New insight on the abundances of metal-bearing molecules in the circumstellar gas

Le Havre (Normandie): UNESCO world heritage site

Mario Hernandez Vera[1], Fabien Dumouchel[1], Jacek Klos[2] and François Lique[1]

[1]*Laboratoire Ondes et Milieux Complexes*
Université du Havre, France

[2]*Dpt. of chemistry and biochemistry*
University of Maryland, USA

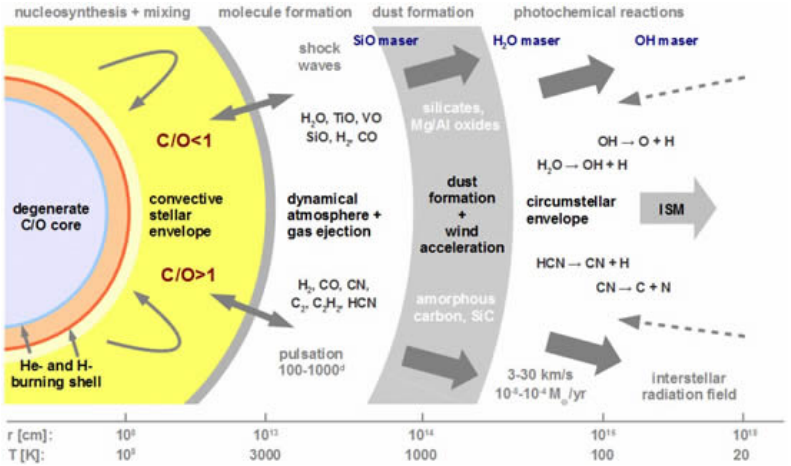
I – Introduction

- Metals are important constituents of the interstellar medium (ISM) and are among the most heavily depleted elements in dense clouds (major component of interstellar dust)
- Metal-bearing molecules in the ISM (including circumstellar gas) are crucial for the evaluation of dust grain composition, ionization balance, mass loss from evolved stars …
- Three families of metal-bearing molecules:

Metal cyanides	*Metal halides*	*Metal monoxides/hydroxydes*
AlCN, MgCN, MgNC, HMgNC, NaCN, SiCN, SiNC, KCN, FeCN	NaCl, KCl, AlCl, AlF	AlO, FeO, AlOH

- **Most common metal bearing molecules** in the circumstellar gas.
- Detection towards circumstellar gas (IRC+10216)

Circumstellar envelope:
Part of the star which has a roughly spherical shape and is not gravitationally bound to the star core.



Schematic chemical structure of the circumstellar shell of an AGB star

I – Introduction

- **Isomerism** occur in many metal cyanides (*Metal cyanides and isocyanides*)

  MgCN/MgNC *AlCN*/AlNC* *SiCN/SiNC*

- Most stable isomer = most abundant (MgCN/MgNC, AlCN/AlNC)
  ✓ **This is not a systematic trend (SiCN/SiNC)**

- Metal cyanides and isocyanides have been **observed in the outer envelope** whereas they are **predicted in the inner enveloppe** (where dust forms)

- Formation of metal cyanides/isocyanides

  Radiative association of M^+ (M=Al, Mg, Si) and cyanopolyynes followed by dissociative recombination (Dumbar & Petrie 2002)

$$M^+ + HC_{2n+1}N \rightarrow MN(C_{2n+1}N)H^+ + h\nu$$
$$\rightarrow M(C_{2n+1}N) + H$$
$$MN(C_{2n+1}N)H^+ + e^- \rightarrow \mathbf{MCN/MNC} + C_{2n}H$$
$$\rightarrow M + HC_{2n+1}N$$

- Chemistry and formation processes of metal cyanides is not well known

- Abundance determined assuming local thermodynamic equilibrium (LTE)

- Abundance ratio of the isomers = line intensity ratio

Molecular abundances of metal cyanides/isocyanides are highly uncertain

* *Not detected but considered in astrochemical modelling*

I – Introduction

➢ New insight on the abundances of metal-bearing molecules

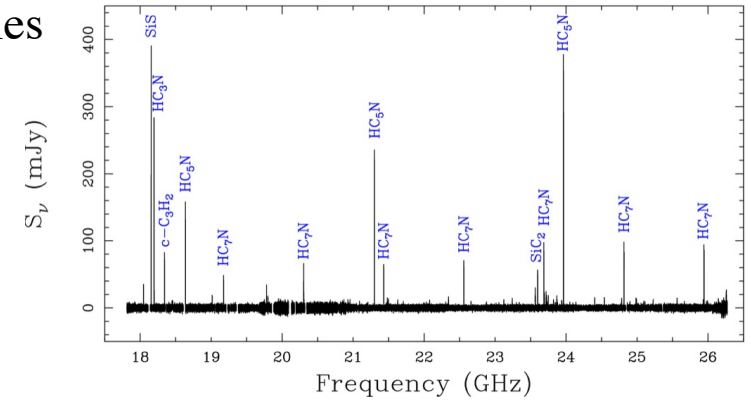
➢ **Spectral lines analysis**

→ Interstellar **molecules identification**

⇨ **Spectroscopic data**

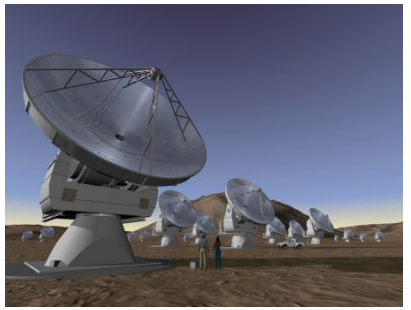
→ **Physical conditions**: Temperature, molecular abundance, gas density …

⇨ **Collisional rate coefficients**



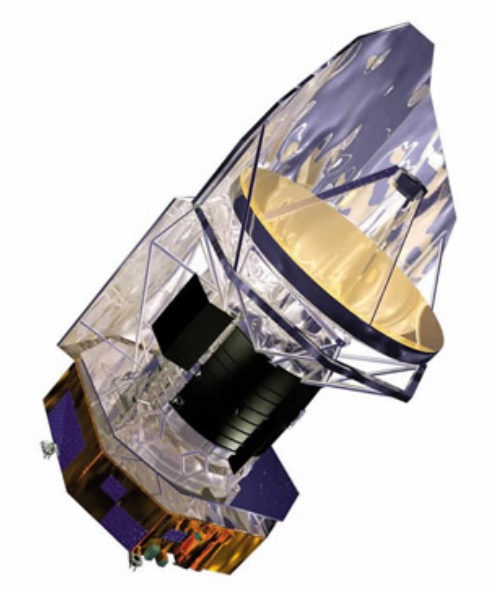
Survey of IRC+10216 (Gong et al. 2015)

Noema Radiotelescope



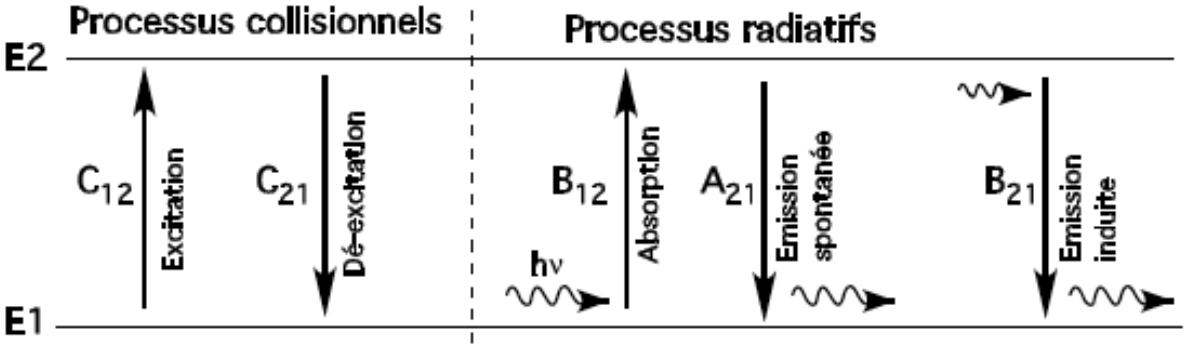
Alma interferometer

I – Introduction



Modeling observational spectra → Molecular abundance
Gaz Density n(H_2)
Temperature

Knowledge of the population of the energy levels of molecules



C_{12} et C_{21} : Rate coefficients B_{12}, B_{21} et A_{12} : Einstein coefficients

Rate coefficients: Boltzmann average of the cross sections

Calculations of rate coefficients for interstellar molecules in collision with He and H_2

I – Introduction

➢ New insight on the abundances of metal-bearing molecules

➢ **Spectral lines analysis**

→ Interstellar **molecules identification**

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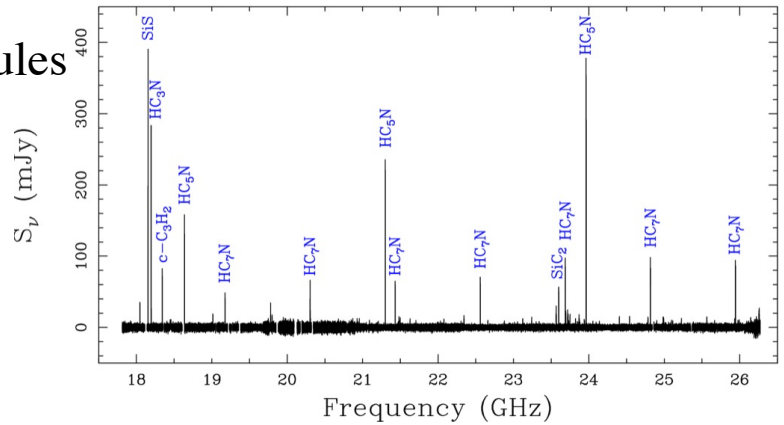
→ **Physical conditions**: Temperature, molecular abundance, gas density …

⇨ **Collisional rate coefficients**



Survey of IRC+10216 (Gong et al. 2015)

