Structured description of uncertainty for chemical reaction products and rates

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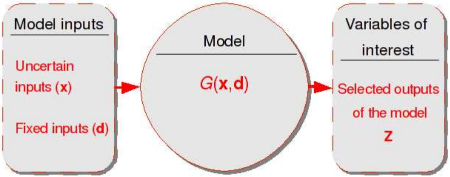
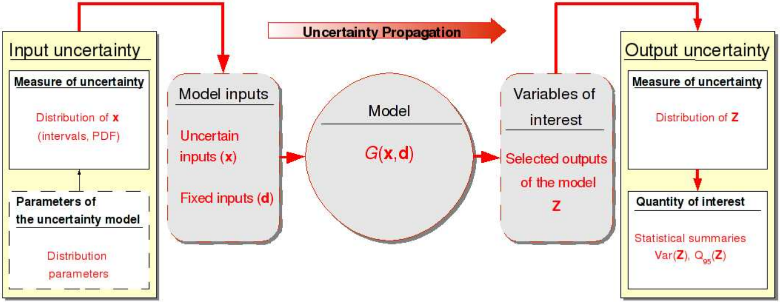
Plan

1. Methodology
   - The Framework
   - Evaluated databases of reaction rates
   - Design of PDF for low-T reaction rates
2. Important reactions in Titan's ionosphere
3. Management of uncertainties for branching ratios
4. Conclusions

Treatment of uncertainty in modelling



Treatment of uncertainty in modelling



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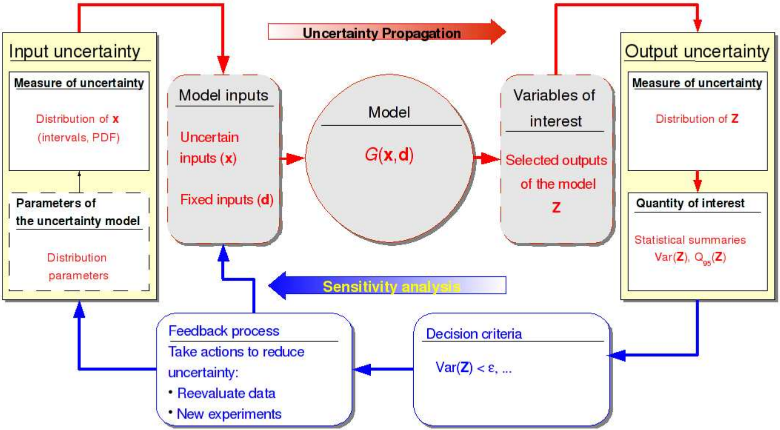

The *key reaction* concept

- Our goal is to *optimally* reduce prediction uncertainty for photochemical models at low T
  - "*optimally*", because low-T experiments are expensive and simulations are computer intensive

- We need to identify parameters of the models (reaction rates, branching ratios...) which are responsible for the large prediction uncertainty on variables of interest
  - the corresponding reactions are the "key reactions" of the UP/SA modeling

- We want to establish an iterative process between modelers and experimentalists
  - pointing out "key reactions" for new experiments should be based on **sane uncertainty analysis**

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Shopping for uncertainties

1. **We need a mathematical representation for uncertain model inputs.**
2. **What have existing databases to offer to uncertainty-aware modelers ?**

Shopping for uncertainties

- **udfa**[06]
  - $k_i(T) = \alpha_i \, (T/300)^{\beta_i} \exp\left(-\gamma_i/T\right)$
  - The accuracy is described by a letter - A, B, C, D, E - where the errors are $< 25\%$, $< 50\%$, within a factor of 2, within an order of magnitude, and highly uncertain, respectively.
  - No T-dependence of uncertainty
  - No pdf proposed

Shopping for uncertainties

- **osu_01_2007**
  - $k_i^0(T) = \alpha_i\,(T/300)^{\beta_i}\exp\left(-\gamma_i/T\right)$
  - $F_i = 1.25, 1.5,\ 2.0$ or 10.0
  - $\log k_i(T) = \log k_i^0(T)\ \pm\ \log F_i$
  - No T-dependence of uncertainty
  - No pdf proposed

