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How Measurements of Rate Coefficients at Low Temperature Increase the Predictivity of Photochemical Models of Titan's Atmosphere[†]

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The predictivity of photochemical models of Titan's atmosphere depends strongly on the precision and accuracy of reaction rates. For many reactions, large uncertainty results from the extrapolation of rate laws to low temperatures. A few reactions have been measured directly at temperatures relevant to Titan's atmosphere. In the present study, we observed the consequences of the reduced uncertainty attributed to these reactions. The global predictivity of the model was improved, i.e., most species are predicted with lower uncertainty factors. Nevertheless, high uncertainty factors are still observed, and a new list of key reactions has been established.

Introduction

The aim of the Cassini–Huygens mission was to increase substantially our knowledge about Titan, in particular regarding the nature of the physical and chemical processes shaping its inscrutable atmosphere. Composed mainly of nitrogen N_2 with a few percent of methane CH_4, its irradiation by solar UV, energetic electrons, and cosmic rays drives a very rich and complex chemistry leading to the formation of aerosols that eventually precipitate on Titan's surface. The Cassini–Huygens mission revealed that the chemical complexity of Titan's atmosphere was even beyond our expectations.[1,2] As many processes are involved (radiative transfer, photodissociations, neutral–neutral thermal reactions, heterogeneous chemistry, microphysics, ...), such a planetary-scale chemical system constitutes a very challenging field of research for modelers and, for the past 25 years, several photochemical models of Titan's atmosphere have been developed independently to tackle the issue of reproducing the observations to the best extent possible and to unveil the processes explaining their origin.[3−11] Despite their quality, these photochemical models of Titan's atmosphere display large discrepancies between their results and the available observations. Lebonnois[8] recently pointed out that the origin of these discrepancies may lie in the adopted photochemical kinetic data itself.

The overall precision of photochemical models of planetary atmospheres has unambiguously been shown to be highly sensitive to the uncertainties in chemical rates.[12−19] Through a comprehensive cross-examination of reaction rate databases, Hébrard et al.[20] recently published a detailed analysis of the different sources of uncertainty in photochemical models of Titan's atmosphere and their evaluation at temperatures representative of such a peculiar environment (50–200 K). Monte Carlo uncertainty propagation enabled Hébrard et al.[9] to assess the effect of these uncertainties on the computed abundances of major chemical species predicted by a 1D photochemical model of Titan's atmosphere. Strikingly, the uncertainties of most of the computed abundances could be much larger than the estimated uncertainties of the abundances gathered from observations, even for basic hydrocarbons like methane CH_4, acetylene C_2H_2, ethylene C_2H_4, and ethane C_2H_6. These calculations were the first to question the predictivity of 1D photochemical models of Titan's neutral atmosphere by establishing that uncertainties related to chemical rate coefficients could affect so significantly the computed concentrations as to preclude any useful comparisons with observations. In this context, as

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Frenklach[21] has stated recently for combustion chemistry, the present frontier of photochemical modeling of planetary atmospheres, or Titan's atmosphere for that matter, is the development of predictive kinetics models capable of accurate numerical predictions with quantifiable uncertainties.[9,15,17,22,23]

At high altitudes, coupled ion−molecule chemistry determines the structure and composition of the ionosphere itself[24,25] but seems also to alter the composition of the neutral atmosphere[26,7,27] and might even play a key role in the formation of aerosols.[2] The parameters of ion−molecule reactions and the density of neutral species were found to be major sources of uncertainty for ionospheric chemistry predictions.[22] A more detailed sensitivity analysis of simulated INMS ion mass spectra with regard to ion−molecule reactions has been performed by Carrasco et al.,[28] who pointed out the lack of information about the reactivity of isomers, the influence of temperature on branching ratios, and heavy ion reactivity. A recent sensitivity analysis including all uncertain reaction rates in the photochemical atmospheric and ionospheric models suggests that neutral−neutral reaction rates are presently the main source of uncertainty for the simulated ion mass spectra (in preparation). Therefore, we focus this study exclusively on thermal neutral−neutral reaction rates.

A major obstacle to precise prediction is the lack of data on the reactivity of neutral species at low temperature (low-*T*); for instance, in state-of-the-art photochemical models of Titan's atmosphere, less than 10% of the rates have been measured in the relevant temperature range. In consequence, photochemical models of Titan's atmosphere are based mostly on low-*T* extrapolations of Arrhenius-type laws. This kind of extrapolation is known to be often inappropriate in this context.[29,30] Low-*T* extrapolations of reaction rates are thus to be treated with great care and considered as very uncertain.

In the present paper, we aim to illustrate the difficulties of low-*T* extrapolation of reaction rates and to underline the importance of low-*T* experimental studies. A dialogue between modellers and experimentalists is necessary to improve the present situation. Considering the difficulty of low-*T* reaction kinetics experiments, the identification of key reactions has to be based on an optimal strategy to improve the predictivity of photochemical models. This can be achieved by global sensitivity analysis, as illustrated recently by Dobrijevic et al.[23,31] The main difficulty of this scheme is that it requires a lot of inputs, mainly reliable evaluation of uncertainties for measured and extrapolated reaction rates. Although a large part of this work has already been achieved by Hébrard et al.,[20] its extension and validation require a group of experts, and a new generation of collaborative kinetic database. The KIDA project,[32] initiated by V. Wakelam for astrochemistry, has been joined by planetologists with similar intentions. A result from KIDA meetings was the reevaluation of the uncertainties associated with measured low-*T* reaction rates. The impact of this database update on the predicted densities of neutrals species in Titan's atmosphere is presented in this article. Database improvement is an iterative process, and a new list of key reactions is issued from the present simulations. These key reactions are guaranteed to have a strong impact on the precision and the accuracy of model predictions, and better estimations of their rates need to be obtained, either experimentally or theoretically.

The body of the paper is organized in four sections. The methods used for photochemical modeling, uncertainty propagation and sensitivity analysis are presented in the next section. A specific section is dedicated to the problem of low-*T* extrapolation of reaction rates and to the evaluations of the uncertainties associated with reaction rates. The reevaluation of uncertainties in the case where low-*T* reaction rate data are available is presented next. The final section analyzes the effects of this database update on the photochemical model predictions and provides the identification of a new list of key reactions.

Methods

The main lines of the 1D photochemical model and statistical procedures for uncertainty propagation and sensitivity analysis are presented here. More details can be found in Hébrard et al.[9] and Dobrijevic et al.[23,31]

1D Photochemical Model. In our 1D photochemical model extending from Titan's surface to 1300 km, the species densities are governed by the altitude-dependent continuity-diffusion equation

$$\frac{\mathrm{d}y_i}{\mathrm{d}t} = P_i - y_i L_i - \mathrm{div}\,\Phi_i \vec{e}_z - C_i \tag{1}$$

where y_i is the density of species i (cm^{-3}), P_i is its (photo)chemical production (cm^{-3} s^{-1}), L_i is its (photo)chemical loss rate (s^{-1}), Φ_i is its vertical flux (cm^{-2} s^{-1}), and C_i is its condensation factor. A detailed description of hydrocarbon, nitrile, and oxygen coupled photochemistry, vertical eddy diffusion, molecular diffusion, and radiative transfer (including Rayleigh scattering by N_2 and aerosols absorption) are included in this model.

