Complex molecules : From the lab to the ISM and back

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pcmi

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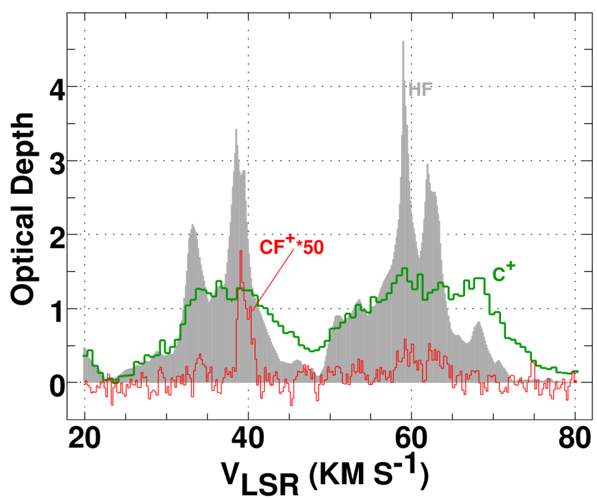
ANR

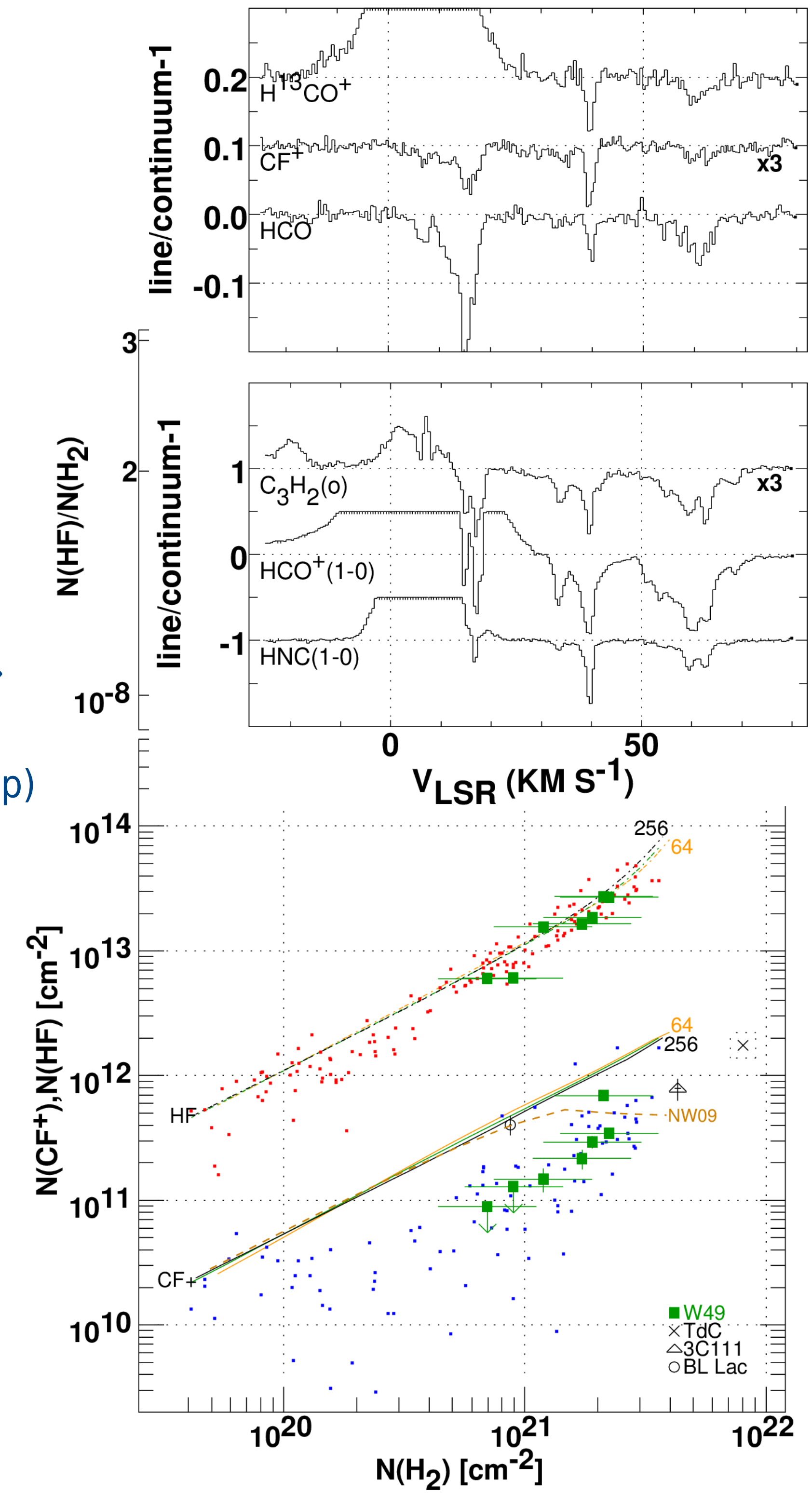
A simple system : CF^+

(Liszt, Guzman et al. submitted)

- Formation $C^+ + HF \rightarrow CF^+ + H$

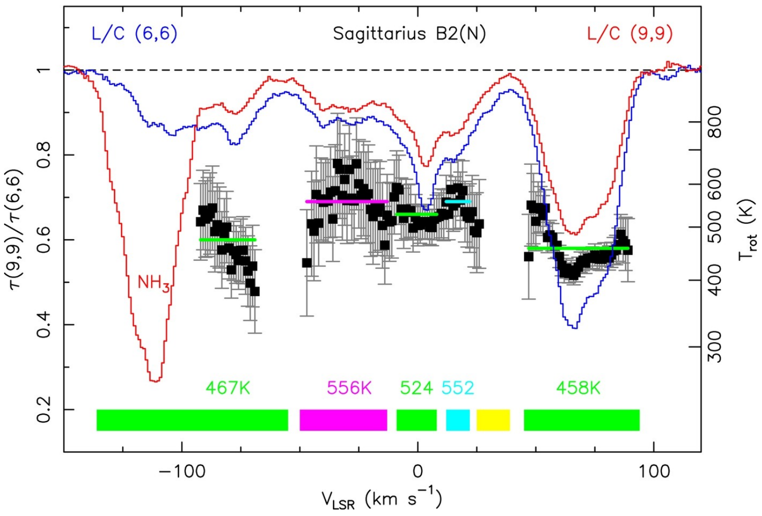
  with rate $k1 = 7.2E\text{-}9\ (T/300\ K)^{-0.15}\ cm^3\ s^{-1}$
- Destruction : $CF^+ + e \rightarrow C + F$; $CF^+ + h\nu \rightarrow C^+ + F$
- In equilibrium : $n(CF^+)/n(HF) = k1n(C^+)/[ken(e) + GD)$
- CF^+ is expected to follow C^+ & H_2 (through HF)
- Observations show a deficit of CF^+ relative to HF by a factor 2 to 4 → reduced formation rate or enhanced destruction rate ?
- Photodissociation rate recently calculated by Dayou & Roueff (in prep)
- Dissociative recombination rate ? Or formation rate ?
- Check The C^+ + HF reaction and CF^+ dissociative recombination