Shopping for uncertainties

- **Neutral reactions : IUPAC - NASA/JPL**, Hébrard*et al.* (JPPC, 2006 ; PSS, 2007)
  - $k_i^0(T) = \alpha_i \, (T/300)^{\beta_i} \exp\left(-\gamma_i/T\right)$

    $F_i(T) = F_i(300\,K) \exp\left(g_i \left|\frac{1}{T} - \frac{1}{300}\right|\right)$
  - F_i is proportional to the **standard** uncertainty, $CI \simeq 67\%$ or $CI \simeq 95\%$
  - “Both uncertainty factors, $F_i(300\,K)$ and g_i, do not necessarily result from a rigorous statistical analysis of the available data.”

Shopping for uncertainties

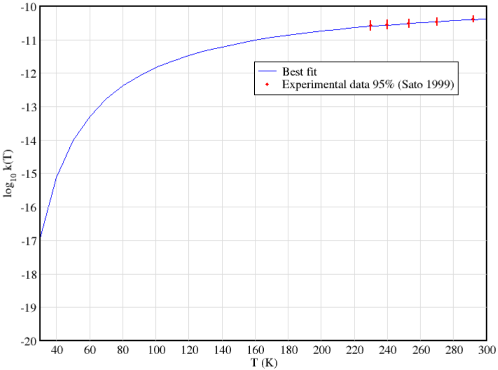
- **Ion-molecule reactions :** Anicich (JPL 2003)
  - Global rate $k_i \pm F_i$ (F_i in percent)
  - Branching ratios $\{b_{ij}\}_{j=1,N}$
  - No reported T-dependence on properties and uncertainties
  - No reported uncertainty on branching ratios

Shopping for uncertainties

- **Electron recombination :** Adams et al. (MSR 2006), Florescu & Mitchell (PR 2006)
  - Global rate $k_i(T) = \alpha_i\,(T/300)^{\beta_i}$
  - Branching ratios $\{b_{ij}\}_{j=1,N}$
  - No uncertainty, search the original literature
  - **Representation by hierarchical Dirichlet distribution**
    Work in progress, see later...

Statistical analysis

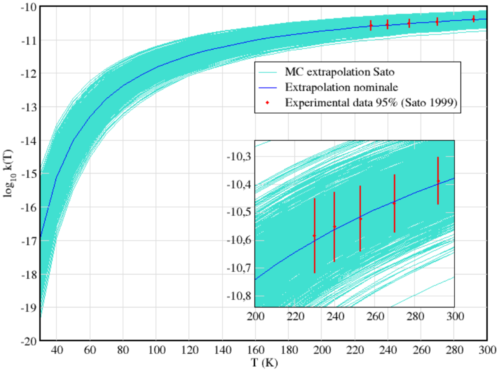
$N(^2D) + C_2H_4 \longrightarrow CH_3CN + H$



	$\ln A$	E_a/R (K)
Best fit	-22.222	504

Statistical analysis

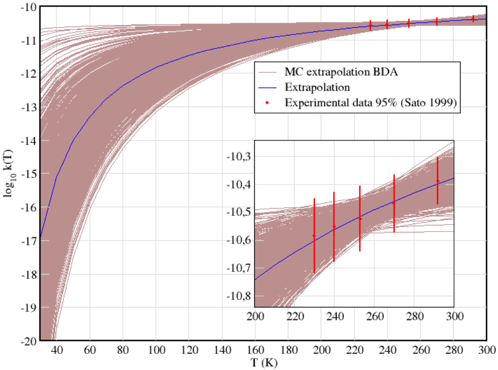
$N(^2D) + C_2H_4 \longrightarrow CH_3CN + H$



