Research report

Electron induced reactivity of major hydride cations in interstellar space

The cold ionized media (CIM), i.e. the interstellar medium (ISM), the supernovae, the early Universe, the planetary atmospheres, the exoplanets, re-entry plasmas near the walls of space krafts, laboratory and fusion plasmas, ion-beam based cancer therapy, etc., containing molecular species are the seat of an extremely rich chemical physics, mainly due to the presence of electrons, cosmic rays, photons and neutral and ionized atomic and molecular species. The successful modelling of these non-equilibrium environments is critically based on the precise knowledge of state-to-state cross sections and rate coefficients of the dominant radiative or collisional elementary processes [1].

Among the many reactive collisional events, the electron driven dissociative recombination (DR) and their competitive processes like ro-vibrational and/or electronic (de-) excitation (RVE or RVdE, as well as EE or EdE) and - at higher collision energies - dissociative excitation (DE), are at the heart of molecular reactivity in these environments, being major molecular ion destruction reactions. They also play an important role in producing the observed atomic metastable states, inaccessible through optical excitations [2]. While DR and DE produces neutral and/or charged smaller fragments, in case of the excitations the target cation's inner degrees of freedom are changed.

The complete theoretical description of the electron induced elementary processes is known to be a serious challenge. It concerns the coherent interaction of several fragmentation continua - electron/ion, neutral/neutral, cation/anion - with several infinite series of super-excited molecular (Rydberg) states, completed with the full inclusion of non-adiabatic couplings between the electronic and nuclear degrees of freedom (rotation, vibration). The best theoretical method that can overcome this complexity is based on the Multichannel Quantum Defect Theory (MQDT) [3].

One of the aims of the present proposal was to tackle the theoretical challenges of refining, developing and extending robust methodologies to be able to study simple *molecular cation + electron* reactions - from diatomic systems towards polyatomic complexes. In addition we applied the developed methodologies to provide collisional data for relevant molecular systems, that are of key importance either because they were recently observed in the the different cold ionised media, or due to the lack of any collisional data, due to the existence of misleading experimental and theoretical data.

The obtained results within the present project are presented in 15 peer-reviewed scientific papers (given in red in the bibliography) with impact factor (11 published and 4 submitted/accepted for publication), 4 papers in scientific journals without impact factor and 3 dissertations (given in blue in the bibliography). A common Hungarian-French PhD thesis is in progress based partly on these results. We have also presented our results at 6 highly ranked international conferences like ICPEAC, POSMOL, ESCAMPIG, GEC or CCMI, given in teal green in the bibliography.

In the followings we briefly outline our main results. The first 8 results (A - H) are connected to reactive processes in electron-molecular cation collisions, followed by electron - neutral molecule collisions (I, J), and ending by showing results for ultracold heavy-heavy collisions (K).

A. H_2^+ and isotopologues

Molecular hydrogen and its cation are among the first species formed in the early Universe. Due to the lack of a dipole moment, in the absence of catalyzing dust grains, the homonuclear molecule H_2 cannot be formed in gas phase by radiative association of two hydrogen atoms, it is formed via the collisions of H^- and H_2^+ [4]. This channel is limited by the destruction of H_2^+ by photodissociation, charge exchange with H atoms, and dissociative recombination (DR) with electrons. In dense molecular clouds where ultraviolet radiation is efficiently absorbed by dust grains, H_2^+ is formed by cosmic-ray ionization of H_2.

The molecular hydrogen cation is also the primary molecular ion formed by photoionization of H_2 in the upper atmospheres and ionospheres of outer gaseous planets in the Solar System and extrasolar giant planets. The recombination of H_2^+ with electrons has also been studied as a source of excited states of atomic hydrogen, in particular H($2p$). In addition, due to the high electron densities, DR of H_2^+ plays an important role also in brown dwarfs atmospheres, planetary nebulae, and HII regions [5].

