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**MOLECULAR DYNAMICS
IN FREE CLUSTERS AND NANOPARTICLES
STUDIED IN MOLECULAR BEAMS**

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MOLECULAR DYNAMICS
IN FREE CLUSTERS AND NANOPARTICLES
STUDIED IN MOLECULAR BEAMS

DSc. Thesis
in Physical Chemistry
by
Michal Fárník

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Abstract

In this Thesis I have summarized our recent research of free clusters and nanoparticles generated by the molecular beam technique in vacuum and investigated by various laser spectroscopic and mass spectrometric methods. The clusters and nanoparticles are of great fundamental interest, since they can provide the link between the individual molecules and the bulk material composed of these molecules by investigating physical and chemical properties as a function of cluster size, ultimately resulting in understanding the transition from the molecule, to the bulk. The work in the field of clusters and nanoparticles in general is relevant to solid state, molecular, atomic and even nuclear physics and chemistry and has practical implications for many areas, e.g., nanoelectronics, surface science, catalysis, environmental studies, biology or even medicine. Besides, the free molecular clusters generated in molecular beams in vacuum poses unique properties, which promote their use for investigations of molecules and processes in complex environments at a detailed molecular level. In this Thesis four main research topics are presented: 1) Photofragmentation in model systems, i.e. hydrogen halides in rare gas clusters; 2) Clusters and nanoparticles of atmospheric relevance; 3) Biologically relevant processes studied in clusters; 4) Novel molecules of rare gas atoms generated in clusters.

The Thesis is based on sixteen recent publications in peer-reviewed international journals. My independent original research started in 2005, when I moved a unique molecular beam experimental apparatus from the Max-Planck Institute in Göttingen to the J. Heyrovský Institute of Physical Chemistry in Prague and founded a new laboratory and experimental *group of Molecular and Cluster Dynamics*, and started a new area of research in the Czech Republic. The focus is, therefore, on the original research accomplished within the last 5 years in our laboratory. However, the present research stemmed from my previous work in Göttingen, therefore, some of this earlier work is outlined in the Thesis as well.

First, to open the Thesis, a brief history of molecular beams and cluster research, and the general motivation for our particular studies is outlined in the *Introduction*. The second chapter *Experiment* is devoted to the description of the apparatus, and the experimental methods are briefly overviewed. The experiment is quite complex and includes several unique and up-to-date methods. The molecular beam techniques are used to generate beams of free molecules, clusters and nanoparticles of various sizes in vacuum. The species in the beams are interrogated by scattering with atoms from a secondary molecular beam, or by electron ionization, or by interactions with UV-photons causing photodissociation and/or photoionization. Various mass-spectrometric methods (quadrupole and time-of-flight mass spectrometers) and energy distribution measurements are implemented to analyze the ongoing processes. Non-trivial laser techniques are employed to generate tunable UV laser beams of high-intensities.

The chapter *Results* of the Thesis outlines the general outcome of our studies which is organized in four sections. The first one *Photodissociation of hydrogen halides in rare gas clusters* summarizes some of our earlier results on the photodissociation of various hydrogen halides (HX, X=Cl,Br,I) in rare gas (Ar and Ne) clusters. These systems provided a detailed understanding of the photodissociation in the cluster environments. Important phenomena, such as *caging* and *cage exit* of the dissociated fragments, have been observed. These model systems facilitated the understanding of the more complicated species, such

as the hydrogen halides in water clusters or functional units of biomolecules in clusters, which are discussed in the following sections.

The section *Atmospherically relevant clusters* summarizes our results on photochemistry of hydrogen halides on ice nanoparticles and pure water clusters photodissociation. Such species play a key role in the ozone depletion process in atmospheric chemistry. Our studies brought the first experimental evidence for the neutral hydronium radical H_3O , which is generated in $\text{HX}\cdot(\text{H}_2\text{O})_n$ species upon UV excitation. The way to the generation of the H_3O radical leads via the acidic dissociation in the ground state to the zwitterionic species $\text{X}^-\cdot\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_{n-1}$. Possible consequences for the atmospheric chemistry models are briefly discussed. The hydronium radical seems to play a central role in the photochemistry of the aqueous systems, which is essential not only to the atmospheric chemistry but also to the other important areas such as the radiation damage of biomolecules.

The section *Biomolecules in clusters* is related to the important issue of photostability of biomolecules. Clusters of small heteroaromatic ring molecules (pyrrole, imidazole, pyrazole) were investigated, which constitute the essential functional blocks and the UV active chromophores in the larger biomolecules. The solvent molecules have a profound effect on the photochemistry of these molecules. Various mechanisms of the solvent induced photostability were revealed, such as closing the dissociation channels by electronic interactions, or stabilization by hydrogen transfer in the excited states.

In the section *Novel rare gas molecules*, the hydride compounds of the type H-Xe-Y (Y is an electronegative atom or group) containing rare gas atom are investigated. These species are stable molecules with partly ionic and partly covalent bonding character. In our experiments they are produced free in the gas phase by photodissociation of the precursor molecules HY on large rare gas Xe-clusters.

The Thesis close with a chapter summarizing some of the general results of our research, and especially with a brief overview of some of the future experiments which were opened for investigation by the introduction of this vital new field of research in our laboratory.

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Chapter 1

Molecular Dynamics in Free Clusters and Nanoparticles Studied in Molecular Beams

1.1 Introduction

In this Thesis I summarize our recent research of free clusters and nanoparticles started in the J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, in 2005, when I received J. E. Purkyně Fellowship of the Czech Academy of Sciences and returned from a long term stay abroad (10 years) spent in several laboratories in Germany and U.S.A. During my last stay at the Max-Planck Institute in Göttingen I worked on an experimental apparatus devoted to the studies of photodissociation of molecules in cluster environments. I have moved this apparatus to Prague and founded a new laboratory with the aim to open the new research field in the Czech Republic. The focus in the Thesis is on the *clusters and nanoparticles in molecular beams and their photochemistry*.¹

Work in the field of cluster and nanoparticles in general is relevant to solid state, molecular, atomic and even nuclear physics and chemistry and has practical implications for many areas, e.g., nanoelectronics, surface science, catalysis, environmental studies, biology or even medicine [14, 15]. The clusters studied in our laboratory are conglomerates of molecules ranging from two constituents (dimers) to large species composed of 10^3 molecules, they can be homogeneous –composed of the molecules of the same type– or heterogeneous –clusters with foreign molecules or smaller clusters embedded in them or deposited on their surfaces. The larger species composed of more than ≈ 10 molecules have dimensions of nanometers, i.e., they are *nanoparticles*. They are produced in our experiment in molecular beams in vacuum where they are studied free of interactions with any substrate. Thus the clusters provide a tool for investigations of various properties as they evolve from an individual molecule to the bulk. In addition, the cluster studies can provide detailed understanding of the observed processes on a molecular level.

The photodissociation of molecules in clusters may serve as an example of how the clusters can be exploited as *nanolaboratories* for studying the photochemical processes in solvent environment. The understanding of photochemistry in condensed media is one of the current challenges in chemical physics both for fundamental and technological reasons.

¹Therefore, not the most significant or the most cited publications of my scientific carrier are covered in this Thesis, but rather some of the most recent ones, which are characteristic for the new research.

A molecular level understanding is difficult to achieve due to the many-body nature of the interactions. A photodissociation process of a diatomic HX molecule is schematically represented in Fig 1.1. A variety of processes can occur ranging from *fragment caging* over closing some dissociation channels or opening new ones due to the *electronic interaction*, to *chemical reactions* of the fragment with the solvent.

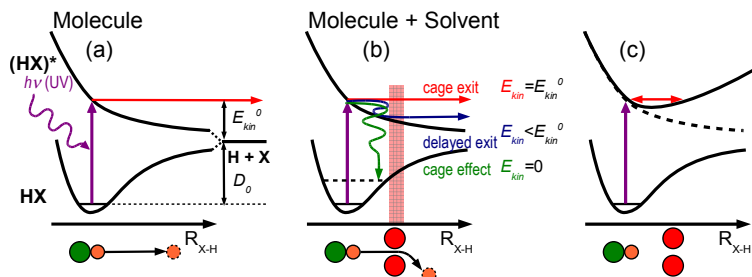


Figure 1.1: Schematic representation of photodissociation of an isolated HX molecule (a), and the possible effects of the solvent molecules on the photodissociation process: mechanical (b) and electronic interaction (c).

When the molecule is photolyzed in a cluster the initial dynamics of the process is essentially the same as in the condensed phase. Nevertheless, the clusters decay during the process and the escaping fragments can be detected, while in the condensed phase the fragments are usually lost from the detection. Thus, in the cluster experiments, observables can be measured not accessible in the bulk studies, e.g., the kinetic energy of the fragments. This energy carries the information about the fragment interaction with the solvent cage. Besides, investigating the process as a function of the cluster size, brings the information about the role of the solvent in the photodissociation. Altogether detailed information about the dynamics of the process in the molecule-solvent system can be gained from such studies [19].

