

Nonadiabatic Nuclear Dynamics in the Ammonia Cation Studied by the Branching Classical Trajectory Method

A. K. Belyaev*^{†1}, O. V. Lebedev* and W. Domcke[‡]

*Department of Theoretical Physics, Herzen University, St. Petersburg 191186, Russia

[†]Department of Physics and Astronomy, Uppsala University, S-75120 Uppsala, Sweden

[‡]Department of Chemistry, Technical University of Munich, Garching, D-85747 Germany

Synopsis The photoinduced nonadiabatic nuclear dynamics of the ammonia cation is studied by the branching classical trajectory approach. The time-dependent populations of different electronic states of the ammonia cation are calculated and are in good agreement with the results of full quantum calculations.

Many important physical and chemical reactions involve nonadiabatic transitions among various adiabatic electronic states. Nonadiabatic effects can be investigated in detail in small systems with numerically exact quantum dynamics methods. However, much less is known about nonadiabatic transitions in larger molecular systems, e.g. the radiationless decay of excited electronic states of polyatomic molecules.

While quantum dynamics calculations are costly or even impossible for somewhat larger molecules, the use of approximate classical or semiclassical methods continues to be an important alternative because of their lower computational costs and the physical insight they provide into the dynamics of a reaction. Mixed quantum-classical techniques are particularly promising. They treat the electronic motion quantum mechanically and the nuclear motion classically.

In the present work, the nonadiabatic radiationless decay dynamics in the ammonia cation is studied in full dimensionality (6D) with classical trajectory surface-hopping calculations. We are interested in the nonadiabatic dynamics which is induced by the photoionization of the neutral ammonia molecule to the 2E excited electronic state. Recently, *ab initio* multi-reference configuration-interaction calculations of the ground state and the degenerate excited state of the ammonia cation have been performed in the six-dimensional space of internal nuclear coordinates, and an analytical anharmonic three-sheeted surface has been constructed in the diabatic representation for this Jahn-Teller and pseudo-Jahn-Teller system [1]. This six-

dimensional three-sheeted potential-energy surface of the ammonia cation is used for the present classical trajectory calculation.

In the branching classical trajectory method, each trajectory branches into two trajectories after each traverse of a nonadiabatic region, the populations in each state being weighted according to the transition probabilities. This approach is similar to that used in Refs. [2, 3, 4] It yields results close to the full quantum treatment in (one-dimensional) atomic collisions. The nonadiabatic transition probabilities are calculated by novel formulae within the Landau-Zener model.

The calculated femtosecond time-dependent populations of different electronic states of the ammonia cation as well as a comparison with the results of full quantum calculations [1, 5] will be presented at the conference.

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References

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¹E-mail: belyaev@herzen.spb.ru