Dissociative recombination is also an important reaction in laboratory astrophysics [6] and cold technological plasmas, since it affects the diagnostics of electric discharges in hydrogen and deuterium mixtures based on the line profile of the hydrogen Balmer series, where this recombination process becomes dominant. The effect has been studied in particular in recombining plasmas where the electron temperature is below 1 eV and therefore relevant for the interstellar medium. These reactions can have an important impact on the behaviour of the plasma near the walls of the ITER-like fusion plasma devices.

The calculations performed on the main low-energy electron-impact processes involving H_2^+ and isotopologues (DR, RVE and RVdE) relevant for the astrochemistry of the early Universe and ISM are the natural continuations and of the already performed studies relevant for the kinetic modelling of these environments [7–9]. In the framework of the stepwise Multichannel Quantum Defect Theory (sMQDT) calculations were performed by fully accounting for all major interactions - Rydberg/valence, rotational and vibronic interactions for the seven most relevant singlet and triplet, gerade and ungerade molecular symmetries. We show results for three different initial ro-vibrational levels of the ground electronic state of both H_2^+ and HD^+ target systems, corresponding to ground state, lowest rotationally excited state and lowest vibrationally excited state respectively [10, 11]. Our calculated DR cross sections are presenting the $1/E$ general trend particular for collisions among low

energy charged particles - Wigner's threshold law - as well as the resonant structures corresponding to the temporary captures of the incident electron into ro-vibrational levels of Rydberg states. The cross section of the resonant elastic collision exceeds the DR by at least two orders of magnitudes, being less affected by resonance and/or target-excitation effects, in contrast to all other reactive processes. The most important ro-vibrational transitions are those having pure "unity" transitions ($\Delta v = 1$ propensity rule) and they are followed by the mixed ro-vibrational excitations. Presently, the calculations for the two isotopologues are finalised up to the lowest 30 ro-vibrational levels. We plan to do the calculations for all ro-vibrational levels of the ground electronic state ($H_2^+ : 283/HD^+ : 331$). In this way we will provide a complete set of ro-vibrationally resolved collisional DR, RVE and RVdE data relevant for the modelling of the early Universe based on vibrationally resolved collisional data.

In order to complete our studies on H_2^+ and isotopologues, we have calculated cross sections between 0.01 meV and 0.3 eV, and consequently thermal rate coefficients between 10 and 1000 K, for DR and rotational excitation/de-excitation (RE/RdE) of electrons with D_2^+ $(X^2\Sigma_g^+)$ ions for their lowest 11 rotational levels and in their ground vibrational level [12]. In our model, we have accounted for previously given all relevant electronic states and symmetries of the cation target, for all relevant rotational and vibronic electronic couplings, by considering the quantum interference among the direct and indirect mechanisms. The obtained rate coefficients show a strong dependence on the initial rotational state of the molecular target. We have compared these DR and RE/RdE coefficients obtained with the similar rate coefficients previously calculated in our group for the H_2^+ and HD^+ isotopologues [8, 9]. They crucially depend on the fine balance between the initial and final channels, the nuclear masses and threshold effects. For RE we observe that heavier the cation, larger the rate coefficient, while for RdE we get only a slight isotopic effect. The strongest initial/final channel dependence can be observed for the DR. The obtained isotopic differences clearly put in evidence the importance of the present results, especially for kinetic modelling of the environments where deuterated species are present. These results complement significantly the recent investigations on the other main competing destructive channels of H_2^+, HD^+, and D_2^+ via their reactions with H_2, HD, and D_2 that produce the H_3^+, H_2D^+, D_2H^+, and D_3^+ triatomic ions, allowing to remove significant uncertainties of previous studies. The numerical data, ready to be used in the kinetic modelling in astrochemistry and cold plasma physics will be uploaded to astrochemical (KIDA) [13] and plasma-related (LxCat, IAEA-Ambdas) [14, 15] databases.

B. SH^+

SH^+ is ubiquitous in the ISM, it was first detected in emission in W3 IRS 5, a region of high-mass star formation [16], and since then in absorption in the diffuse ISM, towards various distant star-forming regions. It is a key building block of the not yet well understood sulfur chemistry of the ISM. However, for SH^+ to be used as a tracer of the physical conditions of the media where it is observed, its chemistry needs to be known in detail and in particular its destruction mechanisms, such as DR.

