Research Report

Ionization and fragmentation processes in free atoms and molecules

Deeper understanding of the dynamics of few-body systems under strong perturbations has relevance for several research fields of fundamental or practical importance such as astrophysics, astrochemistry, atmospheric processes, plasma physics, ion-beam cancer therapy, advanced material manufacturing techniques, etc.. The aim of our research carried out in the framework of the project was to expand our knowledge about the dynamics of molecular processes induced by photons and collisions with charged particles. This was achieved by developments concerning our experimental and theoretical tools, by studying various molecular processes and focusing primarily on small molecules. We have built, developed and tested experimental equipments for our research to be carried out within the framework of the project and in the future. Theoretical methods have also been developed and applied to interpret experimental data and to perform calculations according to the needs of different applications. The obtained results are presented in 44 papers published in refereed international scientific journals. Our activities and results achieved during the project are as follows.

A. Charged particle-molecule collisions

1. *Experimental studies*

Molecular fragmentation in the gas phase: Energy and angular distributions of negatively and positively charged ions emitted from water molecules after irradiation by 6.6 keV O^+ ions were investigated experimentally in an ATOMKI-CIMAP (Centre de recherche sur les Ions, les MAtériaux et la Photonique, Caen, France) collaboration [1]. The distributions of the oppositely charged ions showed great similarity. The H^- to H^+ ratio was found to be 1 : 100 independently on energy and angle. The experimental findings were interpreted theoretically by classical potential scattering and the thermodynamic statistical models. The calculations showed agreement with the experiments and showed that the dominant role of kinetic energy release is stemming from excitations. These observations confirmed our earlier findings that in ion induced fragmentation by singly charged ions, the charge state of the emitted fragments follow simple statistical laws. An important consequence with astrophysical relevance is that negative ion production by collisions with the ions in the dominant kinetic energy range of the stellar wind is a general process.

The fragmentation of water molecules by electron and ion impact is also a phenomenon that has strong astrophysical implications, especially from the point of view of the physico-chemical processes taking place in comets. Naturally, this is also of fundamental importance for the biological effects of ionizing radiation. We performed such ion-impact studies with swift singly charged and slow highly charged ions at the beamlines of different accelerators (VdG-5 in ATOMKI, Debrecen, and the ECR ion source at ARIBE, GANIL, Caen, France) [2]. We found that the Coulomb explosion of the water molecule is dominantly determined by the charge state of the transient molecular ions, and it is almost independent from the primary ionization mechanism.

In collaboration with University College London (UCL), we solved a long-standing problem in measuring the total electron scattering cross section (σ_T) on the water molecule [3]. Despite remarkable efforts, the convergence among earlier measurements of the total cross section remained poor partly due to the variable angular discrimination against forward elastic scattered particles. The measurement was carried out at the Department of Physics and Astronomy of UCL with slightly modified electrostatic positron beam [4], in order to produce an electron beam. The electron beam has an angular divergence of $\simeq 1^o$ and an energy spread of 4%. Its flight path is terminated by a position sensitive detector, which allows the reconstruction of the beam intensity distribution on the plane perpendicular to the beam axis. We found that at energies below 7 eV, our measured σ_T is $28 - 100\%$ higher than all previous measurements confirming the intense peak in the angular distribution of the elastically scattered electrons for H_2O at forward angles. In addition to the angle-resolved measurements of σ_T we reported experimental estimations of the (rotationally and vibrationally summed) elastic differential cross section at around 1.2^o scattering angle, which provided a first point of contact with theories in an angular region crucially important for H_2O and polar molecules in general. Our experimental data were in good agreement with results of the ab initio R-matrix method.