➢ **Evolution of interstellar matter**

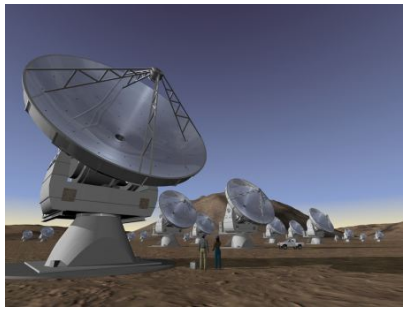
→ Formation of **interstellar molecules**

⇨ **Reactive rate constants**

Noema Radiotelescope

Plan :

- **Structural and spectroscopic properties of metal cyanides / isocyanides**
  - Equilibrium structure, dipole moments and rotational and vibrational
  - Isomerisation pathways
- **Collisional excitation of metal cyanides / isocyanides by He**
  - New *ab initio* potential energy surfaces
  - Collisional rate coefficients
- **Modelling of metal cyanides / isocyanides emission spectra**
- **Conclusion**



Alma interferometer

II – Structural and spectroscopic properties of metal cyanides / isocyanides

➢ Determination of ***energies (E_a, in a.u.), relative energies (E_r, in cm^{-1}), geometries, dipole moments (μ, in D) and rotational (B, in Mhz) and vibrational constants (ω, in cm^{-1})***

Calculations at the (R)CCSD(T)/aug-cc-pV5Z levels using MOLPRO

Al—R—N—C	*l*-AlNC $C_{\infty v}$ $X^1\Sigma^+$	$R = 1.8598$ Å CN = 1.1838 Å $E_a = -334.726820$ $E_r = 0$	$B = 5895.85$ $\mu = 3.3948$ $\omega = 2072(\sigma), 555(\sigma), 96(\pi)$
Al—R—C—N	*l*-AlCN $C_{\infty v}$ $X^1\Sigma^+$	$R = 2.0208$ Å CN = 1.1674 Å $E_a = -334.717798$ $E_r = 1980$	$B = 4966.60$ $\mu = 3.7204$ $\omega = 2174(\sigma), 468(\sigma), 148(\pi)$
Mg—R—N—C	*l*-MgNC $C_{\infty v}$ $X^2\Sigma^+$	$R = 1.9468$ Å CN = 1.1805 Å $E_a = -292.373596$ $E_r = 0$	$B = 5845.5$ $\mu = 4.9514$ $\omega = 2093(\sigma), 527(\sigma), 100(\pi)$
Mg—R—C—N	*l*-MgCN $C_{\infty v}$ $X^2\Sigma^+$	$R = 2.0878$ Å CN = 1.1674 Å $E_a = -292.370602$ $E_r = 657$	$B = 5009.81$ $\mu = 5.3715$ $\omega = 2176(\sigma), 460(\sigma), 163(\pi)$
Si—R—C—N	*l*-SiCN $C_{\infty v}$ $X^2\Pi$	$R = 1.1708$ Å CN = 1.8539 Å $E_a = -381.709176$ $E_r = 0$	$B = 5490.71$ $\mu = 2.8245$ $A_{so} = 66.09^b$
Si—R—N—C	*l*-SiNC $C_{\infty v}$ $X^2\Pi$	$R = 1.7405$ Å CN = 1.1900 Å $E_a = -381.706679$ $E_r = 548$	$B = 6332.76$ $\mu = 2.7290$ $A_{so} = 64.06^b$

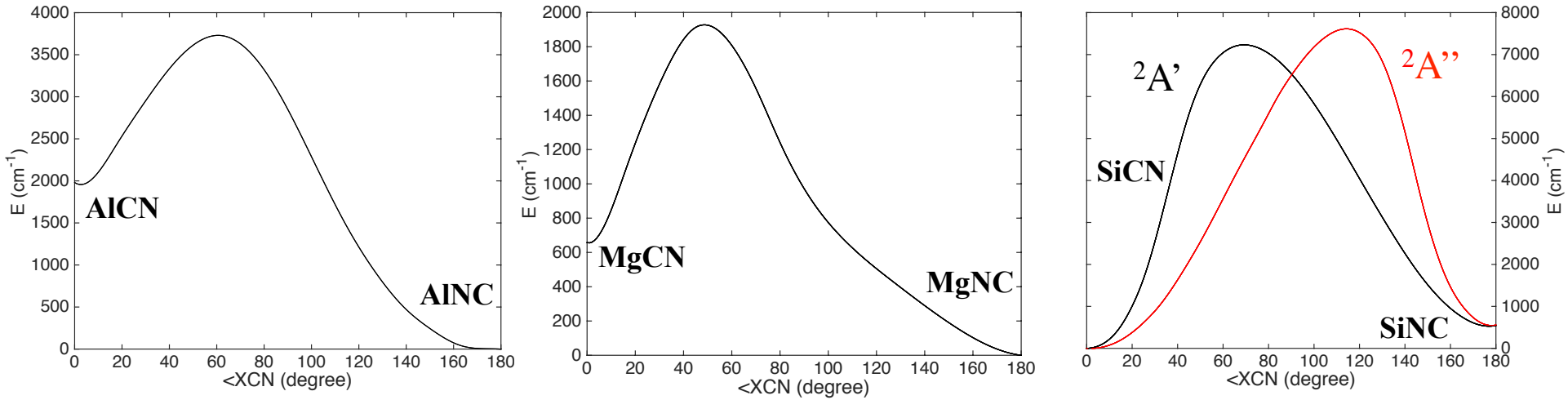
- All compounds are linear
- AlNC, MgNC are more stable than AlCN and MgCN, respectively
- SiCN is more stable than SiNC
- SiNC dipole moment is much higher than that used for astrophysical modelling (2.7 vs. 2.0* D)
- Rotational and vibrational constant are in good agreement with available experimental data

**Largo-Cabrerizo (1988)*

II – Structural and spectroscopic properties of metal cyanides / isocyanides

➢ Computation of the isomerization pathways

Calculations at the (R)CCSD(T)/aug-cc-pV5Z levels using MOLPRO



AlCN/AlNC, MgCN/MgNCand SiCN/SiNC isomerization pathways:
one-dimensional cuts of the potential energy surfaces

➢ Out of linear geometry, the $^2\Pi$ ground electronic state split in two potential energy surfaces of ^{2}A' and ^{2}A'' symmetry.

➢ Isomerization processes are expected to be very slow at typical circumstellar temperatures

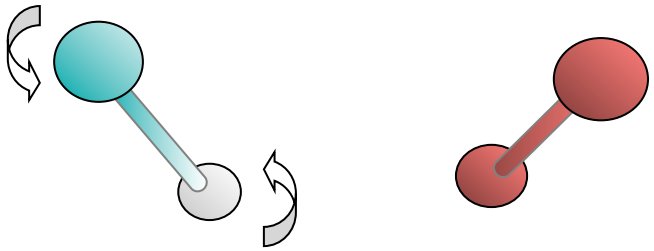
$E_a(AlCN \rightarrow AlNC) \approx 2500\ K$
$E_a(MgCN \rightarrow MgNC) \approx 2000\ K$
$E_a(SiCN \rightarrow SiNC) \approx 11000\ K$

*Senent et al., MNRAS **420**, 1188 (2012)*

⇨ ***Both isomers have to be produced independantly***

III – Collisional excitation of metal cyanides / isocyanides by He

Born-oppenheimer approximation (1927)



2 stages :

ab initio calculation of the potential energy surface between particules

→ Quantum chemistry
Semi-empirical methods

Study of the dynamical of the nuclei

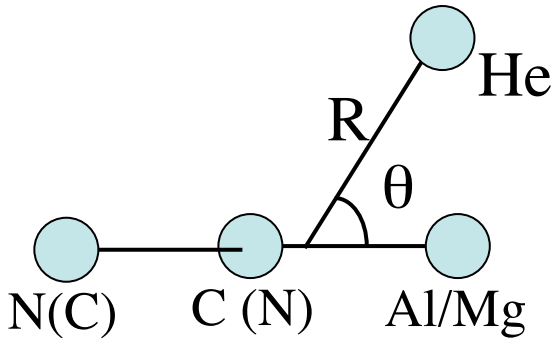
→ Quantum Methods (TI et TD)
Classical methods