Ions are not considered, and the loss and productions are due to photodissociations and bimolecular and termolecular reactions between neutral species. Our model calculates abundances for 127 hydrocarbon, nitrile, and oxygenated species, involved in 676 chemical reactions and 69 photodissociation processes.

The present model is identical to the one used in Dobrijevic et al.[23] All the details about the physical inputs can be found in Hébrard et al.[9]

Uncertainty Propagation. There are many sources of uncertainty in a 1D photochemical model. In the present study, fixed vertical structure, solar irradiance and diffusion coefficients (eddy and molecular) were used throughout the calculations, to focus exclusively on the chemistry issue through the uncertainty of the photodissociation and reaction rates.

The uncertainty in the latter quantities originates in their experimental or theoretical determination and is generally quantified by a standard deviation or a relative uncertainty. Because of the nonlinearity of the chemistry model and the large uncertainties on many parameters, linear uncertainty propagation is not expected to produce valid results. Propagation of distributions by Monte Carlo sampling is better adapted to such problems.[33,34] Due to the positivity constraint on these properties, their distributions are modeled by log-normal probability density functions

$$p(x) = \frac{1}{\sqrt{2\pi}x\sigma}\exp\left(-\frac{(\ln x - \mu)^2}{\sigma^2}\right) \tag{2}$$

with two parameters $\mu = \ln k(T)$, the logarithm of the nominal value of the reaction rate at temperature T, and $\sigma = \ln F(T)$, where $F(T)$ is the geometric standard uncertainty of the log-normal distribution. With these notations, the 67% confidence interval for a reaction rate at a given temperature is $[k(T)/F(T), k(T) \times F(T)]$. It is convenient to relate F to the relative uncertainty $(\Delta k)/(k)$. For small uncertainties, one can write

$$F = \exp(\Delta(\ln k)) \quad (3)$$

$$\simeq \exp\left(\frac{\Delta k}{k}\right) \quad (4)$$

$$\simeq 1 + \frac{\Delta k}{k} \quad (5)$$

Although approximate, the latter equation is convenient to elicit uncertainty factors from relative uncertainties of measured reaction rates: for instance, a 25% relative uncertainty on k corresponds to $F = 1.25$.

The reaction rate coefficients and their associated uncertainty factors, as well as the photodissociation coefficients used in the present study were extracted from the review by Hébrard et al.,[20] including some important revisions detailed in Table 3. Global uncertainty factors $F = 1.5$ were assumed for all photodissociations, in agreement with the lower limit established formerly by Dobrijevic et al.[17]

Long computation times required to reach the convergence of the species densities limit the number of Monte Carlo samples: typically about 500 independent samples are generated. This provides a convergence of average values and correlation coefficients to better than 5%. For each run, one records the reaction rate coefficients (inputs) and neutral mole fractions (outputs) at different altitudes, which are used for statistical uncertainty and sensitivity analysis.

Sensitivity Analysis: A Tool for Key Reactions Identification. Sensitivity analysis is used to detect input parameters (reactions and photodissociation rate coefficients) having strong effects on outputs (species densities). At the present stage of photochemical modeling, we want in particular to identify reactions responsible for large uncertainties in model prediction of some target property. These are called *key reactions* in the following.[31] The main interest of this approach is that it guarantees that the reduction of the uncertainty on the rates of these reactions will have a strong impact on the precision of the target property. This is particularly important to assist in designing new measurement campaigns.

Input−output correlation coefficients provide sensitivity measures well adapted to this key reaction search.[31] They are easy to estimate within the Monte Carlo uncertainty propagation framework and do not require dedicated sampling schemes.[35,36] The input and output samples recorded for uncertainty evaluation can be directly used for the sensitivity analysis. To account for nonlinearities, rank correlation coefficients (RCC) are used. They convert a nonlinear but monotonic relationship into a linear relationship by replacing the values of the sampled inputs/outputs by their respective ranks.[37,36] This method has been recently applied successfully to the chemistry of Titan by Carrasco et al.[22,28] and Dobrijevic et al.[23,31]

Evaluation and Extrapolation of Uncertainties in Chemical Rate Coefficients at Low Temperatures. Even if modern techniques are capable of measuring rate coefficients with a good precision (with quoted uncertainties as small as 10%), data obtained in different laboratories on the same reaction using sometimes the same technique are rarely in agreement to the extent that might be expected from the quoted precision of the measurements. Besides, even if the spread in results among different techniques for a given reaction may provide some basis for evaluating an overall uncertainty, the possibility of identical, or compensating, systematic errors in all the studies must be recognized and make them particularly difficult to detect and to quantify.

Moreover, the reaction rate coefficients and their attached uncertainties are supposed to be constrained within the temperature range of their experimental and/or theoretical determination, which is often not representative of the temperatures of planetary atmospheres. When building a photochemical scheme, modelers have inevitably to extrapolate many chemical rate coefficients, as well as their attached uncertainties, to relevant temperatures. Such an extrapolation constitutes a major source of uncertainty, difficult to quantify, containing basically two contributions:

- a *model uncertainty* due to the fact that the rate law used to represent data within a given temperature range is not necessarily valid outside of this range. Model uncertainty escapes presently any quantitative assessment. It would require the definition of a set of alternative rate laws compatible with a given chemical process. Model averaging of predictions over this set could then be performed. Without such prior restrictions on rate laws, the mathematical behavior of currently available alternative models is diverse enough for model averaged extrapolation to be totally unpredictive. To our knowledge, this kind of approach has not been developed yet and the Arrhenius law $k(T) = A \exp(-B/T)$ or its extended version (Kooij law) $k(T) = A \times T^n \exp(-B/T)$ remain the most widely used rate laws in planetary atmosphere modeling studies.
- a model-dependent *parametric uncertainty* originating in the limited precision of the rate law parameters due to measurement uncertainties. Parametric uncertainty for a given model can be estimated more easily by well established statistical methods. Its main interest is to provide a lower limit for extrapolation uncertainty.

The case of the Arrhenius rate law is presented next to illustrate the importance of parametric uncertainty in low-T extrapolation.

Parametric Uncertainty in Low-Temperature Extrapolation of Reaction Rates and Uncertainties. Our starting point is a set of reaction rates, measured at different temperatures. In all the following, we consider that measurement uncertainties are additive, with normal distributions. Once a rate law is chosen, uncertainty propagation can be used to estimate the effect of measurement uncertainty on prediction uncertainty by this rate law. This is typically done in two stages: (1) estimation of the uncertainty in the rate law parameters (through their probability density function or a variance-covariance matrix) and (2) propagation of the parametric uncertainty to predictions by the rate law. This procedure presents no difficulty, except that both steps are typically performed by different people with different aims. This is often the cause of a major loss of information at the interface, as we will show after an introduction to the statistical tools.