We have developed our specific field-free time of flight experimental setup. We were able to measure two-dimensional velocity distribution of fragment ions emitted from molecules at very low fragment velocities. The corresponding lowest fragment energies that we could measure was 0.1 eV. This and the achieved high accuracy in velocity space enabled us to measure the splitting of binary ridge due to the rotation of the target H_2 molecule in 10 keV $O^+ + H_2$ collisions. The result was published in [5], where we have shown that the rotational levels can be identified by the split and have demonstrated isotopic effects by using D_2 target. Detailed angular dependence of the intensity of the knock out fragment ions was obtained. Target coherence effects were recently noticed in the observed dependencies. Experiments were performed with higher charge state projectiles, also, which lead to observation of higher molecular excitations. These results open up a way to deeper understanding of the dynamics of few-body systems, and will be published in a longer paper together with the interpreting results of classical potential scattering calculation and the thermodynamic model. The experimental apparatus is also able to separate ions with different charge to mass ratio by a retarding grid. This is a slow method and we applied it for H_2 fragmentation only which have shown the dominance of H^+ fragment over H_2^+ emitted from the collisions. We also measured O^{2+} collisions wit O_2 molecules, which are relevant to the processes that take place in the atmospheres of icy moons. The same collision system was also measured at ARIBE GANIL by an electrostatic spectrometer. The experiment were performed as well for different charge states (up to $q = +4$) of the projectile oxygen ions. This technique is suitable for measuring the fragment ions with high kinetic energy and the different charge state could be separated by measuring the flight time of the fragments. Unexpectedly, we observed high fraction of molecular oxygen ions in the emitted particles. The experiments were delayed by the COVID epidemic and could be performed only in the last year of the proposal. A series of supplementary experiments for the high charge state oxygen ions by the TOF technique is still to be done at ATOMKI, where the astrophysically relevant low fragment energy range can be measured, to have complete dataset for astrophysical.

Molecular fragmentation and subsequent chemistry in astrophysical ice analogues: The astrophysical relevance of our gas phase studies has become a more and more important aspect. It was a natural way to extend our research in the direction of astrophysics and astrochemistry by performing ion- and electron-impact experiments in cold astrophysical ice analogues. ATOMKI became a member of a research infrastructure (RI) consortium, which submitted a proposal to the European Commission's Horizon 2020 programme in 2019. This project has been funded, Europlanet 2024 RI, and a multilateral international collaboration was formed (ATOMKI, University of Kent, UK, The Queen's University, Belfast, UK, Queen Mary University of London, Aarhus University, Denmark, University of Miskolc, Hungary). Two experimental setups were completed in ATOMKI within two years: the Ice Chamber for Astrophysics/Astrochemistry (ICA) [6, 7] and the ATOMKI - Queens University Ice chamber for Laboratory Astrochemisty (AQUILA). The ion energy range provided by their supplier accelerators (0.4 keV- 12 MeV) covers the most intense part of the solar wind. In both of these ultra-high vacuum chambers, ice layers can be deposited to cooled ($\sim$ 20 K) surfaces and irradiated by ions and electrons. Their chemical composition can be measured and followed by infrared (FTIR) spectroscopy, while sputtered and desorbed molecules can be analyzed by mass spectrometry (QMS). This methodology opens a unique way to study the fragmentation of the same molecule in both gas and solid phases, and contributing this way to the exploration of the complex, multi-scale scenario of radiolysis.

Fragmentation of molecules by irradiation in ices of different gas mixtures is followed by the chemical interaction of the fragments with the initial molecules and with each other, and we observe this scenario by infrared spectroscopy. Accordingly, our work can be broadly divided into two components: (i) the spectroscopic characterization of astrophysical molecules and materials, and (ii) the physical and chemical changes induced in astrophysical ice analogues by means of irradiation using energetic ions and electrons. Both these aspects of our work are of vital significance, as the former will allow for the production of laboratory spectra which may be used in tandem with data acquired by high-sensitivity instruments such as the James Webb Space Telescope to detect novel molecules in the interstellar medium or outer Solar System environments, while the latter will allow for the study of physical and chemical changes induced by radiation that lead to the formation of molecules of significance to geology or biology.

