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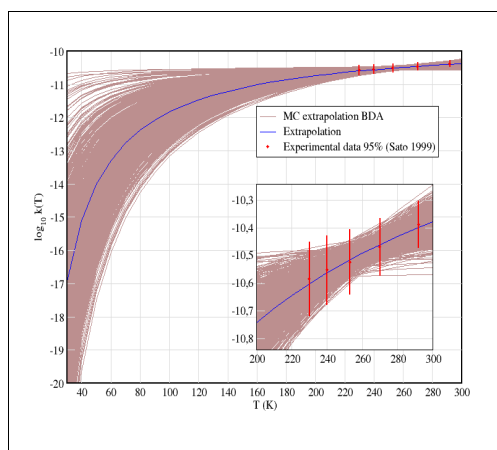
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## How measurements of rate constants at low temperature increase the predictivity of photochemical models of Titans's atmosphere

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Kinetic data measured at low temperatures are very sparse; for instance, in state-of-the-art photochemical models of Titan atmosphere, less than 10% of the rates have been measured in the relevant temperature range (100-200 K) [1-3]. A consequence is that photochemical models rely mostly on low-T extrapolations by Arrhenius-type laws. There is more and more evidence that this is often inappropriate [4], and low T extrapolations are hindered by very high uncertainty [1] (Fig.1). The predictions of models based on those extrapolations are expected to be very inaccurate [2,5].



**Figure 1.** Uncertainty of low temperature extrapolation for the  $N(^2D) + C_2H_4$  reaction rate, from measurements in the range 225 - 292 K [K. Sato *et al.* (1999) *J. Chem. Phys. A* 103, 8650], assuming an Arrhenius law (blue line). The sample of rate laws is generated by Monte Carlo uncertainty propagation after a Bayesian Data re-Analysis (BDA) of experimental data.

A dialogue between modellers and experimentalists is necessary to improve this 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 on Titan atmospheric chemistry [5, 6].

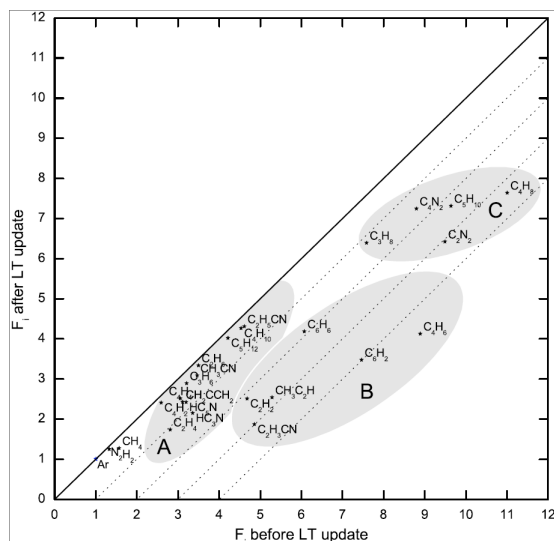
The main difficulty of this scheme is that it requires a lot of inputs, mainly the evaluation of uncertainties for extrapolated reaction rates. Although a large part has already been achieved by Hébrard *et al.* [1], extension and validation requires a group of experts. A new generation of collaborative kinetic database is needed to implement efficiently this scheme. The KIDA project [7], initiated by V. Wakelam for astrochemistry, has been joined by planetologists with similar prospects. A result from these meetings was the reevaluation of the uncertainties associated with *measured* low-T reaction rates [e.g. 8, 9].

The impact of this database update on the predicted densities of neutrals species in Titan's atmosphere is remarkable. There is a general precision improvement (Fig. 2), notably for species of group B in Fig. 2, but some species densities remain poorly predicted (group C in Fig.2). Using these results, we generated a new list of key reactions, *i.e.* having a strong impact on the

precision of model predictions, for which better estimation will have to be obtained, either experimentally or theoretically.

### References

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**Figure 2.** Comparison of uncertainty factors of stable neutral species predicted by a photochemical model of Titan's atmosphere at 1200 km, using the database of Hébrard 2006 [1] (before low-T (LT) update) and the updated database (after LT update). Points close to the diagonal line have a small uncertainty improvement (group A), whereas points far from it have a large uncertainty gain (group B). Species of group C undergo some improvement, but remain very uncertain ( $F > 5$ ).