Statistical Uncertainty Propagation. The most convenient way to store and transfer parametric uncertainty information is through the variance−covariance matrix of the parameters. Heberger et al.[38] claimed more than twenty years ago that "the full correlation matrix should be published in any article dealing with the determination of Arrhenius parameters". This matrix can be used to perform uncertainty propagation by the standard propagation of variances,[33] which is accurate if the rate law expression is linear in its parameters. These considerations introduce some constraints on the choice of a model for data analysis. For instance, the Arrhenius equation $k(T) = A \exp(-B/T)$ is not linear in B, whereas the log-Arrhenius equation $\ln k(T) = \ln A - B/T$ is linear in both $\ln A$ and B, and therefore preferable in the two-stages uncertainty propagation framework. To be more specific, the Arrhenius equation presents two shortcomings with regard to a variance–covariance analysis: the probability density function of A is not normal, and the correlation between A and B is not linear. The variance–covariance matrix of A and B is therefore a very poor statistical summary of their correlated uncertainties, and cannot be relied upon for uncertainty propagation.

We present below a summary of the formulas for temperature-dependent parametric uncertainty extrapolation. Using the log-Arrhenius equation $\ln k(T) = \ln A - B/T$, a standard weighted least-squares (WLS) analysis of a set of measurements $k_i \pm \Delta k_i$ at well-defined temperatures T_i ($i = 1, n$) provides optimal values for the fitted parameters $\ln A$ and B, their standard deviations $\sigma_{\ln A}$ and σ_B as well as for their correlation coefficient ρ (see for instance d'Agostini[39] or Bevington[40] for detailed derivations).

$$\ln A = \frac{\overline{x^2}\cdot\bar{y} - \bar{x}\cdot\overline{xy}}{\overline{x^2} - \bar{x}^2} \tag{6}$$

$$B = \frac{\overline{xy} - \bar{x}\cdot\bar{y}}{\overline{x^2} - \bar{x}^2} \tag{7}$$

$$\sigma_{\ln A} = \sqrt{\overline{x^2}} \Bigg/ \sqrt{(\overline{x^2} - \bar{x}^2)\sum_i {w_i}^2} \tag{8}$$

$$\sigma_B = 1 \Bigg/ \sqrt{(\overline{x^2} - \bar{x}^2)\sum_i {w_i}^2} \tag{9}$$

$$\rho = -\bar{x} \Big/ \sqrt{\overline{x^2}} \tag{10}$$

where $x_i = -1/T_i$, $y_i = \ln k_i$, and $\bar{z} = \sum_{i=1}^{n} {w_i}^2 z_i / \sum_{i=1}^{n} {w_i}^2$ is the weighted mean of any set of z_i variables with weights $w_i = k_i/\Delta k_i$ corresponding to the log-transformation of the rate constants.[38] Note that this linear weight transformation is accurate only for small uncertainties. More accurate transformations have been proposed by Cvetanovic.[41] Alternatively, a weighted nonlinear least-squares procedure can be used with the model $k(T) = \exp(\ln A - B/T)$, for which no weight transformation is necessary. Although this model is nonlinear in $\ln A$ and B, we observed that when the data set contains more than 4–5 measurements, the probability density of the parameters is well approximated by a bivariate normal distribution, validating the use of a variance-covariance matrix.

Using standard propagation of variances,[33] the temperature-dependent standard uncertainty for the log-Arrhenius model is

$$\sigma_{\ln k(T)} = \left({\sigma_{\ln A}}^2 - \frac{2}{T}\rho\,\sigma_{\ln A}\sigma_B + \frac{1}{T^2}{\sigma_B}^2\right)^{1/2} \tag{11}$$

from which one obtains the uncertainty factor $F(T)$ attached to the reaction rate $k(T)$ following $F(T) = \exp(\sigma_{\ln k(T)})$. It is to be noted that the uncertainty factor $F(T)$ depends on the correlation coefficient ρ between the fitted parameters of the linearized Arrhenius equation, as well as on their standard deviations $\sigma_{\ln A}$ and σ_B.

Example: $N(^2D) + C_2H_4$. To illustrate the results of the previous section, we consider the reaction of electronically excited nitrogen atoms $N(^2D)$ with ethylene C_2H_4. Using a pulse radiolysis–atomic absorption method between 225 and 292 K, Sato et al.[42] determined the temperature dependence of the rate constant by a nonlinear least-squares fitting of their experimental data with the Arrhenius equation. For reference, their data set for the title reaction is displayed in Table 1.

TABLE 1: Rate Constant Measurements for the Reaction $N(^2D) + C_2H_4$ from Sato et al.[42]

T(K)	$k \pm \Delta k$ (cm^3 molecule $^{-1}$ s^{-1})
292	4.1 (±0.4) × 10^{-11}
270	3.4 (±0.4) × 10^{-11}
253	3.0 (±0.4) × 10^{-11}
240	2.8 (±0.4) × 10^{-11}
230	2.6 (±0.4) × 10^{-11}

TABLE 2: Arrhenius Parameters for the Reaction $N(^2D) + C_2H_4$

	ln A	B (K)	ρ
Sato et al.[42]	−22.19 ± 0.13	503 ± 50	n/a
this work	−22.23 ± 0.65	500 ± 170	0.996

Results of the Arrhenius fit of this measurements set by Sato et al.,[42] reexpressed in terms of ln A and B, are compared in Table 2 with the results of the WLS analysis. The most striking difference is the very large discrepancy on the parameters' uncertainties between both approaches. Due to the lack of information in the original paper,[42] one can only assume that an *unweighted* nonlinear least-squares analysis was performed, which cannot provide relevant uncertainty estimates.[38,41] Moreover, the correlation coefficient between the fit parameters is not reported. It is therefore impossible to use these results for the purpose of uncertainty propagation/extrapolation, and the whole fitting procedure has to be redone, as we did here.

This situation is unfortunately very common, which, considering the thousands of reactions in photochemical databases and the burden to recover the corresponding original experimental data, limits a generalized use of statistical uncertainty propagation for reaction rate coefficients extrapolation.

The extrapolated rate constant and standard uncertainty are displayed in Figure 1 (top). As expected, uncertainty increases as temperature decreases, which is more easily quantified through the uncertainty factor $F(T)$ plotted in Figure 1 (bottom). This figure compares uncertainty factors obtained by various means: the full/red curve corresponds to our WLS analysis, while the dotted/blue one is obtained using the uncertainties reported by Sato (assuming a null correlation coefficient ρ). This confirms the necessity of a consistent strategy for data analysis and uncertainty propagation to obtain reliable uncertainty extrapolation.

We detailed this example for pedagogical reasons. It shows clearly that parametric uncertainty alone can lead to very large extrapolation uncertainty, depending mainly on the precision and the temperature range of reaction rates measurements. We insist that parametric uncertainty is only a component of extrapolation uncertainty, for which it provides a lower limit. It does not account for systematic measurement errors and/or model uncertainty. An important message to photochemical modelers is therefore: *if you have to use extrapolated reaction rate coefficients, be prepared to account for large uncertainties in your model inputs*.

In general, statistical parametric uncertainty propagation is not a practical way to estimate extrapolation uncertainty, especially when there are measurement and/or theoretical data sets which are in disagreement.

