

THESES OF DISSERTATION

**Quasiclassical Trajectory Study of
Reduced Dimensionality Models of
 $CZ_3Y + X \rightarrow CZ_3 + YX$ Type Reactions**

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Introduction

Molecular reaction dynamics investigates the mechanism of elemental chemical reactions at atomic level. The theoretical studies of the dynamics helps us interpret the experimental results, draw universally applicable conclusions and give us a deeper insight on how the intra- and intermolecular interactions, the masses and the quantum state of reactants influence the microscopic mechanism of a reaction. In most of the investigated systems the Born-Oppenheimer (BO) approximation can be applied, thus the motions of electrons and nuclei can be separated. The sum of selected eigenvalue of the electronic Schrödinger equation (adiabatic state) and the Coulomb interaction energy between nuclei give the Born-Oppenheimer potential energy surface (PES) as a function of nuclear coordinates, which determines the forces between the nuclei. Within the BO approximation the quantum dynamical methods determine the wave function of the nuclear motion, by solving the Schrödinger equation of the nuclei. Nowadays the quantum dynamical simulations of the bimolecular reactions can be routinely performed in full detail (e.g. any total angular momentum value) for 3 and 4 atoms. For systems involving more than 4 atoms reduced-dimensionality (RD) quantum dynamical models need to be applied, in which some, assumedly less important, degrees of freedom are frozen. However it is not known what type of and how large error is caused by this approximation ie. in the determination of reaction cross sections, since we do not have full-dimensional computational results for comparison.

In quasiclassical trajectory (QCT) method of reaction dynamics, the motion of the nuclei is simulated classically on the PES, and the quantization of the vibrations of reactant molecules is taken into consideration by representing the initial state of the molecule by an ensemble of semiclassically quantized classical states which corresponds to the selected quantum state. The classical simulation can be performed without constraints for systems involving larger number of atoms, thus reduced-dimensionality models are usually not used in QCT simulations.

At present, for the description of the 6-atom $\text{CZ}_3\text{Y} + \text{X} \rightarrow \text{CZ}_3 + \text{YX}$ type reactions, the quantum dynamical model with least restrictions is the 8-dimensional model developed by Palma and Clary [*J. Chem. Phys.* 2000, 112 (4), 1859-1867], in which the CZ_3 moiety is constrained to C_{3v} symmetry. In my doctoral work with the aim of testing the goodness of

the Palma-Clary model, I applied that constraint in RD QCT calculations of the $\text{CH}'_3\text{H}'' + \text{H} \rightarrow \text{CH}'_3 + \text{H}''\text{H}$ reaction (H' , $\text{H}'' = \text{H}$ or D) and I compared the results of my RD QCT calculations with those of the FD calculations.

In quasiclassical trajectory methods, the initial ensemble of reactant molecules is usually prepared by the normal mode sampling method, which is based on the harmonic approximation. One of the shortcomings of this method is that the ensembles it yields are not stationary on the real, anharmonic PES of the molecule. In many systems, this non-stationarity of the initial ensembles causes an initial distance dependence of the calculated reaction cross sections, which manifest as waviness superimposed on the excitation function. This issue also arises in both FD and RD QCT simulations of the $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$ and isotopolog reactions and prevents the comparison of the results of the two models. Therefore we comprehensively studied the influence of the nonstationarity of rovibrationally ground-state methane ensembles on the reactivity parameters in the RD and FD cases, and sought for solutions to correct its induced error and to prepare stationary initial ensembles.

Applied Methods

During my doctoral work I wrote and used FORTRAN90 codes to perform the preparation of the initial states of quasiclassical trajectory simulations, the simulation of the trajectories and the evaluation of the trajectory results. Calculations were made on two potential energy surfaces: the ZBB3 PES developed by Bowman et al., and the CBE PES developed by Corchado et al. The integration of the Hamiltonian equations of motion was carried out in space-fixed Descartes coordinates and in the RD simulations the constraints were enforced by constraint forces determined with the Lagrange multipliers method.

Theses and Conclusions

1. As part of our research team, I contributed to the development of a general method based on the normal mode approximation for preparation the reduced- and full-dimensional ensembles of initial states of quasiclassical trajectory calculations and assignment of normal-mode quantum number at instantaneous states of trajectory. The methodology is based on numerical constructed vibrational kinetic energy expression in internal coordinates and therefore it is generally applicable in the knowledge of the coordinate transformation equations of different RD and FD models. I programmed the method into my own FORTRAN90 reaction dynamics codes, and tested its applicability on CZ₃Y (Y, Z = H or D) methane isotopologs in the following 4 RD models, for which I derived the necessary coordinate transformation equations:
 - PC-5Dr model: 5-dimensional model with rectilinear internal coordinates, in which the CZ₃ group is constrained to C_{3v} symmetry.
 - PC-5Dc model: 5-dimensional model with curvilinear internal coordinates, in which the CZ₃ group is constrained to C_{3v} symmetry.
 - PC-4D model: 4-dimensional model with rectilinear internal coordinates, in which the CZ₃ group is constrained to C_{3v} symmetry and the 3 C-Z bond length is frozen at the equilibrium value.
 - RBU-3D model: 3-dimensional model with rectilinear internal coordinates, in which the CZ₃ group is constrained to C_{3v} symmetry, the 3 C-Z bond length is frozen at the equilibrium value and the Y atom is constrained to one of the symmetry planes of the CZ₃ group.
2. We demonstrated in full-dimensional QCT simulations that normal sampling based on harmonic approximation, which is generally applied in preparation of the initial states of quasiclassical trajectory calculations, provides nonstationary ensembles of CH_nD_{4-n} ($n = 0, \dots, 4$) methane isotopologs even in their rovibrational ground state, which is manifested as an oscillation of the ensemble-average C-H/C-D bond lengths in time, while significant energy exchange occurs between the normal modes. The phenomenon was demonstrated both on the less accurate CBE PES which is based on empirical,

