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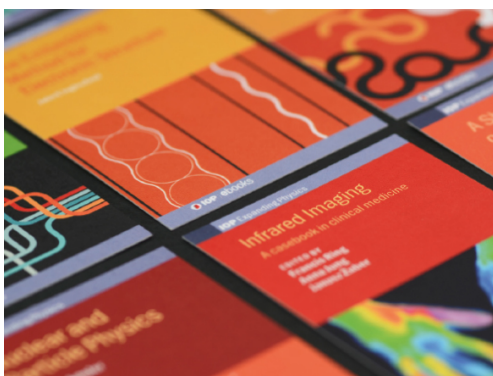
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Probabilistic representations of partial branching ratios: bridging the gap between experiments and chemical models

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Abstract. Dissociative recombination (DR) of polyatomic positive ions with electrons is a very complex process, for which the breakup patterns into neutral fragments are presently unpredictable. Measured branching ratios to the various products channels are thus the only data source for modelers of chemical plasmas. Because of limited detector resolution, data for many ions are incomplete, and implementation of DR processes in chemical models is problematic. In a recent paper [Plessis S *et al.* 2010 *J. Chem. Phys.* **133** 134110], we proposed a novel approach, based on probabilistic trees, enabling modelers to fully account for the hierarchy of available information. For the first time, we were able to build a chemical model for Titan's ionosphere including all available data about DR branching ratios. The improvement on previous models is considerable, and the data needs for Titan are redefined accordingly.

1. Dissociative recombination in chemical models

Despite the accumulation of reference data in the past years [1, 2], there are still major difficulties in the modeling of dissociative recombination (DR) of polyatomic ions in natural or laboratory chemical plasmas [3–11]. The chief problem is the lack of knowledge about branching ratios, mainly due to the difficulty of detection and quantification of neutral fragments, and their isomeric and/or electronic configurations. In the absence of tractable and predictive theories, experimental data are at the moment the only source of information available to modelers. Even for smaller species (3-4 heavy atoms), information is often incomplete: for hydrocarbon ions, the distribution of H atoms between fragments is presently not accessible (see Table 1 and Fig. 1). Also, the isomeric form of the parent ion and the isomeric form and electronic state of the neutral products are generally not known [12]. This lack of information about the chemical identity, and therefore the reactivity, of the products of DR can introduce substantial biases in the predictions of chemical models [13].

Through the production of energetic radicals and heavy neutral species, DR is an important pathway of molecular complexification and diversification. It is therefore crucial to incorporate all the available knowledge about branching ratios into chemical models. This can be difficult, notably when the chemical identity of the fragments are not fully elucidated (see Table 1). If we

Products	Measured probability	Exoergic channels	Selected channels	(b_i)
$C_3NH_x + y H + wH_2$	0.50 ± 0.04	6	$CH_2CHCN + H$	(0.50)
$C_2H_x + CNH_y + zH + wH_2$	0.49 ± 0.04	7	$\left\{ \begin{array}{l} C_2H_2 + HCN + H \\ C_2H_2 + CN + H_2 \end{array} \right.$	$\left. \begin{array}{l} (0.25) \\ (0.25) \end{array} \right.$
$\left\{ \begin{array}{l} C_3H_x + NH_y \\ C_2NH_x + CH_y + zH \end{array} \right.$	0.01 ± 0.01	9	–	
with $x + y + z + 2w = 4$		$\Sigma = 22$	$\Sigma = 3$	

Table 1. Typical experimental results and their interpretation for the branching ratios of the dissociative recombination of a middle-sized ion: CH_2CHCNH^+ [14].

consider recent results about the DR of CH_2CHCNH^+ [14] (Table1), it is striking that from 22 exoergic channels, Vigren *et al.* have selected only three channels for astrochemistry databases, one from the first group of 6, and two from the second group of 7. The latter ones have been given identical branching ratios. This oversimplified description, ignoring all minor channels and plausible isomers (*e.g.* HNC *vs.* HCN), is dictated by the lack of an appropriate representation of such complex data in chemical databases. It can be feared that the systematic use of such simplifications would lead to an artefactual impoverished role of DR in chemical models.

