Fast-beam fragmentation experiments on dissociative recombination

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Abstract. An overview of recent developments is given for storage ring experiments on dissociative recombination using fast merged ion and electron beams. Dynamical aspects of the process are outlined, demonstrating that fast-beam reaction studies can advance the understanding of basic mechanisms holding generally for the fragmentation of electronically excited molecular systems. Experiments yield the collision energy dependence of the process, including rich resonant structure, product branching ratios of the fragmentation, and fragment momenta which also reveal the internal excitation of the fragments. Using cold electron beams and imaging detectors capable of fragment mass recognition at high readout speed, recent detailed fast-beam fragmentation experiments address the dissociative recombination of multielectron diatomic and polyatomic ions. Some of their results are presented together with an outlook on experiments at upcoming storage ring facilities.

1. Introduction
Dissociative recombination (DR) between a molecular cation and a free electron is one of the most important binary reactions in media governed by ion chemistry [1]. Exothermic in nature, it proceeds without an energy barrier and therefore very efficiently down to the lowest temperatures. In their collision, the electron and the ion form a neutral compound state with high electronic excitation, which then relaxes by molecular dissociation through a wide range of coupling mechanisms between electronic and nuclear motion. The cross section of the process and the internal states of the products are sensitive to the various steps in the fragmentation process and depend on the electron impact energy as well as, frequently, also on the initial excitation of the cation. Much information about the underlying reaction mechanisms can be gained from experiments at well-defined collision energy, if possible also for controlled initial states of the ion, and from the analysis of the final product states. Experiments of this type also offer most specific tests of theoretical calculations used to predict the rates and product properties for this reaction.

Comprehensive understanding of DR is, on one hand, motivated by the need of data about this process for modeling gas-phase chemistry in dilute ionized media of astrophysics [2] and low-temperature plasma physics [3]. Both, charged and neutral molecular abundances in these
media often depend strongly on the DR cross section and its products. On the other hand, DR constitutes a test case for our ability to quantum mechanically predict the relaxation of electronic energy by molecular fragmentation, an area where the central importance of rovibronic and non-adiabatic coupling mechanisms is increasingly recognized.

Storage ring experiments with merged beams of molecular ions and electrons [4, 5, 6] offer powerful methods for observing DR reaction rates, branching ratios and fragment momenta. For the diatomic [7, 8] and triatomic [9] hydrogen molecules, experiments revealed many aspects of the quantum dynamics and pointed particularly to the crucial role of molecular Rydberg manifolds [10, 11, 12, 13]. Aside of the energy dependence of the DR cross section, also the outgoing atomic states and specific dynamics, such as angular correlations between the incident electron and the fragmentation direction [8], were investigated. The present paper addresses the extension of detailed dynamical studies to heavier multielectron molecules, both diatomic and polyatomic, where additional phenomena arise in the DR process and where both experiment and theory face the challenge of higher complexity, together with large opportunities for improving our understanding of molecular mechanisms with a wide occurrence in nature.

2. Processes

2.1. Resonant electron capture

The DR of a molecular ion is triggered by its resonant capture of an electron. The basic mechanisms that can occur in a multi-electron system are illustrated in Fig. 1 for the diatomic case. This diagram shows the lowest few potential energy curves of the ion on a common scale with the energy levels of the recombined neutral system. Also indicated is the Franck-Condon (FC) zone that defines the possible initial states of the binary collision. The kinetic energy $E$ of the incident electron is added to the energy of the parent molecular ion in its electronic and vibrational ground state (near label 1 in Fig. 1), while the internuclear distances are defined by the vibrational wave function of the colliding ion. Thus, the initially populated state lies within the indicated area at a height given by the electron collision energy. Pathways for DR are entered from this initial height in the FC zone and, via dissociative neutral potential curves, can terminate in various neutral product states. The difference in total internal energy between the initial and final states defines the kinetic energy gained by the fragments. For a

![Figure 1](image-url)
polyatomic ion, an equivalent map can be constructed with potential energy surfaces (PES) in the multidimensional nuclear coordinate space.

The dissociating potential curves crossing the initial FC zone are electronically doubly excited states of the recombined neutral system. Potential surfaces for such autoionizing states [14] can be obtained in the diabatic representation of the molecule [15], where specific configurations of electronic orbitals are used and configuration mixing is added in later steps of the model. (In this sense, also the initial electronic continuum states in the FC zone are diabatic states.) A diagram such as Fig. 1 can never individually show all neutral PES, as each potential surface of the ion is accompanied by a full series of neutral Rydberg states.