As an example of our spectroscopic work, we have successfully determined that solid-phase purine nucleobases (that are essential components of biomolecules such as DNA and RNA) mid-infrared absorption bands that are, at least in principle, detectable in spectroscopic surveys of interstellar targets. [8]. We have also performed detailed spectroscopic studies of several molecular ices (e.g., SO_2, CO_2, O_3) under a wide range of conditions that are relevant to astrophysical environments [9]. Among the examples of our irradiation experiments, we have demonstrated that the chemistry ensuing as a result of the implantation of sulphur ions into CO_2 ice is dependent on temperature, thus having important implications on the favourability of the formation of sulphur-bearing molecules in different regions of the Solar System [10]. In a separate set of experiments, we were also able to quantify the production of O_3 on icy outer Solar System moons as a result of differences in the initial composition of their icy surfaces [11]. A systematic investigation on the influence of thermal annealing of pure CO_2 astrophysical ice analogues prepared at various temperatures, as well as the effect of temperature on the chemical products after electron irradiation. Such results were directly applicable to studies on the chemistry of interstellar ices, comets, and icy lunar objects, see [12]. We performed comparative irradiations of the amorphous and crystalline ices of different molecules [13, 14]. We found evidence for phase-dependent chemistry, with the radiation-induced exponential decay of amorphous ices being more rapid than that of the crystalline phase. We discussed our results in the contexts of interstellar and Solar System ice astrochemistry and the formation of sulphur allotropes and residues in these settings. Bombarding CO ices with He ions in a wide energy range, we compared the molecular destruction yields with the known cross sections of the primary collision processes (ionization, excitation and electron transfer). Our data suggest that towards low projectile energies, the excitation process is increasingly responsible for molecular fragmentation [15].

2. *Theoretical studies for ionization and fragmentation processes*

CTMC method: In the framework of the project we planned to describe the ion- and photon-induced ionization/fragmentation of molecules by the Classical Trajectory Monte Carlo (CTMC) method. As a first step, we considered the simpler case, i.e., the photoionization of atoms. Starting from our CTMC code for ion-atom collisions we have developed a code for photoionization of atoms based on the Classical Ensemble Approximation (CEA) model. We applied this model for the description of the double ionization of helium induced by 45 fs, 394 nm linearly polarized laser pulses for intensities $(2.5 - 150) \times 10^{14}$ Wcm^{-2} [16]. A reasonable agreement with the experiment of Henrichs *et al.* [17] was achieved by assuming a two-step mechanism: The formation of a transient double excited state in the first step, and the simultaneous release of the two electrons via 'over the barrier ionization' in the second step.

In a further work [18] we have investigated the performance of different versions of the CTMC theory in the description of the single and double ionization of argon induced by 4 fs, 750 nm linearly polarized laser pulses by comparing the calculated quantities with existing experimental data, primarily the results of the systematic measurements of Kübel *et al.* [19], in the intensity range $(1 - 10) \times 10^{14}$ Wcm^{-2}. The comparison involved different one- and two-electron models based on the CEA model. The analysis covered single- and double ionization probabilities and their ratios, longitudinal momentum distributions of the Ar^+ and Ar^{2+} recoiled ions, and the carrier-envelope-phase-dependent asymmetry of the yield of the Ar^+ and Ar^{2+} ions.

We also applied the CTMC method for the study of the effect of higher-order dispersions on photoionization induced by ultrafast laser pulses [20]. Dispersion plays an important role in ultrafast optics [21], it can influence ionisation [22, 23] and dissociation processes [24, 25], or it can be a useful asset at distinguishing the isomers of complex organic molecules [26, 27]. In our calculations we used linearly polarised ultrashort 7 fs laser pulses, 6.5×10^{14}W/cm^2 intensity with a central wavelength of 800 nm. Our results show that electrons with the highest kinetic energies are obtained with transform limited (TL) pulses. The shaping of the pulses with negative second- third- or fourth- order dispersion results in higher ionisation yield and electron energies compared to pulses shaped with positive dispersion values. We have also investigated how the Carrier Envelope Phase (CEP) dependence of the ionisation is influenced by dispersion. We calculated the left-right asymmetry as a function of energy and CEP for sodium atoms employing pulses of 4.5 fs, 800 nm central wavelength, and 4×10^{12}W/cm^2 intensity. We found that the left-right asymmetry is more pronounced for pulses shaped with positive Group Delay Dispersion (GDD). It was also found that shaping a pulse with increasing amounts of GDD in absolute value blurs the CEP dependence, which is attributed to the increasing number of optical cycles.

The first application of our CTMC method extended for photoionization of molecules was an attempt to interpret the results of an experiment carried out in an international collaboration for the study of strong field-ionization of H_2 by a co-rotating two-color laser field [28]. In the experiment the electron momentum distribution has been measured in coincidence with the kinetic energy release of the dissociating hydrogen molecules. The failure of the classical method in the reproduction of the experimental data indicates that dominantly quantum mechanical effects play role in the dissociation process.

