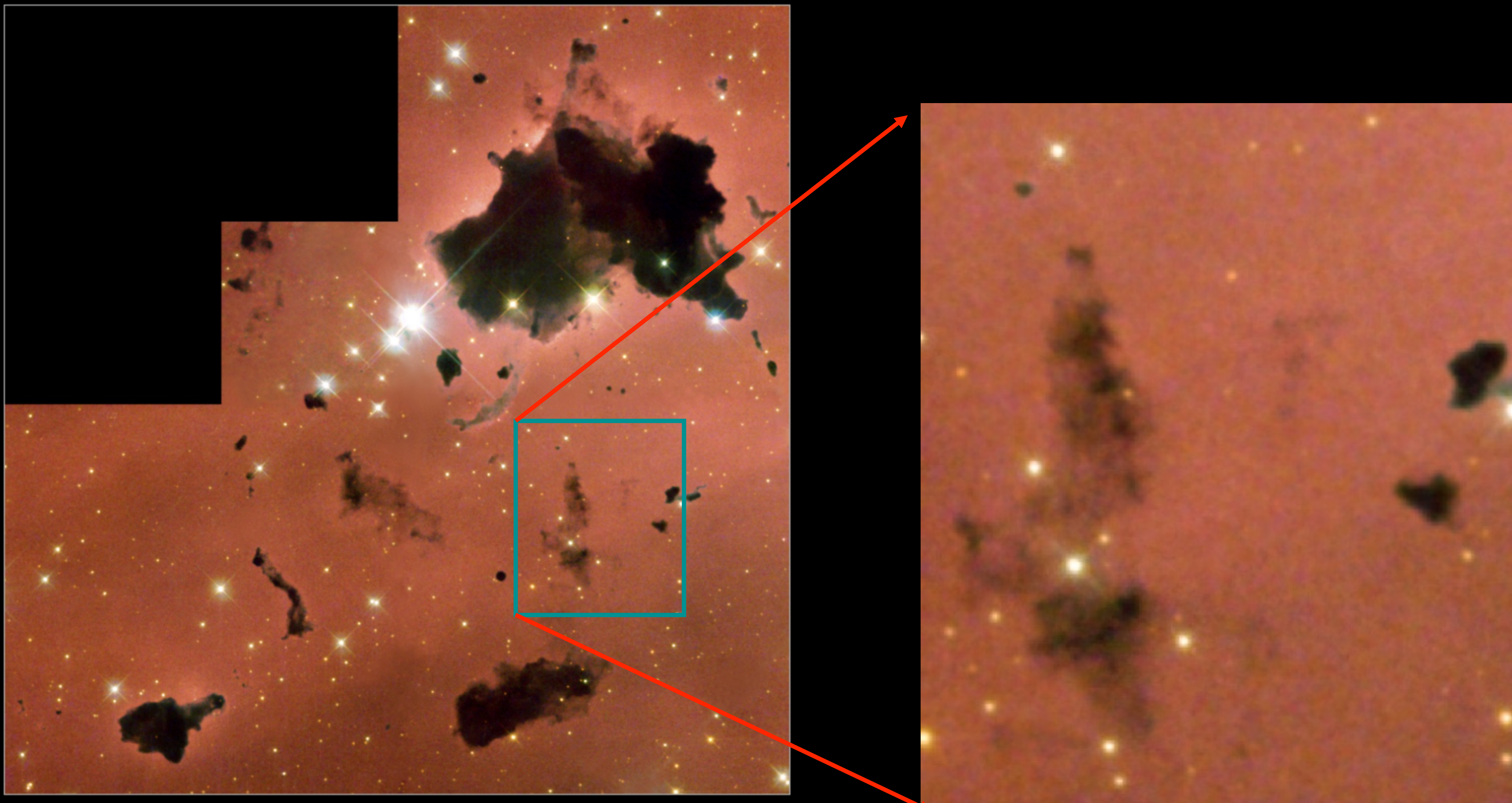
Boissier et al. 2007, *A&A* (comet C/1995 O1 “Hale-Bopp”)

The interstellar life-cycle of gas and dust



Diffuse & translucent clouds…

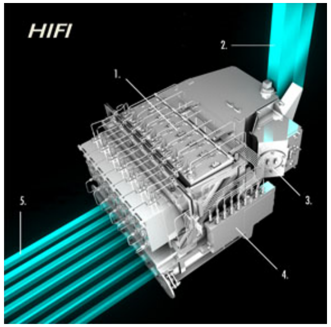
Thackeray's Globules in IC 2944



Hubble Heritage

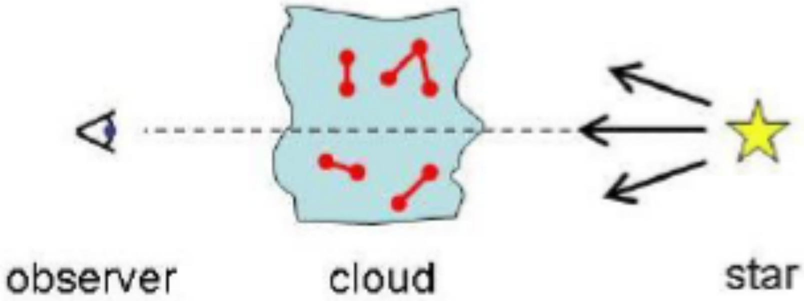
NASA and The Hubble Heritage Team (STScI/AURA) • Hubble Space Telescope WFPC2 • STScI-PRC02-01

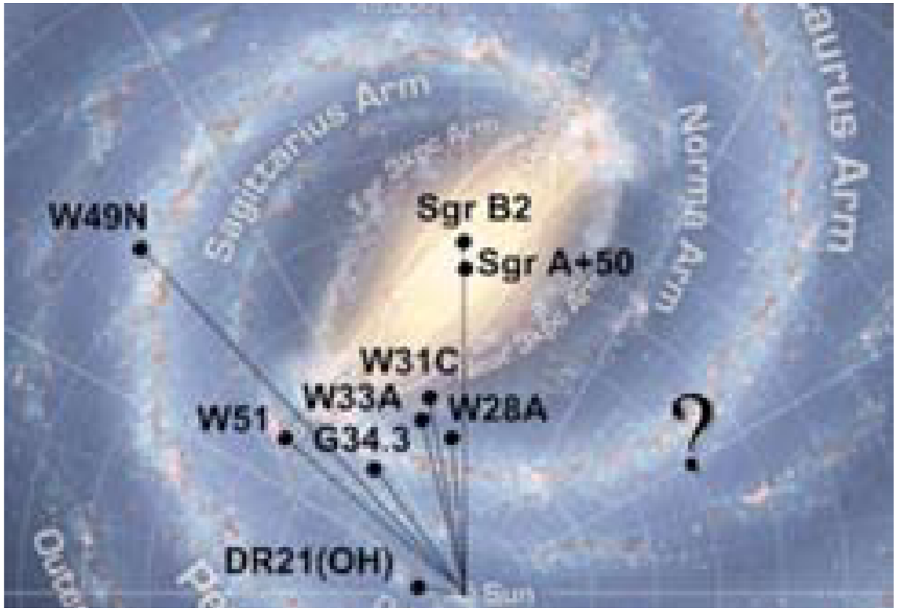
Simple molecules in diffuse ISM

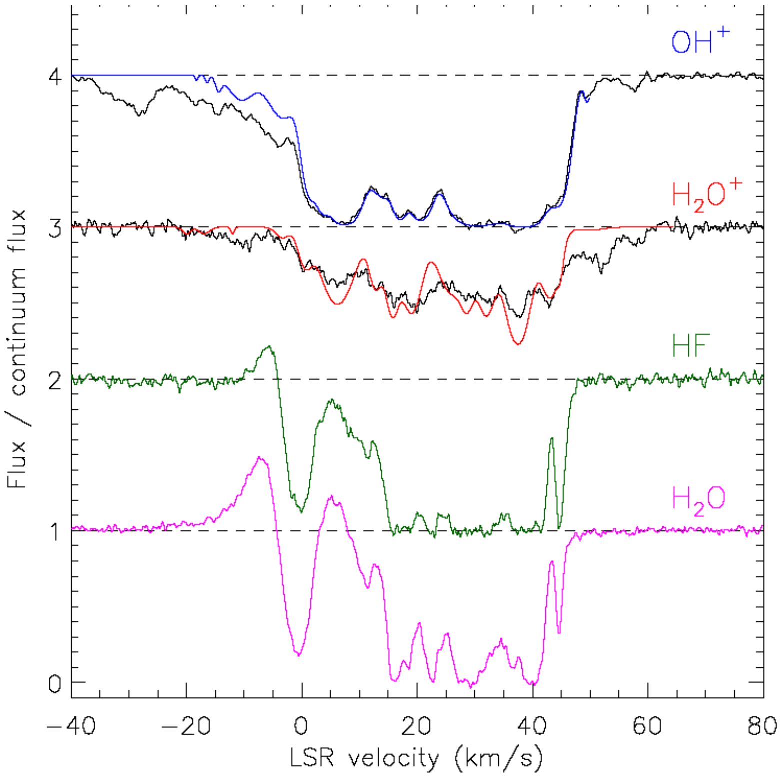


High-resolution (heterodyne) rotational spectroscopy (< 1 km/s resolution)

Far-IR and submm domain: *J*=1-0 transition of light molecules

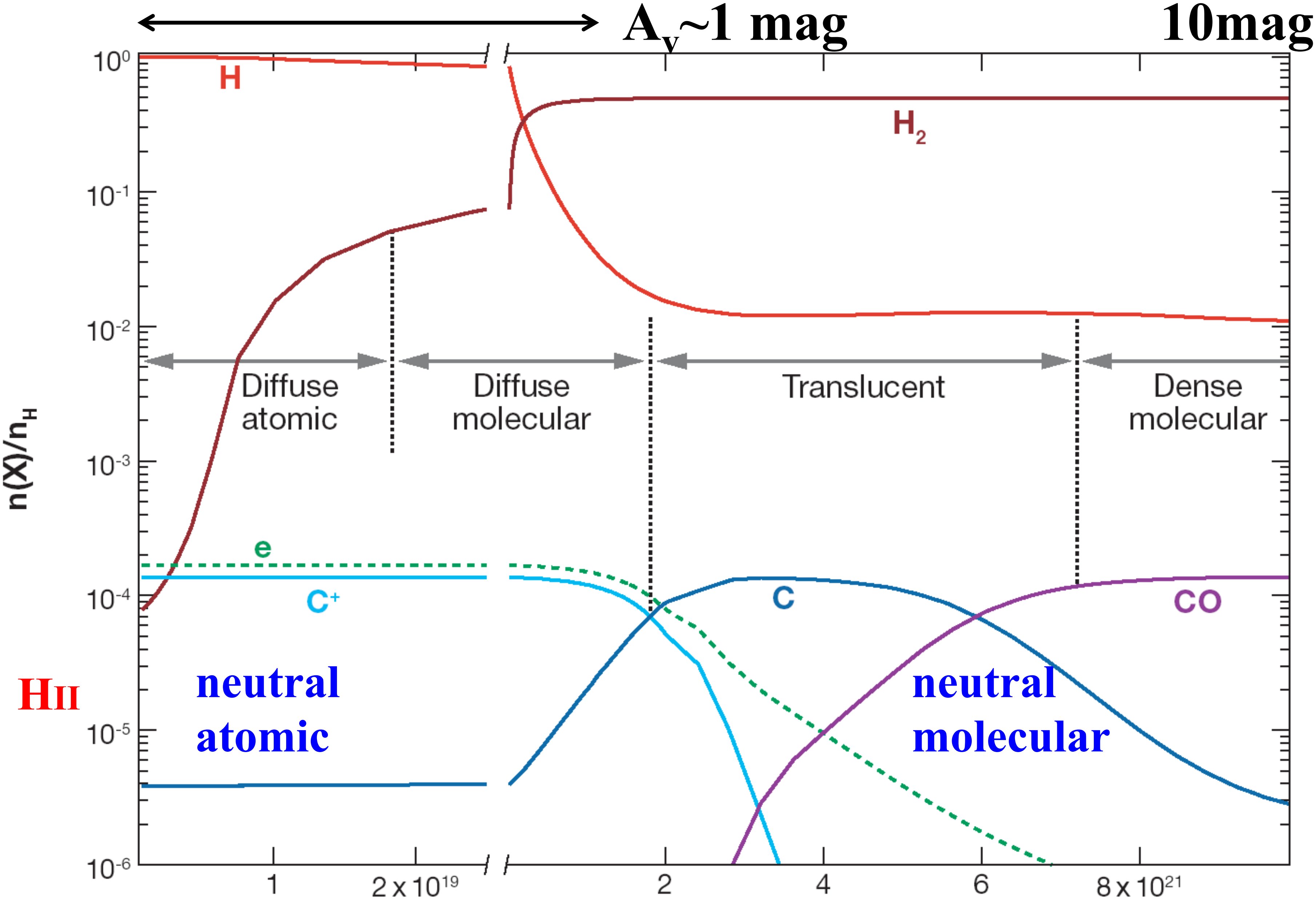






Doppler shift: $f = \left(1 - \frac{v_{\mathrm{s,r}}}{c}\right) f_0$

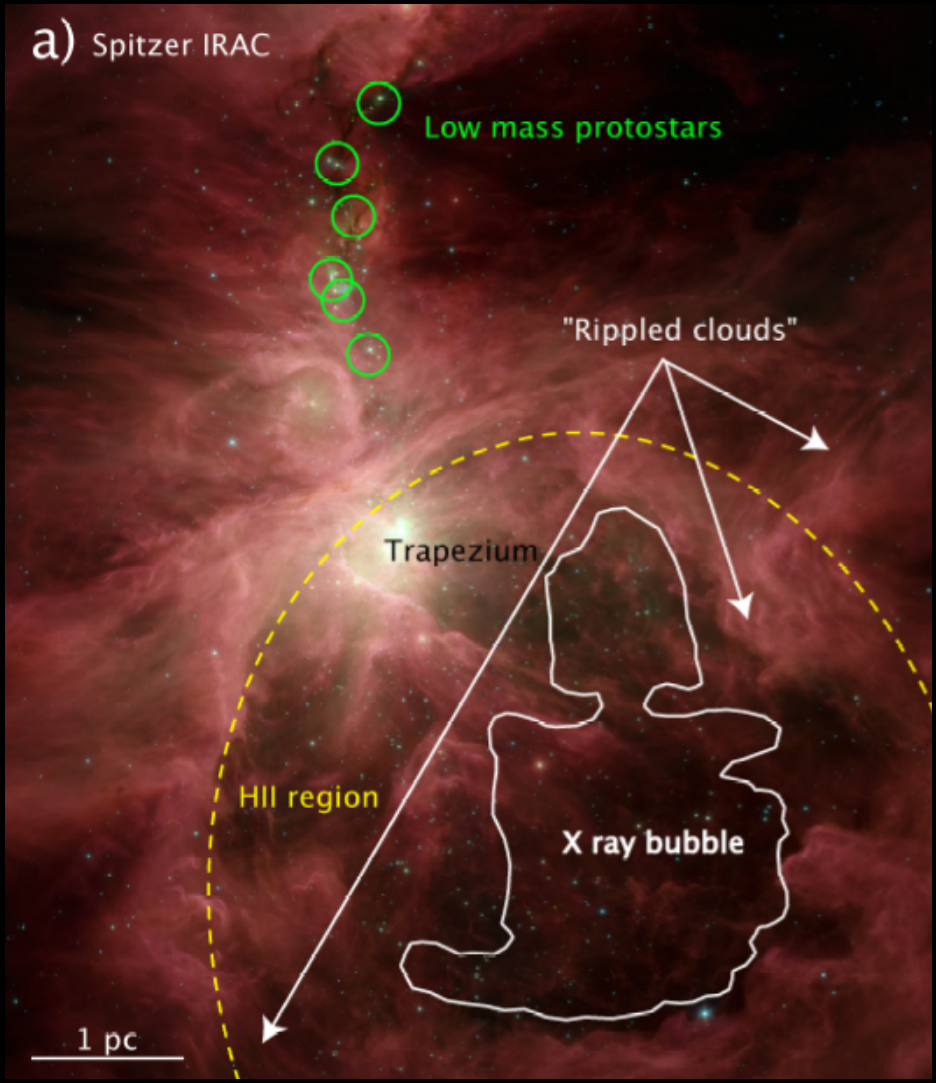
(**Gerin** et al. 2010, **Neufeld** et al., 2010… PRISMAS *Herschel*-KP)



N_H (cm^{-2}) $\approx 10^{21} A_v = n_H$ (cm^{-3}) x lenght (cm)

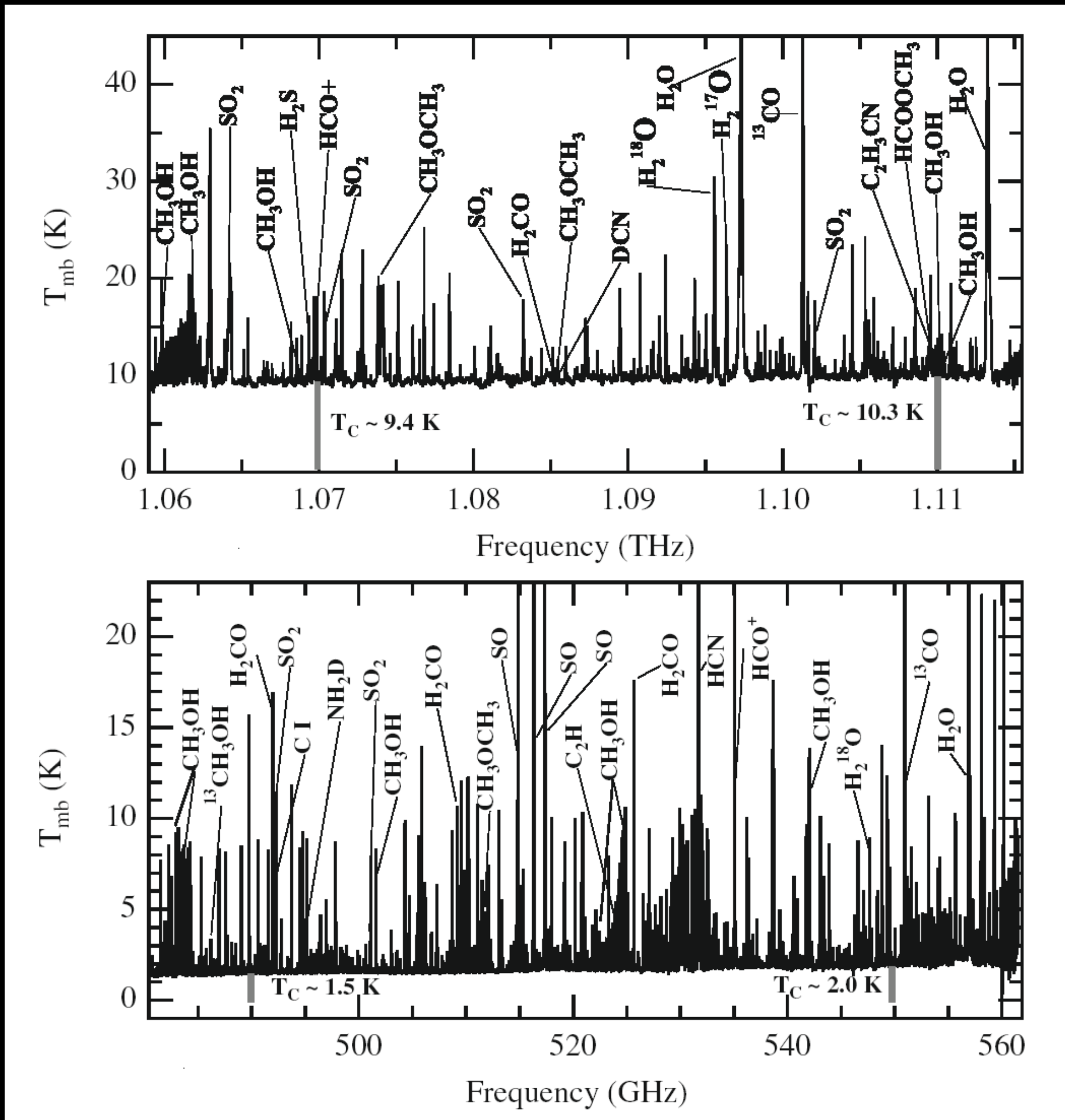
E> 13.6 eV photons ionize H   Only E< 13.6 eV photons penetrate

“Imaging” high-mass star-forming regions



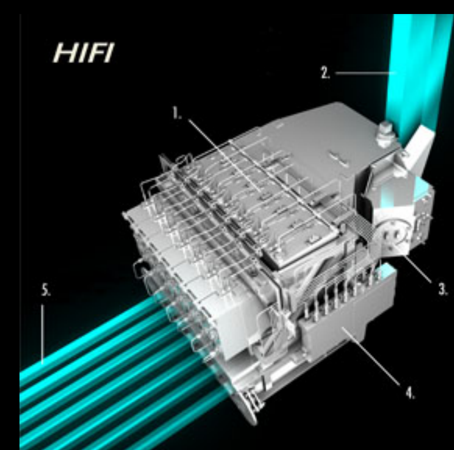
Example: Orion A (M42)

Chemical complexity in SFRs (submm band)



Orion KL/BN

(Bergin et al. 2010, A&A)



THE ASTROPHYSICAL JOURNAL, 652: L141–L144, 2006 December 1

Detection of anion molecules !

LABORATORY AND ASTRONOMICAL IDENTIFICATION OF THE NEGATIVE MOLECULAR ION C_6H^-

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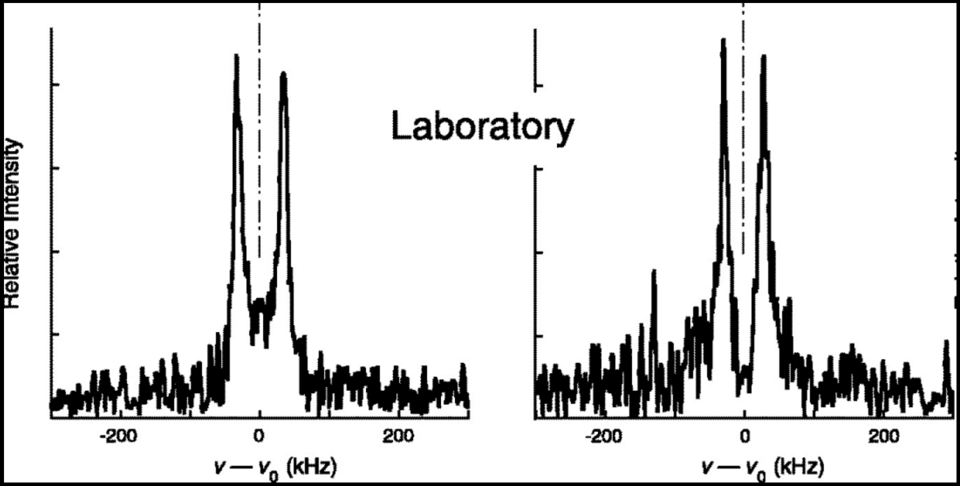
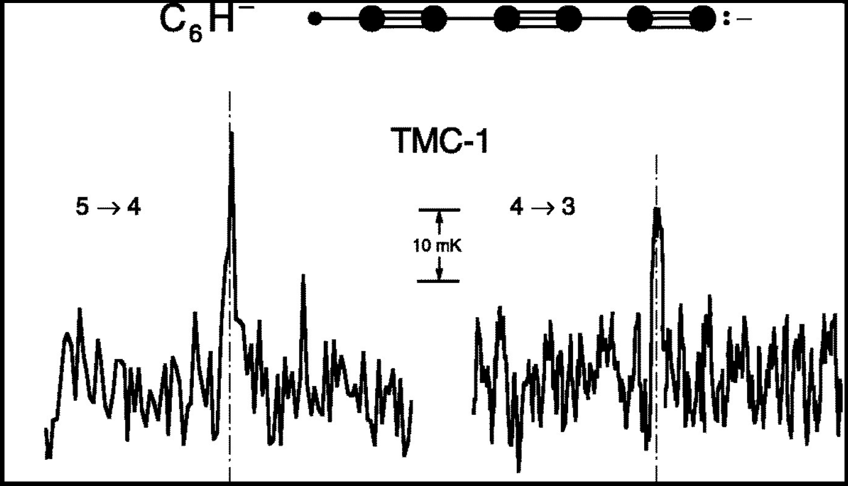
Received 2006 September 28; accepted 2006 October 17; published 2006 November 20

ABSTRACT

The negative molecular ion C_6H^- has been detected in the radio band in the laboratory and has been identified in the molecular envelope of IRC +10216 and in the dense molecular cloud TMC-1. The spectroscopic constants derived from laboratory measurements of 17 rotational lines between 8 and 187 GHz are identical to those derived from the astronomical data, establishing unambiguously that C_6H^- is the carrier of the series of lines with rotational constant 1377 MHz first observed by K. Kawaguchi et al. in IRC +10216. The column density of C_6H^- toward both sources is 1%–5% that of neutral C_6H. These surprisingly high abundances for a negative ion imply that if other molecular anions are similarly abundant with respect to their neutral counterparts, they may be detectable both in the laboratory at high resolution and in interstellar molecular clouds.

