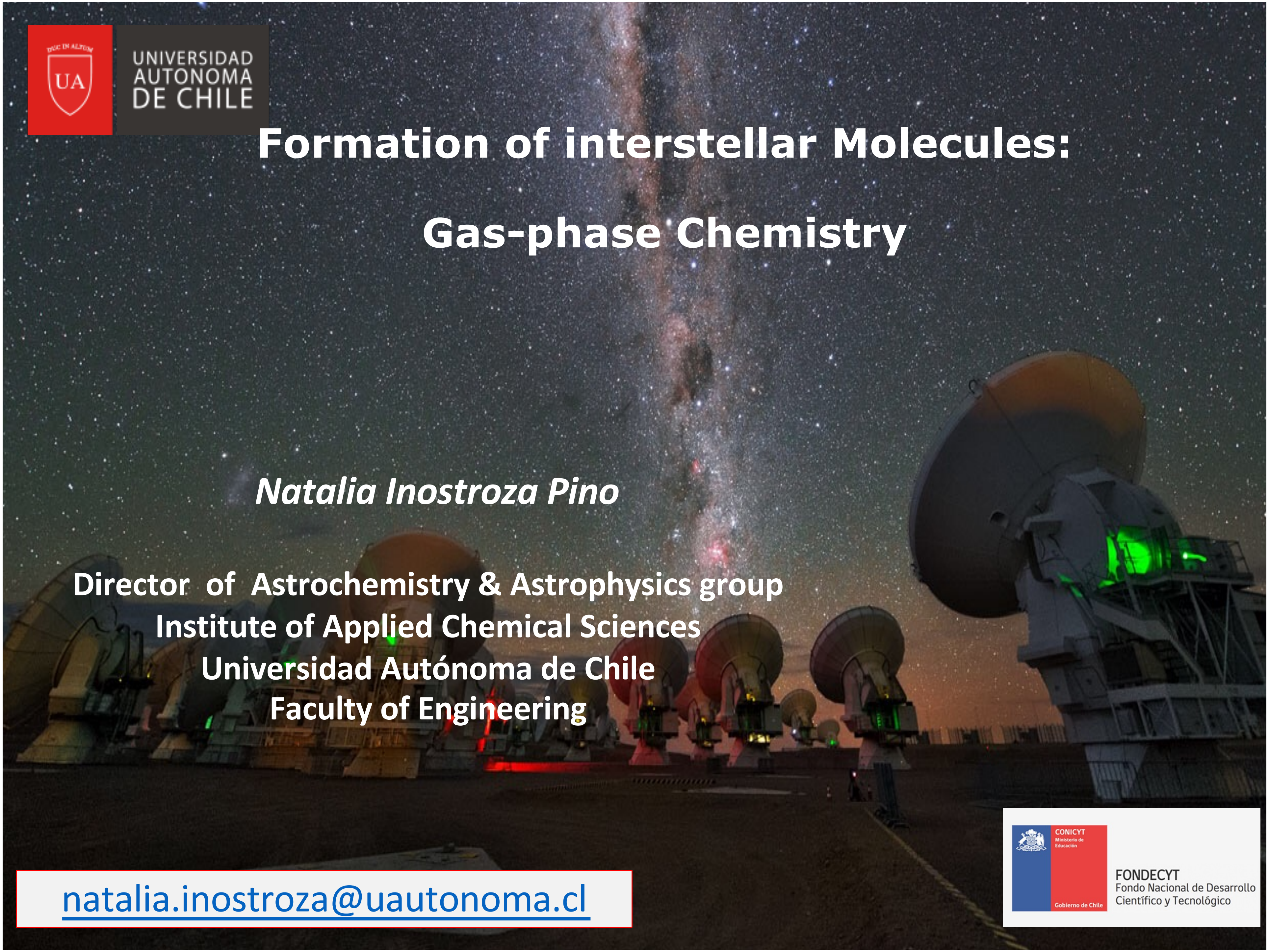

UNIVERSIDAD AUTONOMA DE CHILE

Formation of interstellar Molecules:

Gas-phase Chemistry

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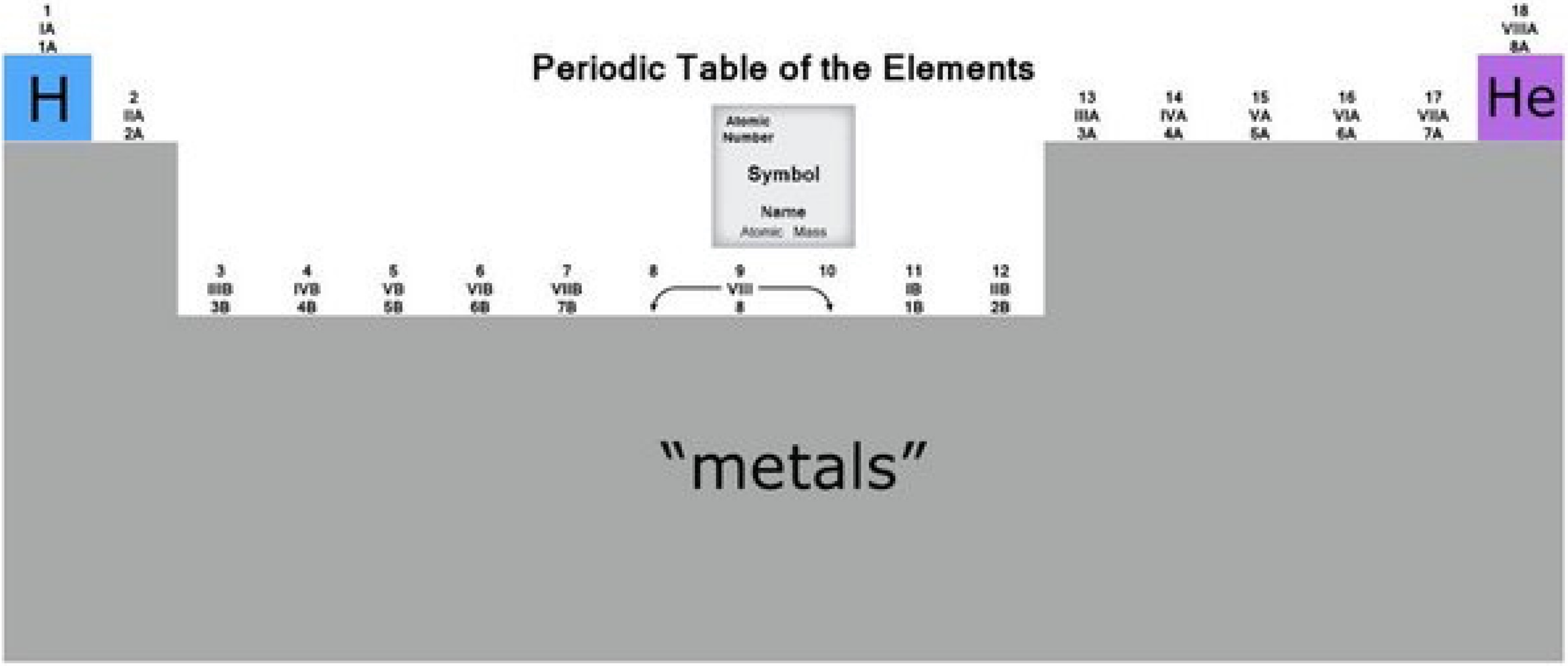
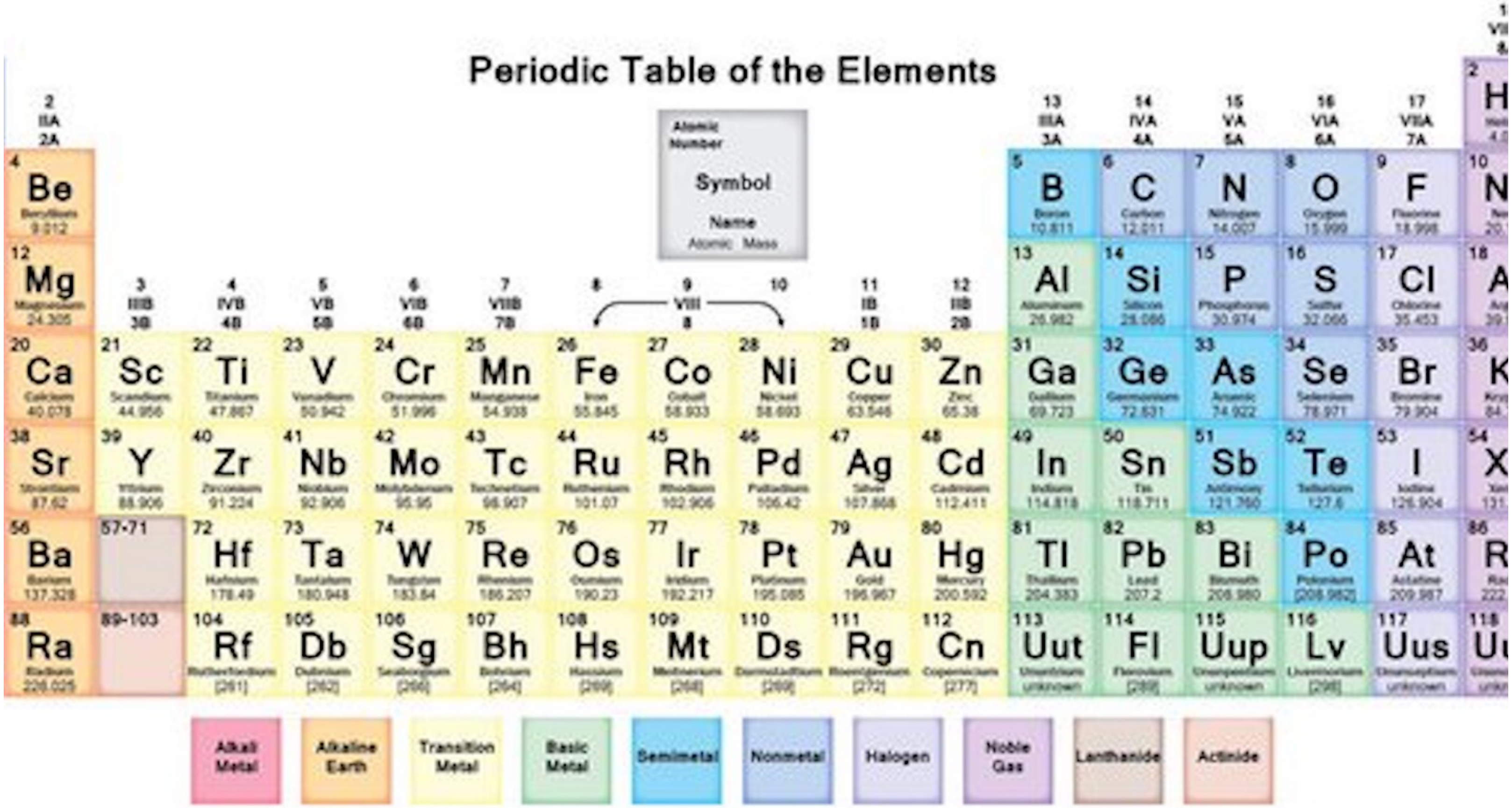


astronomers' periodic table...



2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	1 VII 8
																2 H
4 Be											5 B	6 C	7 N	8 O	9 F	10 N
12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 A
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 K
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 X
56 Ba	57-71	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 R
88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uu

normal periodic table

Molecules in the ISM? Typical Scales

"Size" of a diatomic molecule, $r \approx 2\ \text{Å} = 2\cdot10^{-8}\ \text{cm}$

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

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

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

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

collisions of two molecules $\mathbf{t\ (s) \approx 1 / (\Upsilon\ \mathit{n})} \approx 2$ weeks !!

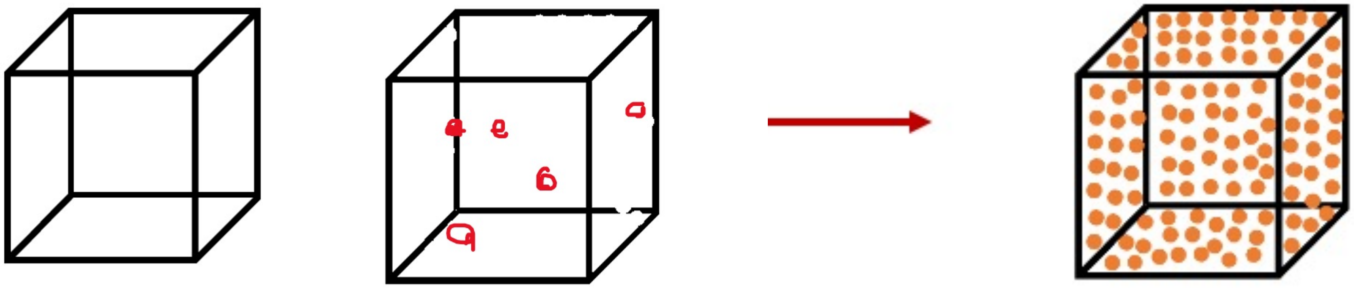
Distance between collisions $\mathbf{d = v\ t} \approx 100{,}000$ km !!

SLOW chemistry,

Astronomers did not expect many molecules in space…

ISM

very low densities, often very low temperatures →



conditions very different compared to Earth !!

- **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 ~10^{5} cm^{-3}

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

→ ISM **chemistry is NEVER in 'thermo-chemical equilibrium**' (solve two body reaction kinetics: **A + B = C + D**)

2 atoms

H_2
AlF
AlCl
C_2
CH
CH^+
CN
CO
CO^+
CP
SiC
HCl
KCl
NH
NO
NS
NaCl
OH
PN
SO
SO^+
SiO
SiS
CS
HF
SH
HD
FeO?
O_2?
CF^+
SiH?
PO

3 atoms

C_3
C_2H
C_2O
C_2S
CH_2
HCN
HCO
HCO^+
HCS^+
HOC^+
H_2O
H_2S
HNC
HNO
MgCN
MgNC
N_2H+
N_2O
NaCN
SO_2
c-SiC_2
CO_2
NH_2
CO_2+
H_3^+
H_2D^+, HD_2^+
SiCN
AlNC
OCS
HCP
CCP

4 atoms

c-C_3H
l-C_3H
C_3N
C_3O
C_3S
C_2H_2
HCCN
$HCNH^+$
HNCO
HNCS
$HOCO^+$
H_2CO
H_2CN
H_2CS
H_3O^+
NH_3
c-SiC_3
CH_3

C_3N^-
PH_3

5 atoms

C_5
C_4H
C_4Si
l-C_3H_2
c-C_3H_2
CH_2CN
CH_4
HC_3N
HC_2NH
HCOOH
H_2CNH
H_2C_2O
H_2NCN
HNC_3
SiH_4
H_2COH^+
C_4H^-
CNCHO

6 atoms

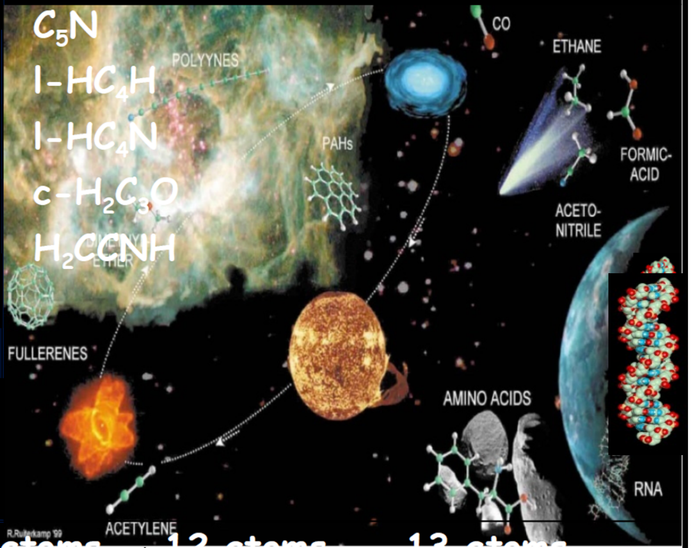
C_5H
l-H_2C_4
C_2H_4
CH_3CN
CH_3NC
CH_3OH
CH_3SH
HC_3NH^+
HC_2CHO
NH_2CHO
C_5N
l-HC_4H
l-HC_4N
c-H_2C_3O
H_2CCNH

7 atoms

C_6H
CH_2CHCN
CH_3C_2H
HC_5N
CH_3CHO
CH_3NH_2
c-C_2H_4O
H_2CCHOH
C_6H^-

8 atoms

CH_3C_3N
$HCOOCH_3$
CH_3COOH
C_7H
H_2C_6
CH_2OHCHO
l-HC_6H
CH_2CHCHO
CH_2CCHCN
NH_2CH_2CN



9 atoms

CH_3C_4H
CH_3CH_2CN
$(CH_3)_2O$
CH_3CH_2OH
HC_7N
C_8H-
SiNC
$CH_3C(O)NH_2$
CH_2CHCH_3

10 atoms

CH_3C_5N
$(CH_3)_2CO$
$(CH_2OH)_2$
CH_3CH_2CHO

11 atoms

HC_9N
CH_3C_6H

12 atoms

C_6H_6
$C_2H_5OCH_3$

13 atoms

$HC_{11}N$

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

About 250 different molecules found in Space, almost everywhere $T_{gas} < 5000$ K

