Theoretical modeling of Penning ionization reaction of molecular hydrogen and metastable helium

(Work plan of Dr. Wojciech Skomorowski)

The goal of the visit is to carry out quantum-dynamical calculations of the Penning ionization rates in the collisions between molecular hydrogen and metastable helium atoms. To this end, we plan to apply a novel method for coupled-channels reactive scattering calculations, developed in the group of Theoretical Chemistry at Radboud University in Nijmegen [1]. We will investigate collisional energies starting from room temperature down to milikelvin regime, and consider different initial rotational states of H_2 molecule and its isotopologues. The proposed theoretical research is directly motivated by ongoing experiments on Penning ionization and cold collisions, conducted in the group of Dr. Ed Narevicius (Weizmann Institute of Science) [2].

Penning ionization is a process in which electronically excited reagent $A^\star$ collides with other species B, causing its ionization:

$$A^\star \ + \ B \ \rightarrow \ A + B^+ + e^-.$$

This type of reaction has been studied experimentally and theoretically since a few decades [3]. However, only recently, experimental methods based on merged molecular beams have been developed and enabled to tune and control the collisional energy of the reagents by a few orders of magnitude. In this way, Penning ionization turned out to be the first *ever* reaction observed experimentally in the energy range spanned from hundreds of Kelvin down to milikelvin [4]. An appealing feature of Penning ionization is the fact that the reaction products are ions, which makes the measurements of rates much easier and results in clean experimental signal. Moreover, the reaction can occur at any temperature, even at ultarcold regime. From the theoretical point of view, particularly interesting is the cold and ultracold regime, where the reaction rates are determined by resonances and quantum threshold laws.

Focus of our study will be Penning ionization rates in the reaction between hydrogen molecule and helium atom in the metastable ^3S state, at low temperature. We will apply a coupled-channels reactive scattering method in which only the reactant arrangement is explicitly taken into account [1]. This approach assumes that once a reactive complex is formed at a sufficiently short intermolecular distance, the reaction proceeds irreversibly. Irreversibility is achieved by applying correct boundary conditions, which allow the flux of colliding particles to disappear into reactive channels. We will test different possible choices of the reactive boundary conditions, based on either linear slop or constant values of adiabatic channels in the short range. The optimal choice of boundary conditions should guarantee invariance of the final reaction rates with respect to small changes in the position of the point which defines the irreversibility of the reactive process.

The method requires knowledge of only the real part of interaction energy. We will apply the interaction potential calculated with a variant of coupled cluster method [CCSD(T)], in which the convergence to the desired excited state is enforced by proper rotation of the occupied orbitals during the initial Hartree-Fock calculation [5]. In the dynamical calculations, the potential will be expanded in terms of Legendre polynomials. The expansion terms will be smoothly connected with long-range van der Waals constants, obtained from separate computation based on a perturbative approach. This step is especially important for ultralow collision energies, where the long-range part of the interaction potential is crucial for the outcome of the collision. We will consider different isotopologues of hydrogen molecule: H_2, HD and D_2. Particularly interesting will be collisions with H_2 molecule, which exists in two isomeric forms (*ortho* and *para*) and each isomer can be investigated in an experiment separately [2]. Due to permutation symmetry of a wave function describing two identical nuclei, only

even rotational states are allowed for $para{-}H_2$ (the lowest state being $J = 0$), and only odd are allowed for $ortho{-}H_2$ (the lowest state being $J = 1$). The spin symmetry implies that anisotropic terms of the interaction potential will couple scattering channels differently in collisions with $para{-}H_2$ and $ortho{-}H_2$, which may lead to significantly distinct reactive behavior, in particularly at low temperature. These symmetry aspects of the collisions will be carefully investigated in our study.

Insights from our theoretical work will serve as a basis to interpret results of ongoing experiments on Penning ionization with hydrogen molecule.

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