Subject headings: ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM





Importance of molecules:

- Exotic chemistry and unique laboratory
- Chemical abundances evolve with *t*

astrochemistry

- Molecules as physical diagnostics (T_{kin}, n, v, B, ζ_{CR}, age, …)
- Gas thermodynamics: gas coolants

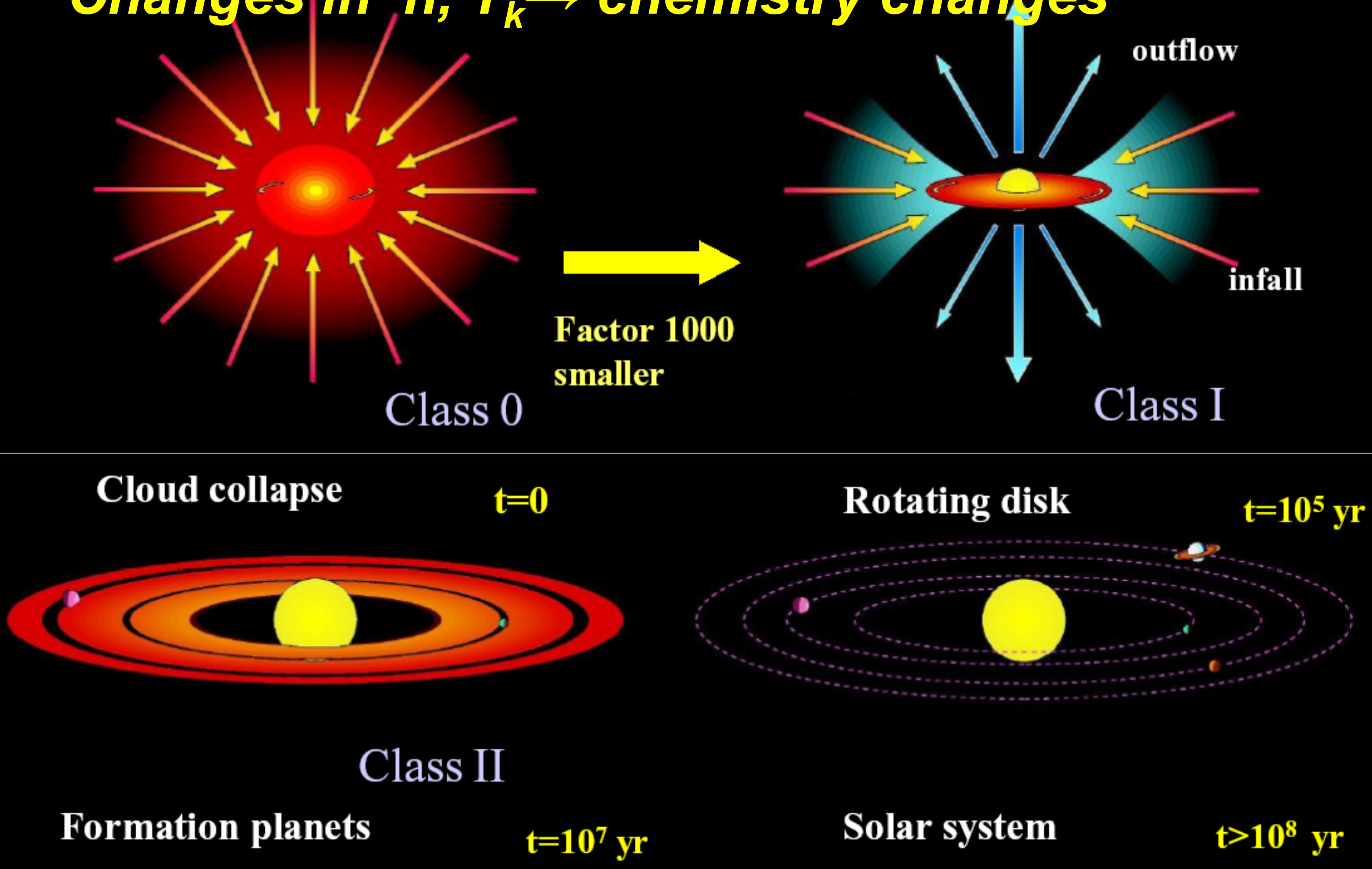
astrophysics

$$CO\,(J=0) \xrightarrow{\text{Collisions}} CO(J=1) \xrightarrow{\text{Radiation}} CO(J=0)$$

Radiation escapes from cloud → net energy lost → gas is cooled
(example: critical to allow gravitational collapse and star formation)

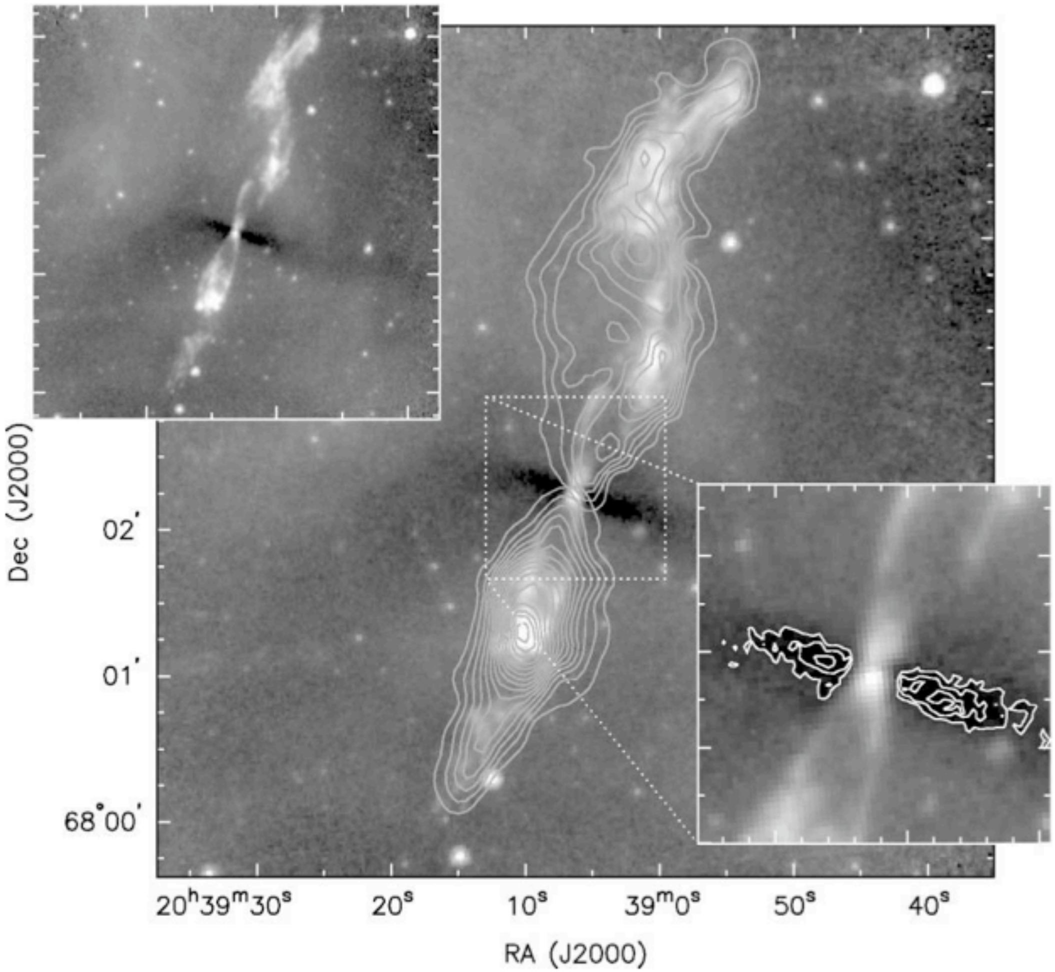
Molecules in Star-forming environments

Changes in n, $T_k \rightarrow$ chemistry changes



Hogerheijde 1998, after Shu et al. 1987

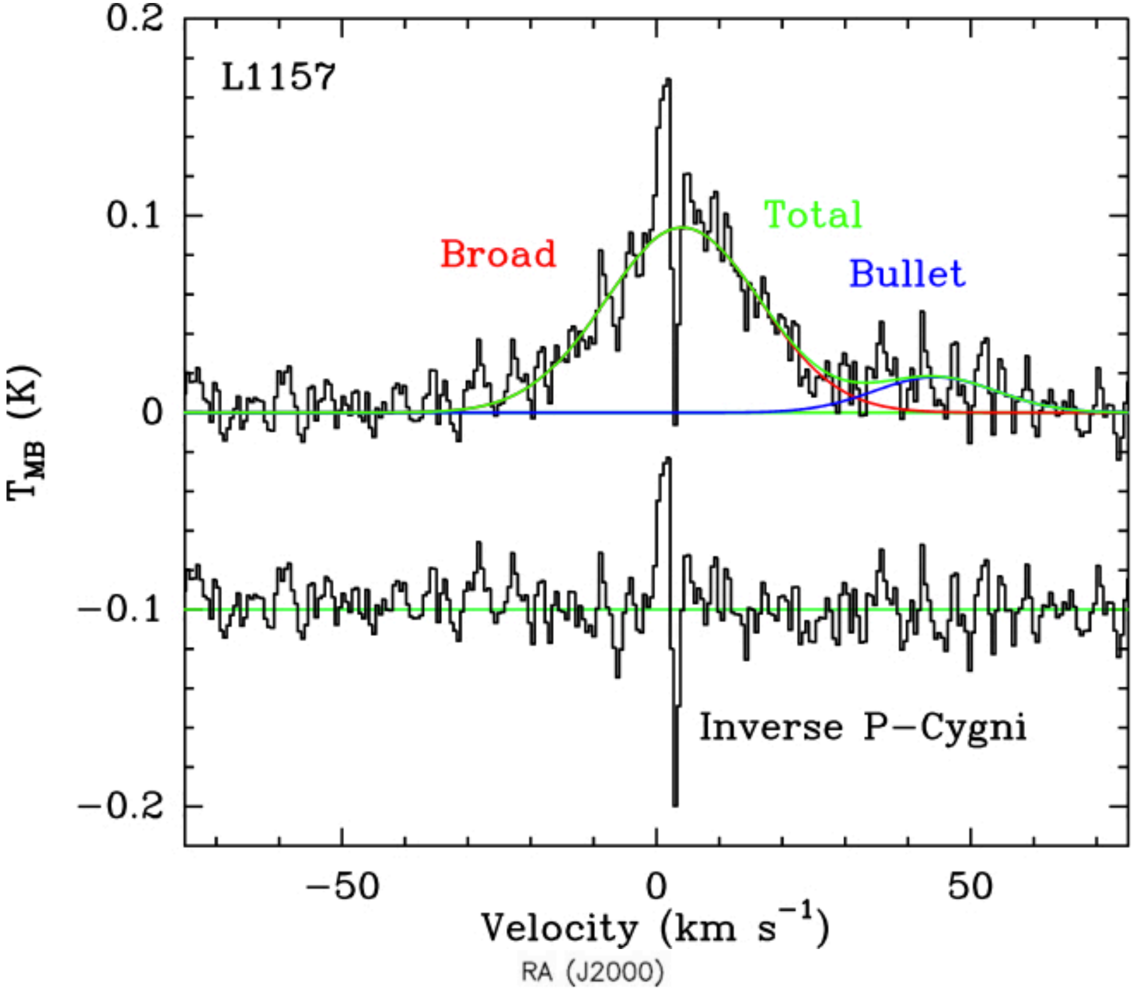
Low-mass stars formation: protostars & outflows



Looney, Tobin & Kwon 2007

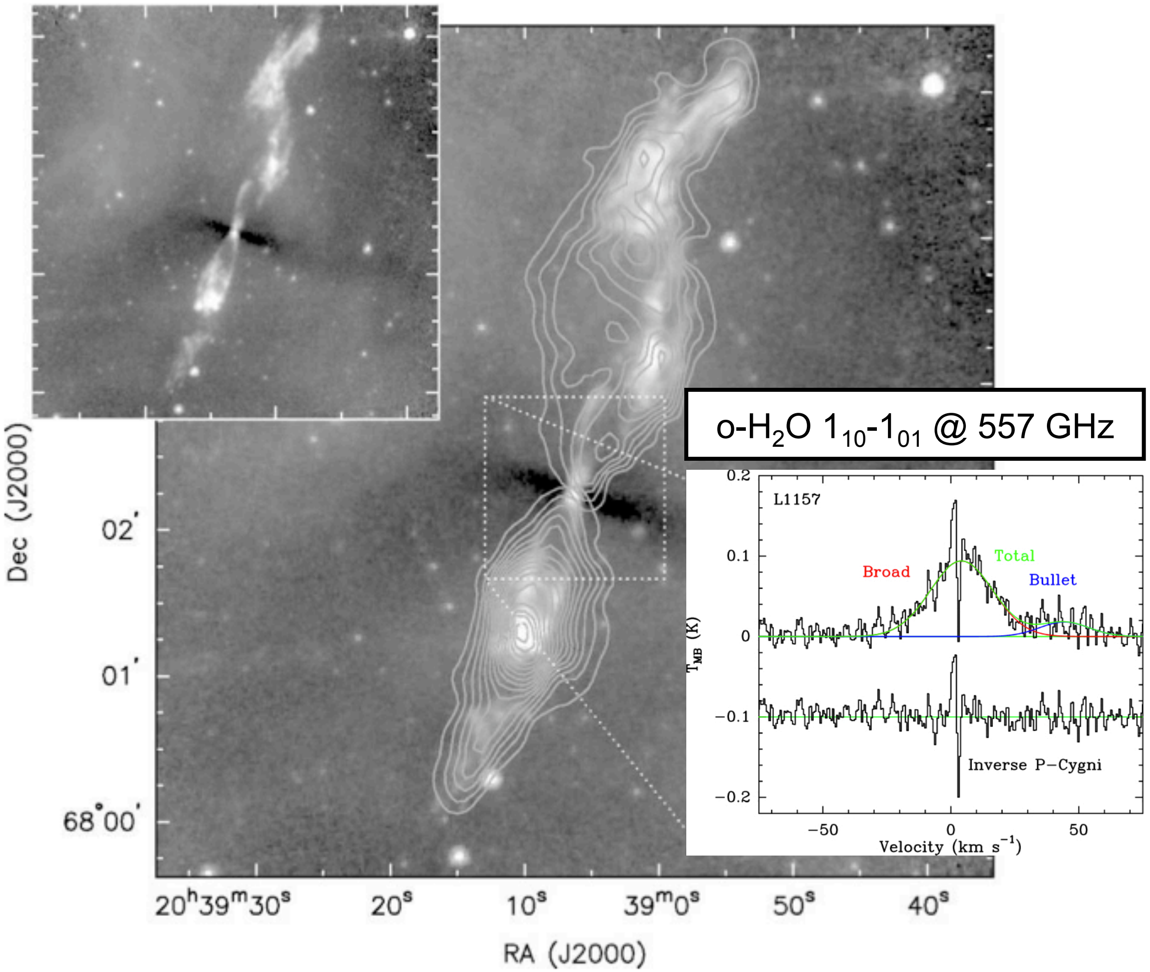
Low-mass stars formation: protostars & outflows

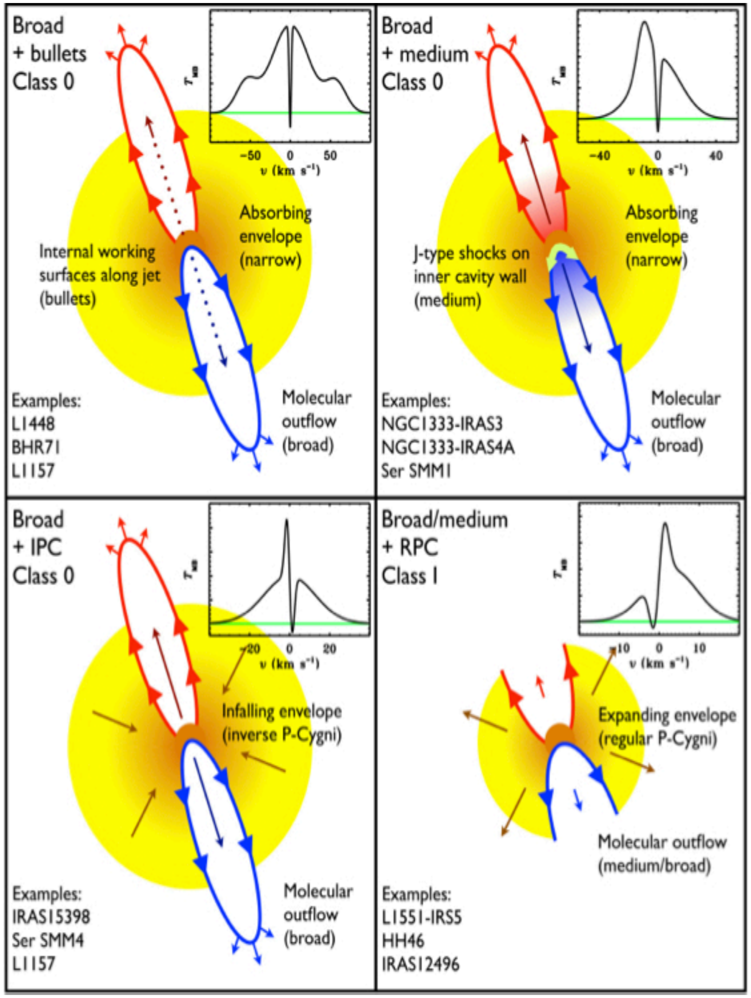
o-H_2O 1_{10}-1_{01} @ 557 GHz



Kristensen et al. 2012

Low-mass stars formation: protostars & outflows

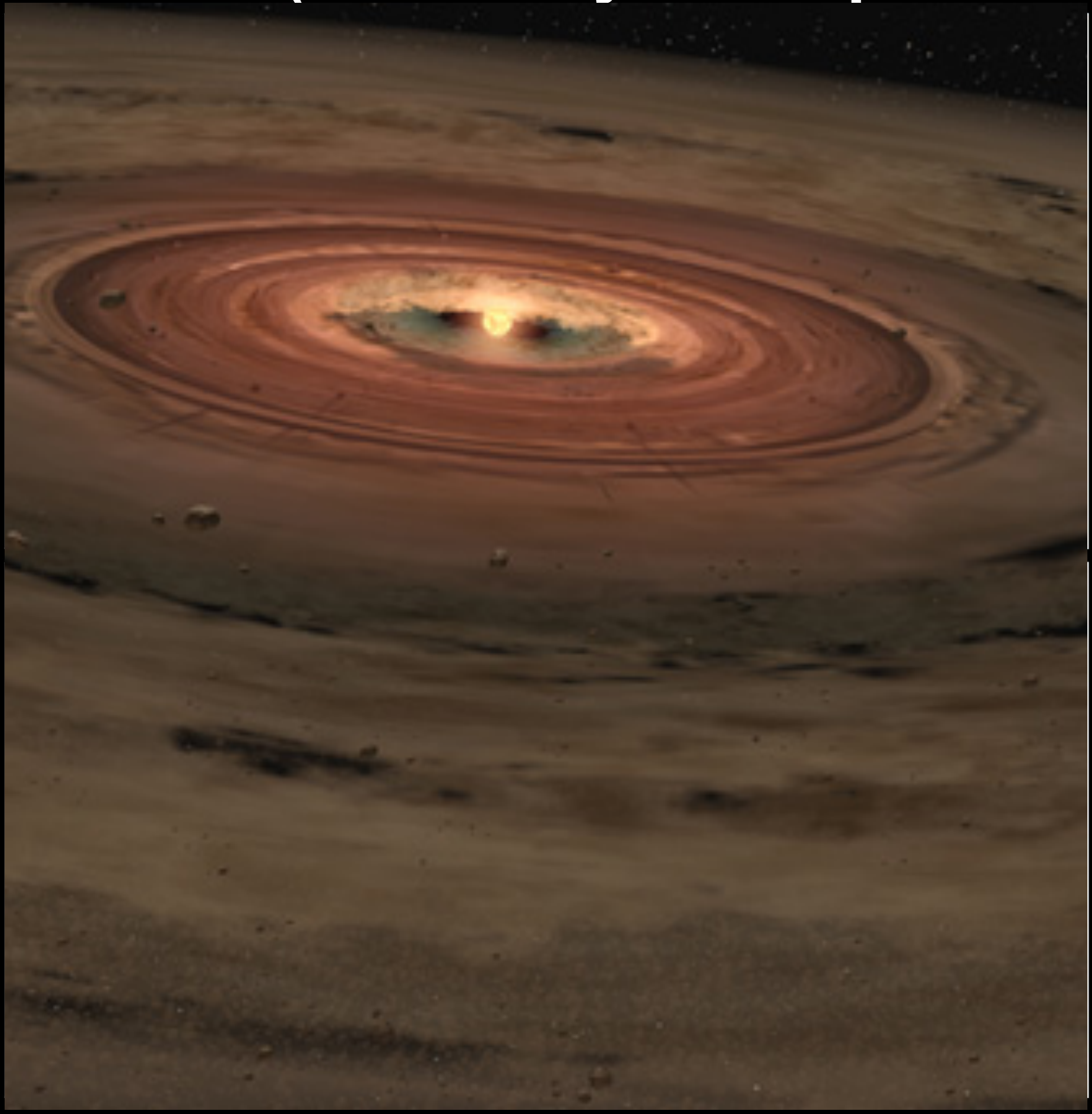


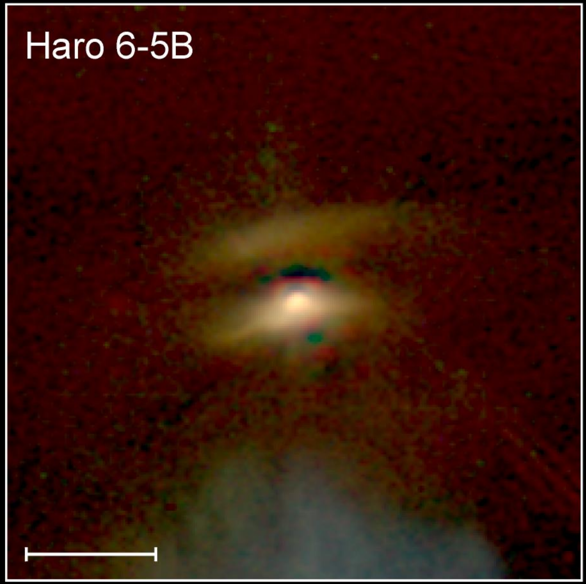


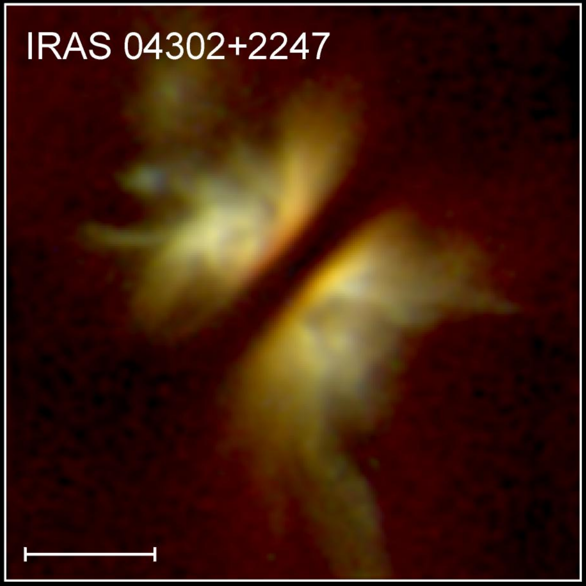
Looney, Tobin & Kwon 2007

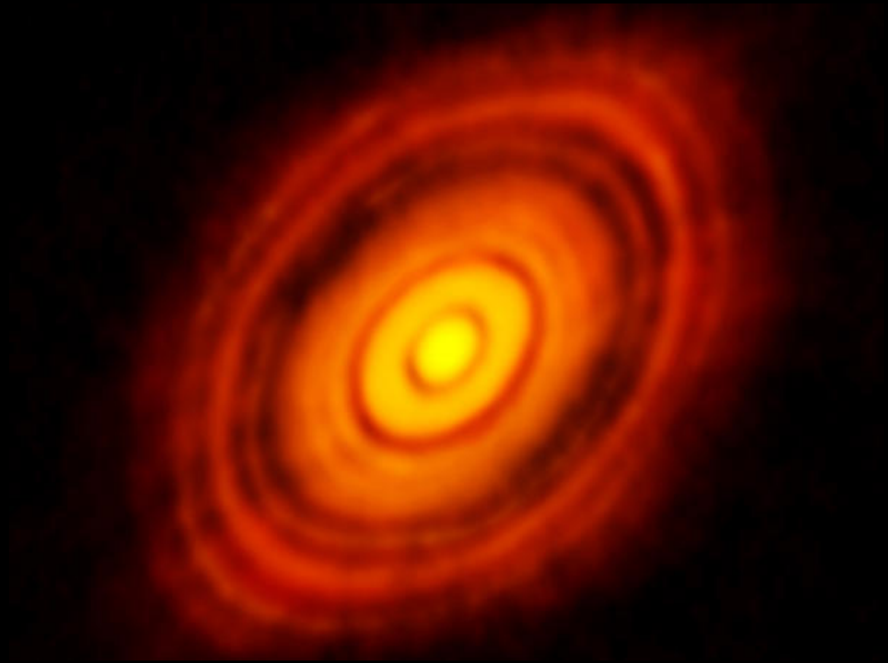
Kristensen et al. 2012

Protoplanetary disks
(chemistry when planets form…)









HL Tau

Protoplanetary disk (35mas resolution)

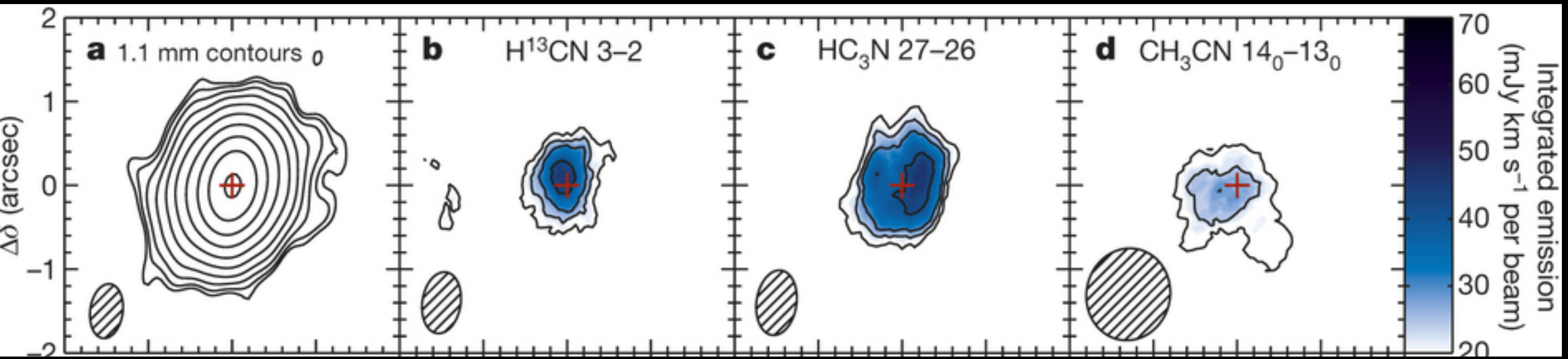
ALMA press release

Dust continuum emission with ALMA

MWC 480 disk

Complex cyanides with ALMA

Öberg et al. 2015, Nature



(rich) faint objects: mid-IR spectroscopy: JWST

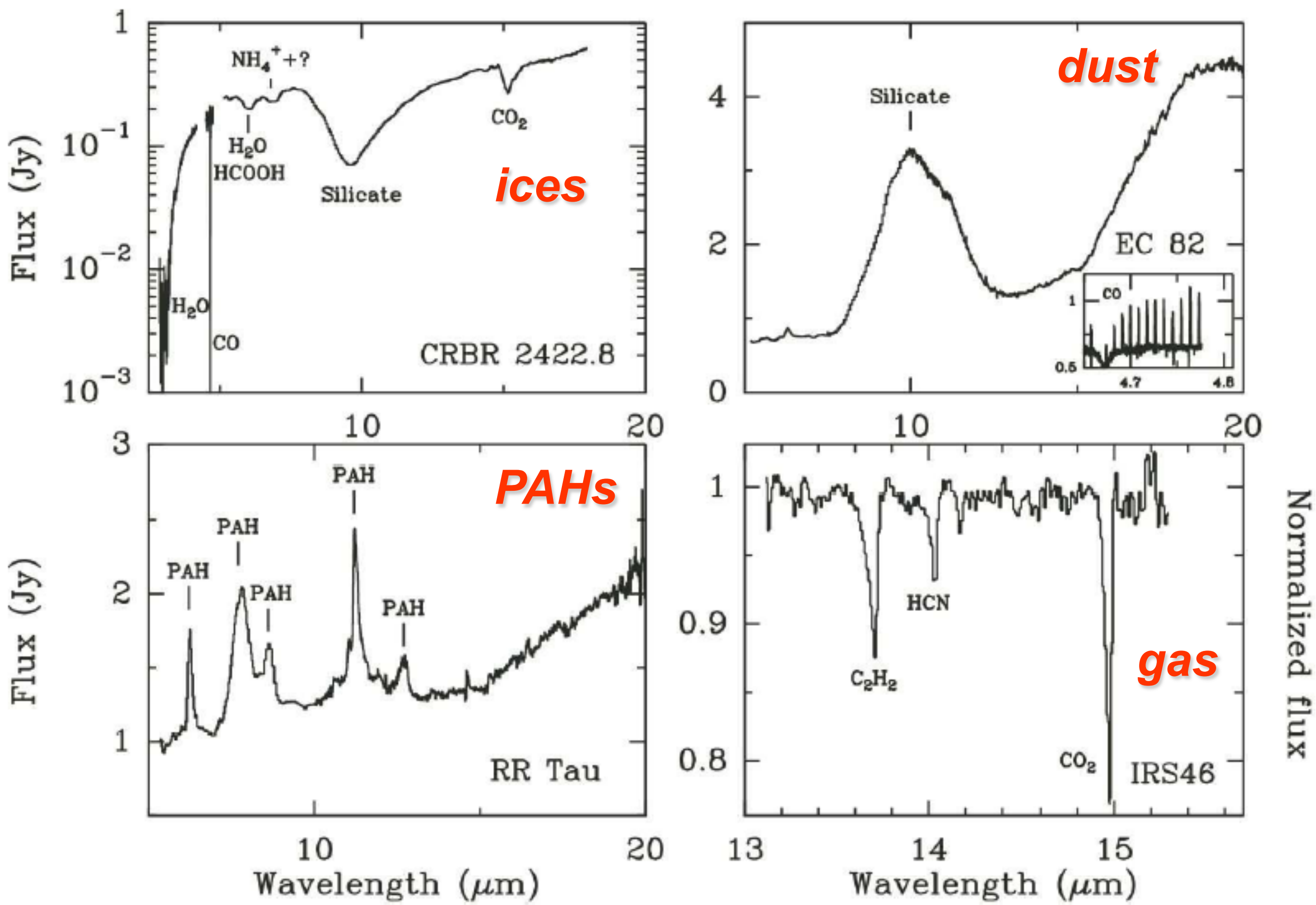


Fig. 3.— *Top left:* ice features toward edge-on disk CRBR 2422.8 -3423. Some absorptions arise in the cold foreground core (*Pontoppidan et al.*, 2005). *Top right:* silicate emission at 10 and 20 μm toward EC 82 (*Kessler-Silacci et al.*, 2006); inset, gas-phase CO v=1-0 emission (*Blake and Boogert*, priv. comm.). *Bottom right:* PAH features toward RR Tau (*Geers et al.*, 2006, in prep.); *Bottom left:* gaseous C_2H_2, HCN and CO_2 toward IRS 46 in Oph (*Lahuis et al.*, 2006);