Stewart and Thompson's[14] study of temperature-dependent uncertainties on reaction rates urged them to estimate the magnitude of the uncertainty factor at a temperature different

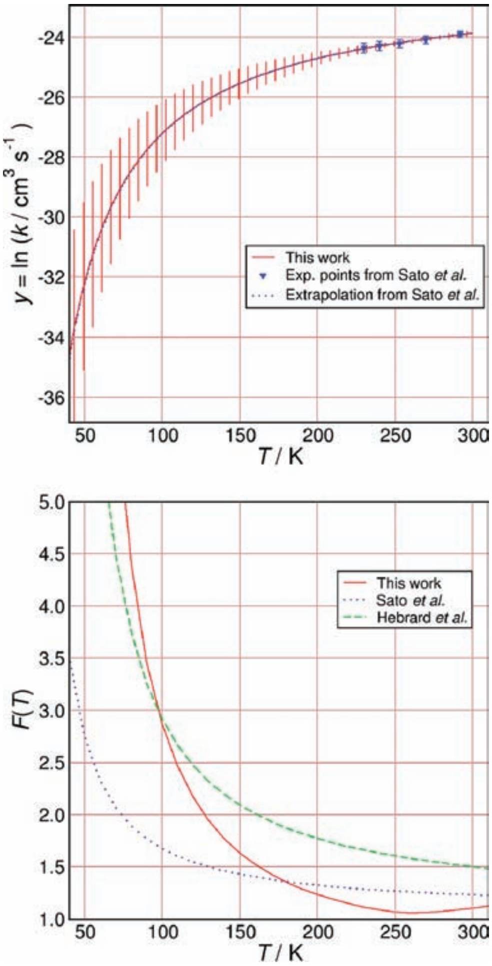

Figure 1. Extrapolation of the Arrhenius law for reaction $N(^2D)$ + C_2H_4. (Top) the full/red line with error bars represents the average value and standard deviations of ln $k(T)$ obtained by the method presented in the text, using Sato et al.[42] experimental data (blue triangles and error bars), and the blue/dotted line represents the extrapolation from the Arrhenius parameters given by Sato et al.[42] (Bottom) uncertainty factors obtained by various methods. The full/red curve corresponds to our WLS analysis, the dotted/blue one is obtained using the uncertainties on Arrhenius parameters reported by Sato et al.,[42] and the dashed/green one corresponds to the independent evaluation by Hébrard et al.[20]

from the one used in the experiments. They introduced an extrapolation method akin to parametric uncertainty propagation but based on critically estimated uncertainties of rate law parameters rather than on statistical analysis. Their study was based on various rate compilations[43,44] providing some Arrhenius coefficients, activation temperatures, and their associated errors at a given temperature. Following DeMore et al.,[44] Stewart and Thompson[14] were then able to evaluate the propagation of the errors at different temperatures, especially at low temperatures, in a model devoted to the Earth's atmosphere. In their critical review, Baulch et al.[45] emphasize, however, the difficulty of estimating these uncertainties on reaction rate coefficients and suggest that many of them, if known, might be underestimated or even misestimated.

Other evaluation techniques have also been proposed by experts, as presented in the following.[14,20,46,47]

Evaluation of Reaction Rates and Their Uncertainties at Low Temperatures. Existing databases for chemical kinetics and photochemical data have been developed with different aims, and optimized for studying Earth's atmospheric chemistry,[48,49] combustion chemistry,[45] or even astrochemistry.[50−52] None of these databases was specifically representative of Titan's atmospheric conditions, nor provided complete uncertainty evaluation. Therefore, Hébrard et al.[20] investigated the different photochemical sources of uncertainty in models of Titan's atmosphere and provided evaluations for relevant temperatures. They provided estimates of the uncertainty factor $F(T)$ of a reaction rate $k(T)$ at any given temperature, following an expression adapted from Sander et al.:[48]

$$F(T) = F(300\text{K}) \exp\left|g\left(\frac{1}{T} - \frac{1}{300}\right)\right| \qquad (12)$$

where $F(300\text{K})$ is the uncertainty in the rate constant $k(T)$ at T = 300 K and g is an "uncertainty-extrapolating" coefficient defined for use with $F(300\text{K})$ in the above expression to obtain the rate constant uncertainty $F(T)$ at different temperatures. These assigned uncertainty factors $F(300\text{K})$ and g have been evaluated to construct the appropriate uncertainty factor, $F(T)$, following an approach based on the fact that rate constants are almost always known with a minimum uncertainty at room temperature. This approach enabled Hébrard et al.[20] to quantify the temperature-dependent uncertainties carried by each reaction rate present in the standard sets of reactions rates in a temperature range adequate for Titan's atmosphere.

It cannot be too strongly emphasized that such an evaluation represents the author's subjective assessment, as it does not result from a rigorous statistical analysis of the available databases, which are generally too limited—or even incomplete as underlined earlier—to enable such an analysis. Hébrard et al.[20] based their evaluation for a fraction of the reactions rate coefficients on previous compilations, in which the uncertainty factors at room temperature $F(300\text{K})$ had been previously evaluated with values included between 1.05 and 12,[53−57] but also on

- the dispersion of available experimental and/or theoretical data for a single reaction as seen in widely used, noncritical databases, such as the NIST Chemical Kinetics Database;[58,59]
- the availability of low temperature experimental data, by seeking to identify specifically the strengths and limitations of the different techniques with respect to their use at such temperatures; and
- the biased estimations that photochemical modelers usually adopt when such low-temperature data are not available.

In the absence of laboratory or theoretical measurements, modelers usually estimate chemical rate coefficients, based on analogies in molecular structures and exothermicities. For example, higher polyyne radicals have been assumed in all previous photochemical models of Titan's atmosphere to be probably less than or as reactive as the ethynyl C_2H radical.[3−5,7,9] In contrast, recent measurements by Berteloite et al.[60] at low and very low temperatures showed that the rate coefficients for the reaction of the butadinyl C_4H radical with various hydrocarbons was systemically larger than those found for reactions of the ethynyl C_2H radical with the same hydrocarbons, illustrating to what extent the previous estimations could be mistaken. Accordingly, Hébrard et al.[20] assumed for these estimated reactions $F(300\text{K})$ = 10.0, the highest imprecision that can be found in their compilation.

