Electron detachment process in collisions of negative hydrogen ions with hydrogen molecules

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Abstract. Investigation of the nonadiabatic nuclear dynamics in collinear and perpendicular collisions of negative hydrogen ions with hydrogen molecules is performed by the branching classical trajectories method. Quantitative assessment of the detachment probability H^- in collisions with H_2 is obtained for energy range 0.5 – 30 eV and the decay mechanisms are analyzed.

1. Introduction

Collisions of negative hydrogen ions with hydrogen molecules are of fundamental interest as a prototype of negative-ion – molecule scattering with the presence of an autoionization channel. In addition, they are of practical importance for the formation and decay of negative ions in plasma, including various astrophysical applications [1].

Theoretical studies of the collision complex H_3^- have more than a 50-year history. In spite of the fact that H_3^- is the simplest polyatomic negative ion, a study of its electronic structure and nuclear dynamics by strict quantum-mechanical methods encounters severe difficulties. This is mainly because of instability of the H_3^- complex with respect to an electron emission. As a result, the ground and electronically excited states of H_3^- are quasi-stationary in a broad region of the configuration space. Conventional *ab initio* calculations of quasi-stationary states are not possible, and alternative theoretical approaches should be used. Such approaches are well developed and successfully applied to quasi-stationary states of diatomic molecules [2], however, their generalization to polyatomic molecules is complicated.

A treatment of the nuclear dynamics of $H^- + H_2$ collisions by strict quantum-mechanical methods also meets severe difficulties. The main reason is in accounting non-adiabatic transitions both between discrete states and between discrete-continuous states. Such transitions are usually neglected or taken into account by means of restricted ways [3-5].

In the present study, nonadiabatic transitions of both types are taken into account. The nonadiabatic nuclear dynamics is studied by means of the branching classical trajectory method which takes into account nonadiabatic transitions between discrete states. Nonadiabatic transitions between discrete and continuous states are taken into account via quasi-stationary widths as a part of the local complex Potential Energy Surfaces (PESs) calculated by means of the Generalized Diatomics-In-Molecule (GDIM) method [6] for the ground and excited states of H_3^- [7]. It should be pointed out that electronic structure calculations are performed «on-the-fly», which does not require performing any analytic fit of the PESs. This approach allows us to perform a nonadiabatic treatment for an arbitrary nuclear configuration, which ultimately makes it possible to calculate the cross section and the rate constant of the process, not only for a distinguished geometries, as it was performed in the past [4,5].

2. Potential energy surfaces

The potential energy surface (PES) of the ground electronic state of H_3^- has been calculated by various methods [6-13] (see also references therein), including standard *ab initio* methods [8-10,13], although standard *ab initio* calculations are reliable only for stationary states. The PESs calculated by this way can be used for nuclear dynamics at low-energy collisions, when nonadiabatic effects are negligible. For electronically excited states (which are predominantly quasi-stationary) and for the ground state in

the regions of quasi-stationarity, PESs cannot be calculated correctly by standard *ab initio* methods. An attempt of the *ab initio* calculation of the first excited state was performed in [10], where the result was a PES of the neutral quasimolecule H_3 with an additional free electron. In case of quasi-stationarity for the ground and excited states, nonadiabatic effects for discrete-continuous transitions can be accounted within the complex potential energy approximation by an imaginary part of a complex PES, the so-called quasi-stationary width.

The H_3^- PESs (as well as the nonadiabatic couplings [3]) were calculated in the full three-dimensional configuration space including the quasi-stationary regions by the conventional Diatomics-In-Molecule (DIM) method [11, 12] and also by the Generalized Diatomics-In-Molecule (GDIM) method [4,6,7]. It should be noted that the GDIM, in contrast to the standard DIM method allows one to calculate not only the real part of the local (and, in general, nonlocal) complex potentials, but their imaginary parts responsible for the decay of quasi-stationary states. In this regard, in order to account for the nonadiabatic effects of both types we have used the local complex PESs of the ground and the first excited states, the PESs calculated by GDIM [7]. In the regions of stationarity of the ground state, the GDIM PES is in a good agreement with the *ab initio* PES [8,9,13], although the former has slightly lower accuracy that does not significantly affect on the nuclear dynamics.