Molecules in Supernova shocks

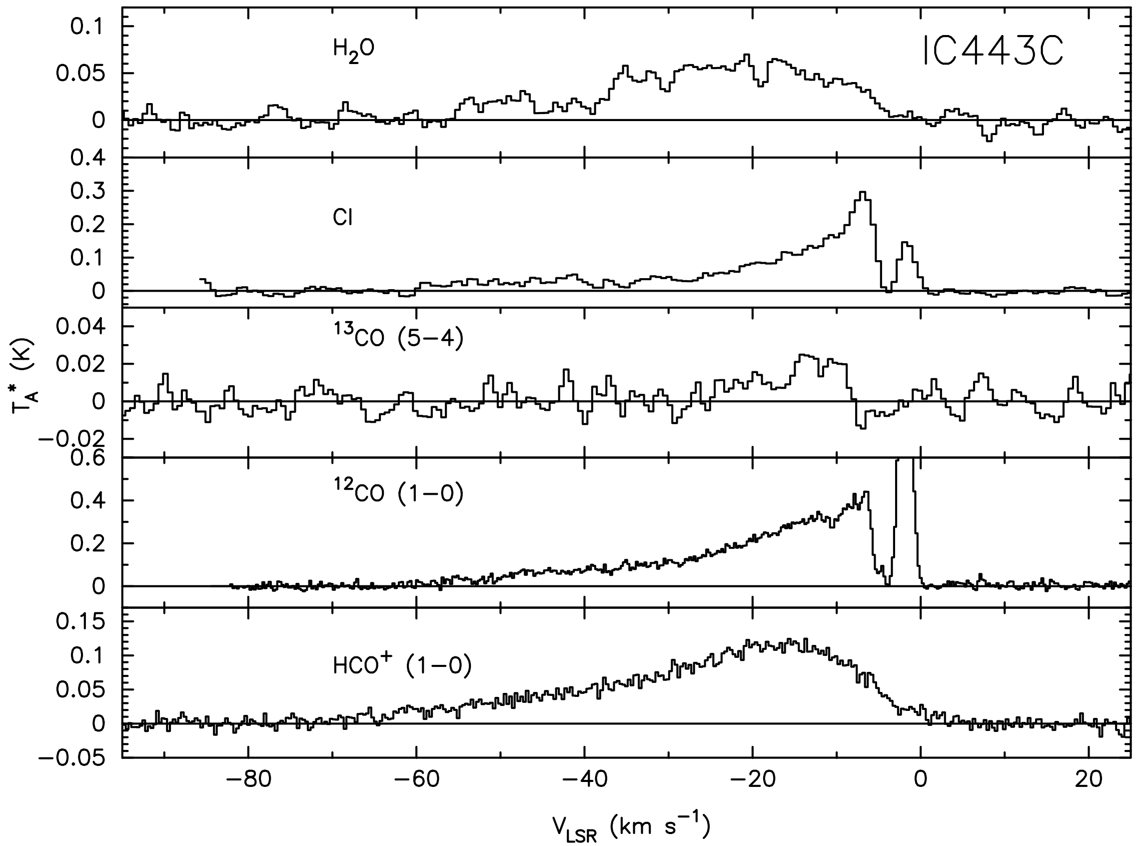
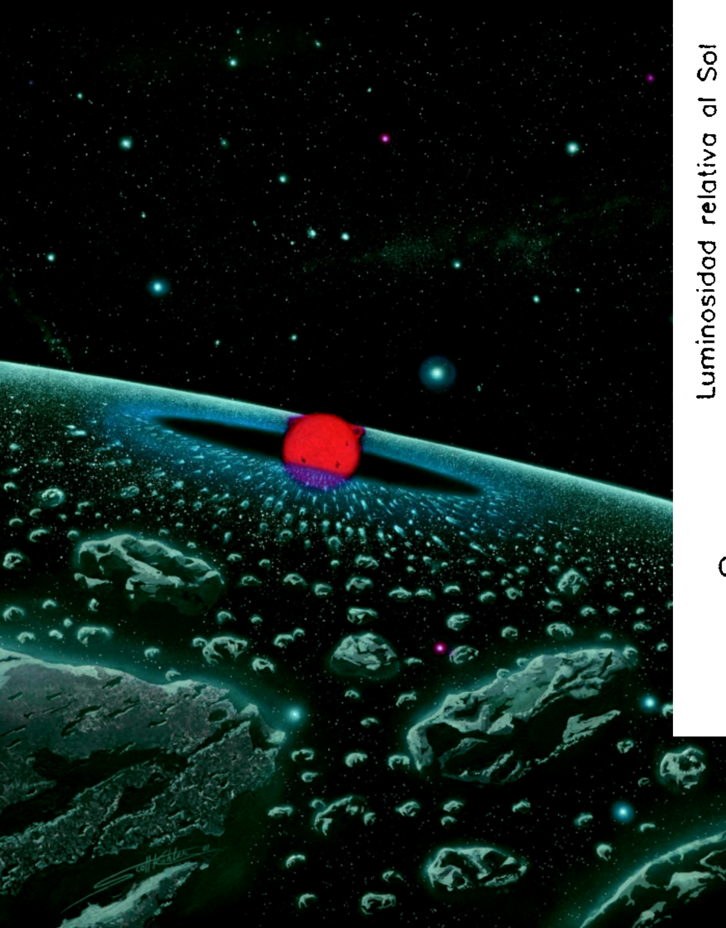


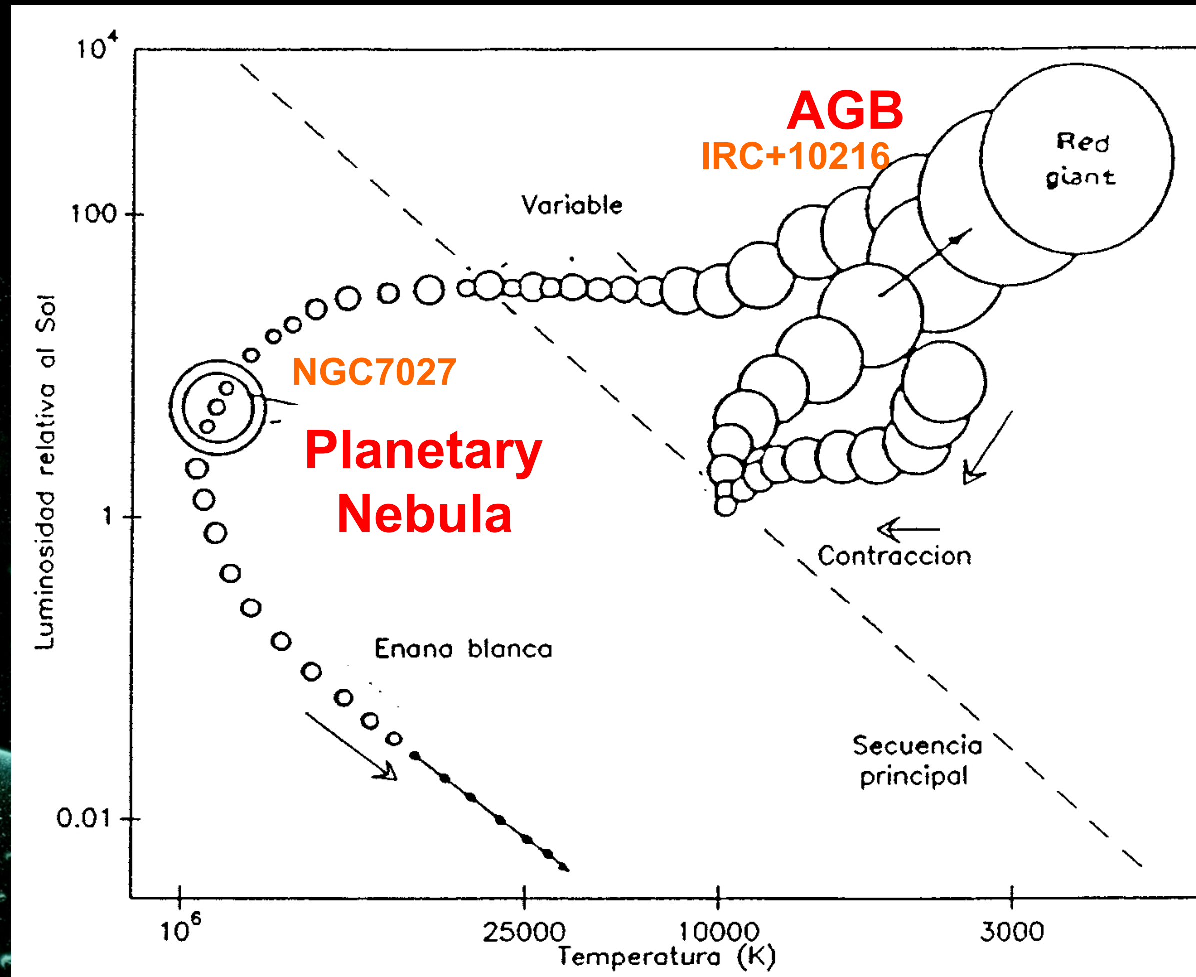
FIG. 2.—Spectra of the $1_{10} \rightarrow 1_{01}$ transition of o-H_2O, the $^3P_1 \rightarrow ^3P_0$ transition of C I, and the $J = 5 \rightarrow 4$ transition of ^{13}CO obtained with *SWAS* toward IC 443C. Also shown are the spectra of the $J = 1 \rightarrow 0$ transition of ^{12}CO and the $J = 1 \rightarrow 0$ transition of HCO^+ convolved to the *SWAS* angular resolution from data obtained at FCRAO toward IC 443G. The coordinates of IC 443C are $\alpha = 6^h17^m44^s.2$ and $\delta = 22°21'49''.1$ (J2000.0).

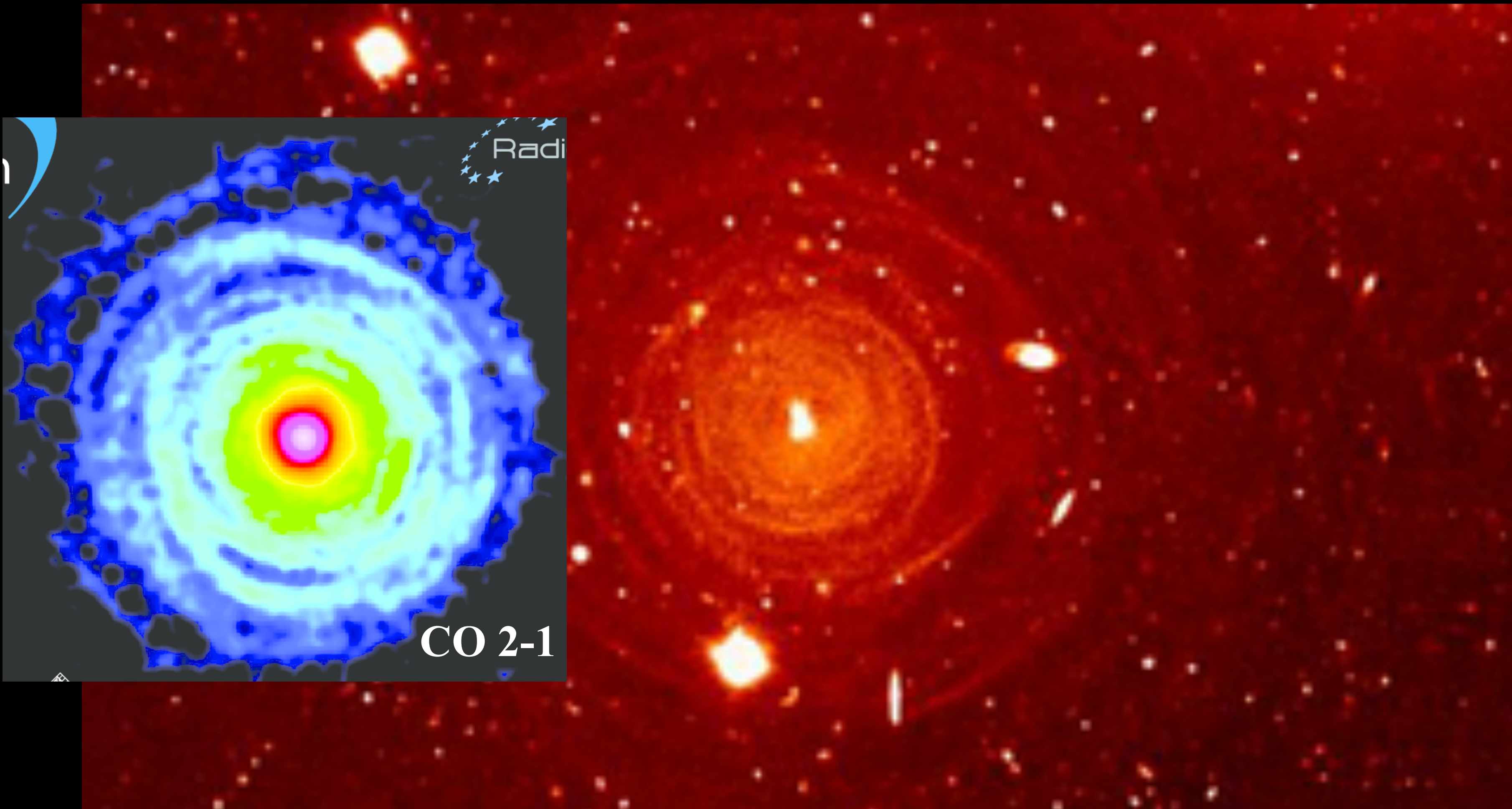
The latest stages of (massive) evolved stars

Chemistry in (Sun-like) evolved stars

(dust grain factories)

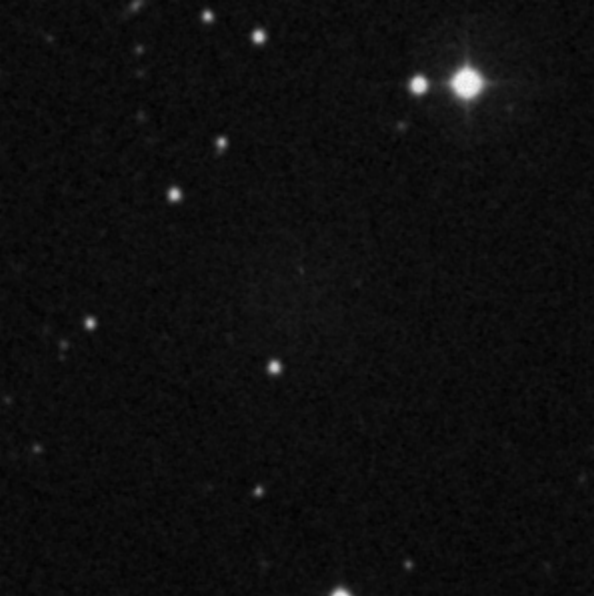




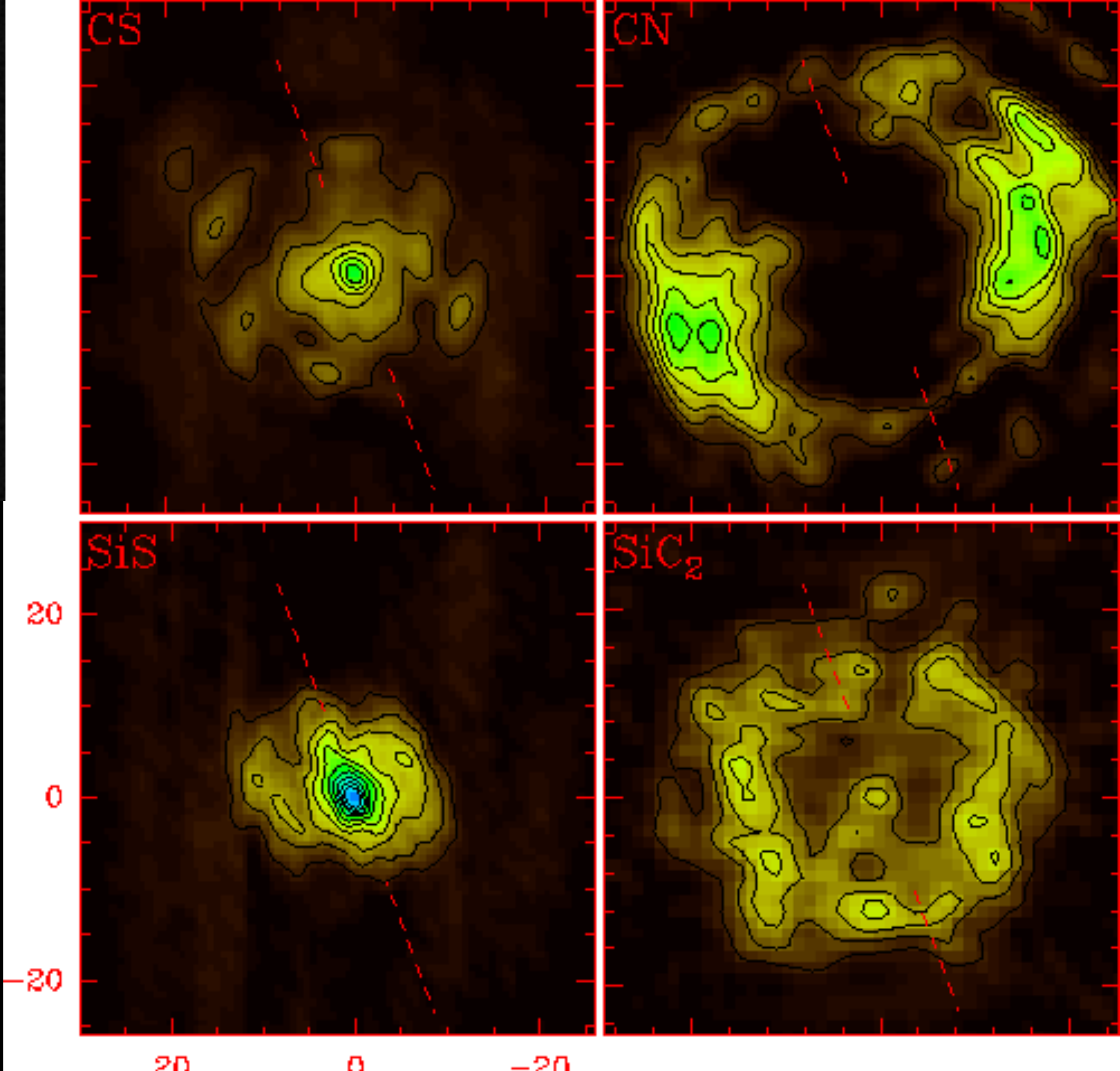


IRC+10216 (or CW Leo) C-rich AGB

Dust formation and Mass-loss into ISM

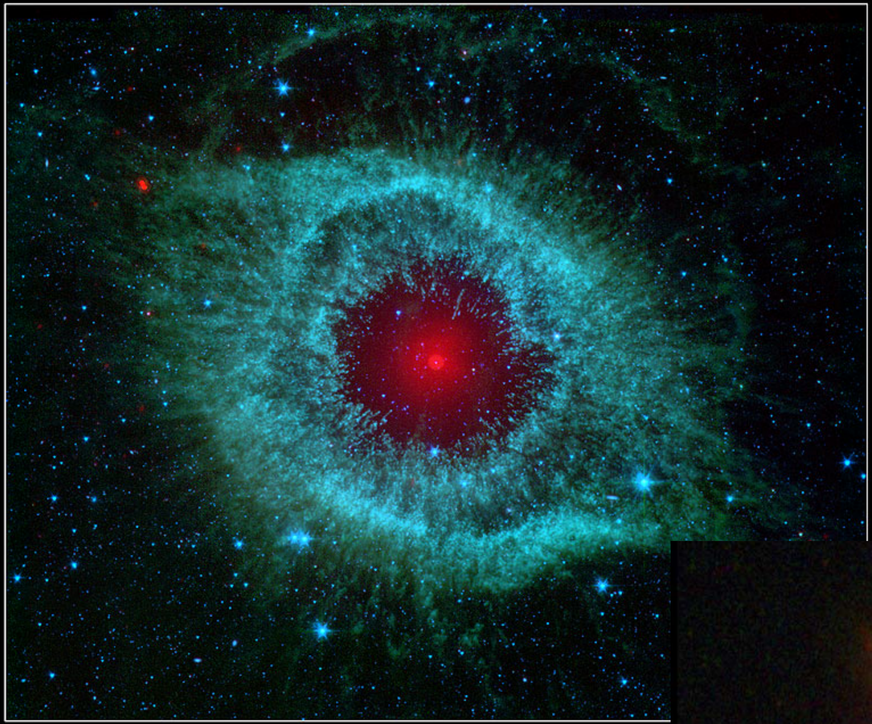


IRAM-NOEMA

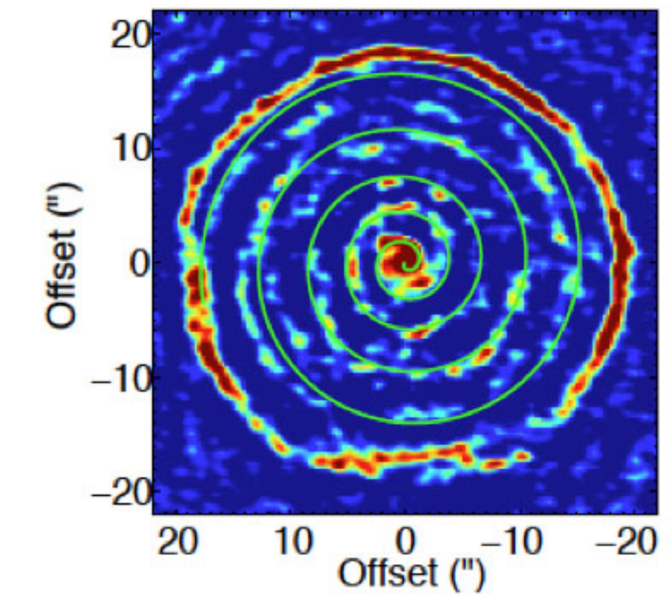


IRc+10216 (or CW Leo) C-rich AGB

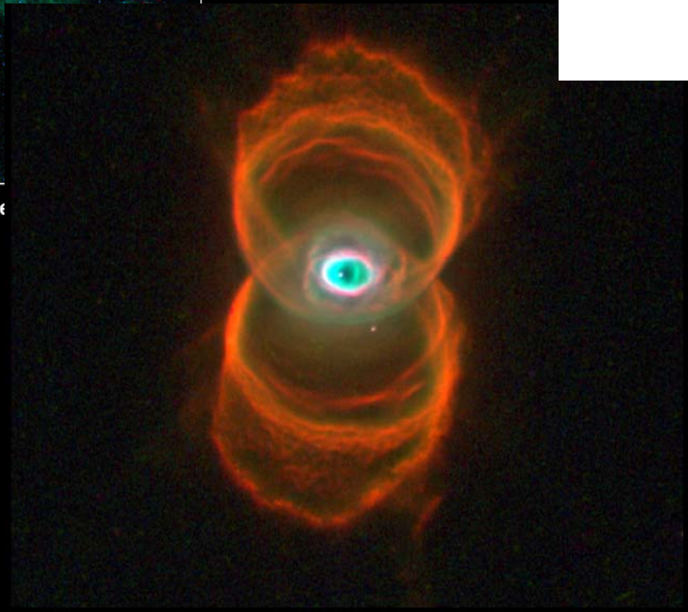
From AGB to Planetary Nebulae



Dusty Eye of the Helix Nebula (NGC 7293) Spitzer Space Tele
NASA / JPL-Caltech / K. Su (University of Arizona)

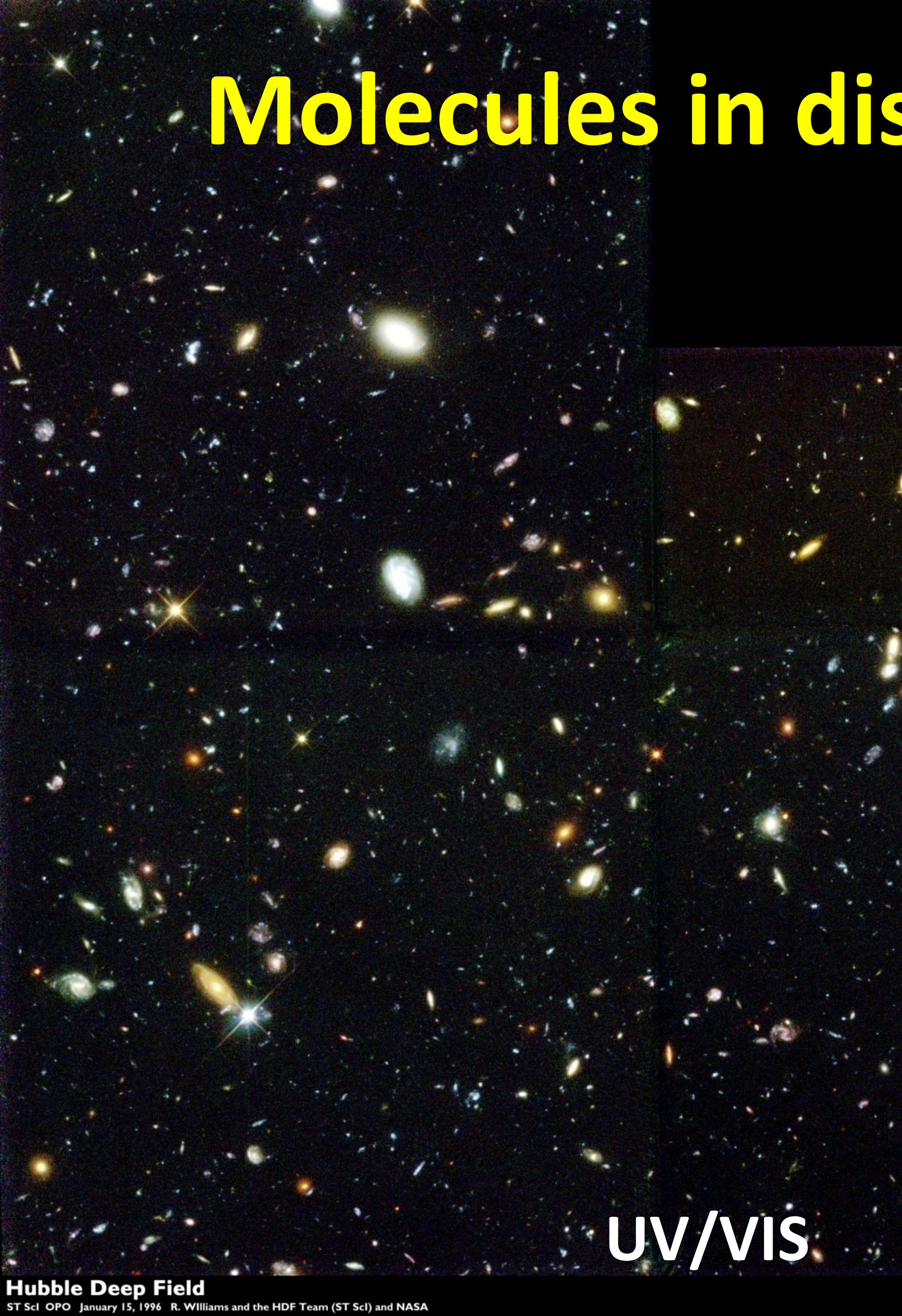


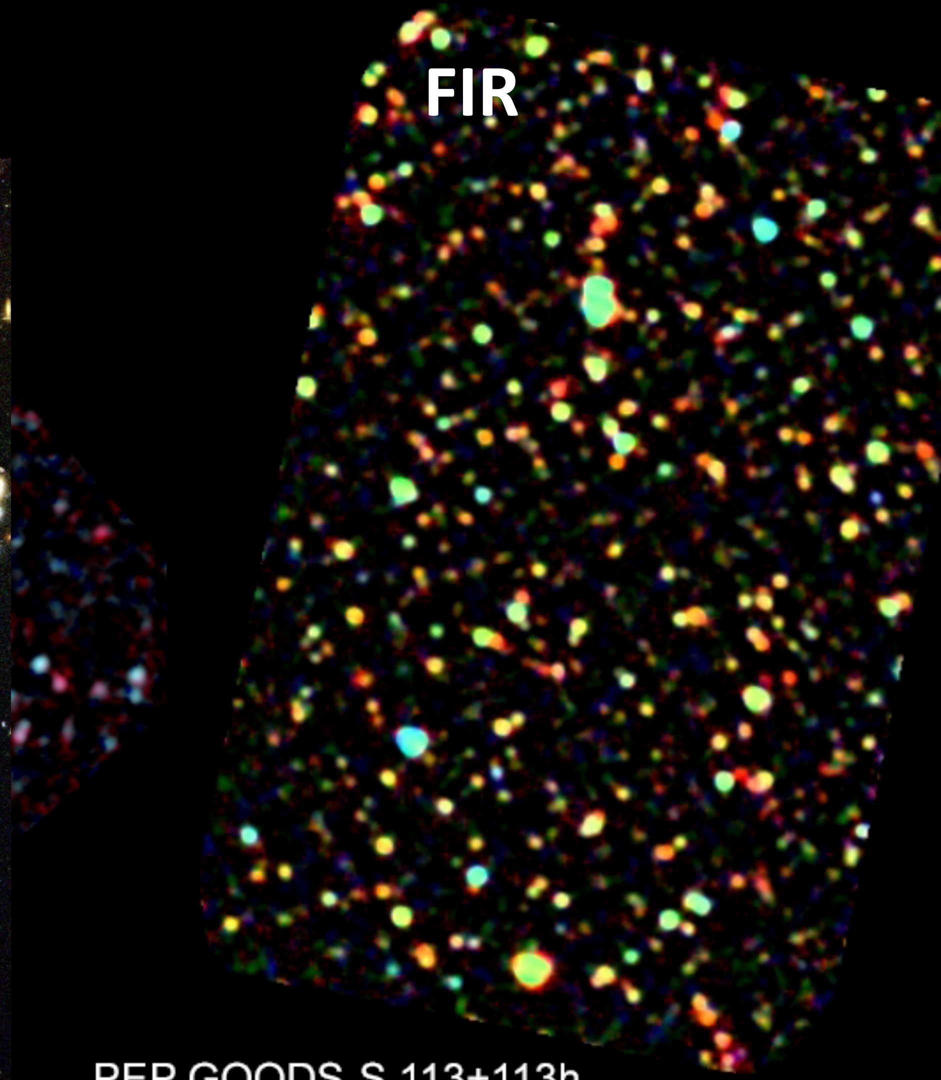
CO
with **ALMA**
(Maercker et al.)