H_2 most abundant species, but actually not detected until 1970's

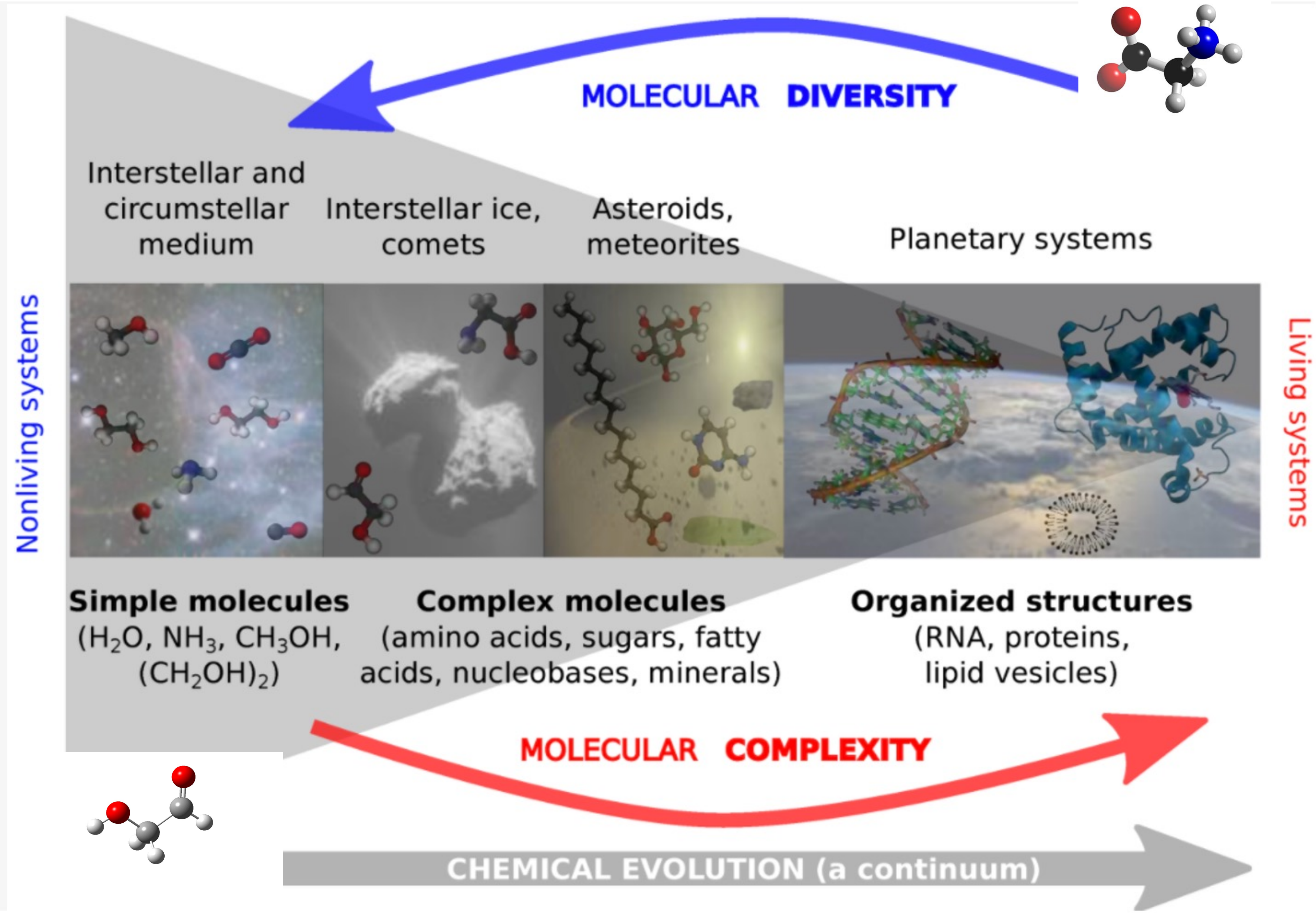
- OH^+, HF, CH^+ simple hydrides → first steps of ISM chemistry

C_3, C_4, … HCN, HC_7N … linear carbon chains

C_6H_6 benzene, simplest aromatic unit ... PAHs

ND_3, CD_3OH doubly and triply deuterated molecules

- NaCl, AlCN, TiO … metal-containing molecules
- $HCOCH_2OH$ glycolaldehyde, simplest sugar + COMs
- NH_2CH_2COOH glycine, simplest aminoacid, but not detected in ISM!



MOLECULAR **DIVERSITY**

Nonliving systems

Interstellar and circumstellar medium

Interstellar ice, comets

Asteroids, meteorites

Planetary systems

Living systems

Simple molecules
(H_2O, NH_3, CH_3OH, $(CH_2OH)_2$)

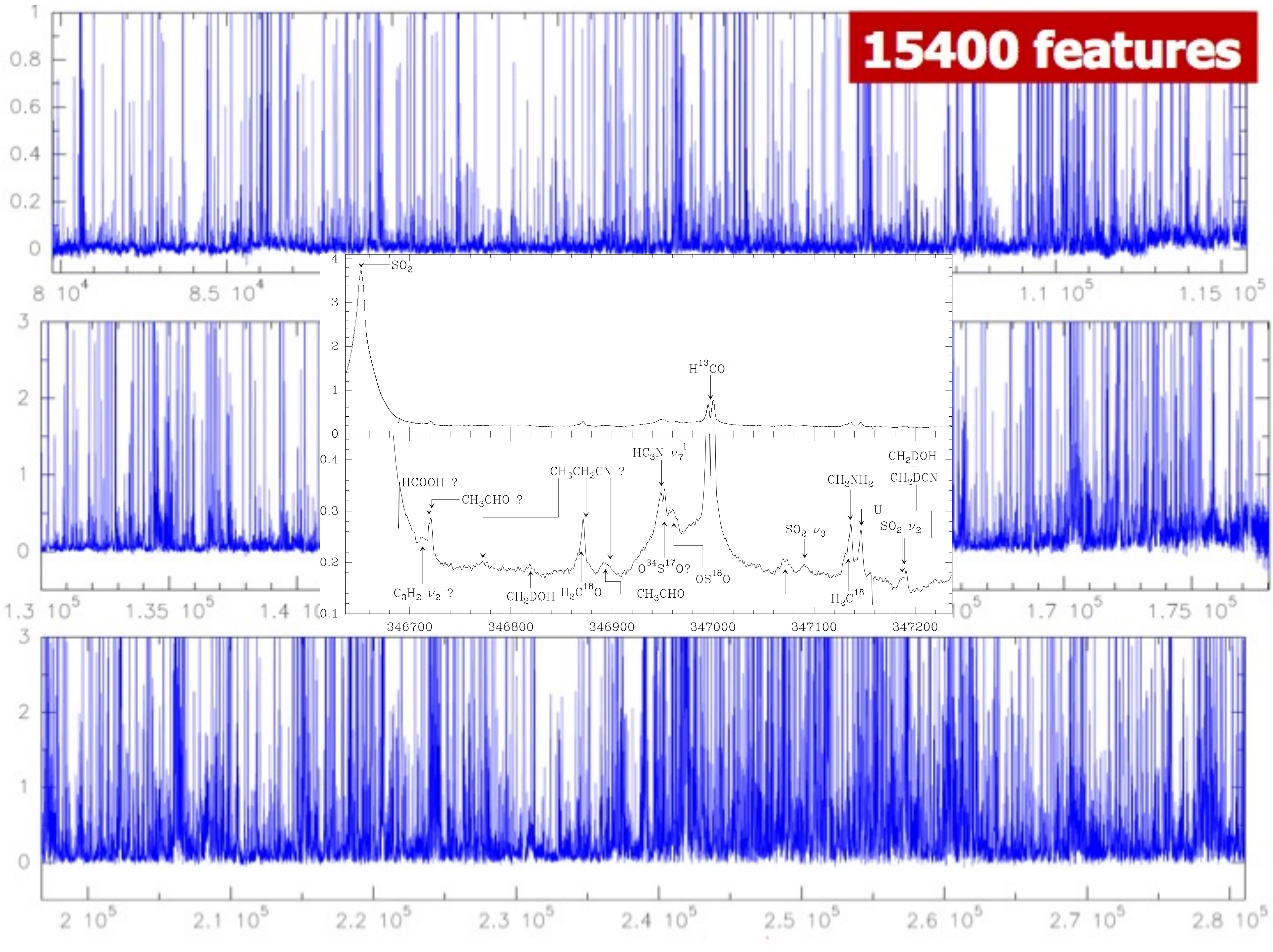
Complex molecules
(amino acids, sugars, fatty acids, nucleobases, minerals)

Organized structures
(RNA, proteins, lipid vesicles)

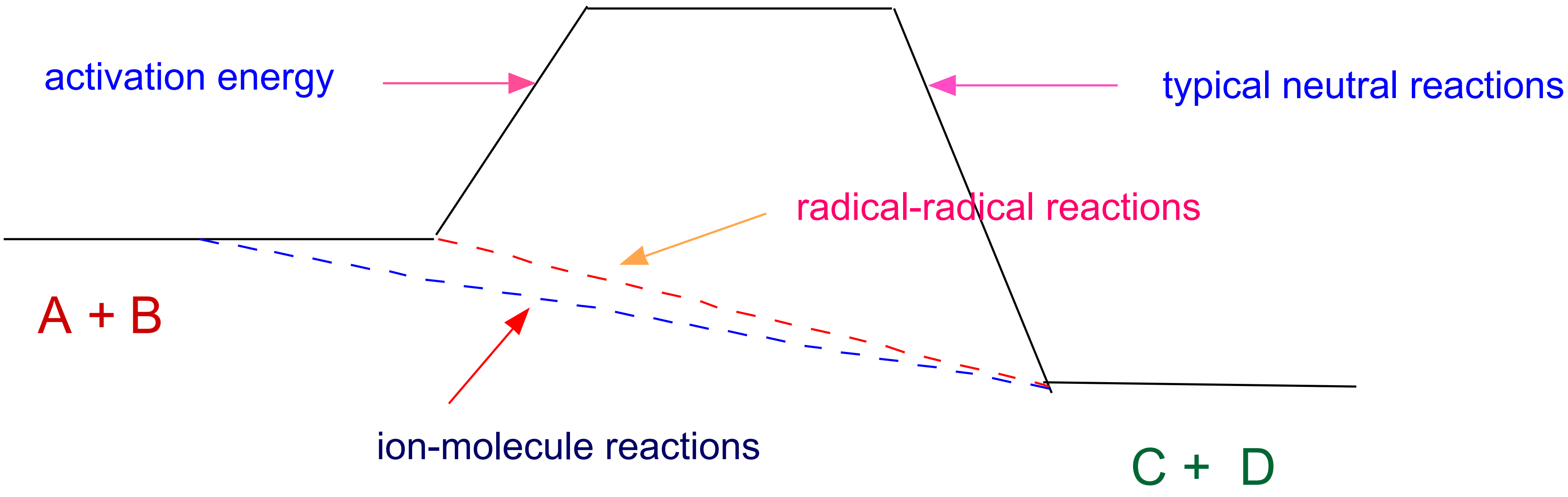
MOLECULAR **COMPLEXITY**

CHEMICAL EVOLUTION (a continuum)

15400 features



POTENTIAL ENERGY OF REACTION



activation energy

typical neutral reactions

radical-radical reactions

A + B

ion-molecule reactions

C + D

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

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

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

Gas phase reactions

$A + crp \rightarrow A^+ + e^-$	Cosmic ray ionization
$A^+ + BC \rightarrow AB^+ + C$	**Ion-neutral reaction**
$A^+ + BC^- \rightarrow AB + C$	Ion-Ion reaction
$A^+ + B \rightarrow A + B^+$	Change transfer reaction
$A + BC \rightarrow AB + C$	Neutral-neutral reaction
$A + B \rightarrow AB + h\upsilon$	Radiative association
$A^+ + e^- \rightarrow A + h\upsilon$	Radiative recombination
$AB^+ + e^- \rightarrow A + B$	Dissociative recombination

complex molecules like the CH_3OH can be formed in gas phase?

Formation models of Molecules

Ion-electron dissociative recombination reactions:

Fast, multiple products, inverse T dependence

Atomic ion-electron radiative recombination recombination:

Neutral complex stabilises by emission of a photon, about 1000 times slower than DR rate coefficients

Radiative association:

$A^+ + B \rightarrow AB^+ + h\nu$

Photon emission more efficient as size of complex grows, therefore can be important in synthesising large molecular ions

$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$

$k(T) = 1.3\ 10^{-13}(T/300)^{-1}\ cm^3\ s^{-1}$

$CH_3^+ + HCN \rightarrow CH_3CNH^+ + h\nu$

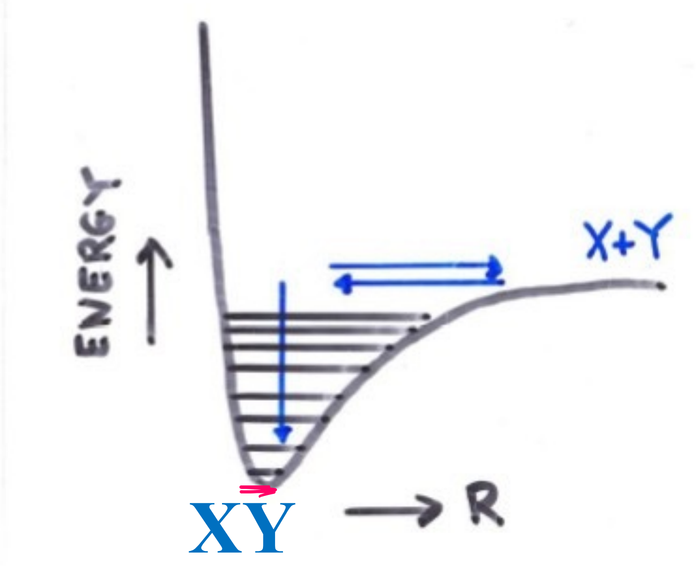
$k(T) = 9.0\ 10^{-9}(T/300)^{-0.5}\ cm^3\ s^{-1}$

Radiative Association (very slow)

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

(XY* =Activated complex)

- 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***

How do we form other gas-phase molecules ?

H_2+ (C, C^+, O, O^+, N, Si, Si^+, S, or S^+)

let us consider the following 2-body reaction…

$$X + Y \rightarrow XY^* \rightarrow XY + h\nu \;??$$

Formation Reaction

$\mathbf{H_2CO + NH_2} \rightarrow H + NH_2CHO$

HNCO + $H_2 \rightarrow NH_2CHO$ (?)

HNCO + 2H —> NH_2CHO

(not feasible by bombardment)

Destruction (included only on gas-phase)

$He^+ + NH_2CHO \rightarrow He + NH_2 + HCO^+$

$H_3^+ + NH_2CHO \rightarrow H_2 + NH_2CH_2O^+$

$C^+ + NH_2CHO \rightarrow N + CH_3CO^+$

$HCO^+ + NH_2CHO \rightarrow CO + NH_2CH_2O^+$

Owing to low gas temperatures ISM, the reaction will occur if the change of energy is ‘positive’

in general, reactions should be

exothermic!!

For example, lets consider the reaction:

$C^+ + H_2 \rightarrow CH_2^+ + h\nu \quad \rightarrow$ slow, k ~10^{-13} cm^3 s^{-1}

what about:

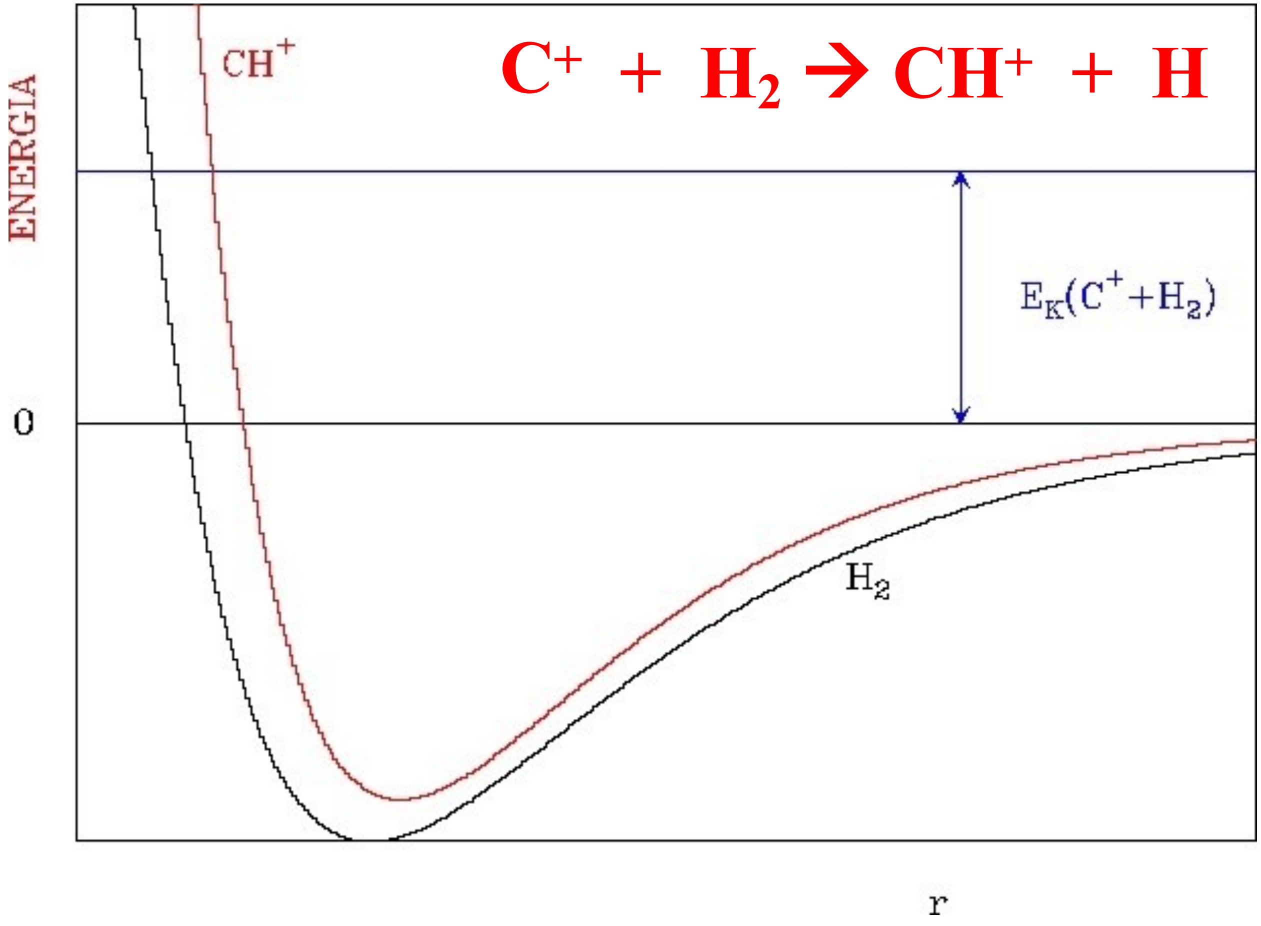
$C^+ + H_2 \rightarrow CH^+ + H$

Is it exothermic?

