Rotational energy transfer in collisions of ammonia with rare gas atoms and H₂

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Synopsis We investigate inelastic collisions of ammonia NH₃ and its isotopologue ND₃ with rare gas atoms or molecular hydrogen. We use state of the art ab initio potential energy surfaces to study the low energy dynamics of the collision by means of the quantum-mechanical close-coupling method. We discuss the experimental implications of our work.

Collisions of ammonia with rare gas atoms and H₂ have been the subject of a large number of studies, both theoretical and experimental, mainly focusing on rotationally inelastic scattering in an astrophysical context. Indeed, NH₃ is often used as a probe of the physical conditions in various interstellar environments [1], and accurate values for the cross sections and rate constants for NH₃-He and NH₃-H₂ collisions are required in order to interpret observations. Recent experimental advances have renewed interest in these systems by allowing measurements of quantum-state-resolved integral and differential cross sections in crossed beam experiments [2, 3, 4], which can be directly compared to theoretical predictions based on accurate potential energy surfaces and quantum-mechanical scattering calculations. The same techniques, combined with a Stark-decelerated beam of NH₃, will allow the measurement of integral and differential cross sections at very low collision energies, where the cross section is dominated by resonances that are very sensitive to the details of the potential energy surface [5]. Finally, inelastic collisions of NH₃ with He and Ne are also of interest in order to understand how the rotational cooling of ammonia in a buffer gas cell proceeds [6,7].

In this context, we have recently investigated the rotationally-inelastic scattering of NH₃ and ND₃ by rare gas atoms or H₂ using new potential energy surfaces obtained by means of the coupled cluster method with single, double and perturbative triple excitations (CCSD(T)) [1, 8]. The close-coupling method is employed to calculate integral and differential cross sections at low collision energy (up to 300 cm⁻¹) corresponding to rotationally inelastic scattering. We compare the theoretical predictions with the experimental data and discuss the implications for the sympathetic cooling of ammonia in collisions with rare gas atoms. We also demonstrate the importance of explicitly taking into account the umbrella (inversion) motion of NH₃ in order to obtain accurate scattering cross sections in the cold regime.

References

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