Hourglass Nebula · MyCn18 HST · WFPC2
PRC96-07 · ST ScI OPO · January 16, 1996
R. Sahai and J. Trauger (JPL), the WFPC2 Science Team and NASA

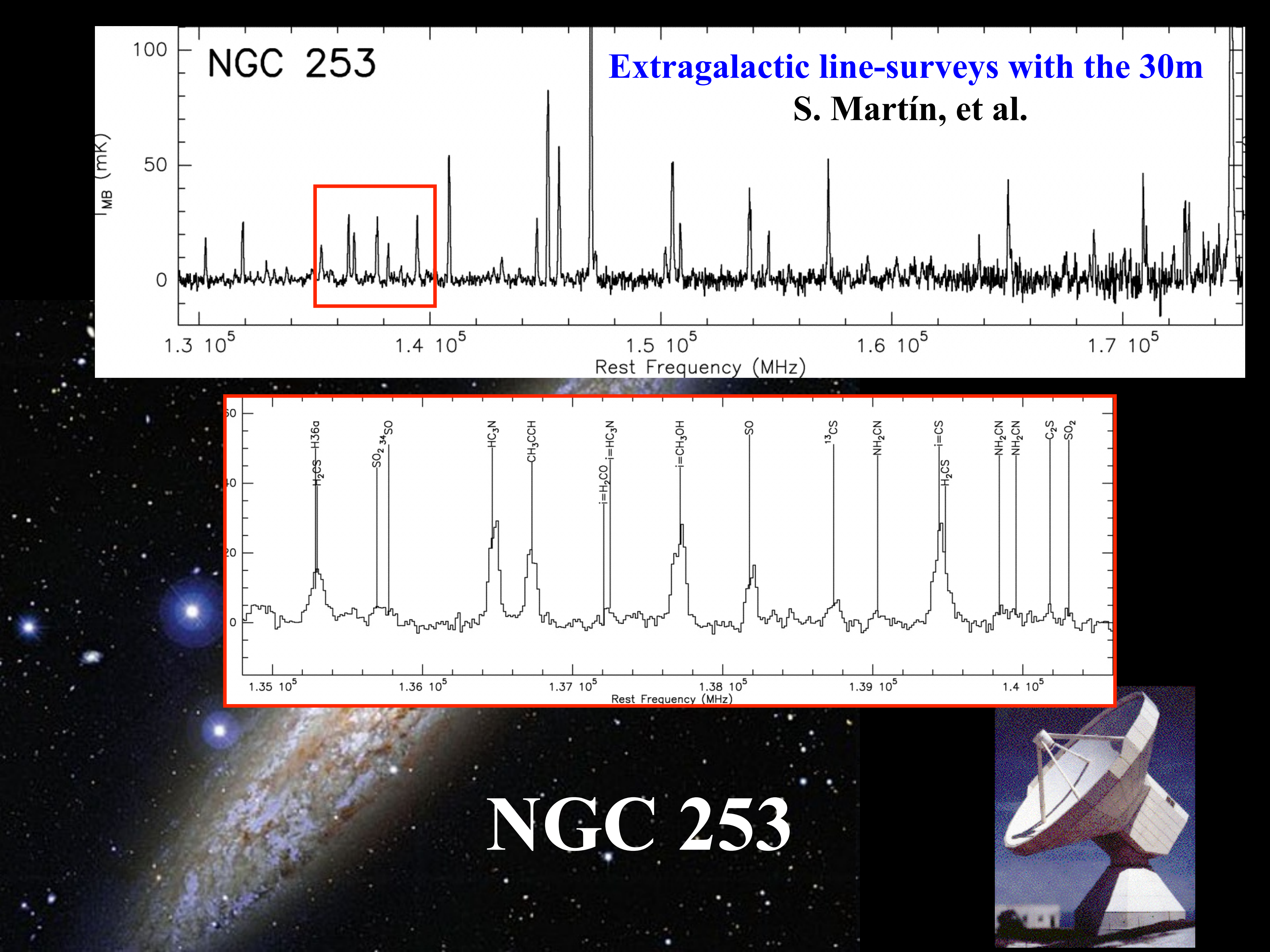
Molecules in distant galaxies?





PEP GOODS-S 113+113h
70+100+160μm
~800 sources

Extragalactic ISM clouds



Extragalactic line-surveys with the 30m
S. Martín, et al.
NGC 253
100
50
0
T_MB (mK)
1.3 10^5
1.4 10^5
1.5 10^5
1.6 10^5
1.7 10^5
Rest Frequency (MHz)
H2CS H36α
SO2 34SO
HC3N
CH3CCH
i=H2CO i=HC3N
i=CH3OH
SO
13CS
NH2CN
i=CS H2CS
NH2CN
NH2CN
C2S
SO2
1.35 10^5
1.36 10^5
1.37 10^5
1.38 10^5
1.39 10^5
1.4 10^5
Rest Frequency (MHz)
NGC 253

How are molecules formed in the interstellar and circumstellar media?

THE NATURE OF THE PROBLEM OF INTERSTELLAR CHEMISTRY

1) Low Temperatures:

Gas phase temperatures from ~10 K (dark, starless clouds)
to ~100-1000 K (UV/shocks…)

2) Low Volume Density:

From ~100 cm^{-3} (diffuse clouds) to ~10^{5-6} cm^{-3} (dense clouds)

3) The Formation of H_2 in gas phase NOT possible (H + H),

- How is H_2 formed?
- How does interstellar chemistry start?

Which are the key processes in ISM chemistry?

1) Need to form the basic molecule, H_2 , how?

2) We need atomic or molecular ions ($H_2 + O^+ \rightarrow OH^+ + H$):
- UV-photons near stars
- But inside dense molecular clouds ?

3) Cold gas ($T < 100$ K) $\rightarrow$ only exothermic reactions work ?

Because of the low temperatures and densities, interstellar chemistry is NOT in thermochemical equilibrium (UV photons, cosmic-ray particles affect the chemistry…) but controlled by 2-body gas-phase reactions (A + B = C + D) → chemical kinetics

Some notation…

BIMOLECULAR REACTIONS (ISM)

$\mathbf{A + B \xrightarrow{k} M + N}$

A,B = atoms, molecules or electron
M = molecule
N = molecule, atom or photon

$\mathbf{M + h\nu \xrightarrow{\beta} \ldots}$

"number density" of molecule "M"?

N(M) = density of "M" molecules ***[n(M)]= (molecules) cm^{-3}***

k = k(T) "rate coefficient" ***[k] = cm^{+3} s^{-1} ~ σ (cm^2) · v(cm s^{-1})***

β = "UV photodissociation rate" ***[β] = (molecules) s^{-1}***

typical β ≈ 10^{-10} s^{-1} → molecule lifetime in diffuse ISM = 1/β ≈ 300 yr! (photochemistry is fast…)

BIMOLECULAR REACTIONS (ISM)

$$A + B \xrightarrow{k} M + N$$

A,B = atoms, molecules or electron
M = molecule
N = molecule, atom or photon

$$M + h\nu \xrightarrow{\beta} \ldots$$

Formation rate of M $= k\, n(A)\, n(B)$ $[cm^{-3}\, s^{-1}]$

Destruction rate of M $= \beta\, n(M)$ $[cm^{-3}\, s^{-1}]$

n(M) as function of time ?

$$\frac{d}{dt}\, n(M, t) = \textit{Formation} - \textit{Destruction} = k\, n(A, t)\, n(B, t) - \beta\, n(M, t)$$

$A + B \xrightarrow{k} M + N$ $\quad\quad\quad$ $M + h\nu \xrightarrow{\beta} \ldots$

d/dt n(M) = Formation – Destruction = k n(A) n(B) – β n(M)

Steady-state → d/dt n(M) = 0 → n(M) = F/β = k n(A)n(B) / β
time-scale ~1/β

PROBLEM: k = k (T) ?? β (cloud position) ??

- k and β can only be determined from quantum calculations and / or through sophisticated laboratory measurements

$k(T) = A(T) \exp(-E_a/kT)$ "*Arrhenius law*" [$cm^3\ s^{-1}$]

$\beta(A_V) \approx \beta_0 \exp(-\alpha A_V)$ [s^{-1}]

HOW DO WE FORM MOLECULE "AB" IN SPACE?

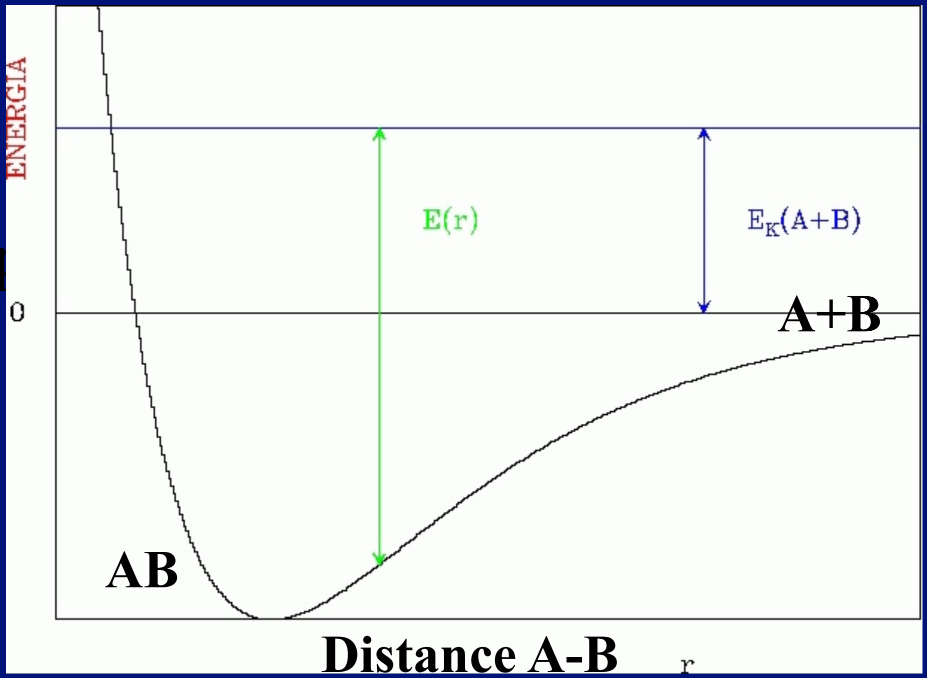
$$A + B \rightarrow AB^* \qquad\qquad AB^* + Z \rightarrow AB + Z$$

In all chemical processes the interaction between two species (atoms or molecules) produces an activated complex (AB^*) that has to loss energy in a very short time period, often similar to the vibration time of the molecule nuclei. There are many ways for the activated complex to loss energy. But, while in terrestrial laboratories catalysers or a third body are available, we will see that in space three body collisions are very uncommon (WHY?).

Let us consider the reaction

$$A + B \rightarrow AB^* \quad (k_1)$$

It may happen that AB^* interacts with a third body (catalyser=Z) to remove the energy excess, $>E_k(A+B)$, produced in the formation of the activated complex. However, AB^* can also dissociate into the initial particles A and B



$$AB^* + Z \rightarrow AB + Z \quad (k_2)$$
$$AB^* \rightarrow A + B \quad (k_3)$$

$k_1 \approx 10^{-11}\ cm^3\ s^{-1}$
$k_2 \approx 10^{-10}\ cm^3\ s^{-1}$,
$k_3 \approx 10^{+11}\ s^{-1}$

Potential energy surface (PES)

EXAMPLE: The simplest trimolecular reaction (H_2 formation)

Let us consider an atomic cloud without dust grains and without radiation field. For t=0 the density of atomic hydrogen is n=n(H) and that of molecular hydrogen is $n(H_2)=0$. The formation of H_2 occurs through the reaction

$$H + H + H = H_2 + H$$

with a k rate of 10^{-32} cm^6 s^{-1}

The formation rate of H_2 is given by **f(t) = "molecular fraction"**

$$\frac{dn(H_2, t)}{dt} = k\, n^3_H(t) \qquad f(t) = \frac{2\, n_{H2}(t)}{n(H)(t) + 2\, n_{H2}(t)} = \frac{2\, n_{H2}(t)}{n(t)}$$

$$\frac{df(t)}{dt} = 2k\, n^2\, (1 - f(t)\,)^3$$

Time to reach f=0.5 ??

EXAMPLE

(Earth at sea level density~10^{19} cm^{-3})

(ultra-high vacuum chamber density~10^5 cm^{-3})

$f(t_0)=0.5$, $t_0=?$

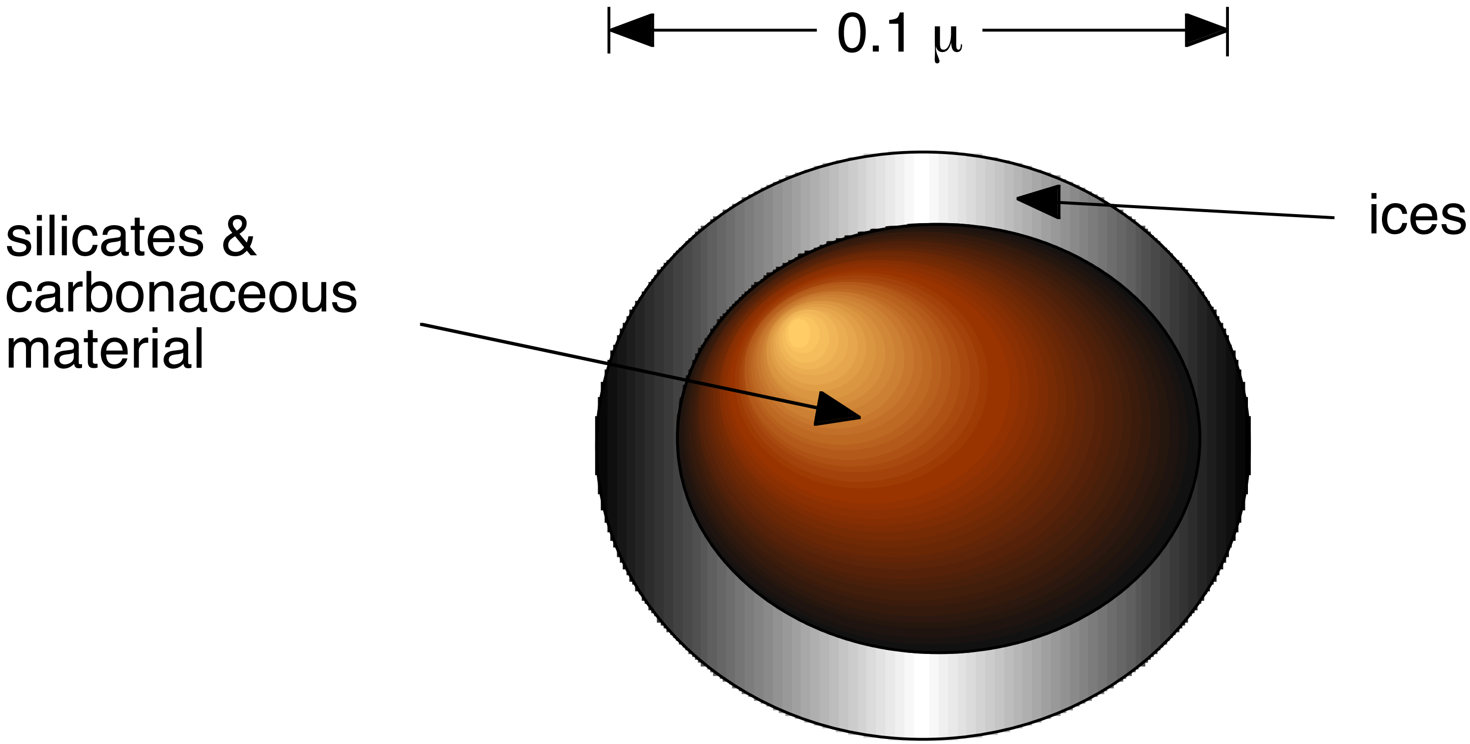
$n_H(cm^{-3})$	…	10^5	10^{10}	10^{12}	10^{15}	10^{16}	10^{18}
t_0 (years)	…	$6\ 10^{14}$	$6\ 10^4$	6	$6\ 10^{-6}$	$6\ 10^{-8}$	$6\ 10^{-10}$
					(600 s)	(6s)	(0.0006s)

3-body reactions are only efficient for densities > 10^{12} cm^{-3}
(not in the ISM)

$H + H + H = H_2 + H$ DOES NOT WORK!

BUT H_2 HAS BEEN DETECTED IN SPACE…

AN INTERSTELLAR GRAIN



M_{gas}/M_{dust}~100 (ISM)

THE ASTROPHYSICAL JOURNAL, 581:276–284, 2002 December 10

Cooling a gas of H atoms and dust grains

FORMATION OF MOLECULAR HYDROGEN ON AMORPHOUS WATER ICE: INFLUENCE OF MORPHOLOGY AND ULTRAVIOLET EXPOSURE

J. E. ROSER,[1] G. MANICÒ,[1,2] V. PIRRONELLO,[2] AND G. VIDALI[1]
Received 2002 April 26; accepted 2002 August 14

ABSTRACT

In this paper, we report on the formation of molecular hydrogen on different types of amorphous water ice. We show that mass spectra of desorbing molecules upon formation are sensitive to the way in which ice is deposited on a cold substrate, to its thermal history, and to the action of UV photons. Implications that these results bear on H_2 formation in dense quiescent clouds are presented and discussed.

Subject headings: astrochemistry — dust, extinction — ISM: molecules — methods: laboratory — molecular processes

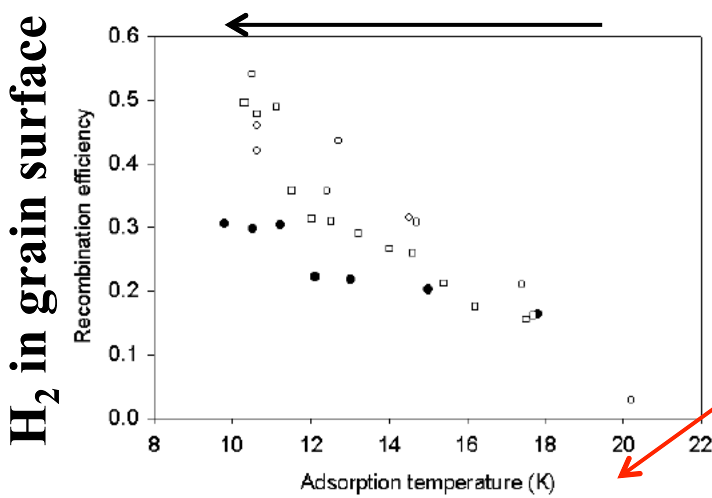


FIG. 3.—Recombination efficiency of molecular hydrogen vs. sample temperature of H atoms. Filled circles are for high-density amorphous ice (Manicò et al. 2001), open circles are for low-density amorphous ice prepared by heating high-density amorphous ice, and open squares are for water vapor–deposited low-density amorphous ice. The error bars are comparable to the size of the symbols. The scatter in the data points reflects the variability in the ice preparation methods.

H atoms are adsorbed and form H_2 in the surface

T typical of cold ISM !

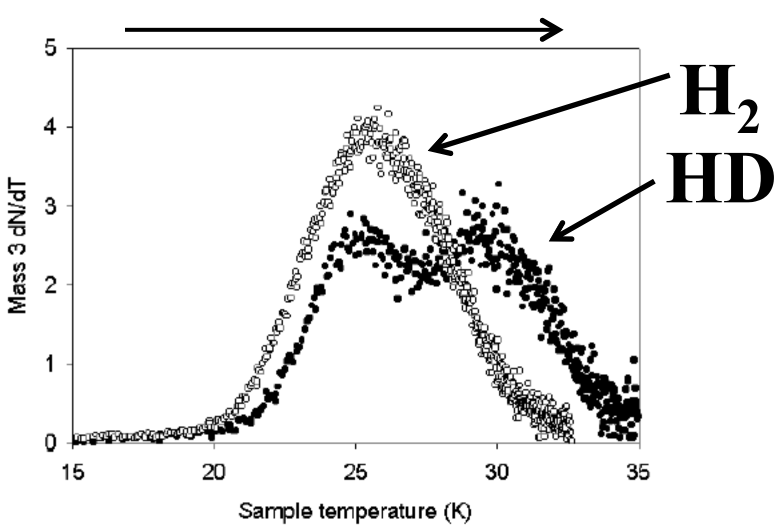


FIG. 4.—Desorption rate (dN_{HD}/dT) vs. ramp temperature after adsorption of H and D for 4 minutes on high-density amorphous water ice at ∼10 K before (*filled circles*) and after (*open circles*) UV exposure for 15 minutes. Traces have been scaled to yield the same area.

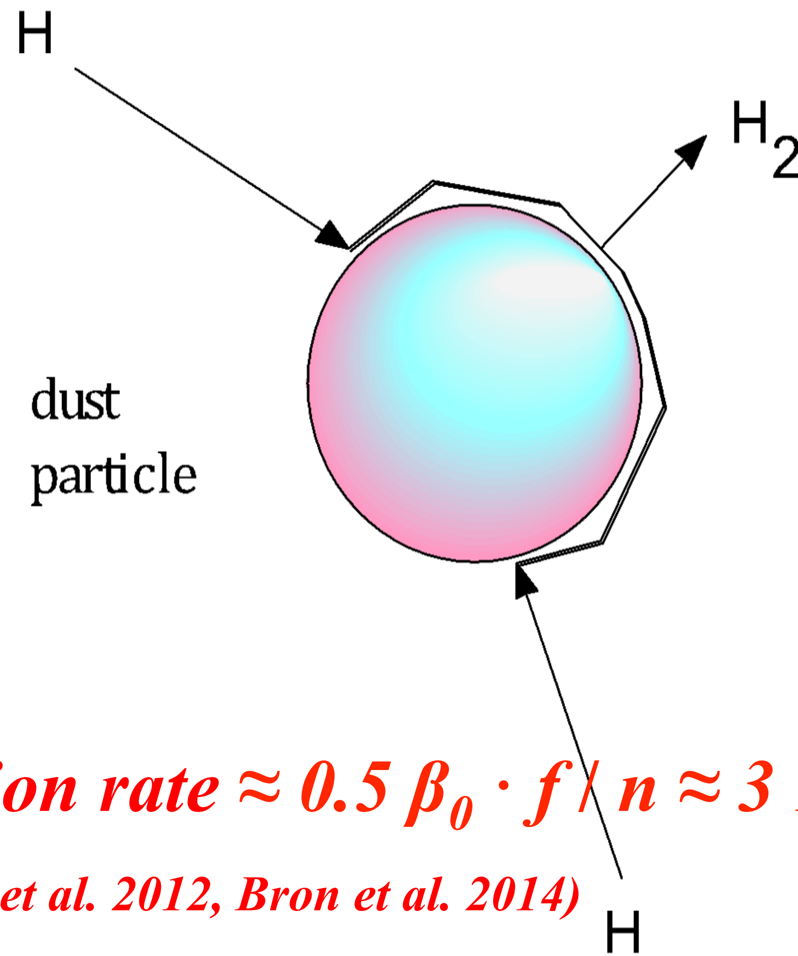
<u>Heating</u> grains with H_2 in their surfaces

H_2 <u>sublimates</u> and leaves the surface!

T typical of ISM !

CO sublimates at T_d~20-30 K
H_2O sublimates at T_d~80-100 K

H_2 formation in the ISM



H_2 formation rate $\approx 0.5\, \beta_0 \cdot f\, /\, n \approx 3\; 10^{-17}\ cm^3\ s^{-1}$

(e.g. Le Bourlot et al. 2012, Bron et al. 2014)

Weakly bound molecules: “diffusion” = “Langmuir-Hinshelwood” mechanism

H_2 is formed on the surface of the dust grains.
How do we form other gas-phase molecules ?

H_2 + (C, C^+, O, O^+, N, Si, Si^+, S, S^+) $\rightarrow$???

A + B $\rightarrow$ AB ??

let us consider the following reaction;

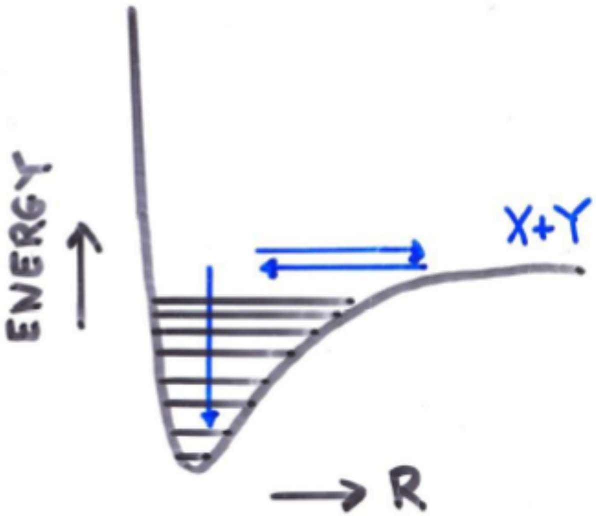
A + B $\rightarrow$ AB + $h\nu$ (*radiative association*)

is it possible?
is it fast enough to be efficient in the ISM?

Radiative Association

- $X + Y \underset{\tau_d}{\overset{\tau_c}{\rightleftarrows}} XY^* \xrightarrow{\tau_r} XY + h\nu$

- Energy conservation → photon must be emitted, which is a very slow process



$\tau_r = 10^{-2}$-10^{-3} s vibrational transition

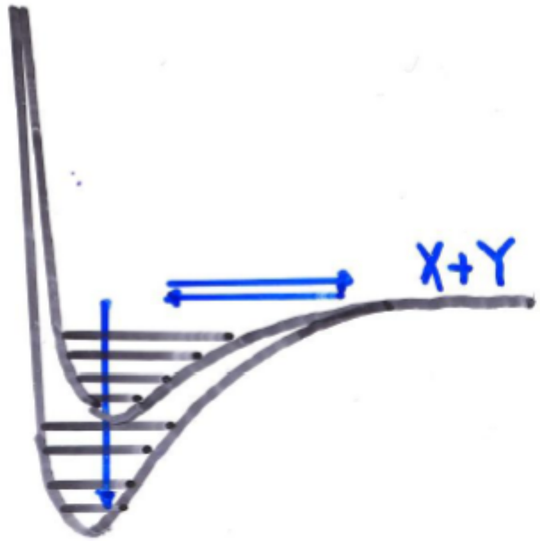
$\tau_{c,d} = 10^{-13}$ s collision time

⇒ ***Molecule formation occurs only 1:10^{10} collisions***

Bond probability = tau_diss / tau_radiate

Radiative Association

- Process becomes more efficient if electronic states available



$\tau_r = 10^{-8}$ s electronic transition

$\tau_{c,d} = 10^{-13}$ s collision time

=> ***Efficiency increased to 1:10^5***

Slow, anyway…

H_2 + (C, C^+, O, O^+, N, Si, Si^+, S, S^+) $\rightarrow$???

The reaction will occur if the change of energy is positive to account for the low temperatures of the interstellar medium (in general, reactions in the ISM should be exothermic!!)

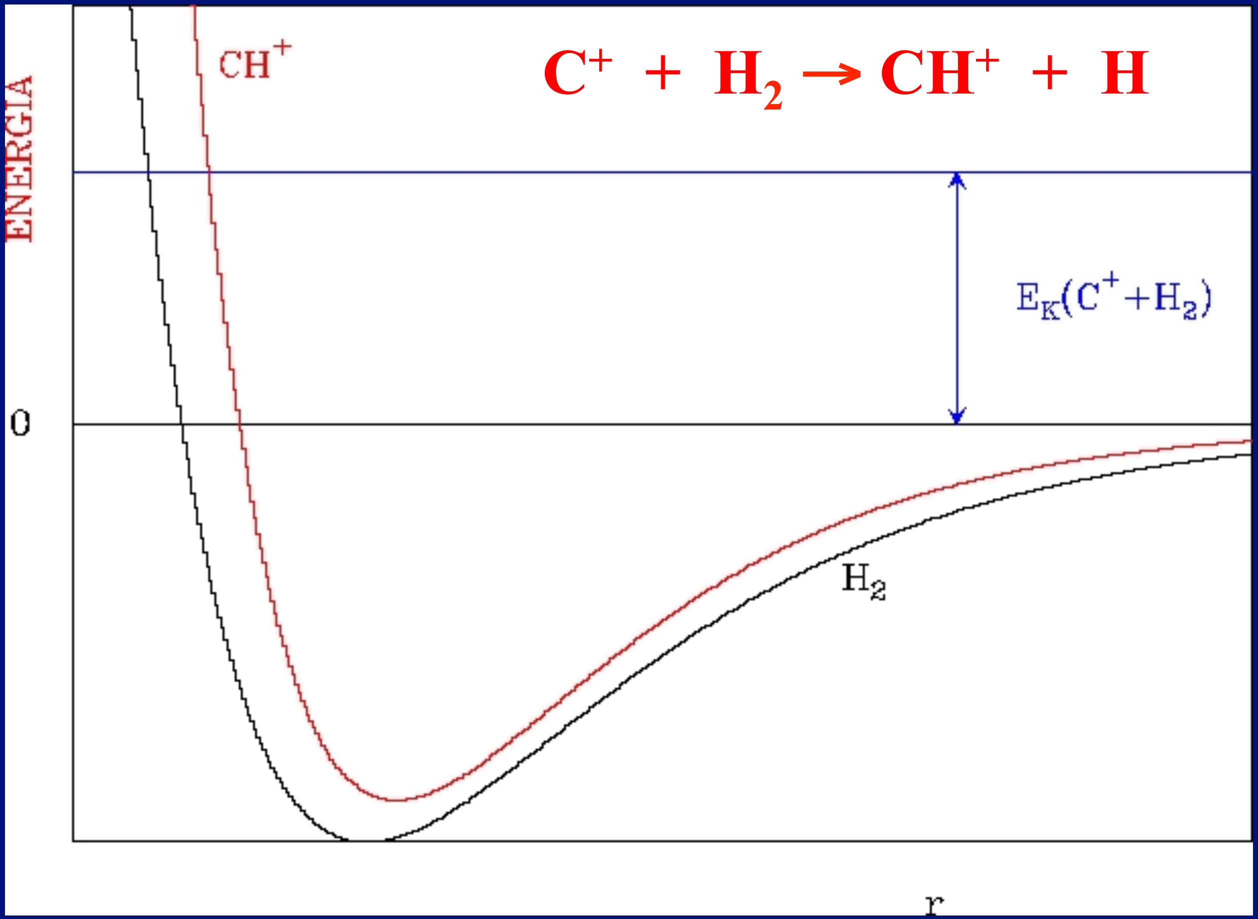
For example, let us consider the reaction:

$C^+ + H_2 \rightarrow CH_2^+ + h\nu$ → **slow**

what about: $C^+ + H_2 \rightarrow CH^+ + H$?