In addition, by including the relativistic description of the ion-induced ionization of the atoms we have studied the collisions of positronium atoms with molecules [29].

CDW-EIS method: It has been shown for atomic targets that theoretical models formulated within the continuum distorted wave with eikonal initial state (CDW-EIS) approximation [30] with Hartree-Fock description of bound and continuum electronic orbitals yield very good agreement with experiments [31, 32]. In [33], we generalized the CDW-EIS method to molecular collisions and applied it to evaluate cross sections for the single ionization of H_2O by energetic bare ion impacts. As in our previous application of the method [34], the initial ground state molecular orbitals have been described with the Gaussian quantum chemistry program package [35] at the Hartree-Fock level. The single center expansion procedure has been used to the ground state electron density, on which the static and exchange contributions to the potential accounting for the multi-center interaction between the unbound electron and the target core was derived. That is compared to our previous application of the CDW-EIS model, where the continuum orbital has been evaluated on the spherically averaged static potential [34], a more realistic anisotropic potential has been considered for accounting the interaction of the released electron with the residual ion. The exchange interaction has been considered by a local energy-dependent potential proposed by Hara [36], which is able to reproduce the essential characteristics of the interaction between bound electrons and the ejected electron. The method has been employed to calculate doubly and singly differential cross sections of the water molecule by energetic H^+, C^{6+} and O^{8+} projectiles, and the discussion of the results has been primarily focused on the emission of low-energy electrons. The great advantage of the present method is that it can easily be extended to study other molecules as well. The orbitals of the active electron both in the initial and final channel are treated by the single-center expansion procedure. The symmetry of the molecule is taken into account in the evaluation of transition amplitudes, which reduce tremendously the time of computing.

Moreover, during the research period various other collision systems have been studied with the previous version of the CDW methods, such as H^+ - He [37], H^+ - H_2 [38], F^{9+}, Si^{12+} - C_{60} [39, 40], Si^{8+} - $C_{13}H_{10}$ [41], in order to test their validity, and to contribute to the understanding of collision mechanisms relevant for applications.

Multichannel Quantum Defect Theory (MQDT): The multichannel quantum defect theory in the present project has been applied with great success to study the electron-induced elementary processes for several diatomic and polyatomic systems having not only key relevance for the astrochemistry, the planetary atmospheres and different types of cold laboratory and technological plasmas, but very demanded by the communities. The obtained results were compared either with other theoretical data or with experimental data measured in storage-ring experiments, and they are also prepared, tabulated and uploaded in databases and shared with the astro and plasma modellers. We have studied the dissociative recombination and ro-vibrational excitation of molecular ions initiating the formation of complex organic molecules relevant for astrochemistry and being key species for life on Earth. In particular, we show how MQDT and R-matrix methods are used to compute cross-sections and rate coefficients for cations in well-defined ro-vibrational levels of the ground electronic state, from sub-meV up to a few eV collision energies for molecular species like CH^+, CO^+, HCO^+, and $CH_2NH_2^+$ [42]. We have pointed on the importance of the molecular rotation (rotational effect) and of the excited electronic states of the target ions (core-excited effects) for the studied elementary processes [42, 43]. By applying our MQDT method we have studied recombination and excitation processes of N_2^+ [44] and BeT^+ [45] relevant for the modelling of the edge fusion plasmas in ITER or ITER-like fusion devices, where the state-to-state cross sections and rate coefficients have shown strong isotopic and vibrational effects, especially in the case of BeH^+ and its isotopologues. Our nitrogen chemistry studies relevant for the interstellar medium (ISM) and/or astrochemistry was continued with electron structure and electron scattering calculations for the SN^+ molecular cation [46], recently discovered in ISM. Bound and resonance states along with corresponding autoionization widths for SN were determined for three different molecular symmetries making possible to study the electron induced dissociative recombination, and rotational and vibrational excitation of SN^+. The first preliminary results obtained for the nuclear dynamics are very promising, we were able to define uncertainties of our calculated recombination and excitation rate coefficients based on the partial wave resolution of the molecular data sets. These new results will be soon published [47]. The last diatomic system we studied in the project is related to one of the most important element of the sulphur chemistry in ISM, namely SH^+ [48]. In the present extended calculation we have proved the importance of the simultaneous inclusion of the rotational and core-excited effects into our models for obtaining realistic rate coefficients for the cold regions of ISM. Moreover, for the first time we managed to obtain branching ratios for the outgoing channels by combing the MQDT with Landau-Zener model, that agree well with the experimental findings.