3. Nuclear dynamics

As mentioned in the Introduction, the branching classical trajectory method [18] is used for studying of the nonadiabatic nuclear dynamics. The method takes into account various nonadiabatic effects. Nowadays, it is generally accepted that the classical trajectory method is an efficient tool to analyze of elementary processes and calculate their quantitative characteristics. In particular, there are many papers, including those devoted to collisions $H^- + H_2$, which demonstrate the high efficiency of the method of classical trajectories, see, e.g., [14-17] and references therein, as a tool to obtain a good quantitative agreement with both accurate quantum-mechanical results and experimental data.

The idea of the branching classical trajectory method implemented in this paper is the following. The classical trajectory starts on the PES of the ground state in the asymptotic region with an asymptotic weight (population). When a local minimum of a splitting between the ground and first excited states PESs is found along a trajectory, the trajectory splits into two trajectories: a child and a parent ones. A population of the child and the parent trajectories are determined by the nonadiabatic transition probability calculated within the Landau-Zener model. Such branching can occur many times, that allows one to take into account nonadiabatic transitions between discrete states. To calculate a nonadiabatic transition probability within the Landau-Zener model, we used a novel formula obtained in [18]

$$P_{if}^{LZ} = exp\left(-\frac{\pi}{2\hbar}\sqrt{\frac{Z_{if}^3}{\ddot{Z}_{if}}}\right), \quad (1)$$

where Z_{if} is a minimum of an adiabatic PES splitting along a trajectory, and $\ddot{Z}_{if}$ is the second derivative with respect to time.

In the case when a trajectory passes a quasi-stationarity region, the system can make a nonadiabatic transition from a discrete state to continuum states (an electron detachment). The nonadiabatic transition probability P_d reads [4]

$$P_d(E_c) = 1 - exp\left(-\frac{1}{\hbar}\int_0^\infty \Gamma[Q(t)]dt\right), \quad (2)$$

where Γ is the quasi-stationary width of the PES along the individual trajectory, Q is the vector of generalized coordinates. The total probability value is then obtained by averaging over all trajectories with regard to their populations.

The generalized coordinates and the equations of motion, given in the paper [19], are used for the classical trajectory calculations. To visualize the trajectories in the case of collinear and perpendicular configurations the Jacobi coordinates were used. The equations of motion are integrated numerically

by the fourth-order extrapolation Adams method with fixed step. To start integration, the fourth-order Runge-Kutta method is used. The accuracy of the numerical solution was estimated by the total energy.

4. Results

The examples of the computed classical trajectories for collinear and perpendicular collisions along PESs for the ground and the first-exited states are shown in Figs. 1 and 2. In the same figures, the quasi-stationary regions of the ground and the first-exited states are shown by the colored contour plots as well. The Jacobi internal coordinates are used for these figures: r is an internuclear distance in the hydrogen molecule, and R is a distance between the nucleus of the hydrogen ion and the center of mass of the target diatomic molecule. It is seen that almost each trajectory along the ground state PES passes the regions of quasi-stationarity where the quasi-stationary width is nonzero. In this case, the electron detachment (discrete-continuum transition) probability is nonzero.