D(products) – D (reactants) > 0 → exothermic
< 0 → endothermic

The dissociation energy of H_2 is 4.48 eV and that of CH^+ is 4.09 eV



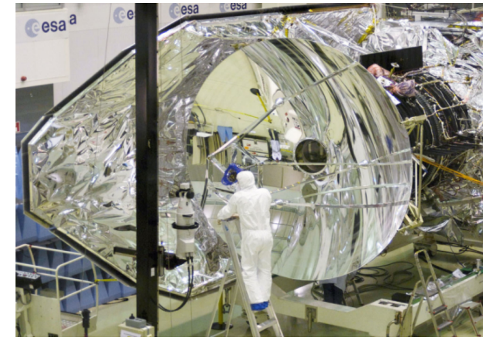
The reaction will be produced if we add 0.39 eV to the system (about 4600 K).

This reaction is endo-thermic and has little probability to occur in the ISM as we need T_{gas} > 4000 K

A&A 521, L15 (2010)
DOI: 10.1051/0004-6361/201015109

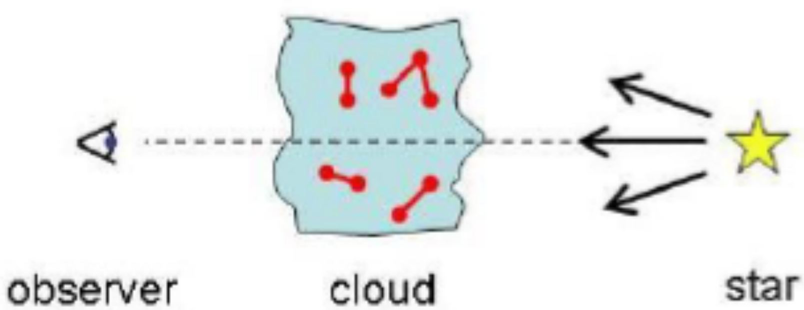
Herschel/HIFI: first science highlights

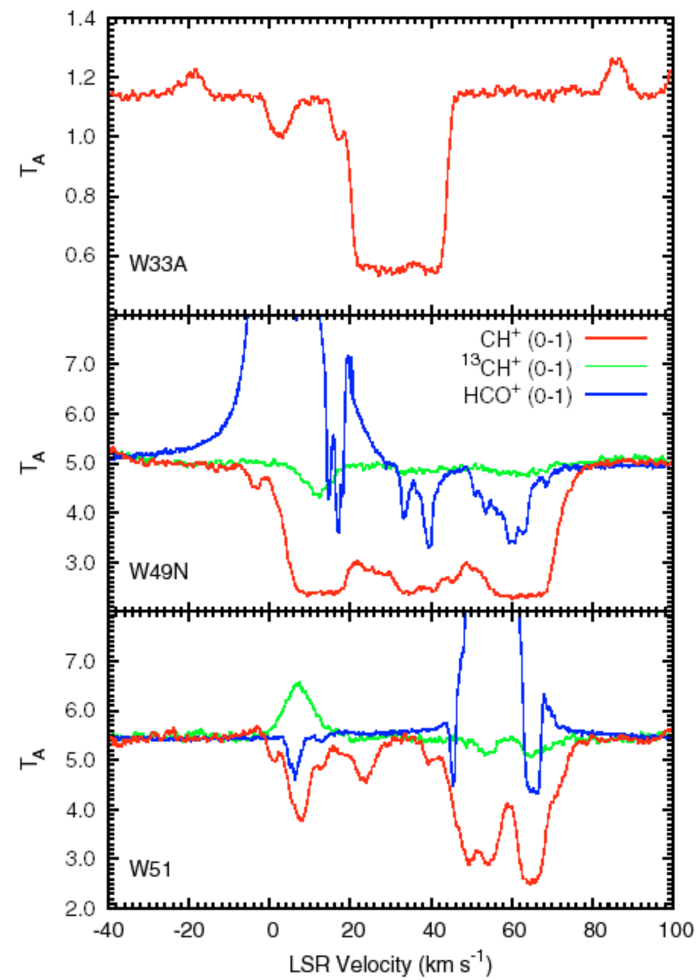
Astronomy & Astrophysics
Special feature



Letter to the Editor

CH^+(1–0) and $^{13}CH^+$(1–0) absorption lines in the direction of massive star-forming regions⋆,⋆⋆





Shocks in diffuse ISM?
(Dissipation of turbulence)

See Falgarone et al. Godard et al.
("TDR models")

The reaction

$$S^+ + H_2 \rightarrow SH^+ + H$$

Has even fewer chances to occur in the ISM

$D(H_2)$=4.49 eV and $D(SH^+)$=3.5 eV

(endothermic by ~10,000 K)

Comparative study of CH^+ and SH^+ absorption lines observed towards distant star-forming regions⋆⋆⋆

B. Godard[1], E. Falgarone[2], M. Gerin[2], D. C. Lis[3], M. De Luca[2], J. H. Black[4], J. R. Goicoechea[1], J. Cernicharo[1], D. A. Neufeld[5], K. M. Menten[6], M. Emprechtinger[3]

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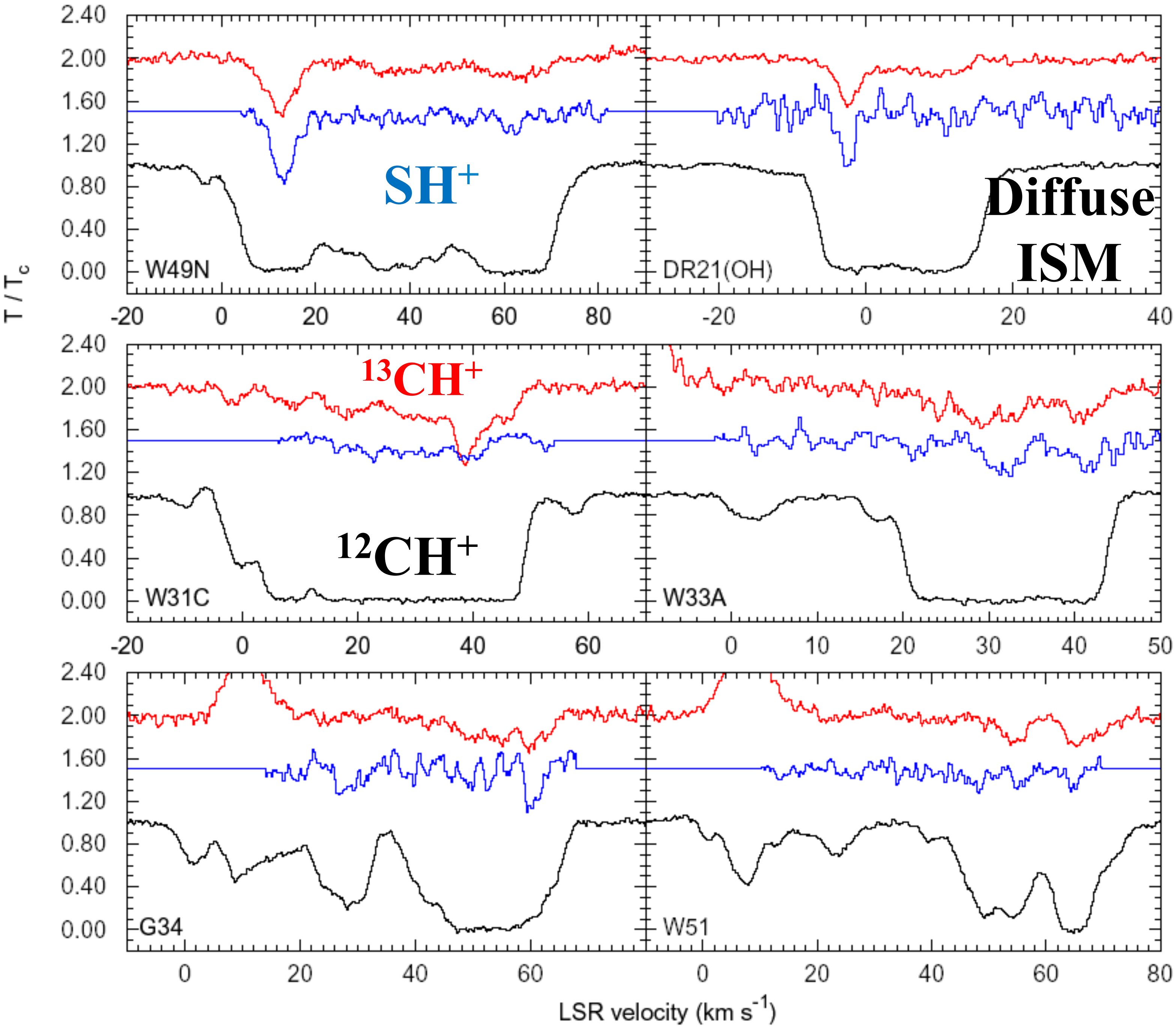
2 LERMA, CNRS UMR 8112, École Normale Supérieure & Observatoire de Paris, Paris, France
3 California Institute of Technology, Pasadena, CA 91125, USA
4 Department of Earth and Space Sciences, Chalmers University of Technology, Onsala Space Observatory, 43992 Onsala, Sweden.
5 The Johns Hopkins University, Baltimore, MD 21218, USA
6 MPI für Radioastronomie, Bonn, Germany.

Godard et al. 2012, A&A

Herschel/HIFI

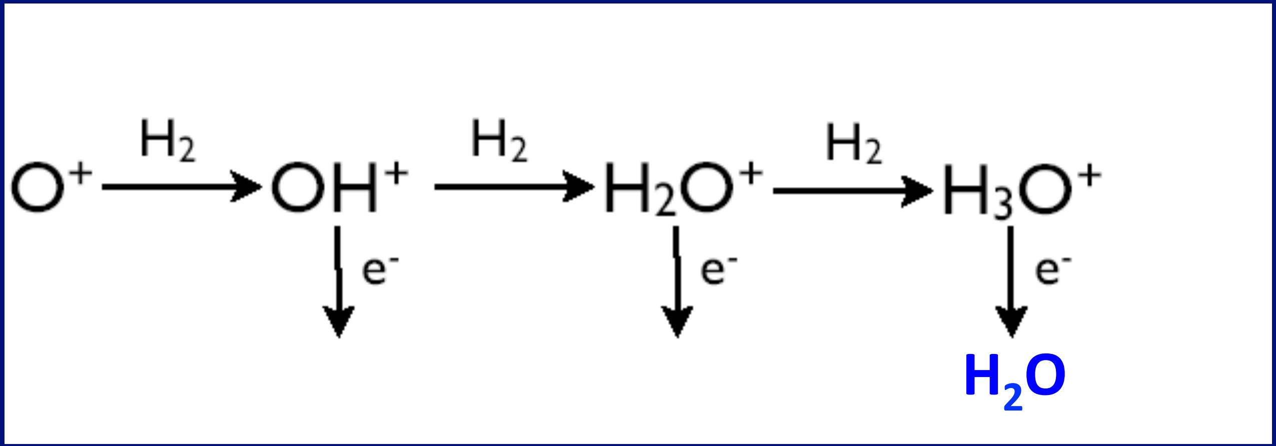


However, the reaction

$$O^+ + H_2 \rightarrow OH^+ + H$$

can occur because $D(H_2)$=4.49 eV, $D(OH^+)$=5.1 eV and it is exothermic by 0.61 eV!

The reaction rate has been measured in the laboratory and is rather fast, $k \approx 1.6\ 10^{-9}$ cm^3 s^{-1}



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Herschel/HIFI: first science highlights

Astronomy & Astrophysics
Special feature

Letter to the Editor

Herschel/HIFI observations of interstellar OH^+ and H_2O^+ towards W49N*: a probe of diffuse clouds with a small molecular fraction

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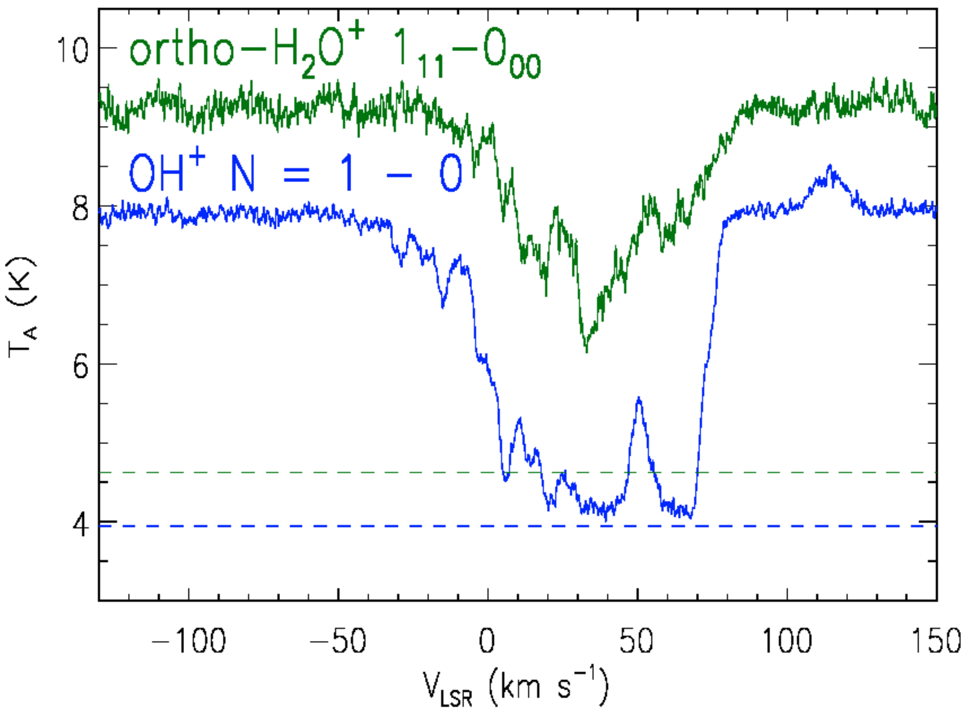
(Affiliations can be found after the references)

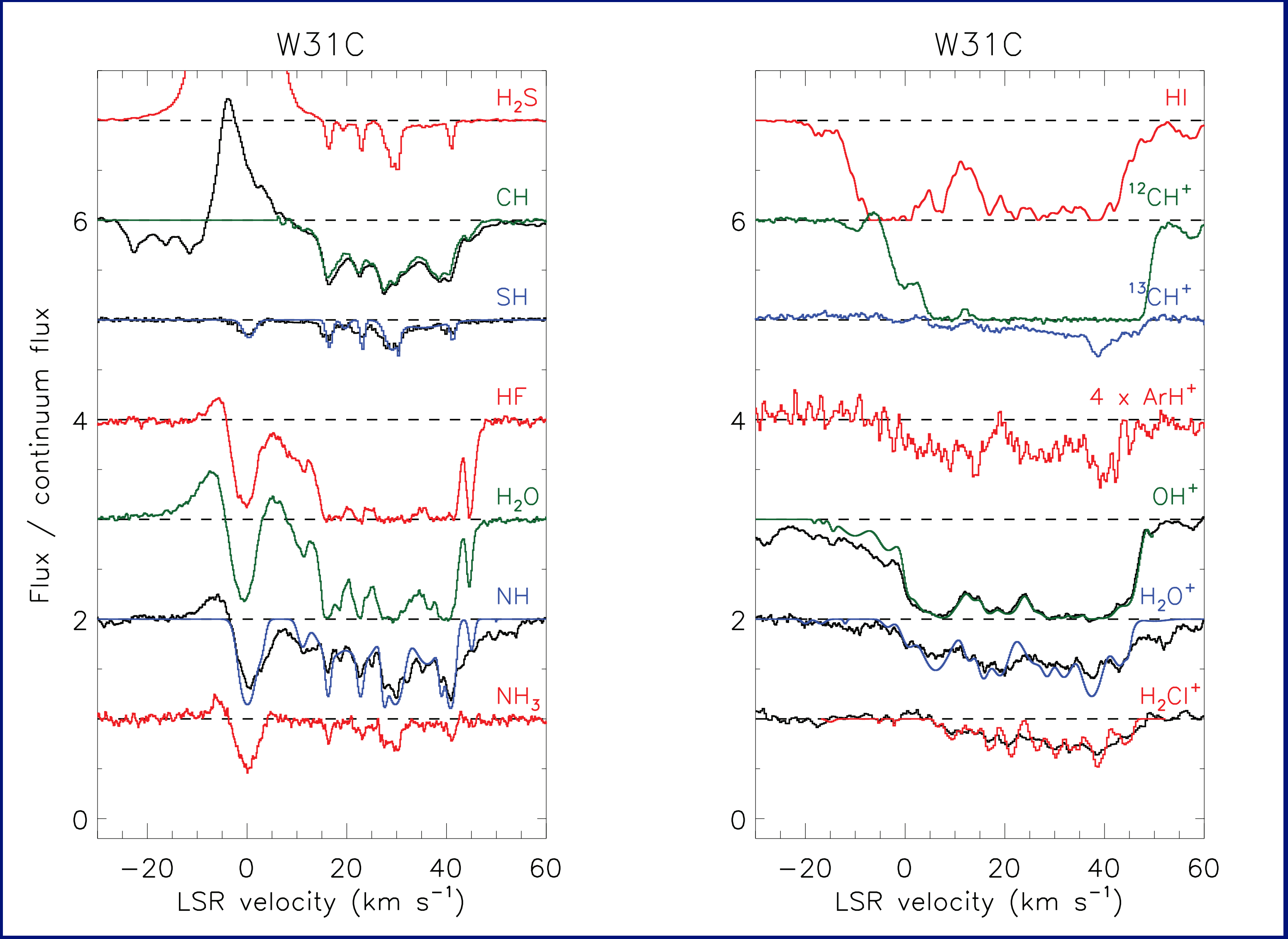


Hydride molecule formation ($X + H_2$ and $X^+ + H_2$)

Element	Ionization Potential (eV)	Endothermicity (Kelvin equivalent = $\Delta E/k_B$) for			Driver
		$X + H_2 \rightarrow XH + H$	$X^+ + H_2 \rightarrow XH^+ + H$	$X + H_3^+ \rightarrow XH^+ + H_2$	
He	24.587	No reaction	Exothermic, but primary channel is to $He + H + H^+$	29000	
C	11.260	11000	4300 ✓		Warm gas
N	14.534	15000	230	10000	Cosmic rays
O	13.618	940 ✓	✓	✓	Warm gas or cosmic rays
F	17.423	✓		10000	None needed
Ne	21.564	No reaction	Exothermic, but primary channel is to $Ne + H + H^+$	27000	
Si	8.152	17000	15000		Warm gas
P	10.487	19000	13000		Warm gas
S	10.360	10000	10000 ✓		Warm gas
Cl	12.968	450	✓		UV with $h\nu > 12.97$ eV
Ar	15.760	No reaction	✓	6400	Cosmic rays

Gerin, Neufeld & Goicoechea, 2016, ARAA, submitted.

Hydride detections in diffuse clouds (*Herschel*, SOFIA…)



Gerin, Neufeld & Goicoechea, 2016, ARAA, submitted.

Are all ion-neutral reactions fast enough?

$$A^{+} + BC \rightarrow AB^{+} + C$$

The formation rate of the product AB^+ is given by

$$A^+ + BC \rightarrow AB^+ + C$$

$$\text{Formation rate } (AB^+) = k\, n(A^+)\, n(BC)$$

Does k [$cm^3\ s^{-1}$] depend on the gas temperature?

Laboratory:

For most of these reactions (exothermic and BC non-polar):

***k* does not depend on the temperature**

and is of the order of $10^{-9}\ cm^3\ s^{-1}$ (high!)

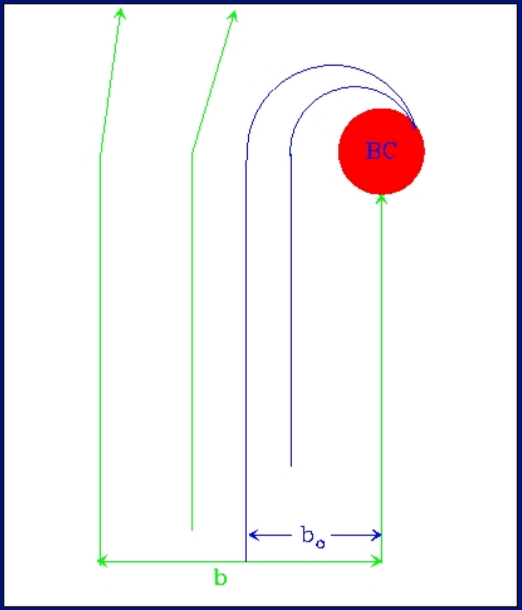
Why?

Start with the classical treatment of the "collision capture" problem.

Let BC be a non-polar molecule.

A^+ induces a dipole moment in BC during the collision process.

The energy produced in the collision reorders the orbitals and overcome any possible activation barrier.



$$A^{+} + BC \rightarrow AB^{+} + C$$

The collisional cross section σ is πb_0^2 (area) and the reaction rate is given by

$$k = \sigma \cdot v = \pi\, b_0^2\, v = \ldots = 2\,\pi\, e\,(\alpha / m)^{1/2} \qquad [cm^3\, s^{-1}]$$

and <u>does not depend on T</u>, only on the polarizability and on the reduced mass of the system !!!

This reaction rate is known as "The Langevin rate" (1905)

Example:

$$O^+ + H_2 \rightarrow OH^+ + H$$

Langevin value $1.6 \cdot 10^{-9}$ cm^{3}s^{-1}
Experimental value $(1\text{-}2) \cdot 10^{-9}$ cm^{3}s^{-1}

The other reaction "channel" :

$$O^+ + H_2 \rightarrow OH + H^+$$

is slightly endothermic

$D(H_2)$=4.48 eV y $D(OH)$=4.39 eV

and thus less probable than the OH^+ formation

What happens in ion-neutral reactions if the BC molecule is polar ?

-Rate coefficients for ion-polar reactions may be factors of 10-100 larger than Langevin values at low T, because $V(R) \propto R^{-2}$

Example:

$$C^{+} + OH \rightarrow CO^{+} + H$$

A classical treatment of the problem ("ADO" = Averaged Dipole Orientations) of the dipole interaction

$$k_{ADO} = 2\pi e \left(\alpha^{1/2} + c\,\mu_D \left(2/\pi kT\right)^{1/2}\right)$$

Where μ_D is the dipole moment of the molecule, T is the gas temperature and c is a function of $\mu_D / \alpha^{1/2}$

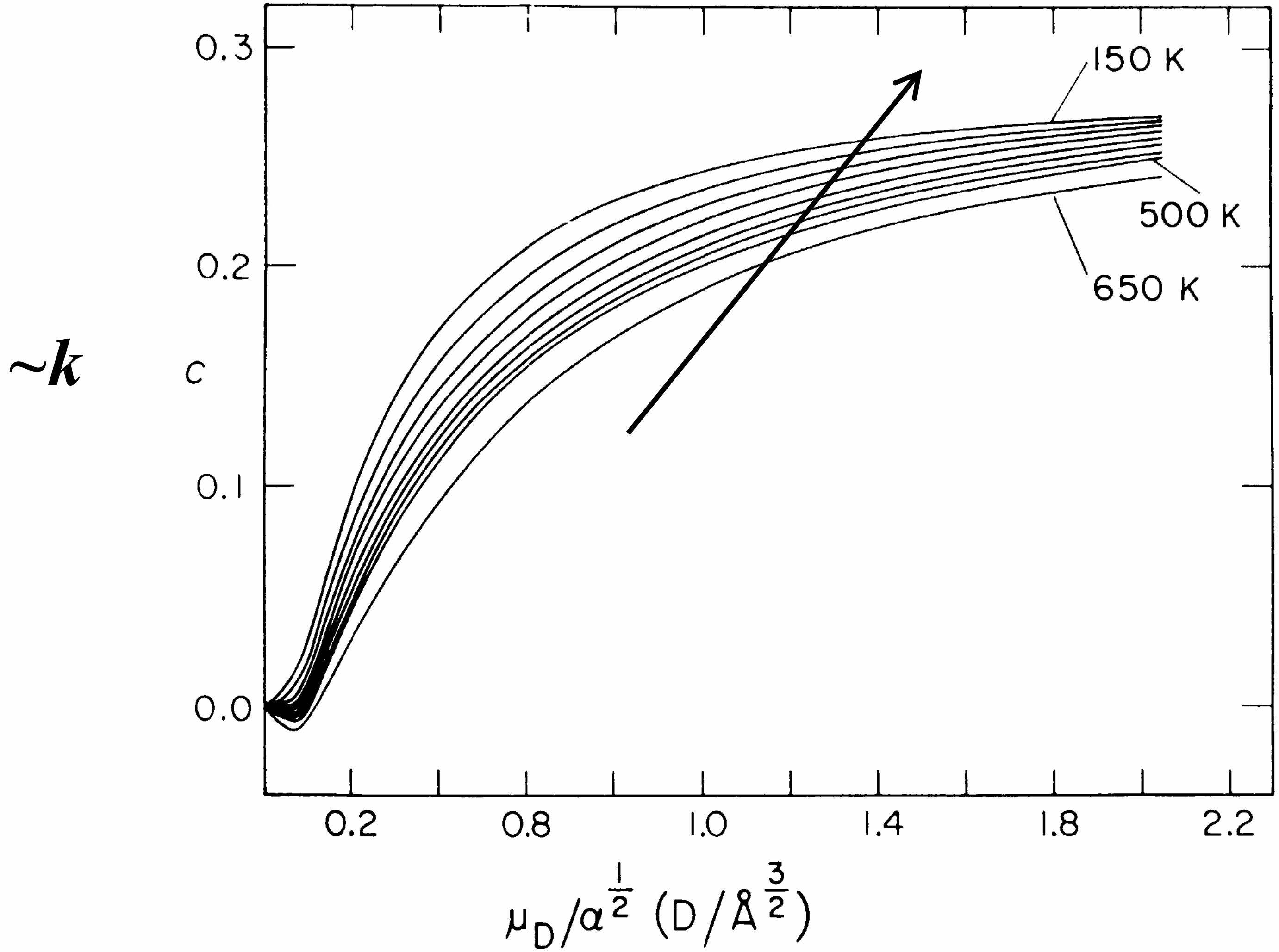


Fig. 3.2 Plot of the constant c against $\mu_D/\alpha^{\frac{1}{2}}$ for temperatures of 150–500 K at intervals of 50 K, and for a temperature of 650 K. (T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, 1975, **17**, 211.)

Reaction rate *k* depends on the gas temperature <u>inversely</u> (ion – polar neutral)

But keep in mind that…

<u>Maybe</u> at low temperatures these simple "semi-classical" theories are just approximations (low velocities and hence long interaction times between the particles, quantum calculations & lab. experiments are needed).

Close interactions between physico-chemists (both laboratory and quantum calculations) and astronomers needed !!

Which are the key processes in ISM chemistry?

1) H_2 is formed on dust grain surfaces
2) We need atomic or molecular ions (ok for diffuse ISM→ UV)

But, how are atoms/molecules ionized *deeply* inside clouds ?

With cosmic rays !!! (e.g. high speed p^+, He nuclei with E~100-1000 MeV)

$$CR + H \rightarrow H^+ + e^- + CR$$

$$CR + H_2 \rightarrow H_2^+ + e^- + CR \quad \text{(unimolecular)}$$

$$H_2 + H_2^+ \rightarrow H_3^+ + H$$

and H_3^+ a key molecule !! Formation_rate(H_3^+) = $\zeta_{CR}\, n(H_2)$
with $\zeta_{CR} \approx 10^{-16} - 10^{-17}\ s^{-1}$ "CR ionization rate"

H_3^+ does not react with H_2, ionization source for other species

THE FORMATION AND DEPLETION OF MOLECULES IN DENSE INTERSTELLAR CLOUDS*

ERIC HERBST† AND WILLIAM KLEMPERER

THE ASTROPHYSICAL JOURNAL, 185:505–533, 1973 October 15

Ionization is produced in dense clouds by cosmic rays sufficiently energetic to penetrate the interior. Since H_2 and He are the dominant species, the major initial ions produced are H_2^+, H^+ (Solomon and Werner 1971), and He^+. The exothermic reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ is rapid (Bowers, Elleman, and King 1969), but the highly exothermic reaction of He^+ with H_2 does not occur for kinetic reasons (Fehsenfeld *et al.* 1966*b*). Thus He^+, unlike H_2^+, will exist in appreciable concentration. Having an electron affinity of 24 eV, He^+ ionizes most neutral species other than H_2 rapidly. The reactions of the primal ions—H^+, H_3^+, He^+—with abundant neutral species such as CO, O, N, O_2, and N_2 produce secondary ions such as C^+, N^+, O^+, N_2^+, O_2^+, HCO^+, and HN_2^+.

$$CR + H_2 \rightarrow H_2^+ + e^- + CR$$
$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

The role of H_3^+ …

PROTON TRANSFER

H_2 has a low proton affinity and the reactions of H_3^+ with neutral species (B) will always produce BH^+ (molecular ions!)

$$H_3^+ + B \rightarrow BH^+ + H_2$$

if the reaction is exothermic (proton transfer).

