Rate Constants: When the problem is not with DFT

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ABSTRACT

The calculation of rate constants using transition state theory is considered chronically difficult, as small variations in the Gibbs free energy barriers translate into reaction rates that can be wrong by orders of magnitude. In this talk, I will concentrate on two problems related to the estimation of rate constants and show that sometimes, one is so obsessed by the accuracy of the underlying calculation that does not realize why the full approach is wrong. The first example relates to the thermal *Z*/*E* isomerization of heteroaromatic azo-based photoswitches [1]. The second example concerns the calculation of luminescence lifetimes of Ru polypyridine complexes [2]. In both cases, DFT is used, and in contrast to previous blames to the quality of DFT, excellent agreement with the experiment is achieved – provided that the correct intermediate species are considered. In summary, it is shown that, calculations can be right for the right reason, even if using DFT…

References

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