Rotational energy transfer in collisions of ammonia with rare gas atoms and H_2

Jérôme Loreau*[1] and Ad van der Avoird†

* Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles (ULB), Brussels, Belgium
† Theoretical Chemistry, Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

Synopsis We investigate inelastic collisions of ammonia NH_3 and its isotopologue ND_3 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 H_2 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, NH_3 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 NH_3-He and NH_3-H_2 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 NH_3, 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 NH_3 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 NH_3 and ND_3 by rare gas atoms or H_2 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 NH_3 in order to obtain accurate scattering cross sections in the cold regime.

References

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[1]E-mail: jloreau@ulb.ac.be