Figure 1 (bottom) displays the evaluation by Hébrard et al.[20] of the temperature-dependent uncertainty factor $F(T)$ for the $N(^2D)$ + C_2H_4 reaction. The uncertainty factor at room temperature $F(300\text{ K})$ for this reaction rate coeficient seems at first to be overevaluated at room temperature, but it is based on several other previously reported determinations. Hébrard

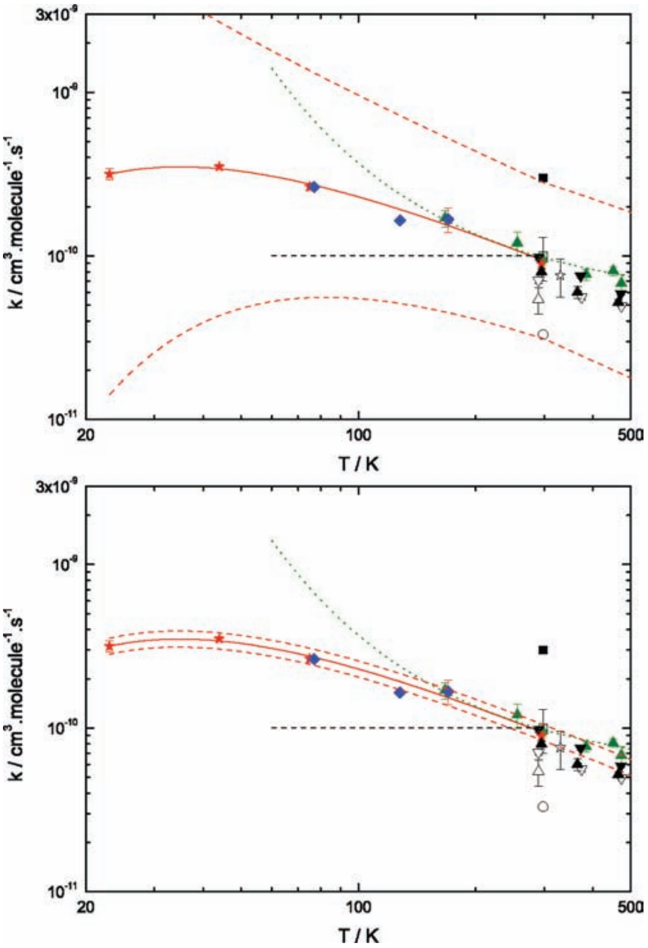

Figure 2. Rate coefficients for the reaction of the methylidine radical CH with methane CH_4 as a function of temperature, displayed on a log−log scale along with associated uncertainties, as estimated in Hébrard et al.[20] (top) and in the present study (bottom). Experimental results obtained in the CRESU apparatus are displayed as red stars[68] and blue diamonds.[69] The red solid line displays the Arrhenius law derived from the CRESU experimental data only.[68] The red dashed lines correspond to the extreme errors limits. The open circle displays the experimental results obtained by Bosnali and Perner,[70] the filled square those obtained by Butler,[71] the open square those of Butler,[72] the green filled triangles those obtained by Berman and Lin,[73] the open triangles those of Anderson,[74] the black filled triangles those obtained by Herbert,[75] the upside-down filled triangles those of Blitz,[76] the upside-down open triangles those obtained by Thiesemann[77] and the open star those of Fleurat-Lessard et al.[78] The black and green dashed lines display the simple extrapolations of Butler[72] and Berman and Lin[73] experimental measurements, respectively, to a temperature range representative of Titan's atmosphere conditions as encountered in some previous models.[3−5]

et al.[20] followed the critical evaluation of Herron[57] by adopting $F(300K) = 1.5$, and recommended $g = 100$. This evaluation of $F(T)$ is, however, undoubtedly underevaluated at low temperatures, as revealed by parametric low-T extrapolation. It can be seen that the large uncertainty factors published in the review by Hébrard et al.[20] are far from being overestimated.

This illustrates again the difficulties of estimating and/or extrapolating the uncertainties on reaction rates to low-temperatures without a rigorous and statistical evaluation of the experimental kinetic data, which is most often impossible with the current state of existing databases.

Reevaluation of Low-Temperature Reaction Rate Coefficients Uncertainties. In an ideal Arrhenius world, high temperature measurements could be used to reduce the uncertainty of the rate law parameters, and thus to improve the precision of low-T predictions (eqs 8 and 9). However, there is now strong evidence that the Arrhenius law is not reliable for low-T extrapolation,[29,30] and low-T measurements are presently unavoidable if we want predictive photochemical models.

To underline specifically the importance of low-T experimental studies in modeling Titan's atmosphere, we proceeded with a reevaluation of the uncertainties estimated for these reactions in Hébrard et al.[20]

Studying important reactions over a wide range of temperatures, especially down to very low temperatures, can assist us in gaining a full understanding of reaction mechanisms in many different planetary environments. Indeed, the evidence strongly suggests that despite the existence of extreme temperatures, there is a rich chemistry occurring in these regions, with molecules being continuously formed and destroyed through chemical reactions. These observations provide a strong stimulus to perform laboratory studies of reaction kinetics at low and very low temperatures.

Essentially, all direct methods for measuring the rates of elementary gas phase neutral−neutral reactions are based either (i) on pulsed laser photolysis and the subsequent observation of transient species in real time through optical spectroscopy or (ii) on the flow method, in which transient species concentrations are measured in steady state at different distances from the point at which the reactants are mixed or generated and the reaction starts. In both cases, it is possible to cool the apparatus cryogenically and thereby fairly routinely reach temperatures as low as 180 K and for a few exceptional cases even as low as 80 K.[61−63] However, it is rather difficult to perform low temperature kinetic measurements in these types of apparatus as any condensable reagents introduced tends to be quickly lost on the reactor walls. Expansion of a gas from a region of high pressure to one of high vacuum through a small orifice drastically cools it, typically to temperatures of ∼10 K or even below.[64] The resultant free jet is effectively "wall-less" but is unfortunately inhomogeneous with respect to both temperature and density, making it difficult to perform accurate kinetic measurements. The use of an appropriately designed, axisymmetric, convergent-divergent, Laval nozzle can provide, however, a supersonic, continuous and uniform flow of relatively dense gas at temperatures well below the ones encountered in the Earth's, but adapted to other interstellar and planetary atmospheres, such as Titan's. Such cooling by a supersonic expansion through Laval nozzles is the central feature of the CRESU (*Cinétique de Réaction en Écoulement Supersonique Uniforme* or Reaction Kinetics in Uniform Supersonic Flow) apparatus.[65,66]

Uncertainty Evaluation of CRESU Measurements. We focused our reevaluation on the reactions that have been experimentally studied with such systems. In contrast with the estimation methodology used in Hébrard et al.,[20] the scattering of experimental and/or theoretical data available in the literature or the biased estimations and/or extrapolations that photochemical modelers may have adopted have not been accounted for in the present reevaluation.

As long as experimental data exist to support its estimation over the appropriate temperature range, the uncertainty factor $F(T)$ does not necessarily increase at lower temperatures and does not have to be temperature-dependent. This is the case for low-T measurements, and temperature-independent uncertainty factors have been directly taken at their published value and the g coefficient was set to 0.

The errors Δk_i usually quoted correspond to a statistical error within one or two standard deviations (67% or 95% confidence interval, respectively). In a CRESU apparatus, systematic errors are essentially due to uncertainties in the control of gas flows and the determination of total gas densities, and they are usually estimated not to exceed 10%.[60,67] In consequence, we systematically combined a 10% error with the statistical errors when there was no further specification about their estimation in the original publication.

Each uncertainty factor F_i was then calculated using the expression $F_i = 1 + \Delta_{\mathrm{mean}}k_i/k_i$, where $\Delta_{\mathrm{mean}}k_i$ represents the mean error (statistical and systematic) reported over the whole experimental temperature range.

