Low-temperature chemistry : modelling with very large uncertainties

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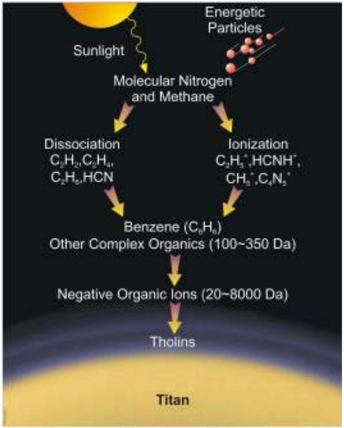
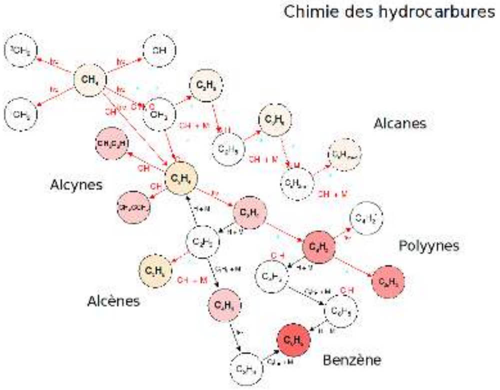
Plan

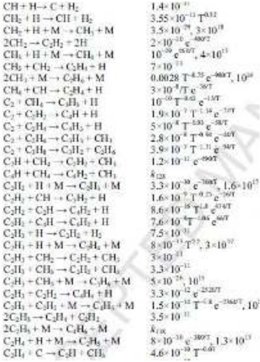
Extra-terrestrial and early-earth chemistry



Tholin formation in Titan's upper atmosphere

Extra-terrestrial and early-earth chemistry





$CH + H \rightarrow C + H_2$	1.4×10^{-11}
$CH_2 + H \rightarrow CH + H_2$	$3.55\times10^{-11}\,T^{0.32}$
$CH_2 + H + M \rightarrow CH_3 + M$	3.5×10^{-29}, 3×10^{19}
$2CH_2 \rightarrow C_2H_2 + 2H$	$2\times10^{-10}\,e^{-400/T}$
$CH_3 + H + M \rightarrow CH_4 + M$	$10^{-29}\,e^{[illegible]/T}$, 4×10^{13}
$CH_3 + CH_2 \rightarrow C_2H_4 + H$	7×10^{-11}
$2CH_3 + M \rightarrow C_2H_6 + M$	$0.0028\,T^{-8.75}\,e^{-[illegible]/T}$, $10^{[illegible]}$
$CH_4 + CH \rightarrow C_2H_4 + H$	$3\times10^{-8}/T\,e^{-38/T}$
$C_2 + CH_4 \rightarrow C_3H_3 + H$	$10^{-10}\,T^{-0.62}\,e^{-15/T}$
$C_2 + C_2H_2 \rightarrow C_4H + H$	$1.9\times10^{-7}\,T^{-1.14}\,e^{-17/T}$
$C_2 + C_2H_4 \rightarrow C_4H_3 + H$	$5\times10^{-8}\,T^{-1.00}\,e^{-58/T}$
$C_2 + C_3H_6 \rightarrow C_4H_3 + CH_3$	$2.8\times10^{-8}\,T^{-0.66}\,e^{-18/T}$
$C_2 + C_3H_8 \rightarrow C_3H_2 + C_2H_6$	$3.9\times10^{-7}\,T^{-1.31}\,e^{-34/T}$
$C_2H + CH_4 \rightarrow C_2H_2 + CH_3$	$1.2\times10^{-11}\,e^{-490/T}$
$C_4H + CH_4 \rightarrow C_4H_2 + CH_3$	k_{128}
$C_2H_2 + H + M \rightarrow C_2H_3 + M$	$3.3\times10^{-30}\,e^{-740/T}$, 1.6×10^{17}
$C_2H_2 + CH \rightarrow C_3H_2 + H$	$1.6\times10^{-9}\,T^{-0.23}\,e^{-16/T}$
$C_2H_2 + C_2H \rightarrow C_4H_2 + H$	$8.6\times10^{-16}\,T^{1.8}\,e^{474/T}$
$C_2H_2 + C_4H \rightarrow C_6H_2 + H$	$7.6\times10^{-8}\,T^{-1.06}\,e^{66/T}$
$C_2H_3 + H \rightarrow C_2H_2 + H_2$	7.5×10^{-11}
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$C_2H_3 + CH_3 \rightarrow C_2H_2 + CH_4$	3.3×10^{-11}
$C_2H_3 + CH_3 + M \rightarrow C_3H_6 + M$	5×10^{-26}, 10^{15}
$C_2H_3 + C_2H_2 \rightarrow C_4H_4 + H$	$3.3\times10^{-12}\,e^{-2520/T}$
$C_2H_3 + C_2H_2 + M \rightarrow C_4H_5 + M$	$1.5\times10^{-12}\,T^{-0.8}\,e^{-2362/T}$, $10^{[illegible]}$
$2C_2H_3 \rightarrow C_2H_4 + C_2H_2$	3.5×10^{-11}
$2C_2H_3 + M \rightarrow C_4H_6 + M$	k_{130}
$C_2H_4 + H + M \rightarrow C_2H_5 + M$	$8\times10^{-30}\,e^{-380/T}$, 1.3×10^{13}
$C_2H_4 + C \rightarrow C_3H + CH_3$	$4.6\times10^{-10}\,T^{-0.07}$