The configuration mixing between diabatic electronic states is crucial for DR: On one side, it can lead to the capture of the free electron – without any dynamic participation of the nuclei required in this step, thus being similar to dielectronic recombination of atomic ions [16]; the neutral states driving these capture processes are also called (electronic) resonances. On the other side, configuration mixing is important in the further evolution of the fragmentation, as any crossings between the diabatic potential curves are converted to avoided crossings in the adiabatic limit, and for moving nuclei dynamical transitions [17] of the Landau-Zener type can occur between the dissociating PES.

As sketched in Fig. 1, such transitions can lead to the splitting of a fragmentation pathway over two or more potential surfaces in the sense of a coherent superposition of the probability amplitudes. This quantum mechanical evolution – distributed over several coherently populated PES – has a crucial effect on the reaction as it is mirrored by the internal (electronic) states of the outgoing fragments and, in the polyatomic case, by their momentum correlations and by the vibrational excitations of molecular fragments; strictly, it can even be a source of quantum mechanical entanglement between the internal states of the outgoing fragments.

The schematic diagram in Fig. 1 translates into a typical DR cross section as a function of the collision energy $E$ as outlined in Fig. 2. The large-scale structure with smooth energy variations in a low-energy region 1 and a high-energy region 3 ($\sim$8-20 eV) results from direct DR [18] into dissociative PES within the initial FC zone. Thus, in region 3 the numerous neutral Rydberg states (or Rydberg resonances) below each of the high-lying dissociative ionic surfaces open many direct pathways as determined by the FC overlap with the initial state. Similarly, in region 1 at small impact energy $E$, direct electron capture into a neutral (resonant) PES intersecting that of the cation near its equilibrium nuclear geometry results in a smooth energy dependence of the cross section, representing the product of the asymptotic threshold energy dependence $E^{-1}$ and a further slowly varying function expressing, among other factors [19, 20], the FC overlap between the incident cation and any resonant states at $E = 0$. The intersection of the cationic PES by a neutral dissociating (diabatic) PES near the cationic potential minimum is a condition
for this direct DR process to occur at low impact energy and at low initial vibrational excitation; however, mechanisms going beyond the purely electronic coupling assumed in this direct electron capture process can in many cases lead to strong low-energy DR even in the absence of an intersection of this type [21].

Apart from dissociating neutral states, also vibrationally bound neutral states can occur whose total energy matches that of the initial collision state; some of such states, attached to neutral bound (diabatic) PES, are indicated in Fig. 1. If suitable mechanisms exist to populate these states, resonant with respect to the total energy and not only its electronic part, sharp structures result in the collision cross section. For contributing to DR, the states of this type must be both autoionizing (in order to appear as a resonance in the electron collision) and predissociating (in order to lead to a fragmentation). Predissociation can occur by any dissociating neutral PES that crosses the neutral bound PES within the range of the vibrational wave function in this resonant state. It can be seen in Fig. 1 that this range can be considerably more extended than the FC zone of the colliding ion, so that the resonant state can act as a doorway to fragmentation paths inaccessible by the direct process. Moreover, the width of the resonant state is determined by the autoionization and predissociation rates, and complicated spectral structures can arise in the continuum if resonances become less separated from each other than by their width. The DR via such vibrationally bound resonances [18, 10] is denoted as the indirect process.

At low collision energy, vibrationally excited Rydberg resonances can be caused in particular by the Rydberg series of neutral PES below the potential surface of the incident cation (see Fig. 1). The mechanism populating such resonances in the electron collision is the vibrational excitation of the ion by the colliding electron, forming an autoionizing, vibrationally excited molecular Rydberg state whose subsequent predissociation leads to DR [18]. This indirect DR mechanism is generally important for diatomic as well as polyatomic ions, reflecting different types of coupling between nuclear and electronic motion. Its particular importance stems from the fact that it leads to strong DR at low impact energy even in the absence of a resonant potential crossing in the FC zone of the ion, as required for the direct process; thus, for many important species (H₂⁺, H₃O⁺, etc.) DR with low-energy electrons proceeds only through the indirect process. High-resolution measurements of the resonant energy dependence could be performed in merged-beams experiments [7, 8, 22], but the observed spectra still resist their definite assignment and detailed reproduction by theoretical calculations, even in such cases as HD⁺ and H₃⁺.