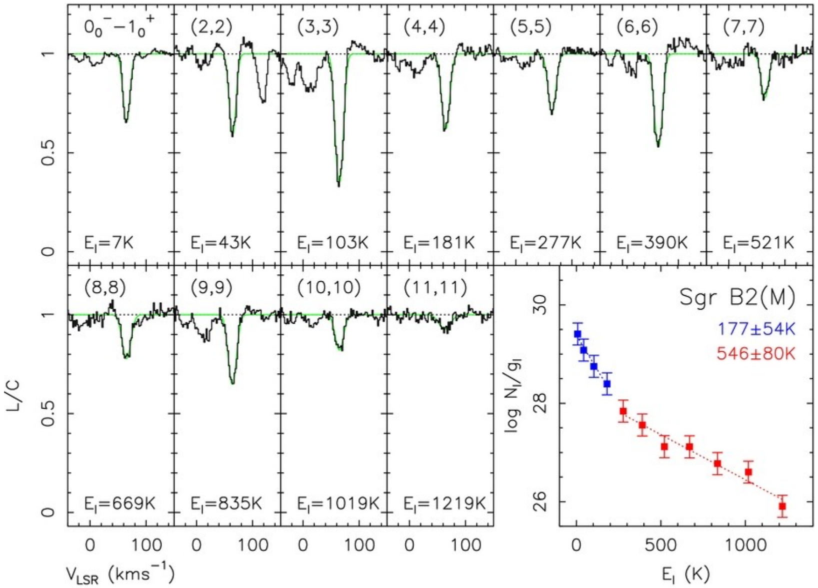


Formation pumping : H_3O^+

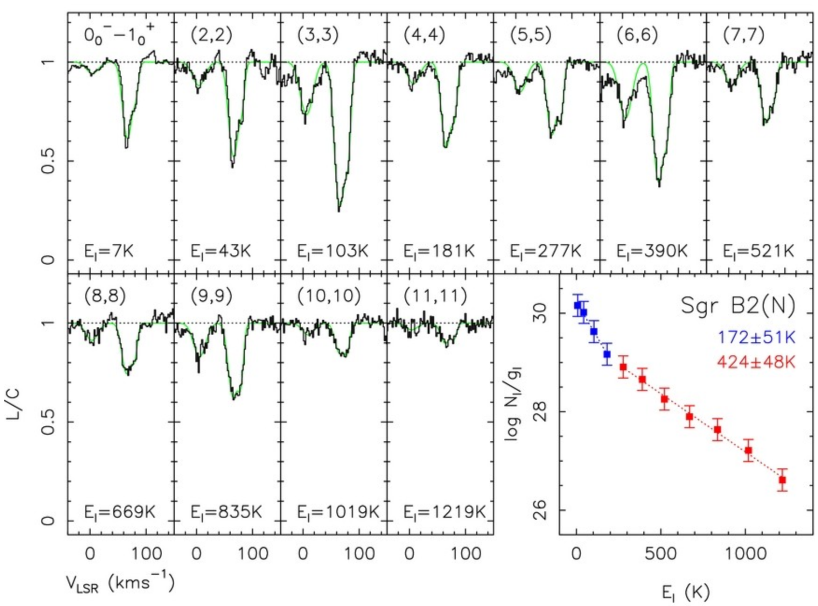
(Lis et al. 2014)



- Symmetric top with high inversion frequency → Lines in the THz range, accessible with Herschel
- NH_3 has similar properties with low inversion frequency
- Detection of absorption in excited levels up to 11,11 > 1200K above ground towards SgrB2
- Other detections in the diffuse ISM, in active galaxies (Arp 220)
- Abundance determination needs all levels
- General phenomenon → formation pumping : the population of the metastable levels has a longer lifetime than the destruction rate. This may also apply to NH_3 in some cases.
- Add a comment in KIDA for species like H_3O^+ ?



$0_0^- - 1_0^+$
(2,2)
(3,3)
(4,4)
(5,5)
(6,6)
(7,7)
E_l=7K
E_l=43K
E_l=103K
E_l=181K
E_l=277K
E_l=390K
E_l=521K
(8,8)
(9,9)
(10,10)
(11,11)
E_l=669K
E_l=835K
E_l=1019K
E_l=1219K
L/C
V_LSR (kms^-1)
Sgr B2(M)
177±54K
546±80K
log N_l/g_l
E_l (K)



