

Influence of rotation and isotope effects on the dynamics of the N(D-2)+H-2 reactive system and of its deuterated variants

Abstract: Integral cross sections and thermal rate constants have been calculated for the N(D-2)+H-2 reaction and its isotopic variants N(D-2)+D-2 and the two-channel N(D-2)+HD by means of quasiclassical trajectory and statistical quantum-mechanical model methods on the latest ab initio potential-energy surface [T.-S. Ho, J. Chem. Phys. 119, 3063 (2003)]. The effect of rotational excitation of the diatom on the dynamics of these reactions has been investigated and interesting discrepancies between the classical and statistical model calculations have been found. Whereas a net effect of reagent rotation on reactivity is always observed in the classical calculations, only a very slight effect is observed in the case of the asymmetric N(D-2)+HD reaction for the statistical quantum-mechanical method. The thermal rate constants calculated on this Potential-Energy Surface using quasiclassical trajectory and statistical model methods are in good agreement with the experimental determinations, although the latter are somewhat larger. A reevaluation of the collinear barrier of the potential surface used in the present study seems timely. Further theoretical and experimental studies are needed for a full understanding of the dynamics of the title reaction. (c) 2005 American Institute of Physics.