THE H_2 + H_3^+ REACTION: DYNAMICALLY BIASED STATISTICAL MODEL FOR THE ORTHO/PARA CONVERSION

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A treatment combining statistical and quasiclassical trajectories methods is here presented[1] to describe the evolution of the title reaction. The work can be considered as a further extension of the previous statistical method by Park and Light[2]. While the nuclear spin selection rules are properly taken into account by the statistical method, the dynamical contribution is introduced in the so-called scrambling probability. The scrambling matrix, which depends on the collision energy, is generated by means of quasiclassical trajectories and determines the probability for the identity/hop/exchange mechanisms to occur.

It is also found that in the quasiclassical calculations the high zero-point energy (ZPE) of the fragments, which is randomly distributed among all the degrees of freedom, shortens the lifetime of the H_5^+ complex. Since reactants and the H_5^+ complex have similar zero-point energies, a new ZPE-biased scrambling matrix is obtained by reducing "artificially" the ZPE in the QCT calculations. This new matrix yields a good agreement with the recent experiments by Crabtree et al.[3] for the hop/exchange ratio at room temperature. At lower temperatures, however, the present simulations predict too high ratios because the biased scrambling matrix is not statistical enough. This demonstrates the importance of applying quantum methods to simulate this reaction at low the temperatures of astrophysical interest.

All the calculations in the present work have been performed on a recent global potential energy surface[4], instead of the long-range ion-induced dipole interaction previously used[2].

References

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