Measurements of the DR cross section as a function of the impact energy for more complex multi-electron ions, in particular diatomic ions with L-shell atoms such C, N, and O, have revealed further narrow structures in the intermediate energy region 2, typically at ∼0.3–2 eV (Fig. 2). The additional resonances are caused by the more complicated electronic structure of these ions, which often have vibrationally bound excited potential surfaces (see Fig. 1). Each of these states is accompanied by a series of electronically doubly excited neutral states, which lie in the initial electronic continuum. Energetically lower members of such series can lead to well separated capture resonances; since their first experimental observations [23, 24, 25] and theoretical [26, 27] studies they are referred to as excited-core Rydberg resonances. The various vibrational levels that lead to capture resonances can again, similar to the low energy case, open dissociation pathways outside the initial FC region, and interesting collision dynamics and energy dependences of the cross section can arise in case of fast, multi-path predissociation. Thus, aside of the interest in DR data of this type for the ion chemistry in warm molecular plasma, the interplay of theoretical and experimental studies regarding such structures also provides a test field for our understanding of coupled electronic and nuclear motion in excited, fragmenting molecules and related quantum phenomena.
2.2. Fragmentation dynamics

Even at near-zero collision energy, DR often leads into various alternative final channels with different chemical compositions and different internal product states. The final-state branching ratios reveal the correlations between the resonant capture state and the product energy levels, which are not uniquely fixed, but depend on possible dynamical transitions between intersecting potential surfaces on the fragmentation pathway. The fragmentation route involves propagation of a quantum wave packet of nuclear motion on one or several potential surfaces, including its coherent splitting at crossings between diabatic potential surfaces (see Fig. 1). Localized multiple dynamical transitions on the way to fragmentation can introduce fast variations of the branching ratios as a function of the collision energy through multi-path interference, so far mainly observed in the related process of ion-pair production in electron-cation collisions [28, 29, 30, 31].

For polyatomic ions, illustration of the reaction by a map similar to Fig. 1 rapidly becomes more difficult as the number of nuclei increases. Experimental observations of branching ratios and, recently, their variations over a wider range of collision energies bring the opportunity of developing theoretical models for the electron capture process and for the relevant potential surfaces along the fragmentation path even in polyatomic cases, up to the propagation of multi-dimensional nuclear wave packets representing the fragmenting molecule. Related work is presented at this conference [32]. The neutral potential surfaces governing fragmentation in the DR of polyatomic ions were surveyed quite extensively over the multidimensional molecular coordinate space for only few cases, including in particular H$_3^+$ [33] and H$_3$O$^+$ [34]; however, even for this case many aspects of the underlying fragmentation dynamics are still only little understood. Ongoing theoretical and experimental studies aim at a much more complete picture of the process for this system and similar polyatomic species.

Merged beams experiments are capable of analyzing the DR process also by measuring the fragment momenta and the resulting kinetic energy release [35]. For polyatomic ions breaking up into three or more products, the momentum correlations between them give further information about the potential landscape leading to fragmentation [36]. Thus, in three-body breakup linear and triangular geometries of the fragment momenta can be distinguished and the full space of possible geometries is spanned by the Dalitz plot representing the kinetic energy sharing between the individual fragments. A number of fragment imaging studies for the three body breakup by DR have been performed. For H$_3^+$, singled out as the most fundamental polyatomic ion, symmetric linear momentum geometries of three H atoms were observed after DR by fragment imaging [37, 38]. For this case, the relation to the fragmentation pathway was studied in considerable detail. Interesting comparisons become possible to three-body fragmentation measurements following the electron capture by H$_3^+$ ions in an atomic gas target, which so far focused on laser-excited levels of neutral H$_3$ [33], but recently also addressed the electron capture into high-lying neutral Rydberg levels of H$_3$ [39]. The momentum geometries for three-body breakup following this type of electron capture are found [39] to strongly resemble those seen after DR at low electron impact energy [38]. This suggests that similar initial neutral states precede the fragmentation in both capture processes. A map of numerous excited potential surfaces was calculated for the neutral H$_3$ system and helps to identify, for the conditions of low-energy DR, a plausible fragmentation pathway [33] via several of them, transforming the molecule from its equilateral triangular shape before the collision to the linear geometry found after its breakup.

