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Modeling of Branching Ratio Uncertainty in Chemical Networks by Dirichlet Distributions

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Validation of complex chemical models relies increasingly on uncertainty propagation and sensitivity analysis with Monte Carlo sampling methods. The utility and accuracy of this approach depend on the proper definition of probability density functions for the uncertain parameters of the model. Taking into account the existing correlations between input parameters is essential to a reliable uncertainty budget for the model outputs. We address here the problem of branching ratios between product channels of a reaction, which are correlated by the unit value of their sum. We compare the uncertainties on predicted time-dependent and equilibrium species concentrations due to input samples, either uncorrelated or explicitly correlated by a Dirichlet distribution. The method is applied to the case of Titan ionospheric chemistry, with the aim of estimating the effect of branching ratio correlations on the uncertainty balance of equilibrium densities in a complex model.

1. Introduction

Simulation of chemical systems relies on parameters such as rate constants, with values mostly evaluated by laboratory experiments. The impact of experimental measurement uncertainties on the outputs of those simulations is receiving increasing attention, for instance in combustion[1−8] or atmospheric chemistry.[9−15] Most of these studies implement Monte Carlo uncertainty propagation (MCUP), which avoids an ensemble of shortcomings of linear local uncertainty propagation. MCUP requires the definition of a probability density function for the input parameters. Random samples of input parameters are generated from this probability density function (PDF) and fed sequentially to the model in order to generate a representative sample of outputs. The design of a representative input PDF, presumably unbiased with regard to available information, is not always unambiguous and should be treated with care.[16]

Modelers gather the values of chemical parameters and the associated uncertainties from periodicals or thematic databases.[18,19] For gas-phase reactions with multiple product channels, databases provide either partial reaction rates (with uncertainty factors, UF)[19] or global reaction rates (with UF) and the corresponding branching ratios (commonly without UF).[20] In all cases, additional information is necessary to process measurement uncertainties in a consistent way. The appropriate type of uncertainty distribution might depend on the experimental technique involved in the measurement or on the combination of results performed by a reviewer. We discussed this point in detail previously for reaction rates and to a lesser extent for branching ratios.[16]

The case of partial rate constants is intricate because in order to define a correct uncertainty pattern one has to link the reported values with their experimental origin, that is, whether they were measured directly or if they are obtained by the product of a global reaction rate and a set of branching ratios. In the first case, the partial rate constants can be treated as independent variables and represented by lognormal or loguniform PDF's. In the second case, one cannot deal any more with independent variables and one has to take into account correlations due to the sum rule of branching ratios.

Branching ratios indeed present a challenge to both experimentalists and modelers. They can be difficult to measure and, if known at all, they can be affected by large uncertainty factors. The uncertainties associated with the measured values are very sparsely available.[20] There is indeed a lack of information to enable the unambiguous specification of a probability density function. In consequence, branching ratios are often taken at face value. However, we have shown previously that neglecting this uncertainty source can lead to a major bias in the uncertainty budget.[16]

Another issue for modelers is the correct treatment of branching ratios as correlated parameters when more than two product pathways are involved.[14,21] At best, the different reactive pathways of a given reaction have been treated as uncorrelated, without control of this approximation. Neglecting correlations between input parameters can be a source of spurious output uncertainty: in linear models, positive correlation of inputs increases the uncertainty of outputs, whereas negative correlation, as implied by the sum rule, has the opposite effect.[22,23] It has to be seen how the nonlinearity of chemical equations affects these rules. For reliable uncertainty propagation, the main problem is to design, from the available experimental information, an unbiased probability density function that accounts for the correlation pattern of branching ratios. Probability density elicitation techniques, as used in Bayesian data analysis, are a tool of choice in this context.[24,25]

We considered recently the Dirichlet distribution for the treatment of branching ratio uncertainties in chemical networks.[16] Other distributions have been proposed in the context of compositional data analysis,[17] mostly to account for complex correlations between variables, which is not necessary in the present case. The Dirichlet distribution provides a simple way to implement a normalization constraint between *any number*

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of variables. This distribution is used widely as a prior PDF in Bayesian inference to enforce the composition structure.[26,27] It has also been used in pharmacokinetics and environmental modeling[28] but seems to have gone unnoticed in the field of chemical simulation. We made use of the total absence of information on the structure of correlation between measured branching ratios to derive an operational model based on the Dirichlet distribution. Two of its advantages are that (i) it can be fully elicited from partial informations and (ii) random samples are obtained easily by standard generators.