Extra-terrestrial and early-earth chemistry

The big picture

- **Origins**
  - complexification of molecules in cold environments
  - formation of biomolecules or their bricks in the interstellar medium
  - atmosphere of the early earth (Titan as a model)
  - apparition of life...
- **At our modest level**
  - predictivity of low-T chemistry models ?

Uncertainty in low-T kinetic modeling

- photochemical models of interstellar or planetary atmospheres are complex (1[-3]D reaction-transport codes
  with 100s to 1000s of stiff coupled nonlinear equations)

- the chemical equations are based on **empirical parameters**
  $A + B \longrightarrow C + D$; $k_{AB}(T, P)$;

  $\frac{da(t)}{dt} = -k_{AB}(T, P)\, a(t)\, b(t)$

- empirical parameters are obtained from experiments and/or **extrapolations**
  $\longrightarrow$ they are always evaluated with **[[very] large] uncertainty**
  $\longrightarrow$ in some models, *estimated* parameters are numerous
  $\longrightarrow$ *in Titan atmospheric model, less than 10% of reaction rates are measured at relevant temperatures*

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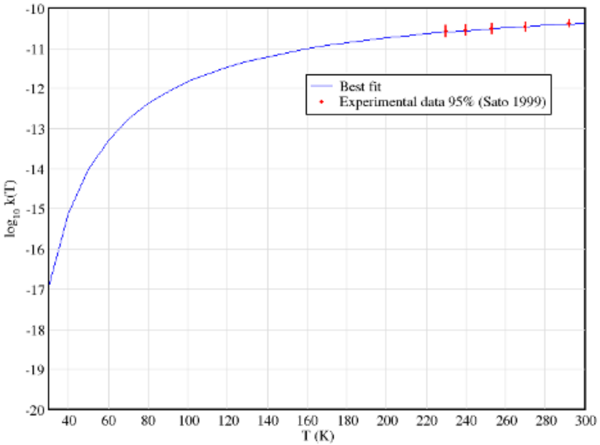
Uncertainty due to extrapolation

Arrhenius law for $N(^2D) + C_2H_4$



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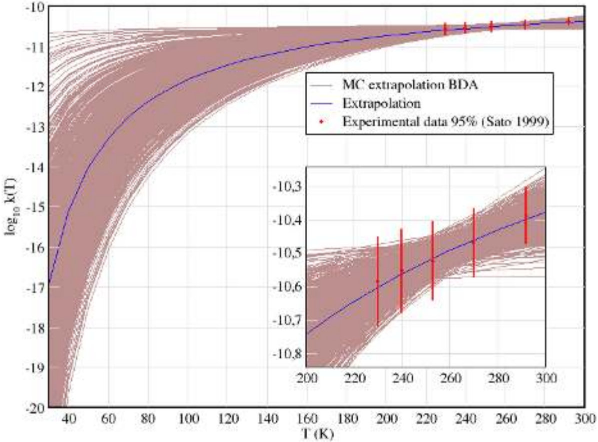
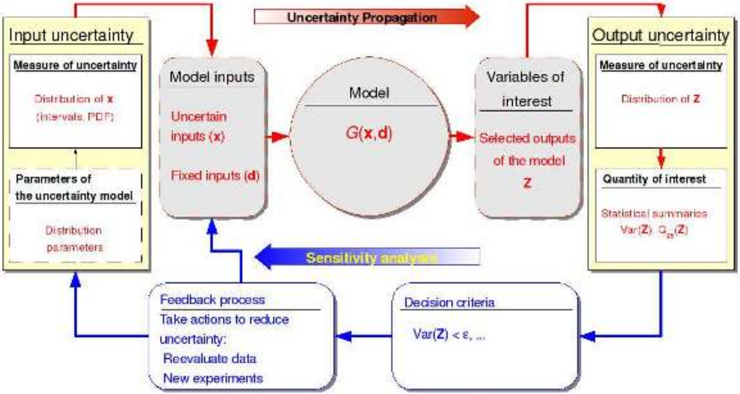