	ln A	E_a/R (K)	Correl
Sato *et al.* (1999)	-22.193 $\pm$ 0.13	503 $\pm$ 50	n/a

Statistical analysis

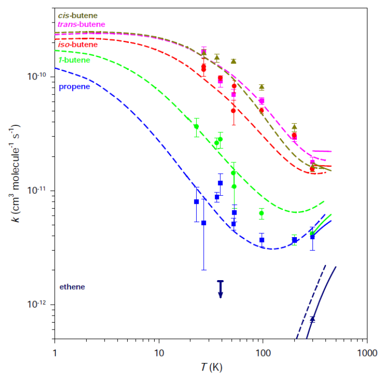
$N(^2D) + C_2H_4 \longrightarrow CH_3CN + H$



	$\ln A$	E_a/R (K)	Correl
Our reanalysis	-22.222 ± 0.66	504 ± 170	0.996

Improper extrapolation laws

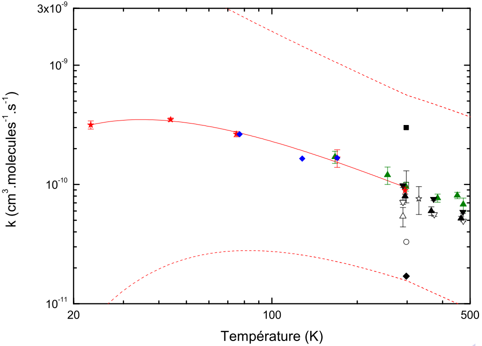
Non-Arrhenius Low-T behaviour of reaction rates



$O(^3P)$ + alkenes : Sabbah et al. (2007) *Science* **317** :102-105.

Conflicting data

$CH + CH_4$



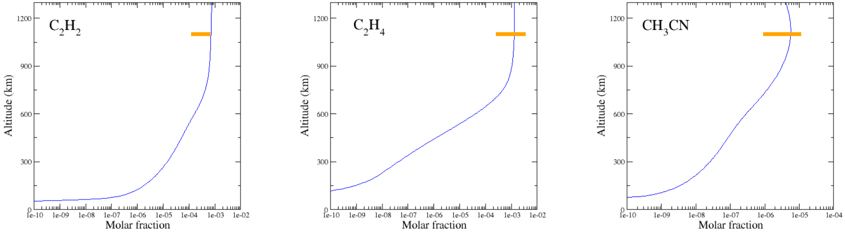
Expert analysis

- Experts are usually trained to estimate "best values"
- Assessing uncertainty (PDF elicitation) is much more difficult :
  - exagerating uncertainty "*just to be on the safe side*" is detrimental to UP/SA ("*Garbage in, garbage out*...")
  - underestimation might lead to wrong "key reactions"
  - might require interaction with elicitation experts

Uncertainty of low-T reaction rates : conclusions

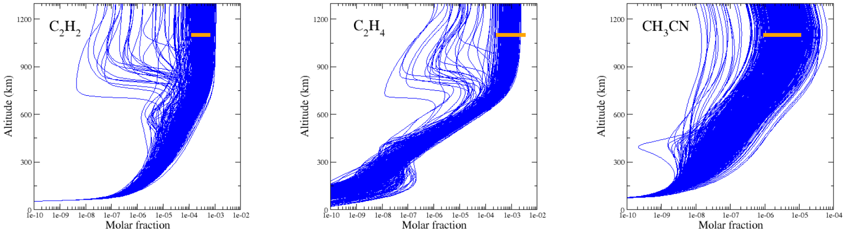
- **Pessimistic**
  - evaluation of 1000s reaction rates and uncertainties by commities of experts will take eons
- **Optimistic**
  - uncertaintywise, few reactions in the model play a dominant role ;
  - sensitivity analysis can help to identify them provided we get reasonable uncertainty assessments ("GIGO") (Dobrijevic *et al.* (2008) *PSS* 56 :1630-1643)
  - iterative process between experiments and simulations