The importance of taking branching ratio uncertainties into account has already been clearly demonstrated.[16] Our aim in the present paper is to study more specifically the effect of the explicit correlation structure imposed by the sum rule on the uncertainty budget for complex chemical systems. After introducing briefly our elicitation method for the Dirichlet distribution, we illustrate the effects of branching ratio correlations, first on a simple pedagogical chemical model and then on a model of Titan ionospheric chemistry with about 600 reactions involving more than 130 species.

2. Method

2.1. Dirichlet Distribution. Typically, for a chemical reaction with n product channels, the partial reaction rates are expressed as $k_i = kb_i$, where k is the global reaction rate and $\{b_i\}_{i=1}^{n}$ are branching ratios characterizing product partitions among channels. Branching ratios form a *composition,* such as $0 \leq b_i \leq 1$ and $\sum_{i=1}^{n} b_i = 1$.[17]

The Dirichlet distribution enables one to represent the fluctuations of quantities, under the condition that their sum remains fixed.[29] As shown in a previous paper,[16] this multivariate distribution can be uniquely parametrized from the estimated branching ratios ($\bar{b}_i$) and an average relative uncertainty (x)

$$(b_1, \ldots, b_n) \sim \text{Dirichlet}\ (\hat{\gamma} \times (\bar{b}_1, \ldots, \bar{b}_n)) \tag{1}$$

where $\hat{\gamma}$ is a precision factor defined by a least-squares equation over the standard uncertainties $\sigma_i = xb_i/2$

$$\hat{\gamma} = \text{argmin}_{\gamma} \sum_i \left(\sigma_i - \left(\frac{\bar{b}_i(1-\bar{b}_i)}{\gamma+1}\right)^{1/2}\right)^2 \tag{2}$$

$$= \frac{4}{x^2}\left(\frac{\sum_i \bar{b}_i(1-\bar{b}_i)}{\sum_i \bar{b}_i\sqrt{\bar{b}_i(1-\bar{b}_i)}}\right)^2 - 1 \tag{3}$$

We expect that choosing $\hat{\gamma}$ by eq 2 will reproduce the available data in many cases. For very uncertain cases, the Dirichlet distribution can become multimodal, which is not desirable. An additional constraint

$$\bar{\gamma} \geq \{\min(\max(\bar{b}_1, 1-\bar{b}_1), \ldots, \max(\bar{b}_n, 1-\bar{b}_n))\}^{-1} \tag{4}$$

is introduced to ensure the unimodality of the Dirichlet distribution.

This elicitation method respects the average values, that is, $<b_i> = \bar{b}_i$, but the Dirichlet distribution cannot reproduce a uniform relative uncertainty for all channels. The relative uncertainty for channel i

$$\hat{x}_i = 2\sqrt{\frac{\left(\frac{1}{\bar{b}_i}\right) - 1}{\hat{\gamma}+1}} \tag{5}$$

has, however, the nice property of being inversely related to the relative abundance of the product. The relative uncertainty (x), which is generally assigned uniformly to all branching ratios, should indeed be considered as an average uncertainty. The Dirichlet distribution contributes to distribute this uncertainty among channels in a pattern that is more consistent with what is expected from measurement uncertainties (the less abundant a product, the larger its uncertainty).