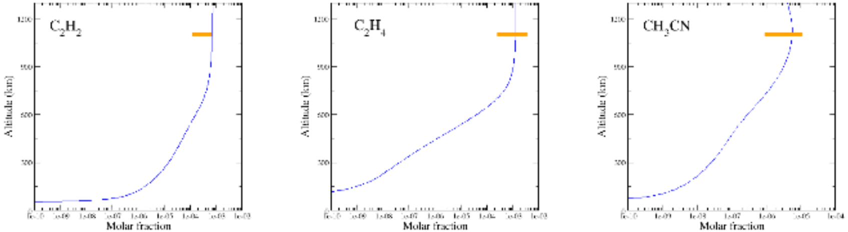
Uncertainty in low-T kinetic modeling

1. What is the impact of empirical parameters uncertainty on the outputs of photochemical models ?
2. Which are the prioritary lab. experiments to perform in order to reduce prediction uncertainty ?
   1. low-T, low-P kinetics experiments are very heavy (time, money)
   2. Goal : experimental design alternating simulations and experiments, based on maximization of information gain for target species

The Framework

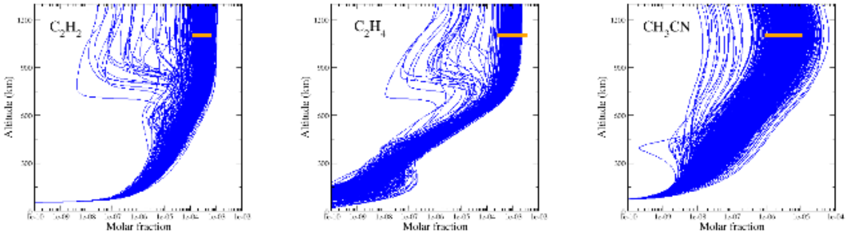


UP on 1D photochemical model



Nominal run

UP on 1D photochemical model



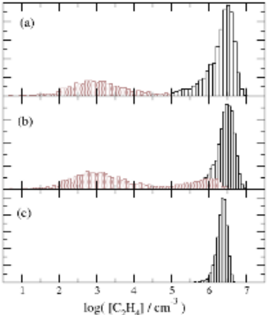
Uncertainty propagation with “Hébrard *et al.* (JPPC 2006)”database

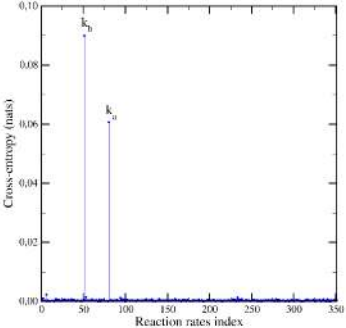
Sensitivity Analysis

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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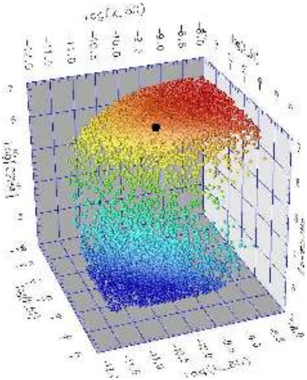
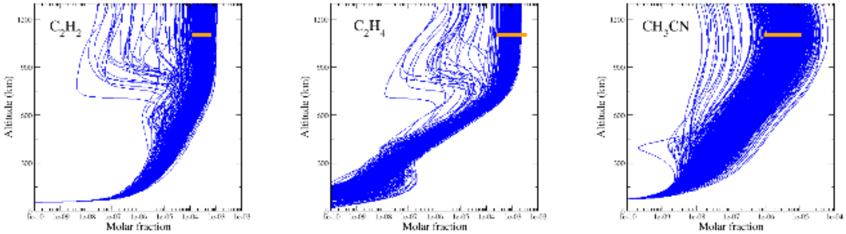