One of the main limitations of the CRESU method when applied to neutral−neutral reactions is that it generally does not provide any information about the branching ratios for multichannel reactions. In some cases, room-temperature measurements, thermochemical considerations, and/or chemical intuition can be used to infer the products with a fair degree of certainty, but this is not always so, and an additional 10−20% uncertainty regarding the reaction products was sometimes adopted. The reevaluated uncertainties are reported in Table 3 in comparison with the previous recommendations by Hébrard et al.[20]

The case of an important reaction, CH + CH_4, is presented in Figure 2. It can be seen how the reevaluation procedure, giving all the weight to low-*T* measurements, might result in spectacular uncertainty reductions.

Results and Discussion

Two Monte Carlo input−output samples were generated to assess the effect of the database update. In the following, we refer to the simulation involving the preupdate database as the *old* simulation, and to the other one as the *new* simulation.

Figure 3 displays the old and new output samples (mole fraction profiles) for two species representative of uncertainty issues in Titan's atmosphere, C_2H_2 and C_2H_3CN. For both compounds, the computed profiles are strongly affected by the

TABLE 3: Uncertainty Factors Reviewed in This Reevaluation

			Hébrard et al., 2006		this evaluation	
Reactions	$k(T)$ (cm^3 molecule^{-1} s^{-1})	refs	F_i(300K)	g_i	F_i(300K)	g_i
C + C_2H_2	$2.9 \times 10^{-10}\,T^{-0.12}$	79, 80	2.0	50	1.20	4
C + C_2H_4	$3.0 \times 10^{-10}\,T^{-0.11}$	79, 80	1.8	50	1.25	2
C + CH_3C_2H	$2.7 \times 10^{-10}\,T^{-0.11}$	81, 80	2.2	100	1.19	0
CH + CH_4	$3.96 \times 10^{-8}\,T^{-1.04}\,e^{-36.1/\mathrm{T}}$	68, 69	3.0	50	1.12	0
CH + C_2H_2	$1.59 \times 10^{-9}\,T^{-0.23}\,e^{-16/T}$	68	2.4	50	1.12	0
CH + C_2H_4	$7.74 \times 10^{-9}\,T^{-0.546}\,e^{-29.6/T}$	68	2.7	50	1.12	0
CH + C_2H_6	$3.8 \times 10^{-10}\,T^{-0.859}\,e^{-53.2/T}$	68, 73	6.0	50	1.23	0
CH + CH_3C_2H	4.6×10^{-10}	69, 72	1.5	100	1.50	0
CH + C_3H_6	4.2×10^{-10}	69	10.0	100	1.50	0
CH + C_4H_8	$8.78 \times 10^{-9}\,T^{-0.529}\,e^{-33.5/T}$	68	2.0	50	1.25	0
C_2H + H_2	$1.2 \times 10^{-11}\,e^{-998/T}$	82	2.0	80	1.60	60
C_2H + CH_4	$1.2 \times 10^{-11}\,e^{-491/T}$	83	1.5	80	1.20	30
C_2H + C_2H_2	$9.53 \times 10^{-11}\,e^{-30.8/T}$	83−86	1.5	50	2.00	0
C_2H + C_2H_4	$7.8 \times 10^{-11}\,e^{134/T}$	82, 85, 87	2.0	50	1.70	0
C_2H + C_2H_6	$5.1 \times 10^{-11}\,e^{-76/T}$	82, 88	1.3	50	1.50	20
C_2H + CH_3C_2H	$1.16 \times 10^{-9}\,T^{-0.3}$	86, 89, 90	1.2	50	1.60	0
C_2H + CH_2CCH_2	$2.0 \times 10^{-9}\,T^{-0.4}$	86, 89, 90	1.1	50	1.80	0
C_2H + C_3H_6	$2.4 \times 10^{-10}\,e^{-76/T}$	85, 87	1.3	50	1.60	20
C_2H + C_3H_8	$9.8 \times 10^{-11}\,e^{-71/T}$	88, 91	1.2	250	1.90	80
C_2H + C_4H_8	$2.1 \times 10^{-9}\,e^{-71/T}$	87, 92	1.3	50	1.50	0
C_2H + C_4H_{10}	$1.23 \times 10^{-9}\,e^{-71/T}$	88, 91	1.1	100	1.31	0
C_2H + C_6H_6	$9.15 \times 10^{-9}\,T^{-0.18}$	93	2.0	100	1.50	30
C_4H + CH_4	$1.7 \times 10^{-12}\,e^{-619/T}$	60	10.0[a]	100[a]	1.22	50
C_4H + C_2H_2	$7.63 \times 10^{-8}\,T^{-1.06}\,e^{-65.8/T}$	60	10.0[a]	100[a]	1.21	0
C_4H + C_2H_4	$1.9 \times 10^{-9}\,T^{-0.4}\,e^{9.5/T}$	60	10.0[a]	100[a]	1.21	0
C_4H + C_2H_6	$3.39 \times 10^{-8}\,T^{-1.24}\,e^{-25.6/T}$	60	10.0[a]	100[a]	1.20	0
C_4H + CH_3C_2H	$3.43 \times 10^{-8}\mathrm{T}^{-0.82}\,e^{-47.2/T}$	60	10.0[a]	100[a]	1.22	0
C_4H + C_3H_8	$2.32 \times 10^{-7}\,T^{-1.35}\,e^{-56.3/T}$	60	10.0[a]	100[a]	1.22	0
CN + CH_4	$5.73 \times 10^{-12}\,e^{-675/T}$	94−96	1.5	80	1.12	30
CN + C_2H_2	$5.26 \times 10^{-9}\,T^{-0.52}\,e^{-20/T}$	94, 96, 97	1.2	60	1.23	0
CN + C_2H_4	$1.36 \times 10^{-8}\,T^{-0.69}\,e^{-31/T}$	94, 96, 97	3.0	30	1.30	50
CN + C_2H_6	$5.94 \times 10^{-12}\,T^{2.2}\,e^{58/T}$	94, 98	10.0	50	1.27	0
CN + CH_3C_2H	4.1×10^{-10}	90	2.0	50	1.3	0
CN + C_3H_6	$1.73 \times 10^{-10}\,e^{102/T}$	94, 96	12.0	80	1.32	30
CN + C_3H_8	$2.4 \times 10^{-14}\,T^{1.19}\,e^{378/T}$	98	1.5	80	1.7	50
H + $^3CH_2$	$3.54 \times 10^{-9}\,T^{0.32}$	99	5.0[b]	600[b]	2.00	100
CH_3 + CH_3 + M	$k_0 = 2.2 \times 10^{-16}\,T^{-3.75}\,e^{-494/T}$	100	1.7[b]	100[b]	1.70	100
	$k_{\mathrm{inf}} = 3.8 \times 10^{-9}\,T^{-0.69}\,e^{-88/T}$		4.1[b]	100[b]	1.30	120
CH_3 + C_2H_3	$k_0 = 3 \times 10^{-11}$	101	2.2[b]	400[b]	2.00	100
CH_3 + C_3H_6	$k_0 = 2.32 \times 10^{-13}\,e^{-4390/T}$	102	1.4[b]	600[b]	2.00	100

[a] In Hébrard et al.'s[20] review, before Berteloite's[60] measurements using the CRESU technique, C_4H + hydrocarbons reactions were directly estimated from C_2H + hydrocarbons, leading to F_i(300K) = 10 and g_i = 100. [b] Hébrard et al.'s[20] evaluation of the uncertainties carried by these reactions echoed the biased estimations photochemical modelers used to adopt. To focus exclusively on experimental- and/or theoretical-uncertainties, these uncertainties have been lowered in the present reevaluation.