3. Experimental method

3.1. Merged beams in ion storage rings

Fast beam fragmentation experiments on DR are based on merging an electron and an ion beam in a collinear overlap region at similar average velocities (Fig. 3), which can be fine adjusted
Figure 3. DR measurements in an ion storage ring. The collision energy $E_d$ is controlled by the ion and electron beam velocities ($v_e, v_i$). The electron temperature $T_e$ represents the spread of the electron velocities, while the internal states of the ions are coupled to the temperature $T_{env}$ of the storage ring walls by blackbody absorption and emission.

by varying the acceleration voltage of the electron beam [4, 5, 6]. They are most efficiently performed inside an ion storage ring: among other benefits, the ion velocities can be made very uniform by phase-space cooling, various methods can be applied for controlling the initial state of the reacting molecules, and the ions can be recycled continuously even if they are produced by a pulsed source with a low duty cycle. In the overlap region, impact energies down to $\sim 1$ meV (corresponding to temperatures as low as 10 K) can be realized, as determined mainly by the velocity spread of the electrons. The neutral fragments from the overlap region, typically $\sim 1$ m long, proceed to a fragment detector installed typically $\sim 10$ m downstream, behind magnetic or electric elements for separating any co-moving charged particles. The neutral fragments of each DR reaction have approximately the velocity of the incident ion, which also defines the motion of the center-of-mass (c.m.) during their propagation to the detector. The mutual distances increase during the drift to the detector and follow from the fragment velocities of the breakup reaction in the c.m. frame, reaching up to several cm at the DR detector. For $\sim 10^6$ stored ions in a continuous coasting beam and an electron density of $10^6$ electrons per cm$^3$, DR reactions occur at rates up to $\sim 10^4$ s$^{-1}$ and, through their high energies in the laboratory frame, the neutral fragments create distinct signals in the various types of counting and imaging detectors used. The measured rates are normalized to the stored ion number and the electron density to derive the beam-beam rate coefficient of the reaction. It is obtained as a function of the collision energy $E_d$ between the two particle beams (see Fig. 3) and represents the average $\langle v\sigma(E) \rangle$ of the DR rate coefficient over the distribution of collision velocities $v$. In contrast to thermal rate coefficients, the beam-beam rate coefficient is obtained at a nearly uniform collision energy, strongly peaked around $E_d$, except for low-energy DR when $E_d$ is set to zero and the average represents the electron temperature.

Depending on the segmentation or position-sensitive readout capabilities of the detectors and their time resolution, fragment multiplicities, transverse fragment positions in the detector plane and arrival time differences can be obtained for individual DR events [35, 36]. Moreover, detectors which are also sensitive to the kinetic energies deposited by the impinging fragments are particularly useful in fast-beam measurements, as the laboratory velocities of all fragments are essentially given by the initial ion velocity and thus, the fragment kinetic energies directly reflect their masses. For DR events in which all fragments are detected and their individual masses can be assigned, the c.m. position in the detector plane can be identified and the possibility of analyzing the momentum geometries in polyatomic breakup is opened up.

The reaction data extracted from fast-beam DR measurements span a wide range. They reach from total DR cross sections as a function of the impact electron impact energy or other parameters, such as the internal states of the parent ion (and thus their storage time since the excited state populations often depend on it) to the analysis of DR branching ratios towards specific fragments, possibly to specific final states within them, and to detailed multi-coincidence fragment momentum measurements. Recent developments in fragment detection and imaging
methods will be discussed in Sec. 3.2.

The recent results presented in this paper were obtained at the Test Storage Ring (TSR) facility operated by the Max-Planck Institute for Nuclear Physics in Heidelberg, Germany, which applies a photocathode electron target [40] to create the co-propagating electron beam [41]. Molecular ion beams with masses up to \( \sim 40 \) amu are produced with electrostatic or radio-frequency accelerators and stored in the TSR at typical kinetic energies of a few MeV. Within fragment imaging experiments, the c.m. positions of DR events are applied to monitor the ion motion in the overlap region with the electron beam [42]. After careful adjustment of the electron beam velocity and its direction during the phase-space cooling, the c.m. positions are in most cases found in a narrow region with a diameter of order 1 mm, indicating very low transverse divergence and size for the stored ion beam. It was shown that at TSR such conditions can be maintained up to high molecular masses of order 30 amu and the extension of efficient phase space cooling to even heavier molecular beams is under continuous study.