From our research, several topics have been selected for presentation in the Thesis:

- (1) Photodissociation of hydrogen halide molecules on rare gas clusters. They provide model systems for investigations of the general question: How does the solvent influence the photodissociation process? Processes, such as *fragment caging* can be studied in these systems.
- (2) Photochemistry of nanoparticles relevant in *atmospheric chemistry*, e.g., in the ozone depletion process. This includes namely photodissociation of hydrogen halide molecules on ice nanoparticles $HX \cdot (H_2O)_n$ ($X = Br, Cl$) and photodissociation in pure $(H_2O)_n$ clusters.
- (3) Photodissociation of basic constituents of *biomolecules* in cluster environments. The photolysis of small heteroaromatic molecules as pyrrole, imidazole and pyrazole was investigated in clusters, with the aim to study the effect of the solvent on the photostability of biomolecules in general.
- (4) Besides, the studies of *novel rare gas compounds* $H-Rg-Y$ generated by photodissociation of precursor molecules HY in rare gas clusters Rg_n were pursued. Investigation of these noble gas compounds is interesting and important from the fundamental point of view, since they substantially enrich our understanding of the chemical bonding.

1.2 Experiment

The experimental setup has essentially been built at the Max-Planck Institute in Göttingen and reassembled in Prague with some minor additions and modifications. It represents a very complex, demanding and complicated experiment featuring several methods which are unique worldwide. Therefore this chapter in the Thesis is devoted to its description, and the experimental methods are briefly overviewed. The apparatus consists of a vacuum system for producing the molecular beams by supersonic gas expansions, and for handling and analyzing them: to perform scattering experiments with atoms or molecules, size select the neutral cluster beams, measure the beam velocity distributions, perform mass spectrometry of clusters ionized by multiphoton ionization (time-of-flight mass spectrometry) or by electron ionization (quadrupole mass spectrometry), and finally to measure the kinetic energy distribution of fragments after the photodissociation of molecules in clusters. The laser system serves to produce light beams of various UV wavelengths to probe the clusters.

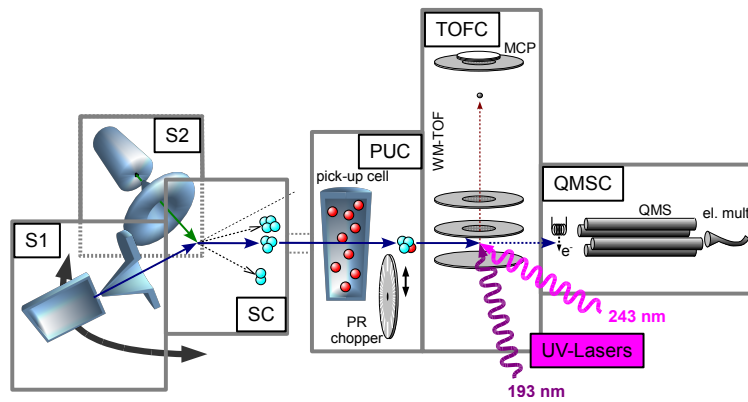


Figure 1.2: The schematic picture of the present experiment: S1–primary beam source chamber; S2–secondary beam source chamber; SC–scattering chamber; PUC–pick-up chamber hosting pick-up cell and pseudorandom (PR) chopper; TOFC–time-of-flight chamber with WM-TOF spectrometer, where laser beams interact with the molecular beam, and the fragments are detected by multichannel plate (MCP); QMSC–quadrupole chamber with QMS, where clusters are ionized by electrons and fragment mass spectra are recorded by electron multiplier.

The schematic picture of the present experiment with its essential parts is shown in Fig. 1.2. The clusters are produced by a supersonic expansion of the corresponding gas molecules through a nozzle into the vacuum. After passing the skimmer, the neutral clusters can be size selected by elastic scattering with a perpendicular beam of rare gas atoms produced in the secondary nozzle. The basic principle of the size selection method is indicated schematically in Fig. 1.2: the smaller (lighter) clusters are scattered to the larger laboratory angles than the larger (heavier) clusters. The whole assembly of the two source vacuum chambers attached to the scattering chamber can be rotated with respect to the rest of the apparatus as indicated. Choosing an appropriate laboratory angle to which the clusters are scattered, clusters of the selected size n are allowed to proceed further through the apparatus. Actually, the angularly selected beam contains also clusters smaller than n and further methods can be employed to obtain a complete size selection of the neutral clusters. It is worth noting that the possibility to obtain explicit information about the

neutral cluster size distribution is one of the unique features of our apparatus.

After the scattering chamber the clusters enter another vacuum chamber, where they can be doped with foreign molecules by passing through a pick-up cell filled with the foreign gas at a low pressure. Then the clusters enter the first detection chamber with a time-of-flight spectrometer of the Wiley-McLaren type (WMTOF). The molecules in the clusters are dissociated and ionized by the laser beams. The ionized fragments are extracted into the WMTOF field free region and detected at the end with a multichannel plate and their TOF spectra are recorded. The WMTOF can be operated as the mass spectrometer when the ions are extracted with a high electric field. However, in the photodissociation experiments it is rather operated in the so called low field mode with a small extraction field, where the kinetic energy distribution (KED) of a particular fragment (e.g., H-atom) can be measured.

The H-fragments are efficiently photoionized at 243 nm (5.1 eV) by a resonance-enhanced multiphoton ionization (REMPI). The molecules in the clusters can be photodissociated previously either by photons of the same wavelength within the same laser pulse or by another laser pulse at 193 nm (6.4 eV). In the photoionization experiments the clusters and/or their fragments are ionized by a non-resonant absorption of several photons from any of the two lasers. Alternatively the mass spectra can be recorded with a quadrupole. For this purpose the clusters proceed into the QMS chamber, where they are ionized by electrons. Further details about the experiment can be found in Refs. [63, 64, 65, 66].

1.3 Results

1.3.1 Photodissociation of hydrogen halides in rare gas clusters

Although the focus is on our present research performed in Prague, this first section of *Results* summarizes some of the experiments performed with the apparatus still in Göttingen. The photodissociation of various hydrogen halides (HX, X= Cl, Br, I) in rare gas clusters represented the prerequisite model systems for the studies of atmospherically relevant species. These systems provided a detailed understanding of the photodissociation of relatively simple diatomic molecules in the cluster environments. The cluster can simulate the solvent effect on the photodissociation process –the rare gas atoms of the cluster represent an archetype structureless solvent. Important phenomena, such as *caging* and *cage exit* of the dissociated fragments, have been observed and analyzed. The detailed understanding of these model systems facilitated the understanding of the more complicated species studied here, such as the hydrogen halides in water clusters or biomolecules in clusters.

Results of HX photodissociation on Ar_n clusters were compared in the Thesis. The comparison is illustrated schematically in Fig. 1.3. First, the comparison of a photodissociation of HBr and HCl molecules on Ar_n clusters at 193 nm is made. While the H-fragments from HBr molecules exhibited significant cage exit no evidence for such process was observed for HCl molecules, where only the caged atoms with near-zero kinetic energy were measured. This could be rationalized by the fact that the smaller HCl molecule fits better into a substitutional position on the Ar_n cluster surface, leading to the higher caging probability.

Second, the comparison between HBr and HI on Ar_n clusters at 243 nm reveals a very similar behavior with both the ground X and the spin-orbit X^* states populated almost equally. While in the case of HBr both states are populated through a perpendicular transition, in the case of HI the ground state I is populated via a perpendicular transition

and the excited state I^* population comes from a parallel transition. Besides, in HI the intensities corresponding to I and I^* populations are mixed by scattering processes from the surrounding Ar atoms of the cluster. This can be rationalized by libration motion and the larger size of the HI molecule, which does not fit into the substitutional position and sits more on the outside of the cluster surface, which in turn leads to the efficient H-fragment scattering. Fig. 1.3 illustrates the hotodissociation of various hydrogen halides

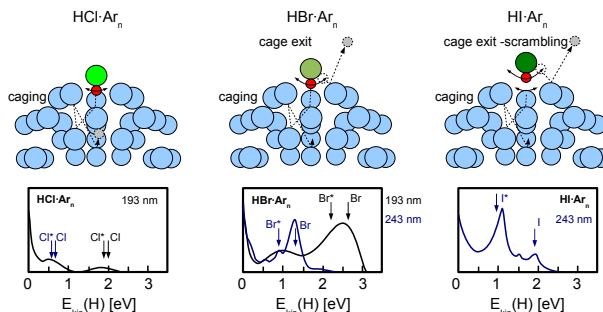


Figure 1.3: Schematic illustration of hotodissociation of various hydrogen halides on Ar_n clusters.

on Ar_n clusters: (a) HCl is buried deep in the substitutional position on the Ar_n cluster surface, leading to the caging of the H-fragment after the photodissociation; (b) HBr does not fit into the substitutional position completely, therefore, part of the fragments from librating HBr molecule can be elastically scattered from the surface and lead to the cage exit; (c) HI sits even more outside on the surface than HBr, therefore, the cage exit is even more pronounced and scrambling of the angular distributions from different polarizations occurs. At the bottom the corresponding representative KEDs are shown to illustrate these effects.

