Uncertainty representation and propagation in chemical networks

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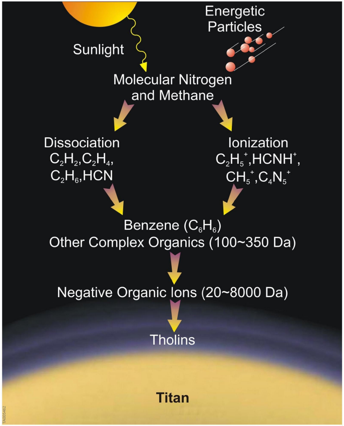
Plan

1. Introduction
2. Uncertainty propagation
3. Treatment of uncertainties for chemical rates
4. Conclusions

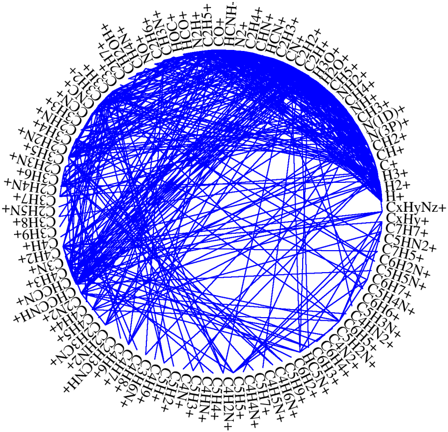
Uncertainties in a chemical model



Tholin formation in Titan's upper atmosphere

- Structural uncertainties
  - Model incompleteness
- Parametric uncertainties
  - transport
  - excitation processes
  - **reaction rates**
    - neutral-neutral
    - ion-molecule

Uncertainties in a chemical model



ca. 680 Ion-molecule reactions in database

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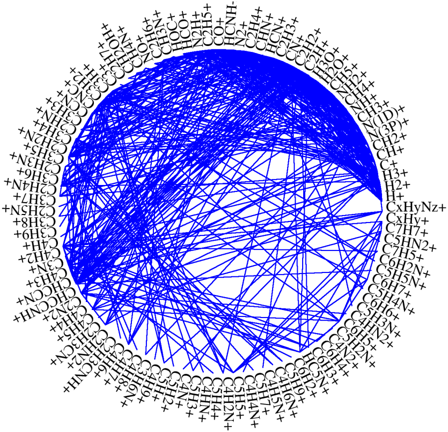

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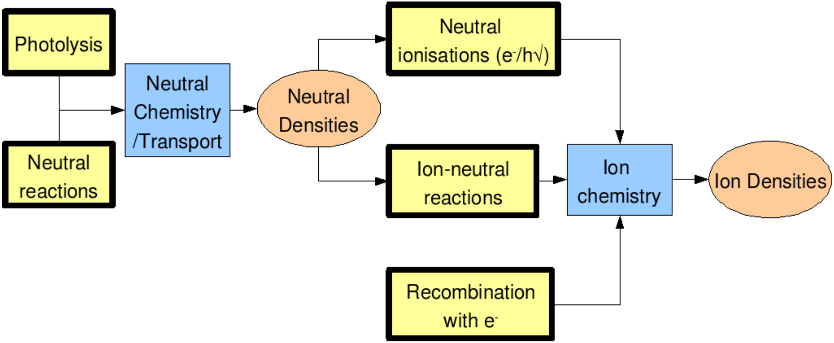
Parametric uncertainty sources



Uncertainty propagation as a tool

- Model predictions to be compared with observational data
  $\longrightarrow$ model predictions as "virtual measurements" : value + incert.
  - *Model assessment* : significative discrepancies can be identified (model improvement) ;
  - *Sensitivity analysis* : major prediction uncertainties can be analyzed to improve input parameters (new lab. experiments...).

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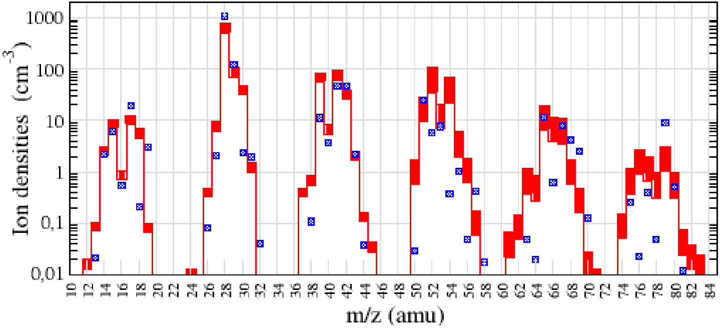
Example : Cassini INMS