In addition to the diatomic studies we have performed calculations for two simple polyatomic molecular cations. Using the polyatomic UK-molecular R-matrix codes electron collisions with the methylene molecular ion CH_2^+ in its bent equilibrium geometry were investigated [49]. We have calculated cross sections for excitation, ionization and dissociation by considering highly excited bound and resonance (Feshbach) states of the neutral complex. In this way we have prepared the study on the dissociative recombination of the target ion. And finally, we have explored the dissociative recombination of N_2H^+ in a two-step theoretical study [50]. In a first step, a diatomic (1D) rough model with a frozen NN bond and frozen angles is adopted, in the framework of the MQDT. The importance of the indirect mechanism and of the bending mode is revealed, in spite of the disagreement between our cross section and the experimental one. In the second step, we use our recently elaborated 3D approach based on the normal mode approximation combined with R-matrix theory and MQDT [42]. This approach results in satisfactory agreement with storage-ring measurements, significantly better at very low energy than the former calculations.

The developments achieved in the present project pave the way for the unified MQDT program package that will simultaneously include all relevant interactions and effects (rotational, vibronic, core excited, spin-orbit) that can be relevant for the reactive elementary processes. In order to include spin-orbit couplings in our model, we plan to use an approximation successfully used for describing fine structure necessary to treat state-to-state processes in ultracold collisions. From experimental point of view the exclusion of reactive processes at ultracold temperatures was timely, thus besides the complete structure of the molecule, we determined state-to-state reaction rates and cross sections for inelastic and elastic processes for collisions between alkali atoms [51].

Moreover, the recent developments (inclusion of core exchange potentials) performed on QUANTEMOL [52] (the electron structure and electron scattering program suite) and MOLPRO [53] - used for calculating the molecular data sets - will make possible to study the electron-impact processes of heavier halogenic molecular species containing chlorines or iodines.

Elastic scattering of electrons on atoms and molecules: The angular variation of differential cross sections for electron scattering by atoms and molecules provides important details about their internal structure and electron density distribution. This knowledge can be extended to better understand their interaction with heavy colliders such as energetic ions. This was our motivation to carry out an extensive theoretical study of elastic electron scattering by some relevant atomic and molecular targets. In [54], we have studied the electron scattering by CF_n ($n = 1 - 4$) molecular target species in the independent atom model (IAM). For the description of the differential cross sections of scattering by the constituent atoms (C and F), we used the Optical Potential (OP) model, which involves the static, exchange, correlation-polarization, scalar-relativistic, spin-orbit as well as the absorption interaction terms (RSEPA framework). Except for the IAM, we also used the simple additivity rule to calculate the integral cross sections, where the electron-molecule scattering cross sections are defined as a sum of the electron-atom cross sections. The amplitudes of electron scattering by the carbon and fluorine atoms of the target molecules are calculated from the corresponding phase shifts by the complex optical potential method, where the potential terms are defined by the atomic properties such as nuclear charge, electron density and static dipole polarizability. The cross sections in the IAM model are calculated at equilibrium internuclear distances of the particular molecules. A good overall agreement was found above $15 - 20$ eV collision energies with respect to the measured differential and total cross sections available in the literature for some of the target species studied in our work [54]. In [55], we report accurate integral and differential cross sections as well as spin-polarization parameters in the case of elastic electron scattering by zinc atom. More than 5 orders of magnitude of collision energies are considered: from 0.01 eV up to 3 keV. We used the relativistic OP model to calculate the scattering amplitudes and elastic cross sections based on the RSEPA interaction potential. The potential terms are determined by the total and valence electron densities of the zinc atom. These densities along with the static dipole polarizability, ionization potential and other atomic properties were calculated in the local approximation of density functional theory, including relativistic effects. We found a strong P-wave shape resonance at low-energis, around $0.19 - 0.20$ eV, with a width of ~ 0.309 and ~ 0.356 eV for the $j = 3/2$ and $j = 1/2$ total electronic angular momenta, respectively. Additionally to differential and integral cross sections, Sherman-functions $S(E, \theta)$ are also computed, which are in a good agreement with the experimental data available in the literature. From the S-functions, five critical minima positions and energies are located. Except for elastic cross sections, in [55] we also reported momentum transfer and viscosity integral cross sections, which is of great importance in interpreting experiments providing them with a benchmark.