The neon clusters represent a border case, where the classical treatment may be sufficient to describe some properties, while the quantum mechanics might be necessary for understanding of some other phenomena. Therefore, it was interesting to investigate the photodissociation process in neon clusters and compare it to the studies in the heavier rare gas clusters. The photodissociation of HBr and HCl molecules on neon clusters pointed to a liquid-like surface layer in large Ne-clusters: the outer surface shells remain liquid also for the larger Ne-clusters, which have frozen solid-like core. The embedded molecule sinks deep into the surface layers, which then hinder the H atom dissociation fragment from leaving the cluster.

The results presented in this section can be found in the corresponding publications [102, 103, 104, 106].

1.3.2 Atmospherically relevant clusters

This section summarizes our results on photochemistry of hydrogen halides in water clusters (ice nanoparticles) $HX \cdot (H_2O)_n$, $\bar{n} \approx 10^2 - 10^3$, and pure water clusters $(H_2O)_n$. These species play a key role in the atmospheric chemistry in the ozone depletion process. We pursue the question of the nature of a hydrogen halide molecule on an ice nanoparticle: Is it covalently bound or acidically dissociated? The quest brought us to the discovery of the neutral hydronium radical H_3O . These species are generated in $HX \cdot (H_2O)_n$ clusters upon UV excitation into an electronic state of charge-transfer-to-solvent character

and subsequent relaxation into a biradical state. Our experiments with isotopic variants of $\text{HX}\cdot(\text{H}_2\text{O})_n$ species provided the first experimental evidence for the H_3O radical generation. Further experiments presented in this Thesis then confirmed its existence and investigated its nature.

The idea of interpreting of our experimental observations in terms of H_3O species followed from the earlier theoretical predictions of H_3O in similar systems by Domcke and Sobolewski [108, 109, 110, 111, 112]. They proposed theoretically the excitation of charge separated species such as the small zwitterionic clusters $\text{Cl}^-\cdot(\text{H}_2\text{O})_3\cdot\text{H}_3\text{O}^+$ to lead to the neutral H_3O radical. Fig. 1.4 depicts the suggested mechanism of the H_3O generation in our experiment: It starts with the acidic dissociation of the HBr molecule, forming a zwitterionic structure $\text{Br}^-\cdot\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_{n-1}$, which is then excited by the 193 nm laser to an excited state of the charge-transfer-to-solvent (CTTS) character [109]. The system then relaxes into a biradical minimum with Br and H_3O neutral radicals, which can ultimately decay into H_2O molecule and the H atom detected [108, 111]. Several experimental findings and further arguments were found to support this mechanism.

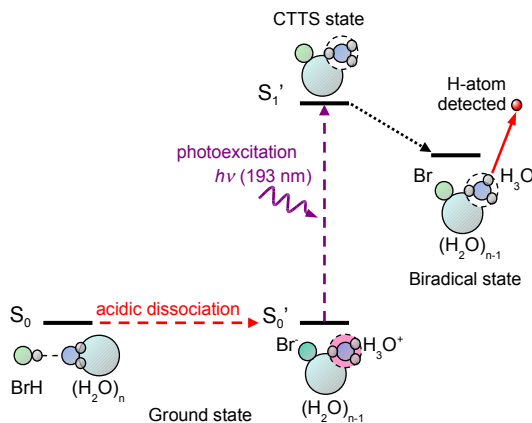


Figure 1.4: Proposed mechanism of the $\text{HBr}\cdot(\text{H}_2\text{O})_n$ cluster photochemistry.

It should be mentioned that our findings can have significant consequences for the atmospheric chemistry models. The experiments and accompanied theoretical calculations demonstrated that the acidic dissociation in $\text{HX}\cdot(\text{H}_2\text{O})_n$ species causes a significant redshift in the absorption spectra of these species. Therefore the HCl adsorbed and acidically dissociated on the ice particles can be a non-negligible direct source of the Cl radical after the UV excitation, without the necessity of converging the reservoir species HCl into the active photolyzable species Cl_2 .

Besides, the evidence for the H_3O molecular radical has been also found in the photodissociation of pure ice nanoparticles. Thus the H_3O species were shown to play a central role in the photochemistry of the aqueous systems, which is essential not only to the atmospheric chemistry but also for other important areas such as the radiation damage of biomolecules.

The results of our investigations of hydrogen halides in ice nanoparticles $\text{HX}\cdot(\text{H}_2\text{O})_n$, which were summarized in this chapter have been published in Refs. [115, 116, 117], and the studies of pure water clusters $(\text{H}_2\text{O})_n$ were published in Ref. [118].

1.3.3 Biomolecules in clusters

The systems studied in this section are related to such important issues as the photostability of biomolecules. Small heteroaromatic ring molecules such as pyrrole, imidazole and pyrazole constitute the essential functional blocks and the UV active chromophores in the larger biomolecules. The pursuit to understand the photochemistry of biomolecules in detail led the researchers to investigations of the photochemistry of these constituent molecules in the gas phase. However, in nature the photochemistry proceeds with these molecules as parts of the larger systems, and also surrounded by the solvent molecules. The solvent molecules can have a profound effect on their photochemistry. Therefore we have investigated these molecules in the clusters where the solvent effects can be studied at the molecular level. Clusters of rare gas atoms were again exploited as archetype structureless solvents. However, since the most important bond in the biological matter is the hydrogen bond, clusters with various hydrogen bond motifs were also studied. Fig. 1.5 shows these bonding motifs for dimers and trimers of structurally very similar molecules: pyrrole, imidazole and pyrazole, investigated in our experiments.

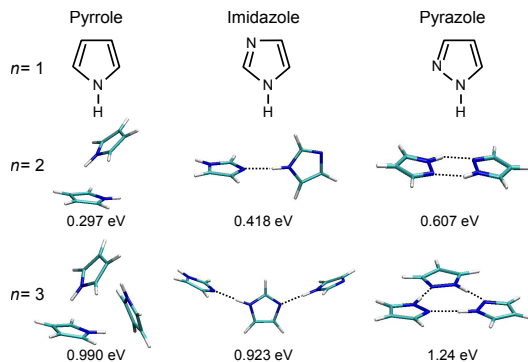


Figure 1.5: Structures and binding energies of the molecules and the different bonding motifs represented by the pyrrole, imidazole and pyrazole dimers and trimers.

Due to their biological relevance, the UV photochemistry of these nitrogen heterocycles was extensively studied in the gas phase both experimentally [119, 120, 121, 122] and theoretically [123, 124, 125, 126]. The general picture of the photochemistry is schematically represented in Fig. 1.6. Upon a low energy excitation, the photodynamics is dominated by the $\pi\sigma^*$ state. This state is asymptotically dissociative and the hydrogen atom is released (hydrogen dissociation, HD, channel). At elongated N-H distances, the $\pi\sigma^*/S_0$ conical intersection occurs. It is, therefore, possible that frustrated dissociation (FD) takes place, and the molecular ground state is recreated. At higher photon energies, the $\pi\pi^*$ state can be populated. A molecular ring distortion (MRD) reaction channel is opened. Subsequently, the molecule quenches into the vibrationally hot ground state where again the hydrogen atom can dissociate or other molecular fragments can be formed. This dynamics leads to a bimodal character of the H-fragment KED spectra from the photodissociation of these molecules. These spectra measured for pyrrole molecule at 243 nm and 193 nm are schematically shown on the insets in Fig. 1.6. The relatively narrow peak of *fast fragments* (around 0.8 eV) originates from the direct dissociation on the $\pi\sigma^*$ surface. The *slow fragments* exhibit a broad distribution peaking near zero. These fragments correspond to statistical decay of the vibrationally hot ground state molecule after the quenching of the

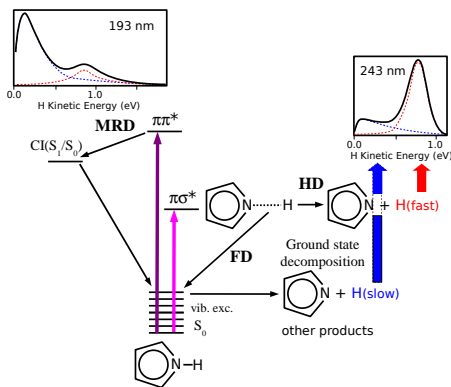


Figure 1.6: Schematic picture of photodissociation processes possible in the studied molecules (pyrrole, imidazole, pyrazole).

$\pi\sigma^*$ or $\pi\pi^*$ state.

We have investigated how these spectra change upon complexation of the molecules in clusters. Figure 1.7 shows examples of the measured H-fragment KEDs from Py (left panels (a) and (b)) and Im (right panels (c) and (d)) clusters at 243 nm. The top panels (a) and (c) correspond to the smaller clusters with the mean sizes of $\bar{n} \approx 3$ produced in expansions with He carrier gas. The bottom panels (b) and (d) correspond to the larger clusters generated in expansions with Ar. The mass spectrometric and scattering experiments in Ar expansions revealed mixed Py_nAr_m clusters with $\bar{n} \approx 4$ and $\bar{m} \approx 8$ for pyrrole, while pure Im_n clusters with $\bar{n} \geq 6$ were generated for imidazole. Clearly, the fast component of KED

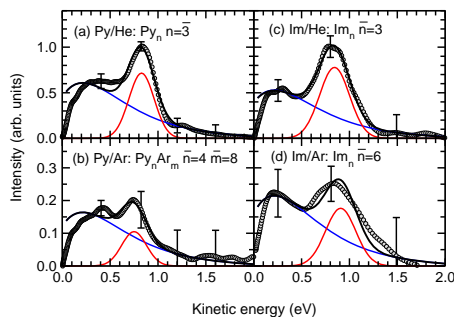


Figure 1.7: Measured KEDs of Py (left panels) and Im (right panels) clusters at 243 nm.

decreases relatively to the slow statistical fragments with the complexation. These changes were rationalized based on theoretical calculations performed in the group of P. Slavíček. For the pyrrole clusters, it has been shown that the conical intersection between $\pi\sigma^*$ and S_0 states cease to exist if the pyrrole molecule is solvated by other species. This effect is independent of the solvent nature, whether it is a structureless rare gas atom or other pyrrole molecule. Therefore, the direct dissociation channel along the N–H coordinate on $\pi\sigma^*$ is closed by the solvent. On the other hand, in case of imidazole and pyrazole clusters the solvent induced photostability is caused by hydrogen and/or proton transfer processes, which occur between the hydrogen bonded cluster constituents in the excited states.