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



$C^+ + H_2 \rightarrow CH^+ + H$

Reaction will proceed if we "add" 0.39 eV to the system (about 4600 K).

This reaction is endothermic and has low probability to occur in the ISM unless $T_{gas} > 1000$ K

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

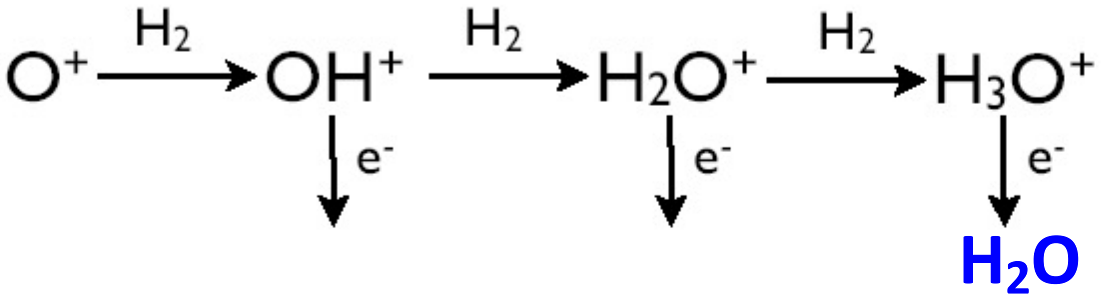
(endothermic by ~1 eV E/k~10,000 K)

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 quite fast, k → $1.6\ 10^{-9}\ cm^3\ s^{-1}$



Molecular Formation of “AB” IN DIFFUSE CLOUDS?

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

The interaction between two species (atoms or molecules) produces an activated complex (AB^*) that is unstable and has to loss energy in a very short time, often similar to the vibration time of the molecule nuclei.

While in the Earth, catalysers or a third body are available, in space three body collisions are very uncommon because of the very low density of ISM clouds.

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

DENSITY is TOO LOW in ISM CLOUDS…
3-BODY REACTIONS DONT WORK IN THE ISM (example: H_2 formation)

Consider an atomic H cloud without dust grains and without radiation field.

At t=0, the density of hydrogen atoms 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} $cm^6\,s^{-1}$

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

$$H + H + H = H_2 + H$$ **DO NOT WORK!**

$$(\text{or } H + H = H_2)$$

GAS-PHASE PRODUCTION OF H_2 IS EXTREMELLY SLOW BUT H_2 HAS BEEN DETECTED IN SPACE…

The role of H_3^* …

PROTON TRANSFER

H_2 has a low proton affinity and the reactions of H_3^+ with neutral species (B) can produce a molecular ion BH^+

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

if the reaction is exothermic (except with H, N and He). e.g.,

$$H_3^+ + CO \rightarrow HCO^+ + H_2$$

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

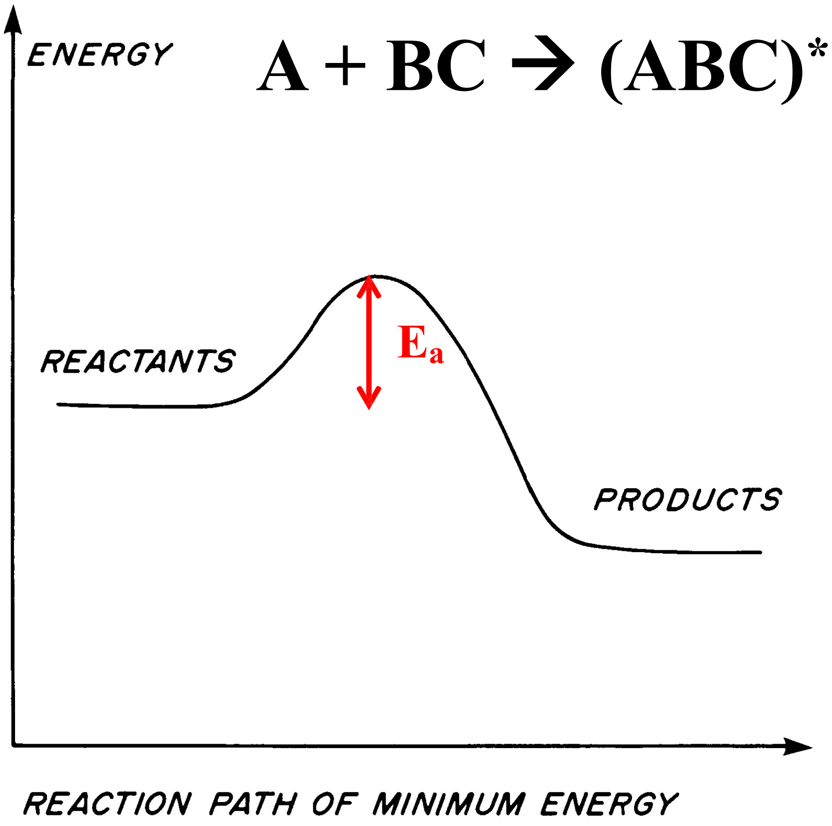
NEUTRAL-NEUTRAL REACTIONS & ENERGY BARRIERS

$A + BC = AB + C$

* 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

$$A + BC \rightarrow (ABC)^* \rightarrow AB + C$$



NEUTRAL-NEUTRAL REACTIONS (Energy Barriers)

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

	$A(cm^3 s^{-1})$	$E_a(K)$
$O + H_2 = OH + H$	$1.0\ 10^{-11}$	5700 (E~-920K)
$OH + H_2 = H_2O + H$	$8.0\ 10^{-12}$	2100

H_2O chemistry: needs high temperature conditions (e.g., shocks in protostellar outflows producing H_2O)

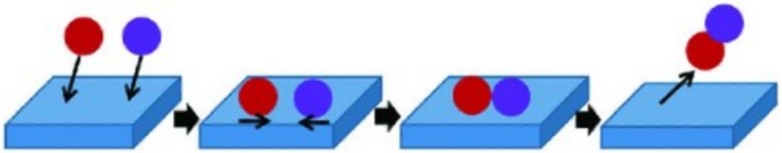
Gas-Phase formation:

$\mathbf{H} + \mathbf{H} \rightarrow \mathbf{H}_2 + h\nu$ very slow, insignificant in ISM

In dust we trust

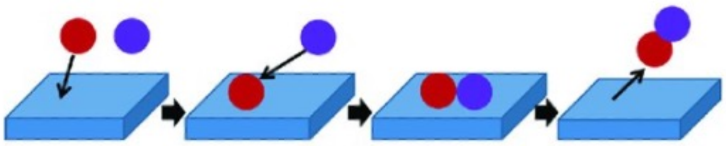
“*Grain surfaces are the watering holes of astrochemistry where species come to meet and mate.*” (Tielens 2005)

Grain surface formation?



Langmuir-Hinshelwood Mechanism

(surface diffusion)



Eley-Rideal Mechanism

(direct hit)

Surface chemistry (cf. Tielens Lecture)

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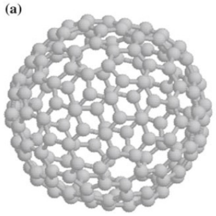
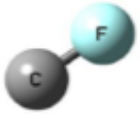
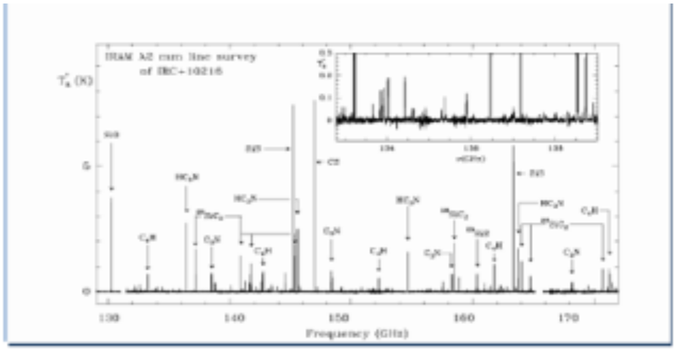
Previous work

(a)

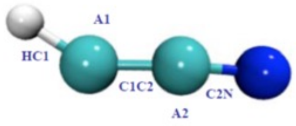




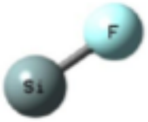
CF^+



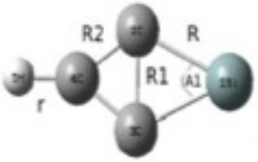
^{28}SiO ^{29}SiO ^{30}SiO

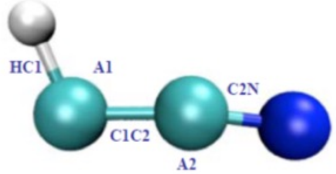


X^3A'' ground state triplet



$^{28}SiF^+$ $^{29}SiF^+$ $^{30}SiF^+$





X^1A' bent singlet

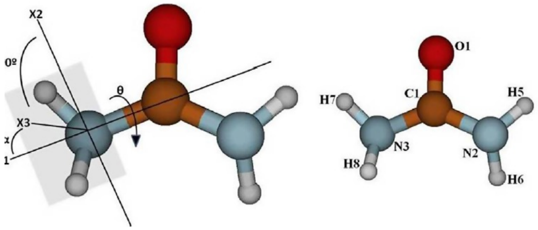
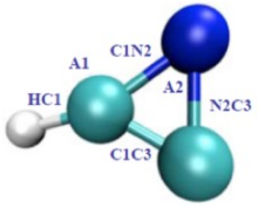
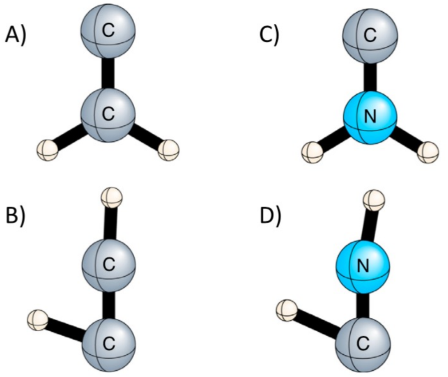
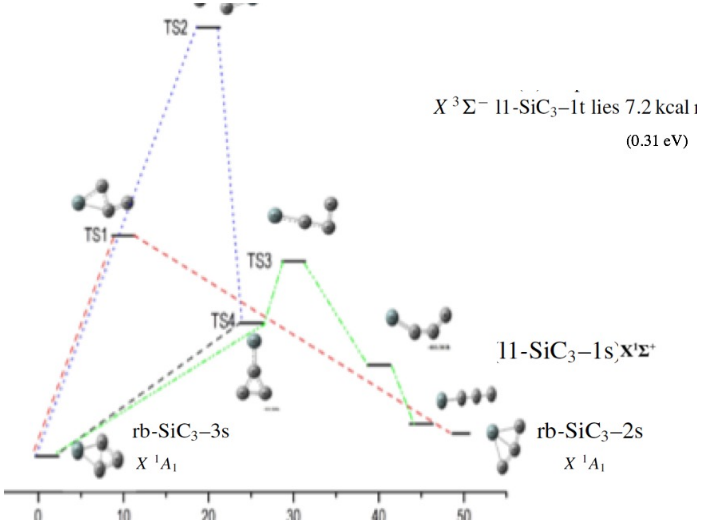


Figure 1. Structural parameters of Urea, definition of NH_2-torsion (θ) and NH_2-wagging (α) coordinates.



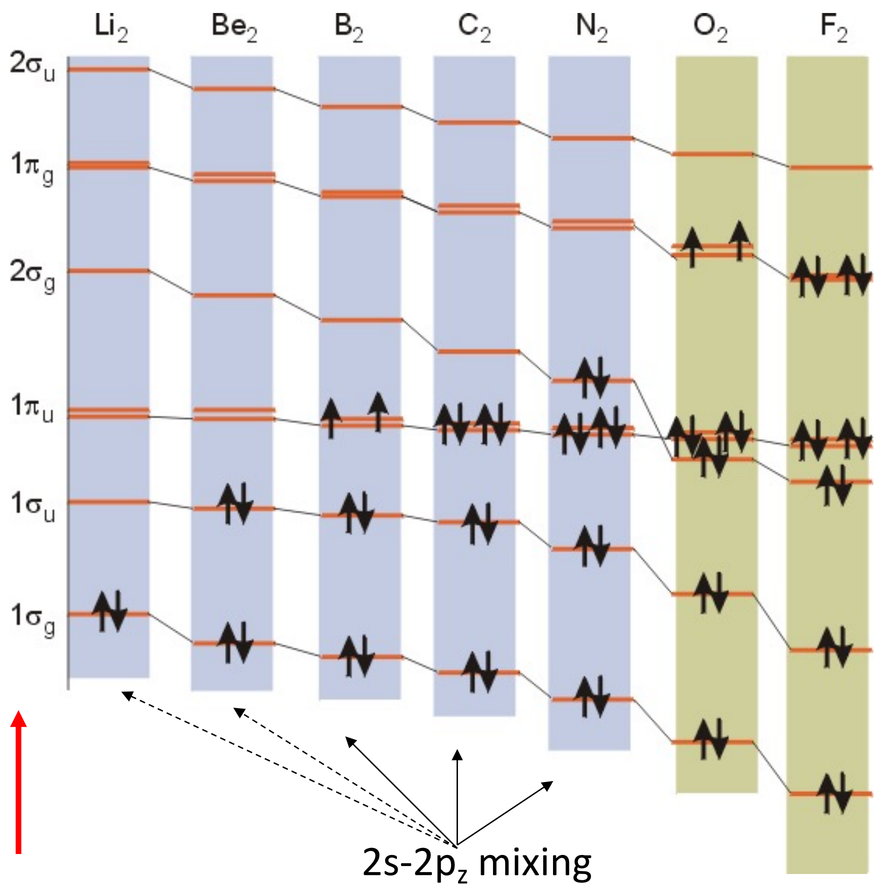
X^1A' cyclic singlet





CSIC

Molecular Orbital Theory Diatomic molecules: MO diagrams for Li_2 to F_2



In this diagram, the labels are for the valence shell only - they ignore the 1s shell. They should really start at $2\sigma_g$ and $2\sigma_u$*.

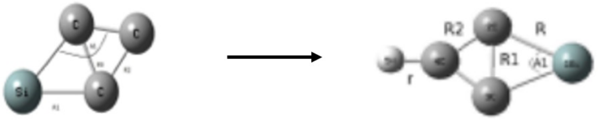
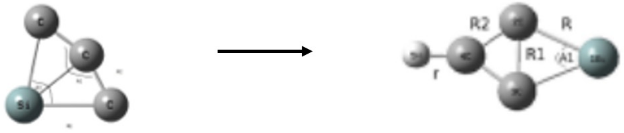
Remember that the separation between the ***n***s and ***n***p orbitals increases with increasing atomic number. This means that as we go across the 2nd row of the periodic table, the amount of mixing decreases until there is no longer any mixing; this happens at O_2. At O_2 the ordering of the $3\sigma_g$ and the $1\pi_u$ MO's changes.

As we go to increasing atomic number, the effective nuclear charge (and electronegativity) of the atoms increases. This is why the energies of the analogous orbitals **decrease** from Li_2 to F_2.

The trends in bond lengths and energies can be understood from the size of each atom, the bond order and by examining the orbitals that are filled.

Molecule	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond Order	1	0	1	2	3	2	1	0
Bond Length (Å)	2.67	n/a	1.59	1.24	1.01	1.21	1.42	n/a
Bond Energy (kJ/mol)	105	n/a	289	609	941	494	155	n/a
Diamagnetic (d)/ Paramagnetic	d	n/a	p	d	d	p	d	n/a

Reaction channels and spectroscopic constants of astrophysical relevant Silicon bearing molecules $SiC_3H,^+$ and SiC_3H

Charge-exchange (10–300K)	[ΔE(kcal mol^{-1})	ΔE(eV)^a
$H^+ + l1\text{-}SiC_3H \rightarrow l1\text{-}SiC_3H^+ + H$	201.5	8.74
$H^+ + rb3\text{-}SiC_3H \rightarrow rb3\text{-}SiC_3H^+ + H$	170.9	7.41
$H^+ + rb2\text{-}SiC_3H \rightarrow rb2\text{-}SiC_3H^+ + H$	192.5	8.35
Ion–neutral (10–41 000K)		
$H_3{}^+ + rb\text{-}SiC_3\text{–}3s \rightarrow rb3\text{-}SiC_3H^+ + H_2$	– 126.7	– 5.50
		
$H_3{}^+ + rb\text{-}SiC_3\text{–}2s \rightarrow rb3\text{-}SiC_3H^+ + H_2$	– 132.2	– 5.73
		

Monthly Notices of the Royal Astronomical Society MNRAS 443, 3127–3133 (2014)

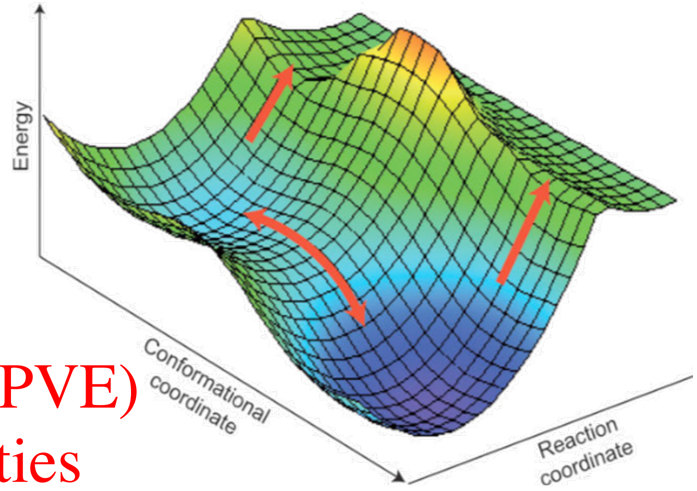
Potential Energy Surface

Vibrational Analysis

Indicate if the structure is

- a minimum (equilibrium structure – all real frequencies)
- a maximum (transition state – one imaginary frequency)
- higher maximum point (more than one imaginary frequency)

$$v_i = \frac{1}{2\pi}\sqrt{\frac{k_i}{\mu}} \quad \text{where} \quad k_i = \frac{\partial^2 E}{\partial^2 l}$$