3.2. Fragment momentum imaging and branching ratios – recent advances

The first storage-ring fast-beam experiments on DR applied unsegmented surface-barrier detectors and analyzed the integral ionization signals from the coincident impact of neutral fragments from individual breakup events, occurring at spatially separated positions of the detector [4]. Signals representing the full kinetic energy of the parent ions in the incident beam signify a DR event. These detectors record each fragment with essentially unit probability; hence, they directly measure the total DR rate provided they fully cover the fragmentation cone around the beam axis. They are also able to reject the rather large background from dissociative excitation of the parent ions in collisions with the residual gas; the neutral fragments of this reaction represent less than the full kinetic energy of the parent ions and thus yield a smaller ionization signal in the detector, which can be used to discriminate the events they create. (A much smaller background from electron capture and dissociation in collisions with the residual gas occurs in addition; this cannot be discriminated directly, but often derived from the collision energy dependence of the measured rate.)

The widely used multichannel plates (MCP) can be applied to read out the fragment impact locations (and with particular upgrades [35] also the impact time differences) for coincident
fragments of individual DR events, but are blind to their laboratory kinetic energies. While these detectors yield very good spatial resolution, their probability to record the individual fragment impacts is clearly below 1 (typically 0.7). In spite of the missing independent fragment mass recognition and the limited observation efficiency, the “monochromatic” impact signals from an MCP can under certain conditions [43] be used to reconstruct the masses belonging to individual fragment hit locations. In a fast-beam experiment with a well cooled ion beam [42] the c.m. motion, conserved in the DR reaction, is very uniform among all stored ions. Thus, the c.m. position of each correctly assigned DR event is expected to lie in a narrow region, defined by the ion beam motion, and by testing all possible mass assignments the one where the correct mass is associated with each hit can be recognized. A high (although not perfect) event-by-event reliability of this method could be achieved for many cases; demonstrations are given by three-body breakup measurements in the DR of D$_2$H$^+$ and H$_2$D$^+$ [44] as well as CH$_2^+$ [45]. Since MCP detectors are wide spread and practical to use, the limits of this method for analyzing multiparticle fragmentation with “monochromatic” imaging detectors warrant careful further exploration.

“Color” imaging in the sense of mass recognition for individual fragments is provided by detectors which are sensitive to fragment kinetic energies while also offering position sensitive readout or segmentation. The first detector of this type introduced for DR experiments is the Energy-sensitive MUltistrip detector system (EMU) [46] at the TSR (see Fig. 4), a multistrip surface-barrier detector with 128 stripes each in horizontal and vertical direction and a kinetic energy resolution shown to be suitable for imaging of separate DR channels on molecules of masses up to \( \sim 30 \). By its high segmentation and its mass resolution, EMU can also be applied to determine branching ratios in polyatomic fragmentation. The data acquisition in EMU measurements proceeds with high count rates, so that new possibilities for the determination of branching ratios as a function of the electron impact energy are opened up, as demonstrated below and in Ref. [46, 47].

Non-imaging methods for the determination of DR branching ratios in fast-beam experiments were applied to already a rather large number of species. In the most widely used technique [36], an unsegmented surface-barrier detector is preceded by a metal plate with a dense pattern of sub-millimeter holes, yielding a grid mask of known geometrical transmission. Since the grid mask randomly blocks individual fragments of a DR event, the integral ionization signal no longer always appears at the full kinetic energy of the parent ion, but is reduced by an amount varying event by event, which corresponds to the mass of the blocked fragments. In a large sample of detected reactions, the relative probabilities of events with various missing fragment masses behind the grid can be analyzed [48] to extract the probabilities at which the product mass combinations occur in DR. Often this reveals the branching ratios. The method was extended to rather large polyatomic ions, including systems such as protonated methanol (in its deuterated equivalent), CD$_3$OD$_2^+$ [49]. The background from dissociative excitation of the parent ions in residual gas collisions cannot be directly rejected event by event in the “grid method”, as it cannot be distinguished from events where a neutral DR fragment was blocked by the grid; it is determined separately and subtracted in the analysis of the probabilities. The branching ratio measurements with EMU [46, 47, 50] can reject this dissociative excitation background event by event, reducing possible uncertainties.

Fast ion beams experiments on cluster fragmentation have demonstrated also another method [51] for analyzing the molecular composition of breakup products with an unsegmented surface barrier detector. Here, both the pulse integral and the rise time (the current amplitude measured at high temporal resolution) were analyzed for ionization signals from carbon cluster fragments. The pulses from fragments of the same total mass, having a fixed pulse integral, turned out to show different discrete values of the current amplitude; it was considerably smaller for a molecular impact at a single position than for the distributed impact of several fragments of
the same total mass. It appears interesting to explore the applicability of this method for DR branching ratio measurements.