These results have been published in a series of articles [127, 128, 129, 132].

1.3.4 Novel rare gas molecules

The hydride compounds of the type H-Rg-Y (Y is an electronegative atom or group) containing rare gas atom (usually Rg= Xe or Kr) represent extremely interesting species from the fundamental point of view extending our understanding of chemical bonding. The bonding in these stable species has partly ionic and partly covalent character. Experimentally, these species are usually produced by dissociation of the HY molecules adsorbed in the rare gas matrices. The precursor molecules can be either UV photolyzed or dissociated by electron bombardment. Then the matrix is annealed by heating, typically from about 10 K to 40 K, to make the hydrogen mobile and recombine to the H-Rg-Y molecule. In 2005 over 20 such molecules prepared in matrices were reviewed in Ref. [54] and their number is ever increasing. However, only three such rare gas molecules have been generated in the gas phase so far: HXeI, HXeCl and HXeCCH, and they were all prepared on the present experimental apparatus [55, 56, 57, 58].

In our experiments these molecules are produced free in the vacuum by photodissociation of the precursor molecules HY on large rare gas clusters Xe_n , $\bar{n} \approx 10^2$ - 10^3 . Besides, after their generation these molecules are oriented in the strong laser fields combined with weak electrostatic fields and detected by this orientation. The production of these molecules in the gas phase proves their stability and their generation in a direct process, and allows investigation of the dynamics of their photodissociation.

Fig. 1.8 shows the schematic picture of generation and orientation mechanism of an H-Xe-Y molecule by HY precursor photodissociation on Xe_n clusters: 1) the HY molecule is photodissociated on the Xe_n cluster; 2) the H fragment is backscattered from cluster atoms and recombines to the HXeY molecule; 3) the HXeY molecule is aligned in the strong laser field by the interaction of the laser electric field vector \vec{E}_L with the polarizability anisotropy of the molecule $\Delta\alpha$, and this alignment is turned into orientation by the interaction of the weak extraction field \vec{E}_S with the dipole moment $\vec{\mu}$ of the molecule; 4) the HXeY molecule is dissociated. The TOF spectrum of H-fragments from the oriented molecule exhibits only the peak of faster fragments (filled red peak), while the spectrum of randomly oriented HY molecule is symmetric (green line). The asymmetry of the measured total spectrum (red line) –which is a sum of the two spectra– is the experimental evidence for the HXeY molecule.

The results of our investigations of rare gas molecules were summarized in Refs. [57, 58, 133, 134].

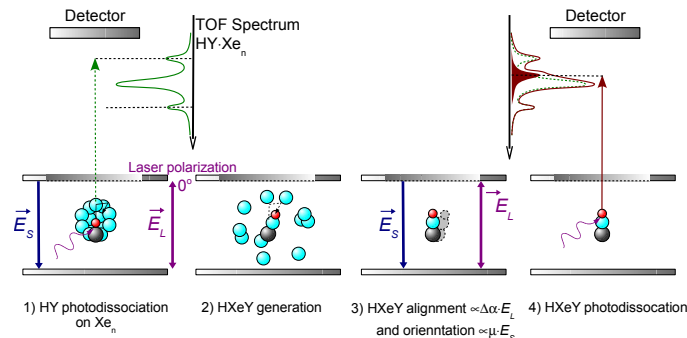


Figure 1.8: Schematic picture of generation and orientation mechanism of an H-Xe-Y molecule by HY precursor photodissociation on Xe_n clusters.

1.4 Conclusions

The experiments with hydrogen halides molecules on rare gas clusters discussed in Sec. 1.3.1 revealed information about the photodissociation dynamics of these species in cluster environments, and such processes as *fragment caging* and *cage exit* were analyzed and well understood. These studies provided an excellent basis for the further investigations of, e.g., the atmospherically and biologically relevant systems discussed in this Thesis.

Our experiments with hydrogen halides on ice nanoparticles in Sec. 1.3.2 have revealed the mechanism of UV excitation leading to the generation of H_3O neutral radical via acidic dissociation in the ground state. The H_3O radical has been also observed in the photodissociation of pure ice nanoparticles. The H_3O was suggested to play a central role in the photochemistry of aqueous systems. Our observations can have significant practical implications in the atmospheric chemistry on ozone depletion models.

In Sec. 1.3.3 we have studied the effect of solvent molecules on photochemistry of small biomolecular units. It has been demonstrated that the presence of solvent molecules can change the photochemistry in various ways: (i) due to the electronic interaction between the studied biomolecule and the solvent a photodissociation channel can be closed, or (ii) in hydrogen bonded system the hydrogen or proton transfer in the excited state can be initiated, which can lead to the excitation energy redistribution and dissipation. Both these effects can lead to the solvent induced stabilization of the molecule in the cluster. Such cluster studies may provide a key to the molecular level understanding of stability of the larger biomolecules in their natural environments.

The last issue treated in this Thesis are the rare gas molecules in Sec. 1.3.4. Here we have demonstrated that some of these interesting species can be generated in the gas phase by photolysis of precursor molecules on large rare gas clusters. Thus their stability and the direct generation mechanism have been proved. Besides, these molecules were oriented in the strong electric fields of laser combined with the weak electrostatic fields. Finally, also the photodissociation dynamics of these species has been studied.

Numerous possible future experiments and investigation directions have been suggested in the concluding chapter of the present Thesis, illustrating the potential of the new vital field of research started by the author five years ago in the J. Heyrovský Institute of Physical Chemistry, AS CR.

Bibliography

- [1] Forsén, S. In *Nobel Lectures, Chemistry 1981-1990*; Frängsmyr, T., Malmström, B. G., Eds.; World Scientific Publishing Co.: Singapore, **1992**.
- [2] Stern, O. *Z. Phys.* **1920**, *2*, 49.
- [3] Stern, O. *Z. Phys.* **1920**, *3*, 417.
- [4] Stern, O.; Gerlach, W. *Z. Phys.* **1922**, *9*, 349.
- [5] Scoles, G. *Atomic and Molecular Beam Methods*; Oxford: New York, **1988**.
- [6] Pauly, H. *Atom, Molecule and Cluster Beams*; Springer: Berlin, **2000**.
- [7] Bernstein, R. B. *Chemical Dynamics via Molecular Beam and Laser Techniques*; Oxford University Press: Oxford, **1982**.
- [8] Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford University Press: Oxford, **1982**.
- [9] Düren, R.; Lackschewitz, U.; Milošević, S.; Waldapfel, H.-J. *Chem. Phys.* **1990**, *140*, 199.
- [10] Mestdagh, J. M.; Gaveau, M. A.; Gée, C.; Sublemontier, O.; Visticot, J. P. *Int. Rev. Phys. Chem.* **1997**, *16*, 215.
- [11] Hurley, S. M.; Dermota, T. E.; Hydutsky, D. P.; Castleman, A. W. *Science* **2002**, *298*, 202.
- [12] Hurley, S. M.; Dermota, T. E.; Hydutsky, D. P.; Castleman, A. W. *J. Chem. Phys.* **2003**, *118*, 9272.
- [13] Buck, U.; Steinbach, C. *J. Phys. Chem. A* **1998**, *102*, 7333.
- [14] Castleman, A.; Keesee, R. *Science* **1988**, *241*, 36.
- [15] Jena, P.; Castleman, A. W. *Proc. Nat. Acad. Sci. USA* **2006**, *103*, 10560.
- [16] Haberland, H. *Clusters of Atoms and Molecules*; Springer: Berlin, **1994**.
- [17] Toennies, J. P.; Vilesov, A. F. *Angew. Chem. Int. Ed.* **2004**, *43*, 2622.
- [18] Dong, F.; Miller, R. E. *Science* **2002**, *298*, 1227.
- [19] Buck, U. *J. Phys. Chem. A* **2002**, *106*, 10049.