In a recent paper [15], we proposed an original solution to this problem by treating partial knowledge about branching ratios as an uncertainty source. Accordingly, probabilistic representations were designed to account for the various uncertainty patterns identified through an extensive review of the literature [15]. In order to deal with partial branching ratios data and their hierarchical structure, we used probabilistic trees. This enabled us to design and run the first chemical model of Titan’s ionosphere implementing all available data about DR.

In the following, we present the main steps of the method, and through our main results for Titan’s ionosphere, we demonstrate how they contribute to redefine the data needs for the modeling of chemical plasmas.

2. Probabilistic representation of partial sets of uncertain branching ratios

This work extends the previous study by Carrasco and Pernot [18] about the representation of uncertain branching ratios in chemical models, where the necessity of a good description of correlations between these parameters was underlined in the context of uncertainty propagation and sensitivity analysis [13]. Our new developments acknowledge the fact that information on branching ratios, or lack thereof, has often a hierarchical structure which can be translated into probabilistic trees incorporating all available data.

The first step in our approach is to consider that reaction rates and branching ratios are typically measured by different experiments/techniques [1, 2]. Good practice in uncertainty management is to keep an explicit separation of uncertainty sources. Therefore, we will not consider here the problem of the rate coefficients [15].

For a reaction with n products channels, the branching ratios b_i have two constraints ($b_i \geq 0$ and $\sum_{i=1}^n b_i = 1$), which define them as probabilities. The sum-to-one is essential to ensure that, when estimating uncertainties of the outputs of a chemical model, uncertainties on branching ratios of a given process do not propagate to products not directly related to this process [15, 18, 19].

In the following, we call *probabilistic tree* a hierarchy of branching ratios, such that, at each node (represented in the schemes by an opening brace ‘{’), all contributions sum to 1.

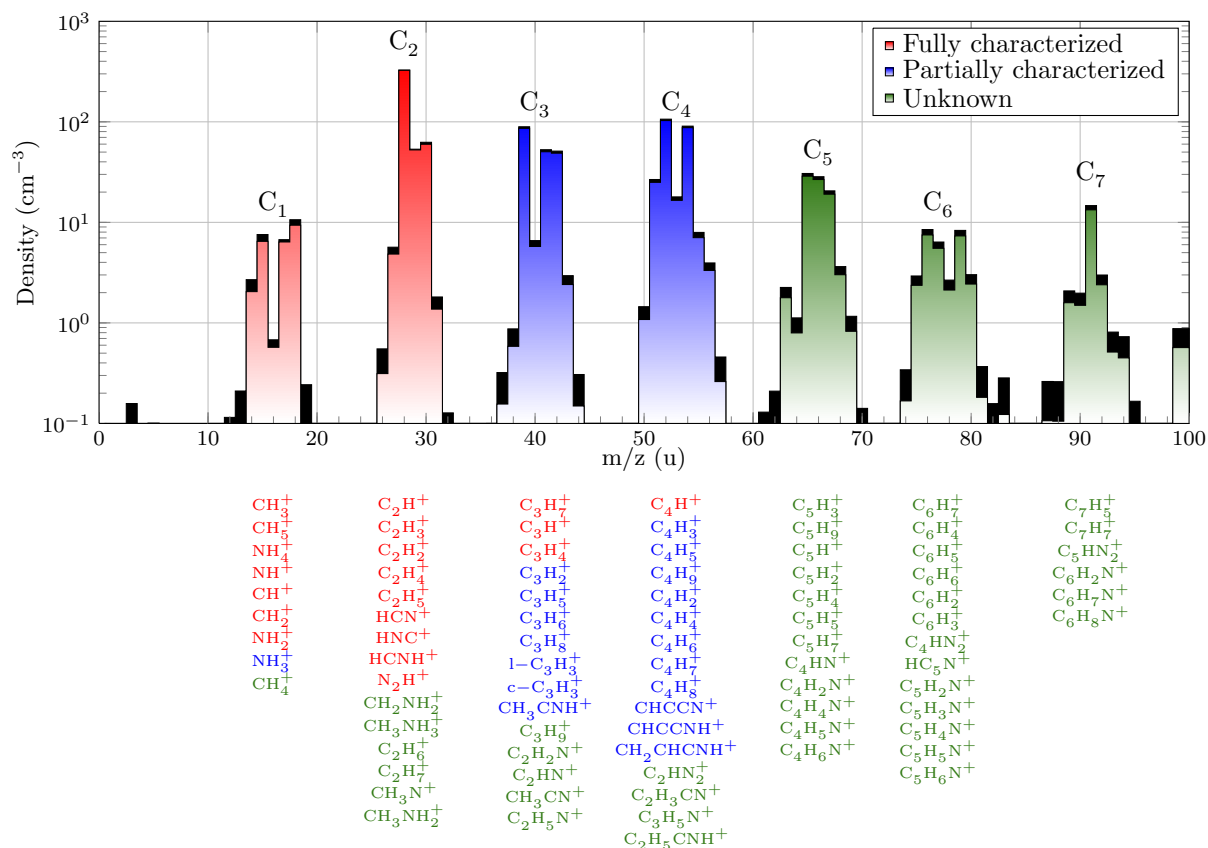
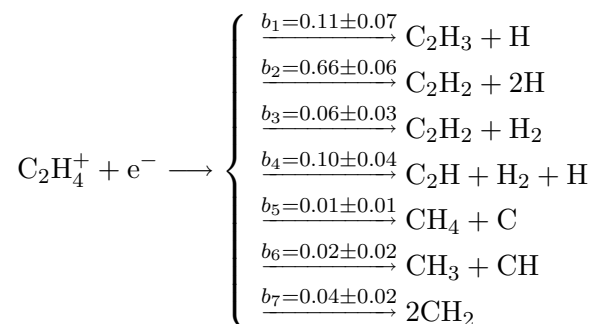