2.2. Monte Carlo Uncertainty Propagation. Uncertainty propagation is performed by Monte Carlo sampling. A sample of inputs is generated by a program independent of the chemical simulation code and stored in a file. This program reads a database of reactions, containing all relevant parameters (stored as preferred values and relative uncertainties), and enables one to select different elicitation schemes by keywords. Monte Carlo uncertainty propagation needs very few modifications to the chemistry models. The chemistry code is slightly modified in order to implement a loop over the input samples and the storage of the output samples in a file. Output samples are treated by a series of independent codes to generate statistical summaries (mean, variance, quantiles...), probability density estimates (histograms or kernel estimation), and empirical cumulative density functions.

Samples from the Dirichlet distribution (eq 1) are generated by the Gamma algorithm,[30] where n independent random numbers are generated from Gamma distributions $B_i \sim$ Gamma($\hat{\gamma}\bar{b}_i$, 1). The branching ratios are obtained as normalized ratios of these numbers, $b_i = B_i/\sum_i B_i$.

3. Case Studies

A simple chemical system is considered first in order to display the consequences of neglecting branching ratio correlations on the uncertainties of kinetic traces. In a second part, we consider a large equilibrium chemical system related to Titan ionospheric chemistry.

3.1. Pedagogical Example. We consider a simple chemical system involving two parallel unimolecular reactions $X \rightarrow Y_1$ and $X \rightarrow Y_2$, with rates $k_1 = kb_1$ and $k_2 = kb_2$, respectively.

At first, the global rate constant, k, is assumed to be measured with great accuracy and is kept fixed throughout the analysis. With branching ratios $\bar{b}_1 = {}^1/_3$, $\bar{b}_2 = {}^2/_3$, and a precision factor $\hat{\gamma} = 45$ (corresponding to relative uncertainty of about 40% for $\bar{b}_1$ and 20% for $\bar{b}_2$), the input parameters are distributed according to $(b_1, b_2) \sim$ Dirichlet (15, 30).

We compare the time-dependent concentrations for (a) the correlated case $(b_1, b_2) \sim$ Dirichlet (15, 30) and (b) for the uncorrelated case where b_1 and b_2 are generated independently from their marginal densities, $b_1 \sim$ Beta(15, 30) and $b_2 \sim$ Beta(30, 15) (cf. the Appendix).

The time-dependent concentrations, shown in Figure 1, are given by

$$x(t) = x_0 \exp(-k(b_1 + b_2)t) \tag{6}$$

$$y_i(t) = \frac{x_0 b_i}{(b_1 + b_2)}(1 - \exp(-k(b_1 + b_2)t));\ i = 1, 2 \tag{7}$$

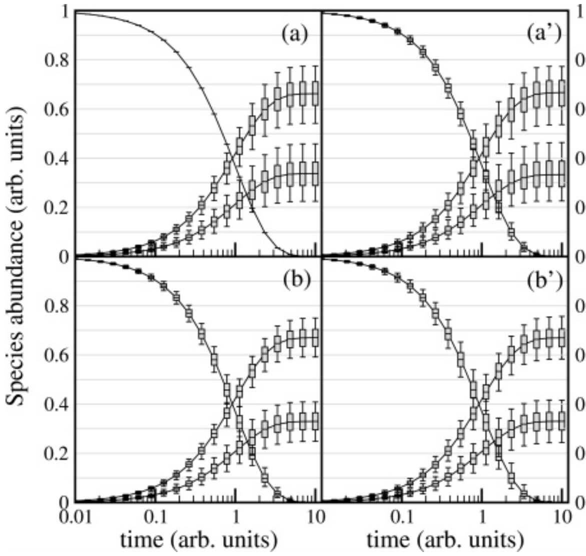

Figure 1. Time-dependent concentrations for a system involving two parallel unimolecular reactions ($x_0 = 1$). Left column: fixed global rate constant $k = 1$, (a) exact treatment of branching ratios, $(b_1, b_2) \sim$ Dirichlet (15, 30); (b) fixed reaction rate and uncorrelated branching ratios $b_1 \sim$ Beta (15, 30) and $b_2 \sim$ Beta (30, 15). Right column: same as left column, but with 20% uncertainty on the global rate constant, k.