Predicted ion mass spectrum with all uncertainty sources vs. Cassini's INMS (T5@1200km)

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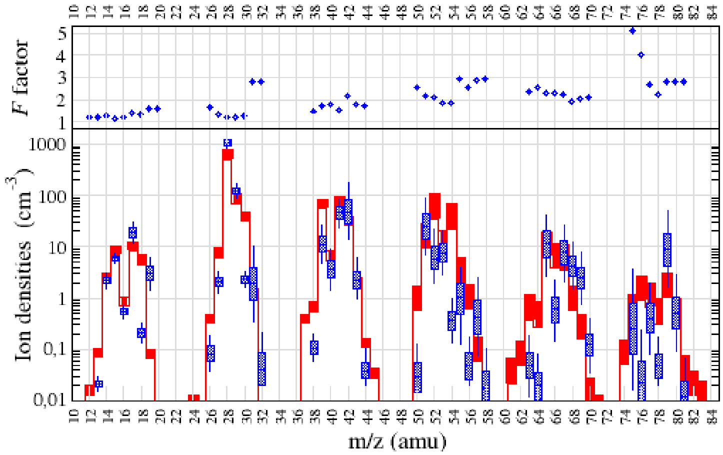


Predicted ion mass spectrum with all uncertainty sources vs. Cassini's INMS (T5@1200km)

Local Uncertainty Propagation

1. **List all sources of uncertainty**

2. **Characterize uncertainty sources and estimate standard uncertainties**

   1. *Type A* : statistical analysis of a sample
   2. *Type B* : all the rest
      u_x from designed pdf

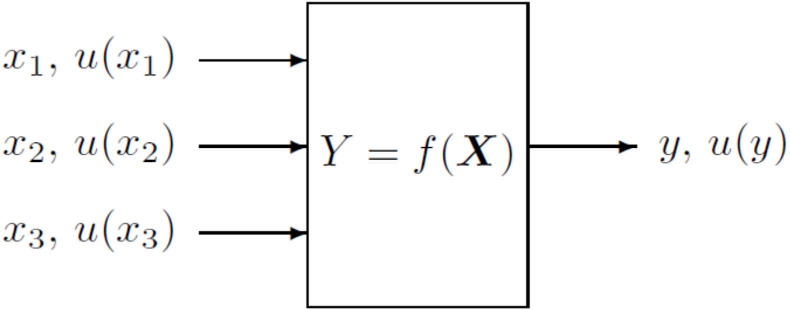
3. **Combine standard uncertainties**

$$\hat{y} = F(\hat{x}_1, \hat{x}_2, ...)$$

$$u_y^2 = \sum_i \left(\frac{\partial y}{\partial x_i}\right)^2_{\hat{x}_i} u_{x_i}^2 + \sum_{i \neq j} \left(\frac{\partial y}{\partial x_i}\right)_{\hat{x}_i} \left(\frac{\partial y}{\partial x_j}\right)_{\hat{x}_j} cov(x_i, x_j)$$

Guide to the expression of **U**ncertainty in **M**easurement (BIPM *et al.*, 1995)

Local Uncertainty Propagation



Guide to the expression of **U**ncertainty in **M**easurement (BIPM *et al.*, 1995)

Global Uncertainty Propagation

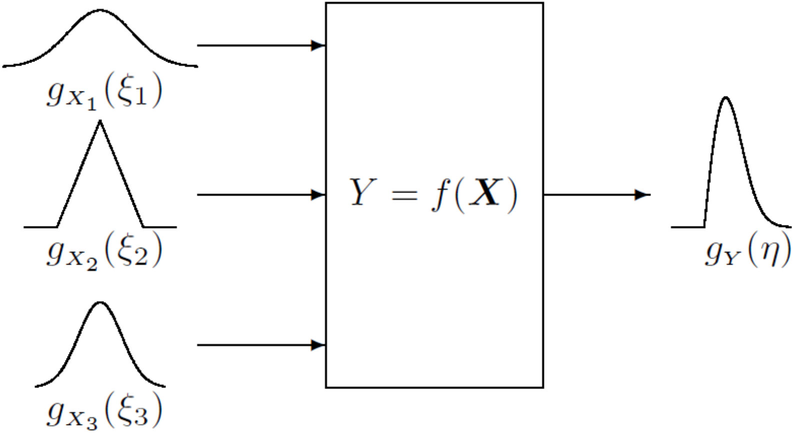
1. **List all sources of uncertainty**
2. **Represent uncertainty sources by pdf** $g_{\{x_i\}}(\{\xi_i\})$
3. **Perform uncertainty propagation**

$$g_y(\eta) = \int d\,\{\xi_i\}\;\delta(\eta - f(\{\xi_i\}))\,g_{\{x_i\}}(\{\xi_i\})$$