Figure 1. Typical mass spectrum of ions in Titan's ionosphere, as recorded by Cassini INMS at an altitude of ca. 1100 km [16]. The ionic species, identified by chemical modeling [17], are specified below each C_x block of peaks, where x is the number of heavy atoms in the ions. Ions are colored according to the available information on their DR products. Blocks of peaks are colored according to the status of the dominant ions.

2.1. Representation of branching ratios by probabilistic trees

We consider a few typical cases extracted from the literature and see how they can be incorporated into our representation scheme.

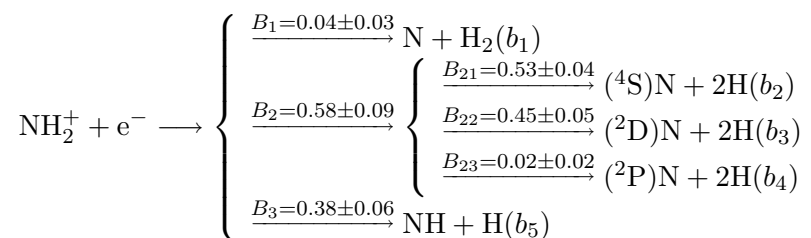
2.1.1. Fully characterized products. A few ions (up to class C₄, Fig. 1) have fully characterized branching ratios. For instance, the branching ratios for seven exoergic products pathways for C₂H₄⁺ have been measured[20]



In this case, the representation is simple and does not require a hierarchy.

2.1.2. Combining complementary experiments. NH_2^+ is an interesting case, where we have to combine two sets of branching ratios coming from different experiments. The main channels have been measured first: $B_1(\text{N} + \text{H}_2) = 0.04 \pm 0.03$, $B_2(\text{N} + 2\text{H}) = 0.58 \pm 0.09$ and $B_3(\text{NH} + \text{H}) = 0.38 \pm 0.06$ [21, 22]. In a second stage, the spin state of N through the second channel was elucidated: $B_{21}({}^4S)\text{N} + 2\text{H}) = 0.53 \pm 0.04$, $B_{22}({}^2D)\text{N} + 2\text{H}) = 0.45 \pm 0.05$ and $B_{23}({}^2P)\text{N} + 2\text{H}) = 0.02 \pm 0.02$ [22].