In the framework of the sMQDT we have studied the relevance of the $^4\Pi$ symmetry states of SH for the DR and VE of SH^+ at low energy/temperature [17]. This study is a natural continuation of our previous study on the $^2\Pi$ symmetry states of SH [18] and it is meant to complete and increase its accuracy. We have found that this symmetry has a far smaller contribution to the cross sections/rates than the $^2\Pi$ ones. Therefore, the comparison between theory and experiment did not change after the present study: an overall good agreement from 10 meV to 1 eV, and a disagreement increasing progressively up to one order of magnitude when the energy is decreased from 10 to 0.1 meV. We produced for the first time the branching ratios, and we considered the redistribution of the probability fluxes at the crossing between the PECs of the two dissociative states. A spectacular inversion in the branching ratios takes place, resulting in a satisfactory agreement between our theoretical MQDT-Landau-Zener final results and those produced by the Test Storage Ring (TSR) equipment from Heidelberg, Germany, at very low energy. More than two third of the recombination events result in ground state sulphur atoms. For the first time, we have also computed vibrational excitation cross sections and rate coefficients. This process is largely dominated by dissociative recombination below 1000 K. Moreover, to facilitate their use in kinetic modelling, we have fitted their temperature dependence by using the Arrhenius-type formula. The tabulated numerical data, ready to be used are uploaded to astrochemical databases. In addition, for the first time we have started to do uncertainti studies on the calculated cross sections related to the precision of the molecular data sets. These preliminary results were shown in the thesis of two BSc students [19, 20] from University of Debrecen. The calculated DR and VE rate coefficients were uploaded to KIDA [13] database.

Further studies will be devoted to account the rotational effects, which may result in a better agreement between theory and experiment, especially in the very low energy range.

C. N_2H^+ and isotopologues

N_2H^+ is a closed-shell, linear, three-atomic inorganic cation that was one of the first charged polyatomic species observed in the interstellar medium (ISM), and is less known in terrestrial environments. It is a key member of the nitrogen astrochemistry, and it gives astronomers information about the fractional ionization of gas clouds and the chemistry that happens within those clouds, and it is often used as a tracer for molecules that are not as easily detected due to a lack of permanent dipole moments, such as N_2. Thus, it is crucial to know in details the different formation and/or destruction pathways of N_2H^+. Moreover, in recent years, there was a growing interest in the isotopic ratio of interstellar nitrogen (^{14}N vs. ^{15}N) in the view of establishing to which degree the planetary systems inherit their chemical composition from their parent interstellar clouds [21]. One of the main challenges is to determine the sources of isotopic ratio variations of nitrogen in star-forming regions and protoplanetary disks. One hypothesis was, that dissociative recombination of N_2H^+ with slow electrons might be responsible for isotope-selective depletion.

In order to elucidate the major destruction pathways of N_2H^+, we have explored its DR in a two-step theoretical study [22]. In a first step, a diatomic (1D) rough model with a frozen N-N bond and frozen angles is adopted, in the framework of our sMQDT method. The molecular data relevant for DR via the "N_2" pathway (a frozen N-N bond and frozen angles) was calculated by Talbi et al. [23]. The importance of the indirect mechanism and of the bending mode was revealed, in spite of the disagreement between our cross section and the experimental one, we have obtained DR cross sections that underestimates the CRYRING, Stockholm, Sweden measurements by more than two orders of magnitude. In the second step, we used our recently elaborated 3D approach based on the normal mode approximation combined with R-matrix theory and MQDT [24]. The obtained 3D model results, including the symmetric and asymmetric stretching and bending vibronic modes, are in very good agreement with the CRYRING storage-ring experiments at low collision energies providing better cross sections in these energy regions compared with other theoretical results.