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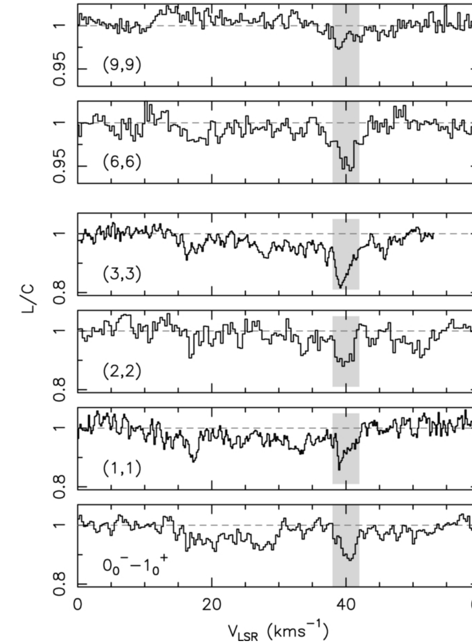
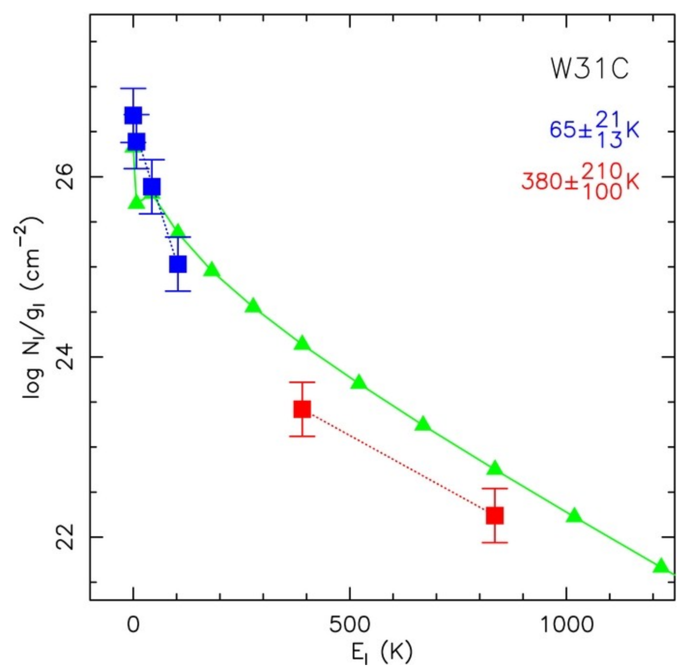
E_l=669K
E_l=835K
E_l=1019K
E_l=1219K
L/C
V_LSR (kms^-1)
Sgr B2(N)
172±51K
424±48K
log N_l/g_l
E_l (K)



(9,9)
(6,6)
(3,3)
(2,2)
(1,1)
$0_0^- - 1_0^+$
L/C
V_LSR (kms^-1)



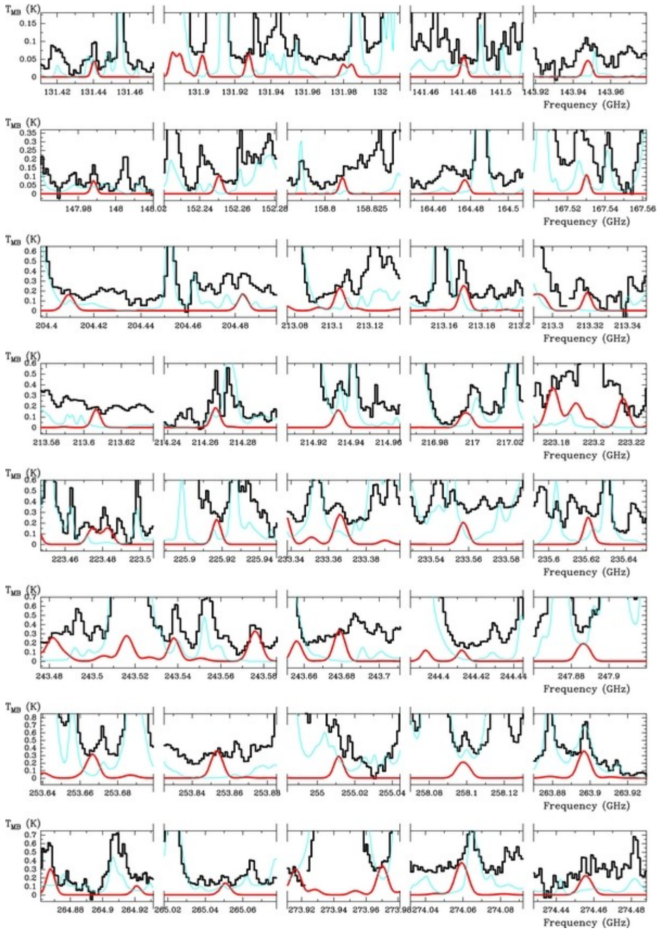
W31C
65^{+21}_{-13}K
380^{+210}_{-100}K
log N_l/g_l (cm^-2)
E_l (K)