anharmonic force field formulas and on the ZBB3 PES which was fitted to the results of high-level *ab initio* calculations.

3. We showed that, as a consequence of the bond-length oscillations, the reactivity parameters (reaction probability, reaction cross-section) of the $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$ and isotopolog reactions determined in QCT simulations also oscillate periodically as a function of the initial distance of the reactants, leading to significant uncertainty in their determination and giving rise to unphysical minima and maxima on the calculated excitation functions. We pointed out that this uncertainty may also be significant in other reactions when the passage of the trajectory through the strong interaction region is sufficiently rapid compared to the periodic time of the stretching vibrations of the breaking bonds. Consequently, we proposed that before starting the reactivity calculations, it is advisable to examine whether the initial ensembles of reactant molecules are stationary, namely whether oscillation occurs in the average length of the breaking bond or in any other parameter which affects the reactivity of the molecule.
4. I proposed an *ad hoc* method to get unambiguous reactivity parameters that are insensitive to the choice of the initial distance of the reactants, in the case when the ensembles of reactant molecules prepared by the standard normal mode sampling method are nonstationary and thus remove the unphysical extremes from the excitation functions. The method is based on the averaging of the reactivity parameters over an entire period of the mean C–H/C–D bond length oscillation. We introduced the 1PA name for the method as the abbreviation of ‘one-period averaging’.
5. I performed the normal mode analysis of CZ_3Y ($\text{Y}, \text{Z} = \text{H}$ or D) methane isotopologs on the CBE and ZBB3 PESs with the PC-5Dr, PC-5Dc, PC-4D and RBU-3D reduced-dimensional models. By the comparison with the full-dimensional normal vibrations and normal frequencies, I arrived at the following conclusions:
 - For the CH_4 and CD_4 isotopologs, which belong to the T_d symmetry group in full dimension, the totally symmetric stretch mode remains intact in the 5-dimensional models. The triply degenerate stretching and the triply degenerate deformation modes become nondegenerate asymmetric stretching and

umbrella modes, respectively, with unchanged frequencies. Instead of the doubly degenerate deformation mode of the FD model, a doubly degenerate rocking mode with slightly different frequency appears. In the 4-dimensional model the doubly degenerate rocking mode of the 5-dimensional models remains unchanged and a local C-H stretching mode appears instead of the symmetric and asymmetric stretching modes. In the 3-dimensional model the degeneracy of the rocking mode disappears, but all the frequencies of the 4-dimensional model remain unchanged.

- For the CH₃D and CD₃H isotopologs, which belong to the C_{3v} symmetry group in full dimension, the totally symmetric modes remain unchanged in the 5-dimensional models, while the frequency of the doubly-degenerate rocking mode changes slightly and the other doubly-degenerate deformation and stretching modes of the CZ₃ group disappear. In the 4-dimensional model, the umbrella mode and the doubly-degenerate rocking mode of the 5-dimensional model remain unchanged, while the frequency of the local CH stretching mode slightly changes and the local CZ₃ symmetric stretching mode disappears. In the 3-dimensional model the degeneracy of the rocking mode disappears, but all the frequencies of the 4-dimensional model remain unchanged.
6. I found that the nature of the rocking and umbrella normal mode vibrations of methane in the rectilinear (PC5Dr model) and curvilinear (PC-5Dc model) 5-dimensional models differ, which causes that the initial average bond lengths of the normal mode sampled ensembles also differ for the two models. I demonstrated, that the average C-H/C-D bond lengths of the 5-dimensional methane ensembles also oscillates in time, however in the case of the PC-5Dc model, the amplitude of the oscillation is much higher than that of the PC-5Dr model.

By the comparison of the time evolution of the average C-H/C-D bond lengths and normal mode quantum numbers of methane ensembles prepared by normal mode sampling with the PC-5Dr, PC-4D and RBU-3D models, I found that by reducing the number of degrees of freedom, the energy exchange between the modes does not cease and the relaxation of the ensembles become slower. This can be explained by the fact that the initial phase coherence of the ensemble is lost more slowly in systems with a simpler phase space structure as the vibrations are less chaotic.