Also you can get

- IR and Raman spectra
- zero-point vibrational energy (ZPVE)
- useful thermochemical quantities
- Reaction rate coefficients
- Tunneling corrections

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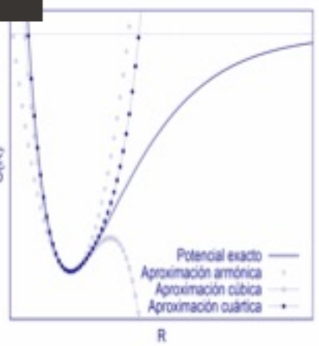
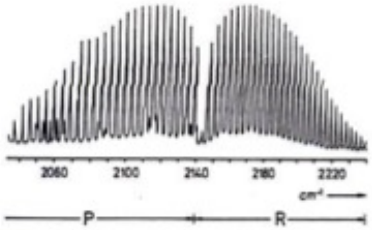
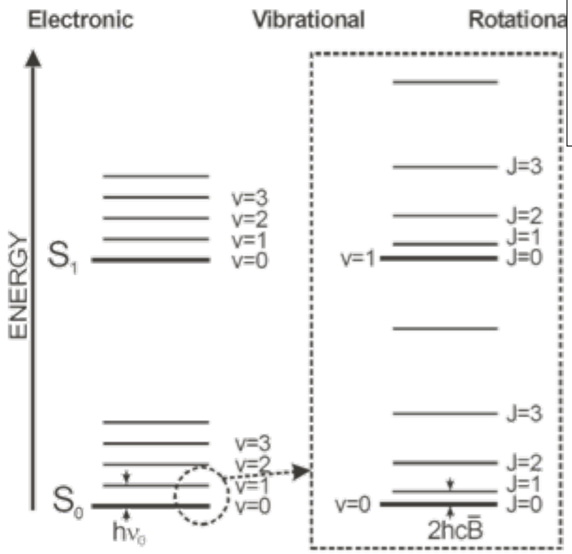
METODOLOGIA: AB initio







MRCI+Q MRCI CASSCF CCSD(T)
aug-cc-pVXZ, cc-pVXZ, X=TZ, QZ, 5Z
***MOLPRO, Gaussian, Games**

$\Delta E_{CASSCF\text{-}MRCI}$ =7.33 eV (169.203 kcal/mol), $\Delta E_{MRCI\text{-}MRCI+Q}$=0.379 eV (8.748 kcal/mol

MRCI+Q/aug-cc-pV5Z para el ión CF+ versus la curva calculada con el método Rydberg-Klein-Rees (RKR)

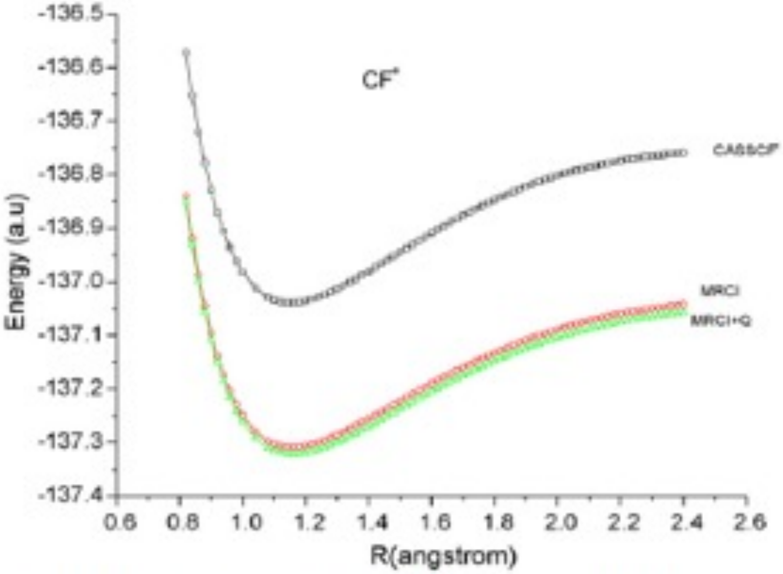
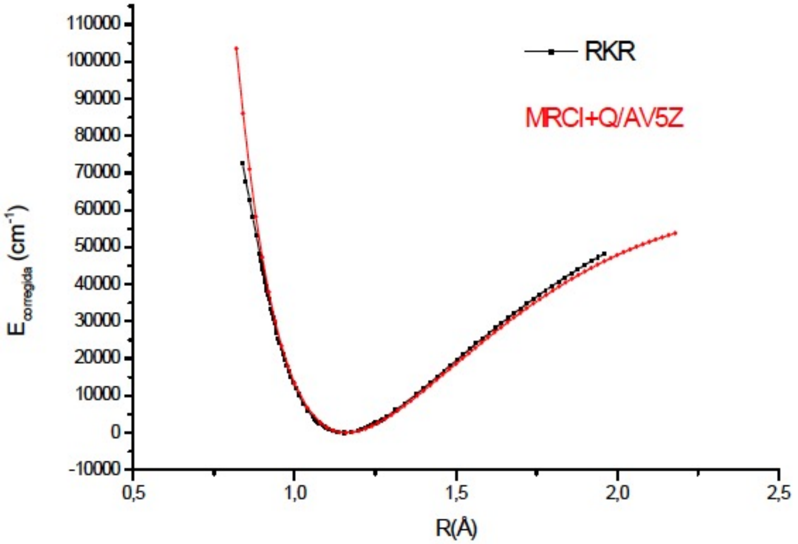
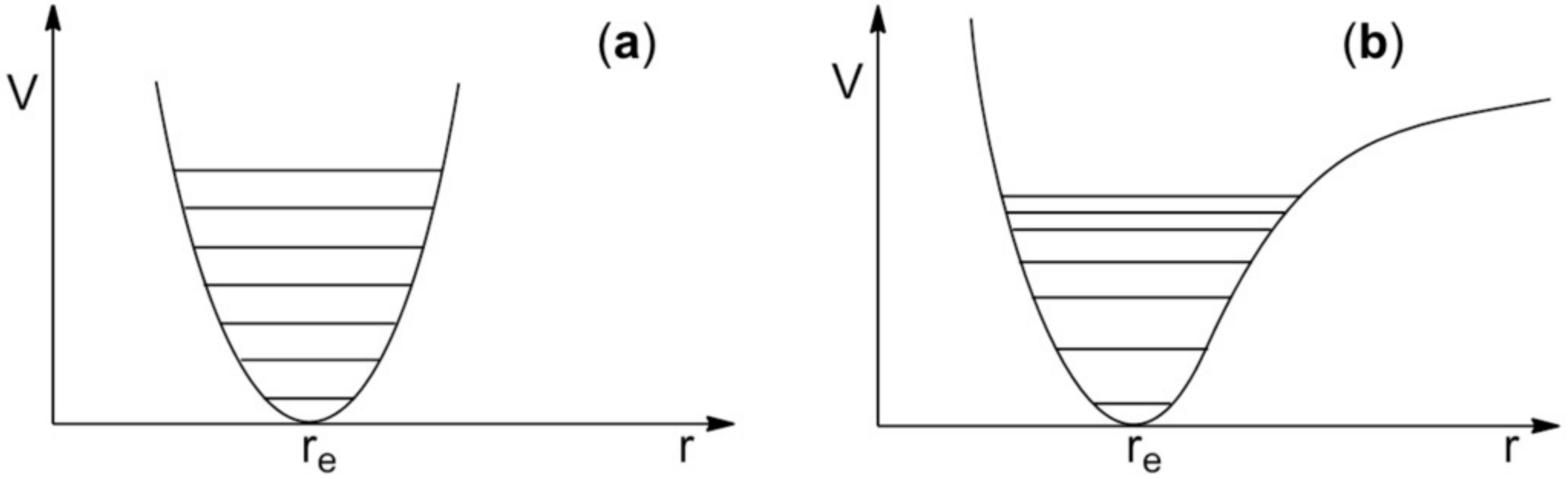


Fig. 1 Potential energy functions of CF⁺ using aug-cc-pV5Z basis set



CASSCF (10,8). 328 funciones de estado de configuración (CSFs) 792 determinantes, 3136 estados intermedios
MRCI N° de configuraciones internas: 328 N° de configuraciones singles: 144816 N° de configuraciones dobles: 486480

Harmonic vs. Anharmonic Energy Levels

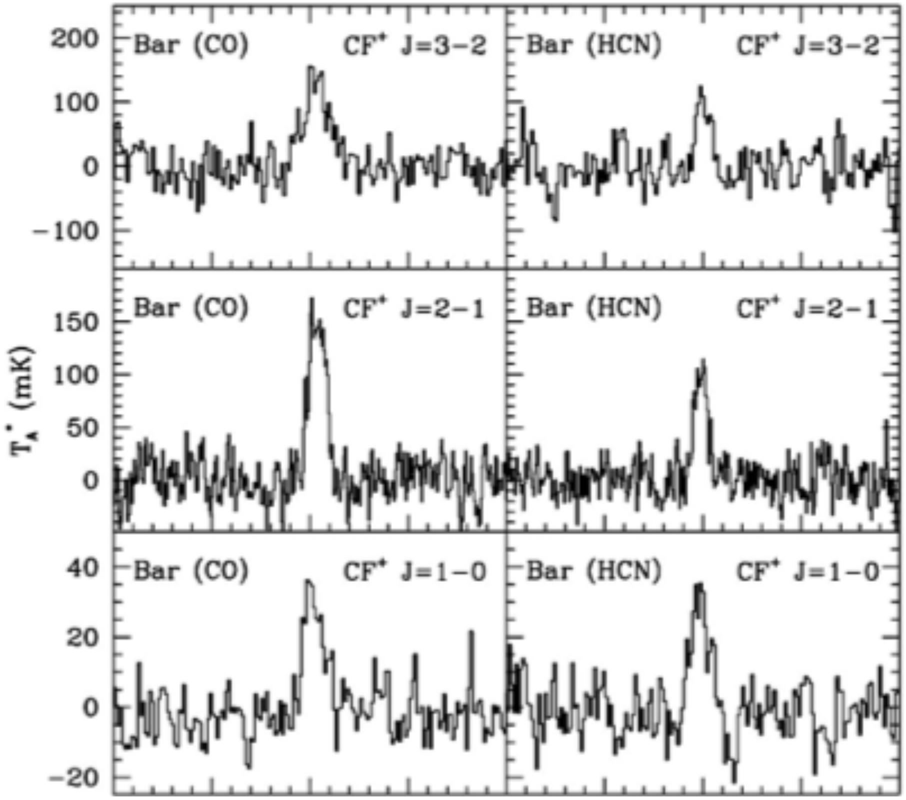


$$E(\nu) = \sum_k \omega_k \left(\nu_k + \frac{1}{2}\right) \qquad E(\nu) = \sum_k \omega_k \left(\nu_k + \frac{1}{2}\right) + \sum_{k \leq l} x_{kl} \left(\nu_k + \frac{1}{2}\right)\left(\nu_l + \frac{1}{2}\right)$$

- The spacing between vibrational energy levels for a harmonic oscillator is a constant → ω_k
- The spacing between energy levels for VPT2 decreases according to the anharmonic constants x_{kl}

Transiciones Rotacionales

OBSERVACIONES EN LA BARRA DE ORION



Espectro estelar para $^{12}CF^+$ $J = 1$ -0,$J= 2 - 1$ (IRAM 30 m) and J =3−2 (APEX 12m) obtenido en barra de Orion. (temperatura antena/estándar local reposo)

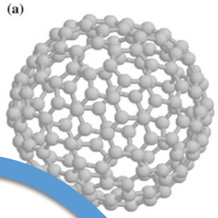
Our results	Exp. results Neufeld y col.
304.2 [GHz]	307.7 [GHz]
203.1 [GHz]	205.2 [GHz]
102.0 [GHz]	102.6 [GHz]

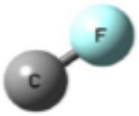
$$\nu = 0, J_2 - J_1 = 1$$

N.Inostroza*a, J.R.Letelier, P.Fuentealba, M.L.Senentd, *Spectrochimica* Acta Part A-Molec. and Biomolecular Spectroscopy, 71, 798 (2008).

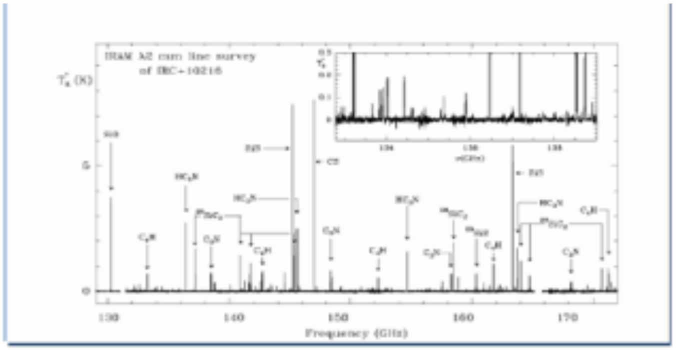
Previous work

(a)

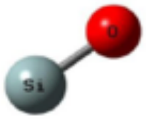


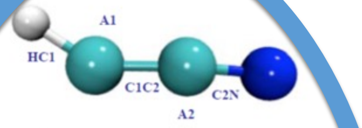


CF⁺



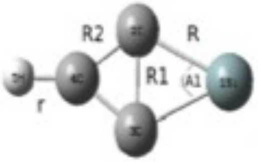
^{28}SiO ^{29}SiO ^{30}SiO

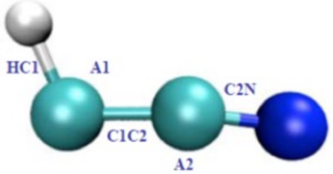




X^3A'' ground state triple

$^{28}SiF^+$ $^{29}SiF^+$ $^{30}SiF^+$





X^1A' bent singlet

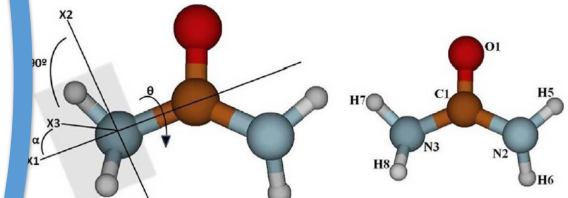
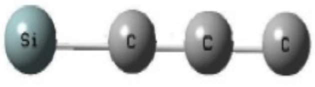
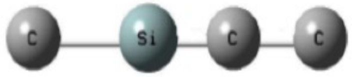
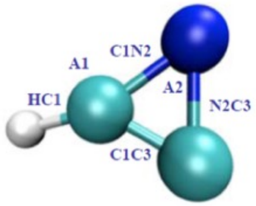


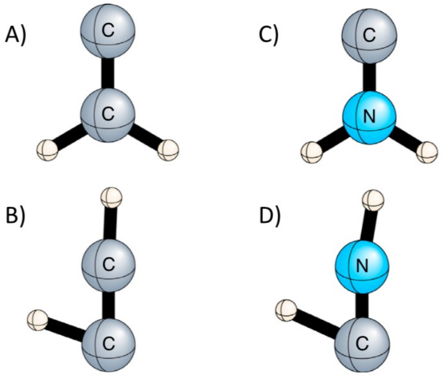
Figure 1. Structural parameters of Urea, definition of NH_2-torsion (θ) and NH_2-wagging (α) coordinates.

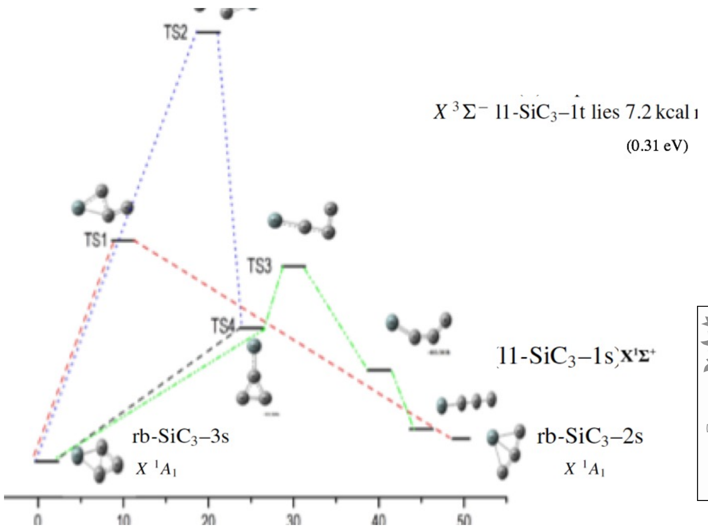






X^1A' cyclic singlet





SPECTRO

At a stationary point, the potential can be expanded in terms of force constants $f_{ij\ldots}$, up to quartic level: (the s could be any appropriate coordinates: Cartesian, internal, normal, symmetry internal)

$$V = \frac{1}{2}\sum f_{ij} s_i s_j + \frac{1}{6}\sum f_{ijk} s_i s_j s_k + \frac{1}{24}\sum f_{ijkl} s_i s_j s_k s_l$$

For asymmetric tops, vibrational frequencies (relative to ground state) are given by:

$$E_v = \sum_i v_i \omega_i + \sum_{i \le j} X_{ij} (v_i v_j + (v_i + v_j)/2)$$

i=1, …, number of normal modes.

Lee J. T.