From linear uncertainty propagation, one gets the time-dependent variance for $x(t)$

$$\sigma_x^2(t) = x_0^2 k^2 t^2 \exp(-2k(b_1 + b_2)t)\,(\sigma_{b_1}^2 + \sigma_{b_2}^2 + 2\mathrm{cov}(b_1, b_2)) \qquad (8)$$

In the correlated case (a), the variances and covariance of the branching ratios cancel because $\sigma_{b_1}^2 = \sigma_{b_2}^2 = -\mathrm{cov}(b_1, b_2)$ (eq 11), and, as expected, the variance of $x(t)$ is null.

When the correlation is neglected, $\sigma_x^2(t)$ vanishes at $t = 0$ and $t = \infty$ and presents a maximum at $t = 1/(k(b_1 + b_2))$. One thus has a spurious uncertainty of the concentration of the parent species because of the violation of the sum rule.

Considering the final concentrations of the products, $y_i(\infty) = x_0 b_i/(b_1 + b_2)$, the variances are $\sigma_{yi}^2 = x_0^2\mathrm{Var}(b_i/(b_1 + b_2))$. Because of the sum rule, $\sigma_{yi}^2 = x_0^2\mathrm{Var}(b_i)$ in the correlated case. In absence of correlation, $\mathrm{Var}(b_i/(b_1 + b_2))$ can be developed as

$$\mathrm{Var}\left(\frac{b_i}{b_1 + b_2}\right) = \mathrm{Var}(b_i) \times (\bar{b}_i^2 + (1 - \bar{b}_i)^2) \le \mathrm{Var}(b_i) \qquad (9)$$

Therefore, the uncertainty on the concentrations of the products in the uncorrelated case is smaller that in the exactly correlated case. Neglecting the correlation thus produces an underestimation of variance, which is the opposite of what is expected from linear uncertainty propagation. This effect is maximal (by a factor of 2) when $\bar{b}_1 = \bar{b}_2 = 0.5$. Because it is related to the positive covariance between b_i and $\sum b_i$, the effect is also maximal in the case of two product channels.

A 20% relative uncertainty on the global rate constant k has then been introduced in order to simulate a more realistic scenario. The resulting uncertainties on the time-dependent concentrations are shown in Figure 1a′ and b′. We first note that branching ratios are the main contributors to overall uncertainty and then that the effect of correlation is still marked, as in cases a and b.

By neglecting the correlation between the branching ratios in the case of two parallel unimolecular reactions, we observed an overestimation of the uncertainty on the global rate constant, and, simultaneously, an underestimation of the uncertainty on the final product concentrations. Thus, the sum rule for branching ratios can produce opposite effects according to the observed property of a chemical system. It is thus practically impossible to estimate beforehand the effect of neglecting branching ratio correlations on the uncertainty budget of complex chemical networks.

3.2. Titan Ionospheric Chemistry.

Model. In a coupled model of Titan’s atmosphere and ionosphere,[31] the stationary densities for ions are calculated by solving iteratively (i) the ion equations with current neutral densities and (ii) the neutral equations with the production and loss terms estimated at step (i). In a recent paper,[16] we presented the first evaluation of uncertainties on ion densities calculated by the model of Banaszkiewicz et al.,[31] due to the parameters involved in bimolecular reactions, that is, rate constants and branching ratios.

The model involves 33 neutral and 102 ionic species, including two pseudo-ions representing heavy hydrocarbons ($C_xH_y^+$, $x \ge 7$) and heavy nitriles ($C_xH_yN_z^+$, $x \ge 6$). Only reactions with rates available in the literature are included, on the basis of the comprehensive survey compiled by Anicich and McEwan.[32] The reaction scheme comprises 589 reactions, with 738 kinetic parameters (315 rate constants and 423 branching ratios). More than 50% of the 315 global reactions have two product pathways or more (up to seven), which emphasizes the necessity of a correct treatment of branching ratio uncertainties.