In a second study we were focusing on the isotopic effects in the dissociative recombination and vibrational excitation of the astrochemically relevant N_2H^+ molecular cation, by changing the masses of all atomic ingredients [25]. By using a 3D model calculation in the framework of the normal mode approximation combined with R-matrix theory and MQDT we have determined the DR and VE cross sections and thermal rate coefficients for 8 isotopologues by considering all three normal modes: the doubly degenerate bending and symmetric and asymmetric stretching. Our calculations show that the relative differences respective to the main isotopologue are below 1% for the hydrogen-containing isotopologues, and reach about 30% for the heaviest deuterated isotopologue ($^{15}N_2D^+$). This study concludes that dissociative recombination is not responsible for the peculiar isotopic ratios ($N_2H^+/^{15}NNH^+$ and $N_2H^+/N^{15}NH^+$) observed in the interstellar medium, suggesting that crucial fractionation processes, in the gas or on the surface of the icy grains, are still missing in the current astrochemical networks.

D. NH^+

Controlling heat load on the plasma facing components is a major issue in large magnetically controlled fusion devices like ITER, and is needed to protect the walls from thermal damage. Injection of impurities like nitrogen, and noble gases like neon and argon are being increasingly used and tested for this purpose [26]. Injected impurity gases can interact with the plasma giving rise to different hydrides, since H, D and T is used as fuel. Significant amounts of NH, NH^+ and their isotopologues are expected to form in the vicinity of the walls, thus detailed collision data is required for the plasma flow modelling.

NH and its cation is a relevant member of the nitrogen chemistry in ISM. It was first observed in the interstellar medium at the beginning of the 1990s by Meyer and Roth [27] and since then it was found in different protostars [16] and photon dominated regions. Moreover, it is the minority final product of the electron impact dissociative recombination of N_2H^+, another key member of the nitrogen astrochemistry of ISM [22]. In contrary, NH^+ was not yet observed in the ISM. One possible explanation can be for example the relative high DR rate coefficients making its fragmentation an important and fast process. However, an indirect proof of its presence is the observation of the protonated ammonium cation, since its reactive collision with H_2 is an important stop in the formation chain.

The production of collisional data relies on prior knowledge of the potential energy curves (PECs) corresponding to the ion's ground state as well as that of the dissociative states of the neutral molecule and of its mono-excited Rydberg states. These latter states, which we can organize in Rydberg series, each of them characterized by geometry-dependent quantum defects. Additionally, the electronic couplings between the dissociation and ionization continua (referred as Rydberg-valence couplings) are needed. With the aim of identifying Rydberg states and resonant states of NH, in the present work we have undertaken detailed electron scattering and structure calculations in the frame work of the R-matrix theory [28]. We have identified and characterised valence and Rydberg states belonging to 9 different symmetries that can be relevant for the DR. Finer details on the variation of the effective quantum numbers of the Rydberg states with the internuclear distance R, which provides deeper insights into their nature than the PECs are also provided and some of the valence states have been identified. We have also made detailed calculations on the resonant states and the resonance widths, and their continuation as bound states below the target NH^+ ion. These have been used to derive complete diabatic states of $^1\Sigma^+$,$^1\,\Pi$,$^1\,\Sigma^-$ and $^3\Sigma^+$ symmetries. The details of the Rydberg states, the resonant states, their widths and the full diabatized curves which serve as primary data for processes like dissociative recombination, dissociative excitation, resonant vibrational excitation and de-excitation have been obtained here for the first time.

E. NS^+

While NS was among the first diatomic molecules observed in the ISM, NS^+ cation was only recently detected, and now it is known to be ubiquitous in these environments. Moreover, sulphur is the tenth and nitrogen is the fifth most abundant element in the Universe, thus their chemistry is of key importance for astronomical environments. A challenge for astrochemistry is to understand the mechanisms and rates of formation and destruction of both neutral and cationic molecules.