UP on 1D photochemical model



Nominal run

UP on 1D photochemical model



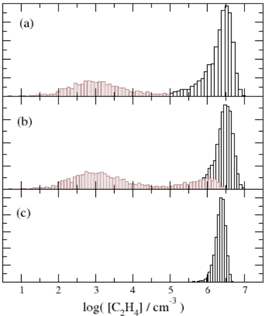
Uncertainty propagation with "Hébrard *et al.* (JPPC 2006)" database

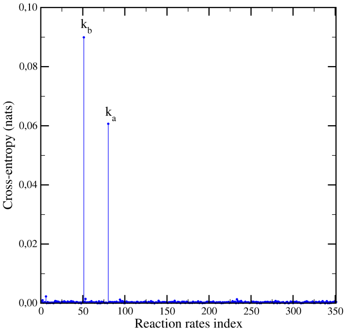
Sensitivity Analysis

Which input parameters are most affected by the filtering of low C_2H_4 densities ?

Cross-entropy analysis : only 2 reactions involved !

- $CH + CH_4 \longrightarrow C_2H_4 + H$; $F_a = 12.7$
- $CH + H \longrightarrow C + H_2$; $F_b = 6.8$





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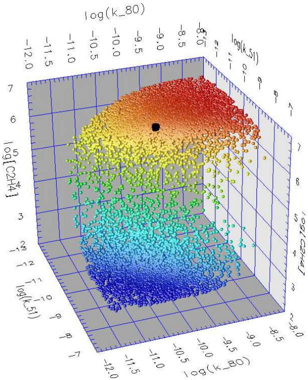
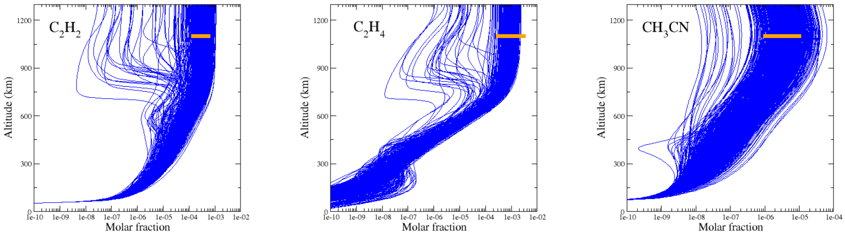


Alternative filtering methods

- "Chemical Filtering" : $k_a[CH_4] > k_b[H]$
- Uncertainty reduction : $F_a = F_b = 2$

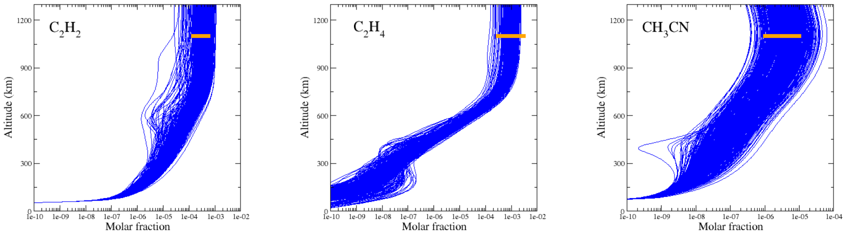
UP on 1D photochemical model



Uncertainty propagation with "Hébrard *et al.*" database

(M. Dobrijevic *et. al.*, submitted)

UP on 1D photochemical model

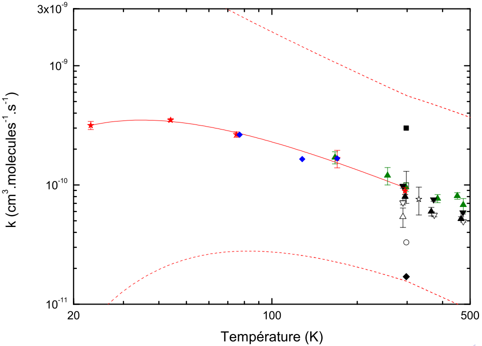


Uncertainty propagation with filtering

(M. Dobrijevic *et. al.*, submitted)

Effects of update of rate database ?