Probability Density Assignment for Branching Ratios. Two cases occur in the review of Anicich[20] for ion−molecule gas-phase reaction kinetics: branching ratios of a reaction have either been determined experimentally or products have been detected but not quantified. In the first case, a preferred value *without* uncertainty is reported.

To quantify the uncertainties of branching ratios, we analyzed the literature: by comparison of different experimental studies of a same reaction[16] and in the absence of further information, we retained an average relative uncertainty of $x = 50\%$ for all channels (cf. Section 2.1). Moreover, it has been observed that uncertainties were inversely related to the abundance of the products, which is automatically simulated by the Dirichlet distribution (see eq 3).

Effect of the Correlation. Ignoring branching ratio uncertainties affects the uncertainty balance of the predicted ion densities significantly,[16] and it can also drastically affect the uncertainty of the density profiles of some major ions in the Titan ionosphere (see, for instance, the $C_2H_4^+$ density profile in Figure 2). This should be a major concern for uncertainty propagation and sensitivity analysis studies.

To emphasize the effect of the correlation of branching ratios, the global rate constants have been fixed at their nominal value. We generated two samples:[34] a correlated sample from the Dirichlet distribution (eq 1), and an uncorrelated sample from the marginal 1D Beta distributions, $b_i \sim \mathrm{Beta}(\hat{\gamma}\bar{b}_i, \hat{\gamma}(1 - \bar{b}_i))$ (cf. the Appendix). Histograms and empirical cumulative density functions (CDF) for the relative uncertainties of all ion densities at 1200 km are reported in Figure 3, and their difference for each ion is reported on the radar plot in Figure 4.

Comparison of the CDF’s indicates a small increase of average uncertainty when correlation is neglected: the median uncertainty is 30% in the case of uncorrelated inputs, against 15% in the case of correlated inputs. A qualitative effect is observed for primary ions (i.e., those only consumed by ion−molecule reactions): when the correlation is enforced, these ions disappear with a reaction rate that is independent of branching

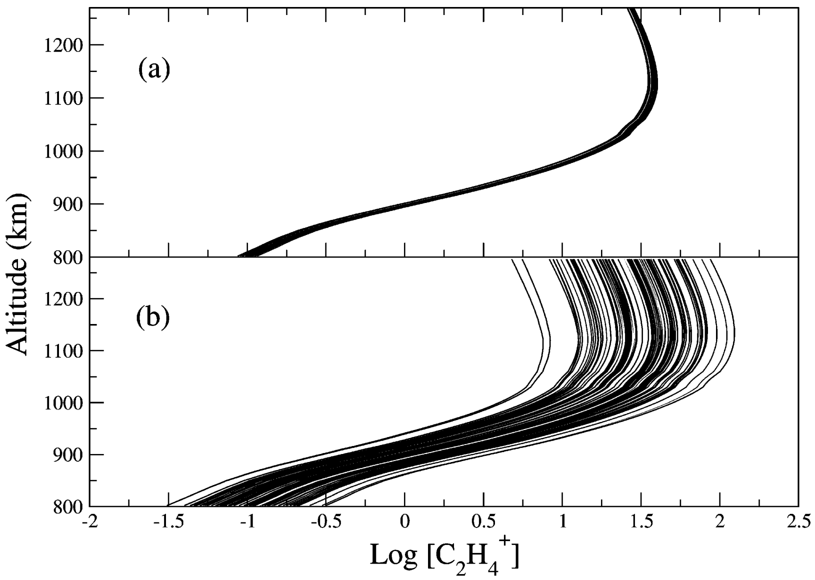

Figure 2. Samples of $C_2H_4^+$ density profiles by day-time chemistry obtained by uncertainty propagation of (a) rate constant uncertainties and (b) both rate constants and branching ratio uncertainties.