Alternative filtering methods

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

Checking the identified reactions



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

(M. Dobrijevic *et. al.*, 2008)

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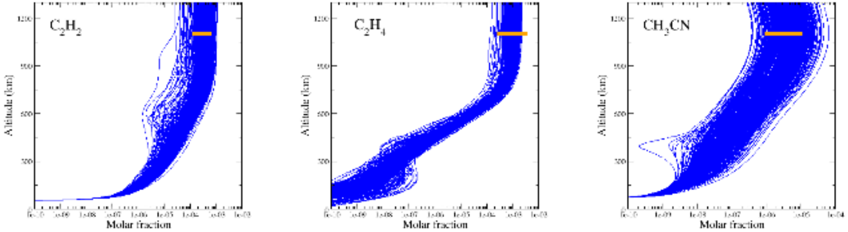


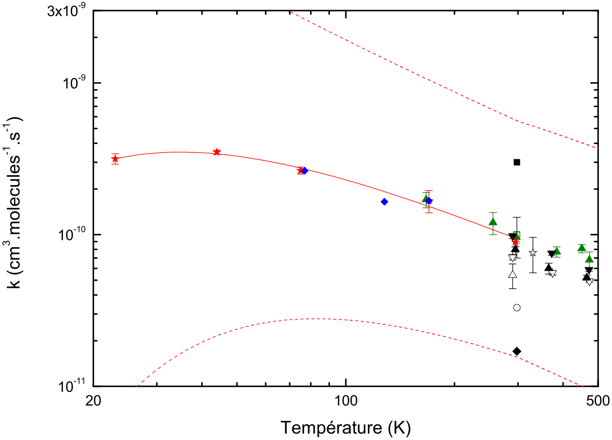
Uncertainty propagation with filtering

(M. Dobrijevic *et. al.*, 2008)

Update of database in favor of low-T experiments

Reduction of uncertainty on all reaction rates measured at low temperature

$CH + CH_4$



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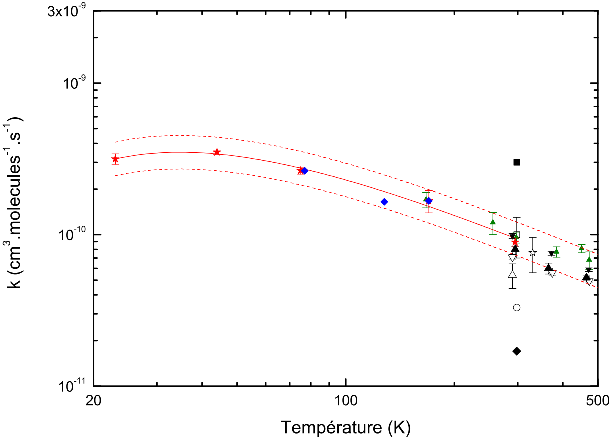
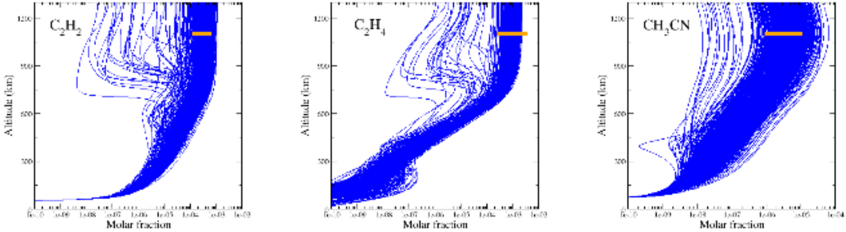


Effect of the database update



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

(E. Hébrard *et. al.*, in prep)