$CH + CH_4$



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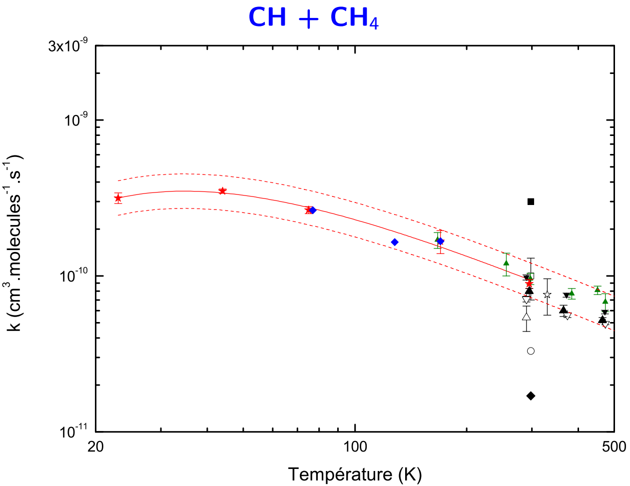

Parametric uncertainties of branching ratios

$$A + B \longrightarrow P_1 \,;\; k$$

- **Partial rate constants** $k_i = k * b_i; \;\sum_i b_{,i} = 1$
- Usual representation in databases ("1 line, 1 reaction")
  - if uncertainty is given, it is thus a combination of F_k and F_{b_i}

Parametric uncertainties of branching ratios

$$A + B \longrightarrow P_1\,;\ k,\ b_1$$
$$\longrightarrow P_2\,;\ k,\ b_2$$

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Parametric uncertainties of branching ratios

$$
\begin{aligned}
A + B &\longrightarrow P_1\,;\ \ k,\ b_1 \\
&\longrightarrow P_2\,;\ \ k,\ b_2
\end{aligned}
$$

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Branching ratios and the sum rule

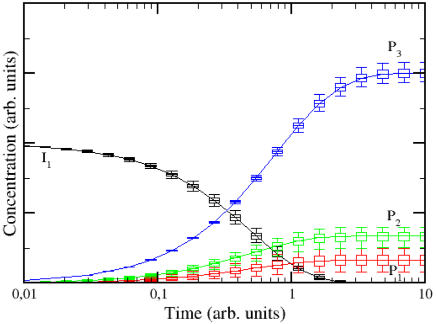
$$I_1 + M_1 \longrightarrow P_1\,;\;\; k_1,\; b_{11}$$
$$I_1 + M_1 \longrightarrow P_2\,;\;\; k_1,\; b_{12}$$
$$I_1 + M_2 \longrightarrow P_3\,;\;\; k_2$$

$$[M_i] \gg [I_i]$$

$$F_k \ll F_b$$

Branching ratios and the sum rule

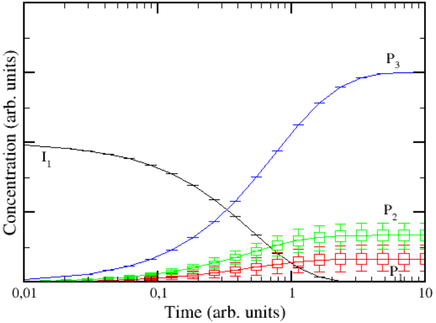
Uncorrelated partial rates



$$k_{11} = k_1 * b_{11} = 0.33 \pm 0.12, \; k_{12} = k_1 * b_{12} = 0.67 \pm 0.12$$