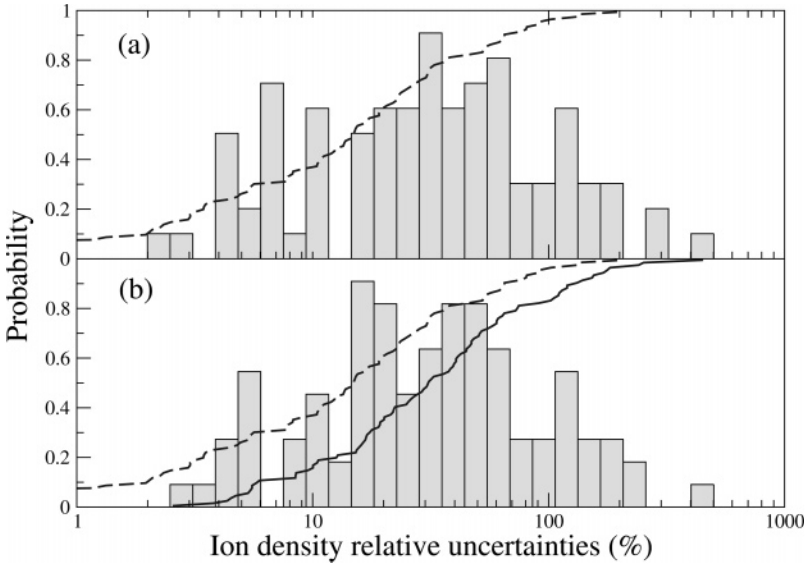

Figure 3. Histograms and empirical cumulative density functions from the relative uncertainties of all ion densities (day-time chemistry; altitude 1200 km; logarithmic scale) for correlated (a) and uncorrelated (b) branching ratio elicitation methods. The cumulative density function obtained by simulation with the correlated distribution is reported in the lower graph (dotted line) for comparison.

ratio uncertainty. Their equilibrium density is therefore simulated without uncertainty. This is at the origin of the step at low uncertainties observed on the CDF's for correlated inputs. When omitting the correlation, the total reaction rate is no longer constant, and those ions get uncertain equilibrium densities.

When looking at a finer scale, we see that the relative uncertainty on the ion densities can be overestimated or underestimated by at most 0.1 (Figure 4). The primary ions, such as N^+, N_2^+, H^+, and H_2^+, have their uncertainty slightly overestimated, in agreement with the effect observed for the parent ions in the pedagogical case. Similarly, some terminal ions, such as $C_2H_2N^+$, $C_4H_6^+$, $C_5H_7^+$, or $C_5H_4N^+$, have underestimated uncertainties (Figure 4). In the latter case, there is, however, no strict rule because the pathways to these species combine numerous opposite contributions on reactant and product uncertainties, as detailed in the pedagogical case. This confirms that in the case of complex chemical networks it seems impossible to predict the effect of neglecting branching ratio correlation on uncertainty propagation beforehand.

Pointing out the most uncertain outputs is a preliminary step to sensitivity analysis. In the present system, there is apparently a scrambling of uncertainties between the correlated and uncorrelated cases. To quantify this scrambling, we calculated rank correlation coefficients[33] for ion densities between the correlated and uncorrelated samples and plotted the correlation diagram (Figure 5a). Points that lie apart from the $x = y$ line of the graph indicate a modification in the order of ions between both simulations, which is a direct effect of correlation. Figure 5a shows that the ordering of ion densities suffers very few alterations. Indeed, only four permutations are observed: for example, ions 19 and 24 (respectively, $C_3H_4^+$ and $C_4H_3^+$) exchange their 17th and 18th positions in the list. The correlation coefficient is equal to 0.99, very close to identity. As expected, the explicit correlation between branching ratios does not influence the average values of the outputs significantly.