Quantum Harmonic Oscillator

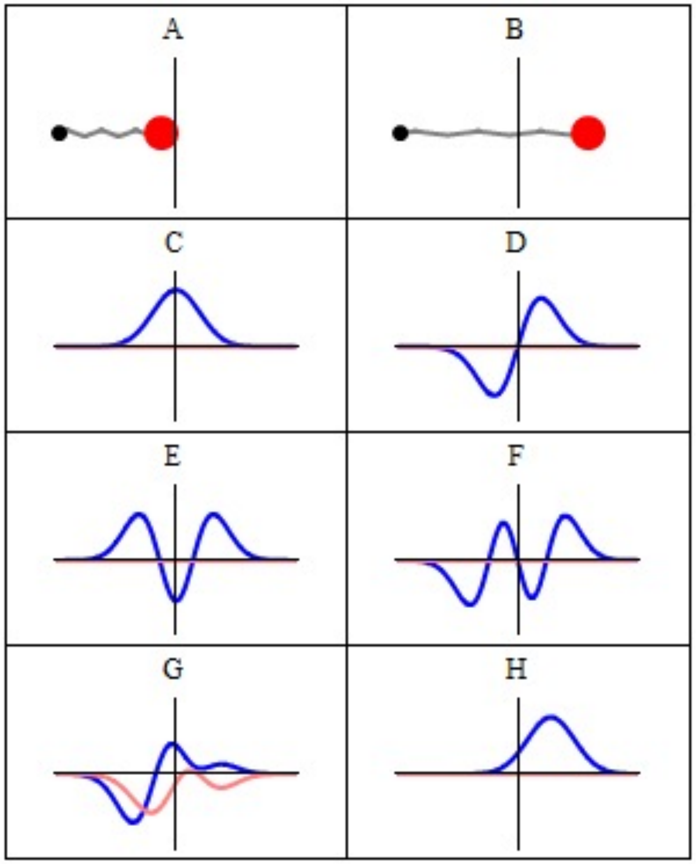
HΨ = EΨ

H = T + V

where T is the kinetic energy operator and

$$V = \frac{1}{2}\sum_{i,j}^{3N} F_{ij}X_iX_j$$

$$E(\nu) = \sum_k \omega_k \left(\nu_k + \frac{1}{2}\right)$$



where ω_k is the kth eigenvalue (harmonic frequency) or normal mode and v_k is the quantum number for the kth normal mode

Lee J. T.

GIF by Sbyrnes321 - Own work, CC0, https://commons.wikimedia.org/w/index.php?curid=14059905

Anharmonicities – VPT2

For the simplest treatment of anharmonicities, V is given by

$$V = \frac{1}{2}\sum_{i,j}^{3N}\left(\frac{\partial^2 V}{\partial X_i \partial X_j}\right) X_i X_j$$

$$+ \frac{1}{6}\sum_{i,j,k}^{3N}\left(\frac{\partial^3 V}{\partial X_i \partial X_j \partial X_k}\right) X_i X_j X_k$$

$$+ \frac{1}{24}\sum_{i,j,k,l}^{3N}\left(\frac{\partial^4 V}{\partial X_i \partial X_j \partial X_k \partial X_l}\right) X_i X_j X_k X_l$$

$$\left(\frac{\partial^2 V}{\partial X_i \partial X_j}\right) = F_{ij}$$

$$\left(\frac{\partial^3 V}{\partial X_i \partial X_j \partial X_k}\right) = F_{ijk}$$

$$\left(\frac{\partial^4 V}{\partial X_i \partial X_j \partial X_k \partial X_l}\right) = F_{ijkl}$$

and the energy levels are given by

$$E(v) = \sum_k \omega_k \left(v_k + \frac{1}{2}\right) + \sum_{k \le l} x_{kl} \left(v_k + \frac{1}{2}\right)\left(v_l + \frac{1}{2}\right)$$

where the x_{kl} are the anharmonic constants

Lee J. T.

Anharmonicities – VPT2

$$x_{kk} = \frac{1}{16}\phi_{kkkk} - \frac{1}{16}\sum_{m}(\phi_{kkm})^2\left[\frac{8\omega_k^2 - 3\omega_m^2}{\omega_m\left(4\omega_k^2 - \omega_m^2\right)}\right],$$

$$\begin{aligned} x_{kl} = {} & \frac{1}{4}\phi_{kkll} - \sum_{m}\frac{\phi_{kkm}\phi_{llm}}{4\omega_m} \\ & - \sum_{m}\frac{(\phi_{klm})^2\omega_m\left(\omega_k^2 + \omega_l^2 - \omega_m^2\right)}{2\Omega_{klm}} \\ & + \sum_{\alpha}B_{\alpha}^{e}(\zeta_{kl}^{\alpha})^2\left[\frac{\omega_k}{\omega_l} + \frac{\omega_l}{\omega_k}\right], \end{aligned}$$

$$\begin{aligned} \Omega_{klm} = {} & (\omega_k + \omega_l + \omega_m)(-\omega_k + \omega_l + \omega_m) \\ & \times(\omega_k - \omega_l + \omega_m)(\omega_k + \omega_l - \omega_m), \end{aligned}$$

$$B_{\alpha}^{e} = \frac{h}{8\pi^2 c I_{\alpha}^{e}},$$

where φ are the force constants transformed into the normal coordinate basis and the I^e_a are the moments of inertia.

Lee J. T.

Especially, the vibrational fundamentals, first overtones, and combinational bands are:

$$\nu_i = \omega_i + 2X_{ii} + \frac{1}{2}\sum_{k \neq i} X_{ik}$$

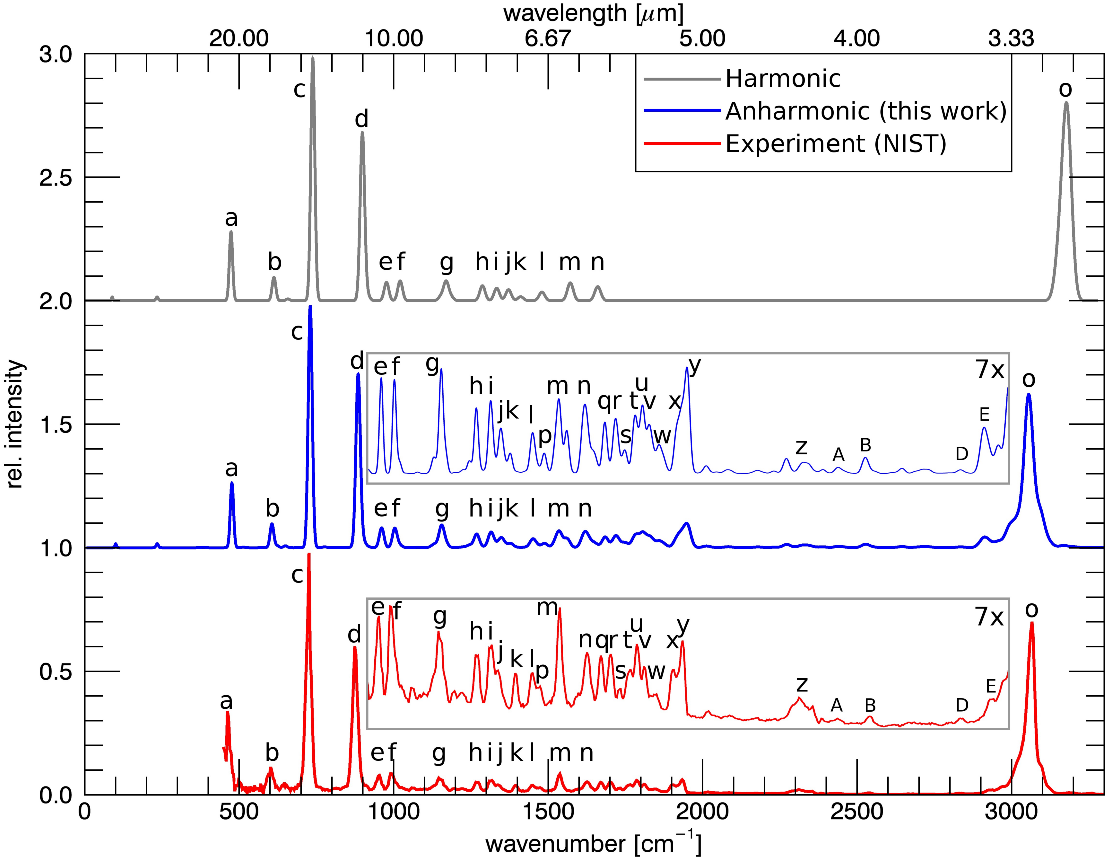
$$2\nu_i = 2\omega_i + 6X_{ii} + \sum_{k \neq i} X_{ik}$$

$$\nu_i + \nu_j = \omega_i + \omega_j + 2X_{ii} + 2X_{ij} + 2X_{jj} + \frac{1}{2}\sum_{k \neq i,j} X_{ik} + X_{jk}$$

Lee J. T.

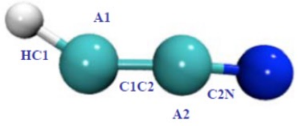
PAH Anharmonicities: Anthracene

- The overall agreement between the anharmonic spectrum and experiment is very good.
- Unlike the harmonic spectra the anharmonic spectra are essentially not scaled.
- The region from about 1600 2500 cm^{-1} is solely due to combination bands



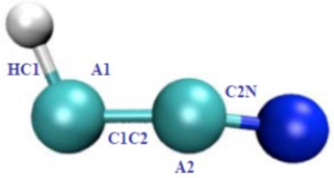
- The computed anharmonic relative IR intensities are also very good compared to experiment (except for the C-H stretch region)
- The C-H stretch region is dominated by resonance polyads – will be discussed in comparison to high-resolution experiments.
- Lee J. T. et al ApJ 2018

Accurate ab initio quartic force fields of cyclic and bent HC2N isomers



X^3A'' ground state triplet

The grids for each electronic state consisted of 743 distinct geometries and these were used to fit our best QFFs.
CCSD(T) or **RCCSD(T)** **/cc-pVX Z, X = 3,4,5,**

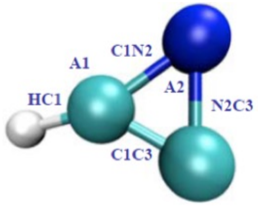


X^1A' bent singlet

$$E(l) = E(TQ5) + E(rel - nrel) + E(mtcc - nmtcc),$$

scalar relativistic effects

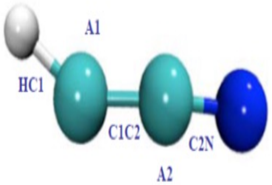
core-correlation correction

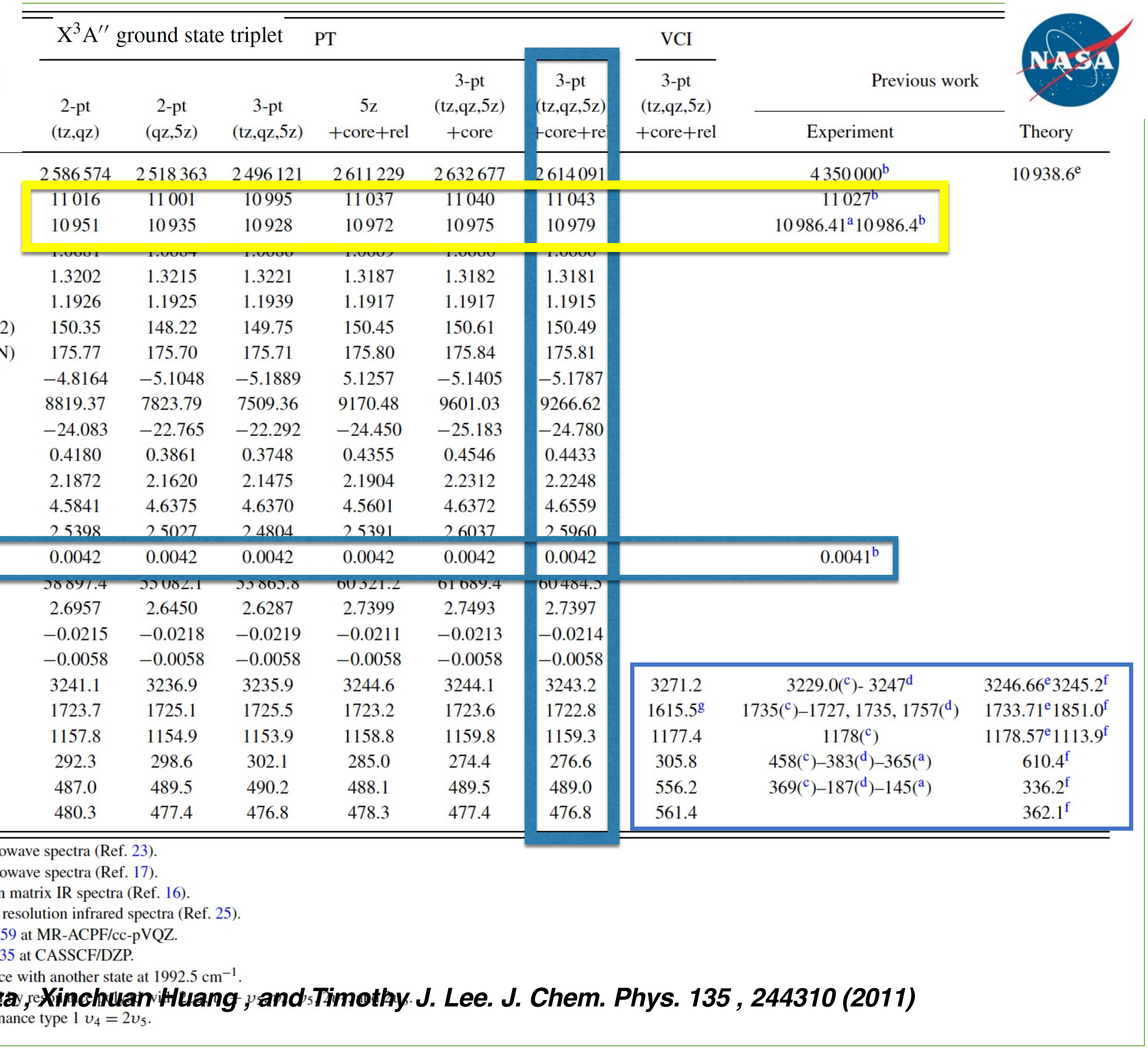


X^1A' cyclic singlet

The QFFs were used together with second-order **perturbation theory (PT) (SPECTRO)** and **variational methods (MULTIMODE)** to solve the nuclear Schrödinger equation.

Natalia Inostroza , Xinchuan Huang , and Timothy J. Lee. J. Chem. Phys. 135 , 244310 (2011)



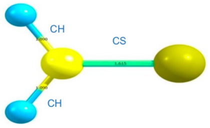


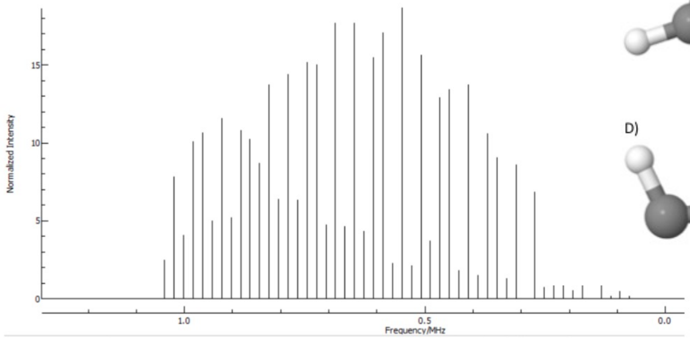
X^3A'' ground state triplet	PT						VCI	Previous work	
	2-pt (tz,qz)	2-pt (qz,5z)	3-pt (tz,qz,5z)	5z +core+rel	3-pt (tz,qz,5z) +core	3-pt (tz,qz,5z) +core+re	3-pt (tz,qz,5z) +core+rel	Experiment	Theory
A_0	2 586 574	2 518 363	2 496 121	2 611 229	2 632 677	2 614 091		4 350 000[b]	10 938.6[e]
B_0	11 016	11 001	10 995	11 037	11 040	11 043		11 027[b]	
C_0	10 951	10 935	10 928	10 972	10 975	10 979		10 986.41[a] 10 986.4[b]	
HC1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
C1C2	1.3202	1.3215	1.3221	1.3187	1.3182	1.3181			
C2N	1.1926	1.1925	1.1939	1.1917	1.1917	1.1915			
A1(HC1C2)	150.35	148.22	149.75	150.45	150.61	150.49			
A2(C1C2N)	175.77	175.70	175.71	175.80	175.84	175.81			
$10^{10}H_J$	−4.8164	−5.1048	−5.1889	5.1257	−5.1405	−5.1787			
H_K	8819.37	7823.79	7509.36	9170.48	9601.03	9266.62			
10^6H_{JK}	−24.083	−22.765	−22.292	−24.450	−25.183	−24.780			
H_{KJ}	0.4180	0.3861	0.3748	0.4355	0.4546	0.4433			
$10^{10}h_1$	2.1872	2.1620	2.1475	2.1904	2.2312	2.2248			
$10^{11}h_2$	4.5841	4.6375	4.6370	4.5601	4.6372	4.6559			
$10^{11}h_3$	2.5398	2.5027	2.4804	2.5391	2.6037	2.5960			
D_J	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042		0.0041[b]	
D_K	58 897.4	55 082.1	53 865.8	60 321.2	61 689.4	60 484.5			
D_{JK}	2.6957	2.6450	2.6287	2.7399	2.7493	2.7397			
10^3d_1	−0.0215	−0.0218	−0.0219	−0.0211	−0.0213	−0.0214			
10^3d_2	−0.0058	−0.0058	−0.0058	−0.0058	−0.0058	−0.0058			
$\upsilon_1(A')$	3241.1	3236.9	3235.9	3244.6	3244.1	3243.2	3271.2	3229.0(c)- 3247[d]	3246.66[e] 3245.2[f]
$\upsilon_2(A')$	1723.7	1725.1	1725.5	1723.2	1723.6	1722.8	1615.5[g]	1735(c)–1727, 1735, 1757(d)	1733.71[e] 1851.0[f]
$\upsilon_3(A')$[h]	1157.8	1154.9	1153.9	1158.8	1159.8	1159.3	1177.4	1178(c)	1178.57[e] 1113.9[f]
$\upsilon_4(A')$[i]	292.3	298.6	302.1	285.0	274.4	276.6	305.8	458(c)–383(d)–365(a)	610.4[f]
$\upsilon_5(A')$	487.0	489.5	490.2	488.1	489.5	489.0	556.2	369(c)–187(d)–145(a)	336.2[f]
$\upsilon_6(A'')$	480.3	477.4	476.8	478.3	477.4	476.8	561.4		362.1[f]

[a] From microwave spectra (Ref. 23).
[b] From microwave spectra (Ref. 17).
[c] From argon matrix IR spectra (Ref. 16).
[d] From high resolution infrared spectra (Ref. 25).
[e] From Ref. 59 at MR-ACPF/cc-pVQZ.
[f] From Ref. 35 at CASSCF/DZP.
[g] In resonance with another state at 1992.5 cm^{-1}.
[h] [illegible]
[i] Fermi resonance type 1 $\upsilon_4 = 2\upsilon_5$.