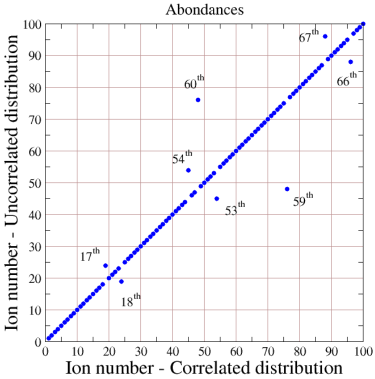
Branching ratios and the sum rule

Correlated partial rates



$$\{k_{11}, k_{12}\} = k_1 * \{b_{11}, b_{12}\} \sim \mathrm{Diri}\,(15, 30)$$

Effect of sum constraint on UP for a complex system



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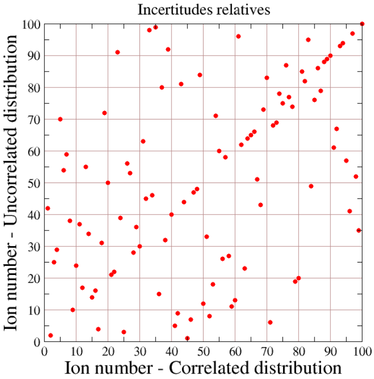
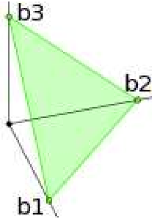


PDFs for branching ratios

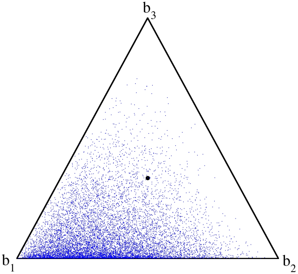
Implementing the sum constraint



Carrasco *et al.*, *PSS* (2007)

Preferred values and precision

$$\{b_{i,j}\} \sim \mathrm{Diri}\left(\{\alpha_{i,j}\}\right) \quad \propto \prod_j b_{i,j}^{\alpha_{i,j}-1}$$



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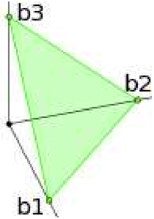
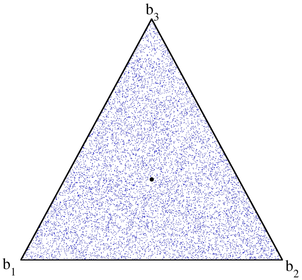


Carrasco *et al.*, *PSS* (2007)

No preference : total uncertainty

$$\{b_{i,j}\} \sim \mathrm{Diri}\,(1, 1, ..., 1)$$



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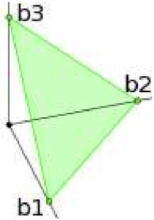
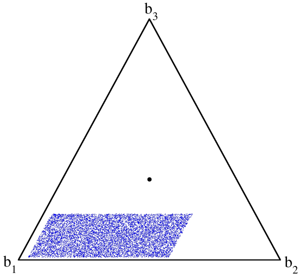


Carrasco *et al.*, *PSS* (2007)

Preferred intervals

$$\{b_{i,j}\} \sim \text{Diut}\left(\left\{b_{i,j}^{min}, b_{i,j}^{max}\right\}\right)$$



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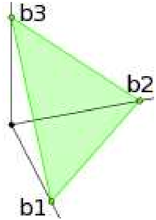
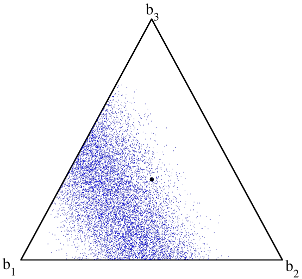


Carrasco *et al.*, *PSS* (2007)

Partial "total uncertainty"

$$\{b_{i,j}\} \sim \text{Diri}\left(\alpha_{i,1}, \alpha_{i,2} * \text{Diri}\left(1,1\right)\right)$$



Partial determination of dissociative recombination products

Coupling ion and neutral chemistry

$$\begin{aligned} A + e^-(h\nu) &\longrightarrow A^+ + e^- + e^-(h\nu) \\ A^+ + B &\longrightarrow C + D^+ \\ A^+ + e^- &\longrightarrow X + Y + \ldots \end{aligned}$$

$$\begin{aligned} X + e^-(h\nu) &\longrightarrow X^+ + e^- + e^-(h\nu) \\ X^+ + A &\longrightarrow E + F^+ \\ &\vdots \end{aligned}$$

