Using long-range TST for predicting the rate constants of barrierless reactions at low temperatures

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Abstract

Modelling of the chemistry in the interstellar media requires as input the rate constants for all the reactions that are likely to influence that chemistry. Because of the very low temperatures, only reactions that proceed on a potential energy surface without any barrier separating the reactants and the products are important. In these conditions the conventional Arrhenius-like expressions of the rate constants in terms of the properties in the vicinity of the saddle point are not applicable. Experimental measurements of the rate constants at such temperatures are also very difficult. In this talk we discuss the application of a form of variational transition state theory appropriate for long-range interactions to the barrierless reactions important to astrochemistry. We demonstrate, using the reactions of $O(^3P)$ with alkenes, $CN+C_2H_6$, and H_3^+ with O and CO as examples, that this long-range TST, in conjunction with state-of-the-art electronic structure calculations and a two-transition-state model, allows one to reliably predict the rate constants of barrierless reactions in the temperature range from 10 to 100 K and higher.

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