4. **Estimate uncertainties of model outputs from** $g_y(\eta)$

Evaluation of measurement data - Supplement 1 to the GUM (BIPM *et al.*, 2006)

Global Uncertainty Propagation



Evaluation of measurement data - Supplement 1 to the GUM (BIPM *et al.*, 2006)

Limitations of local and global UP

Local approach, pb. with :

- asymmetrical pdfs (ex. lognormal) ; $\exists$ improved versions of standard formula
- nonlinear models (large uncertainties) ;
- nonlinear correlations (ex : prescribed sum).

Most of the above apply to chemical networks of interest here...

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Most of the above apply to chemical networks of interest here...

Global approach

- more complex (pdf design)
- grid-based methods (polynomial chaos, Galerkin...)
  - curse of dimensionality
  - pb. with positivity constraints
- sampling based methods
  - pb. if model $y = F(x)$ computer intensive

Monte Carlo, Latin Hypercube Sampling (LHS)...

$$g_{\{x_1,\ldots,x_n\}}(\xi_1,\xi_2,\ldots,\xi_n)$$

$$\downarrow$$

$$\overbrace{\begin{array}{cccc} \xi_1^{(1)} & \xi_2^{(1)} & \ldots & \xi_n^{(1)} \\ \xi_1^{(2)} & \xi_2^{(2)} & \ldots & \xi_n^{(2)} \\ \vdots & \vdots & & \vdots \\ \xi_1^{(m)} & \xi_2^{(m)} & \ldots & \xi_n^{(m)} \end{array}}$$

Monte Carlo, Latin Hypercube Sampling (LHS)...

$$g_{\{x_1,\dots,x_n\}}(\xi_1, \xi_2, \dots, \xi_n)$$
$$\downarrow$$
$$\begin{array}{cccccc}
\multicolumn{4}{c}{\overbrace{\hspace{12em}}} & F & \\
\hline
\xi_1^{(1)} & \xi_2^{(1)} & \dots & \xi_n^{(1)} & \longrightarrow & \eta^{(1)} \\
\hline
\xi_1^{(2)} & \xi_2^{(2)} & \dots & \xi_n^{(2)} & & \\
\vdots & \vdots & & \vdots & & \\
\xi_1^{(m)} & \xi_2^{(m)} & \dots & \xi_n^{(m)} & &
\end{array}$$

Sampling based uncertainty propagation

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\hline
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Monte Carlo, Latin Hypercube Sampling (LHS)...

$$
\begin{array}{c}
g_{\{x_1,\ldots,x_n\}}(\xi_1,\xi_2,\ldots,\xi_n) \\
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\overbrace{
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\begin{array}{c}
F \\
\longrightarrow \\
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\\
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\\
\\
\end{array}
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\\
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\downarrow \\
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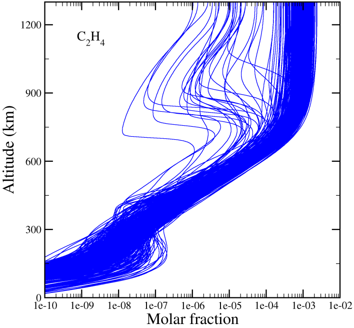
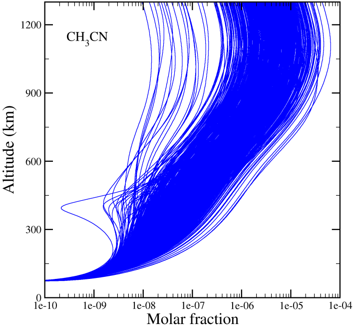
\end{array}
\right|
$$

Global UP : Titan photochemistry





Bimodality of outputs PDF : out of reach of local UP

Global UP provides extensive exploration of parameter space

Hébrard. *et al.*, *JPPC* (2006), *PSS* (2007)