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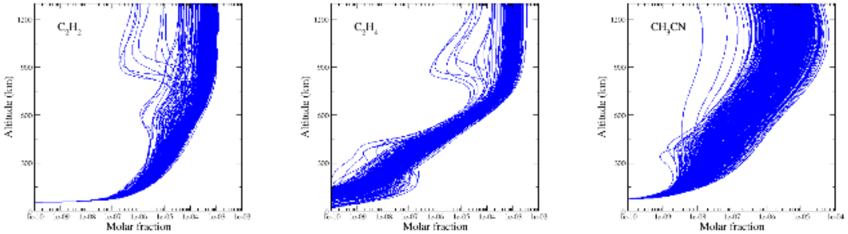


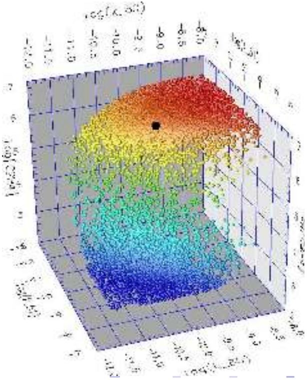
Uncertainty propagation updated database

(E. Hébrard *et. al.*, in prep)

Sensitivity Analysis

Which reaction(s) responsible for residual bimodality at high altitude ?

- Cross-entropy analysis : only 1 reactions involved
  - $CH + H \longrightarrow C + H_2$
- This is clearly a key reaction to be better studied...



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")

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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Parametric uncertainties of branching ratios

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

- **Reaction rates and branching ratios are mostly measured by different experiments/techniques**
  - larger uncertainties for branching ratios (more difficult to measure than rates) ;
- **Keep an explicit separation of uncertainty sources**
  - T-dependence of k different from b_i ;
  - more pertinent sensitivity analysis (key parameters) ;
  - easier to manage the sum rule wrt. uncertainties.

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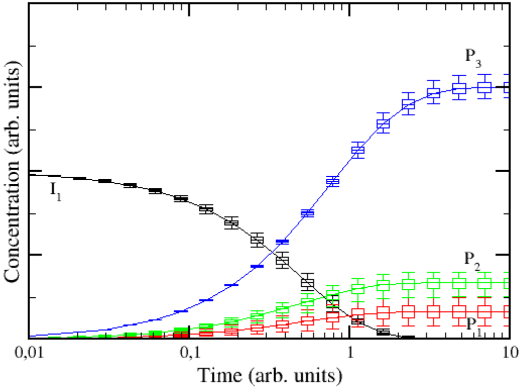
Branching ratios and the sum rule

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

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

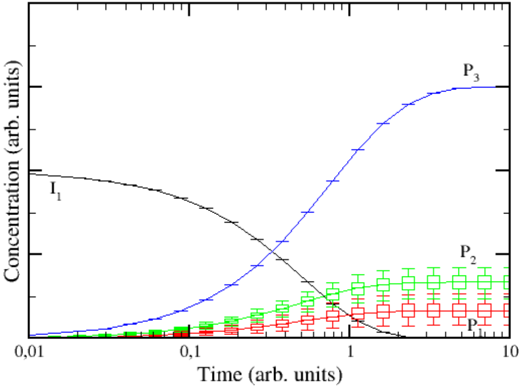
$$F_k \ll F_b$$

Branching ratios and the sum rule



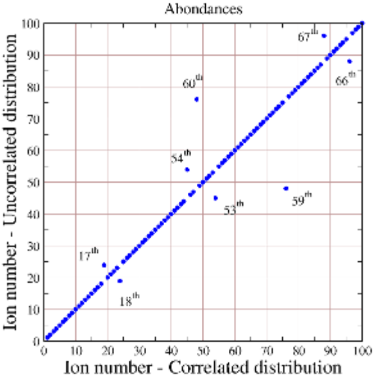
Uncorrelated partial rates : $b_{11} = 0.33 \pm 0.12$, $b_{12} = 0.67 \pm 0.12$

Branching ratios and the sum rule



Correlated partial rates : $\{b_{11}, b_{12}\} \sim \mathrm{Diri}\,(45 \times \{0.33, 0.67\})$

Effect of sum constraint on UP for a complex system



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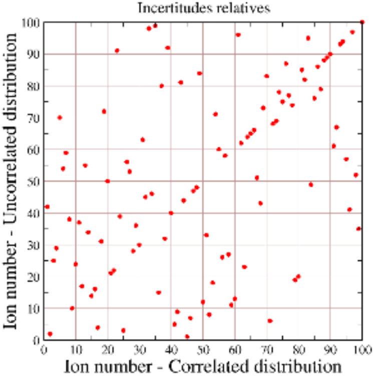
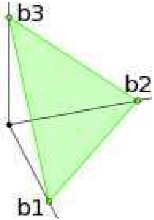


