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The effect of spin-forbidden transitions in N(²D)+H_2 collisions: a trajectory surface hopping analysis

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INTRODUCTION

The reactions of N(²D) play an important role in plasma and atmospheric chemistry.[1] The rate constants for the quenching of such radical have been measured via multiple reactions[1], and the specific case of quenching via N(²D) +H_2→NH($X^3\Sigma^-$)+H has found good agreement among different experiments.

Theoretically, there are 5 electronic potential energy surfaces (PESs) that correlate to the N(²D) +H_2 channel, but normally only the lowest (²A") state of NH_2 is considered. However, nonadiabatic effects can play a role in reaction dynamics in multiple ways. For example, the first two electronic PESs of NH_2 (²A" and ²A') are Renner-Teller coupled, and this effect has been studied in reaction dynamics[2]. In this work we study, for the first time, another nonadibatic coupling on this benchmark system: the spin-orbit induced transitions. This will allow the prediction of how much N(²D) can be quenched to the ground N(⁴S) state by the title collision, which may be experimentally detectable.

METHODS

In this work we employ two accurate analytic PESs for NH_2[3,4]: the ²A" and ⁴A". These PESs are eigenvalues of the spin-free Hamiltonian. The coupling between them comes from the spin-orbit operator (H_{SO}), and its matrix elements are computed at the MRCI level with the aug-cc-pVQZ basis set over a set of 600 NH_2 geometries, which were fitted to a Gaussian-type function. The dynamics are then performed with the quasiclassical trajectory method, and whenever a doublet/quartet crossing is reached, the Landau-Zenner transition probability is calculated in order to determine whether a hopping occurs.

RESULTS AND DISCUSSION

The cross sections for the spin-forbidden reaction[5] is given in Figure 1. It is found that the reaction threshold is reduced by rotational excitation on H_2. For higher translational energies, this excitation inhibits the spin-forbidden cross section, due to a lower hopping probability[5]. The formation of long-lived complexes is also studied, which enhances reaction probability for specific initial conditions. Further details on the collision will also be explored.

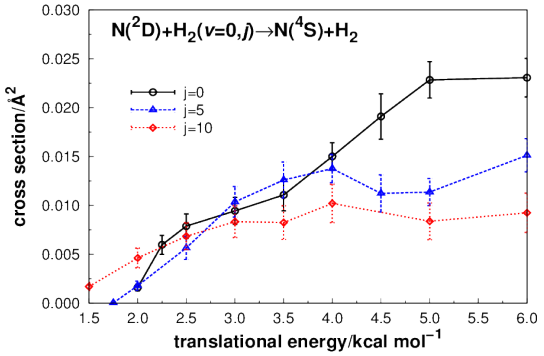

Figure 1. Excitation function for the spin-forbidden reaction.

CONCLUSIONS

We have performed the first theoretical predictions of the spin-orbit coupling for the NH_2 system. High level *ab initio* calculations of the SO coupling were performed and fitted to an analytic function. This fit was employed to study the dynamics of the N(²D)+H_2→N(⁴S)+H_2 reaction.

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