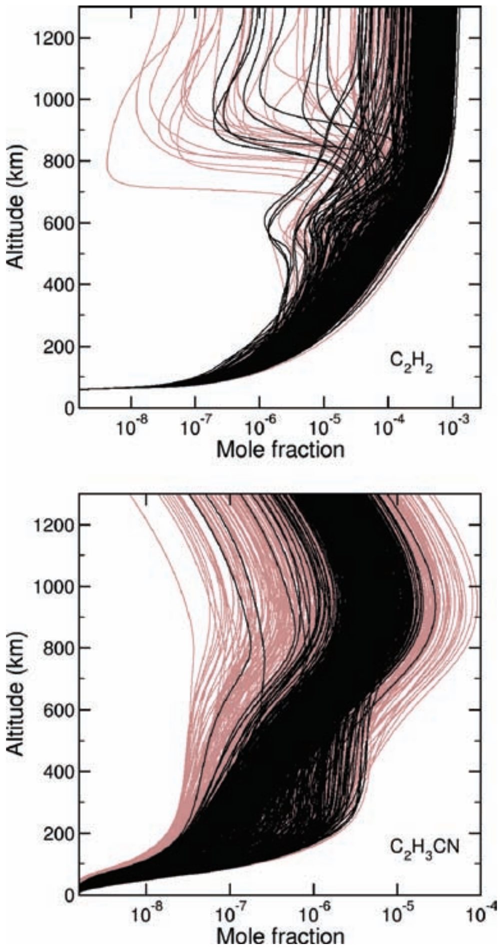

Figure 3. Abundance profiles of C_2H_2 and ethylene C_2H_3CN as a function of altitude obtained after 500 Monte Carlo runs of the 1D photochemical code: (brown/gray) old simulation;[20] (black) new simulation (this work).

uncertainties carried by the photochemical parameters, even after the database update. The particular features observed at high altitudes for C_2H_2 will be discussed below.

Effects of the Database Update. Propagation of the reevaluated uncertainties in chemical reaction rate coefficients on the results of our photochemical model of Titan's atmosphere are now examined in closer detail.

Figure 4 summarizes the effects of the database update. It displays the uncertainty factors F of the mole fractions of the main stable neutral species at an altitude of 1200 km, before and after the database update. As all points lie below the diagonal, the reevaluation has a clear effect on the overall precision of the photochemical model. It is, however, difficult to qualify this effect. For instance a strong effect would be for the confidence intervals of most species to be reduced by at least a factor of 2. For log-normal variables, this is represented by $F_{new} \leq F_{old}^{1/2}$. As seen in Figure 4, only one species (C_2H_3CN) reaches this state. To analyze the other species, it is convenient to consider uncertainty factor reductions $\Delta F = F_{new} - F_{old}$ (parallel lines in Figure 4). About 37% of all species experience $\Delta F \leq -1$. Chemically inert species as N_2 and Ar are not significantly affected. The most impacted stable neutral species is butadiene C_4H_6, with $\Delta F = -4.75$.

We observe in Figure 4 that the stable neutral species are grossly distributed in classes separated by a $F_{old} \simeq 4.5$ threshold. In the old simulation, about 50% of the species have an uncertainty factor $F_{old} \geq 4.5$, whereas the proportion reduces to about 25% in the new simulations. Although there is no justification for this value, it can be conveniently used to discriminate three classes of compounds:

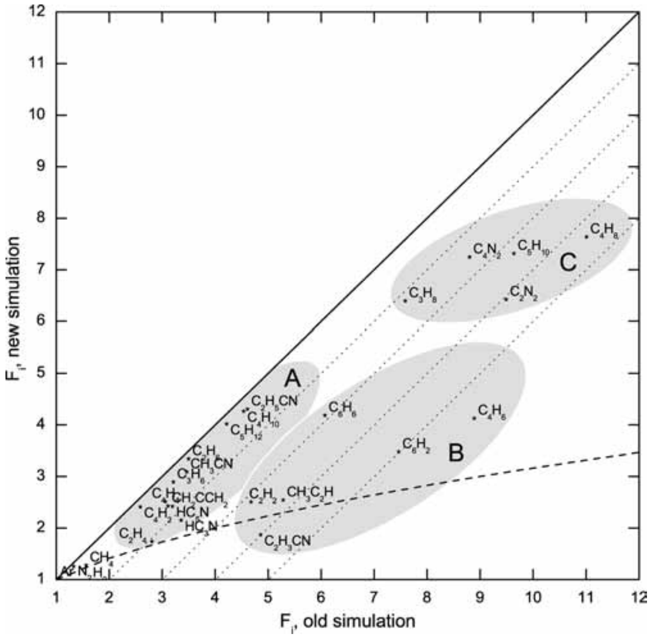

Figure 4. Evolution of the uncertainty factors F_{y_i} attached to the abundances distribution y_i of every neutral stable species at 1200 km: (solid line) no precision increase nor decrease; (dotted lines) uncertainty decrease by steps of $\Delta F = -1$; (dashed line) $F_{new} = F_{old}^{1/2}$.

- Class A: species with $2 \leq F_{old} \leq 4.5$. About half of the stable $C_xH_yN_z$ species are aggregated in this zone, and they underwent rather minor precision improvements ($0 > \Delta F \geq -1$).
- Class B: uncertainty factor decreasing from $F_{old} > 4.5$ to $F_{new} < 4.5$. This set of species underwent a notable precision improvement ($\Delta F \leq -2$), which reflects that their uncertainty was directly driven by one or more of the updated reaction rates. By a direct effect, we mean that key reactions for these species in the old simulation are in the panel of updated reactions, and that they do not appear any more in the list of key reactions in the new simulation. The following reactions are in this case:

$CH + CH_4$ for C_2H_2, CH_3C_2H, C_4H_6 and C_6H_6

$C_4H + C_2H_4$ for C_6H_2 and C_6H_6

$CH + C_2H_4$ for CH_3C_2H

$CH + C_3H_6$ for C_4H_6

$C_4H + C_2H_2$ for C_6H_2

$CN + C_2H_4$ for C_2H_3CN

- Class C: $F_{new} \geq 4.5$. These large uncertainties are due to a combination of large uncertainties associated with estimated reaction rates and large uncertainties in the densities of some intermediate species. For instance, for C_4H_8, seven key reactions contribute with identical contributions (rank correlation coefficients around 0.3 in absolute value). There is little hope to obtain a major improvement for these species in the near future. For most of these species, some precision improvement can

TABLE 4: Key Reactions Responsible for the Large Uncertainty in C_2H_2 and C_2H_4 Mole Fractions at 1200 km (RCC: Rank Correlation Coefficient)

reaction	F	RCC	
		C_2H_2	C_2H_4
$N_2 + h\nu \rightarrow N(^2D) + N(^4S)$	1.5		−0.25
$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2$	1.5	0.28	0.41
$CH_4 + h\nu \rightarrow CH_3 + H$	1.5		0.30
$H + CH \rightarrow C + H_2$	12.7	−0.40	−0.30
$C_3H_2 + CH_4 \rightarrow C_3H_3 + CH_3$	12.7	0.26	0.29
$C_3H_2 + C_2H_4 \rightarrow C_5H_5 + H$	12.7		−0.27

nevertheless be traced back to the database update (notably to the reaction $CH + CH_4$). For nitriles, the quenching reaction $N(^2D) + Ar$ appears also as a key factor, although it is rather well-known ($F = 2$).