As a first step, we have determined the bound and resonance states along with corresponding autoionization widths for nitrogen sulphide (NS) molecules, using electron and NS^+ cation scattering calculations [30]. The calculations were performed for the $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ point-group symmetries using the *ab initio* R-matrix method for both bound and continuum states. The resonance states yield dissociative potential curves which, when considered together with their widths, provide input for models of different electron-cation collision processes including dissociative recombination, and rotational and vibrational excitations. Curves and couplings which will lead directly to DR are identified. Resonance positions and auto-ionization widths were calculated for e+NS^+ system depending on the internuclear separation. The Rydberg series that converge to the

ion ground state were computed together with the corresponding effective principal quantum numbers. The use of a dense grid produces numerous resonances and bound states in great detail, which facilitate the identification of dissociative states and singly excited Rydberg manifolds. To our knowledge, this is the first time when relevant molecular data sets were calculated to study electron-induced reactive elementary processes in NS^+.

In a second step we have performed nuclear dynamics calculations for the SN^+ molecular cation [31] using the sMQDT method with the previously calculated molecular data sets. We have calculated electron induced dissociative recombination cross sections and rate coefficients for the first two vibrational levels of the target cation for collision temperatures relevant in ISM. We have estimated the uncertainty of our MQDT calculations caused by the global electronic couplings unresolved in the angular momentum of the incident electron. Comparing our results with those obtained for the similar molecular cation NO^+ and with values given in the KIDA database [13], suggests that the database values are too high. We suggest that rate coefficients obtained through sMQDT for NS^+ and NO^+ are likely to be more reliable than those currently recommended in the KIDA database. The relatively moderate DR rate we have evaluated explains—at least partially—the ubiquitous presence of NS^+ in interstellar space.

F. NeH^+

The use of noble gases like neon or argon as impurities for controlling heat load on the plasma facing components in large magnetically controlled fusion devices like ITER is more and more general. The injected impurities can interact with the plasma giving rise to different hydrides, since H, D and/or T is used as fuel. Significant amounts of NeH and/or ArH and their isotopologues are expected to form in the vicinity of the walls, thus detailed collision data is required for the plasma flow modelling.

Unlike HeH^+ (one of the oldest molecule in the Universe) and ArH^+, NeH^+ remains undetected in the ISM. The formation of NeH^+ is expected to be heavily dependent on the abundance of HeH^+, which is more prevalent due to the significant presence of helium and atomic hydrogen in the environment. Another possible explanation for the non-detection of NeH^+ may lie in its dissociative recombination behavior. A high dissociative recombination rate coefficient at temperatures relevant for the interstellar medium could significantly reduce its steady-state concentration, making detection more challenging.

HeH^+ recombines with electrons exclusively through electron capture into Rydberg states, without having a diabatic dissociative neutral state that crosses the cation. For ArH^+ we have found such states which become open for dissociation at non-zero collision energies [32]. Nevertheless, on TSR Heidelberg it was measured low but non-negligible DR rates into the ground state of ArH, claiming the mechanism of non-adiabatic coupling between the ionization continuum and the ground electronic state. In order to understand which mechanism drives the recombination of NeH^+ at ISM temperatures, we have calculated the potential energy curves for the $^1\Sigma^+$ ground state of NeH^+ ion and for the lowest five $^2\Sigma^+$ states and two $^2\Pi$ states of NeH molecule and the non adiabatic couplings among them with high precision using standard quantum chemistry packages [33]. These couplings are essential for the future sMQDT calculations that will provide cross sections and rate coefficients in low-energy collisions between electrons and NeH^+.

G. BeH^+ and isotopologues

Beryllium and tungsten are considered as major plasma-facing materials for the ITER reactor which, once released, act as plasma impurities. The ejected impurities can interact with the plasma giving rise to different hydrides, since H, D and T are used as fuel. Significant amounts of BeH and its cations, together with their isotopologues are expected to form in the vicinity of the walls, thus detailed collision data is required for the plasma flow modelling.

In the framework of the sMQDT we have performed nuclear dynamics calculations for electron induced reactive processes of BeH^+ [34] and BeD^+ [35] and more recently for BeT^+ [36], from low to moderate collision energies. In this way we have ended a series of studies on the DR, VE and VdE of BeH^+ and isotopologues with electrons of low to moderate collision energy, for all initial vibrational levels of the target cation. In this way we have obtained the vibrational and isotopic dependence of the DR, VdE and VE rate coefficients of the beryllium-monohydride cations [11]. Moreover, these results enables us to derive an isotopic scaling law from this data-set, which greatly facilitates the use of this detailed information for the modellers of the ITER-like fusion plasmas.