- [20] Molina, M. J.; Tso, T. L.; Molina, L. T.; Wang, F. C. Y. *Science* **1987**, *238*, 1253.
- [21] Tolbert, M. A.; Rossi, M. J.; Malhotra, R.; Golden, D. M. *Science* **1987**, *238*, 1258.
- [22] Tolbert, M. A.; Rossi, M. J.; Golden, D. M. *Geophys. Res. Lett.* **1988**, *15*, 847.
- [23] Leu, M.-T. *Geophys. Res. Lett.* **1988**, *15*, 17.
- [24] Peter, T. *Ann. Rev. Phys. Chem.* **1997**, *48*, 785.
- [25] Solomon, S.; Garcia, R. R.; Rowland, F. S.; Wuebbles, D. J. *Nature* **1986**, *321*, 755.
- [26] Lu, Q.-B.; Madey, T. E. *J. Chem. Phys.* **1999**, *111*, 2861.
- [27] Lu, Q.-B.; Sanche, L. *J. Chem. Phys.* **2004**, *120*, 2434.
- [28] Lu, Q.-B.; Sanche, L. *Phys. Rev. Lett.* **2001**, *87*, 078501.
- [29] Weimann, M.; Fárník, M.; Suhm, M. A. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3933.
- [30] Fárník, M.; Weimann, M.; Suhm, M. A. *J. Chem. Phys.* **2003**, *118*, 10120.
- [31] Devlin, J. P.; Fárník, M.; Suhm, M.; Buch, V. *J. Phys. Chem. A* **2005**, *109*, 955.
- [32] Devlin, J. P.; Uras, N.; Sadlej, J.; Buch, V. *May* **2002**, *417*, 269.
- [33] Buch, V.; Sadlej, J.; Aytemiz-Uras, N.; Devlin, J. P. *J. Phys. Chem. A* **2002**, *106*, 9374.
- [34] Kang, H.; Shin, T. H.; Park, S. C.; Kim, I. K.; Han, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 9842.
- [35] Blank, D. A.; North, S. W.; Lee, Y. T. *Chem. Phys.* **1994**, *187*, 35.
- [36] Cronin, B.; Nix, M. G. D.; Qadiri, R. H.; Ashfold, M. N. R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5031.
- [37] Wei, J.; Kuczmann, A.; Riedel, J.; Renth, F.; Temps, F. *Phys. Chem. Chem. Phys.* **2003**, *5*, 315.
- [38] Wei, J.; Riedel, J.; Kuczmann, A.; Renth, F.; Temps, F. *Faraday Discuss.* **2004**, *127*, 267.
- [39] Papadakis, V.; Kitsopoulos, T. N. *Rev. Sci. Instrum.* **2006**, *77*, 083101.
- [40] Lippert, H.; Ritzel, H.-H.; Hertel, I. V.; Radloff, W. *Chem. Phys. Chem.* **2004**, *5*, 1423.
- [41] Barbatti, M.; Vazdar, M.; Aquino, A. J. A.; Eckert-Maksić, M.; Lischka, H. *J. Chem. Phys.* **2006**, *125*, 164323.
- [42] van den Brom, A. J.; Kapelios, M.; Kitsopoulos, T. N.; Nahler, N. H.; Cronin, B.; Ashfold, M. N. R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 892.
- [43] Crespo-Hernandez, C. E.; Arce, R.; Ishikawa, Y.; Gorb, L.; Leszczynski, J.; Close, D. M. *J. Phys. Chem. A* **2004**, *108*, 6373.

- [44] Crespo-Hernandez, C. E.; Cohen, B.; Hare, P. M.; Kohler, B. *Chem. Rev.* **2004**, *104*, 1977.
- [45] Fárník, M.; Davis, S.; Nesbitt, D. J. *Faraday Discuss.* **2001**, *118*, 63.
- [46] Fárník, M.; Nesbitt, D. J. *J. Chem. Phys.* **2004**, *121*, 12386.
- [47] Fárník, M.; Steinbach, C.; Weimann, M.; Buck, U.; Borho, N.; Suhm, M. A. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4614.
- [48] Sobolewski, A. L.; Domcke, W. G. *J. Phys. Chem. A* **2007**, *111*, 11725.
- [49] Schultz, T.; Samoylova, E.; Radloff, W.; Hertel, I. V.; Sobolewski, A. L.; Domcke, W. *Science* **2004**, *306*, 1765.
- [50] Markwick, P.; Doltsinis, N. *J. Chem. Phys.* **2007**, *126*, 175102.
- [51] Schwalb, N.; Temps, F. *J. Am. Chem. Soc.* **2007**, *129*, 9272.
- [52] Dermota, T. E.; Zhong, Q.; Castleman, A. W. *Chem. Rev.* **2004**, *104*, 1861–1886.
- [53] Gerber, R. B. *Annu. Rev. Phys. Chem.* **2004**, *55*, 55.
- [54] Pettersson, M.; Khriachtchev, L.; Lundell, J.; Räsänen, M. In *Inorganic Chemistry in Focus II*; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley-VCH: Weinheim, **2005**; page 15.
- [55] Baumfalk, R.; Nahler, N. H.; Buck, U. *J. Phys. Chem.* **2001**, *114*, 4755.
- [56] Nahler, N. H.; Buck, U.; Bihary, Z.; Gerber, R. B.; Friedrich, B. *J. Chem. Phys.* **2003**, *119*, 224.
- [57] Nahler, N. H.; Fárník, M.; Buck, U. *Chem. Phys.* **2004**, *301*, 173.
- [58] Poterya, V.; Votava, O.; Fárník, M.; Ončák, M.; Slavíček, P.; Buck, U.; Friedrich, B. *J. Chem. Phys.* **2008**, *128*, 104313.
- [59] Friedrich, B.; Herschbach, D. *Phys. Rev. Lett.* **1995**, *74*, 4623.
- [60] Sakai, H.; Safvan, C.; Larsen, J.; K.M. Hiilligsø e, K. H.; Stapelfeldt, H. *J. Chem. Phys.* **1999**, *110*, 10235.
- [61] Larsen, J. J.; Hald, K.; Bjerre, N.; Stapelfeldt, H.; Seideman, T. *Phys. Rev. Lett.* **2000**, *85*, 2470.
- [62] Friedrich, B.; Nahler, N. H.; Buck, U. *J. Mod. Opt.* **2003**, *50*, 2677.
- [63] Baumfalk, R.; Buck, U.; Frischkorn, C.; Gandhi, S. R.; Lauenstein, C. *Ber. Bunsenges. Phys. Chem.* **1997**, *101*, 606.
- [64] Baumfalk, R.; Buck, U.; Frischkorn, C.; Gandhi, S. R.; Lauenstein, C. *Chem. Phys. Lett.* **1997**, *269*, 321.
- [65] Lohbrandt, P.; Galonska, R.; Kim, H. J.; Lauenstein, M. S. C.; Buck, U. In *Atomic and Molecular Beams. The State of the Art 2000*; Campargue, R., Ed.; Springer: Berlin, **2001**; page 623.

- [66] Nahler, N. H. *PhD Thesis, GA Universität Göttingen* **2002**.
- [67] Wiley, W. C.; McLaren, I. H. *Rev. Sci. Instrum.* **1955**, *26*, 1150.
- [68] Christen, W.; Rademann, K. *Phys. Rev. A* **2008**, *77*, 012702.
- [69] Christen, W.; Rademann, K. *Phys. Scripta* **2008**, *80*, 048127.
- [70] Toennies, J. P.; Vilesov, A. F.; Whaley, K. B. *Physics Today* **2001**, *2*, 31.
- [71] Póczik, I. *Z. Phys. D* **1991**, *20*, 395.
- [72] Hagen, O. F. *Surf. Sci.* **1981**, *106*, 101.
- [73] Hagen, O. F. *Z. Phys. D* **1987**, *4*, 291.
- [74] Hagen, O. F. *Rev. Sci. Instrum.* **1992**, *63*, 2374.
- [75] Buck, U.; Krohne, R. *J. Chem. Phys.* **1996**, *105*, 5408.
- [76] Bobbert, C.; Schütte, S.; Steinbach, C.; Buck, U. *Europ. Phys. J. D* **2002**, *19*, 183.
- [77] Schütte, S.; Buck, U. *Intern J. Mass Spectr.* **2002**, *220*, 183.
- [78] Farges, J.; de Feraudy, M. F.; Raoult, B.; Torchet, G. *Sur. Sci.* **1981**, *106*, 95.
- [79] Torchet, G.; Farges, J.; de Feraudy, M. F.; Raoult, B. In *The Chemical Physics of Atomic and Molecular Clusters*; Scoles, G., Ed.; North-Holland: Amsterdam, **1990**; page 513.
- [80] Torchet, G.; Schwartz, P.; Farges, J.; de Feraudy, M. F.; Raoult, B. *J. Chem. Phys.* **1983**, *79*, 6196.
- [81] Brudermann, J.; Buck, U.; Buch, V. *J. Phys. Chem.* **2002**, *106*, 453.
- [82] private communication. Buck, U. **2007**.
- [83] Gough, T. E.; Mengel, M.; Rowntree, P. A.; Scoles, G. *J. Chem. Phys.* **1985**, *83*, 4958.
- [84] Behrens, M.; Fröchtenicht, R.; Hartmann, M.; Siebers, J. G.; Buck, U. *J. Chem. Phys.* **1999**, *111*, 2436.
- [85] Nahler, N. H.; Baumfalk, R.; Buck, U.; Vach, H.; Slavíček, P.; Jungwirth, P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3394.
- [86] Buck, U.; Meyer, H. *Phys. Rev. Lett.* **1984**, *52*, 109.
- [87] Buck, U.; Meyer, H. *J. Chem. Phys.* **1986**, *84*, 4854.
- [88] Buck, U. *J. Phys. Chem.* **1988**, *92*, 1023.
- [89] Steinbach, C.; Fárník, M.; Buck, U.; Brindle, C. A.; Janda, K. C. *J. Phys. Chem. A* **2006**, *110*, 9108.
- [90] Buck, U. In *Advances in Molecular Vibrations and Collision Dynamics*; Bowman, J. M., Bačić, Z., Eds.; JAI Press Inc.: Stanford, **1998**; page 127.