Natalia Inostroza , Xinchuan Huang , and Timothy J. Lee. J. Chem. Phys. 135 , 244310 (2011)

Theoretical Rovibrational Characterization of the cis/trans-HCSH and H_2SC Isomers of the Known Interstellar Molecule Thioformaldehyde





Espectro N°6 Espectro rovibracional tioformaldehido *CCSD(T)-F12/cc-pVTZ-F12*
300 K

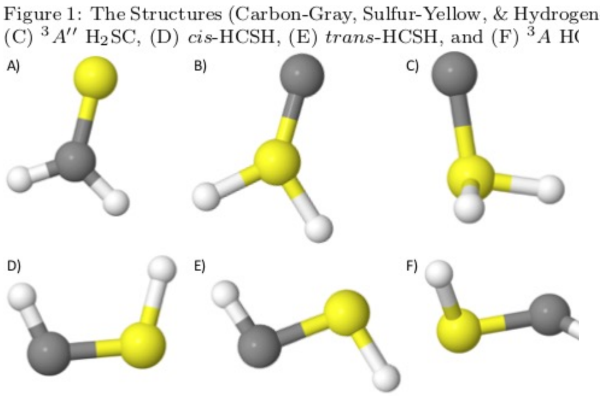


Figure 1: The Structures (Carbon-Gray, Sulfur-Yellow, & Hydrogen-White) of (A) H_2CS, (B) $^1A_1$ H_2SC, (C) $^3A''$ H_2SC, (D) *cis*-HCSH, (E) *trans*-HCSH, and (F) ^3A H(

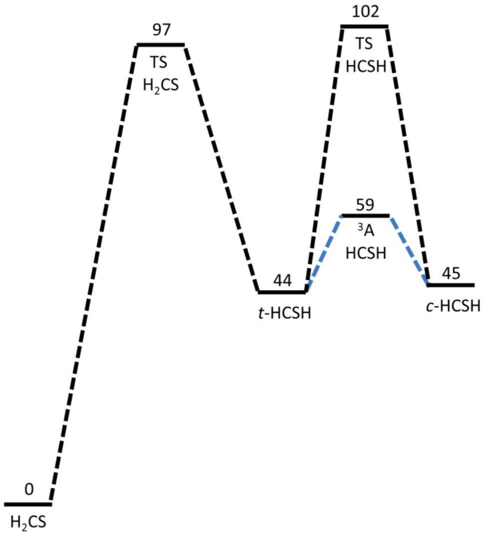
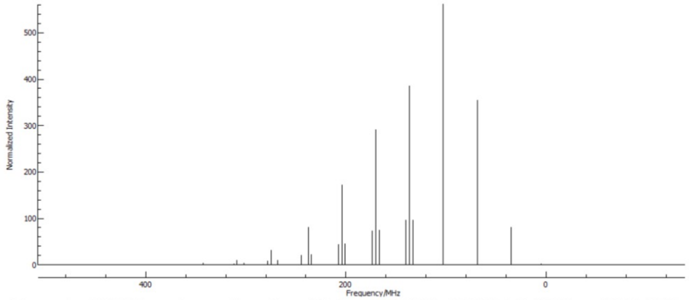
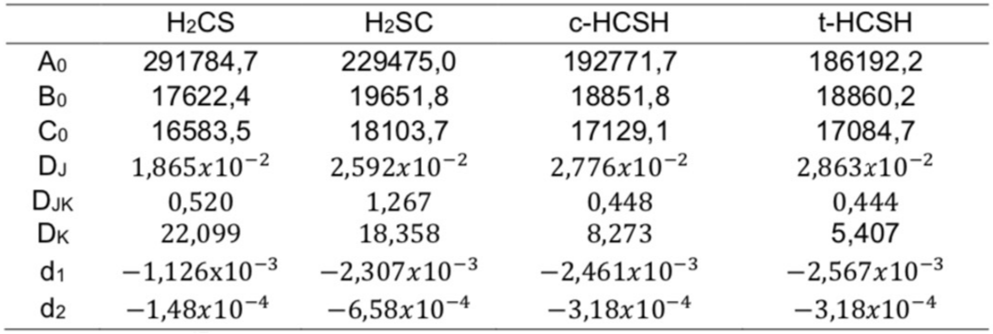


Fig. 2. The potential energy surface for conversion of H_2CS into *cis*- and *trans*-HCSH in kcal/mol.



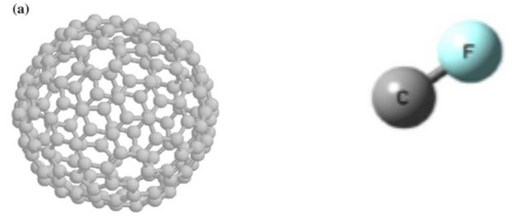
Espectro N°7 Espectro rovibracional tioformaldehido *CCSD(T)-F12/cc-pVTZ-F12*
10 K



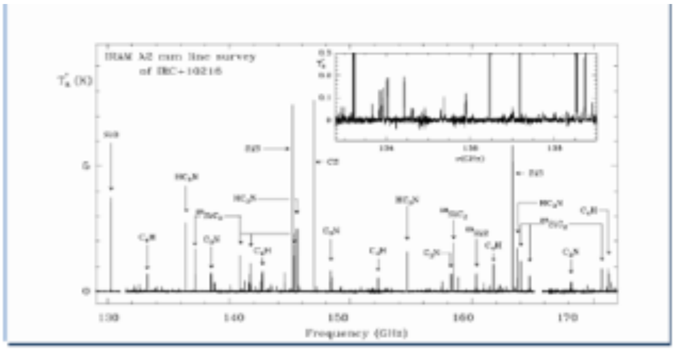
	H_2CS	H_2SC	c-HCSH	t-HCSH
A_0	291784,7	229475,0	192771,7	186192,2
B_0	17622,4	19651,8	18851,8	18860,2
C_0	16583,5	18103,7	17129,1	17084,7
D_J	$1{,}865x10^{-2}$	$2{,}592x10^{-2}$	$2{,}776x10^{-2}$	$2{,}863x10^{-2}$
D_{JK}	0,520	1,267	0,448	0,444
D_K	22,099	18,358	8,273	5,407
d_1	$-1{,}126x10^{-3}$	$-2{,}307x10^{-3}$	$-2{,}461x10^{-3}$	$-2{,}567x10^{-3}$
d_2	$-1{,}48x10^{-4}$	$-6{,}58x10^{-4}$	$-3{,}18x10^{-4}$	$-3{,}18x10^{-4}$

N. Inostroza-Pino, T. J Lee, C.Palmers and R. Fortenbery, / Journal of Molecular Spectroscopy 369 (2020) 111273

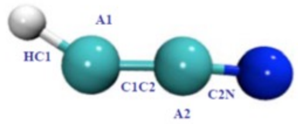
Previous work



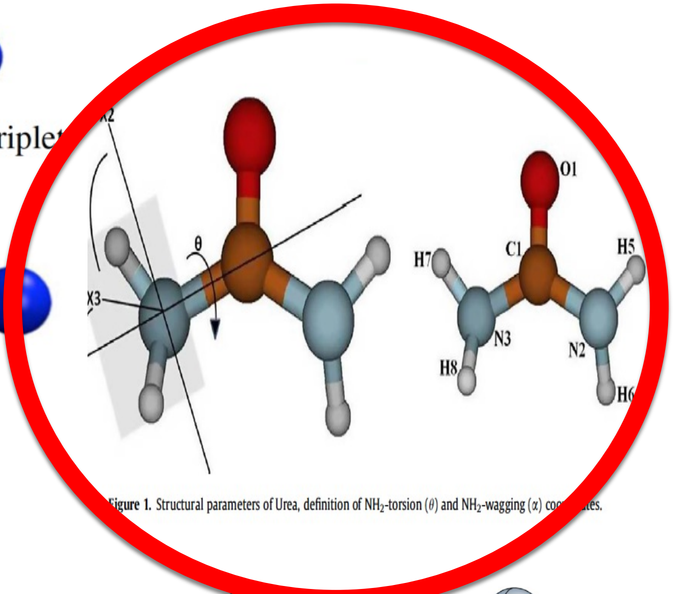
CF$^+$



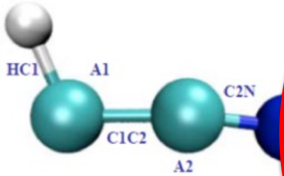
^{28}SiO ^{29}SiO ^{30}SiO



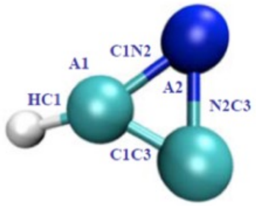
X^{3}A$''$ ground state triplet



igure 1. Structural parameters of Urea, definition of NH$_2$-torsion (θ) and NH$_2$-wagging (α) co tes.

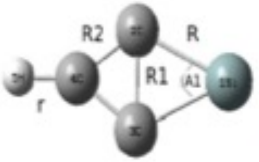


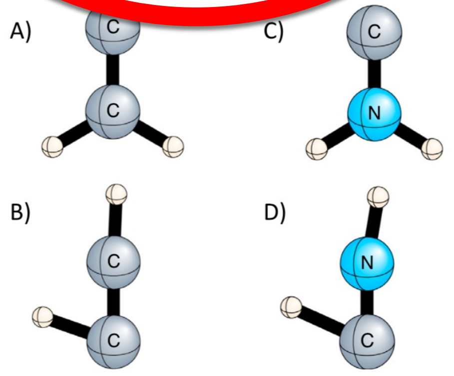
X^{1}A$'$ bent singlet

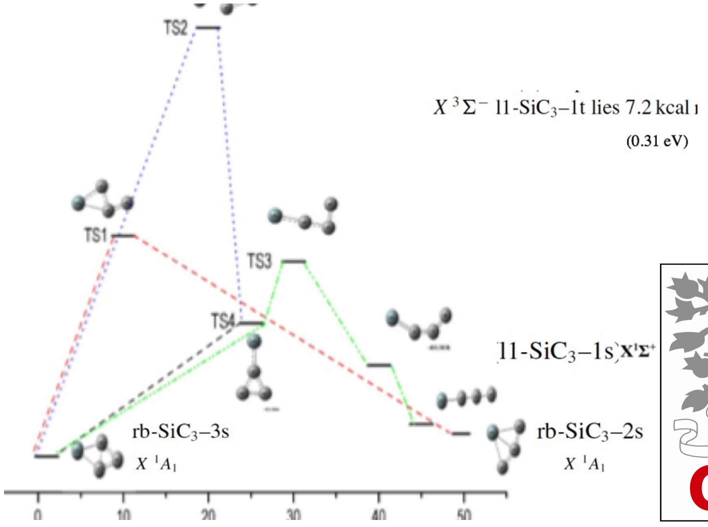


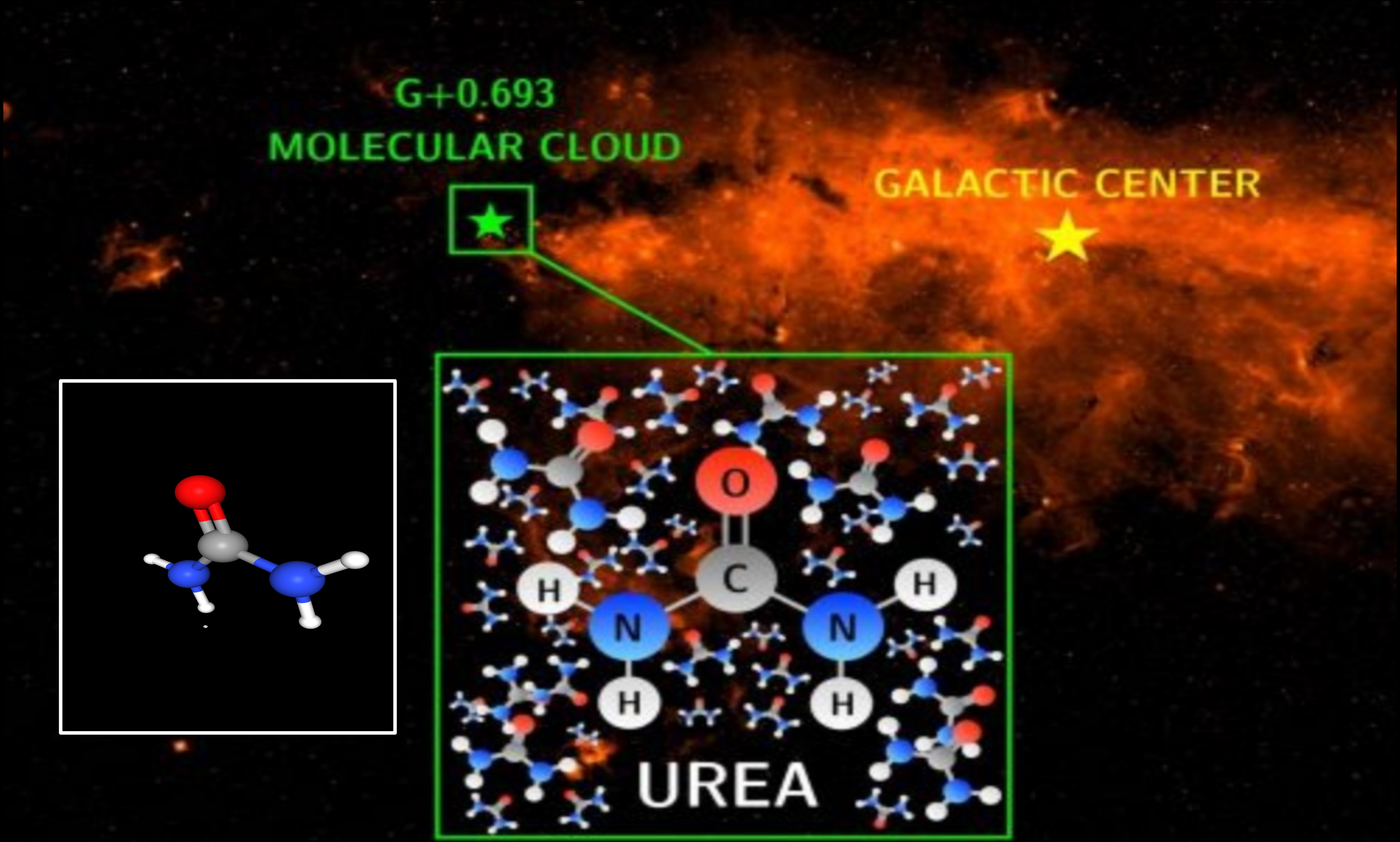
X^{1}A$'$ cyclic singlet

^{29}SiF$^+$ ^{30}SiF$^+$









Rivilla et al apj 2020

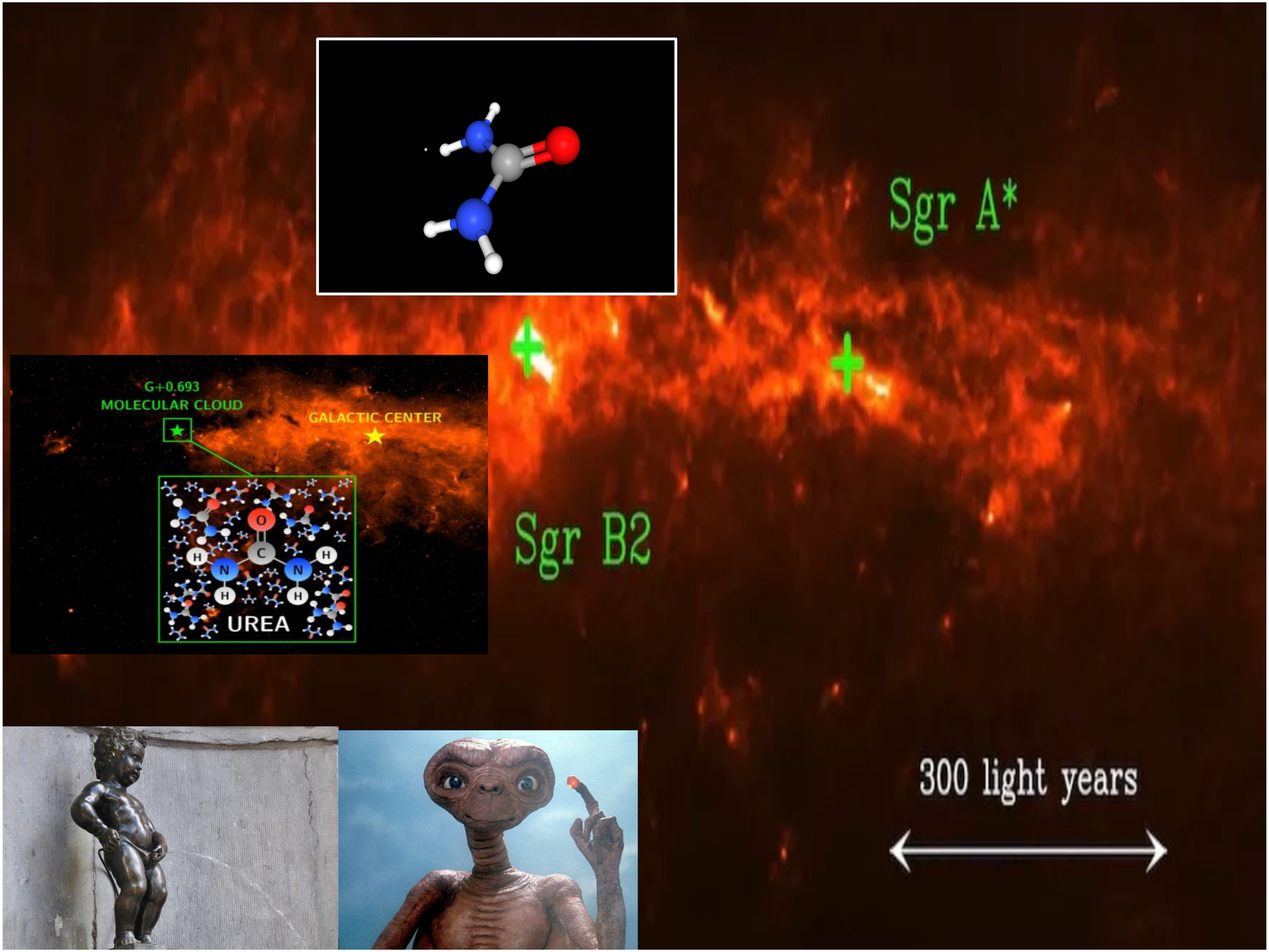
Inostroza &senent ChemPhys 2012

FIT-ESPEC

FIT:Genera una Superficie de Potencial analítica a partir de las energías electrónicas de un grid de geometrías (coordenadas internas)

$$V(Q_i, Q_j \ldots Q_n) = \frac{1}{2}\sum_i f_{ij} Q_i Q_j + \frac{1}{6}\sum_i \sum_j \sum_k f_{ijk} Q_i Q_j Q_k + \frac{1}{24}\sum_i \sum_j \sum_k \sum_l f_{ijkl} Q_i Q_j Q_k Q_l + \ldots$$

ESPEC: se obtienen los parámetros espectroscópicos Ro-vibracionales mediante Teoría de Perturbaciones


Sgr A*
G+0.693
MOLECULAR CLOUD
GALACTIC CENTER
O
C
H
N
N
H
H
H
UREA
Sgr B2
300 light years

Large amplitude vibrations of Urea in gas phase

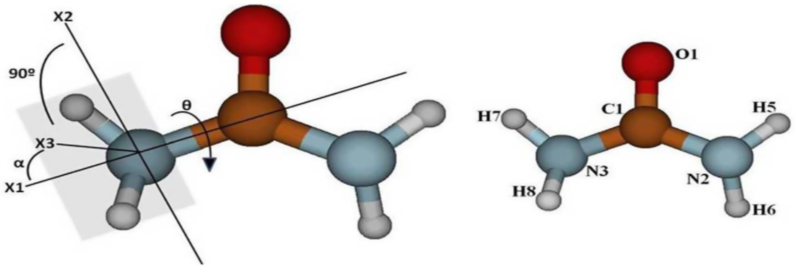


Figure 1. Structural parameters of Urea, definition of NH$_2$-torsion (θ) and NH$_2$-wagging (α) coordinates.