Collisional cross sections calculations: $\sigma_{ij}(E_k)$

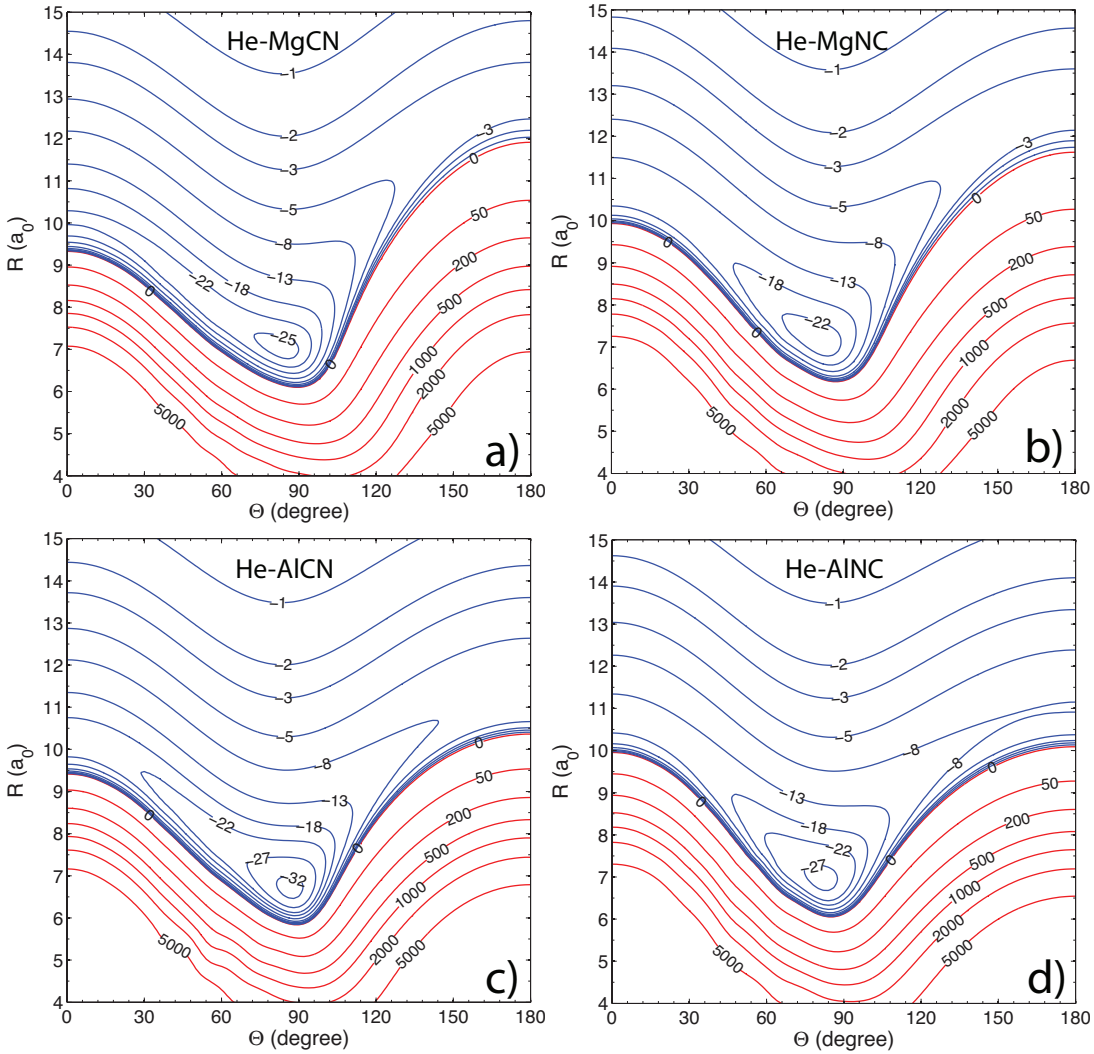
Accuracy ↓

- **Close Coupling** (Exact calculations; CPU time : (Channel number)^3)
- **Coupled states** (Neglect coupling between rotational momentum and angular momentum)
- **IOS** (Neglect rotation of the molecule during collision)

III – Collisional excitation of metal cyanides / isocyanides by He

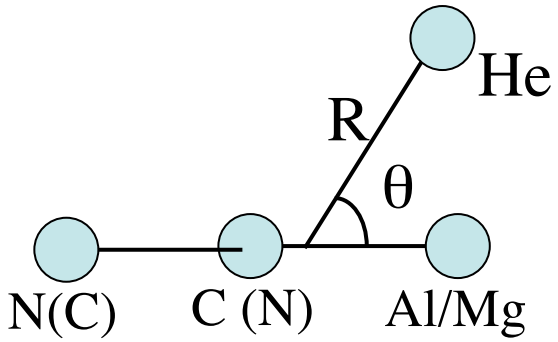


- 2 degrees of freedom : R et θ
- AlCNHe ground electronic state: ^{1}A'
  MgCNHe ground electronic state: ^{2}A'
- Monoconfigurational (MCSCF)
  ➡ ***Coupled Clusters can be used***
- Calculations done with MOLPRO
- aug-cc-pVTZ basis set + bond func.
- BSSE corrections



Contour plots of the MgC-He (a), MgNC-He (b), AlCN-He (c) and AlNC-He (d) potential energy surface

III – Collisional excitation of metal cyanides / isocyanides by He



- 2 degrees of freedom : R et θ
- AlCNHe ground electronic state: ^{1}A'
  MgCNHe ground electronic state: ^{2}A'
- Monoconfigurational (MCSCF)
  ➡ ***Coupled Clusters can be used***
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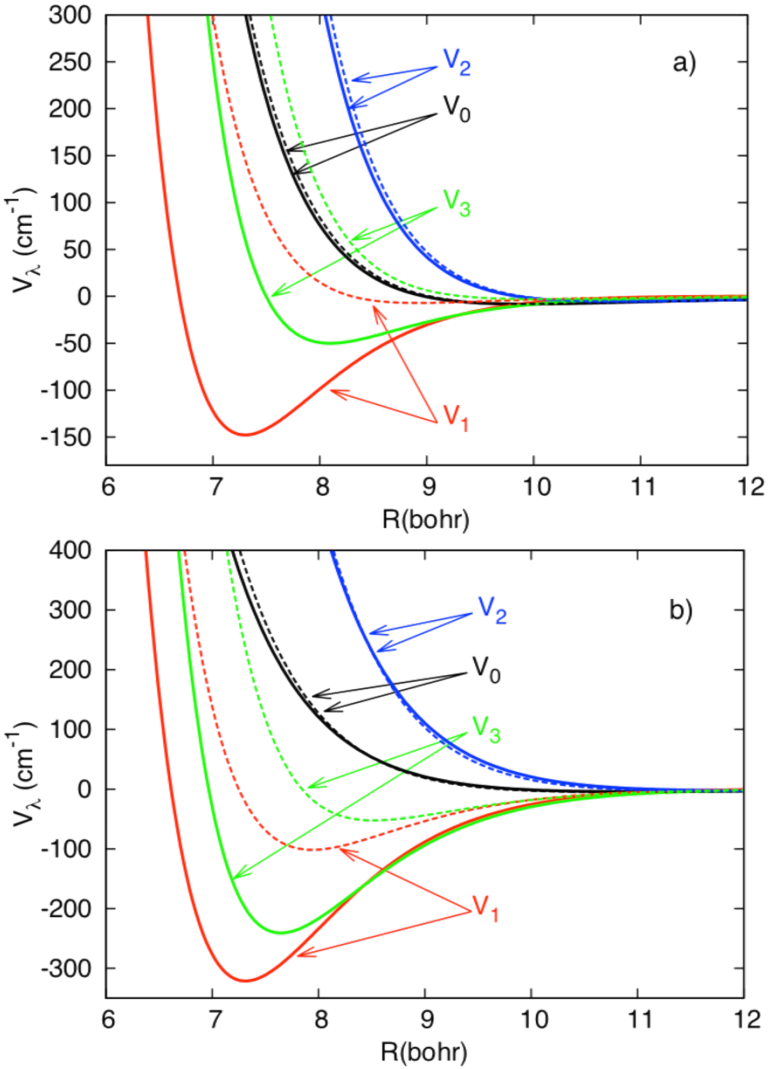
➢ Legendre polynomials expansion:

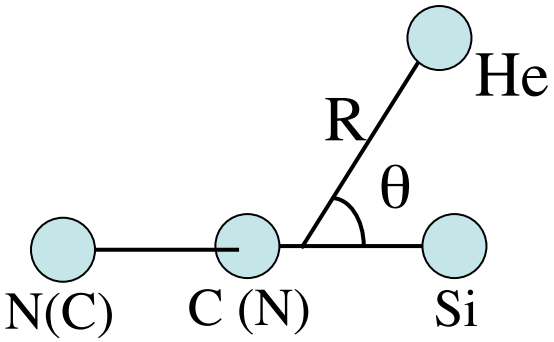
$$V(R,\theta) = \sum_{\lambda} V_{\lambda}(R) P_{\lambda}(\cos\theta)$$

⇨ **Significant differences between X-CN/NC-He interaction**



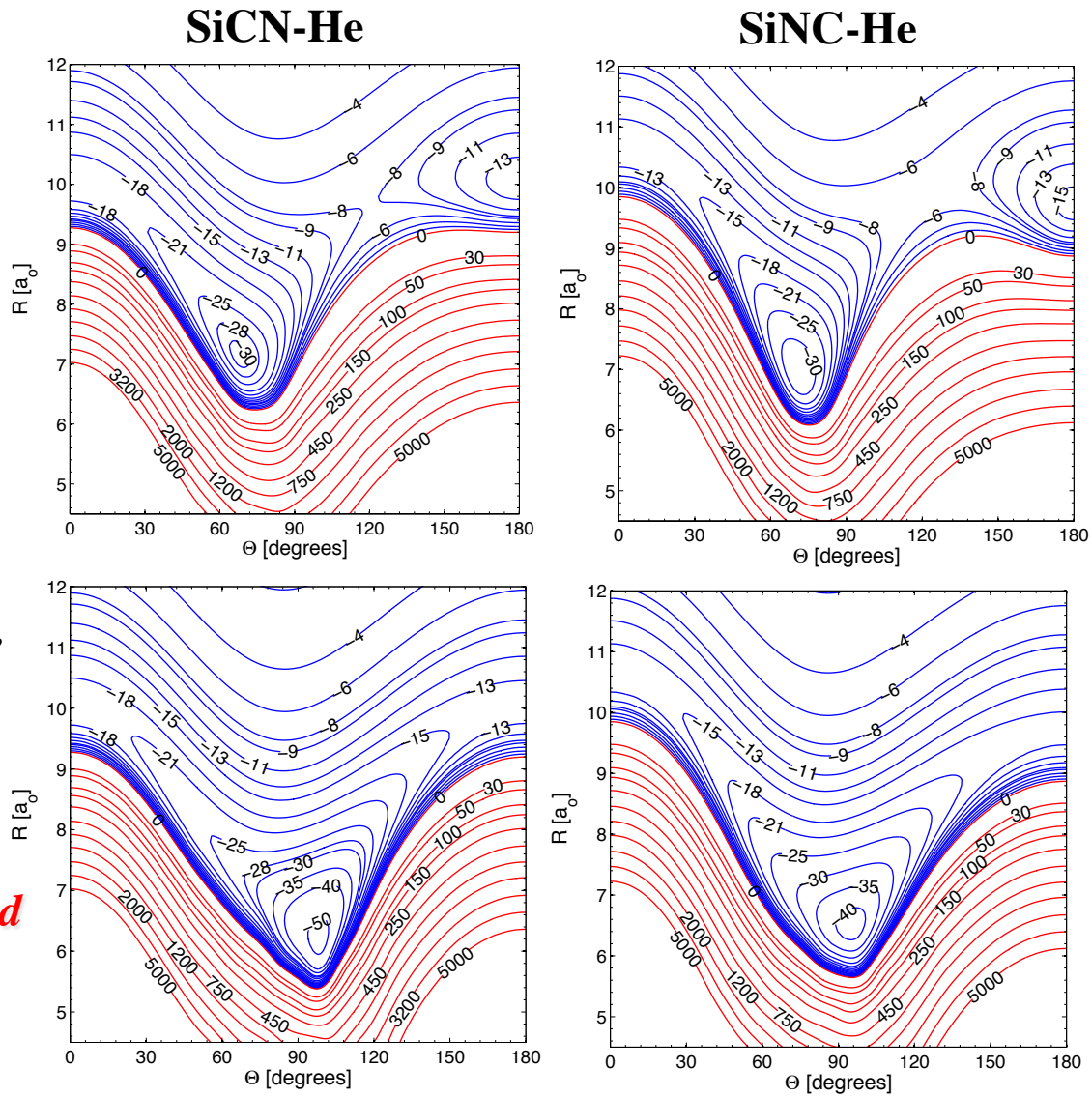
Plot of the first radial coefficients(λ=0 … 3) as a function of R. (a) The solid lines denote AlCN-He while the dashed lines denote AlNC-He. (b) The solid lines denote MgCN-He while the dashed lines denote MgNC-He