Interstellar Compounds

Number of atoms	Molecule
2	AlCl, AlF, C_2, CF+, CH (and CH+), CN, CO (and CO^+), CP, CS, FeO, H_2, HCl, HF, HN, HO, KCl, N_2, NO, NS, NaCl, O_2, PN, PO, SH (and SH^+), SO (and SO^+), SiC, SiN, SiO, SiS, O_2, TiO.
3	H_3^+, AlNC, CH_2, C_3, C_2H, C_2O, C_2S, CO_2, H_2C, H_2O, H_2S, HCN, HCO (and HCO+), HCP, HCS^+, HNC, HN_2^+, HNO, HOC^+, KCN, MgCN, MgNC, NH_2, N_2H^+, N_2O, NaCN, OCS, H_2Cl^+, CO_2, c-SiC_2, SiCN, SiNC, SO_2, C_2H^-, FeCN, HO_2, TiO_2.
4	CH_3, l-C_3H, c-C_3H, C_3N (and C_3N^-), C_3O, C_3S, C_2H_2, H_3O^+, H_2CN, $HCNH^+$, H_2CO, H_2CS, HCCN, $HCNH^+$, $HOCO^+$, HNCO, HNCS, NH_3, c-SiC_3, HOOH, HMgNC, NH_3D^+, i-C_3H^+, CH_3O.
5	C_5, C_4N, CH_4, c-C_3H_2, l-H_2C_3, H_2CCN, H_2C_2O, H_2CNH, H_2COH+, C_4H (and C_4H^-), HC_3N, HCCNC, HCOOH, HNC_3, NH_2CN, SiC_4, SiH_4, NH_2CO^+, HNCNH.
6	c-C_3H_2O, C_2H_4, CH_3CN, CH_3NC, CH_3OH, CH_3SH, l-H_2C_4, HC_3NH^+, $HCONH_2$, C_5H, C_5O, C_5N (and C_5N^-), HC_2CHO, HC_4N, CH_2CNH, E-HNCHCN.
7	c-C_2H_4O, CH_3C_2H, H_3CNH_2, CH_2CHCN, H_2CHCOH, C_6H (and C_6H^-), HC_4CN, CH_3CHO.
8	H_3CC_2CN, $H_2COHCHO$, CH_3OOCH, CH_3COOH, H_2C_6, C_2H_6, CH_2CHCHO, CH_2CCHCN, CH_3C_3N, C_7H, H_2NCH_2CN, $(NH_2)_2CO$.
9	CH_3C_4H, CH_3OCH_3, CH_3CH_2CN, CH_3CONH_2, C_8H (and C_8H^-), HC_6CN, CH_3CHCH_2, CH_3CCCN, C_2H_5SH.
10	$(CH_3)_2CO$, CH_3CH_2CHO, CH_3C_5N, $HOCH_2CH_2OH$.
11	HC_8CN, CH_3C_6H, C_2H_5OCHO, $CH_3OC(O)CH_3$.
12	$CH_3OC_2H_5$, C_6H_6, C_3H_7CN.
13 and more	$HC_{10}CN$, $C_6H_7^+$ … and $C_{14}H_{10}^+$, C_{60}, C_{70}.

Finding new species : line surveys

- Increased instantaneous spectral bandpass :
  - “Easy” coverage of tens of GHz at good spectral resolution ~ 200kHz
  - Automatic line fitting procedures and removal of artefacts (ghosts, interferences, etc.)
- Strong spectral confusion in hot cores : high densities and temperature (200 K), significant population in excited levels up to ~ 1000K & including vibrational states, isotopologues,
- A confirmed detection requires many lines from different excitation levels and no missing lines.
  - CH3CH2SH in Orion (Koleniskova et al 2014)
- High angular resolution helps by separating the sources (NOEMA /ALMA)
- Cold cores : lower excitation conditions & narrow lines → reduced spectral confusion. Optimum sources for isotopologues (D, 15N, …) . Presence of some complex molecules (CH3CHCH2, CH3O, CH3CHO …)
- PDRs : medium excitation conditions, narrow lines → reduced spectral confusion. Optimum sources for UV-driven chemistry. Presence of some complex molecules (CH3CN, CH3CHO, …)



Method 1 : Lab to Space

- Analysis of the chemistry
- Selection of possible species
- Chemical Synthesis for species not commercially available (may need to be produced in situ)
- Laboratory spectroscopy

  starting from low frequency predictions, up to THz frequencies) + assignment, derivation of rot constants, line list
- Astrophysical search through line surveys or dedicated observations

Long time scale (few years) , success not guaranteed

Method 2 : Space to lab

- Astrophysical observations (line survey) & line identification from catalogs
- Set of U lines (not assigned)
- Derivation of possible spectroscopic parameters
- Comparison with existing calculations or measurements
- Proposition of a new detection
- If no laboratory spectroscopy is available, the confirmed assignment needs a dedicated laboratory measurement.