PDF DESIGN

- type of PDF depends on the nature of the parameters
  - discrete vs. continuous
  - interval of definition
    $]-\infty, +\infty[$, $[0, +\infty[$, $[a, b]$...
- PDF of outputs depends on PFDs of inputs,
  tempered by "Central Limit Theorems"
- the joint PDF of all uncertain parameters can be factorized in groups of independent parameters

$$g_{\{x_i\}}\left(\{\xi_i\}\right) = \prod_k g_{\{x_j\}_{j\in k}}\left(\{\xi_j\}_{j\in k}\right)$$

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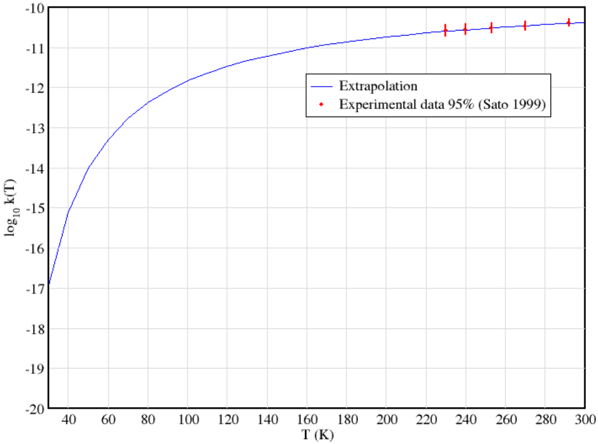
Parametric uncertainties of reaction rates

Analysis of measured rate constants

- Example. *Arrhenius* $\ln k = \ln A - \vartheta / T$
  - Data analysis provides $\{\ln A, \vartheta\} \sim \mathrm{Norm}\left(\left\{\overline{\ln A}, \overline{\vartheta}\right\}, \Sigma\right)$
    Σ : variance/covariance matrix
  - sample of k from $\{\ln A, \vartheta\}$ and stat. analysis
    or
    $u_{\ln k}^2 = u_{\ln A}^2 + u_{\vartheta}^2 / T^2 - 2/T * \mathrm{Cov}(\ln A, \vartheta)$
  - Note : $\mathrm{Cov}(\ln A, \vartheta)$ generally large (>0.9), very important for UP !

Arrhenius UP example : $N(^2D) + C_2H_4$



	$\ln A$	E_a/R (K)	Correl
Bayesian	-22.222 $\pm$ 0.66	504 $\pm$ 170	0.996

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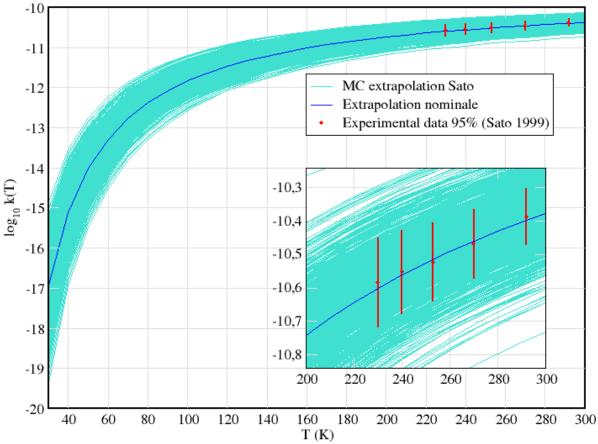

	$\ln A$	E_a/R (K)	Correl
Sato *et al.* (1999)	-22.193 $\pm$ 0.13	503 $\pm$ 50	n/a

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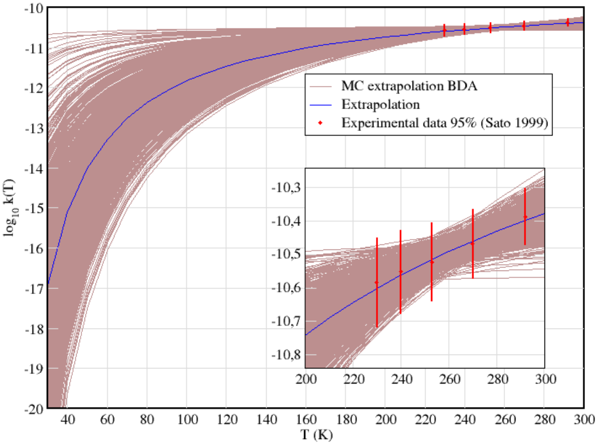