III – Collisional excitation of metal cyanides / isocyanides by He



When interacting with He, the doubly-degenerate Π electronic state is split into two states of A' and A" symmetry corresponding to the singly occupied π orbital lying in, or perpendicular to, the tetratomic plane, respectively.

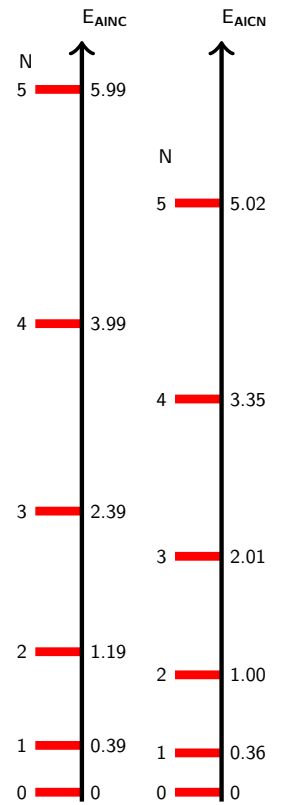
- 2 degrees of freedom : R et θ
- Monoconfigurational (MCSCF)
  - ➡ ***Coupled Clusters can be used***
- Calculations done with MOLPRO
- aug-cc-pVTZ basis set + bond func.
- BSSE corrections



Contour plots (in cm^{-1}) of the SiCN-He and SiNC-He A' (upper panel) and A" (lower panel) potential energy surface.

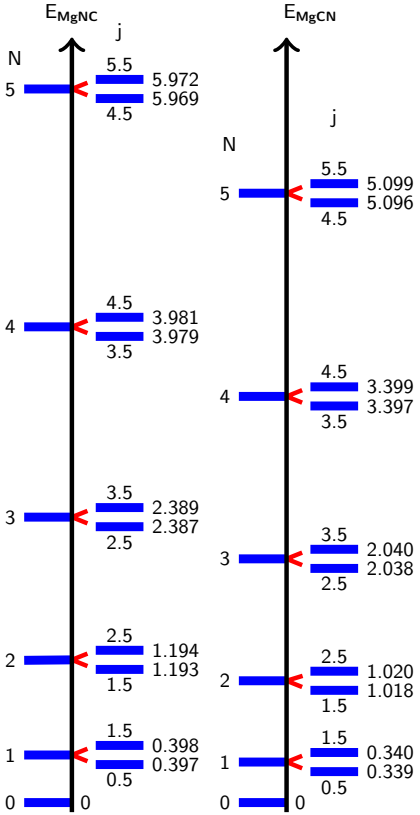
III – Collisional excitation of metal cyanides / isocyanides by He

➢ Rotational structure of AlCN / AlNC / MgCN / MgNC / SiCN / SiNC molecules



$AlCN/NC(X^1\Sigma^+)$

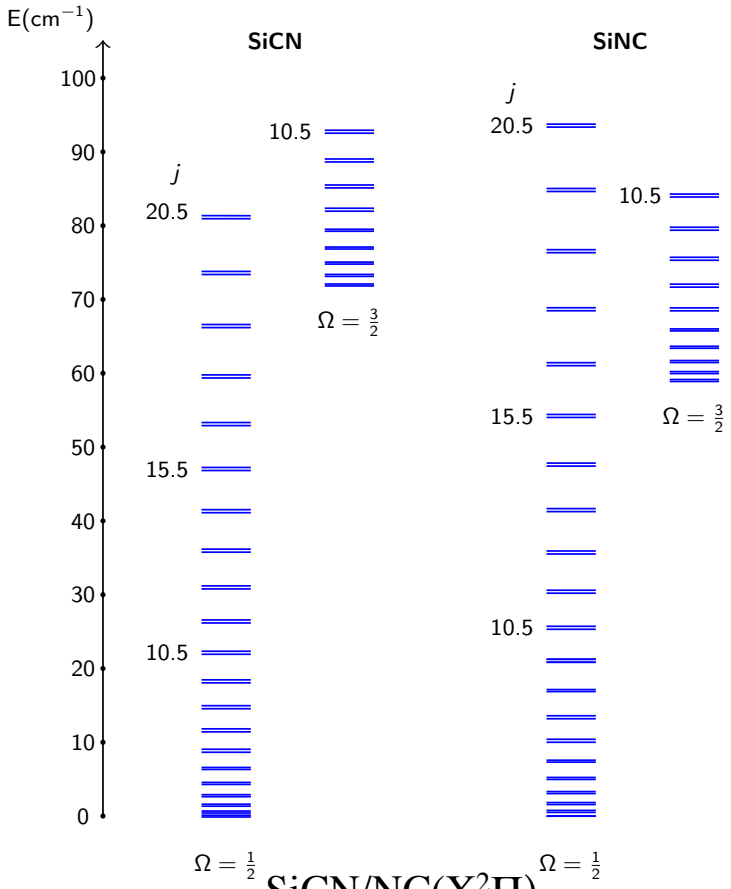
N : rotation



$MgCN/NC(X^2\Sigma^+)$

j = N + S

total — **rotation** — **spin**



$SiCN/NC(X^2\Pi)$

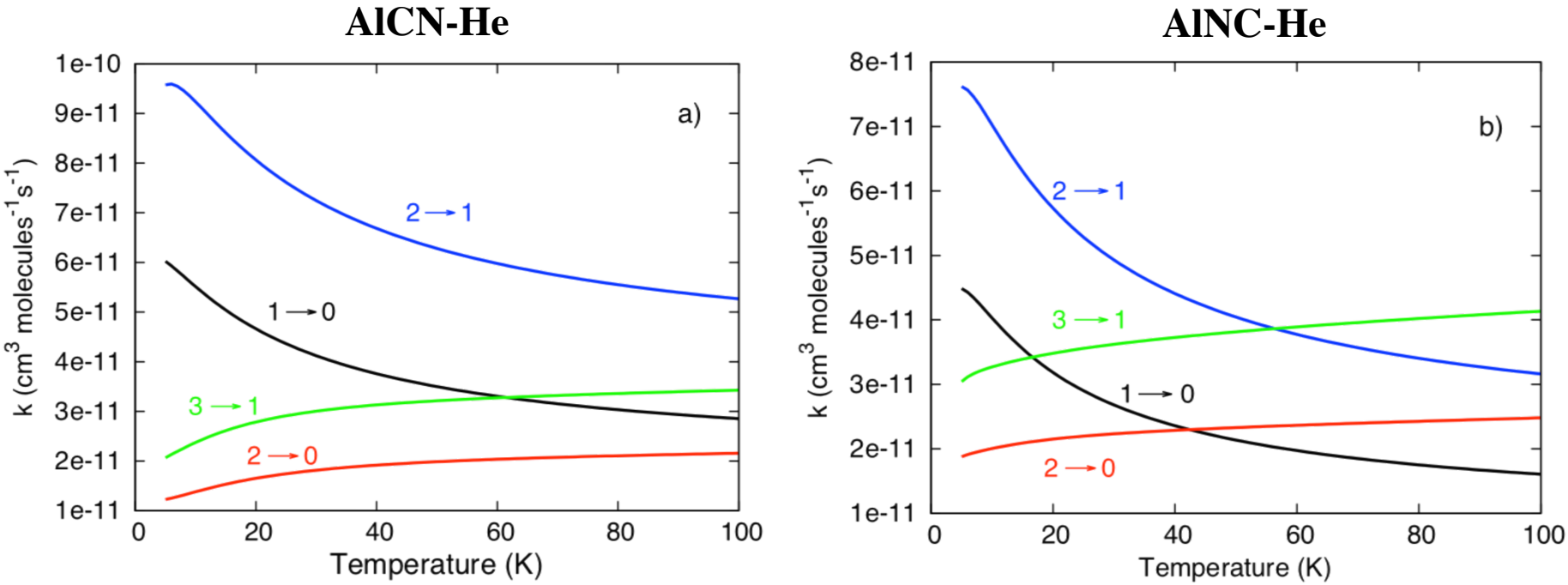
2 spin orbit manifolds :

