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Comment on "Photodestruction of PAHs in the interstellar medium I. Photodissociation rates for the loss of an acetylenic group"

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In the beginning of this paper (Allain et al. 1996), the authors make a comparison between their results concerning the photofragmentation of PAHs and the predictions of an older paper on the same topic "Photo-thermo-dissociation..." (Léger et al. 1989) hereafter referred as PTD. However, it appears that the basis of this comparison is not clearly defined, which can induce some confusion for a reader not acquainted with the formalism of unimolecular reactions.

A rapid glance in Fig. 2 of Allain et al., and in the text related to it, would lead to the conclusion that the PTD model, based on the Inverse Laplace Transform (ILT) method (Forst 1972) is definitely not a good one, since it gives numerical results up to ten orders of magnitude too low. But, what is not stated clearly, neither in the caption, nor in the text, is that the different methods of calculation of the rate are applied to different fragmentation pathways: the ILT method is used to calculate the rate of loss of a single carbon atom, while the RRK formalism is used for the loss of an acetylenic group. This point deserves two comments.

On the one hand, concerning the fragmentation pathway, the paper PTD was "not directly based on reactions with PAHs" merely because no experimental data concerning the photofragmentation of PAHs was published at the time it was written. Besides the dehydrogenation process, the only pathways for which data could be available, by extrapolation of properties of bulk graphite, were the losses of C, C_2 and C_3. With the increasing number of experiments, it now appears that these processes are not relevant for the destruction of PAHs, but this has nothing to do with the choice of any particular method of rate evaluation. Moreover, at the end of the PTD paper, we clearly stated that, owing to the experimental results of Ruhl et al., the loss of C_2H_2 "would have to be taken into account in the determination of the minimum size of PAH".

On the other hand, if one wants to compare the accuracy of different calculations, the comparison has to be done on the same physical process. In the present case, this could have been done for the dehydrogenation process. All the coefficients needed to calculate the rate of hydrogen atom loss from an arbitrary PAH are summarised in the paper Allain et al. As an example, Fig. 1 compares, for naphthalene and coronene, the dehydrogenation rates obtained using the RRK and ILT formalism. As can be seen, the discrepancy between the two methods is now not larger than two orders of magnitude. This uncertainty does not exceed the range that can be expected for any model only using two parameters (E_0, k_0) to deal with the whole PAH family, without accounting for the particularity of each molecule. Moreover, it can be noticed that, if the experimental data of Jochims et al. (1994) is closer to the RRK result for coronene, the opposite is true in the case of naphthalene.

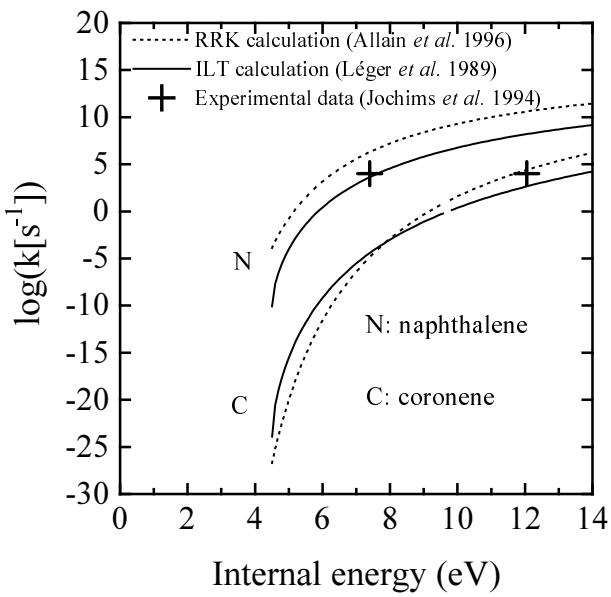

Fig. 1. Rates of hydrogen loss for two PAH cations, calculated from RRK and ILT methods.

Then the ILT calculation appears to work at least as well as the RRK one when applied to the same process. But, it has to be reminded that, while the RRK parameters have been fitted to reproduce experimental data, those used in the ILT calculation are only based on the knowledge of the binding energy and on statistical physics considerations. The PTD model has then a

predictive nature. This is possible because, in the ILT formula, E_0 is the dissociation energy, the same which appears in the Arrhenius law[1]. On the opposite, the RRK formula is based on the so-called classical approximation for the density of state. To compensate for the poor quality of this approximation, the parameter E_0 has to be modified and becomes a mere fitting parameter, "only approximately related to the bond dissociation energy".

Therefore, the criticisms of the ILT calculation are not founded. This formalism, based on parameters with a clear physical meaning, gives dissociation rates with at least the same accuracy than the RRK one. Moreover, if both calculations are based on experimental results, the ILT method becomes better, especially for the evolution of the rate near the dissociation threshold, which cannot be reproduced correctly using the RRK formula.

References

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[1] E_0 is actually the dissociation energy and not "the sum of the dissociation energy and the zero point energy" as erroneously stated by Allain et al.

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