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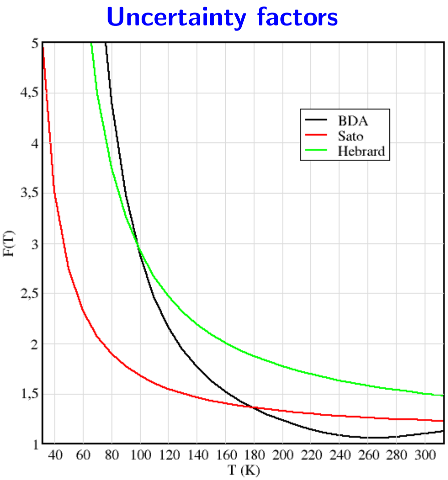

Choice of pdf for evaluated rates

Distributions implementing positivity constraint

- **Preferred value** k_i^0, estimated uncertainty factor F_i^0

$$k_i \sim \text{Lognormal}(k_i^0, F_i^0)$$

  - $\text{P}(k_i^0/(2F_i^0) < k_i < k_i^0 * 2F_i^0) \simeq 0.95$
  - k_i^0 is *median* of pdf, not *mean* (Stewart and Thompson, 1994)
  - **modelers truncate to $2 * F_i^0$ or $3 * F_i^0$ to avoid "exotic" rates**

- **Preferred interval**

$$k_i \sim \text{Loguniform}(k_i^{min}, k_i^{max})$$

  - no preferred value within an interval (dispersed experimental data)
  - $k_i^{min} = k_i^0/(2F_i^0)$, $k_i^{max} = k_i^0 * (2F_i^0)$

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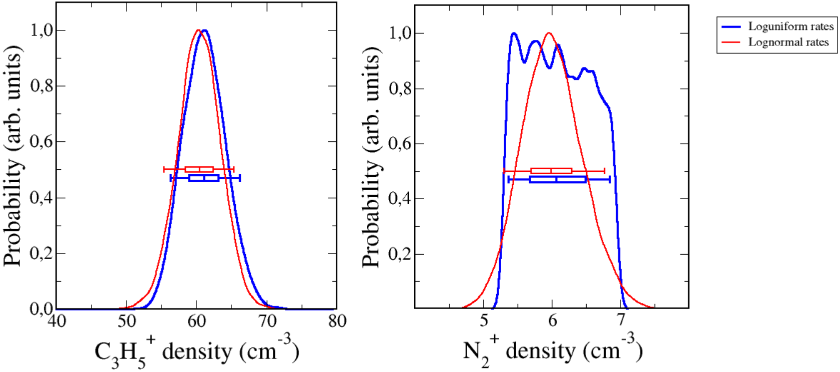
Lognormal vs. Loguniform



Output pdf depends on the place of the species in the network
Might have an impact on sensitivity analysis

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

Parametric uncertainties of branching ratios

Multi-pathway reactions

$$k_{i,j} = k_i * b_{i,j}; \sum_j b_{i,j} = 1$$

- **Reaction rates and branching ratios are mostly measured by different experiments/techniques**
  - larger uncertainties for branching ratios (more difficult to measure than rates).

- **In such cases, it is better to keep an explicit separation of uncertainty sources**
  - more pertinent sensitivity analysis (key parameters) ;
  - easier to manage the sum rule wrt. uncertainties ;
  - T-dependence of k_i different from $b_{i,j}$
  - safer update of databases when new branching ratios or rate available.

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PDFs for branching ratios

Distributions implementing the sum rule

- **Preferred values and precision**

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

- **No preference**

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

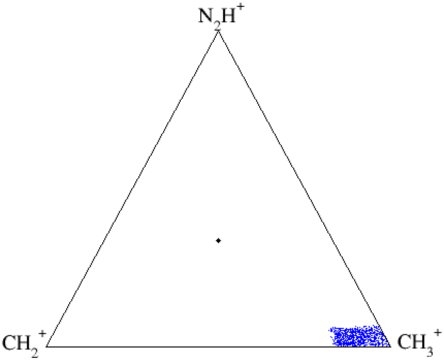
ex : low-T extrapolation for ion-molecule reactions