$^2\Pi_{1/2}$ **(F_1)** and $^2\Pi_{3/2}$ **(F_2)**

Rotation-spin-orbit levels **j** are doubly degenerated (**e** and **f** parity)

III – Collisional excitation of metal cyanides / isocyanides by He

AlCN-He and AlNC-He: rate coefficients



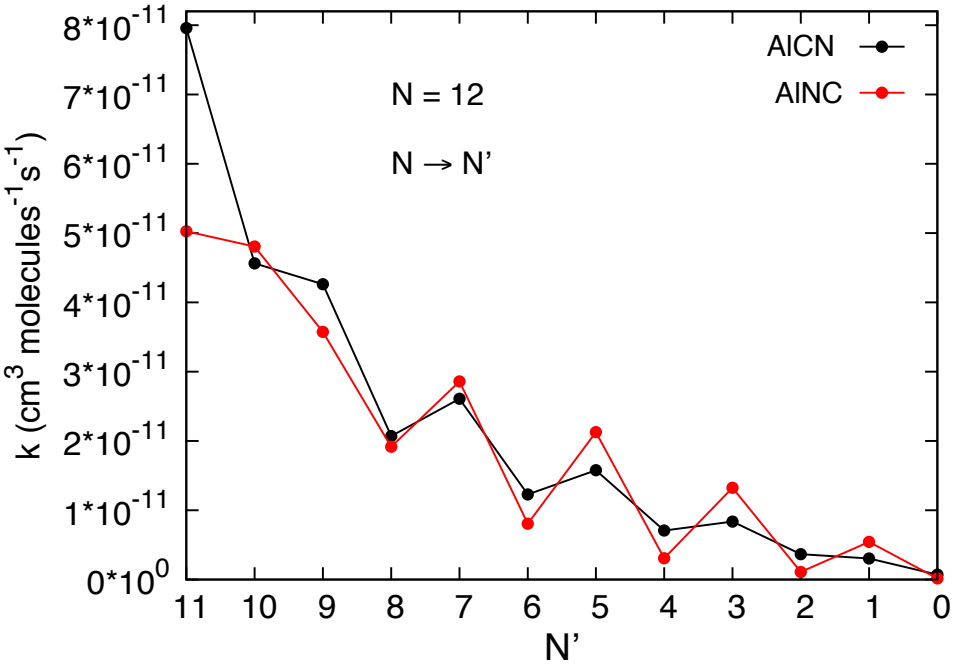
Temperature variation of AlCN-He and AlNC-He rate coefficients

- Similar order of magnitude and similar temperature variation
- Same propensity rules in favor of odd ΔN transitions
- Significant differences for ΔN=1 transitions ($k_{AlCN}(T) > k_{AlNC}(T)$)

ΔN=1 transitions: radiative transitions ➡ ***Impact on radiative transfer calculations ?***

III – Collisional excitation of metal cyanides / isocyanides by He

AlCN-He and AlNC-He: rate coefficients



AlCN-He and AlNC-He de-excitation rate coefficients from N = 12 at 50 K

- Similar order of magnitude and similar temperature variation
- Same propensity rules in favor of odd ΔN transitions
- Significant differences for ΔN=1 transitions ($k_{AlCN}(T) > k_{AlNC}(T)$)

ΔN=1 transitions: radiative transitions ➡ ***Impact on radiative transfer calculations ?***

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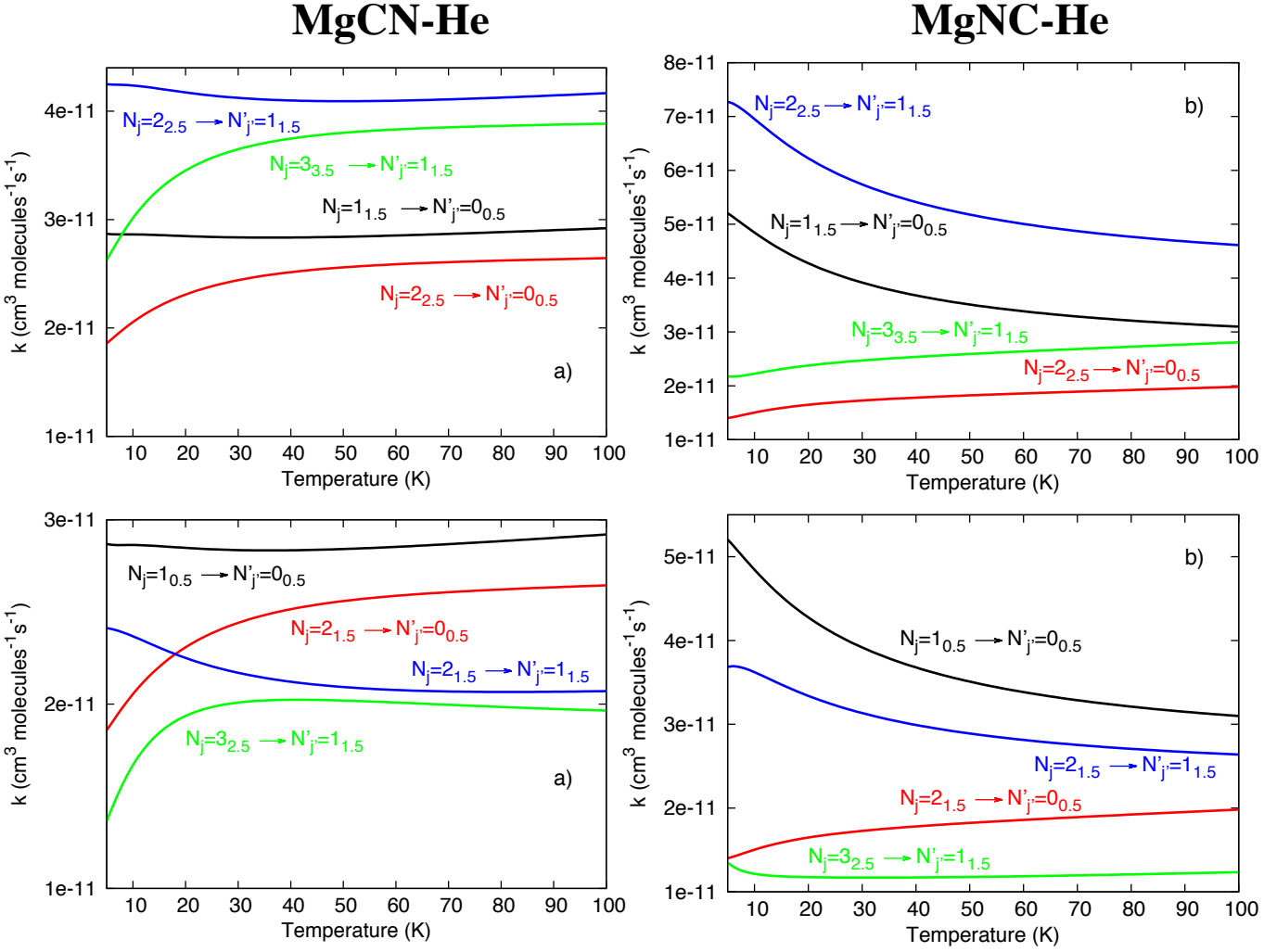
MgCN-He and MgNC-He: rate coefficients



- Propensity rules in favor of $\Delta j = \Delta N$ transitions
- Different variation with temperature
- Different propensity rules with respect to odd and even ΔN transitions
- Selection rules explained by PES:
  anisotropic PES: $\Delta N = 1$
  isotropic PES: $\Delta N = 2$

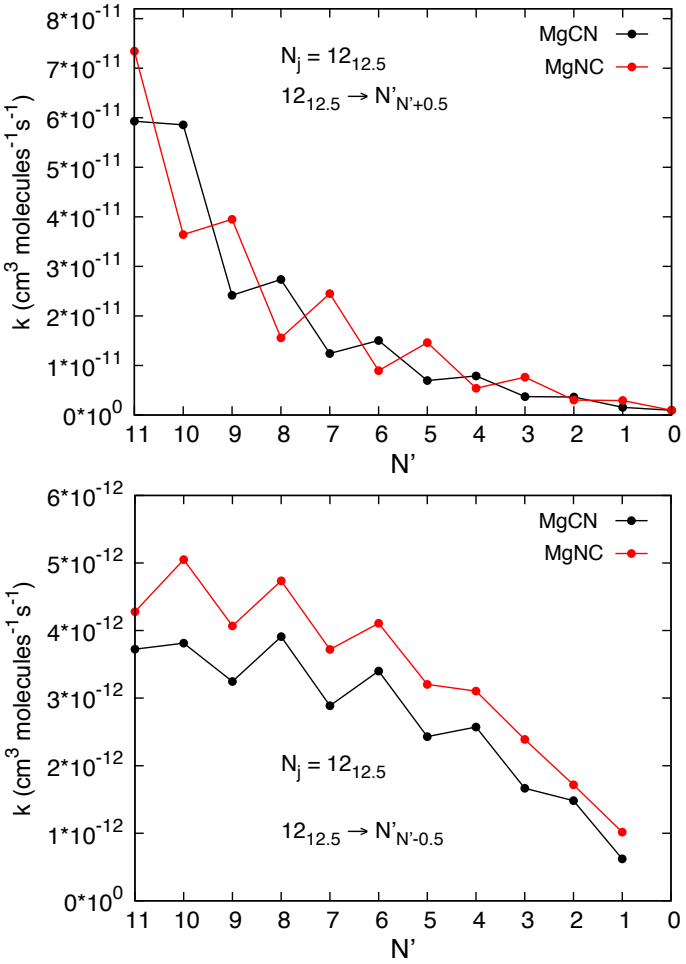
⇨ ***Specific calculations should be performed for the two isomers***

Temperature variation of MgCN-He (a) and MgNC-He (b) rate coefficients; Upper panels: $\Delta j = \Delta N$ transitions ; lower panels: $\Delta j \neq \Delta N$