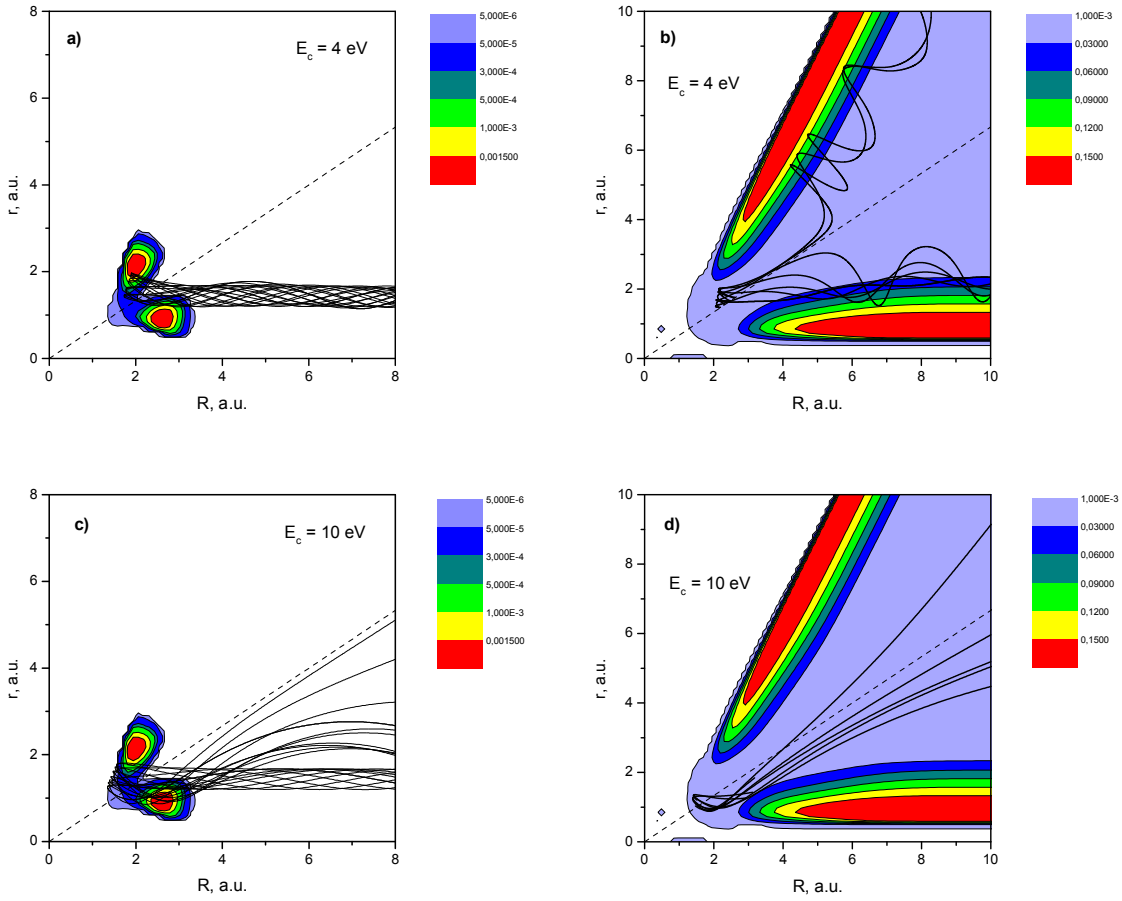

Figure 1. Classical trajectories in Jacobi coordinates along PESs of the ground (a, c) and the first excited states (b, d) for collinear collisions at the energies of 4 eV and 10 eV. The quasi-stationary widths (in atomic units) for the ground and the excited states are shown by the colored contour plots.