Long time scale (few years). Often leads to surprises (e.g. unexpected species CH2CHCH3 propylene)

Finding new species : which strategy ? I

Using gas phase chemical models and searching for the predicted species not detected yet

- Hydrogen abstraction reactions :
  - OH^+, H_2O^+, H_3O^+ (eg Gerin et al; 2010, Indriolo et al. 2015)

    $O^+ + H_2 \rightarrow OH^+ + H$; $OH^+ + H_2 \rightarrow H_2O^+ + H$; $H_2O^+ + H_2 \rightarrow H_3O^+ + H$
  - NH_4^+ through NH_3D^+ (Cernicharo et al. 2013)
  - HCl^+, H_2Cl^+ (De Luca et al., Lis et al.)
- Protonation reactions
  - $HOCO^+$ indicates the presence of CO_2
  - H_2NCO^+ (Gupta et al. 2013)
- Predicted products of gas phase networks
  - C_2 (Souza et al. 1977)
  - HF (Neufeld et al. 1997)
- N chemistry
  - NO^+ (Cernicharo et al. 2014)

    Too much HNO ! What is missing ? NCO is predicted, no detection so far while HNCO is abundant

This works for relatively simple species. For more complex ?

Finding new species : which strategy ? II

Using a simple chemical reasoning

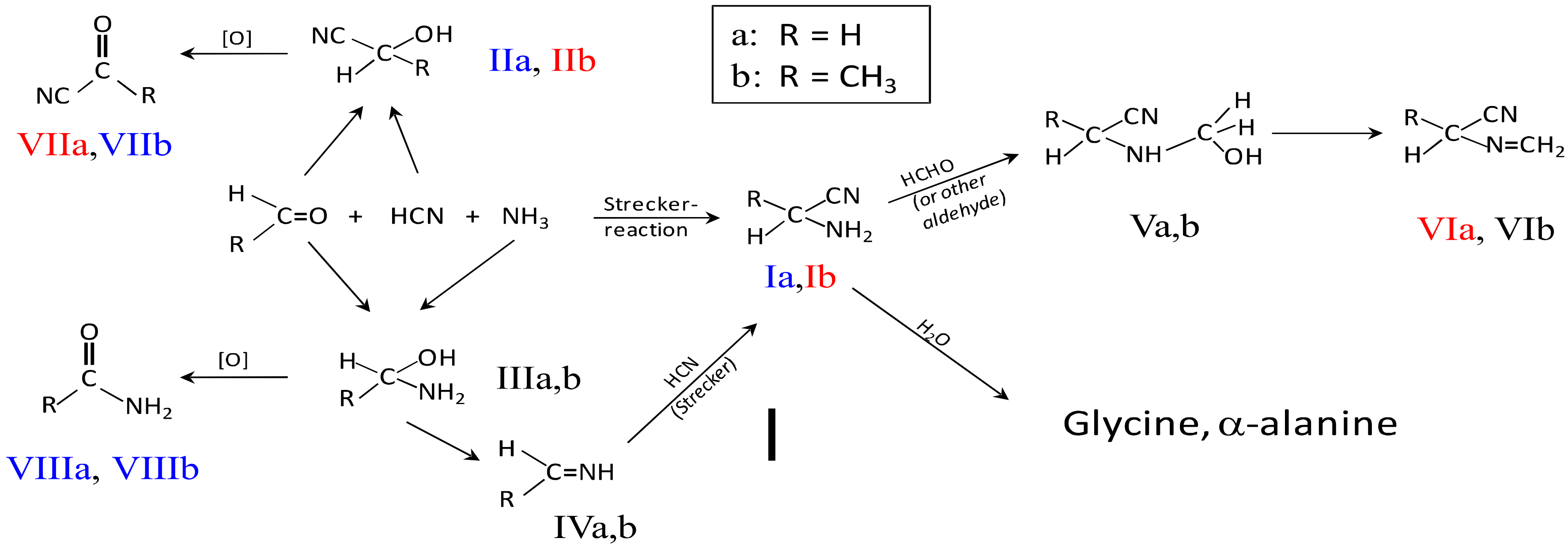
- Isomers :
  - HCN / HNC
  - HNCO, HOCN, HCNO
  - c-C_3H_2, l-C_3H_2
  - HCCCHO, c-C_3H_2O (no CH2CCO so far !)
- Chemical families
  - Carbon chains & cycles C_nH, C_nH_2
  - Cyanopolyynes HC_nN
  - Aldehydes H_2CO, CH_3CHO, ...
  - Alcohols ... CH_3OH, CH_3CH_2OH
  - Cyanides and isocyanides CH_3CN, CH_3NC, CH_3CH_2CN ,