- [91] Buck, U.; Huisken, F. *Chem. Rev.* **2000**, *100*, 3863.
- [92] Fárník, M.; Weimann, M.; Steinbach, C.; Buck, U.; Borho, N.; Adler, T. B.; Suhm, M. A. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1148–1158.
- [93] Poterya, V.; Fárník, M.; Buck, U.; Bonhommeau, D.; Halberstadt, N. *Int. J. Mass Spec.* **2009**, *280*, 78.
- [94] Janeček, I.; Cintavá, S.; Hrivňák, D.; Kalus, R.; Fárník, M.; Gadea, F. X. *J. Chem. Phys.* **2009**, *131*, 114306.
- [95] Peoux, G.; Monnerville, M.; Duhoo, T.; Pouilly, B. *J. Chem. Phys.* **1997**, *107*, 70.
- [96] Pouilly, B.; Monnerville, M. *Chem. Phys.* **1998**, *238*, 437.
- [97] Rakitzis, T. P.; Samartzis, P. C.; Toomes, R. L.; Kitsopoulos, T. N. *J. Chem. Phys.* **2004**, *121*, 7222.
- [98] Baumfalk, R.; Buck, U.; Frischkorn, C.; Nahler, N. H.; Hüwel, L. *J. Chem. Phys.* **1999**, *111*, 2595.
- [99] Baumfalk, R.; Nahler, N. H.; Buck, U.; Niv, M. Y.; Gerber, R. B. *J. Chem. Phys.* **2000**, *113*, 329.
- [100] Fárník, M.; Poterya, V.; Votava, O.; Ončák, M.; Slavíček, P.; Dauster, I.; Buck, U. *J. Phys. Chem. A* **2009**, *113*, 7322.
- [101] Zhong, Q.; Castleman, A. W. *Chem. Rev.* **2000**, *100*, 4039.
- [102] Slavíček, P.; Jungwirth, P.; Lewerenz, M.; Nahler, N. H.; Fárník, M.; Buck, U. *J. Chem. Phys.* **2004**, *120*, 4498.
- [103] Nahler, N. H.; Fárník, M.; Buck, U.; Vach, H.; Gerber, R. B. *J. Chem. Phys.* **2004**, *121*, 1293.
- [104] Fárník, M.; Nahler, N. H.; Buck, U.; Slavíček, P.; Jungwirth, P. *Chem. Phys.* **2005**, *315*, 161.
- [105] Schmidt, M.; Kusche, R.; von Issendorff, B.; Haberland, H. *Nature* **1998**, *393*, 238.
- [106] Slavíček, P.; Jungwirth, P.; Lewerenz, M.; Nahler, N. H.; Fárník, M.; Buck, U. *J. Phys. Chem. A* **2003**, *107*, 7743.
- [107] Baumfalk, R.; Nahler, N. H.; Buck, U. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2372.
- [108] Sobolewski, A. L.; Domcke, W. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4.
- [109] Sobolewski, A. L.; Domcke, W. *J. Phys. Chem. A* **2003**, *107*, 1557.
- [110] Sobolewski, A. L.; Domcke, W. *Phys. Chem. Chem. Phys.* **2005**, *7*, 970.
- [111] Sobolewski, A. L.; Domcke, W. *J. Chem. Phys.* **2005**, *122*, 184320.
- [112] Sobolewski, A. L.; Domcke, W. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3818.
- [113] Nee, J. B.; Suto, M.; Lee, L. C. *J. Chem. Phys.* **1986**, *85*, 4919–4924.

- [114] Cheng, B. M.; Chung, C. Y.; Bahou, M.; Lee, Y. P.; Lee, L. C. *J. Chem. Phys.* **2002**, *117*, 4293–4298.
- [115] Ončák, M.; Slavíček, P.; Poterya, V.; Fárník, M.; Buck, U. *J. Phys. Chem. A* **2008**, *112*, 5344.
- [116] Poterya, V.; Fárník, M.; Slavíček, P.; Buck, U.; Kresin, V. V. *J. Chem. Phys.* **2007**, *126*, 071101.
- [117] Fárník, M.; Buck, U. *Phys. Scripta: Comm. At. Mol. Opt. Phys.* **2007**, *76*, 73.
- [118] Poterya, V.; Fárník, M.; Ončák, M.; Slavíček, P. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4835.
- [119] Ashfold, M. N. R.; Cronin, B.; Devine, A. L.; Dixon, R. N.; Nix, M. G. D. *Science* **2006**, *312*, 1637–1640.
- [120] Devine, A. L.; Cronin, B.; Nix, M. G. D.; Ashfold, M. N. R. *J. Chem. Phys.* **2006**, *125*, 184302.
- [121] Schwell, M.; Jochims, H.-W.; Baumgärtel, H.; Leach, S. *Chem. Phys.* **2008**, *353*, 145.
- [122] Jagoda-Cwiklik, B.; Slavíček, P.; Cwiklik, L.; Nolting, D.; Winter, B.; Jungwirth, P. *J. Phys. Chem. A* **2008**, *112*, 3499.
- [123] Machado, F.; Davidson, E. *J. Chem. Phys.* **1992**, *97*, 1881.
- [124] Serrano-Andres, L.; Fulscher, M.; Roos, B.; Merchan, M. *J. Phys. Chem.* **1996**, *100*, 6484.
- [125] Su, M. D. *J. Phys. Chem. A* **2007**, *111*, 1567.
- [126] Barbatti, M.; Lischka, H.; Salzmann, S.; Marian, C. *J. Chem. Phys.* **2009**, *130*, 034305.
- [127] Poterya, V.; Profant, V.; Fárník, M.; Slavíček, P.; Buck, U. *J. Chem. Phys.* **2007**, *127*, 064307.
- [128] Profant, V.; Poterya, V.; Fárník, M.; Slavíček, P.; Buck, U. *J. Phys. Chem. A* **2007**, *111*, 12477.
- [129] Poterya, V.; Tkáč, O.; Fedor, J.; Fárník, M.; Slavíček, P.; Buck, U. *Int. J. Mass Spec.* **2010**, *2010*, 85.
- [130] Rubio-Lago, L.; Zaouris, D.; Sakellariou, Y.; Sofikitis, D.; Kitsopoulos, T. N.; Wang, F.; Yang, X.; Cronin, B.; Devine, A. L.; King, G. A.; Nix, M. G. D.; Ashfold, M. N. R. *J. Chem. Phys.* **2007**, *127*, 064306.
- [131] Lipciuc, M. L.; Wang, F.; Yang, X.; Kitsopoulos, T. N.; Fanourgakis, G. S.; Xantheas, S. S. *Chem. Phys. Chem.* **2008**, *9*, 1838.
- [132] Poterya, V.; Profant, V.; Fárník, M.; Šišťák, L.; Slavíček, P.; Buck, U. *J. Phys. Chem. A* **2009**, *113*, 14583.

- [133] Buck, U.; Fárník, M. *Int. Rev. Phys. Chem.* **2006**, *25*, 583.
- [134] Slavíček, P.; Ončák, M.; Poterya, V.; Fárník, M. *Chem. Listy* **2008**, *102*, 467.
- [135] Friedrich, B.; Herschbach, D. *J. Phys. Chem. A* **1999**, *103*, 10280.
- [136] Friedrich, B.; Herschbach, D. *J. Chem. Phys.* **1999**, *111*, 6157.
- [137] Khriachtchev, L.; Pettersson, M.; Runeberg, N.; Lundell, J.; Räsänen, M. *Nature* **2000**, *406*, 874.
- [138] Kumar, A.; Kolaski, M.; Kim, K. *J. Chem. Phys.* **2008**, *128*, 034304.
- [139] David, O.; Dedonder-Lardeux, C.; Jouvét, C.; Kang, H.; Martrenchard, S.; Ebata, T.; Sobolewski, A. *J. Chem. Phys.* **2004**, *120*, 10101.
- [140] David, O.; Dedonder-Lardeux, C.; Jouvét, C. *Int. Rev. Phys. Chem.* **2002**, *21*, 499.
- [141] Carrera, A.; Nielsen, I. B.; Carcabal, P.; Dedonder, C.; Broquier, M.; Jouvét, C.; Domcke, W.; Sobolewski, A. L. *J. Chem. Phys.* **2009**, *130*, 024302.
- [142] Frutos, L.; Markmann, A.; Sobolewski, A.; Domcke, W. *J. Phys. Chem. B* **2007**, *111*, 6110–6112.
- [143] Sanche, L. *Nature* **2009**, *461*, 358.
- [144] Whitaker, B. *Imaging in Molecular Dynamics*; Cambridge University Press: Cambridge, **2003**.