7. I recognized that depending on whether the normal mode sampling of the initial methane ensembles was done with rectilinear or curvilinear coordinates, different excitation functions are obtained for the $\text{CZ}_3\text{Y} + \text{H} \rightarrow \text{CZ}_3 + \text{YH}$ ($\text{Y}, \text{Z} = \text{H}$ or D) reaction in QCT calculation for both the FD and RD cases, even if the effect of the average bound length oscillation is corrected by the 1PA method. I pointed out that standard normal mode sampling method using Cartesian coordinates also leads to a different excitation function than the normal mode sampling using rectilinear or curvilinear internal coordinates. Consequently, it can be concluded that the normal mode initial state preparation in lab Cartesian coordinates, which is commonly applied in QCT calculations brings some kind of arbitrariness into the results.

I demonstrated that stationary ensembles prepared by adiabatic switching on the anharmonicity in rectilinear or curvilinear internal coordinates lead to the same excitation functions both in full-dimensional and reduced-dimensional QCT simulations.

8. Using the stationary methane ensembles prepared by the adiabatic switching method with the PC-5Dr and PC-5Dc models I performed RD QCT calculations of the $\text{CZ}_3\text{Y} + \text{H} \rightarrow \text{CZ}_3 + \text{YH}$ ($\text{Y}, \text{Z} = \text{H}$ or D) reactions with the constraints of the Palma-Clary model on the CBE and ZBB3 PESs and compared the results with those of FD QCT calculations. I concluded that the Palma-Clary model gives a qualitatively good description, as for both PESs and for all isotopologs the shape of the excitation functions, opacity functions and product angle distributions agree well with the FD results. However for the majority of the cases the results of the RD model underestimate the FD ones.

Publications and Presentations

Publications forming the basis of the thesis:

- 1) Vikár, A.; Nagy, T.; Lendvay, G. Testing the Palma-Clary Reduced Dimensionality Model Using Classical Mechanics on the $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$ Reaction. *J. Phys. Chem. A* **2016**, *120*, 5083–5093.
- 2) Nagy, T.; Vikár, A.; Lendvay, G. Oscillatory Reaction Cross Sections Caused by Normal Mode Sampling in Quasiclassical Trajectory Calculations. *J. Chem. Phys.* **2016**, *144*, 014104
- 3) Nagy, T.; Vikár, A.; Lendvay, G. A General Formulation of the Quasiclassical Trajectory Method for Reduced-Dimensionality Reaction Dynamics Calculations. *Phys. Chem. Chem. Phys.* **2018**, *20* (19), 13224–13240.

Publications without impact factor on the topic of the theses:

- 4) Vikár, A.; Nagy, T.; Lendvay, G. Reduced-dimensionality study of the reaction of methane with H atom. In: Proceedings of the 7th European Combustion Meeting, Budapest, Hungary, 30.03-02.04.2015, Budapest, Hungary, Hungarian Section of the Combustion Institute, 2015. Paper P1-19. 6 p. (ISBN: 978-963-12-1257-0)

Additional publications:

- 1) Ziolkowski, M.; Vikár, A.; Mayes, M.L.; Bencsura, Á.; Lendvay, G.; Schatz, G.C. Modeling the electron-impact dissociation of methane. *J. Chem. Phys.* **2012**, *137*, 22A510

Presentations related to the thesis:

- 1) Vikár, A., Nagy, T., Lendvay, G. Quasiclassical reduced dimensionality studies of the methane + H reaction (poster presentation),
11th Central European Symposium on Theoretical Chemistry, Mariapfarr, Ausztria, September 2012.
- 2) Vikár, A.; Lendvay, G. Redukált-dimenziós reakciódinamikai modellek vizsgálata (oral presentation),
Seminar of Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, April 2013.
- 3) Vikár, A.; Nagy, T.; Lendvay, G. Reduced Dimensional Study of the Methane + H Reaction (poster presentation),
23rd International Symposium on Gas Kinetics and Related Phenomena, Szeged, July 2014.
- 4) Vikár, A.; Nagy, T.; Lendvay, G. $CZ_3Y + X \rightarrow CZ_3 + YX$ típusú reakciók dinamikájának elméleti leírása redukált-dimenziós módszerekkel (oral presentation),
Meeting of MTA Reaction Kinetics and Photochemistry Working Group, Debrecen, March 2015.
- 5) Vikár, A.; Nagy, T.; Lendvay, G. Reduced-dimensionality study of the reaction of methane with H atom (poster presentation),
Proceedings of the 7th European Combustion Meeting, Budapest, March 2015.
- 6) Nagy, T.; Vikár, A.; Lendvay, G. Sampling initial states for quasiclassical trajectory calculations using adiabatic switching (poster presentation),
European Conference on the Dynamics of Molecular Systems, Toledo, Spain, September 2016.

Additional presentations:

- 1) Vikár, A.; Lendvay, G. A metán fotodissociációjának elméleti vizsgálata (oral presentation),
Meeting of MTA Reaction Kinetics and Photochemistry Working Group, Siófok, April 2012.