Preserving the measurement uncertainties and the norm constraint for each experiment leads to a natural embedding of the data into a probabilistic tree



For a given pathway, the branching ratio is obtained by multiplication of the probabilities from the root to the terminal leave, *e.g.* $b_1 = B_1$, or $b_4 = B_2 * B_{23}$. Note that the spin state is left unspecified for the first pathway, an inconsistency that can be resolved by the method exposed in the next example.

2.1.3. Dealing with partial measurements. When one has partial measurements, as in Table 1, one can build a hierarchy similar to the one in the previous case, with measured values of branching ratios at the first level. This defines a partition of the products in a number of classes, and within each class, one can use unspecified (totally uncertain) branching ratios.

The example of C_3H_2^+ is developed in steps (1,2) of Fig. 2. One has measurements for two heavy atoms configurations $B_1(\text{C}_3)$ and $B_2(\text{C}_2 + \text{C})$ [23, 24]. For the C_3 pathway, three exoergic channels are considered with unknown branching ratios: $(\text{C}_3 + \text{H}_2)$, $(\text{C}_3 + 2\text{H})$ and $(\text{C}_3\text{H} + \text{H})$, and for the $\text{C}_2 + \text{C}$ pathway, two channels are invoked: $(\text{C}_2\text{H}_2 + \text{C})$ and $(\text{C}_2 + \text{CH}_2)$, also with unknown proportions.

In the resulting representation, the branching ratio to channel $(\text{C}_3 + \text{H}_2)$, $b_1 = B_1 * B_{11}$, lies between 0 and 0.88 ± 0.02 . The same is valid for the two other channels in its class, b_2 and b_3 , with the constraint that $b_1 + b_2 + b_3 = 0.88 \pm 0.02$. By construction, this representation incorporates all available information and respects the experimental data.

2.1.4. Empirical rules for increased precision. An important property of the probabilistic trees is that one can implement constraints locally (within a branch) without disturbing other parts of the tree. In particular, any constraint at the lower levels will not affect the fact that the experimental data at the first level are respected.

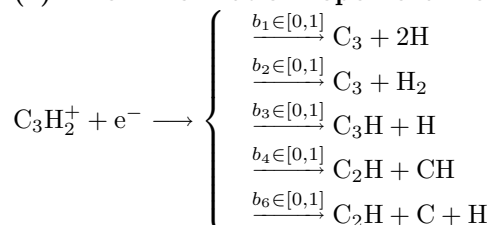
It is therefore possible to implement *empirical rules*, notably through order constraints ($b_1 \geq \dots \geq b_n$). We emphasize that this is a strong point of this approach that non-numerical information can be incorporated in the representation to increase its predictivity.

Unfortunately, empirical rule correlating the values of branching ratios to easily estimated properties, are still mostly nonexistent. There is clearly no straight correlation between the exothermicity of products channels and their branching ratios. Using more complex indicators, weak correlations between thermodynamics and preferred breakup patterns have been detected by Vigianno *et al.* [25] and Roueff [26]. Implementation of these weak correlations in our framework is under study.

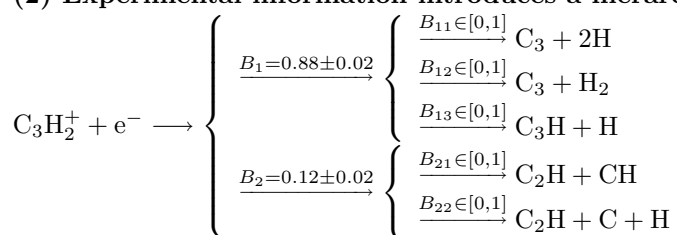
The only empirical rule we have used so far is the so-called “ $2\text{H} \geq \text{H}_2$ ” rule [15], which states that the production of two hydrogen atoms is always more probable than one hydrogen molecule.