*Vera et al., MNRAS **432**, 468 (2013)*

III – Collisional excitation of metal cyanides / isocyanides by He

MgCN-He and MgNC-He: rate coefficients



MgCN-He and MgNC-He de-excitation rate coefficients from N = 12 at 50 K for Δj=ΔN (upper panel) and Δj≠ΔN (lower panel) transitions

- Propensity rules in favor of Δj=ΔN transitions
- Different variation with temperature
- Different propensity rules with respect to odd and even ΔN transitions
- Selection rules explained by PES:
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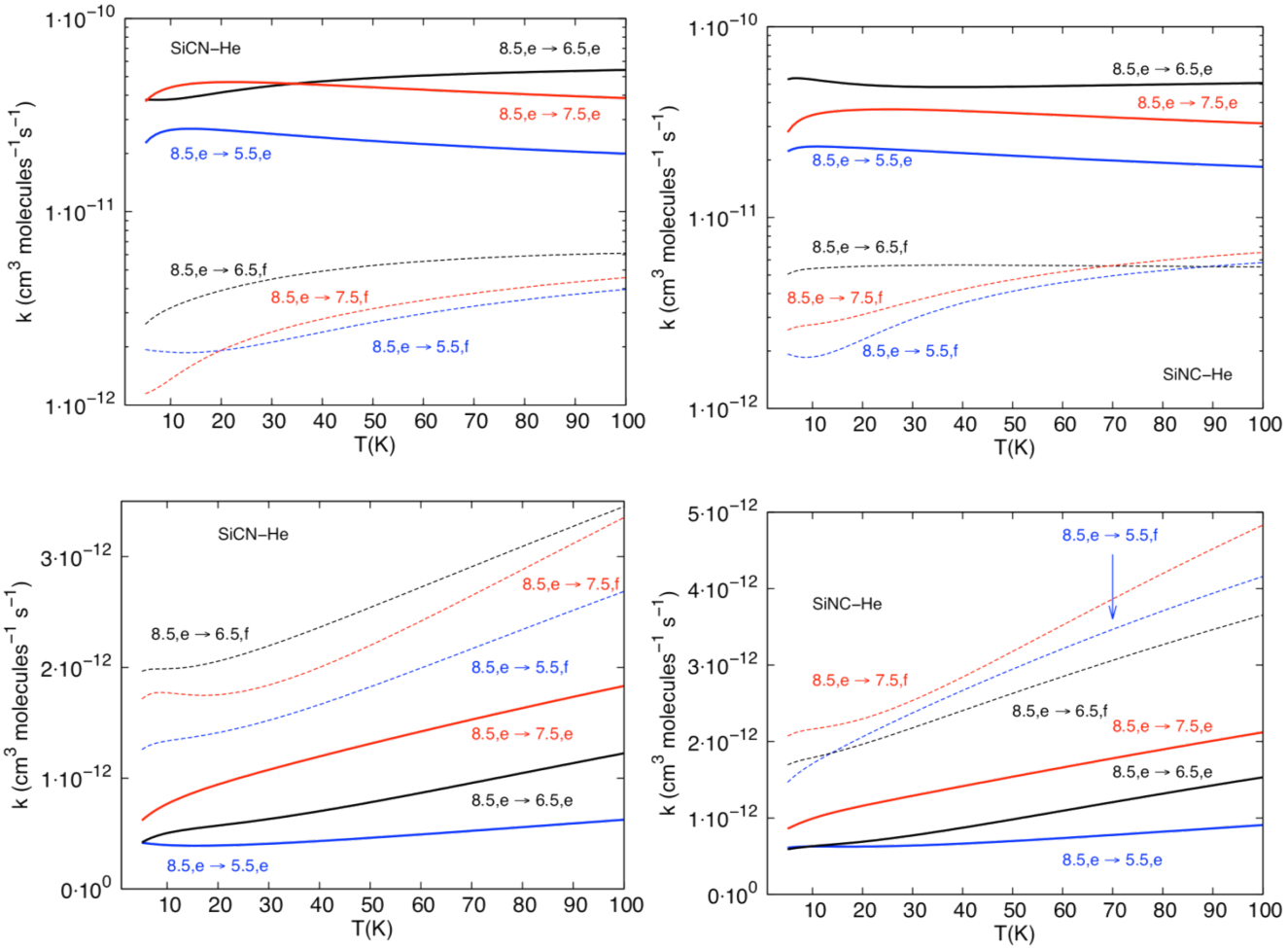
III – Collisional excitation of metal cyanides / isocyanides by He

SiCN-He and SiNC-He: rate coefficients

SiCN-He **SiNC-He**



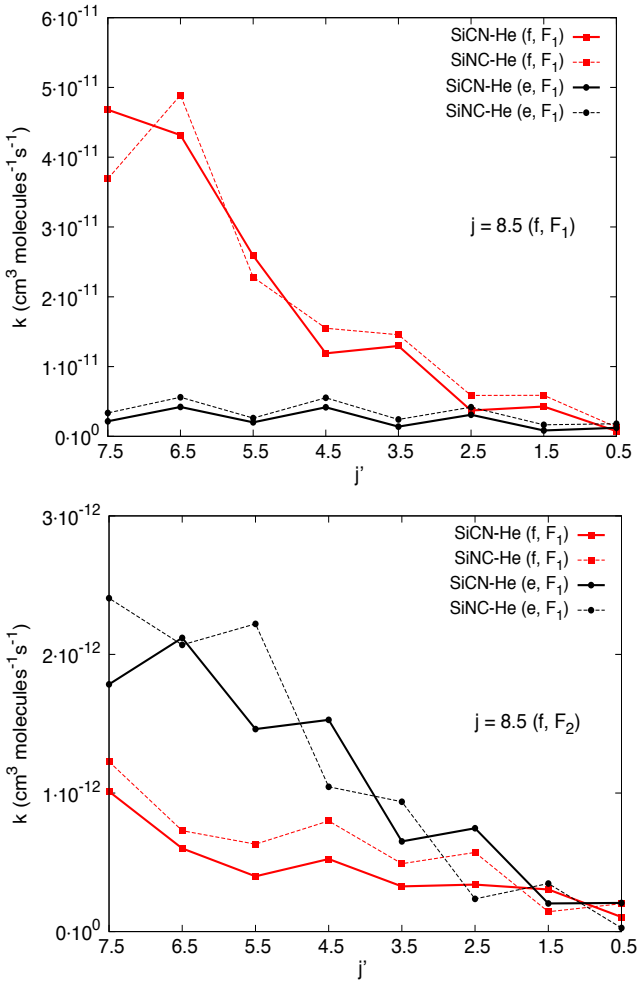
- Propensity rules in favor spin-orbit conserving transitions
- Propensity in favor of Λ-doublet conserving labels (e → e / f → f) for spin-orbit conserving transitions
- Global agreement for the two sets of data
- SiCN-He: Δj = 1 favored
  SiNC-He: Δj = 2 favored

⇨ ***Moderate differences: impact on radiative transfer calculations ?***

Temperature variation of SiCN-He and SiNC-He rate coefficients; Upper panels: spin orbit conserving transitions ; lower panels: spin orbit changing transitions

III – Collisional excitation of metal cyanides / isocyanides by He

SiCN-He and SiNC-He: rate coefficients



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⇨ ***Moderate differences: impact on radiative transfer calculations ?***

SiCN-He and SiNC-He de-excitation rate coefficients at 25 K from j = 8.5 f (F_1) (upper panel) and from j = 8.5 f (F_2) (lower panel)

IV – Modelling of metal cyanides / isocyanides spectra

Radiative transfer

- ISM and circumstellar enveloppes are out of Local Thermodynamic Equilibrium (LTE)
- Population of molecular levels given by radiation field and density (collisions depend on the density)
- Or, radiation field is also given by population of molecular levels …

⇨ **Solve simultanously statistical equilibrium + transfer equation**

⇩

Radiative transfer code : LVG (RADEX - van der Tak et al., 2007)

⇩

Determine intensity of spectra for en **3 physical parameters** (for a given geometry of the molecular cloud) :
Column density **N** or **abondance**, gas density **n(H_2)**, Temperature **T**

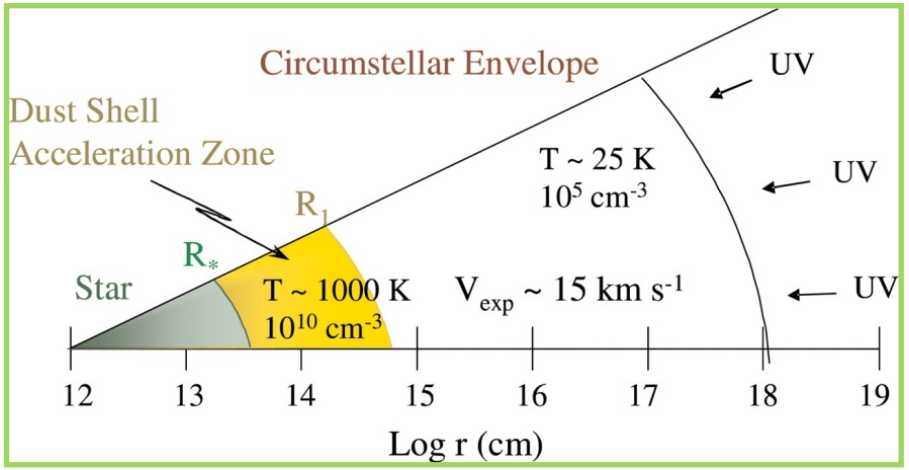
Intensity are given in brightness temperature T_B $\left(T_B = \frac{c^2}{2k\nu^2} I\nu \right)$

The excitation temperature (T_{ex}) is the temperature at which we would expect to find a system with this ratio of level populations ➡ *LTE is valid when $T_{Ex} = T$*

IV – Modelling of metal cyanides / isocyanides emission spectra

- Metal cyanides and isocyanides have been observed in the **outer envelope of IRC+10216**