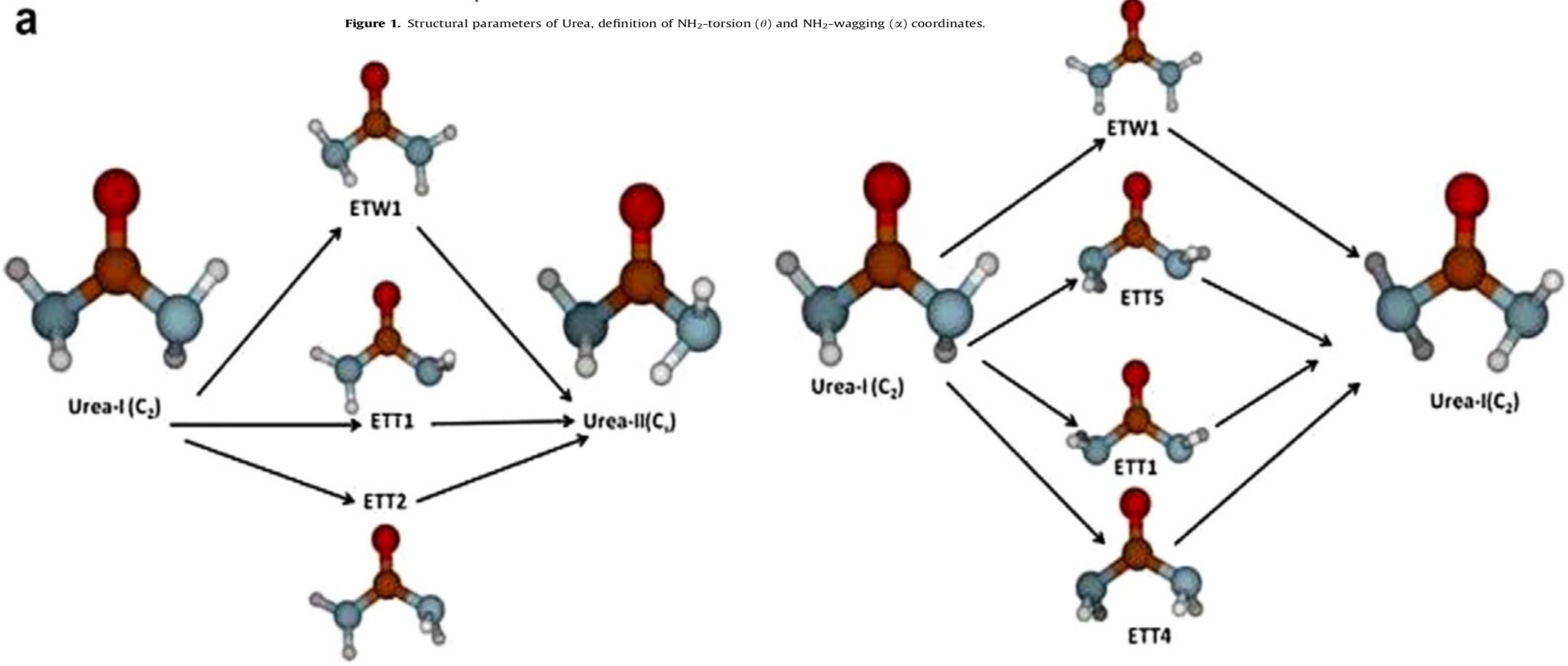
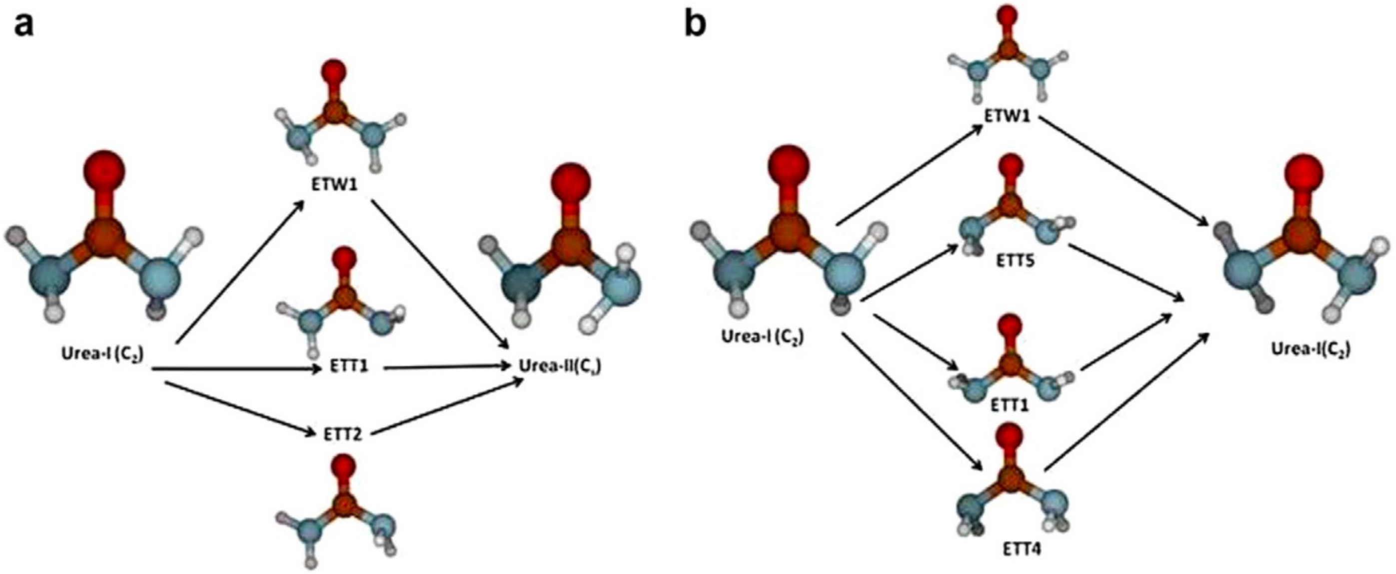


Figure 2. Conversion channels and transition states for the processes (a) Urea-I → Urea-II; (b) Urea-I → Urea-I.

Inostroza, N., & Senent, M. L. (2012). *Chemical Physics Letters*, *524*25-31.



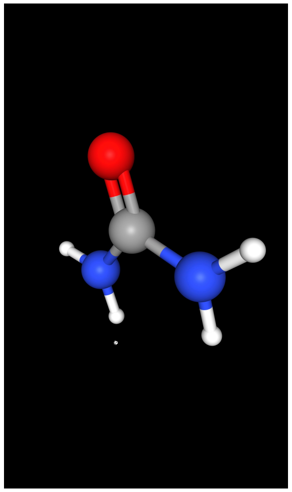


Figure 2. Conversion channels and transition states for the processes (a) Urea-I → Urea-II; (b) Urea-I → Urea-I.

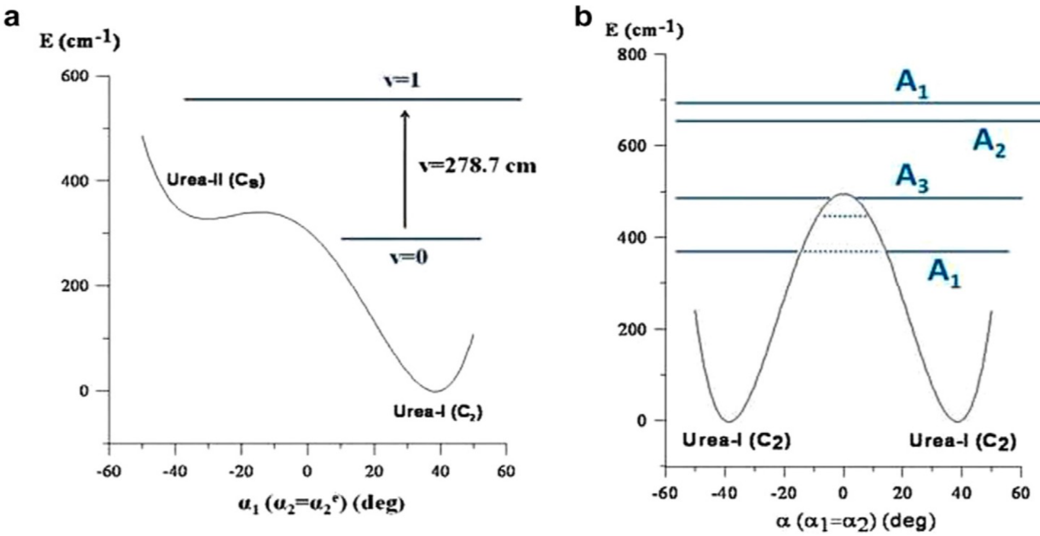
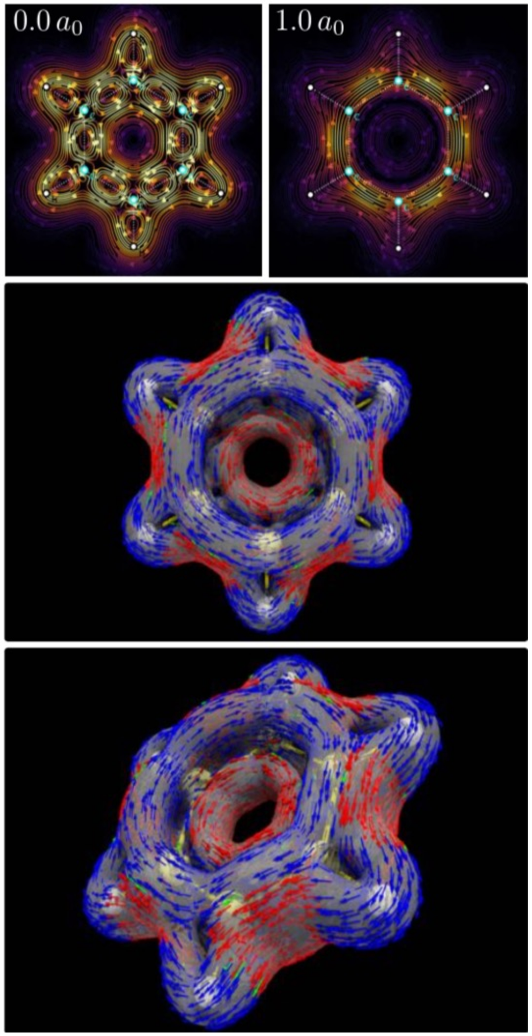


Figure 3. One-dimensional cuts of the MP2 potential energy surfaces: (a) depending on the C–N torsion; (b) depending on the NH_2-wagging coordinate.

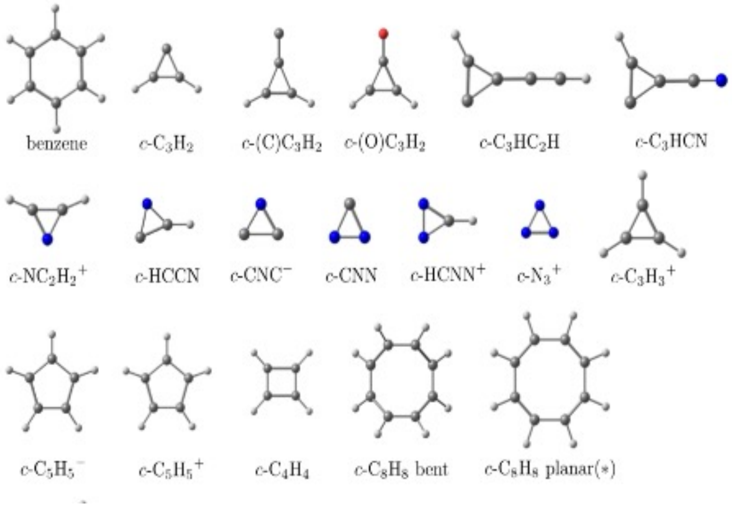
A&A 662, A106 (2022)

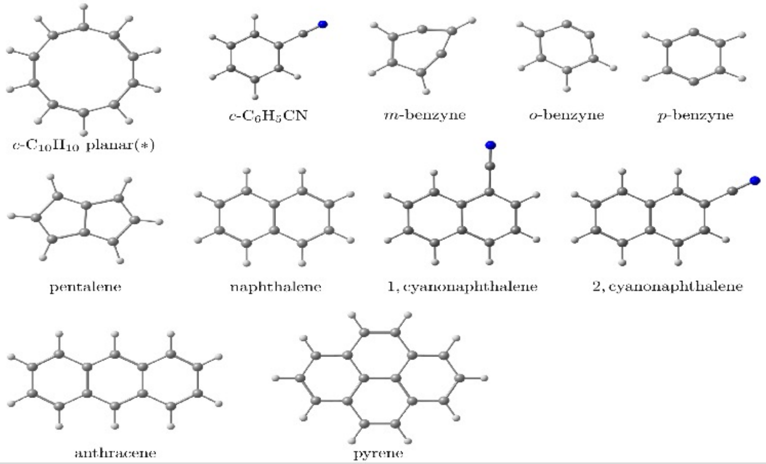
Quantification of molecular aromaticity as a predictive factor of astrophysical significance

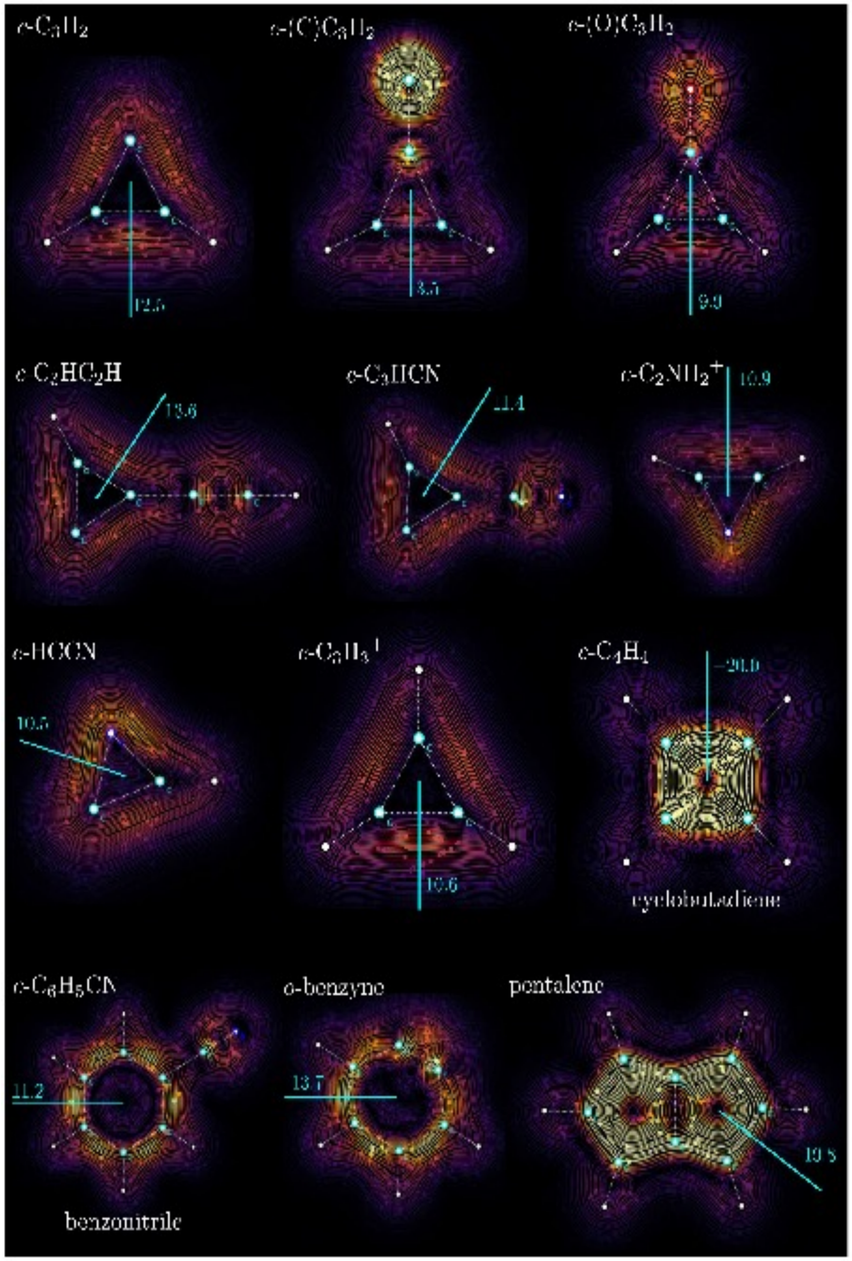
Luis Alvarez-Thon[1], Timothy J. Lee[2], Ryan C. Fortenberry[3] and Natalia Inostroza-Pino[4]