The same procedure was also applied to the uncertainties of the ion densities. In contrast to the previous case, Figure 5b displays an important effect of branching ratio correlations on

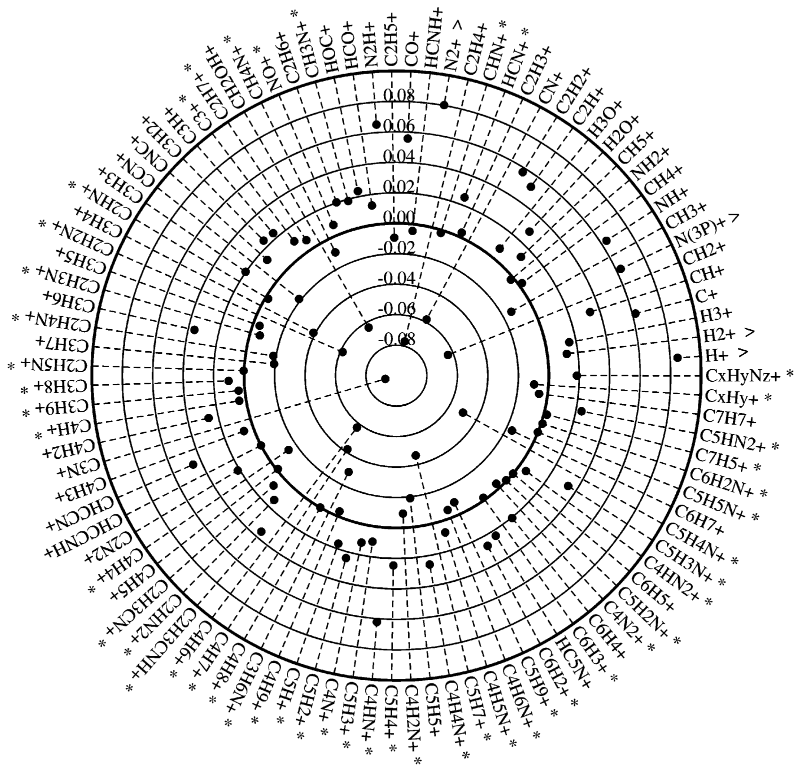

Figure 4. Difference of relative uncertainties on ion densities ("uncorrelated'' *minus* "correlated''). Positive values correspond to an overestimation of the relative uncertainty in the uncorrelated case. Values vary from −0.1 to 0.1, the central bold line being the zero value. Primary ions are indicated with an arrow ">'', and terminal ions with a star "*''.

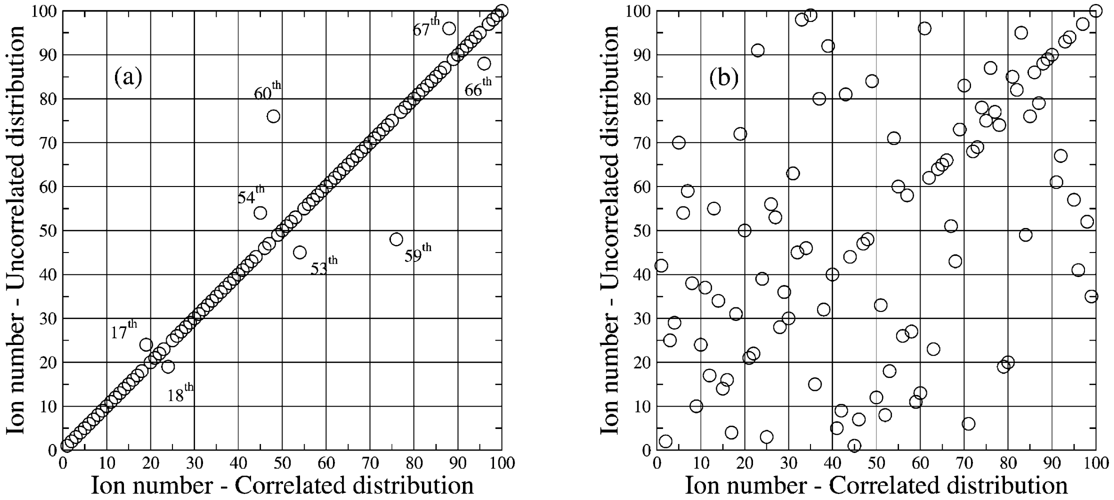

Figure 5. Effect of branching ratio correlation on ion densities and their relative uncertainties. The ordered ions list, from uncorrelated branching ratio distribution, is plotted against the ordered ions list, from correlated branching ratio distribution. Coordinates along both axes are the database indexes of the ions. Ions are ordered (a) by decreasing density and (b) by decreasing relative uncertainty.

the simulated uncertainties. Few ions preserve their position in both correlated and uncorrelated samples, and the correlation coefficient is indeed quite low (0.44).