Partial determination of dissociative recombination products

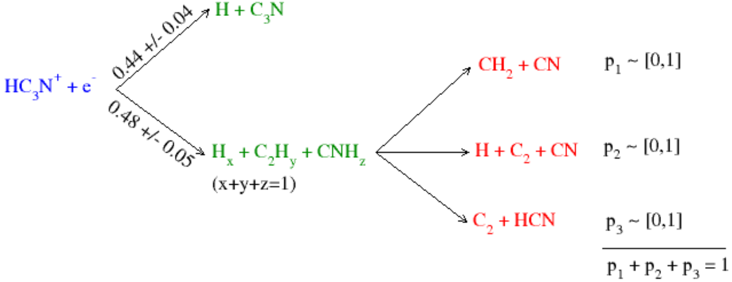
Branching Ratios of the DR of $DCCCN^+$

	Products	Branching Ratio
....	$C_3N + D$	0.44 ± 0.04
....	$DCC + CN$, $D + C_2 + CN$, $DCN + C_2$	0.48 ± 0.05
....	$C_2N + DC$, $N + C_3D$	0.02 ± 0.01
....	$D + C + C_2N$	0.04 ± 0.02
....	$DC_2N + C$	0.02 ± 0.01
....	$ND + C_3$	0.00 ± 0.01

W. D. Geppert at al., *Astroph. J.* (2004)

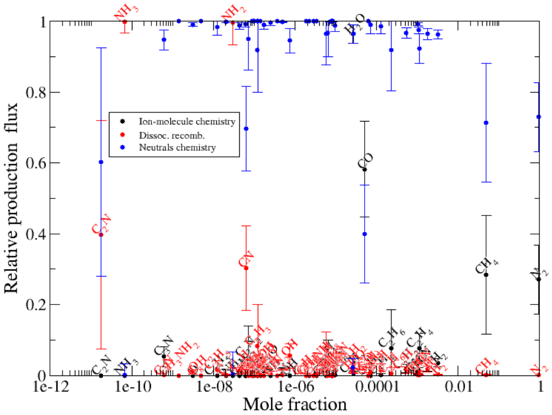
Partial determination of dissociative recombination products

Hierarchical Dirichlet modeling (Carrasco et Pernot, *JPCA* 2007)



Partial determination of dissociative recombination products

Application to Titan ionosphere (work in progress)



Partial rates or Branching ratios ?

$$A + B \longrightarrow P_1\,;\ \{k,\ b_1\} \text{ or } k_1?$$
$$\longrightarrow P_2\,;\ \{k,\ b_2\} \text{ or } k_2?$$

- **if reaction rates and branching ratios are measured by different experiments/techniques**
  - keep separated uncertainty statements and representation in database
- **if not, proceed as usual ("1 line, 1 reaction")**
- Advantages of keeping an explicit separation of uncertainty sources
  - T-dependence of k might be different from b_i ;
  - more pertinent sensitivity analysis (key parameters) ;
  - easier to manage the sum rule wrt. uncertainties.

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Conclusions

- photochemical models should not ignore the large uncertainty in chemical parameters :
  - low-T extrapolation of reaction rates
    need uncertainty-aware kinetics database
  - products distributions / branching ratios
    very important to enforce sum constraint
    the larger the uncertainties, the more important the conservation laws
- uncertainty propagation and sensitivity analysis are powerful tools for improving model precision
- *key reactions* are identified by their majority contribution to model imprecision
- this requires adapted uncertainty representation and a new generation of kinetics database (KiDA)

Beloved collaborators and funding agencies

- N. Carrasco, E Hébrard (SA, Verrières-le-Buisson)
- S. Plessis (LCP, Orsay)
- M. Dobrijevic, V. Wakelam (LAB, Bordeaux)

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- CNES
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