B. Photoionization

Higher order effects: Theoretical and experimental studies of photoelectron angular distribution (PAD) at photon energies of a few hundred of eV are generally explained in the framework of the dipole approximation (DA). With the advances of synchrotron sources and experimental techniques, new observations emerged of which the precise interpretation can only be explained by going beyond the DA [56–58]. Moreover, it was found that excited states cannot be neglected while trying to understand angular differential cross sections [59]. In fact, the interference effects between the direct photoionization and resonant processes can greatly affect the photon energy dependent behavior of the dipole parameters [60]. To interpret the experimental results we have developed a theoretical model of atomic photoionisation, considering the channel interaction effects between direct ionization and autoionization process for the case of Kr including multipole contributions beyond the DA. In the studied photon energy range both the direct ionization of the $4p$ outer subshell and the excitation of the inner $3p$ subshell is possible, followed by a resonant Auger-decay process. Thus channel interactions occur between the direct and the excitation-decay pathways. The calculated dipole and non-dipole parameters characterizing the PADs were compared with the experimental results for the two fine structure components of the Kr $4p$ state [61] measured with the ESA22 electron spectrometer [62] at the DORIS III, in Hamburg. With this unique experimental setup we were able to determine for the first time the photon energy dependence of the dipole and non-dipole angular anisotropy parameters. We found that both the dipole and the non-dipole parameters show a different behavior as a function of the photon energy than the existing theoretical models, including ours, predict. The experimental observations also show stronger octupole contribution than predicted by theory. The resonance structures for the considered multipole parameters could give a qualitative evidence for channel interaction effects, but couldn't account for all of the observed structures in the experiment. The discrepancies are possibly due to the fact that multielectron correlation effects are not included in our model as well as the appearance of two-electron excitations of the $3d$ subshell, which also lie in the studied photon energy range. The PAD is very sensitive to changes in the anisotropy parameters, thus future experiments with good angular resolution are needed to obtain more accurate values. The spectrometer was recently upgraded by installing a large position sensitive detector which allows a more detailed measurement of PAD in the future.

Study of biologically relevant molecules: Tetrahydrofuran (THF, C_4H_8O) can be used as a model molecule representing the deoxyribose group in DNA backbone and therefore has significant interest [63–65]. It was also discovered that secondary electrons induced by ionizing radiation with energies well below the ionization threshold can cause strand breaks in the DNA [66]. This shows the importance of the properties of photoelectron emission from THF. In our study [67] energy and angular distributions of photoelectrons from THF ionized by a He(I) vacuum ultraviolet (VUV) photon source were measured and compared with other available experimental results. We were the first group having measured the angular distribution from THF in the $0^o - 360^o$ angular region and determined the β asymmetry parameters. Numerical calculations were also performed to study the process. The prominent peaks in the energy spectra of photoelectrons were identified according to their binding energy and symmetry with the help of outer valence Green's function calculations. Theoretical calculations performed for the binding energies of orbitals and photoelectron intensities are in reasonable agreement with measurement. The observed angular distributions show the determining role of dipole transition mechanism in the whole electron ejection energy range in agreement with the theoretical calculation.