This study reveals that branching ratio correlations, when properly accounted for by the Dirichlet distribution, have no major impact on the predicted ion densities themselves. However, the uncertainties of these predictions are strongly dependent on it. The Dirichlet distribution is thus an essential contribution to reliable uncertainty budgets and sensitivity analysis.

4. Conclusions

Correlation between branching ratios for products of a reaction had not been previously explicitly considered for uncertainty propagation in complex chemical systems. Using our Dirichlet model of branching ratio uncertainties, we have shown on a simple system that the effect of branching ratio correlations is multifaceted. Under- and overestimations of output uncertainties are observed, depending on whether the reactants or products are considered. Moreover, negative correlation as implied by the sum rule for branching ratios does not necessarily lead to a decrease in output uncertainty. This is expected to be even more important when considering time-resolved observables than for equilibrium properties. In the former case, neglecting the correlation leads to an overestimation of the uncertainties of reactants during the time course of the reaction, whereas it produces an underestimation of the uncertainties of final concentrations of the products.

It thus seems difficult to assess a general behavior for a complex system. Through the application to a model of Titan ionospheric equilibrium chemistry, we have shown that no major impact on the predicted equilibrium densities is to be expected when neglecting branching ratio correlations. The main effect, a second-order one, is observed on the uncertainty budget of the model outputs. The Dirichlet distribution therefore appears as an important contribution to the reliability of the results of uncertainty and sensitivity analysis in complex chemical networks.

This study contributes to underline the difficulty for modelers to extract reliable information on branching ratio uncertainties from chemical reactivity databases. This is due in part to the almost complete lack of reporting of such uncertainties but also to the inappropriate reporting of partial rate constants instead of the branching ratios from which they are derived (this does not concern partial rates that are directly measured). This forces modelers to make crude assumptions on the branching ratio uncertainties, which certainly have a non-negligible impact on the final uncertainty budget. There is indeed a crying need for reference databases of evaluated branching ratios with their uncertainties.

The branching ratio uncertainty elicitation we developed on the example of Titan ionospheric chemistry could be directly applied to other complex chemistry models such as those occurring in combustion, plasmas, and atmospheric or interstellar media. Moreover, it can also be easily extended to other correlated properties in physical chemistry, such as quantum yields and relative abundances, for which the treatment of uncertainties does not seem to have yet received the deserved attention.

In any case, the proposed Dirichlet method is very simple to implement within a Monte Carlo uncertainty propagation framework and does not require significant computation overcharge.

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Appendix

Properties of Dirichlet Distribution. Basic statistical properties for variables distributed according to[17,30]

$$(b_1, \ldots, b_n) \sim \text{Dirichlet}\,(\hat{\gamma} \times (\bar{b}_1, \ldots, \bar{b}_n)) \tag{10}$$

with parameters $\sum_i \bar{b}_i = 1$, and $\hat{\gamma} > 0$:

$$\mathrm{E}(b_i) = \bar{b}_i$$

$$\mathrm{Var}(b_i) = \sigma^2_{b_i} = \frac{\bar{b}_i(1 - \bar{b}_i)}{(\hat{\gamma} + 1)}$$

$$\mathrm{cov}(b_i, b_j) = -\frac{\bar{b}_i\,\bar{b}_j}{(\hat{\gamma} + 1)}\,(i \neq j) \tag{11}$$

The univariate marginal distributions are[29]

$$b_i \sim \mathrm{Beta}(\hat{\gamma}\bar{b}_i, \hat{\gamma}(1 - \bar{b}_i))$$

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(34) The convergence of the outputs has been tested with 10^3, 10^4, and 10^5 samples. Cumulative density functions used for this test were satisfyingly converged for 10^4 samples.