Appendix A

Thesis publications

(Number of citations/without selfcitations **Impact Factor**)

3.1 Photodissociation of hydrogen halides in rare gas clusters

1. Slavíček, P.; Jungwirth, P.; Lewerenz, M.; Nahler, N. H.; Fárník, M.; Buck, U.
J. Chem. Phys. **2004**, *120*, 4498 – 4511.
Photodissociation of hydrogen iodide on the surface of large argon clusters: The orientation of the librational wave function and the scattering from the cluster cage
12/3, **3.149**
2. Nahler, N. H.; Fárník, M.; Buck, U.; Vach, H.; Gerber, R. B.
J. Chem. Phys. **2004**, *121*, 1293 – 1302.
Photodissociation of HCl and small (HCl)_m complexes in and on large Ar_n clusters
11/8, **3.149**
3. Fárník, M.; Nahler, N. H.; Buck, U.; Slavíček, P.; Jungwirth, P.
Chem. Phys. **2005**, *315*, 161 – 170.
Photodissociation of HBr on the surface of Ar_n clusters at 193 nm
10/2, **1.961**
4. Slavíček, P.; Jungwirth, P.; Lewerenz, M.; Nahler, N. H.; Fárník, M.; Buck, U.
J. Phys. Chem. A **2003**, *107*, 7743 – 7754.
Pickup and Photodissociation of Hydrogen Halides in Floppy Neon Clusters
15/8, **2.871**

3.2 Atmospherically relevant clusters

5. Fárník, M.; Buck, U.
Phys. Scripta: Comm. At. Mol. Opt. Phys. **2007**, *76*, 73 – 78.
Photodissociation of HBr molecules in clusters: from rare gas clusters to water nanoparticles
1/1, **0.970**
6. Poterya, V.; Fárník, M.; Slavíček, P.; Buck, U.; Kresin, V. V.
J. Chem. Phys. **2007**, *126*, 071101.
Photodissociation of hydrogen halide molecules on free ice nanoparticles
11/5, **3.149**
7. Ončák, M.; Slavíček, P.; Poterya, V.; Fárník, M.; Buck, U.
J. Phys. Chem. A **2008**, *112*, 5344–5353.
Emergence of charge-transfer-to-solvent band in the absorption spectra of hydrogen halides on ice nanoparticles: spectroscopic evidence for acidic dissociation
3/1, **2.871**

8. Poterya, V.; Fárník, M.; Ončák, M.; Slavíček, P.
Phys. Chem. Chem. Phys. **2008**, *10*, 4835 – 4842.
Water photodissociation in free ice nanoparticles at 243 nm and 193 nm
4/3, **4.064**
- 3.3 Biomolecules in clusters**
9. Poterya, V.; Profant, V.; Fárník, M.; Slavíček, P.; Buck, U.
J. Chem. Phys. **2007**, *127*, 064307.
Experimental and theoretical study of the pyrrole clusters photochemistry: Closing the $\pi\sigma^$ dissociation pathway by complexation*
12/8, **3.149**
10. Profant, V.; Poterya, V.; Fárník, M.; Slavíček, P.; Buck, U.
J. Phys. Chem. A **2007**, *111*, 12477 – 12486.
Fragmentation dynamics of size selected pyrrole clusters prepared by electron impact ionization
6/3, **2.871**
11. Poterya, V.; Profant, V.; Fárník, M.; Šišťík, L.; Slavíček, P.; Buck, U.
J. Phys. Chem. A **2009**, *113*, 14583 – 14590.
Photoinduced Processes in Hydrogen Bonded System: Photodissociation of Imidazole Clusters
0/0, **2.871**
12. Poterya, V.; Tkáč, O.; Fedor, J.; Fárník, M.; Slavíček, P.; Buck, U.
2010, *2010*, 85 – 93.
Mass spectrometry of hydrogen bonded clusters of heterocyclic molecules: Electron ionization vs. photoionization NA, **2.445**
- 3.4 Novel rare gas molecules**
13. Nahler, N. H.; Fárník, M.; Buck, U.
Chem. Phys. **2004**, *301*, 173 – 183.
Search for oriented HXeX molecules from the photolysis of HCl and HBr in xenon clusters
10/8, **1.961**
14. Buck, U.; Fárník, M.
Int. Rev. Phys. Chem. **2006**, *25*, 583 – 612.
Oriented xenon hydride molecules in the gas phase
12/10, **6.892**
15. Poterya, V.; Votava, O.; Fárník, M.; Ončák, M.; Slavíček, P.; Buck, U.; Friedrich, B.
J. Chem. Phys. **2008**, *128*, 104313.
Generation and orientation of organoxenon molecule H-Xe-CCH in the gas phase
12/10, **3.149**
16. Slavíček, P.; Ončák, M.; Poterya, V.; Fárník, M.
Chem. Listy **2008**, *102*, 467 – 473.
Syntéza v létajících nanoreaktorech: Hydridy vzácných plynů
0/0, **0.593**

Statement about the authorship of the presented publications: The research covered in this thesis represents a very complex, demanding and complicated experiment accompanied by theoretical interpretations based on state-of-the art calculations. Therefore the presented publications resulted from the collaboration of several coauthors, and usually independent experimental and a theoretical groups were involved. However, it should be noted that in the majority of the presented publications the contribution of the author of these Thesis was pivotal. In most cases the author was responsible for making the experimental proposal, measuring and evaluating the experimental data, he was strongly involved in the experimental interpretations, and finally responsible for writing the publications themselves. This is reflected by the fact that he was the corresponding author of 8 publications and the lead author of further 2 publications from the 16 publications covered in this thesis. His role in the remaining 6 publications was also essential. This is further detailed in a separate document submitted with the application and signed by the coauthors.

Appendix B

List of publications by M. Fárník

Scientific journals with Impact Factor only

Total number of publications = 46

Total number of citations = 528

Current H-factor = 14

1. M. Sadílek, J. Vančura, M. Fárník, and Z. Herman: *Beam Scattering Study of the Charge Transfer Process N^{2+} (He , He^+) N^+ at Low Collision Energies*. Int. J. Mass Spectrom. Ion Processes 100, (1990), 197–207.
2. M. Fárník, Z. Herman, T. Ruhaltinger, J. P. Toennies, and R. G. Wang: *Single electron charge transfer between He^{2+} and NO . Population of vibrational states of NO^+ ($^1\Sigma^+$) product from high-resolution scattering experiments*. Chem. Phys. Lett., 206, (1993), 376–380.
3. M. Fárník, Z. Dolejšek, Z. Herman, and V. E. Bondybey: *Beam scattering investigation of hydride-ion transfer processes. Reaction of $CH+3^+$ and $CD+3^+$ with C_2H_6* . Chem. Phys. Lett., 216, (1993), 458–464.
4. Z. Dolejšek, M. Fárník, and Z. Herman: *Dynamics of chemical reactions of doubly charged ions: CF_2D^+ formation in collisions of CF_2^{2+} and D_2* . Chem. Phys. Lett., 235 (1995), 99–104.
5. M. Fárník, T. Ruhaltinger, Z. Herman, and J. P. Toennies: *Single electron transfer in collisions of He^{2+} with: Vibrational state Population of NH_3^+ and H_2S^+* . J. Chem. Phys., 103, (1995), 3495–3500.
6. J. ?abka, M. Fárník, Z. Dolejšek, J. Polách, and Z. Herman: *Dynamics of the hydride ion transfer reaction between CD_3^+ and CH_4 : A crossed beam study*. J. Phys. Chem., 99, (1995), 1559–15601.
7. M. Fárník, U. Henne, B. Samelin, and J. P. Toennies: *Comparison between positive and negative charging of helium droplets*. Z. Phys. D, 40, (1997), 93–98.
8. M. Fárník, U. Henne, B. Samelin, and J. P. Toennies: *Difference in the Detachment of Electron Bubbles from Superfluid 4He Droplets versus Nonsuperfluid 3He Droplets*. Phys. Rev. Lett., 81, (1998), 3892.
9. M. Fárník, B. Samelin, and J. P. Toennies: *Measurements of the lifetimes of electron bubbles in large size selected $^4He_N^-$ droplets*. J. Chem. Phys., 110, (1999), 9195.
10. Z. Herman, J. Žabka, Z. Dolejšek, and M. Fárník: *Dynamics of chemical and charge transfer reactions of molecular dications: beam scattering and total cross section data on CF_2D^+ (CF_2H^+), CF_2^+ , and CF^+ formations in $CF_2^{2+} + D_2$ (H_2) collisions*. Int. J. of Mass Spectrometry, 192, (1999), 191.
11. S. Davis, M. Fárník, D. Uy, and D. J. Nesbitt: *Concentration modulation spectroscopy with a pulsed slit supersonic discharge expansion source*. Chem. Phys. Lett., 344, (2001), 23–30.
12. M. Fárník, S. Davis, and D. J. Nesbitt: *High-resolution near IR studies of hydrogen bonded clusters: Large amplitude dynamics in $(HCl)_n$* . Faraday Discuss. 118, (2001), 63–78.
13. M. Fárník, S. Davis, M. D. Schuder, and D. J. Nesbitt: *Probing potential surfaces for hydrogen bonding: Near-IR combination band spectroscopy of van der Waals stretch (ν_4) and geared bend (ν_5) vibrations in $(HCl)_2$* . J. Chem. Phys., 116, (2002), 6132–6145.
14. M. Fárník, S. Davis, M.A. Kostin, O.L. Polyansky, J. Tennyson, and D. J. Nesbitt: *Beyond the Born-Oppenheimer approximation: High-resolution overtone spectroscopy of H_2D^+ and D_2H^+* . J. Chem. Phys., 116, (2002), 6146–6158.
15. M. Weinman, M. Fárník, and M.A. Suhm: *A first glimpse at the acidic proton vibrations in HCl -water clusters via supersonic jet FTIR spectroscopy*. Phys. Chem. Chem. Phys., 4, (2002), 3933–3937.
16. M. Fárník and J. P. Toennies: *The influence of embedded atoms, molecules and clusters on the lifetime of electron bubbles in large 4He droplets*. J. Chem. Phys., 118, (2003), 4176–4182.