- **Preferred intervals**

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

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

EXAMPLE : $N_2^+ + CH_4$



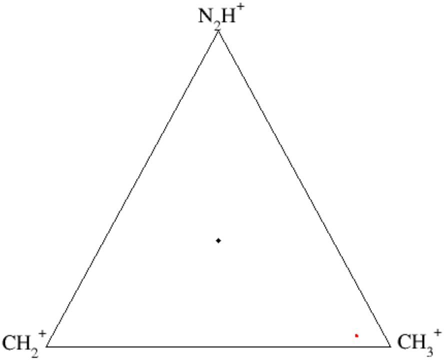
CH_3^+	CH_2^+	N_2H^+
0.89	0.08	0.03
10%	100%	100%

Standard elicitation

$$1 \leq 10\ \% \leq 0.5$$
$$0.5 < 30\ \% \leq 0.1$$
$$0.1 < 100\ \% \leq 0$$

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

Example : $N_2^+ + CH_4$

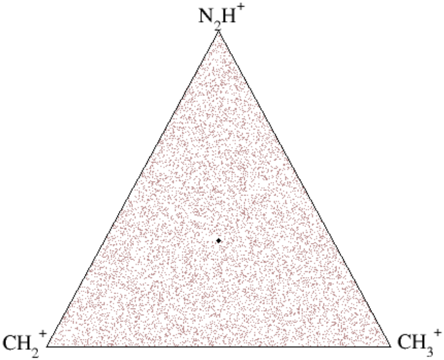


CH_3^+	CH_2^+	N_2H^+
0.89	0.08	0.03
2%	10%	10%

Improved elicitation
according to Nicolas (PhD Thesis, 2002)

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

Example : $N_2^+ + CH_4$



CH_3^+	CH_2^+	N_2H^+
1/3	1/3	1/3
100%	100%	100%

Full uncertainty

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

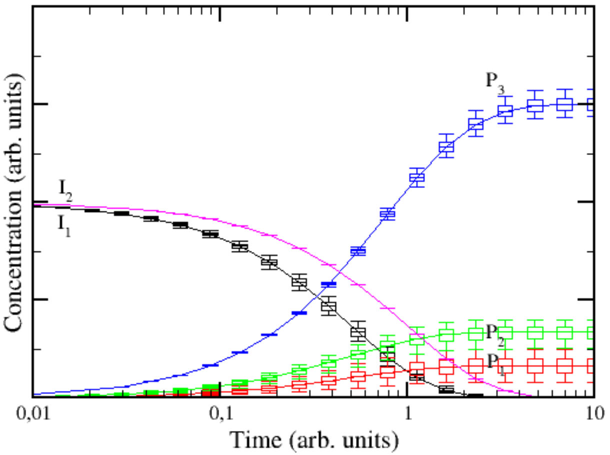
Branching ratios and the sum rule

$$I_1 + M_1 \longrightarrow P_1\ ;\ \ k_1,\ b_{11}$$
$$I_1 + M_1 \longrightarrow P_2\ ;\ \ k_1,\ b_{12}$$
$$I_1 + M_2 \longrightarrow P_3\ ;\ \ k_2$$
$$I_2 + M_2 \longrightarrow P_3\ ;\ \ k_3$$