PDFs for branching ratios

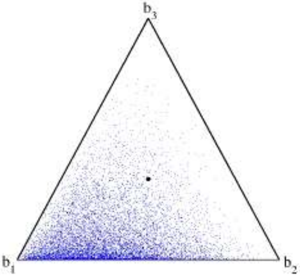
Implementing the sum constraint



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

Preferred values and precision

$$\{b_i\} \sim \mathrm{Diri}\left(\{\alpha_i\}\right) \quad \propto \prod_i b_i^{\alpha_i - 1}$$



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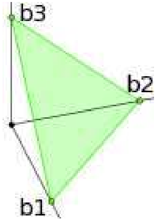
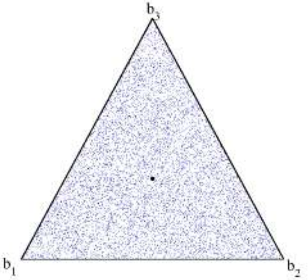


Carrasco *et al.*, *PSS* (2007)

No preference : total uncertainty

$$\{b_i\} \sim \mathrm{Diri}\,(1, 1, ..., 1)$$



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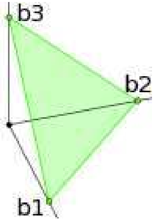
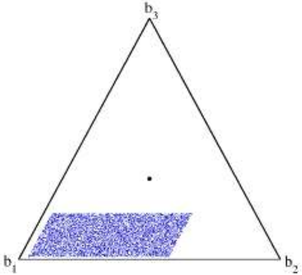


Carrasco *et al.*, *PSS* (2007)

Preferred intervals

$$\{b_i\} \sim \mathrm{Diut}\left(\left\{b_i^{min}, b_i^{max}\right\}\right)$$



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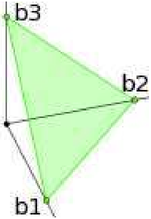
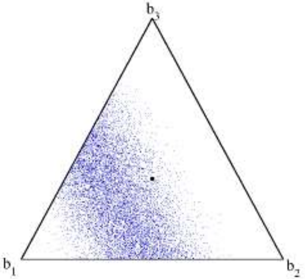


Carrasco *et al.*, *PSS* (2007)

Partial "total uncertainty"

$$\{b_1, b_2, b_3\} \sim \text{Diri}\left(\alpha_1, \alpha_2 * \text{Diri}\left(1, 1\right)\right)$$



Elicitation of Dirichlet pdf (1)

From data $\{\overline{b}_i\}$ and global relative uncertainty x

$$\{b_i\} \sim \mathrm{Dirichlet}\left(\gamma \times \{\overline{b}_i\}\right)$$

- γ is obtained by least squares

$$\gamma = \frac{1}{x^2}\left(\frac{\sum_i \overline{b}_i(1-\overline{b}_i)}{\sum_i \overline{b}_i\sqrt{\overline{b}_i(1-\overline{b}_i)}}\right)^2 - 1$$

  with additional constraint for unimodality

$$\gamma \geq \left\{\min\left(\max\left(\overline{b}_1, 1-\overline{b}_1\right), \ldots, \max\left(\overline{b}_n, 1-\overline{b}_n\right)\right)\right\}^{-1}$$

- **sampling** by direct algorithm : draw n independent variates $B_i \sim \mathrm{Gamma}(\hat{\gamma}\overline{b}_i, 1)$, and normalize $b_i = B_i / \sum_i B_i$.

Carrasco et Pernot, *JPCA* 2007

Elicitation of Generalized Dirichlet pdf (2)

From data $\{\overline{b}_i\}$ and standard uncertainties $\{u_i\}$

$$\{b_i\} \sim \mathrm{DirG}\left(\{\nu_i, \mu_i\}\right)$$

- with parameters

$$\nu_i = \frac{\overline{b}_i}{u_i^2} \text{ and } \mu_i = \frac{\overline{b}_i^2}{u_i^2}$$

- **sampling** by direct algorithm : draw n independent variates $B_i \sim \mathrm{Gamma}(\nu_i, \mu_i)$, and normalize $b_i = B_i / \sum_i B_i$.
  - much more efficient than rejection algorithm to sample over prescribed intervals ;
  - but no strict boundaries...