PROTON AFFINITIES

H	2.69	O_2	4.34
H_2	4.34	CO	6.20
He	1.82	NO	4.99
O	5.03	C_2	7.20
C	6.46	CN	4.99
N	4.21	N_2	5.03
		CS	7.57

H_3^+ will transfer protons to all atoms (except N, H y He) and to most molecules

e.g., $H_3^+ + CO \rightarrow HCO^+ + H_2$

RADIATIVE RECOMBINATION [SLOW!]

$X^+ + e^- \rightarrow X + h\nu$ (reverse of photoionization)

These mechanisms produce neutral species from a chemistry based on ion-neutral reactions.

In this reaction the energy excess of the system is released as radiation.

e.g. (deep in molecular clouds) $Fe^+ + e^- \rightarrow Fe + h\nu$

IP =7.9eV

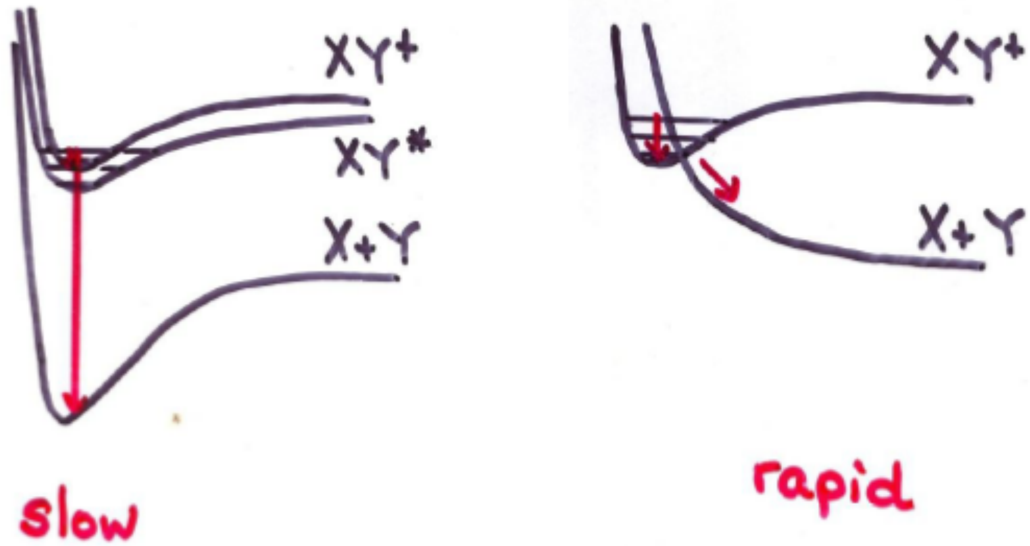
Typical reaction rates are slow $k_{RR} \approx 10^{-12}\ cm^3\ s^{-1}$

Molecular ions recombine much faster through other mechanism…

- Molecular ions: $XY^+ + e \rightarrow XY + h\nu$
  $\rightarrow X + Y$

Radiative: slow

Dissociative: rapid at low T



- Need curve crossing between XY^+ and repulsive XY potential for reaction to proceed fast

DISSOCIATIVE RECOMBINATION

Molecular positive ions recombine with electrons to dissociate into neutral species (not by radiating a photon)

$$ABC^{+} + e^{-} \rightarrow BC + A$$

Reaction rates have a $T^{-1/2}$ dependence!

Typical values for the dissociative recombination rate are

$$k_{DR} \approx 10^{-6} - 10^{-7}\ \mathrm{cm^{3}\ s^{-1}}\ \ \text{(fast)}$$

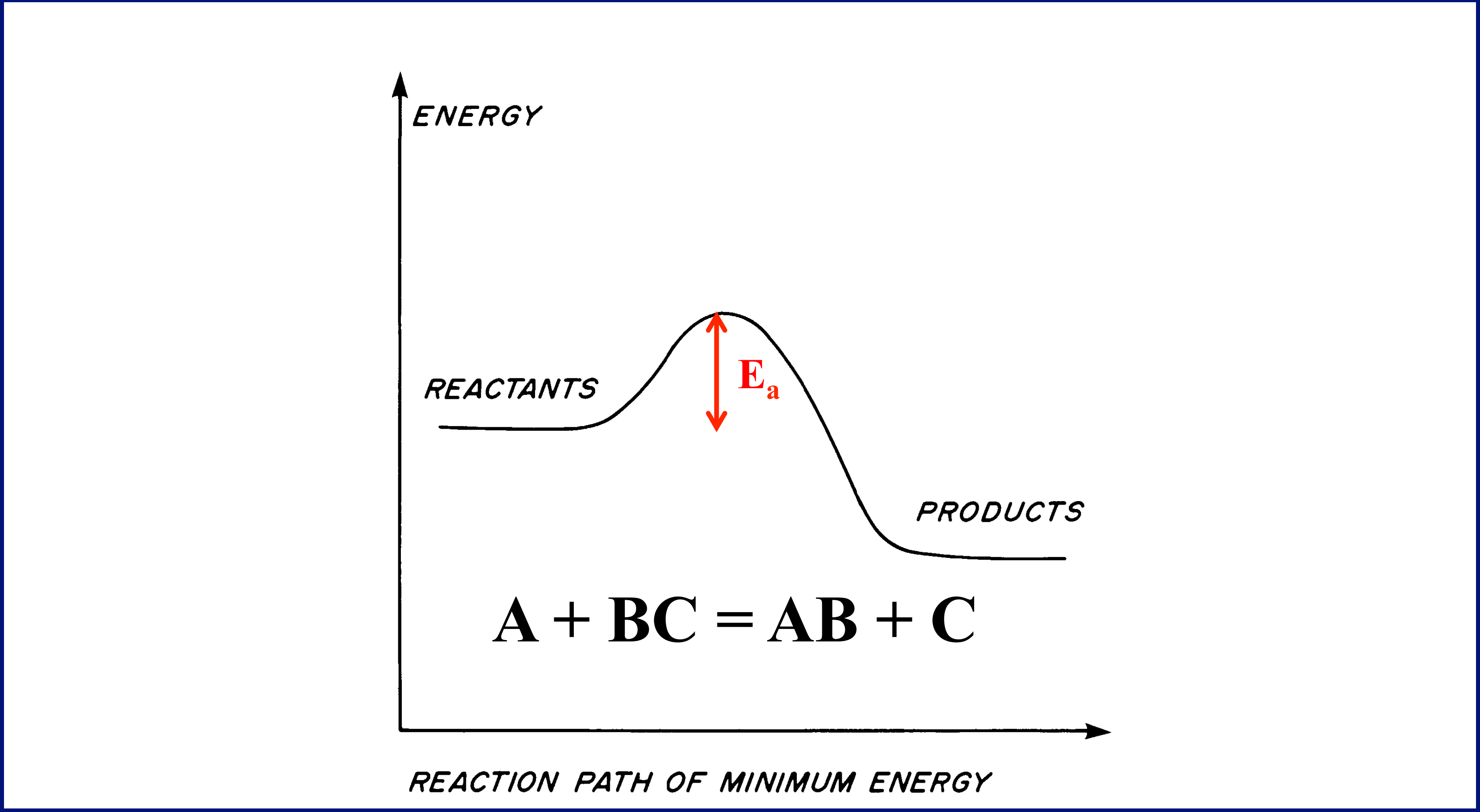
e.g. $HCO^{+} + e^{-} \rightarrow CO + H$

These reactions are very important in ISM even if $n(e^{-})/n_H \sim 10^{-4}$-$10^{-8}$ (ionization fraction)

NEUTRAL-NEUTRAL REACTIONS

$$A + BC = AB + C$$

* Long-range attraction weak: van der Waals interaction $\sim 1/R^6$
* Strong temperature dependence has been found for many of these reactions + activation energy barriers E_a



NEUTRAL-NEUTRAL REACTIONS (Energy Barriers)

$$k(T)=A(T)\ \exp\ (-E_a\ /kT)$$

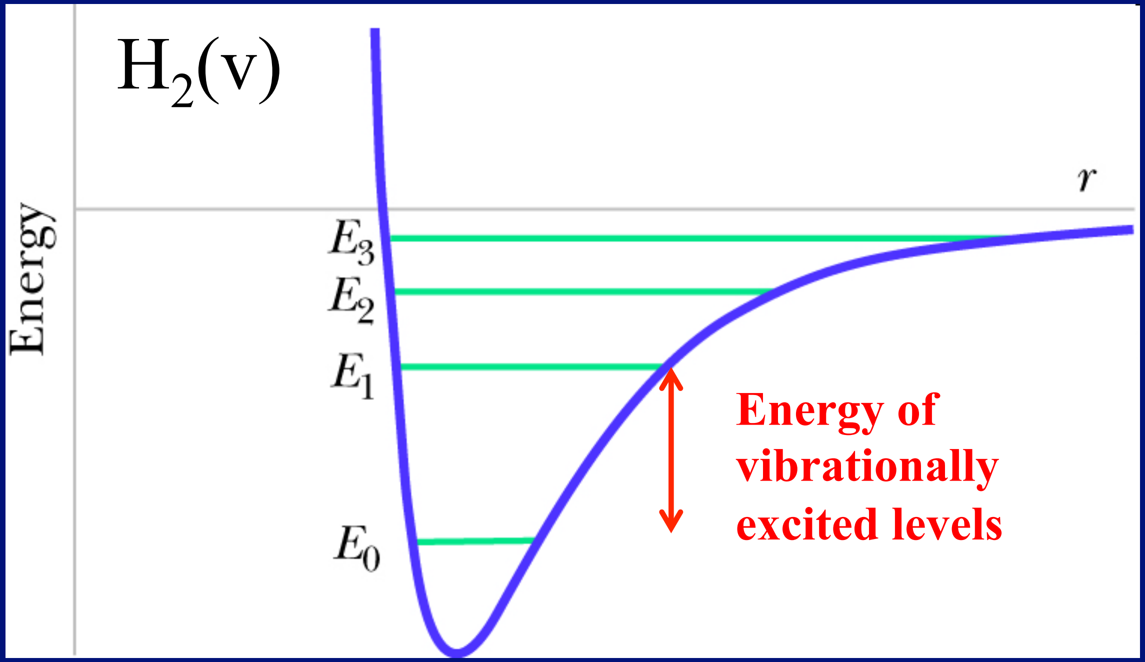
	$A(cm^3s^{-1})$	$E_a(K)$	
$H + H_2CO = H_2 + HCO$	$2.7\ 10^{-11}$	1300	
$H + H_2S = H_2 + SH$	$1.3\ 10^{-11}$	860	
$H + O_2 = OH + O$	$3.7\ 10^{-10}$	8500	
$O + H_2 = OH + H$	$1.0\ 10^{-11}$	5700	(E~-920K)
$O + H_2S = OH + SH$	$6.6\ 10^{-13}$	900	
$OH + CO = H + CO_2$	$5.1\ 10^{-13}$	300	

ISM: need high temperature conditions
(e.g., shocks in protostellar outflows)

State-to-state chemical reactions
(Vibrationally excited H_2)

"Non-thermal reactions" may overcome endothermicities or activation energy barriers E_a

H_2 (v=0) + C^+ $\rightarrow$ CH^+ + H (endothermic by 0.39 eV or 4600 K)



The H_2 (v=1) level has an energy of ~0.5 eV (~5800 K)

- In some particular cases the H_2 (v>0) levels can be significantly populated e.g. by absorption of UV photons in Photodissociation Regions.

State-to-state chemical reactions

(effects of UV-pumped vibrationally excited H_2)

THE ASTROPHYSICAL JOURNAL, 713:662–670, 2010 April 10 doi:10.1088/0004-637X/713/1/662

THE CHEMISTRY OF VIBRATIONALLY EXCITED H_2 IN THE INTERSTELLAR MEDIUM

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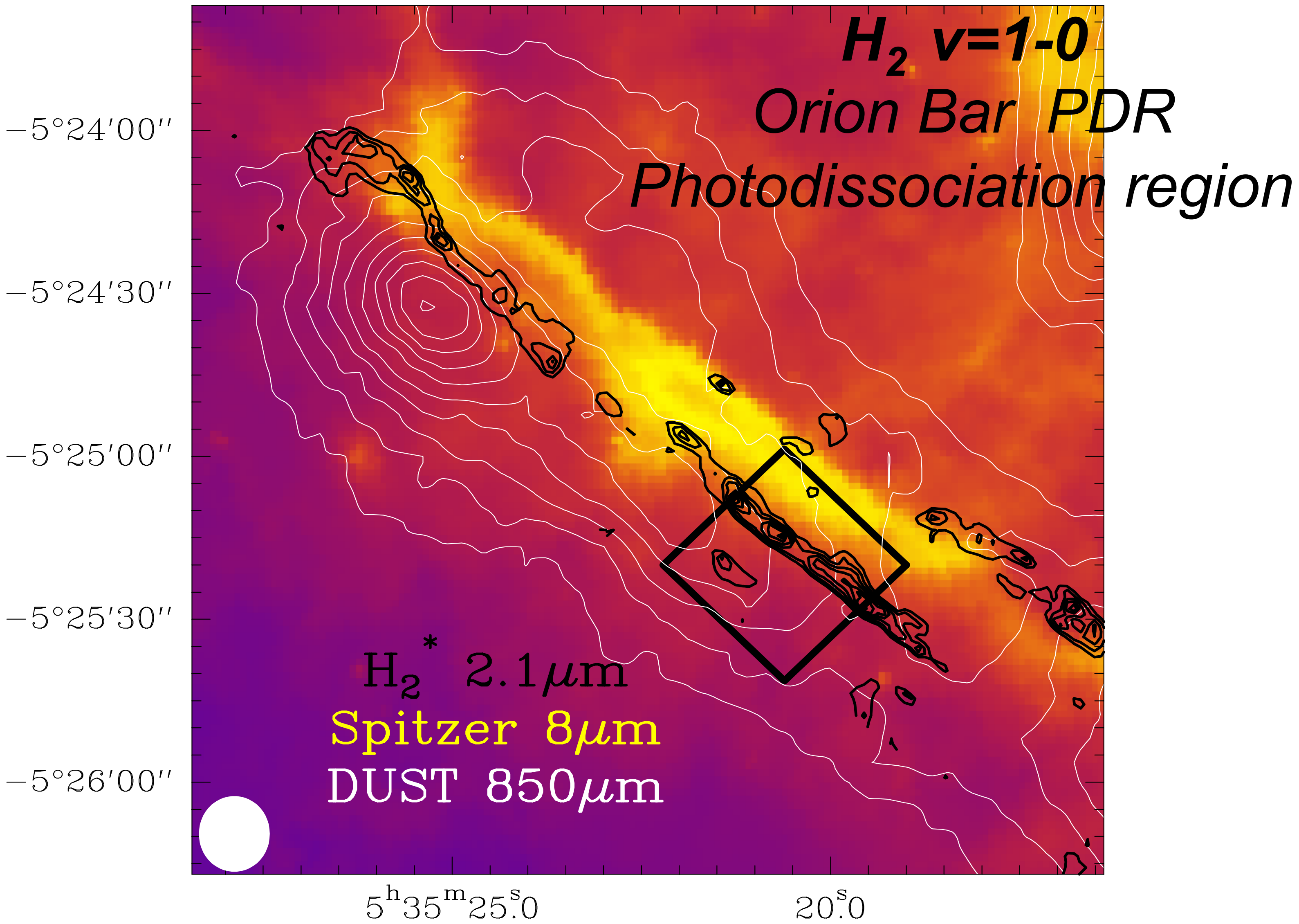
H_2 $(v \geq 1) + C^+ \rightarrow CH^+ + H$ (exothermic !!)

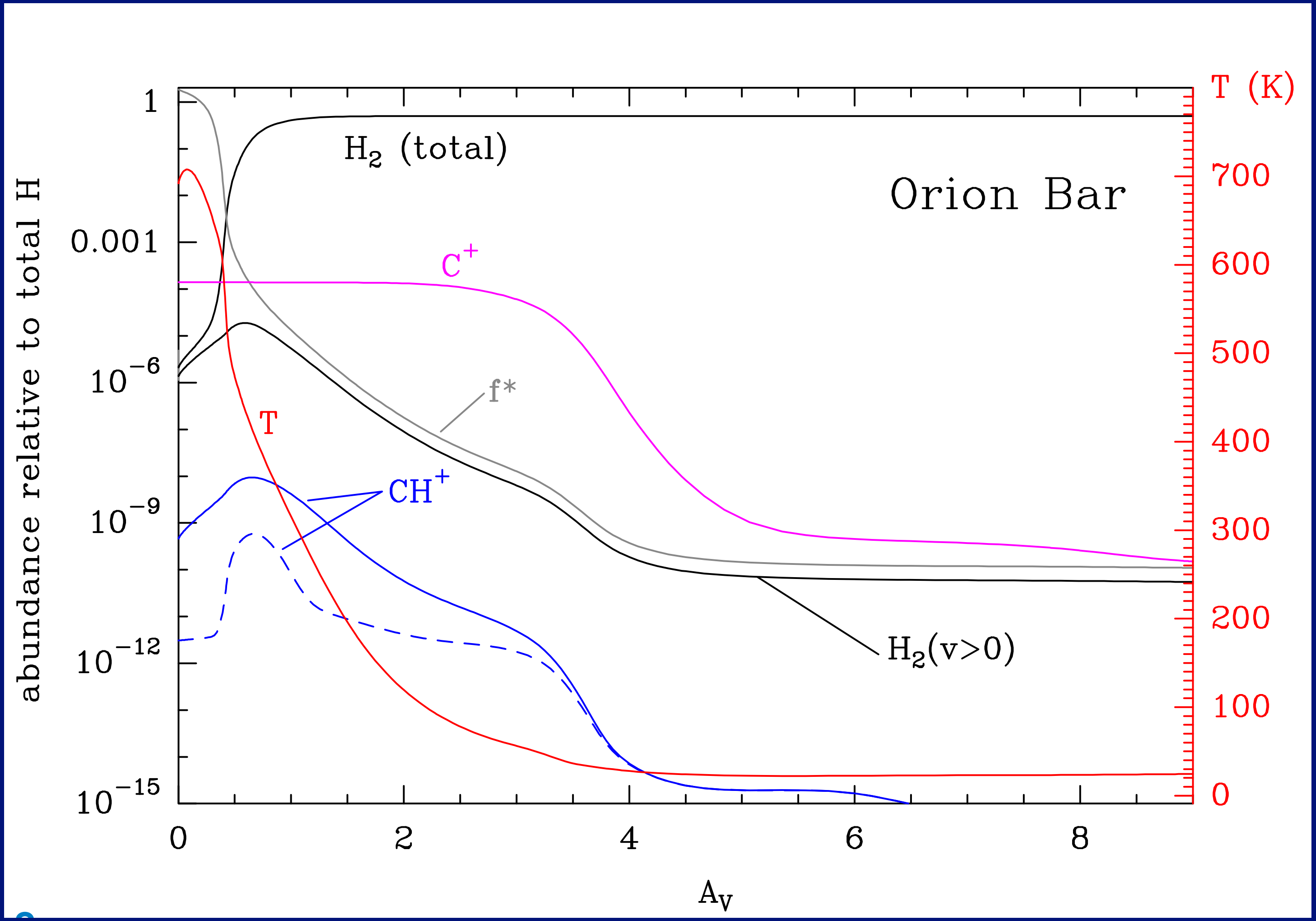
State-to-state chemical reactions

(effects of UV-pumped vib. excited H_2)



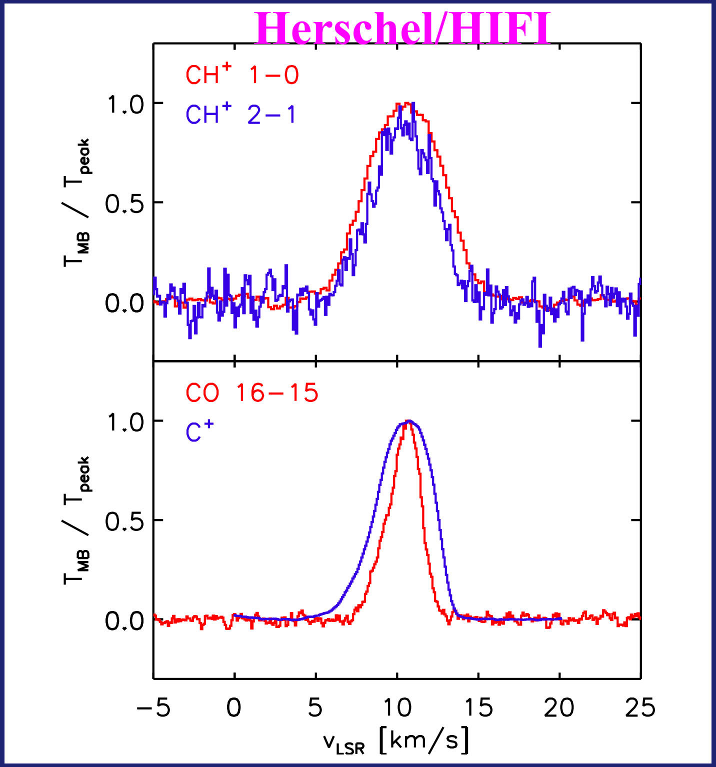
Non-thermal reactions may overcome endothermicities or activation energy barriers E_a

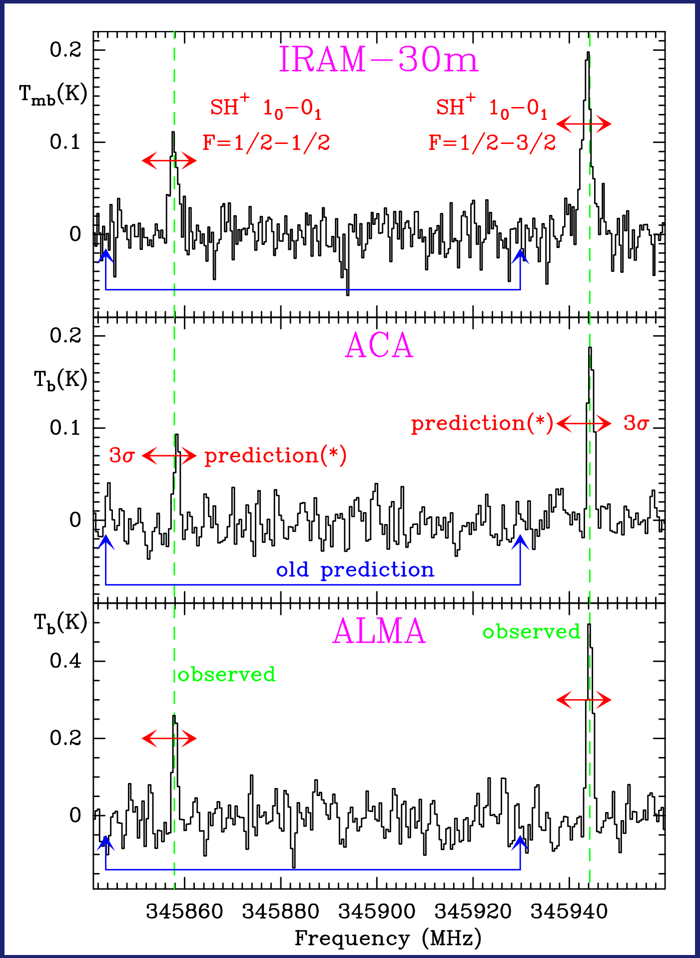
Agúndez, Goicoechea et al. 2010, ApJ (Orion Bar)



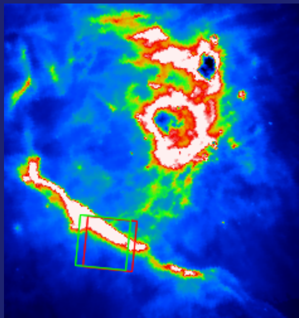
Effect of $H_2\ (v \geq 1) + C^+ \rightarrow CH^+ + H$

CH^+, SH^+ in the Orion Bar





Confirmation of UV-pumped H_2 (v ≥ 1) reactions with C^+ and S^+

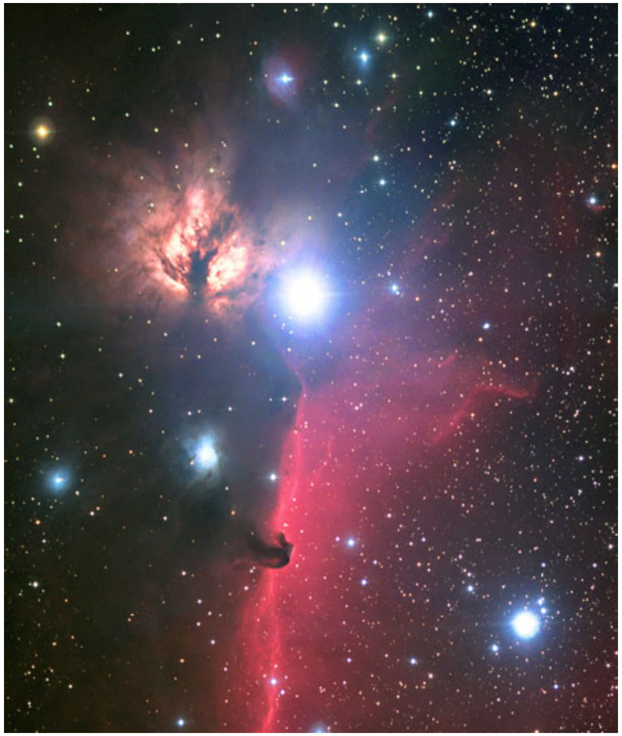


Models with H_2^* : Agúndez et al. 2010, ApJ, Zanchet et al. 2013, AJ

***Detections*:** Nagy et al. 2013, A&A; Müller, Goicoechea et al. 2014, A&A

UV photodissociation and photoionization (PDRs)

The main path to destroy molecules in UV illuminated gas is photodissociation and photoionization



<u>What do we need to know ?</u>

1) The electronic, vibrational and rotational levels of each molecule

2) The <u>far-UV radiation</u> field >911 A (<13.6eV)
(higher E photons ionize H atoms in HII regions)

- Experiments available for stable molecules, but not for radicals or ions
- Small molecules: quantum chemical calculations of potential surfaces of excited states + transition dipole moments, followed by nuclear dynamics to obtain cross sections

Phtodissociation (PDR) models

Where physics and chemistry are driven by FUV photons (13.6-6 eV)

UV-PROCESSES:

1) FUV flux attenuation

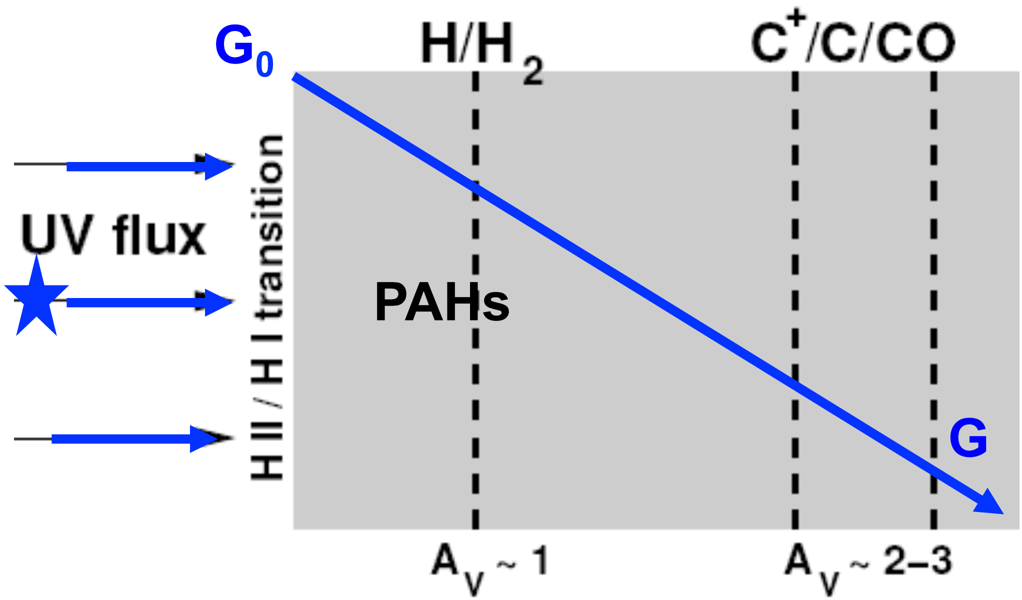
(dust extinction but also H_2 lines)

2) Chemistry

(photochemistry)

3) Gas heating and cooling → T_{gas}

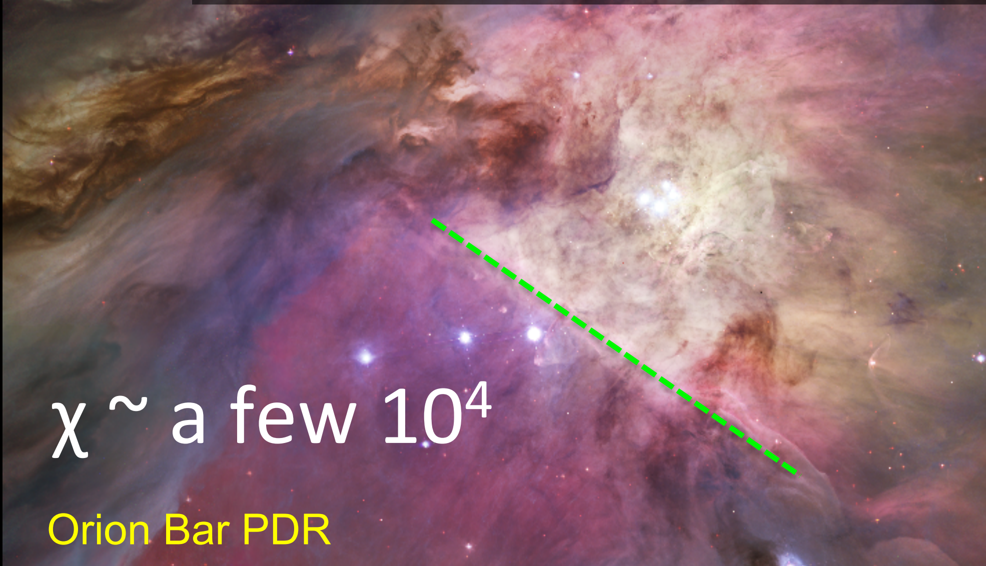
(photoelectric effect, line cooling, ...)