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

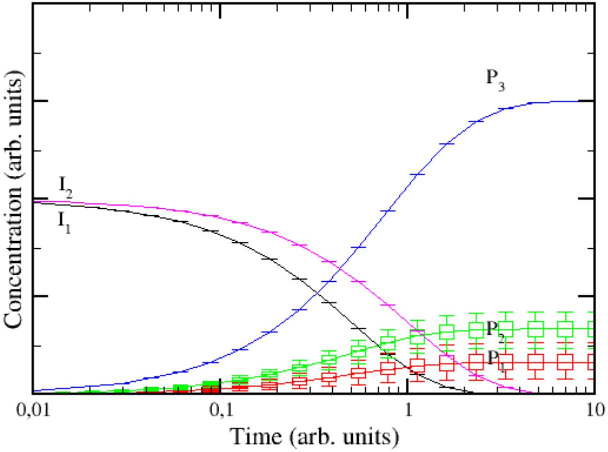
$$F_k \ll F_b$$

Branching ratios and the sum rule



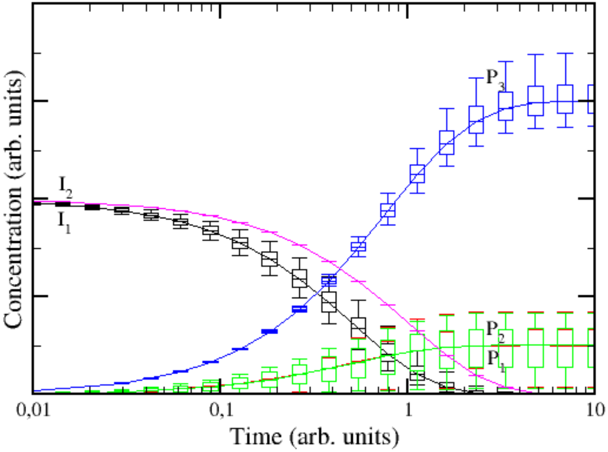
Uncorrelated partial rates : $b_{11} = 0.33 \pm 0.12$, $b_{12} = 0.67 \pm 0.12$

Branching ratios and the sum rule



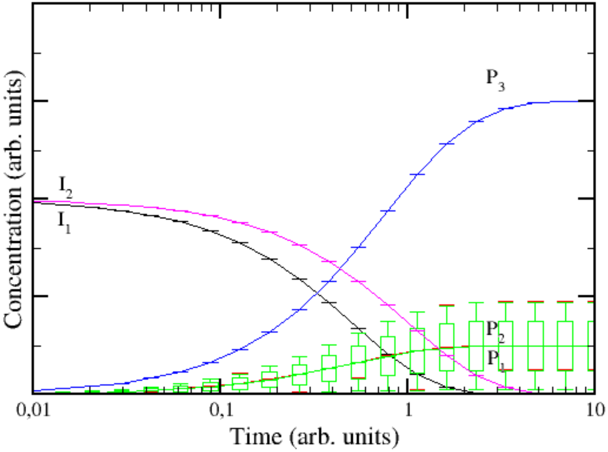
Correlated partial rates : $\{b_{11}, b_{12}\} \sim \mathrm{Diri}\,(15, 30)$

Branching ratios and the sum rule



Uncorrelated partial rates : $b_{11} \sim b_{12} \sim \mathrm{Unif}\,(0, 1)$

Branching ratios and the sum rule



Correlated partial rates : $\{b_{11}, b_{12}\} \sim \mathrm{Diri}\,(1,1)$

Shopping for rate uncertainty

What have existing databases to offer to MCUP-aware modelers ?

- **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

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

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

What have existing databases to offer to MCUP-aware modelers ?

- **IUPAC - NASA/JPL**
  - $k_i(T) = k_i^0 \exp\left(-E_i/T\right)$

    $F_i(T) = F_i^0 \exp\left(g_i \left|\frac{1}{T} - \frac{1}{T^0}\right|\right);\ T^0 = 298\,K$
  - F_i is an **expanded** uncertainty, $CI \simeq 95\%$
  - "The assignment of the uncertainties is a subjective assessment of the evaluators. *They are not determined by a rigorous statistical analysis of the database.*"
  - No pdf proposed

What have existing databases to offer to MCUP-aware modelers ?

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

    $F_i(T) = F_i(300\,K)\,\exp\left(g_i\left|\frac{1}{T} - \frac{1}{300}\right|\right)$
  - F_i is a **standard** uncertainty, $CI \simeq 67\%$
  - "Both uncertainty factors, $F_i(300\,K)$ and g_i, do not necessarily result from a rigorous statistical analysis of the available data."
  - No pdf proposed, but
    - $\log k_i = \log k_i(T) + \epsilon\,\log F_i(T)$; $\epsilon \sim \mathrm{Norm}(0,1)$, in Hébrard *et al.* (*PSS*, 2007)

Conclusions

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  - Monte Carlo UP is now recognized as a standard tool in metrology
- **Utility of MCUP depends on adapted PDFs**, with
  - a correct description of inputs uncertainty
    - amplitude (not too small, not too large...)
    - distribution shape (to a minor degree, but we need more experiences in SA to conclude)
  - a structure reflecting experimental uncertainty sources
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- **Existing databases have not be designed with MCUP in mind**
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Remerciements

- N. Carrasco (SA, Verrières)
- S. Plessis & Ch. Alcaraz (LCP, Orsay)
- M. Dobrijevic (LAB, Bordeaux)
- E. Hébrard (LISA, Crétail)
- M. Banaszkiewicz (SRC, Warsaw)
- R. Thissen & O. Dutuit (LPG, Grenoble)
- V. Vuitton & R. Yelle (LPL, Tucson)

- CNRS
- CNES
- EuroPlaNet
- Programme National de Planétologie