In addition we have extended our previous studies [34–36] of BeH^+ and its isotopologues on the reactive collisions with electrons by considering higher collision energies facilitating the study of the dissociative excitation, occurring above the dissociation threshold of the molecular ion target [37]. Starting from the original molecular data sets and using simple scaling laws we have enlarged our set of molecular states participating in the fragmentation dynamics, resulting in a more realistic description of the dissociation and excitation of the molecular target. We produced cross sections and rate coefficients for DR, DE, VE, and VdE processes up to 12 eV collision energy. By applying these developments for the other isotopologues we will be able to provide fully resolved state-to-state collisional data up to collision energies characterizing the plasma close to the walls (and divertor region) of the ITER-like fusion devices.

H. CH^+, CH_2^+ and C_2H^+

Many low temperature plasma environments have hydrocarbon molecules, radicals and molecular cations as important constituents, like JET-like fusion plasma devices, cold technological plasmas or ISM. Collision of electrons with molecules and

their ions in these environments are important processes that play a fundamental role in initiating chemistry, particle balance and transport.

In a recent review paper [3] we have pointed on the importance of the higher-ordered effects (rotational, core excited and/or spin-orbit effects) combined with multiple symmetries/states in the cross sections and rate coefficients for DR of CH^+. The comparison of our results and the most recent Cryogenic Storage-Ring in Heidelberg, Germany reveals the need for more detailed studies. In the focus is the low temperature part of the rate coefficients, below 100 K. Our preliminary results [38, 39] have confirmed that all the above higher-order effects have to be considered simultaneously in order to obtain good agreement with the state-selective storage-ring results. The necessary developments of the sMQDT method are in progress.

CH_2^+ is a very important constituent in low temperature ionized/plasma environments. It is a key cation of hydrocarbon-based molecular plasmas and a major building block of carbon astrochemistry leading to complex organic molecules. Despite its importance, very little is known about the electron-induced elementary collisional processes of the cation. We have provided a reliable set of cross sections for the electronic excitation, ionization, and electron impact dissociation of the CH_2^+ molecular cation in the frame work of the R-matrix theory [40]. In fact, none of these cross sections have ever been reported before by any ab initio calculation. Additionally, we have also calculated the positions and widths for some of the Feshbach resonances in the e+CH_2^+ system. These Feshbach resonances, as is well known, are the principal routes to dissociative recombination of the ion targets. CH_2^+ is an open-shell molecular cation, and the eigenphase sums calculations show the presence of resonance states at almost "zero" collision energies of the e+CH_2^+ molecular system, putting in evidence the importance of the direct mechanism of DR. The treatment of DR and related processes in this case requires more comprehensive calculations, this is the subject of an ongoing project.

In order to understand how small radicals formed in the non-equilibrium hydrocarbon plasmas are affecting the plasma properties, we have started to investigate the reaction dynamics between free electrons and the C_2H^+ radical. In the frame-work the R-matrix theory we will evaluate the electronic excitation, ionization, and electron impact dissociation of the C_2H^+ molecular cation. Using the polyatomic method developed for the very similar molecular cation N_2H^+ - normal mode approximation combined with R-matrix theory and MQDT - we plan to obtain the dissociative recombination and rotational/vibrational/electronic excitation cross sections and rate coefficient.

I. CF_n

The fluorine-containing radicals are the key components of the different gas-discharge and low-energy plasma environments. In the C_nF_m based plasmas the molecules undergo fragmentation processes due to inelastic collisions, which lead to the production of ionized and neutral radicals, including CF, CF_2 and CF_3.