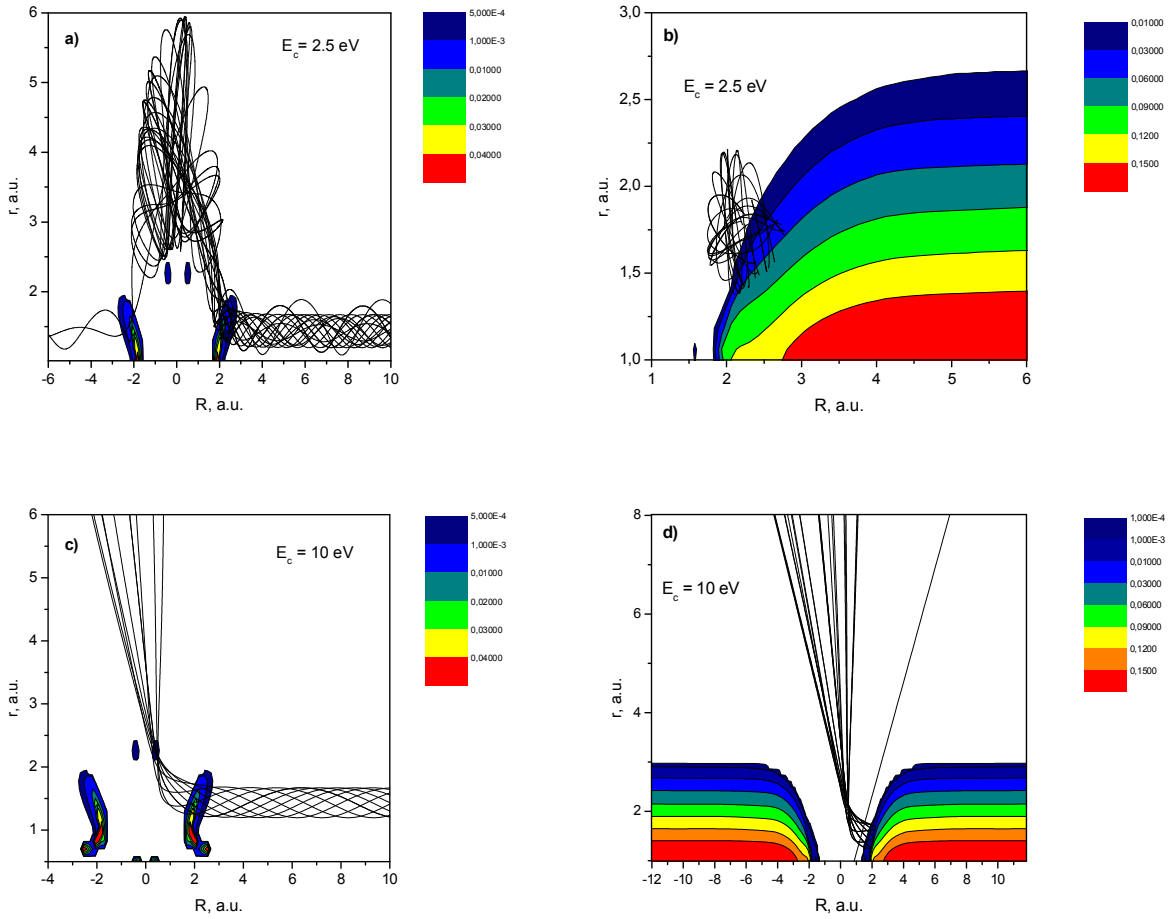

Figure 2. Classical trajectories in Jacobi coordinates along PESs of the ground (a, c) and the first excited states (b, d) for perpendicular collisions at the energies of 2.5 eV and 10 eV. The quasi-stationary widths (in atomic units) for the ground and the excited states are shown by the colored contour plots.

Figure 3 represents the calculated probabilities of a negative-hydrogen-atom decay in collinear collisions with a hydrogen molecule. The solid line 1 shows the result due to the direct mechanism: the detachment processes is based on quasi-stationarity of the ground state only. It is seen that the electron detachment process due to the direct mechanism has the energy threshold about 1 eV, the energy at which the trajectories get reaching the region of quasi-stationarity of the ground state. With increasing of the collision energy, the trajectories pass the regions with higher values of the quasi-stationary width. This increases the electron detachment probability. The probability has a maximum is around 2.5 eV. The further increasing of collision energy reduces time for a trajectory being in the quasi-stationary region, finally, this reduces the detachment probability. Note the peaks of the probability, in particular, the peak in the vicinity $E_c = 1$ eV. That peaks are the result of classical trajectories resonances due to the nuclei motion between two valleys of the ground state PES. These resonances involve the quasi-stationary regions in these valleys, and consequently increase the residence time of the anion in the quasi-stationary region.

Figure 3 also shows the electron detachment probability due to the alternative mechanism in addition to the direct mechanism (the dashed line). The alternative mechanism includes nonadiabatic transitions between the ground and the exited discrete states and the quasi-stationarity of the excited

states. The quasi-stationary width of the exited state is much larger than that for the ground state, therefore the detachment probability of the excited state is higher than the detachment probability for the ground state. However, at low collision energies E_c, the nonadiabatic transitions probability from the ground state to the excited state is relatively small, and the contribution of the alternative mechanism is negligible (see. Fig. 3). With increasing the collision energy, the nonadiabatic transition probability between the ground and first excited states increases, and the contribution of the alternative mechanism becomes more significant.