Bimodality of Density Profiles. As seen in Figure 4, the Monte Carlo sampling procedure reveals outlying profiles of the mole fraction of some species as C_2H_2. The dispersion of the profiles may extend over several orders of magnitude from 600 km up to 1300 km. With the new simulations, these profiles are filtered out to some extent.

Studying the origin of such high-altitude outlying profiles for C_2H_2 and C_2H_4, Dobrijevic et al.[23] showed that the chemical system may explore two different chemical regimes, because of the large uncertainties taken for two key reactions, $CH + CH_4$ (R1) and $CH + H$ (R2). It was also shown that this behavior could be avoided if the product of the uncertainty factors could be lowered from $F_{R1} \times F_{R2} = 3.4 \times 12.7 = 43.2$ to $F_{R1} \times F_{R2} < 1.4$ at 1200 km. The update of reaction R1, reducing its uncertainty factor from 3.4 to 1.12 (see Table 3) is insufficient to reach this threshold, and the bimodality can still be observed in the new simulations, although with a reduced amplitude (Figure 4).

The list of key reactions at 1200 km for C_2H_2 and C_2H_4 is reported in Table 4. The reaction $CH + H$ is still present, whereas the reaction $CH + CH_4$ is not. A notable feature of this list of key reactions is that the reactions responsible for the large uncertainty in C_2H_2 and C_2H_4 densities are not systematically the most uncertain ones. The uncertainty factors at 1200 km reported in Table 4 range from 1.5 to 12.7. Moreover, this list emphasizes the fact that the key reactions specifically correlated to the considered compounds are not necessarily their primary production or loss mechanisms but could well be reactions further along in the reaction network.

Identification of New Key Reactions. Establishing a new list of key reactions is the best way to stimulate an improvement in model predictivity. We recall that key reactions are those that affect most strongly the precision of model predictions.

Dobrijevic et al.[23] targeted their study of key reactions on the important neutral species C_2H_2 and C_2H_4 with bimodal concentrations at high altitude, as shown in the previous section. In the present study, we aim at a general improvement of model predictivity, and we are therefore looking for globally important reactions. Such reactions can be identified as the ones that have significant correlation coefficients with the densities of numerous species.

Table 5 lists the reactions contributing significantly (with a RCC larger than 0.2 in absolute value) to the uncertainties of more than 15 species, for a representative set of altitudes (300, 600, 900, and 1200 km). Reactions appearing as important at a single altitude only have been omitted from the list. The procedure was applied to the old and new simulations to ascertain the effect of the database update on the list of key reactions.

TABLE 5: Most Influential Reactions at Selected Altitudes[a]

	reactions	300 km		600 km		900 km		1200 km	
		old	new	old	new	old	new	old	new
I	$H + {}^3CH_2$			14		27		28	
	$CH + CH_4$	14		33		46		45	
	$CH_3 + CH_3$	37		26					
	$C_4H + C_2H_4$			19		16		16	
II	$H + C_2H_2 + M$	49	50	19	21	16	19	16	18
	$C_3H_2 + CH_4$	13	17	25	23	35	36	43	41
	$N_2 + h\nu$			14	17	20	24	25	28
	$CH_4 + h\nu$				11	16	20	21	25
III	$C_6H_6 + h\nu$		18		19		12		13
	$H + CH$				15		23		20
	$C_3H_2 + C_2H_4$						16		19

[a] The influence of a reaction is quantified by the number of species having input−output absolute rank correlation coefficients larger than 0.2 with this reaction. Only reactions with one score larger than 15 are reported.

For instance, at 1200 km in the new simulations, the reaction $C_3H_2 + C_2H_4$ contributes significantly to 41 species, i.e., about one-third of all 127 species, which is much more than all other reactions at this altitude. At the same altitude, $CH + H$, identified above as a key reaction for C_2H_2 and C_2H_4 contributes to one-sixth of all species.

The set of globally influential reactions is rather small. We can distinguish three classes of reactions:

(I) reactions that were considered as key reactions in the old simulations and lost this status following the database update,

(II) reactions with unchanged key reaction status, and

(III) reactions that became globally important following the database update.

Set I is the clear illustration that the study at low-T has a strong impact on model predictivity. All reactions in this class were key reactions for the old simulation, with a strong impact in a large range of altitudes. For instance $CH + CH_4$ has the highest scores in Table 5, previously affecting more than 45 species in the ionosphere. A consequence of the update of their uncertainty factors in agreement with low-T measurements is that their impact is now considerably reduced to the point where they are not key reactions any more, at any altitude.

Sets II + III constitute the new list of key reactions, which should be studied in priority in representative conditions of Titan's atmosphere ($T = 71-175$ K, $P < 0.2$ Torr and N_2 as background atmosphere). Two reactions have already been studied at room temperature but are in need of low-T measurements: $H + CH$ and $H + C_2H_2 + M$.

Only two key reactions have *estimated* reaction rate coefficients: $C_3H_2 + CH_4$ and $C_3H_2 + C_2H_4$. It is noticeable that the sensitivity analysis is a very selective process, in the sense that it does not select *all* reactions with large uncertainty factors, especially in the case of estimated reaction rate coefficients, but only important ones.

The remaining three are the photolyses of N_2, CH_4, and C_6H_6. We adopted in the present work a lower limit $F = 1.5$ for the uncertainty factors related to the whole set of photodissociation processes. To lower this value would greatly improve the accuracy of the modeling of Titan's atmosphere, but this would require lowering the uncertainty factors associated with the absorption cross sections, the quantum yields, and the actinic flux, which requires an extensive investigation beyond the frame of the present study.

Conclusion

Following Hébrard et al.,[20] we have reevaluated the uncertainties on rate coefficients of reactions with low-*T* measurements. We have shown that this database update improves considerably the precision of model predictions. However, many species are still affected by large uncertainties. A set of key reactions responsible for this state of affairs has been highlighted. These are reactions for which an improvement in low-*T* rate constant precision is expected to produce a global improvement in the model. Among those, only two are reactions with *estimated* rate constants. For these reactions, experimental studies or theoretical estimations are pressingly needed. Photolyses of major species appear more and more as a limiting factor in the quest for improved accuracy and precision.

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