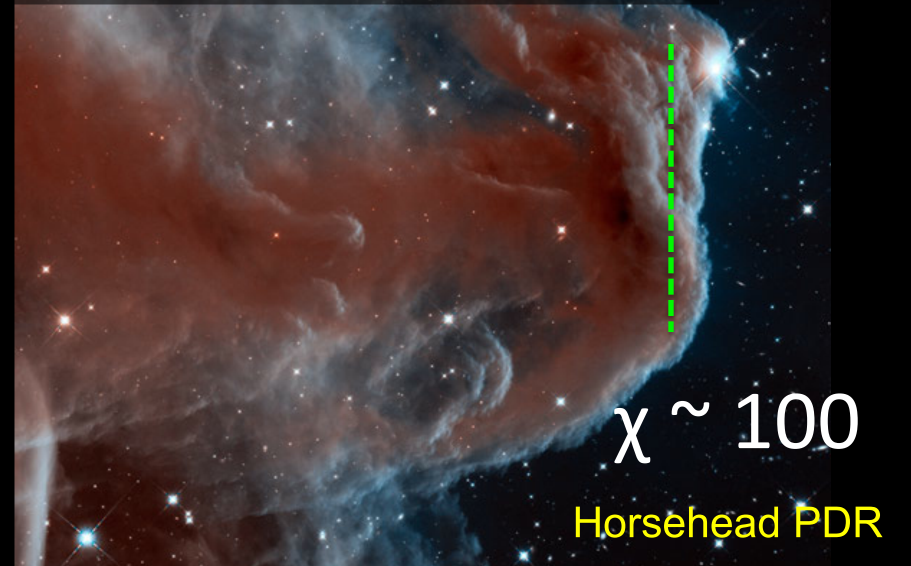


DETAILED PDR MODEL: **Meudon PDR CODE** http://pdr.obspm.fr/PDRcode.html

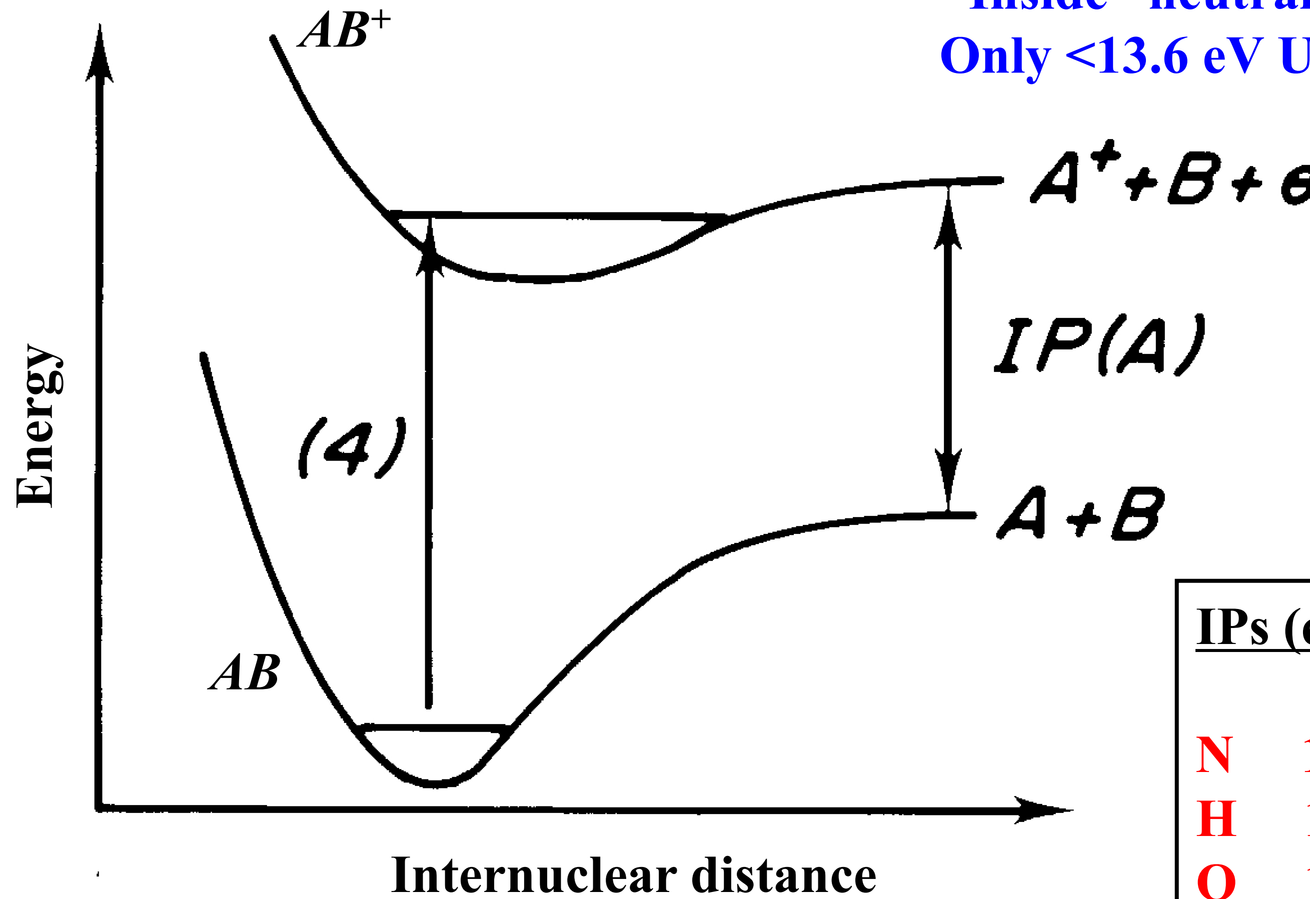
Le Petit et al. (2006), *Goicoechea & Le Bourlot (2007).* **Review: Hollenbach & Tielens 1999**

Templates to understand the emission from distant/unresolved UV-regulated environments





Inside "neutral" clouds:
Only <13.6 eV UV photons

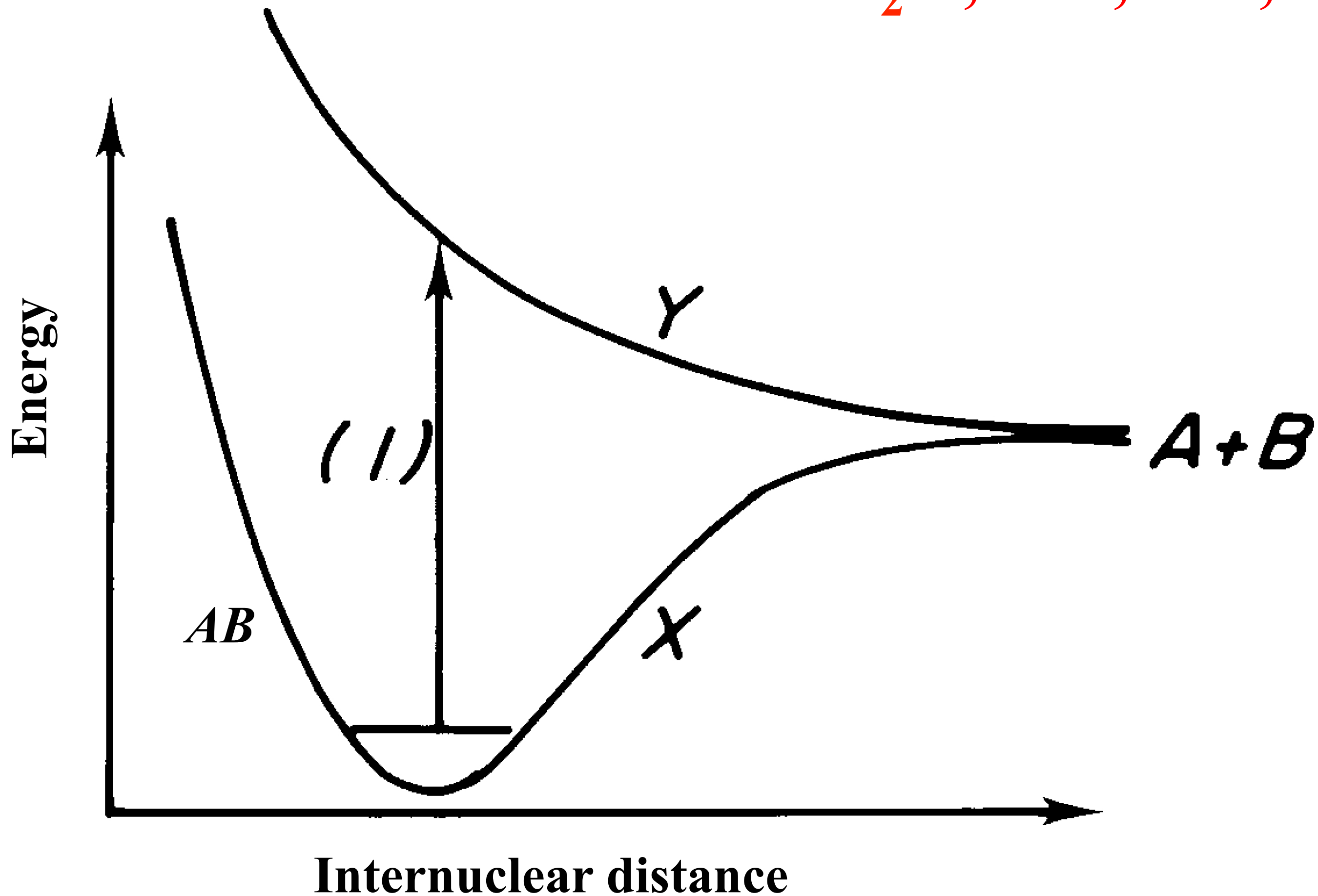


IPs (eV)	
N	14.6
H	13.6
O	13.6
C	11.3
S	10.4
Mg	7.7
H_2	15.4
CO	14.0
H_2O	12.6

"Photoionization"

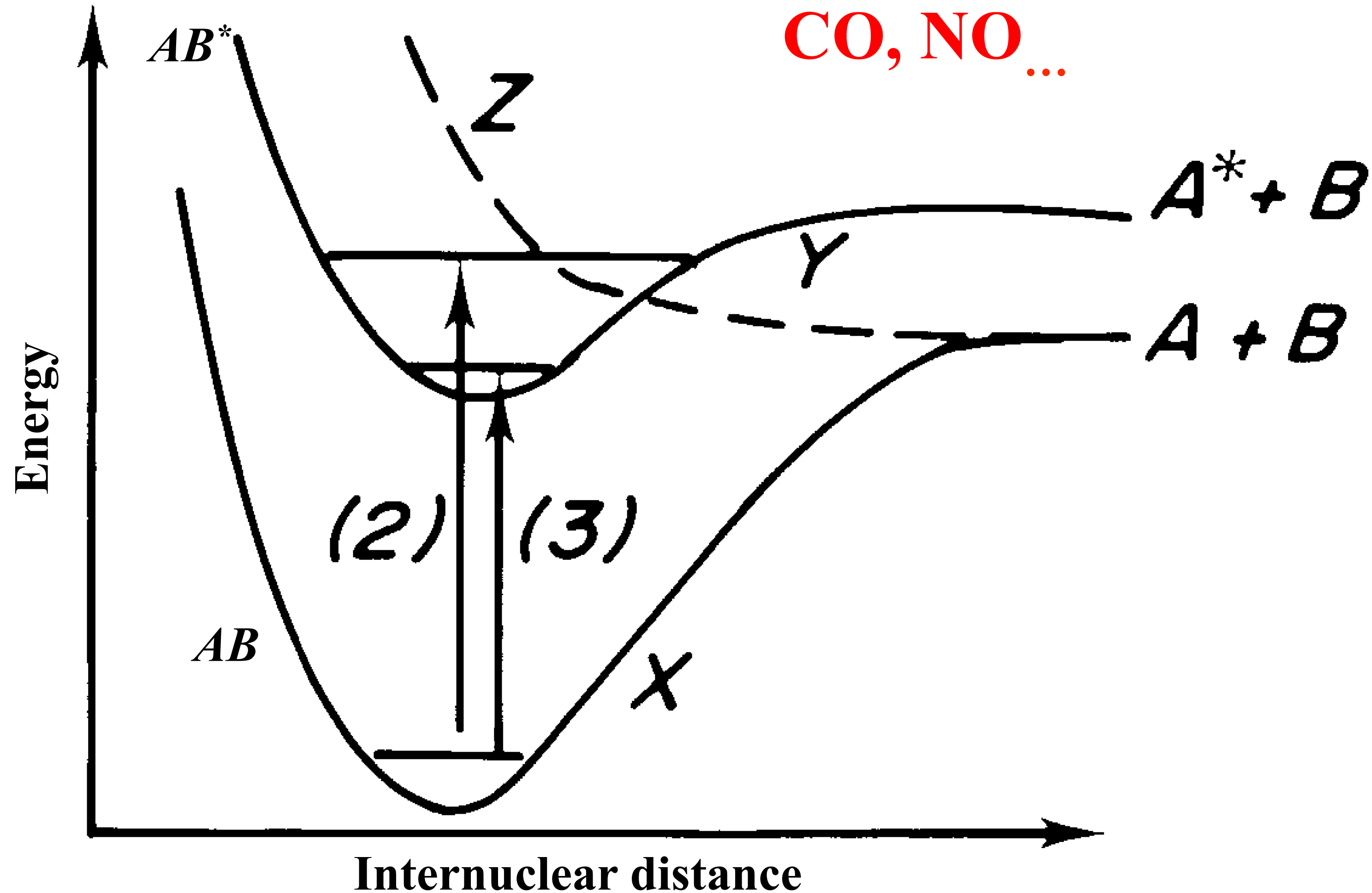
$$\mathrm{AB} + h\nu \xrightarrow[\beta]{} AB^+$$
$$\mathrm{C} + h\nu \longrightarrow C^+$$

H_2O, OH, CH, CH_2...



"Direct Photodissociation"

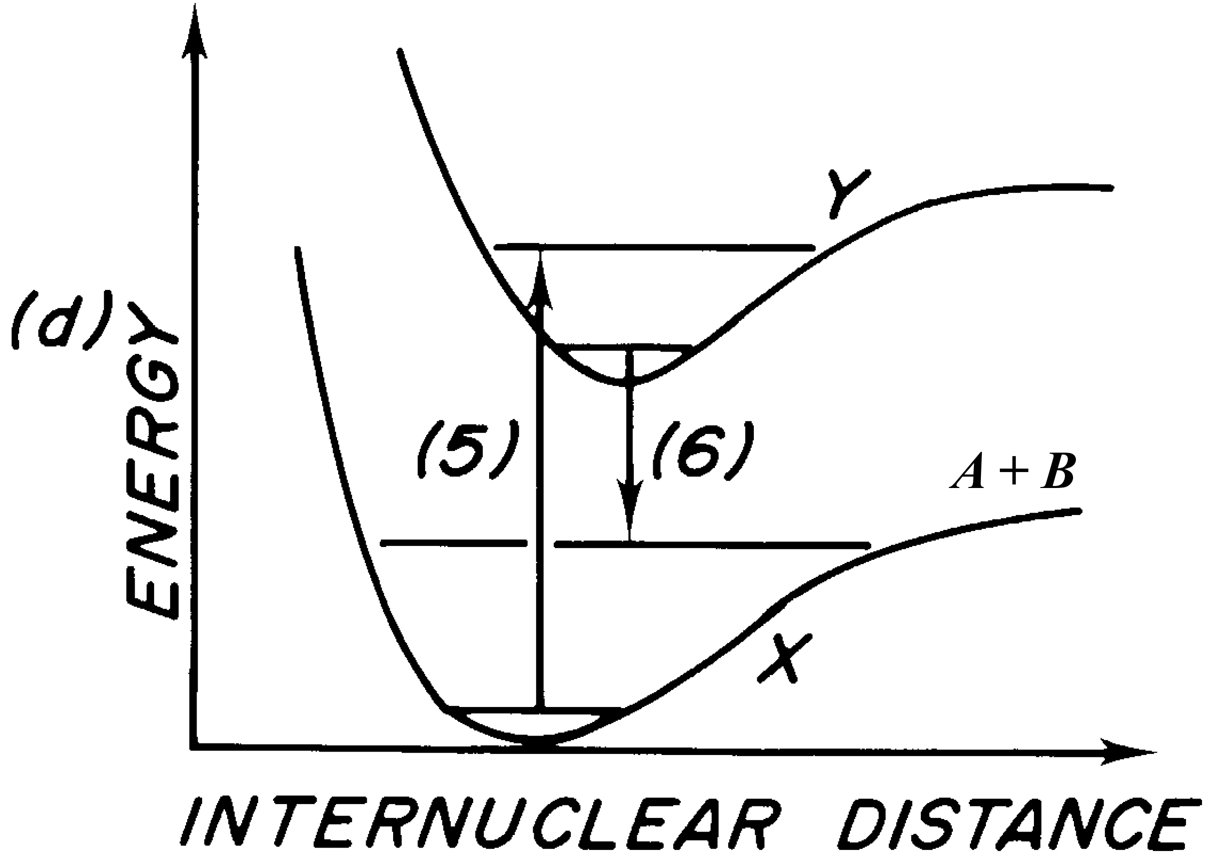
$$AB + h\nu \underset{\beta}{\longrightarrow} A + B$$



“Photo-Predisociation”

$$\mathbf{AB} + \boldsymbol{hv} \xrightarrow[\beta]{} \boldsymbol{AB^*} \rightarrow \boldsymbol{A} + \boldsymbol{B}$$

H_2



“Dissociation via fluorescent emission”

$$\mathbf{AB} + \boldsymbol{h\nu} \xrightarrow[\beta]{} \boldsymbol{A} + \boldsymbol{B}$$

H_2 photodissociation

$H_2(X^1\Sigma_g^+, v''=0) + h\nu \rightarrow H_2(B^1\Sigma_u^+, v')$ $\lambda < 1109A$
$\rightarrow H_2(C^1\Pi, v')$ $\lambda < 1109A$

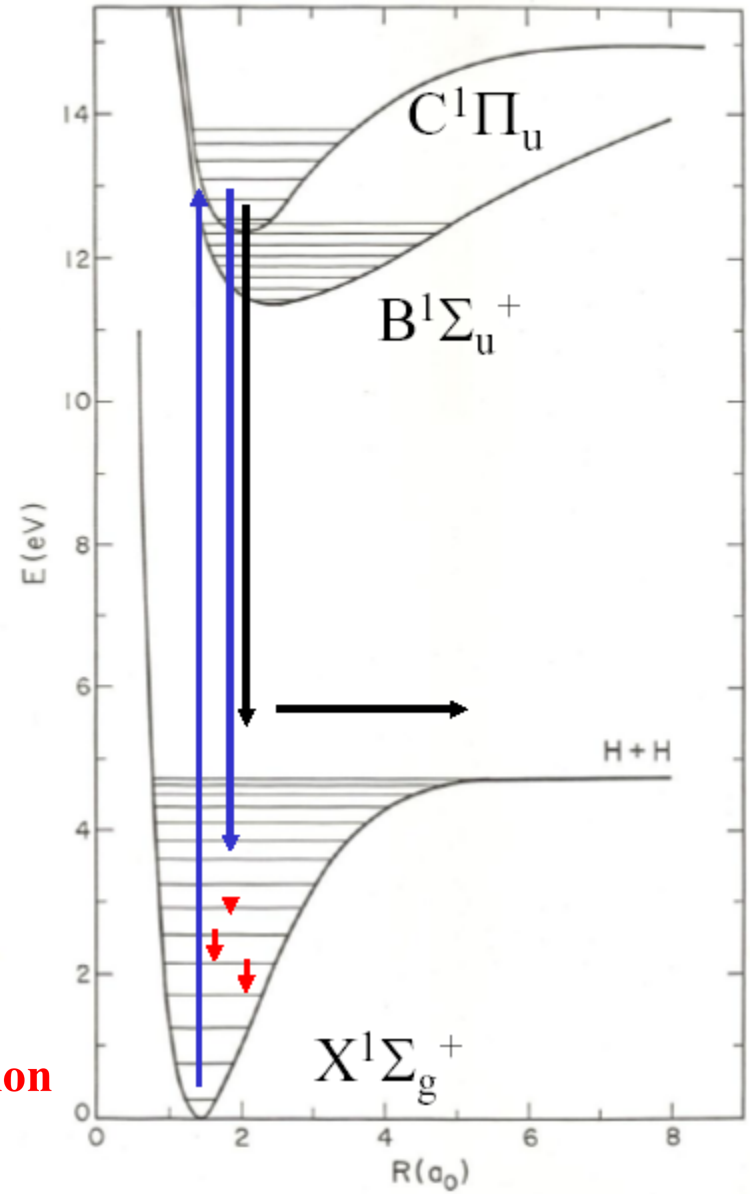
"Lyman and Werner bands"

There are *not* allowed electric dipole transitions from $X^1\Sigma_g^+$ to repulsive electronic states with energies <13.6 eV !!

$H_2(B^1\Sigma_u^+, v') \rightarrow H_2(B^1\Sigma_g^+, v'') + h\nu$
$\rightarrow H + H + h\nu$

and

$H_2(B^1\Pi_u^+, v') \rightarrow H_2(B^1\Sigma_g^+, v'') + h\nu$
$\rightarrow H + H + h\nu$



90% of absorptions into B and C states are followed by emission back into bound vibrational levels of the X state 10% of the absorptions are followed by emission into the unbound vibrational continuum, leading to dissociation

The Astrophysical Journal, 628:750–757, 2005 August 1

Fluorescent H_2 emission in the FUV

FLUORESCENT MOLECULAR HYDROGEN EMISSION IN IC 63: *FUSE*, HOPKINS ULTRAVIOLET TELESCOPE, AND ROCKET OBSERVATIONS

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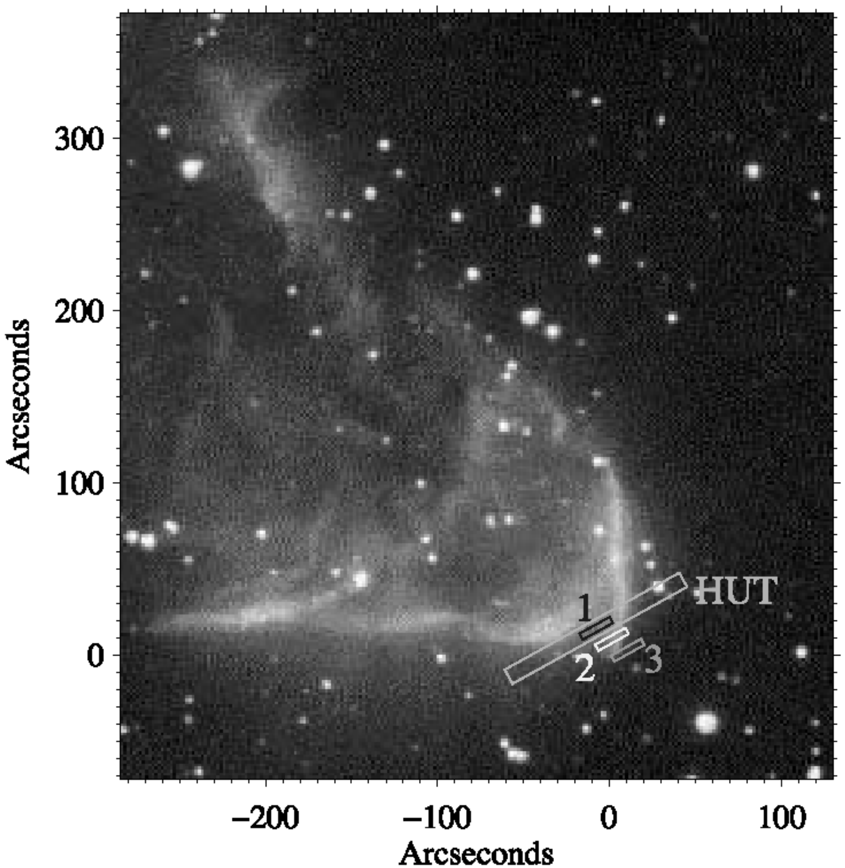
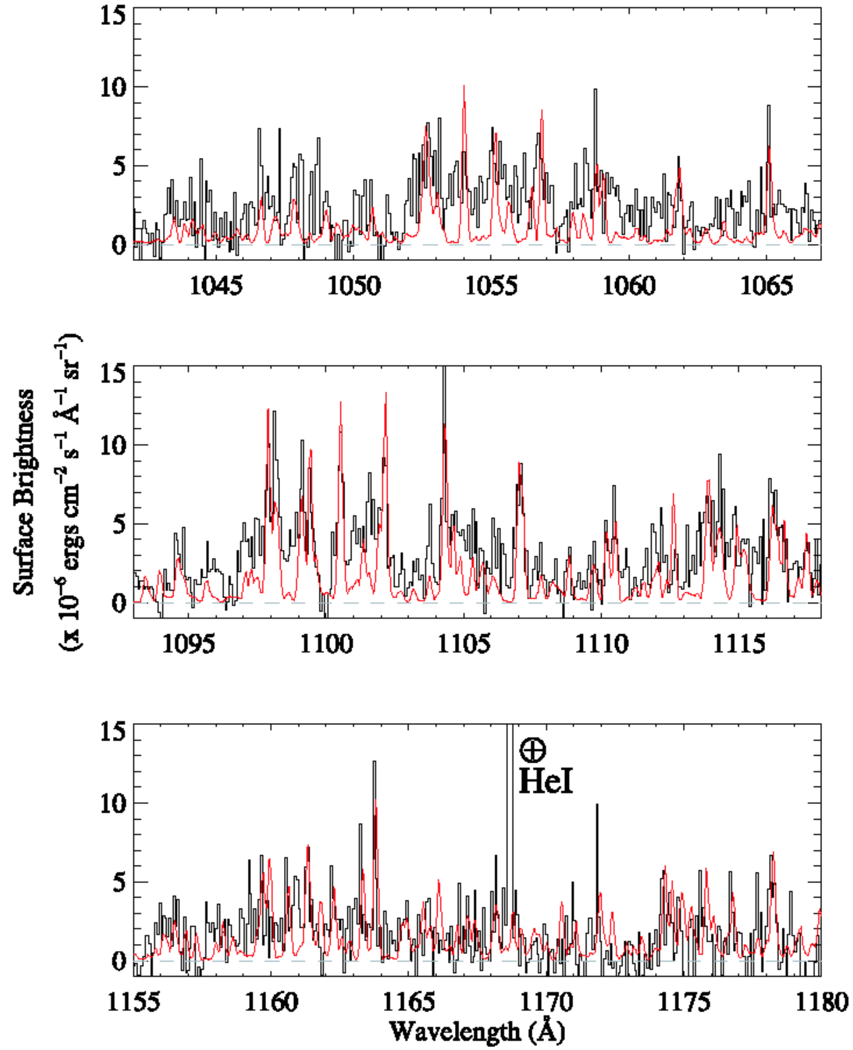
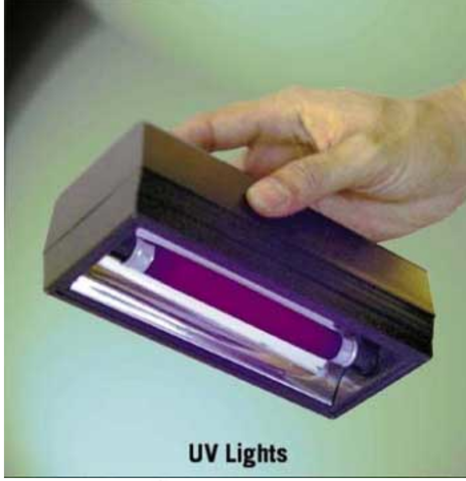