The integral cross sections of elastic electron scattering by the CF, CF_2, CF_3 and CF_4 molecular targets are calculated in the independent atom model (IAM) with additivity rule approach, while for the differential cross sections the IAM approach is used [41]. A good agreement was observed while comparing our integral cross sections with the measured data. The level of the agreement however strongly depends on the target molecule, and a good consistency is observed typically above certain collision energies: from 10 eV in case of CF_2, above 15-20 eV for CF_3 and from 40 eV in case of CF_4. Similar tendencies were found in case of the differential cross sections for a wide range of scattering angles at collision energies above 10 eV in case of CF_2, above 15–20 eV for CF_3, while in case of CF_4 – above 20 eV.

J. HDO

Water, $H_2^{16}O$ or H_2O, is ubiquitous in the Universe, in gas phase and also solid phase, and it is the third most abundant molecule after H_2 and CO. The singly deuterated form of water, HDO, is much less abundant (by typically two to five orders of magnitude) but it is also detected in a variety of astrophysical environments, including interstellar and circumstellar regions, planetary and cometary atmospheres. Observing H_2O and HDO in the same source is particularly interesting because the HDO/H_2O ratio is a unique probe of the water history and, in (exo)planets, of the evolution of their atmospheres. To the best of our knowledge, there is neither theoretical nor experimental study for the (ro)vibrational excitation of HDO.

Cross sections for electron-impact excitation of the 16 low-lying vibrational levels of the HDO isotopologue of the water molecule were computed using a theoretical approach based only on first principles, normal mode approximation combined with R-matrix theory and MQDT. It is the first application of the polyatomic electron-molecular cation method to neutral targets. Thermally-averaged rate coefficients were derived from the calculated cross sections for temperatures in the 10-10000 K interval and analytical fits for rate coefficients were provided for convenience of use. The H/D isotopic substitution was found to have a large impact in general, so that the rate coefficients for H2O could not be used reliably for HDO. In order to employ these rate coefficients in modelling non-LTE spectra of HDO in various astrophysical environments, uncertainty estimations were performed.

K. Ultracold K+Cs and Li+Ba^+ collisions

Ultracold temperatures in dilute quantum gases opened the way to an exquisite control of matter at the quantum level. We focus on the control of ultracold atomic collisions using a laser to engineer their interactions at large interatomic distances. We have shown that the entrance channel of two colliding ultracold atoms can be coupled to a repulsive collisional channel by the laser light so that the overall interaction between the two atoms becomes repulsive: this prevents them to come close together

and to undergo inelastic processes, thus protecting the atomic gases from unwanted losses [43]. We have illustrated such an optical shielding mechanism with ^{39}K and ^{133}Cs atoms colliding at ultracold temperature (< 1 μK). The process is described in the framework of the dressed-state picture and we then solve the resulting stationary coupled Schrödinger equations. The role of spontaneous emission and photoinduced inelastic scattering is also investigated as possible limitations of the shielding efficiency. We predict an almost complete suppression of inelastic collisions over a broad range of Rabi frequencies and we have found that the polarization of the shielding laser has a minor influence on this efficiency. This proposal could easily be formulated for other bialkali-metal pairs as their long-range interaction are all very similar to each other.

Hybrid atom-ion systems are a rich and powerful platform for studying chemical reactions, as they feature both excellent control over the electronic state preparation and readout as well as a versatile tunability over the scattering energy, ranging from the few-partial wave regime to the quantum regime. In this work, we make use of these excellent control knobs, and present a joint experimental and theoretical study of the collisions of a single $^{138}Ba^+$ ion prepared in the $5d^2D_{3/2,5/2}$ metastable states with a ground state ^{6}Li gas near quantum degeneracy [44]. We show that in contrast to previously reported atom-ion mixtures, several non-radiative processes, including charge exchange, excitation exchange and quenching, compete with each other due to the inherent complexity of the ion-atom molecular structure. We present a full quantum model based on high-level electronic structure calculations involving spin-orbit couplings. Results are in excellent agreement with observations, highlighting the strong coupling between the internal angular momenta and the mechanical rotation of the colliding pair, which is relevant in any other hybrid system composed of an alkali-metal atom and an alkaline-earth ion.

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Debrecen, 31.01.2025

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