4. Recent experimental results

4.1. Excited-core neutral Rydberg resonances

Motivated by the strong interest in low-temperature media, such as in astrophysics, many studies of DR focused on the lowest collision energies achievable. However, substantial DR rates are also found at higher collision energies up to several eV (see Fig. 2). In this context, for multi-electron ions, excited-core neutral Rydberg resonances become important, as they can contribute to significant DR rates in a temperature range where molecular ions survive under plasma conditions [3, 53]. In fast-beam measurements, such contributions were identified for the DR of, e.g., OH$^+$ [24], CH$^+$ [25], N$_2^+$ [54], NO$^+$ [55] and, in a recent measurement at much higher energy resolution, CF$^+$ [52] (see Fig. 5). In CF$^+$, the lowest peaks from excited-core neutral Rydberg resonances occur near 1.6 eV as a prominent doublet in which the single peaks have an energy width below 0.2 eV; above, a highly structured resonance pattern continues up to $\sim$8 eV. The beam-beam rate coefficient for DR drops at the vertical excitation energy to the $a^3\Pi$ bound excited state of the CF$^+$ parent ion, which probably indicates the series limit of neutral Rydberg levels below this state, as well as the adiabatic dissociation energy of CF$^+$, indicating the competition of ionic dissociation with DR. This demonstrates the high complexity and the large amount of information on molecular levels and their dissociation dynamics that are revealed by the DR cross section at higher impact energies. Similar high-resolution studies, complementing earlier experiments [54, 55], are desirable for other multi-electron molecules such as the atmospheric species N$_2^+$, NO$^+$, O$_2^+$ and others. Since higher temperatures are involved, also studies for ions in specific excited vibrational states are of interest. Theoretical studies of the CF$^+$ DR spectrum appear highly useful in the development of reliable methods for predicting DR via excited-core neutral Rydberg resonances.

4.2. Fragment imaging studies

4.2.1. Fragment and parent excitation in low-energy collision studies

Since its implementation at the TSR, fragment imaging using the EMU detector, combined with mass recognition, has brought out important aspects regarding the DR of polyatomic ions as well as the conditions under which such ions are investigated in ion storage rings. This will be discussed on the example of fragment imaging for the DR of D$_3$O$^+$ with cold electrons, corresponding to a thermal

Figure 5. DR rate coefficient for CF$^+$ measured at TSR [52] with structure from excited-core Rydberg resonances. The vertical excitation energy from the CF$^+$ ground state to CF$^+ (a^3\Pi)$ and the ionic dissociation threshold to C$^+$ + F are marked. A strong doublet peak, shown at a higher resolution in the lower plot, occurs near 1.6 eV. Fragment imaging reveals that for the lower component of the doublet the product channel C$^1P$ + F is by far the dominant one, while for the upper component the dominant product channel is C$^1D$ + F [52].
distribution of impact energies of ~10 K. Similar to previous ion storage ring experiments on this species [56, 57] as well as on other polyatomic ions, a discharge ion source is used to produce the parent ion beam, which is then kept circulating in the ion storage ring for several seconds before the start of the merged-beams measurement, giving excited ions the opportunity to relax by radiative emission. Since substantial lifetimes of many seconds or more can occur for rotational decay, the population of excited levels in this degree of freedom cannot generally be excluded after the initial storage period. Thus, it is desirable that DR measurements with such parent ions are accompanied by sensitive tests for their internal excitation, similar to those applied for H$^+$ and its isotopomers [38, 44].

In the low-energy DR of D$_3$O$^+$, three fragmentation channels occur with sets of branching ratios, slightly differing between the experiments, obtained already in earlier measurements [56, 57]. Thus, about 70% of the reactions lead into the three-body channel OD + D + D, while the remaining reactions produce the channels D$_2$O + D or OD + D$_2$ at, roughly, the same probabilities. While “monochromatic” fragment imaging with an MCP detector cannot distinguish between both two-body channels and, in addition, records a significant fraction of the three-body fragmentations as two-body breakup events, imaging with the EMU detector uniquely identifies all three product channels. Moreover, it is operated at a high readout speed and can determine the dependence of the product branching ratios on the electron impact energies over a wide range [47]. Furthermore, it also can unambiguously identify the background from ion collisions with residual gas molecules.