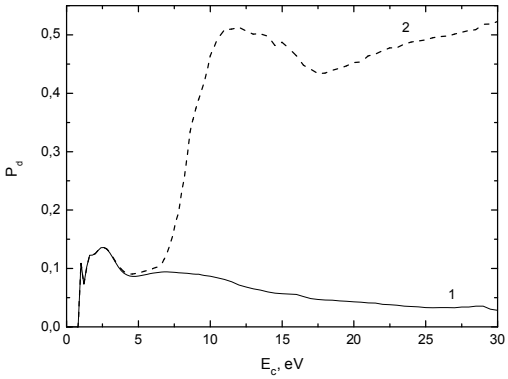

Figure 3. The negative hydrogen ion detachment probability in collinear collisions with hydrogen molecules as a function of the collision energy: 1 – calculation based only the quasi-stationarity of the ground state only; 2 – calculation taking into account the quasi-stationarity of both the ground and the first excited states of the anion, as well as non-adiabatic transitions between these discrete states.

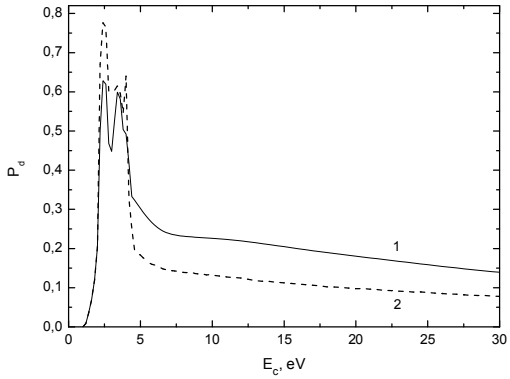

Figure 4. The same as in Fig. 3, but for perpendicular collisions.

At collision energies below 4 eV, the trajectories in the excited state are trapped in the potential well, where the quasi-stationary width significantly lower than in the asymptotic region. At the energy of 4 eV, dissociative channels get open for the excited state having a large value of quasi-stationary widths, resulting a significant increase for the electron detachment probability (see. Fig. 3). At energies greater than 7 eV, the alternative mechanism becomes dominant and determines the electron detachment process.

Figure 4 shows the detachment probability of the negative hydrogen ions at perpendicular collisions with hydrogen molecules. As in the case with collinear collisions, the threshold value of the detachment probability for the perpendicular geometry is about 1 eV. In the energy range from 2 to 4 eV the detachment probability reaches a maximum and has a resonance structure. At energies of 4 eV and higher, the probability begins to decrease. An interesting feature is the fact that the inclusion of an excited state in this case leads to reduce the probability, as compared with the detachment probability due to the quasi-stationary ground state (switched off nonadiabatic interaction between the ground and excited states). This can be explained by the fact that after the opening of the dissociative channels for the excited state, trajectories pass mainly through the region in which the width of the quasi-stationary has negligible values, that leads to small values of the electron detachment probability.

Both Figs. 3 and 4 shows that the electron detachment probabilities can reach substantial values, up to the value of 0.8, even at low collision energies. This clearly indicates that the electron-detachment channel should be taken into account in considerations of all processes in collisions of negative hydrogen ions with hydrogen molecules.

5. Conclusion

The investigation of the nonadiabatic nuclear dynamics in collinear and perpendicular collisions of a negative hydrogen ion with a hydrogen molecule is performed by the branching classical trajectories method. The quantitative assessment of the probability for decay of H^- in collisions with H_2 is obtained and the decay mechanisms is analyzed. It is proved that for low-energy collisions (from 1 to 5 eV) the direct mechanism associated with the quasi-stationarity of the H_3^- ground state dominates, whereas at high energies (higher than 5 eV), the alternative mechanism related to nondiabatic transitions between the ground and the excited discrete electronic states and with the quasi-stationarity of the excited state provides more significant contribution.

Acknowledgments

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