Partial determination of dissociative recombination products

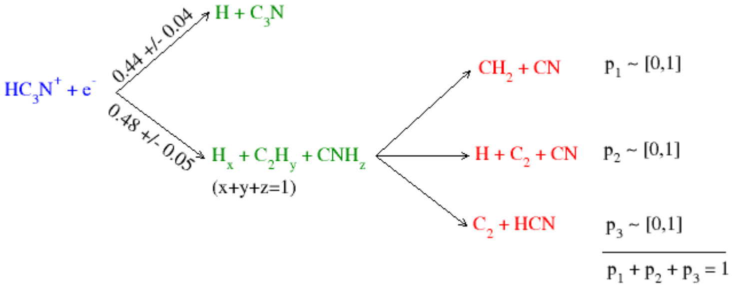
Branching Ratios of the DR of $DCCCN^+$

	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)

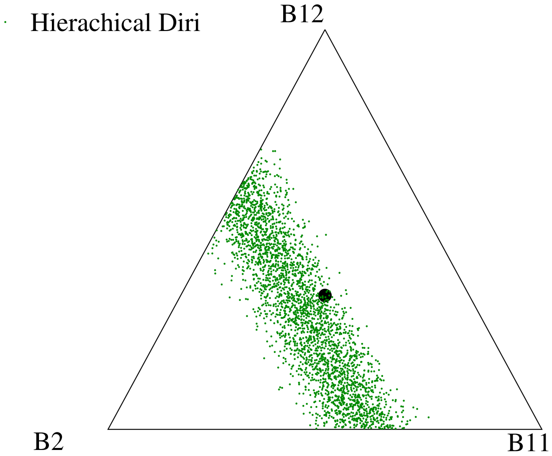
Partial determination of dissociative recombination products

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



$$\{b_{i,j}\} \sim \text{Diri}\left(99 * \{0.48,\ 0.52 * \text{Diri}\left(1,1,1\right)\}\right)$$

Hierarchical vs. all-at-once



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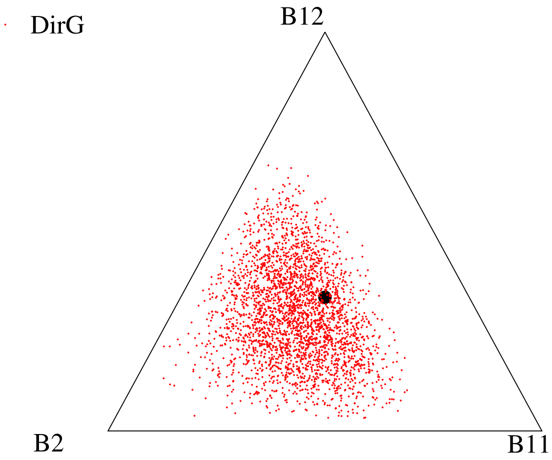

Conclusions

Uncertainty and photochemical modeling @ low-T

- we have to handle very large uncertainties
  - due to the necessity to extrapolate from room-T measurements
  - due to unspecified products distributions
- explicit enforcement of conservation equations is a necessity for reliable Uncertainty Propagation and Sensitivity Analysis
- we are exploring various elicitation techniques of chemical information through Dirichlet distributions and variants
  - **all advices wrt. elicitation, sampling, optimization... are welcomed !**

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- we are exploring various elicitation techniques of chemical information through Dirichlet distributions and variants
  - **all advices wrt. elicitation, sampling, optimization... are welcomed !**

Conclusions

Uncertainty and photochemical modeling @ low-T

- we have to handle very large uncertainties
  - due to the necessity to extrapolate from room-T measurements
  - due to unspecified products distributions
- explicit enforcement of conservation equations is a necessity for reliable Uncertainty Propagation and Sensitivity Analysis
- we are exploring various elicitation techniques of chemical information through Dirichlet distributions and variants
  - **all advices wrt. elicitation, sampling, optimization... are welcomed !**

Beloved collaborators and funding agencies

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

- CNRS
- CNES
- EuroPlaNet
- Programme National de Planétologie