Main steps in generating a probabilistic tree for branching ratios

(1) Prior information: open channels



(2) Experimental information introduces a hierarchy



(3) Using empirical rule(s)

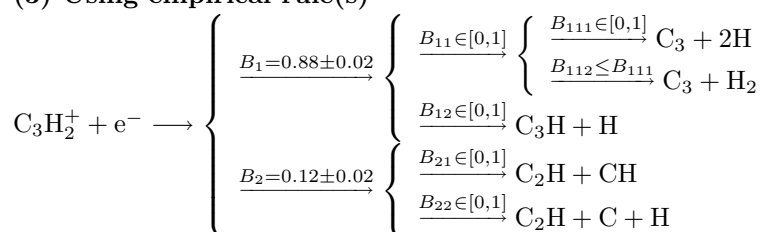


Figure 2. Probabilistic tree structure of the available information on branching ratios for the dissociative recombination of C_3H_2^+ .

This rule is validated by all experimental data for the ions considered in Titan’s ionosphere, at the exception of NH_4^+ . Implementation of this rule for C_3H_2^+ is presented in Fig. 2(3).

However modest in its scope, each instance of this rule in a tree contracts the space of accessible branching ratios by a factor two. Ordering of more than two channels would result in still better uncertainty reduction. Considering their practical renewed interest, the search for empirical rules should be actively pursued.

2.2. Managing probabilistic trees in chemical models

For numerical applications, the treatment of probabilistic trees requires to generate representative samples to be used in a Monte Carlo Uncertainty Propagation framework [18, 19, 27]. We designed and use a toolbox of *knowledge-adapted* Dirichlet-based distributions [15]. As an illustration, the nested Dirichlet representation of the tree in Fig. 2(3) is translated in the database to

$$\{b_1, \dots, b_5\} \sim \text{Dirg}(0.88 \otimes \text{Diri}(0.5 * \text{Dior}(2), 0.5; 2), 0.12 \otimes \text{Diun}(2); 0.02, 0.02),$$

where Dirg, Diri, Dior and Diun are different “flavors” of the Dirichlet distribution: Dirg, the generalized Dirichlet distribution, is used when we have a set of branching ratios and their uncertainties; Diun is the uniform Dirichlet distribution, to be used in absence of information; Dior is the ordered version of Diun; and Diri is the standard Dirichlet distribution. This expression is parsed by a code, which generates random numbers at each node and makes the

adequate products to compute the b_i 's. This code is available upon request to the corresponding author.

3. Application to Titan's ionosphere

The mass spectrometers (INMS and CAPS) aboard the Cassini probe have revealed the presence in Titan's ionosphere of unexpectedly high densities of positive ions with m/z as large as 300 u [16, 35]. Typical INMS data are shown in Fig. 1, along with the tentative identification of the measured ions. In ionospheric pressure and temperature conditions, DR is a major pathway for the destruction of ions to produce heavy neutral species and/or (smaller) highly reactive radicals. The observations demonstrate also the importance of representing minor channels in the DR products, because the density range of INMS mass spectra covers at least 2 orders of magnitude: a one percent channel of a major ion might contribute as much to a given product as a 99 percent channel of a minor ion.

In fact, the extreme complexity of DR products formation is in sharp contrast with the fact that none of the ion-neutral coupled models for Titan's ionosphere integrates the multi-pathway nature of this process [28–34]. With only few exceptions, the present paradigm is to consider the H-loss channel as the only pathway for all H-bearing ions: $MH^+ + e^- \rightarrow M + H$, which is at best a severe approximation. Recent experimental studies have clearly shown that DR could not only break bonds between heavy atoms efficiently, but also break more than one bond (Fig. 3) [1, 2]. As our probabilistic approach enables to implement a DR scheme accounting for all plausible pathways, we tested it in a ionospheric chemistry model of Titan [19, 27], comparing the production rates of neutral species to those of the H-loss approximation. This is the first model implementing all available DR data for Titan's ions (58 species) [15].