Physical conditions in the outer enveloppe of IRC+10216
T = 20 – 50 K
$N(H_2)= 10^4 – 10^5$ cm^{-3}
Line width : ≈ 29 km s^{-1}



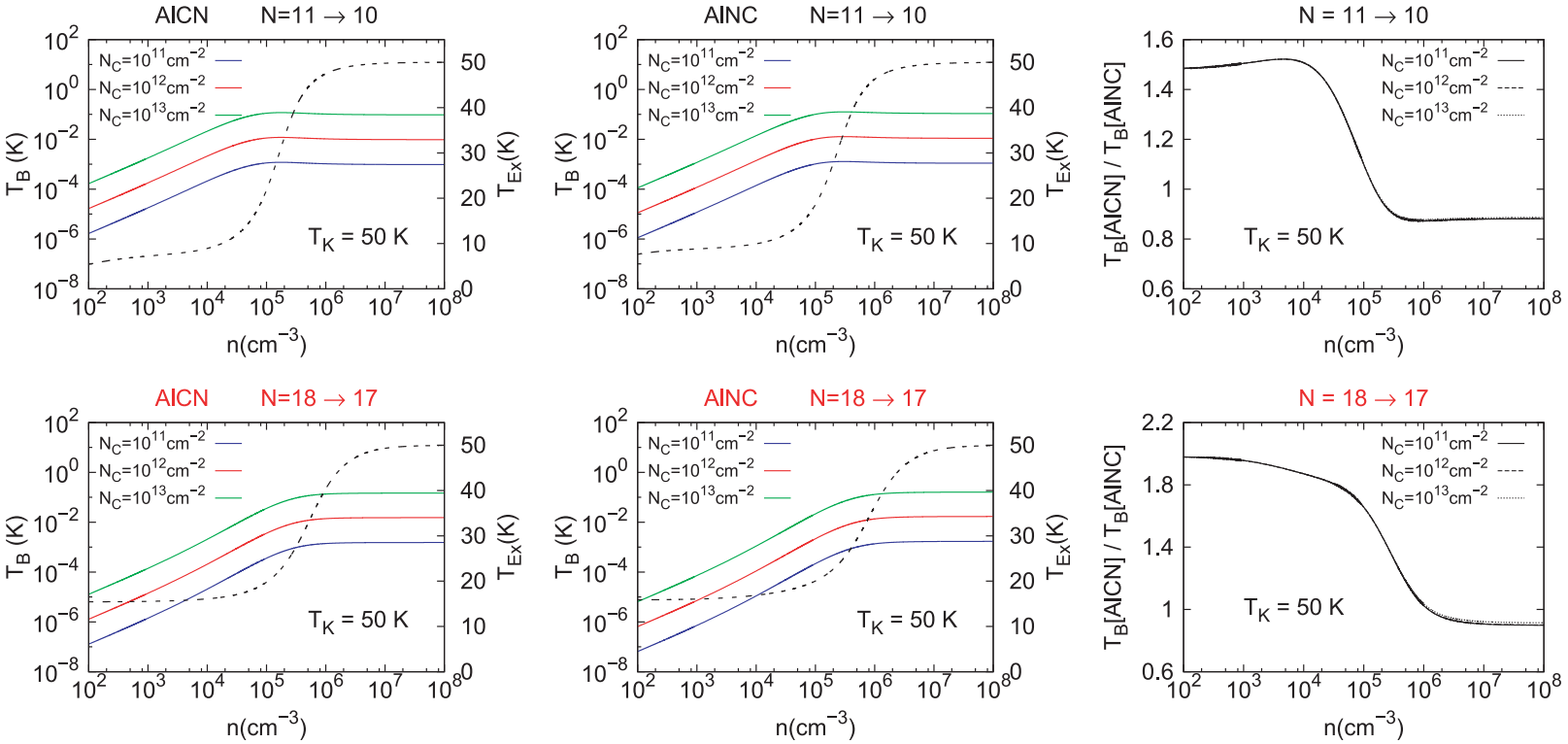
Circumstellar enveloppe of of IRC+10216

	AlNC	AlCN	MgNC	MgCN	SiNC	SiCN
Observed lines	*11 → 10* *12 → 11* *13 → 12* *18 → 17* *21 → 20*	Not detected	*7 → 6* *8 → 7* *9 → 8* *12 → 11* *13 → 12* *14 → 13* *19 → 18*	*9 → 8* *10 → 9* *11 → 10*	6.5 → *5.5* 7.5 → *6.5* 8.5 → *7.5* 10.5 → *9.5* *All within F_1 manifold*	7.5 → *6.5* 8.5 → *7.5* 9.5 → *8.5* *All within F_1 manifold*
N	9 10^{11} cm^{-2}		5 10^{13} cm^{-2}	2 10^{12} cm^{-2}	2 10^{12} cm^{-2}	2 10^{12} cm^{-2}

Physical conditions explored : T = 20 - 100 K ; $n(H_2) = 10^2 – 10^8$ cm^{-3} ; $N=10^{11} - 10^{13}$ cm^{-2}

IV – Modelling of metal cyanides / isocyanides spectra

AlCN and AlNC excitation in circumstellar media

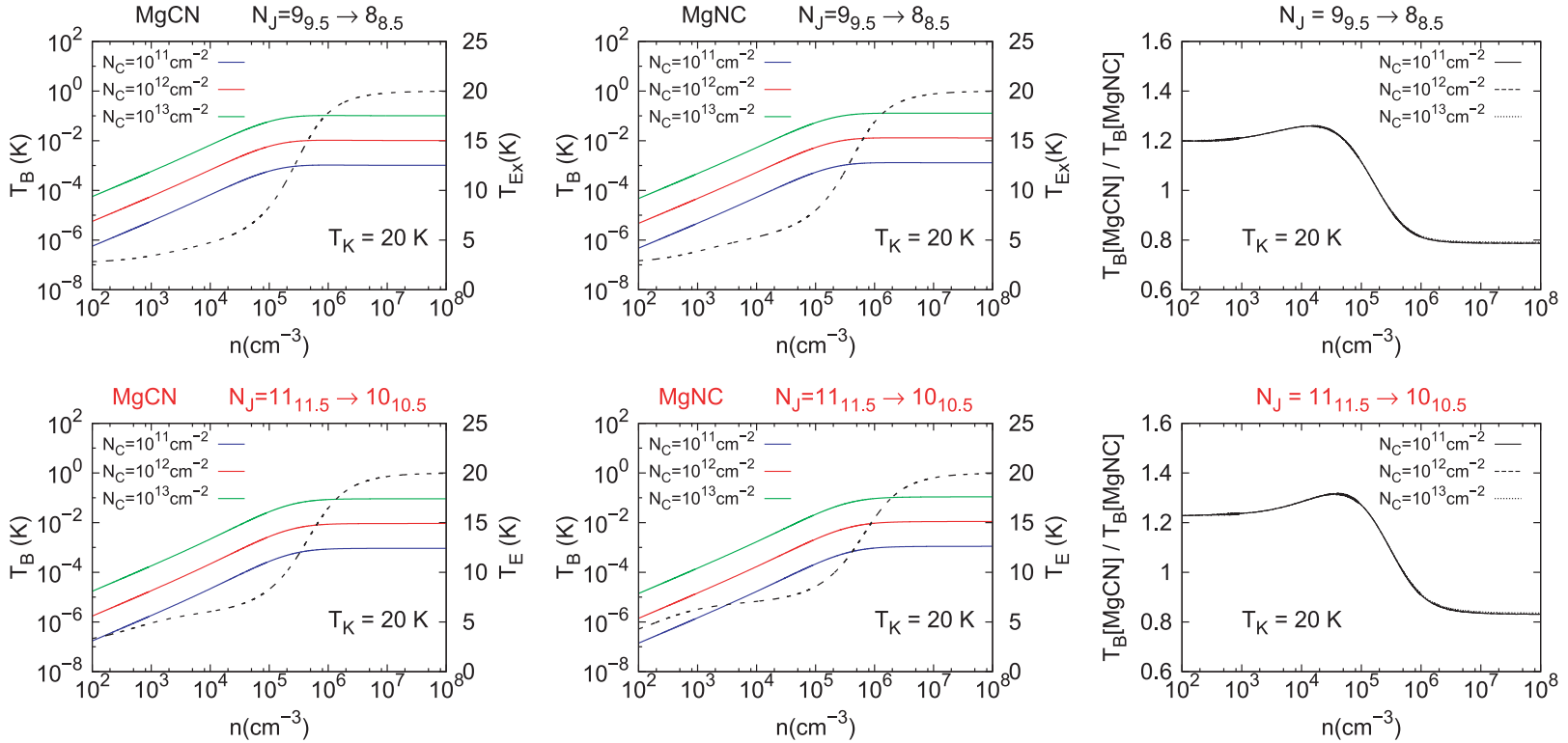


Excitation temperature (T_{Ex}, dashed lines), brightness temperature (T_B, solid lines) and brightness temperature ratios for two lines of AlCN and AlNC. The linewidth is 30 km s^{-1}.