Finding new species : which strategy ? III

- Functional groups
  - Methyl derivatives : HCN, CH_3CN ...
  - Thio hydrocarbons CH_3SH
  - Cyanides / aldehydes /alcohols ...
  - Amine (NH_2)

- Analogs of laboratory chemical synthesis
  - e.g; Strecker reaction
  -

Strecker synthesis



Ia & IVb on going Margulès & Guillemin
VIa (A&A 559, A44 (2013) , Ib (A&A 538, A51 (2012)
IVc (EtCH=NH) on going.

Detection : Ia, IVa, IVb
No detection IIa, VIa
No synthesis for lab spectroscopy : IIIa,b (can be done in matrices)

Some species with known spectroscopy, no detection

- $HOCH_2CN$: hydroxyacetonitrile.
  - Formed in laboratory ice experiments. Competes with aminomethanol (NH_2CH_2OH) and aminoacetonitrile (H_2NCH_2CN). Is a glycine precursor through the Strecker synthesis (Danger et al. 2012).

    Not detected in line surveys in the best sources (Orion, SgrB2, comets …) although the spectroscopic data are excellent up to ~ 500 GHz…
  - Desorption ? Reactivity ?

- A HCN trimer $(CN)_2CHNH_2$
  - $NCCH_2CN$ malonitrile

  and its isomer socyanoacetonitrile $CNCH_2CN$
  - Simple and relatively small species, the HCN dimer E-cyanomethanimine is detected in SgrB2 (Zaleski et al.).
  - Species with 2 N are relatively rare ? Why ?

Some species with known spectroscopy, no detection

- CH_3CH_2NC: ethyl isocyanide.
  - Cyanides like CH_3CH_2CN , CH_2CHCN are very abundant in hot cores. Isocyanides are much less abundant than their cyanide isomers, but are of interest for ISM and Titan atmosphere.
  - CH3NC is detected in the horsehead nebula at the 10% level relative to CH_3CN ?
  - Cyanide / isocyanide chemistry needs further work

- CH_3CONCO: acetyl isocyanate
  - HNCO is present in many environments, 2 isomers are detected, OCN^- is a mantle component, acetone CH_3COCH_3 is detected in hot cores, hence this is a reasonable candidate.

    Species with a large number of C, N & O atoms, may have a very low abundance or be below the current detection limit.

    Revise solid state chemistry ?

Some current projects & suggestions

- Radicals
  - CH_3O (Cernicharo et al. 2012) → CH_2OH (Difficult synthesis and spectroscopy)
  - HCCO (Agundez et al. 2015) (10% of ketene H2CCO), Other radicals ?
- N chemistry (following NO^+ detection (Cernicharo et al. 2014). Too much HNO in the models → missiing N species
  - NCO. Known spectroscopy ; no detection
  - HNO^+, H_2NO^+ ?
  - H_2NCO^+ , $HNCOH^+$?
- D Species
- 13C species
- Vibrationally excited transitions
- Metal bearing species (in circumstellar envelopes) associated with the formation of grains
- Sulfur bearing species : thio-formates ROC(S)H and RSC(O)H
- Chiral molecules ? following the detection of the branched species iso-propyl-cyanide i-C_3H_7CN (Belloche et al. 2014)
-

Spectroscopic developments in Lille & Paris

- Frequency coverage up to 1.9 THz using frequency multiplier developed for space (HIFI, JUICE, …)
- Spectroscopy with heterodyne detection (as done for the tests and characterization of HIFI mixers) Test with Schottky mixers ; comparison of sensitivity
- Fast Scan : 3 days to record the full band 150 – 1500 GHz at ~ 20 to 150 kHz sampling