Our “full scheme” includes 448 partial DR reactions producing 62 neutral species. From it, we derived an “H-loss” scheme with 63 partial reactions and 48 neutral products. This comparison showed unambiguously that the “H-loss” scheme dampens the production of radicals and favors the production of heavy stable neutral species. By contrast, the full model produces much more reactive radicals which could boost the neutral chemistry in the ionosphere. Preliminary tests in a coupled ion-neutrals models show indeed that the densities of N-bearing species are very sensitive to this flow of radicals [36]. The effect is less marked for hydrocarbons. In addition, DR is globally much more efficient than bimolecular ion-molecule reactions to produce radicals.

We also observe a “cascade” effect, where heavier ions contribute significantly to the formation of smaller neutral species. In absence of data about their DR branching ratios, most heavy species are not presently included in the model. Their breakup patterns by DR and their role in the chemistry of Titan's ionosphere is therefore a major open issue.

4. Conclusions and data needs

Probabilistic tree representation of branching ratios is a powerful method to deal with partial measurements and to implement empirical rules. In combination with Monte Carlo methods, this is a very promising tool for consistent kinetic modeling of chemical plasmas.

A major result of this study is that we are able to deal with partial measurements, which is a reason to redefine data needs for Titan's ionosphere.

To understand the major fluxes in the ionospheric chemistry, notably the impact of heavy ions on the neutral chemistry, it is *not* a priority to get exhaustive measurements of branching ratios for individual ions. If one considers the groups of ions in Fig. 1, it is much more important to get partial branching ratios for heavy ions $C_{x-y}N_yH_z^+$ ($x \geq 5$) or smaller unmeasured ions, than to get fully characterized branching ratios for already partially characterized ions (*i.e.* green-to-blue rather than green/blue-to-red, in terms of group colors).

Several strategies can be invoked to complement the experimental data. Analogies with other dissociative processes [37] and isotopomers [38] can provide precious information. Identification

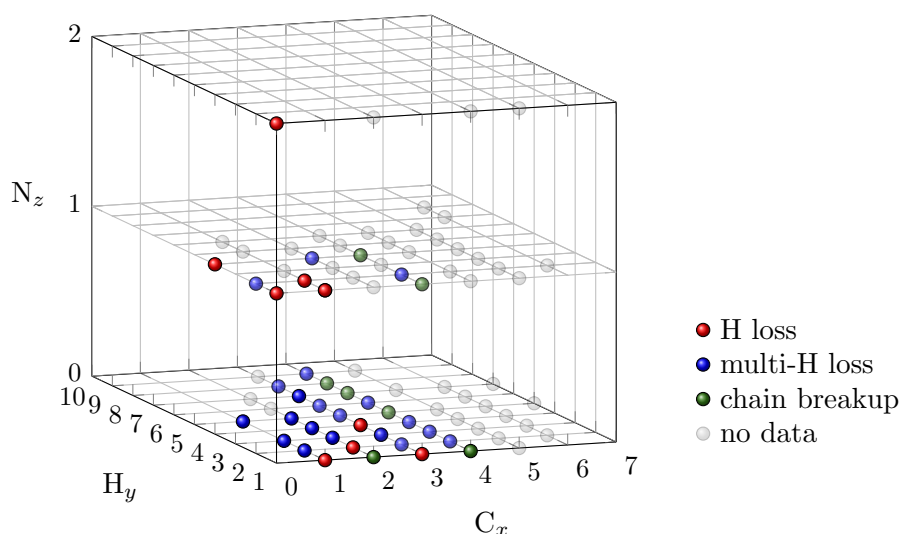


Figure 3. Major breakup patterns for $C_xH_yN_z^+$ ($x + z \neq 0$ and $y \neq 0$) ions assigned in INMS mass spectra.

of tendencies in breakup patterns would enable us to propose a first level of nesting, and thus constrain the role of heavier ions.

Empirical rules constraining the relative behavior of several branches within an inner level of nesting have also the potential to increase dramatically the model's predictivity (*e.g.* the “ $2H \geq H_2$ ” rule). Production of “isomers” (*e.g.* HCN/HNC, $^1CH_2/^3CH_2$, spin states of N) is an ubiquitous consequence of DR, and data on their relative production are strongly needed.

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