The fragment position distributions in the detector plane, as measured for the DR with cold electrons, can be analyzed [50] to determine the distributions of the kinetic energy release (KER) shared by the fragments, shown for the three breakup channels in Fig. 6. As illustrated in Fig. 7, considering the initial and final energies of the reaction, the observed fragment kinetic energies result from several contributions. They basically result from the reaction energies starting in the ground state of the parent ion and proceeding to the ground-state products in the three relevant product channels, as shown. However, any internal excitation energies of the molecular products are subtracted from these values, leading to a lower KER, while an internal excitation energy of...
the parent ion is added and increases the KER. Thus, the conclusions from the measured KER distributions are different for the three channels. For \( \text{D}_2\text{O} + \text{D} \), Fig. 6(a), the difference between the maximum KER of 6.3 eV and the measured one reveals very high internal excitation of the \( \text{D}_2\text{O} \) molecular products; the reaction energy towards \( \text{OD} + \text{D} + \text{D} \) also appears in the KER distribution for this channel as it marks the internal energy above which \( \text{D}_2\text{O} \) molecules can dissociate into \( \text{OD} + \text{D} \). For \( \text{OD} + \text{D}_2 \), Fig. 6(b), the interpretation is similar [50], but the internal energies of the two molecular products add up. Finally, the KER distribution for \( \text{OD} + \text{D} + \text{D} \), Fig. 6(c), reflects the internal excitation of the OD fragment as it extends to lower energies. On the other hand, however, it also extends to significantly higher values than given by the reaction energy; this tail is interpreted as the distribution of internal excitation energies of the \( \text{D}_3\text{O}^+ \) parent ions, corresponding to an internal temperature as high as \( \sim 3000 \) K. The observed tails can be shown unambiguously not to result from background reactions of the \( \text{D}_3\text{O}^+ \) ions in the residual gas, contradicting the result of previous similar studies [58] which concluded that the stored \( \text{D}_3\text{O}^+ \) ions were internally cold.

Analysis of the transverse fragment position distributions for three-body breakup, as discussed above, has in recent years been used to probe the parent ion excitation in DR experiments for a number polyatomic species. Three-body breakup is considered since, in the smaller systems studied, all or most of the fragments are atomic and therefore (if any) have only few, well defined excited states. Thus, the transverse kinetic energy distribution extends up to the limit given by the reaction energy between the ground-state species and can be sensitively probed for any tails. For \( \text{H}_3^+ \), this fragment imaging method clearly reveals the high parent-ion temperatures around 3000 K obtained with standard discharge ion sources [38] and the effect of buffer-gas cooling obtained by using a cold ion source for \( \text{H}_3^+ \), down to the level of \( \sim 300 \) K [59, 22]. The asymmetric isotopologues of this ion are found cold (\( \sim 300 \) K) even with the standard sources by radiative relaxation during a few seconds of storage [44]. Similar completion of radiative relaxation has been confirmed for other dihydrides, such as \( \text{CH}_2^+ \) [60, 45] and, very recently, \( \text{D}_2\text{F}^+ \) [61]. In contrast, high internal temperatures were observed in stored ion beams from discharge ion sources over up to 30 s of storage time for \( \text{D}_3\text{O}^+ \) [50], \( \text{D}_2\text{HO}^+ \) [62] and \( \text{DCND}^+ \) [63]. Hence, although all these species have a permanent dipole moment in their ground state and their vibrational modes are infrared active, a number of significantly populated, slowly decaying rotationally excited levels is revealed for them by the observations. Extended calculations for \( \text{D}_3\text{O}^+ \) and \( \text{D}_2\text{HO}^+ \) [64] suggest the co-existence of short and much longer lived rotational levels for both these systems; long radiative lifetimes (due to the large moment of inertia) are also derived [63] for the linear \( \text{DCND}^+ \) ion. By the method of Coulomb explosion imaging, incomplete internal relaxation was moreover observed for \( \text{DCO}^+ \) [65], in this case finding the bending vibration to remain excited at roughly 2000 K during \( \sim 12 \) s. This survey of observations demonstrates the need to consider parent excitation in DR measurements with great care for many species. Even in larger polyatomic ions, long-lived ro-vibrationally excited levels appear to become relevant, although they may co-exist with much faster decay of infrared active excitations.