17. M. Fárník, M. Weinman, and M.A. Suhm: Acidic protons before take-off. A comparative jet FTIR study of small HCl- and HBr-solvent complexes J Chem. Phys., 118, (2003), 10120–10136.
18. M. Fárník, S. Davis, and D. J. Nesbitt: *Probing hydrogen bond potential surface for out-of-plane geometries: Near-infrared combination band torsional (ν_6) spectroscopy in (HCl) $_2$* . J. Chem. Phys., 118, (2003), 10137–10148.
19. P. Slavíček, P. Jungwirth, M. Lewerenz, N. H. Nahler, M. Fárník, U. Buck: *Pickup and Photodissociation of Hydrogen Halides in Floppy Neon Clusters* J. Phys. Chem. A (2003), 107, 7743 – 7754.
20. P. Slavíček, P. Jungwirth, M. Lewerenz, N.H. Nahler, M. Fárník, and U. Buck: *Photodissociation of hydrogen iodide on the surface of large argon clusters: The orientation of the librational wave function and the scattering from the cluster cage* J. Chem. Phys. (2004), 120, 4498 – 4511.
21. N.H. Nahler, M. Fárník, and U. Buck: *Search for oriented HXeX molecules from the photolysis of HCl and HBr in xenon clusters* Chem. Phys., 301, (2004), 173 –182.
22. N. H. Nahler, M. Fárník, U. Buck, H. Vach, R. B. Gerber: *Photodissociation of HCl and small (HCl) $_m$ complexes in and on large Ar $_n$ clusters* J. Chem. Phys. (2004), 121, 1293 – 1302.
23. M. Fárník, C. Steinbach, M. Weinman, U. Buck, N. Borho, and M.A. Suhm: *Size selective vibrational spectroscopy of methyl glycolate clusters: comparison with jet FTIR spectroscopy*. Phys. Chem. Chem. Phys., 6, (2004), 4614–4620.
24. M. Fárník and D. J. Nesbitt: *Intramolecular energy transfer between oriented chromophores: High-resolution infrared spectroscopy of HCl-trimer* J. Chem. Phys, 121, (2004), 12386–12395.
25. M. Fárník and J. P. Toennies: *Flying nano-cryo-reactors: Ion-molecule reactions in 4He droplets*. J. Chem. Phys., 122, (2005), 014307. (selected for publication in Virtual Journal of Nanoscale Science and Technology, Vol. 10, Iss. 26, December 27, 2004)
26. J.P. Devlin, M. Fárník, M.A. Suhm, and V. Buch: *Comparative FTIR spectroscopy of HX adsorbed on solid water: Ragout-jet water clusters vs. ice nanocrystal arrays*. J. Phys. Chem. A, 109, (2005), 955–958.
27. M. Fárník, N.H. Nahler, P. Slavíček, U. Buck, and P. Jungwirth: *Photodissociation of HBr molecules on Ar $_n$ clusters at 193 nm*. Chem. Phys., 315, (2005), 161–170.
28. M. Fárník, M. Weinman, C. Steinbach, U. Buck, N. Borho, T.B. Adler, and M.A. Suhm: *Size-selected methyl lactate clusters: Fragmentation and spectroscopic fingerprints of chiral recognition*. Phys. Chem. Chem. Phys., 8, (2006), 1148–1158.
29. M. Weimann, M. Fárník, M.A. Suhm, M.E. Alikhani, and J. Sadlej: *Cooperative and anticooperative mixed trimers of HCl and methanol*. J. Mol. Structure, 790, (2006), 18–26.
30. C. Steinbach, M. Fárník, I. Ettischer, J. Siebers, and U. Buck: *Isomeric transition in size-selected methanol hexamers probed by OH-stretch spectroscopy*. Phys. Chem. Chem. Phys., 8, (2006), 2752–2758.
31. C. Steinbach, M. Fárník, U. Buck, C.A. Brindle, and K.C. Janda: *Electron impact fragmentation of size-selected krypton clusters*. J. Phys. Chem. A, 110, (2006), 9108–9115.
32. U. Buck and M. Fárník: *Oriented xenon hydride molecules in the gas phase*. Int. Rev. Phys. Chem., 25, (2006), 583–612.
33. V. Poterya, M. Fárník, P. Slavíček, U. Buck and V. Kresin: *Photodissociation of hydrogen halide molecules on free ice nanoparticles*. J. Chem. Phys., 126, (2007), 071101. (selected for publication in Virtual Journal of Nanoscale Science and Technology, Vol. 15, Iss. 8, February 26, 2007)
34. M. Fárník and U. Buck: *Photodissociation of HBr molecules in clusters: from rare gas clusters to water nanoparticles*. Phys. Scr., 76, (2007), C73–C78.
35. V. Poterya, V. Profant, M. Fárník, P. Slavíček, and U. Buck: *Experimental and theoretical study of the pyrrole cluster photochemistry: Closing the $\pi\sigma^*$ dissociation pathway by complexation*. J. Chem. Phys., 127, (2007), 064307. (selected for publication in Virtual Journal of Biological Physics Research, Vol. 14, Iss. 4, August 15, 2007)
36. V. Profant, V. Poterya, M. Fárník, P. Slavíček, and U. Buck: *Fragmentation dynamics of size selected pyrrole clusters prepared by electron impact ionization: Forming a solvated dimer ion core*. J. Phys. Chem. A, 111, (2007), 12477.
37. V. Poterya, O. Votava, M. Fárník, M. Ončák, P. Slavíček, U. Buck, and B. Friedrich: *Generation and orientation of organoxenon molecule H-Xe-CCH in the gas phase*. J. Chem. Phys., 128, (2008) 104313.
38. P. Slavíček, M. Ončák, V. Poterya, and M. Fárník: *Syntéza v létajcích nanoreaktorech: Hybridy vzácných plynů*. Chem. Listy, 102 (2008) 467–473.
39. M. Ončák, P. Slavíček, V. Poterya, M. Fárník, and U. Buck: *Emergence of Charge-Transfer-to-Solvent Band in the Absorption Spectra of Hydrogen Halides on Ice Nanoparticles: Spectroscopic Evidence for Acidic Dissociation*. J. Phys. Chem. A, 122 (2008) 5344–5353.

40. V. Poterya, M. Fárník, M. Ončák, and P. Slavíček: *Water photodissociation in free ice nanoparticles at 243 nm and 193 nm*. Phys. Chem. Chem. Phys., 10 (2008) 4835–4842.
41. V. Poterya, M. Fárník, U. Buck, D. Bonhommeau, N. Halberstadt: *Fragmentation of size-selected Xe clusters: Why does the monomer ion channel dominate the Xe_n and Kr_n ionization?*. Int. J. Mass Spectrometry, 280 (2009) 78–84.
42. M. Fárník, V. Poterya, O. Votava, M. Ončák, P. Slavíček, I. Dauster and U. Buck: *Solvent induced photostability of acetylene molecules in clusters probed by multi-photon dissociation*. J. Phys. Chem. A, 113 (2009) 7322 – 7330.
43. I. Janeček, S. Cintavá, D. Hrivňák, R. Kalus, M. Fárník, F. X. Gadea: *Post-ionization fragmentation of rare-gas trimers revisited with new theoretical approaches*. J. Chem. Phys., 131 (2009) 114306.
44. V. Poterya, V. Profant, M. Fárník, L. Šišťík, P. Slavíček, and U. Buck: *Photoinduced processes in hydrogen bonded system: Photodissociation of imidazole clusters*. J. Phys. Chem. A, 113 (2009) 14583 – 14590.
45. V. Poterya, O. Tkáč, J. Fedor, M. Fárník, P. Slavíček, and U. Buck: *Mass spectrometry of hydrogen bonded clusters of heterocyclic molecules: electron ionization vs. photoionization*. Int. J. Mass Spectrometry, 290 (2010) 85 – 93.
46. M. Fárník, P. Slavíček, and U. Buck: *Photodissociation of Molecules in Hydrogen Bonded Clusters: Probing the Excited State*. Invited chapter in the book: *Excited-State: Hydrogen Bonding and Hydrogen Transfer*, Eds. K.-L. Han and G.-J. Zhao, Wiley, p. 1137-1176, accepted 2010.