

Long-Range Transition State Theory at Low Temperatures.

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Reliable predictions for the abundance of chemical species in the interstellar media and their time-evolution requires accurate estimates of the rate constants for hundreds of gas-phase reactions. Theoretical calculations of these rate constants are complicated by two facts. First, in the relevant temperature range (10-50 K), the important reactions are barrierless, which implies that the transition state for such a reaction is not automatically defined by the critical features of the potential energy surface such as saddle points. Instead, the transition state for such reactions should be determined variationally as a function of the conserved values of the total energy and angular momentum. Second, relatively weak effects, such as the spin-orbit electronic coupling and its interference with the long-range potential energy terms, which are usually neglected at higher temperatures, must now be properly accounted for. Recently, we have developed a simplified version of variational transition state theory, termed long-range transition state theory (LR-TST), which is applicable at moderately low temperatures when the "capture bottle neck" lies in the long-range interaction region. While this theory is purely classical, it is still applicable for most of the reactions of interest at the temperatures important for astrochemistry. For some reactions, however, the classical description is not sufficient and in this talk we discuss how to generalize the theory to properly account for quantum effects. We also discuss two important types of reactions for which the quantum effects are important. One type involves a reactant with a large rotational constant. Examples of such species are the important free radicals $\text{CH}(^2\Pi)$, $\text{OH}(^2\Pi)$, or $\text{NH}(^3\Sigma^-)$. We show how to obtain a low temperature limit for such reactions. Quantum effects are also important when one of the reactants is an open shell atom. Usually, the main multipole interaction term for such a reaction is the interaction of the atomic quadrupole with the electric field of the second species. This interaction, however, interferes with the spin-orbit coupling of the atom. We show how to take into account the interplay between these two interactions in the potential energy calculation. As an example of this calculation we consider the capture rate for the $\text{O}(^3P) + \text{OH}(^2\Pi)$ reaction.

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