- T_{Ex} are independent of N / T_B is proportional to N ➡ The lines are optically thin
- LTE conditions are reached for n(H_2) > 10^6 cm^{-3}
- AlCN presents a stronger emission than the AlNC ➡ Line intensities ratios cannot provide abundance ratio ⇨ **AlNC is much more abundant than AlCN (else it would be detected !)**

IV – Modelling of metal cyanides / isocyanides spectra

MgCN and MgNC excitation in circumstellar media



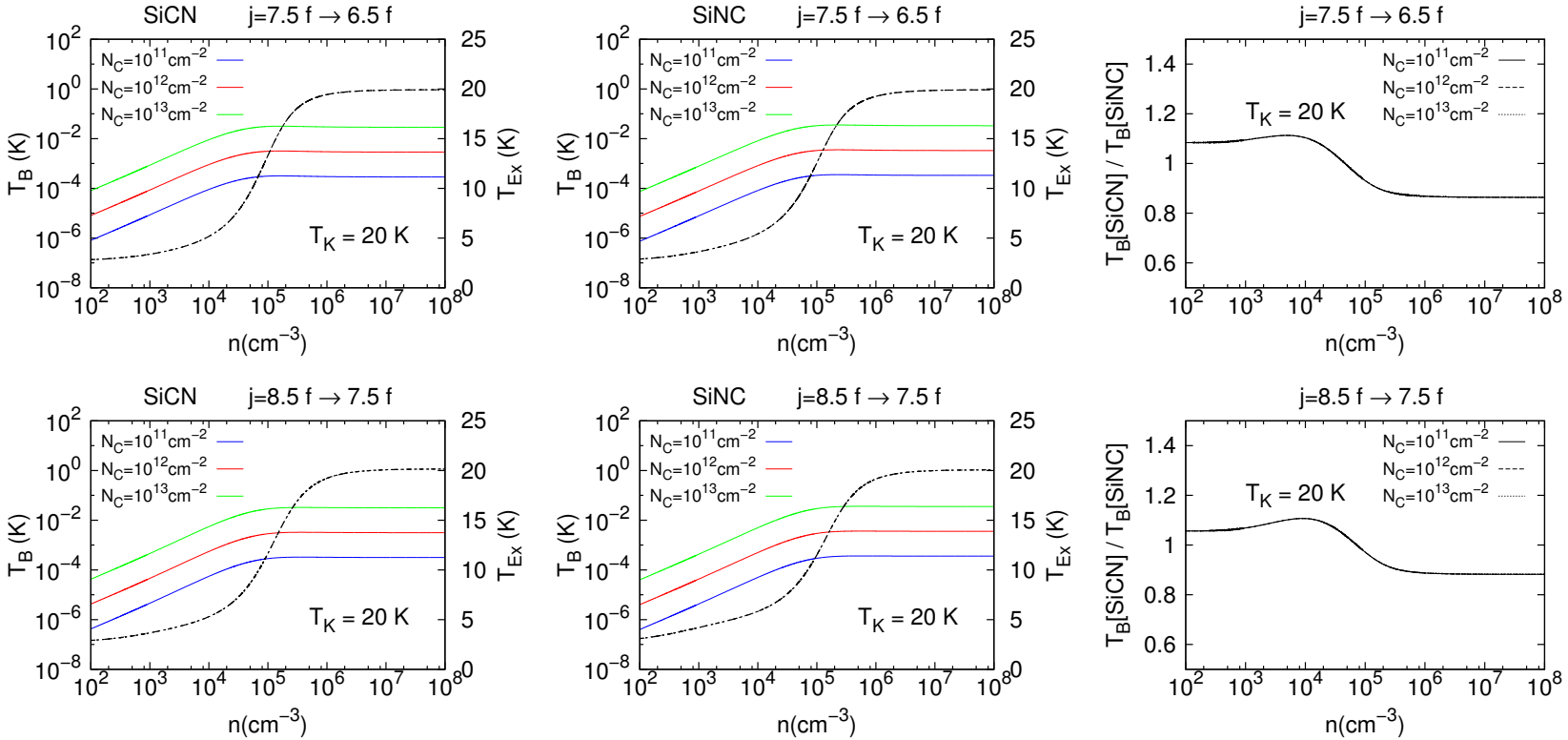
Excitation temperature (T_{Ex}, dashed lines), brightness temperature (T_B, solid lines) and brightness temperature ratios for two lines of MgCN and MgNC. The linewidth is 30 km s^{-1}.

- T_{Ex} are independent of N / T_B is proportional to N ➡ The lines are optically thin
- LTE conditions are reached for n(H_2) > 10^6 cm^{-3}
- MgCN presents a stronger emission than MgNC at low n(H_2) and a slightly weaker emission than MgNC at high n(H_2)

*Vera et al., MNRAS **448**, 2438 (2015)*

IV – Modelling of metal cyanides / isocyanides spectra

SiCN and SiNC excitation in circumstellar media

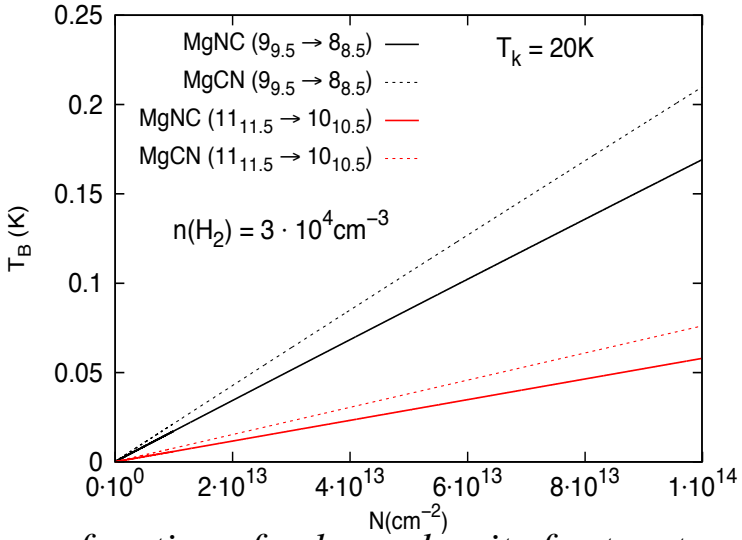


Excitation temperature (T_{Ex}, dashed lines), brightness temperature (T_B, solid lines) and brightness temperature ratios for two lines of SiCN and SiNC. The linewidth is 30 km s^{-1}.

- T_{Ex} are independent of N / T_B is proportional to N ➡ The lines are optically thin
- LTE conditions are reached for $n(H_2) > 5\ 10^5$ cm^{-3} *Vera et al., MNRAS in press (2015)*
- SiCN and SiNC emission is similar. SiCN presents a slightly stronger emission than SiNC at low $n(H_2)$ and a slightly weaker emission than SiNC at high $n(H_2)$

IV – Modelling of metal cyanides / isocyanides spectra

MgCN / MgNC



T_B as a function of column density for two transitions of MgCN and MgNC

Column density dependance of T_B is different !

- Previous estimation (Ziurys et al. 1995):

$$\frac{N[MgNC]}{N[MgCN]} = \frac{T_B[MgNC]}{T_B[MgCN]} = 22 \pm 3$$

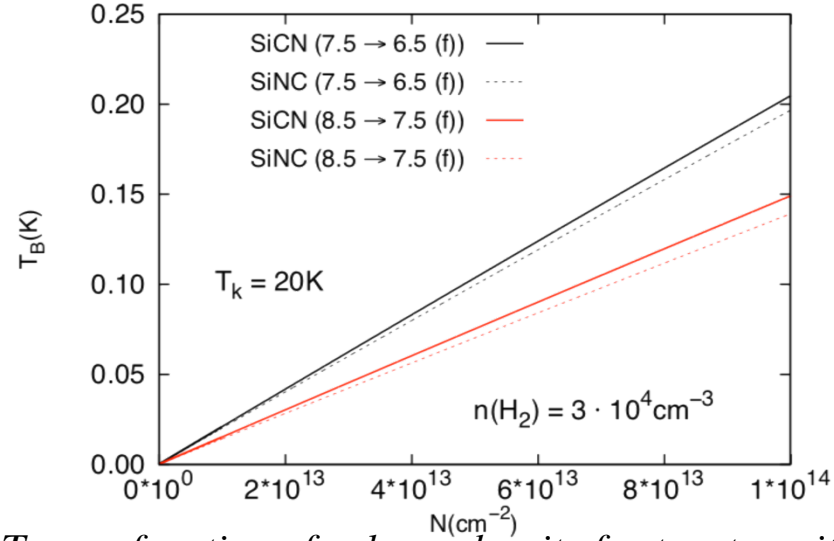
- Present estimation: *α_i : slope of the curve*

$$\frac{N[MgNC]}{N[MgCN]} = \frac{\alpha_{MgCN}}{\alpha_{MgNC}} \frac{T_B[MgNC]}{T_B[MgCN]}$$

$$\Rightarrow \quad \frac{N[MgNC]}{N[MgCN]} \approx 30$$

Lowering of the MgCN/ MgNC abundance ratio

SiCN / SiNC



T_B as a function of column density for two transitions of SiCN and SiNC

Column density dependance of T_B is similar

- Previous estimation (Guelin et al. 2004):

$$\frac{T_B[SiCN]}{T_B[SiNC]} \approx 2 \Rightarrow \frac{N[SiCN]}{N[SiNC]} \approx 1$$ *(Corrected from different μ)*

- Present estimation:

$$\Rightarrow \quad \frac{N[SiCN]}{N[SiNC]} \approx 2$$

SiCN is 2 times more abundant than SiNC !

V – Conclusions and outlook

- New spectroscopical data / Isomerization pathways
- New collisional data (first published for metal cyanides)
- New set of radiative transfer calculations for the excitation of metal cyanides
- Non-LTE calculations are required for each isomer
- Selective cyanides chemistry in favor of the most stable isomers

  Branching ratio of $MN(C_{2n+1}N)H^+ + e^- \rightarrow$ ***MCN/MNC*** $+ C_{2n}H$ *reaction favor the most stable isomer ?*

- Computation of collisional rate coefficients of metal cyanides/isocyanides with H_2 (differences may be larger as in the case of HCN/HNC)
- Performed similar study for other metal cyanide/isocyanides such as NaCN / KCN / FeCN
- Review metal-bearing molecules chemistry in the circumstellar gas (in particular determination of branching ratio of $MN(C_{2n+1}N)H^+ + e^- \rightarrow$ ***MCN/MNC*** $+ C_{2n}H$ reaction)
- New observations of metal cyanides and isocyanides toward IRC+10216 and others circumstellar enveloppes

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