Interstellar radiation field



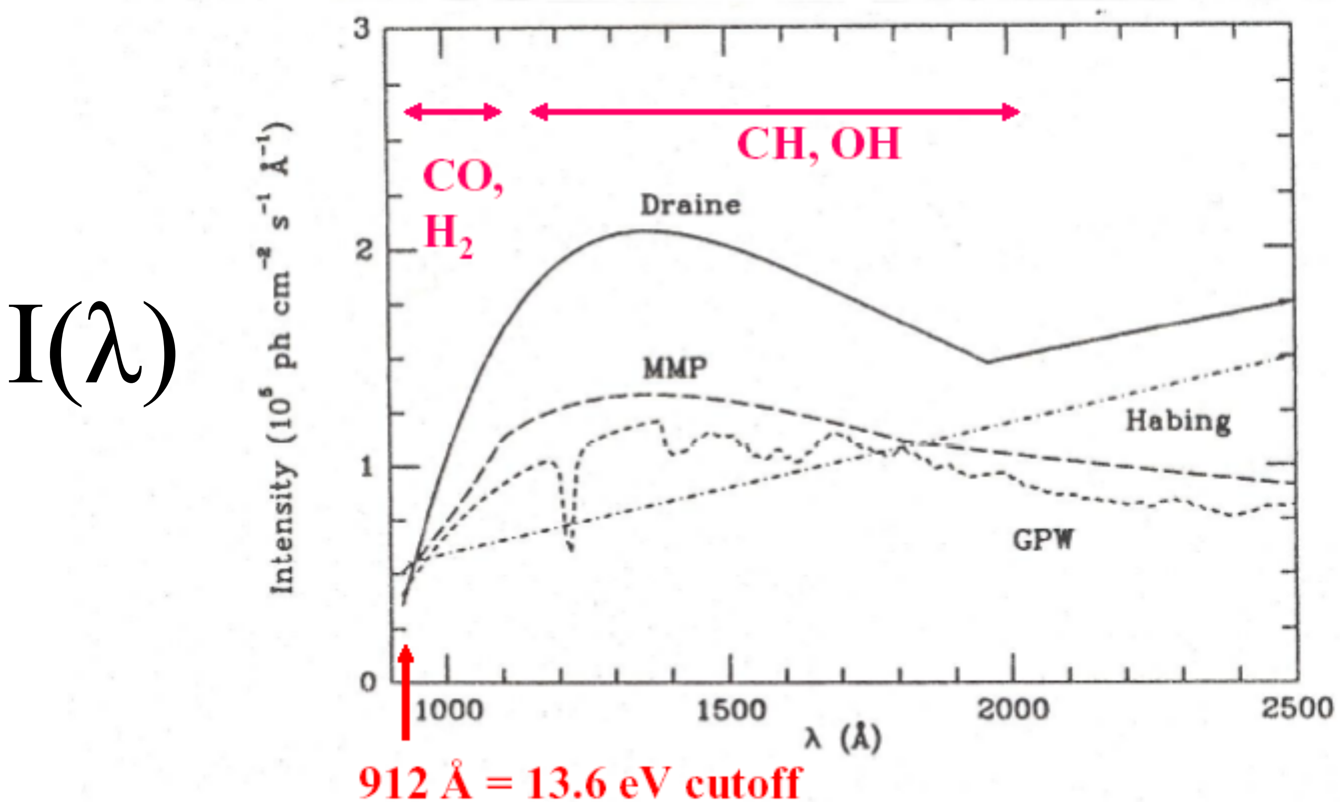
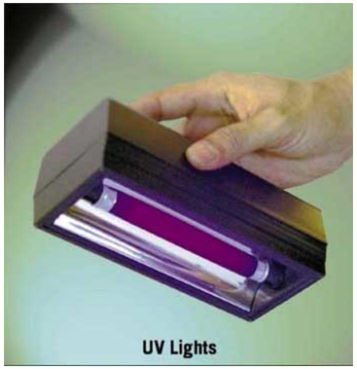


Figure 5. *The intensity of the interstellar radiation field as a function of wavelength cf. Draine (1978) (full line), Mathis et al. (1983) (long–dashed line), Gondhalekar et al. (1980) (short–dashed line) and Habing (1968) (dash–dotted line).*

Average radiation provided by young O + B stars



far-UV field
I =I (λ)
decreases
with
Av

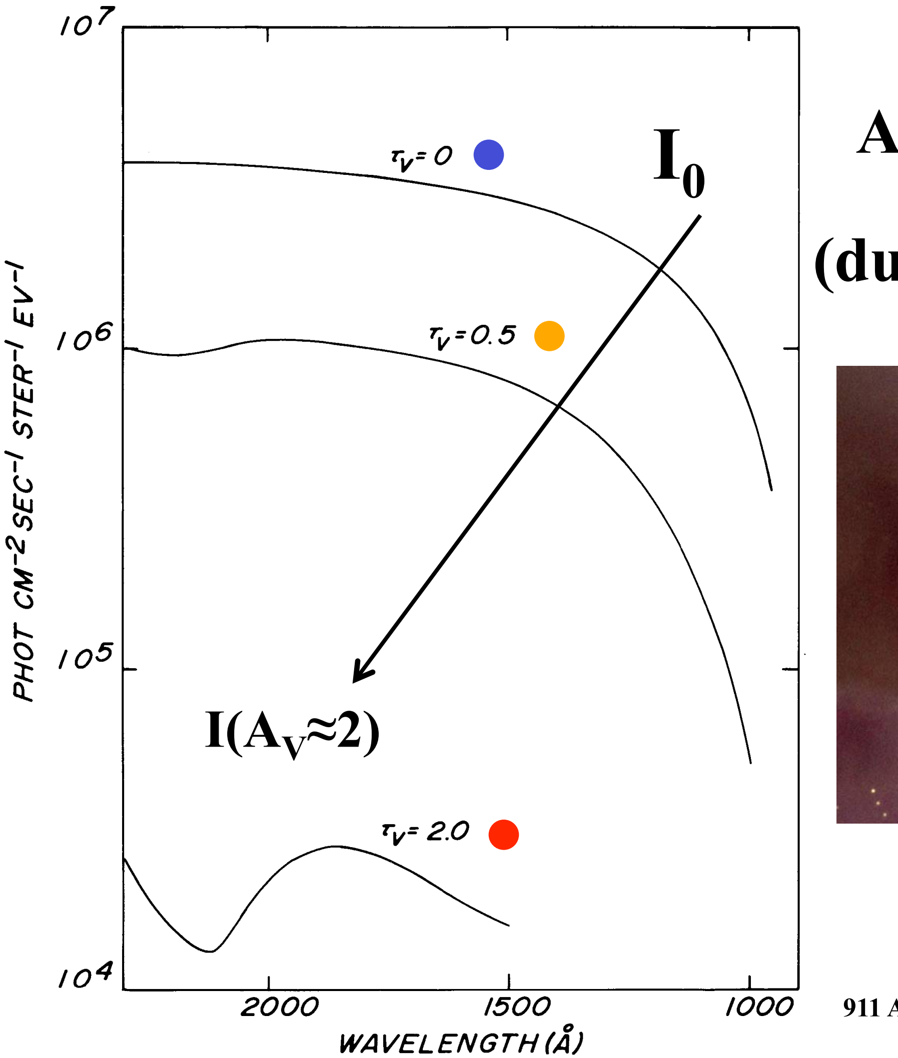
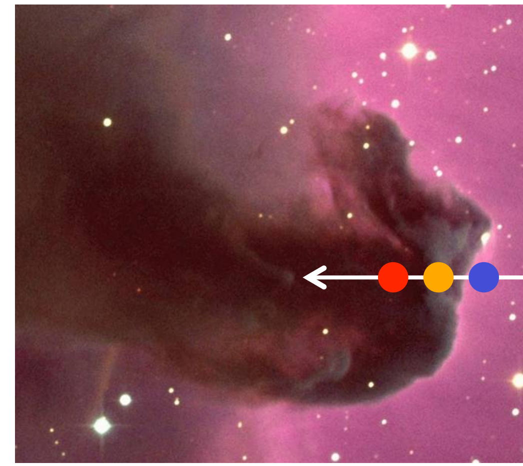


Fig. 4.4 The interstellar radiation flux $F(E)$ photons $cm^{-2}s^{-1}eV^{-1}ster^{-1}$ in unobscured regions of the interstellar medium, in a typical diffuse cloud with $\tau_v \approx 0.5$, and in a denser cloud with $\tau_v \approx 2$.

$A_V = 1.086 \cdot \tau_V$

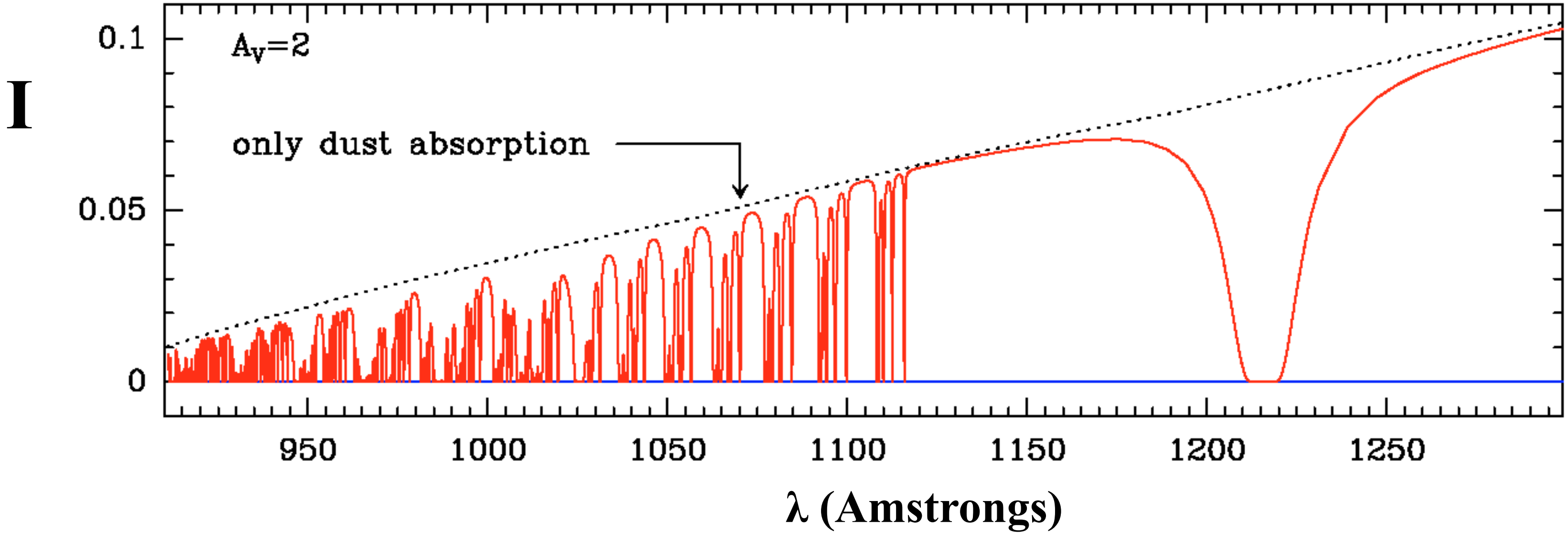
(dust attenuation)



FUV photons are mainly absorbed by dust grains

κ_{pd} photodissociation rate (<u>complex</u> calculation)

$$\beta = \kappa(A_V) = 4\pi \int_0^{13.6eV} I(E, A_V)\sigma_{PD}(E)\,dE$$



Goicoechea & Le Bourlot 2007, A&A

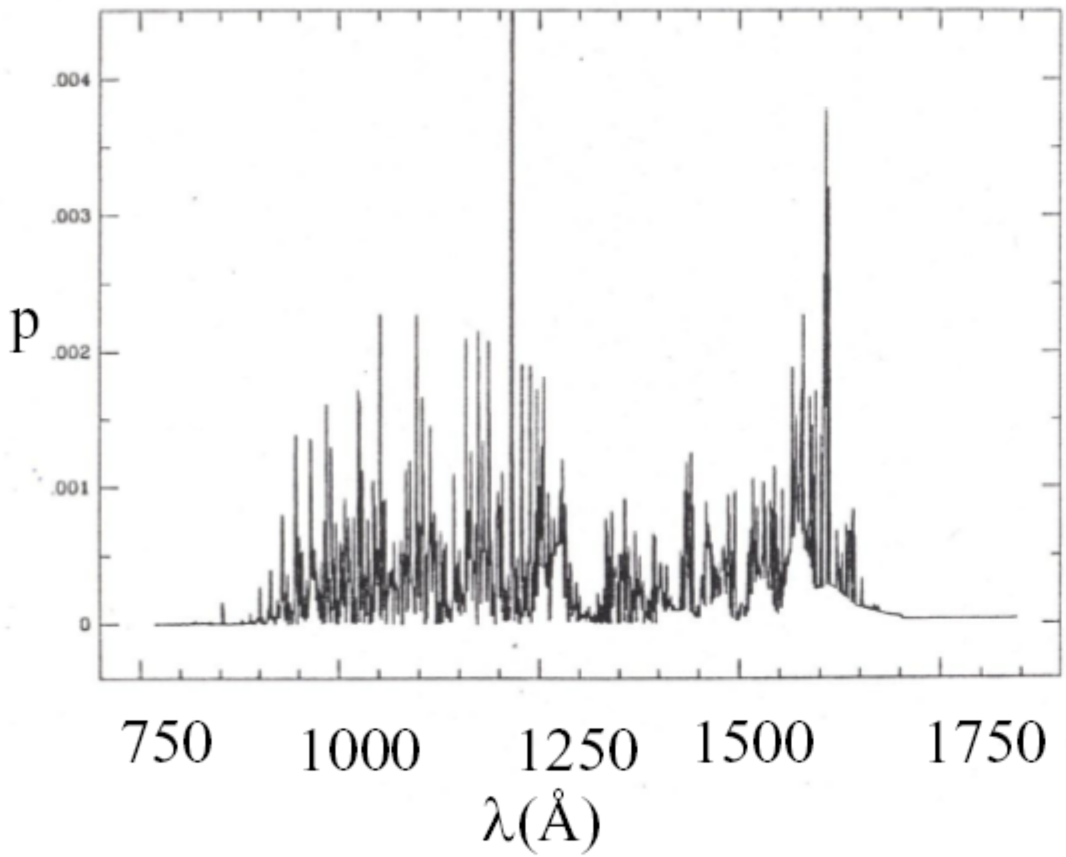
σ_{PD}= molecule photodissociation cross-section [cm^{-2}]

$$\kappa_{pd} = \beta_0 \exp(-\alpha A_V) \quad (s^{-1})$$

Table 4.1 Dissociation rates, β_0, and α [equation (4.14)] for simple molecules exposed to the unshielded interstellar radiation field. (S. S. Prasad and W. T. Huntress, Jr, *Astrophysical Journal Supplement Series*, 1980, **43,** 1.)

Molecule	β_0 (s^{-1})	α	Molecule	β_0 (s^{-1})	α
H_2	5×10^{-11}	—	HCN	1×10^{-10}	1.8
HD	5×10^{-11}	—	HCO	8.8×10^{-10}	1.6
CH	1.4×10^{-10}	1.5	H_2CO	8.8×10^{-10}	1.6
CO	5×10^{-12}	3.0	NH_3	5.5×10^{-10}	2.0
CN	5×10^{-11}	1.7	H_2O	3.2×10^{-10}	1.7
			CH_3^+	2×10^{-9}	1.7

Cosmic-ray induced radiation
(UV "secondary photons" in cloud interiors)



$H_2 + CR \Rightarrow H_2^+ + e^*$

$H_2 + e^* \Rightarrow H_2^* + e$

$H_2^* \Rightarrow H_2 + h\nu$

Prasad & Tarafdar 1983
Gredel et al. 1987

-Detailed line + continuum spectrum peaking around 1600 Å and continuing below 912 Å

$G_0 = 10^{-4}\ G_{ISM}$ → no *UV-dark* environment exists

Astrochemical models

- **Astrochemical models** contain thousands of reactions but only a few type of different reaction types:

- Formation of bonds **reaction rate k(T):**
  - Radiative association: 10^{-13} cm^{3}s^{-1} $X^+ + Y \rightarrow XY^+ + h\nu$
  - Associative detachment $X^- + Y \rightarrow XY + e$
  - Grain surface: 10^{-17} cm^{3}s^{-1} $X + Y{:}g \rightarrow XY + g$
- Destruction of bonds
  - Photo-dissociation: 10^{-9}–10^{-12} s^{-1} $XY + h\nu \rightarrow X + Y$
  - Dissociative recombination: 10^{-6} cm^{3}s^{-1} $XY^+ + e \rightarrow X + Y$
  - Collisional dissociation: $XY + M \rightarrow X + Y + M$
- Rearrangement of bonds
  - Ion-molecule reactions: 10^{-9} cm^{3}s^{-1} $X^+ + YZ \rightarrow XY^+ + Z$
  - Charge-transfer reactions: 10^{-9} cm^{3}s^{-1} $X^+ + YZ \rightarrow X + YZ^+$
  - Neutral-neutral reactions: 10^{-12} cm^{3}s^{-1} $X + YZ \rightarrow XY + Z$

Astrochemical reaction data bases

Mainly gas-phase:

~5000 reactions between ~450 species up to 13 atoms

http://udfa.ajmarkwick.net (**UMIST**-UDFA, T. Millar et al.)

http://www.physics.ohio-state.edu/~eric/research.html (**OSU**, E. Herbst et al.)

http://kida.obs.u-bordeaux1.fr (**KIDA**-Bordeaux, Wakelam et al.)

http://home.strw.leidenuniv.nl/~ewine/photo/ (**Photo-rates,** E. van Dischoeck)

$$k(\mathrm{T})=a(\mathrm{T}/300)^{b}\ \exp\ (-c/k\mathrm{T})\ [\mathrm{cm}^{3}\ \mathrm{s}^{-1}]$$

$$k_{ph}(\mathrm{A_v})=a\ \exp\ (-c\ \mathrm{A_v})\ [\ \mathrm{s}^{-1}]$$

Computational chemistry

$$A + B \xrightarrow[k_{AB}]{} X + Y$$

$$X + C \xrightarrow[k_{XC}]{} D + E$$

$$X + h\nu \xrightarrow[\beta_X]{} \text{products}$$

(on grains: $A_{grain} + B_{grain} \rightarrow X_{grain} + Y_{grain}$; $X_{grain} + h\nu / T \rightarrow X$)

One differential equation per species in the network: (non-linear, *stiff* problem)

$$d/dt\ \ n_X = F - D = \Sigma_A \Sigma_B\, k_{AB}\, n_A\, n_B - (\Sigma_C\, k_{XC}\, n_C + \beta_X)\, n_X \quad (only\ gas)$$

+ Conservation equations:

Carbon $n_C = n(C^+) + n(C) + n(CO) + n(CH) \ldots + 2n(C_2) + 2_n(C_2H) + \ldots$

…

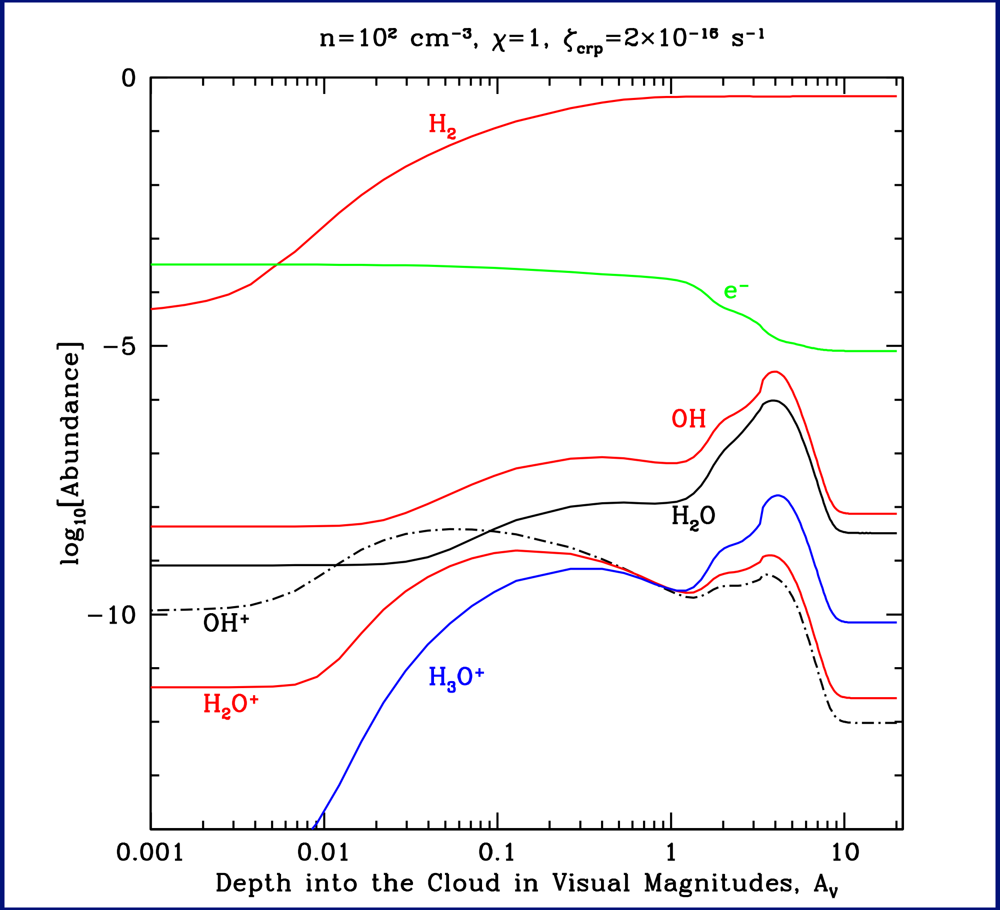
Charge $n_e = n(C^+) + n(H^+) + n(H_3^+) + \ldots$

SOLVED ITERATIVELY

(*eg.* Netwon-Raphson techniques when dn/dt = 0 steady-state)

Astrochemical codes: e.g., Meudon PDR code, Cloudy...

- ***Input*** radiation field (UV) → ***output*** radiation field (atomic/molecular line emission)
- Thermodynamics (heating and cooling) → T_{gas} , T_{dust}
- Chemical kinetics (gas + grain) → atomic/molecular abundances



Several iterations needed

But remember, rates are sometimes uncertain…,
→ Model predictions are uncertain (factors ~2 to 10)
See e.g. Wakelam et al. 2005

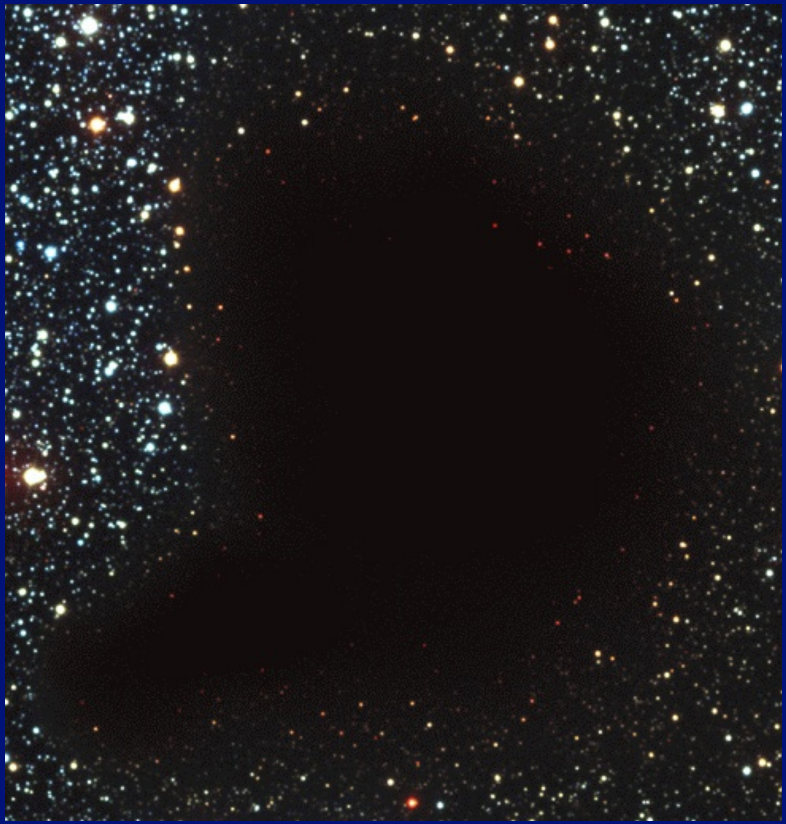
Hollenbach et al. 2012, ApJ

Diffuse clouds

Low densities, warm gas
UV dissociation, CR ionization, turbulence…

Simple hydrides: OH^+, CH^+ …
Seen in absorption

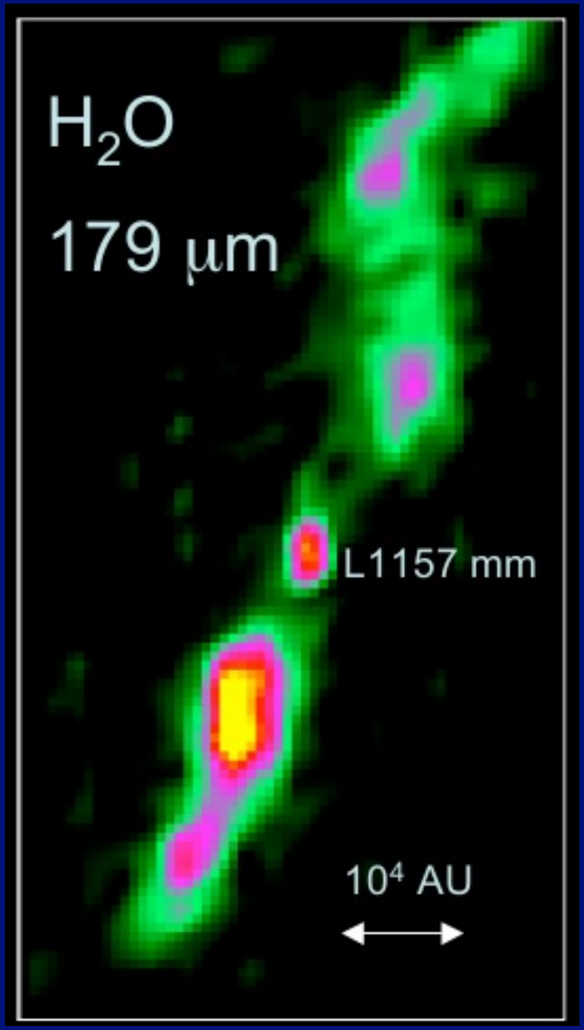
Dense clouds



High densities, cold gas
Depletion, CR ionization…

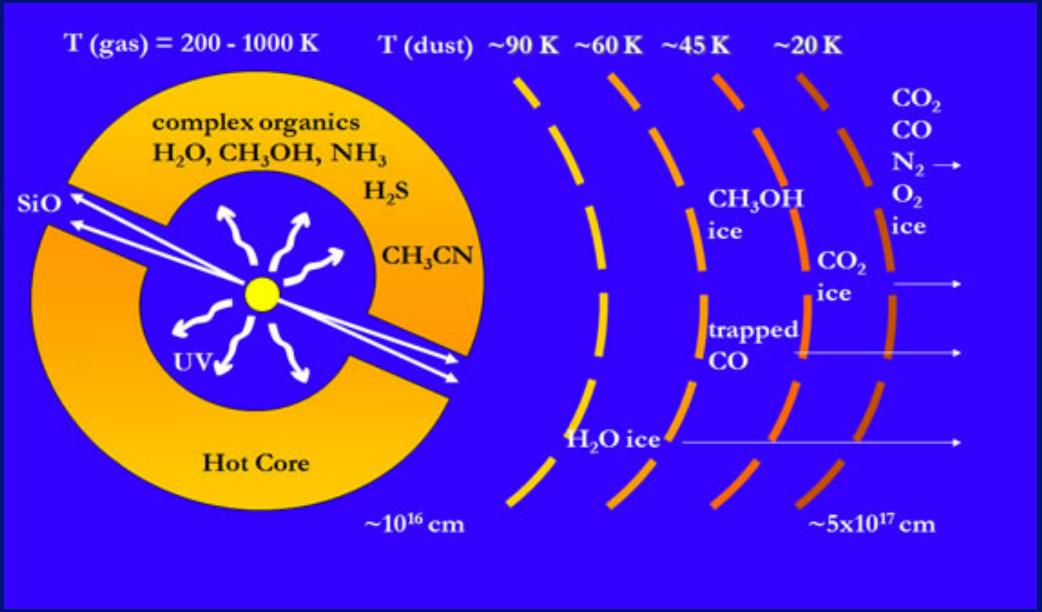
Heavier molecules: N_2H^+…
Deuterated isotopologues: N_2D^+ …

Shocks



High-Temperature chemistry
Grain sputtering
H_2O, OH, SiO and hot CO …

Hot Cores



Ice-mantle evaporation
Warm-temperature chemistry
CH_3OH, NH_3, complex organics…

UV-irradiated clouds (PDRs)

Photochemistry,
Ion-molecule chemistry

PAHs, C^{+}, O,
reactive ions (CO^{+} , HOC^{+} …),
hydrocarbons (C_3H^{+} …)

Circumstellar envelopes around evolved stars

High densities, dust formation

with metals: NaCl…
refractory: TiO, SiC…

Summary:

Which are the key processes in ISM chemistry?

1) Need to form the basic molecule, H2 in grain surfaces.

2) We need atomic or molecular ions (H2 + $O^+ \rightarrow OH^+$ + H):

- far-UV photons (<13.6 eV) near stars

- Cosmic-ray <u>particles</u> in shielded clouds

and we prefer exothermic reactions…

- Chemistry is <u>not</u> in thermochemical equilibrium but controlled by 2-body gas-phase reactions (X^+ + H2 $\rightarrow$ XH^+ + H) $\rightarrow$ **reaction kinetics**

Gas-phase molecules are (predominantly) synthesised in exothermic reactions in the gas and on the surfaces of tiny dust grains.