4.2.2. Product channels traced along increasing collision energy Through the parallel readout of many detection channels, the new EMU detector also allows product channel branching ratios to be efficiently traced along the electron impact energy \( E \). Thus, as the energy available for the molecular breakup increases, a much more complete picture of the DR process and of the excited potential curves of the molecular system is accessed. On one hand, additional final levels or chemical compositions of the reaction products are reached energetically. On the other hand, also new electron capture resonances become effective, and the nuclear velocities during the breakup change, together with the transition probabilities at crossings between diabatic potential surfaces and the phases in possible multi-path interferences; moreover, additional crossings leading to
alternative breakup pathways can be accessed (see Fig. 1). While earlier experimental work on the quasi-continuous energy dependence of fragment branching ratios are scarce (H$_3^+$ was studied [48]), measurements with the new fast detector system can be performed at much higher energy resolution and investigate the systematics for a much wider range of species, including D$_2$H$^+$ [46] and D$_3$O$^+$ [47]. The ion DCO$^+$ has become the first test system for experimental and theoretical studies on the resonant potential surfaces leading to DR at higher impact energy [32].

Also fragment imaging measurements under continuous variation of the impact energy $E$ have become possible with the fast EMU detector. The data samples are sufficiently large and detailed that, for two-body breakup, two-dimensional representations of the fragment distance distributions can be obtained with the collision energy as a second variable. Preliminary results are given in Fig. 8 for the DR of NH$^+$ ions. Although the fragment distance in this measurement is projected onto the detector plane, events for which the dissociation is approximately transverse to the beam direction clearly indicate the size of the KER. In this diatomic case, the KER represents the various atomic excited levels of the outgoing N and H fragments as indicated. Energetic openings of new final states, their relative populations, and also the occurrence of new electron capture resonances are reflected by the structures in these two-dimensional data, which will reveal an extraordinarily complete picture of the DR process for this ion in the ongoing analysis.

5. Outlook: upcoming facilities
Fast beam fragmentation experiments on DR at ion storage rings have seen a strong development and recently further advances in the development of electron sources and fragment detection techniques. They shed new light on the rich diversity of phenomena that exist in the DR of polyatomic ions and of multi-electron molecular systems. While studies of DR cross sections and product branching ratios for cold electron collisions meanwhile cover a large number of molecular ions, assessing and quantifying the relevance of the reaction in ion chemical environments for the specific species, these data are far from being complete. For heavier polyatomics, the branching ratio results become less comprehensive [67] and the masses too high for efficient use of the storage ring technique. Moreover, the internal states of the products and the collision energy dependences of the process, tracing new electron capture routes and changes in the final channels of the reaction, were much less investigated, even for the lighter systems. Furthermore, the initial states of the parent ions are far from being controlled precisely in these studies; the excitation temperatures mostly correspond at least to room-temperature through the blackbody radiation field in the laboratory devices, and often to much higher values. This holds for light ions as well as for heavier polyatomics, where the uncertainties about the internal states in the experiment increase as the configuration space grows.
New storage ring facilities are becoming available for future studies at ion storage rings along these considerations. The large magnetic storage and cooler rings at high-energy heavy-ion and radioactive beam facilities, such as the GSI in Darmstadt, Germany, and the Heavy Ion Research Facility in Lanzhou (HIRFL), China, offer much higher magnetic deflection power than the ion storage rings so far used in DR experiments. Hence, with suitable molecular ion injectors, merged electron-ion beam experiments at similar beam velocities can be performed with significantly higher molecular masses. The molecular physics program [68] under planning at the storage ring CSRe at HIRFL [69] can be expected to extend the accessible mass range by a factor 6, corresponding to the gain in magnetic deflection power for this machine.

A different approach is taken by the project of the Crogenic Storage Ring (CSR) at the Max-Planck Institute for Nuclear Physics in Heidelberg, Germany [70, 71, 72]. Using compact electrostatic deflection and focusing devices, the storage ring is operated in a low-temperature surrounding with wall temperatures of ∼10 K and cryopumping at 2 K. The ion beam kinetic energy is reduced from typically 2 MeV at the TSR to 300 keV, where electrostatic acceleration from well accessible ion source platforms with a wide range of cold molecular ion sources is possible. The CSR includes a merged-beam electron target for phase-space cooling and electron collision studies, further developing the technology of the photocathode electron target of the TSR at envisaged electron beam energies down to 1 eV. Internally relaxed molecular ions from the cold sources can be kept cold during their storage, avoiding their heating by black-body radiation via infrared-active modes. With the low-energy electron beam, DR studies on stored and cryogenically cooled molecular ions are expected to become possible for molecular masses up to ∼160 amu with this new facility.

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