C. Instrumental developments for experiments

The development of experimental devices turned out somewhat differently from our plans. We originally aimed to design two time-of-flight (TOF) systems, one for the molecular physics beam of the ECR ion source, and a 2nd for the similar beamline of the VdG-5 accelerator. In addition, an energy dispersive spectrometer that works with a combination of electrostatic and magnetic fields was also planned to put into operation at the same VdG-5 beamline. Unfortunately, the VdG-5 accelerator fell into a critical state after a waterlogging in April 2019, and - due to the lack of financial resources for its complete renovation - it was shut down in November of that year. In the same period, we became involved in the investigation of molecular fragmentation for studying astrochemical scenarios. Together with our collaborators we developed and installed two high-value, complex measuring stations with the help of the Europlanet 2024 RI project and support from HUN-REN. We have not used the support of the present OTKA project for their construction, but we did use it in a limited extent for the implementation of the scientific programs (for purchasing some consumables) and the presentation of the results at international conferences. The above changes in the boundary conditions forced us to reconsider our instrumental plans. In addition, the COVID pandemic significantly slowed down both the collaboration activities and the lead time for the purchase and production of the ordered investment tools. We are grateful that these effects were in large part compensated by the one-year extension of the present OTKA project. Fortunately, together with our French collaborators, we were able to implement the dispersive spectrometer - based on the combination of electrostatic and magnetic fields - at the ECR ion source of the ARIBE GANIL. Our measurements there provided astrophysically relevant results by finding a general collisional production mechanism for negative ions. Unfortunately, COVID intervened our travel program, and only recently became possible to continue the measurements again. A TOF-based spectrometer assembly, targeting multiple coincidence measurements was specifically designed for the 1000 mm diameter measurement chamber at the VdG-5 beamline. However, this measuring chamber - together with its auxiliary equipment - takes up so much space that it could not be relocated next to the Tandetron accelerator. Other conditions also changed (the existing detector turned out to be slow for TOF application), so we reconsidered the structure of the spectrometer and requested a cost reallocation at the end of 2020, which made it possible to purchase a fast detector-electronics system. Procurement of this system has slowed considerably due to COVID. In the meantime, the demand that the new TOF spectrometer should be suitable for measuring larger fragments of more complex molecules was gradually expressed, thus ensuring the parallel examination of fragmentation with ice samples by bombarding the gas (vapor) and solid phases of the same material, with the same ions. This demand involved another, almost complete redesign. Based on the new plans developed after the simulations, the TOF spectrometer was finally put into production in the fall of this year, and was completed this November. We believe that this unusually late realization of this instrumental development will support our novel approach of experimental multiscale studies already in the near future, performing experiments early in 2024. The implementation of the field-free TOF spectrometer has proven to be a great success, providing opportunity to examine the collisions of small molecules in fine detail. This is a unique facility, with an efficient magnetic shielding ($B < 1$ mGs) and a contact-potential free arrangement for all internal surfaces including the collision area of the crossed ion-beam and the effusive target gas jet, and the meshes in front of a position sensitive multichannel plate detector. The target gas jet can be cooled to liquid N_2 temperatures for reducing the initial momentum scattering of the molecules. Two-dimensional velocity distribution of fragment ions emitted from molecules can be measured at very low fragment velocities (≥ 0.1 eV). This and the achieved high accuracy in velocity space enabled us to measure the splitting of binary ridge due to the rotation of the target H_2 molecule in 10 keV $O^+ + H_2$ collisions, where we have shown that the rotational levels can be identified by the split and isotopic effects were demonstrated by D_2 target.

ESA-22 electron spectrometer: Our measurements on the THF molecule [67] showed that the relatively large size and low intensity of the VUV beam in the target area at $h\nu = 40.81$ eV photon energy (He II) would not allow accurate measurement of the 3D angular distribution of photoelectrons ejected from the outer shells of noble gases. Therefore, we started with the substantial developments that increased the sensitivity of the spectrometer, and which were also necessary to make the equipment suitable for another experimental program planned at high power XUV beamlines. The channeltron detectors were replaced by a channel plate detector for improving the angular resolution, allowing detection of electrons simultaneously over a wider energy range, increasing detection efficiency and reducing the measuring time. Most of those upgrades have been performed from another financial sources aiming to prepare the spectrometer for studying photoionization at the ELI-ALPS Laser Center in Szeged. After calibrating the spectrometer by comparing elastic electron scattering data and electron-impact induced Auger spectra with reference data, ESA-22 was transported to Szeged. There we installed it at the SYLOS LONG XUV beamline of the ELI-ALPS Laser Center. Recently, we performed the first test measurement for the photoionization of the argon atom and N_2 molecule by photon impact in the $30 - 90$ eV energy range.

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