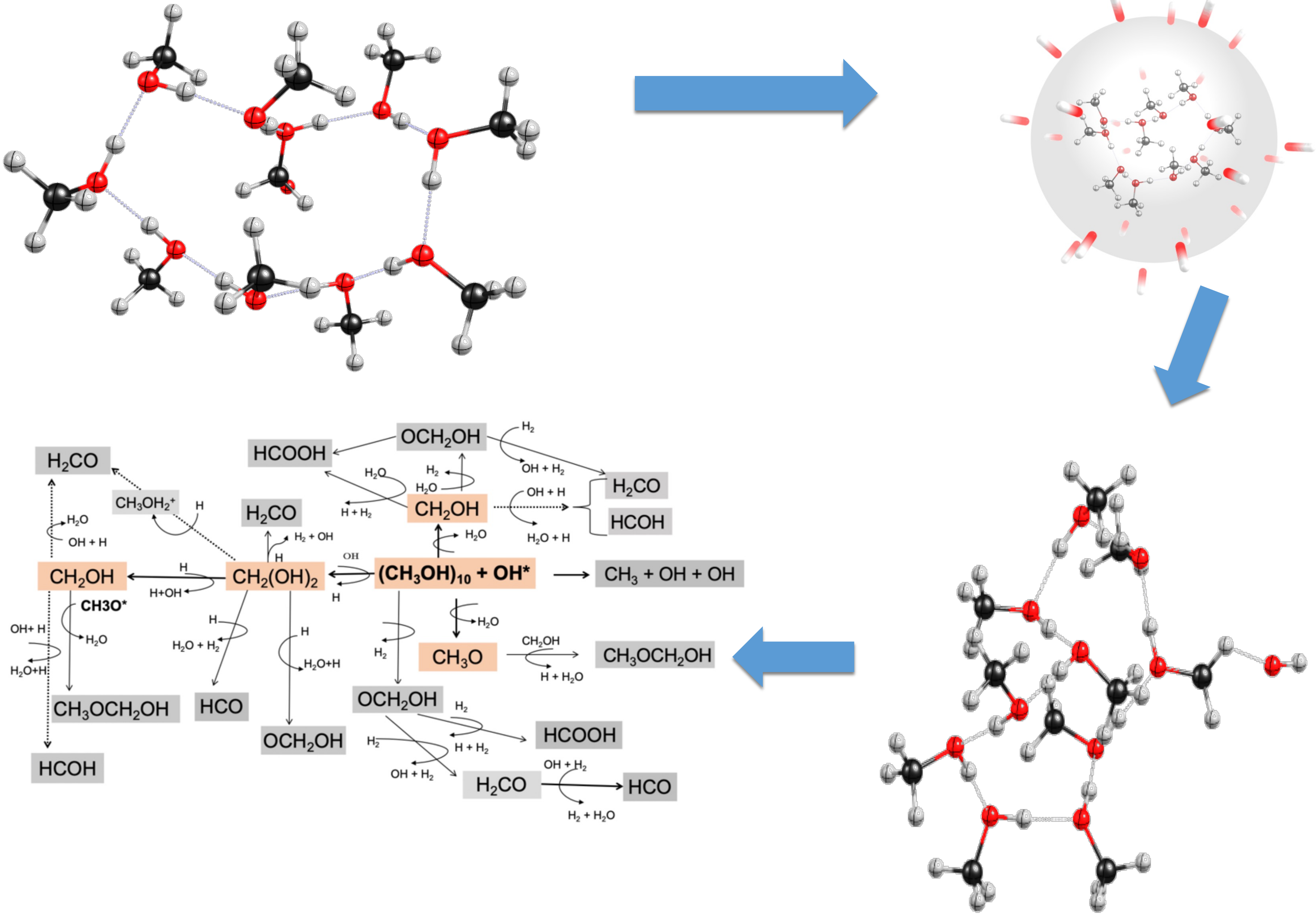
Density functional theory (DFT) calculations at the B3LYP/aug-cc-pVTZ level provide optimized structures and the wave-functions needed to provide the RCS values for the molecules analyzed.


benzene
c-C_3H_2
c-(C)C_3H_2
c-(O)C_3H_2
c-C_3HC_2H
c-C_3HCN
c-$NC_2H_2^+$
c-HCCN
c-CNC^-
c-CNN
c-$HCNN^+$
c-N_3^+
c-$C_3H_3^+$
c-$C_5H_5^-$
c-$C_5H_5^+$
c-C_4H_4
c-C_8H_8 bent
c-C_8H_8 planar(*)


c-$C_{10}H_{10}$ planar(*)
c-C_6H_5CN
m-benzyne
o-benzyne
p-benzyne
pentalene
naphthalene
1, cyanonaphthalene
2, cyanonaphthalene
anthracene
pyrene


c-C_3H_2
c-(C)C_3H_2
c-(O)C_3H_2
12.5
3.5
9.9
c-C_3HC_2H
13.6
c-C_3HCN
11.4
c-$C_2NH_2^+$
10.9
c-HCCN
10.5
c-$C_3H_3^+$
10.6
c-C_4H_4
−20.0
cyclobutadiene
c-C_6H_5CN
11.2
benzonitrile
o-benzyne
13.7
pentalene
19.8

$(Methanol)_{10}$-Ice-mantle



10 eV

$$CH_3OH + OH^- \longrightarrow CH_3O^- + H_2O$$

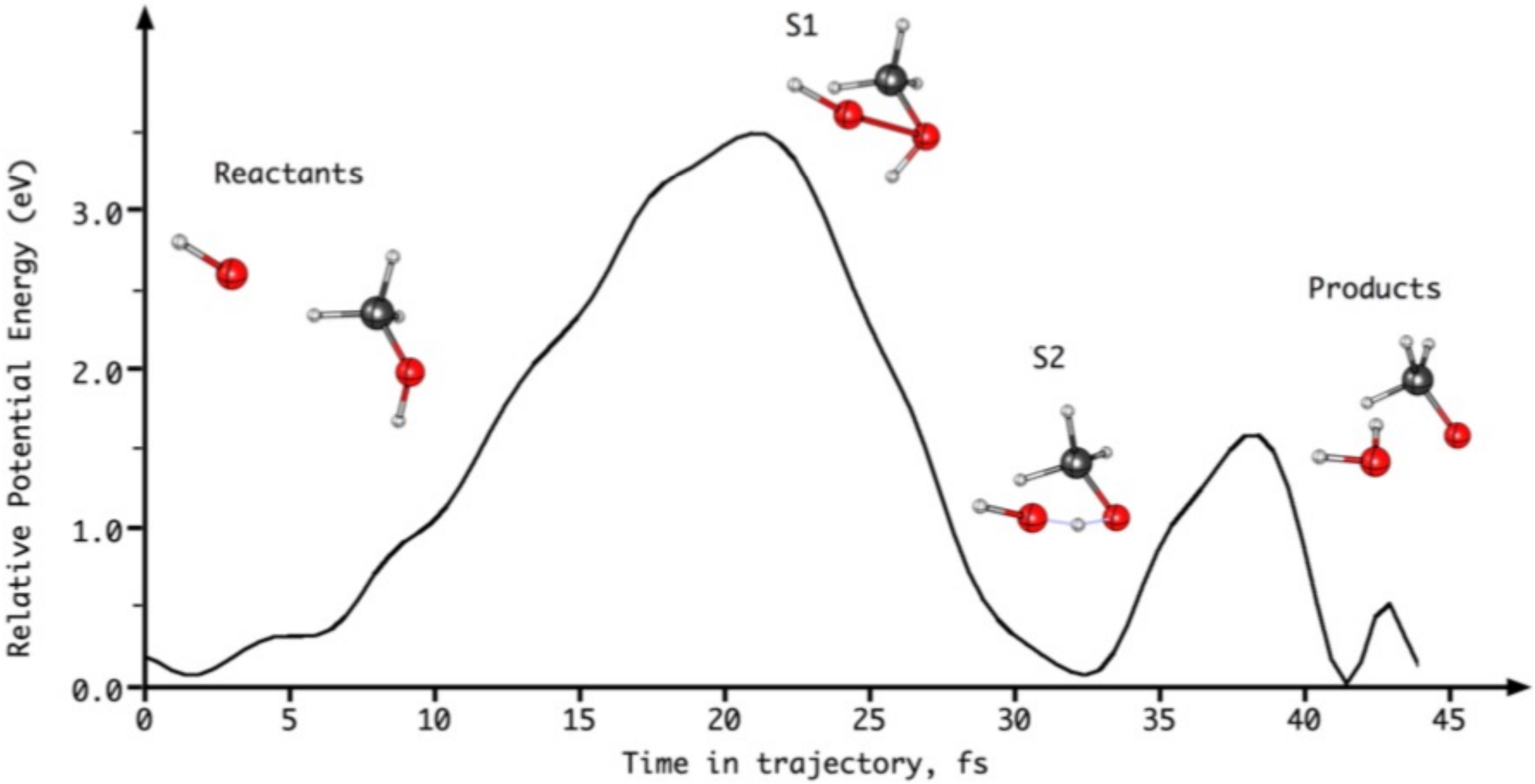
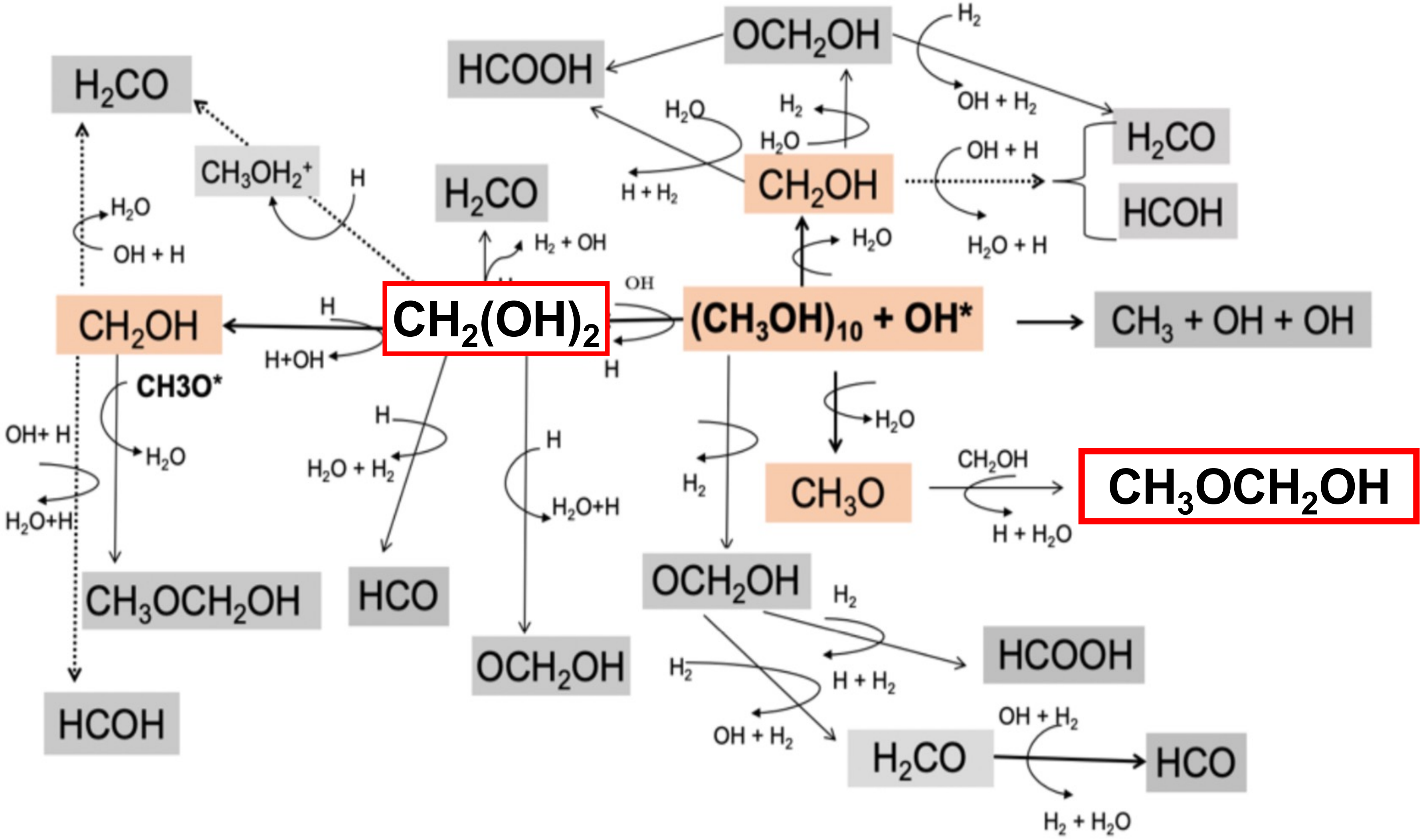


Fig. 3. Diagram illustrating $CH_3OH + OH^- \xrightarrow{CH_3OH--O--H} CH_3O^- + H_2O$ outcomes at 10 eV in a BOMD simulation.

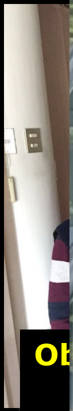
CH_3OH + OH radical

A&A 641, A14 (2020)



Reading

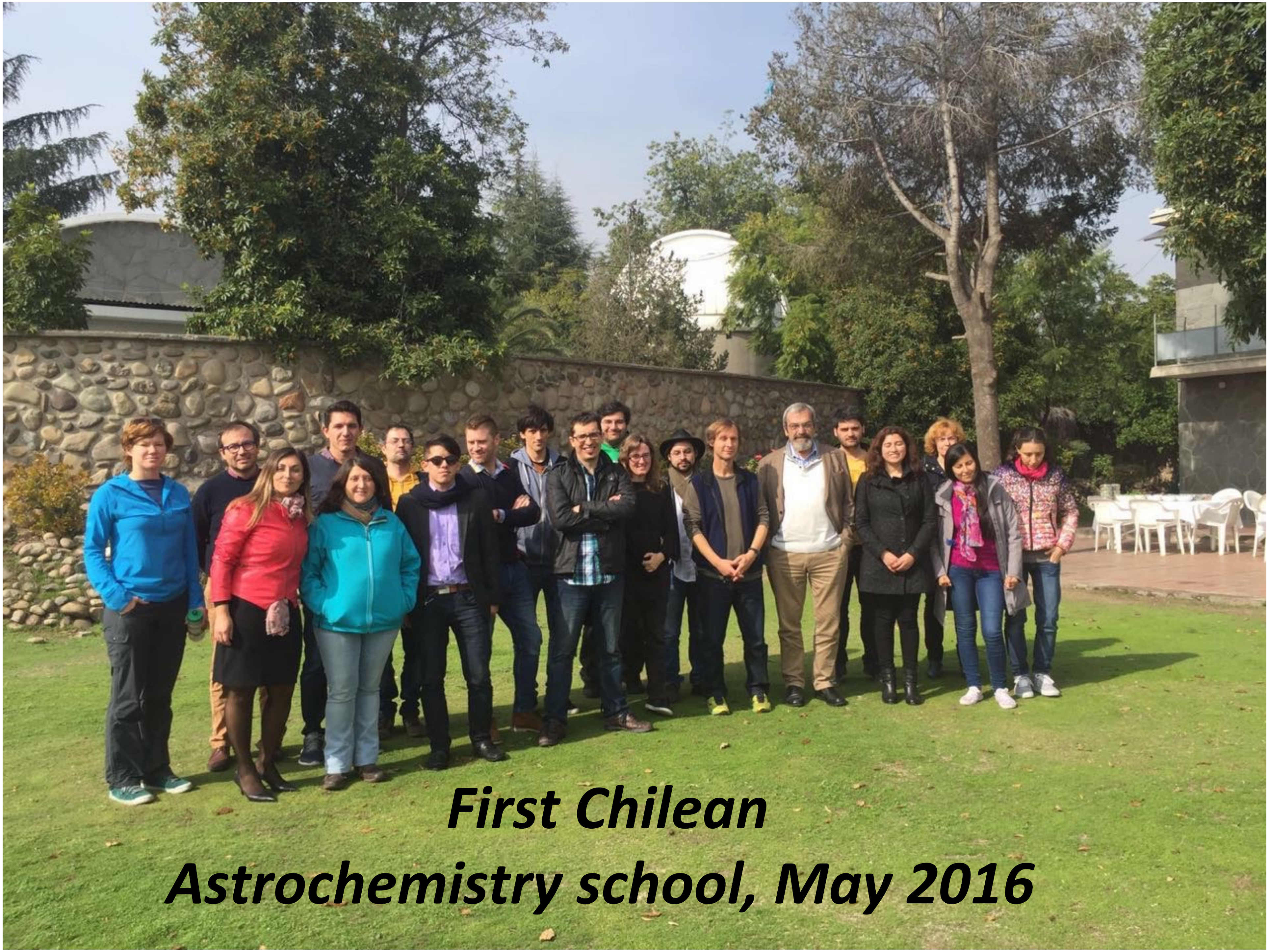
- More advanced astrochemistry chapters in “The Physics and Chemistry of the Interstellar Medium”, A. G. G. M. Tielens, ISBN 0521826349. Cambridge, UK: Cambridge University Press, 2005.



Ob

G

0113
TMOS



First Chilean
Astrochemistry school, May 2016

II International
Astrochemistry school, October 2018

Gracias

@nucleoastrochem