Molecular ion recombination in merged beams: experimental results on small systems and future perspectives

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Abstract: This paper discusses the application of the merged-beam technique to the study of dissociative recombination. After a description of the experimental method, attention is turned to H\textsubscript{2}\textsuperscript{+} and its isotopomers. The apparent perfect agreement between experiment and theory which seemed to prevail in the early 1990s has had to give way to an agreement which is satisfactory but far from perfect. The consistent set of data for HD\textsuperscript{+} from merged electron-ion beams in four different ion storage rings is very satisfying, while it is difficult to reconcile single-pass data for H\textsubscript{2}\textsuperscript{+} with those from an ion storage ring.

1. Introduction
Dissociative recombination (DR) is a process for which the cross section scales essentially as the inverse of the incident electron energy in the rest frame of the ion. Thus, because of the large cross section at very low electron energies, it is desirable to have access to a technique which allows measurements at these energies. In some experiments one wishes to probe properties of the DR process at a fixed, and very low and well defined, electron energy. In other experiments one is more interested in measuring the cross section as a function of electron energy over a broad energy range. In order to resolve resonances in the cross section, which can occur as a result of interferences between the direct and indirect mechanisms, high resolution is required. In other words, electrons with a narrow velocity distribution are required. The merged-beam technique is tailor made to meet these requirements.

There are ions that cannot be studied by means of afterglow techniques. The best example is the H\textsubscript{2}\textsuperscript{+} ion, the simplest of all molecules. The reason is that H\textsubscript{2} is rapidly converted to H\textsubscript{3} in any hydrogen plasma. In the comprehensive review of dissociative recombination in 1970, Bardsley and Biondi [1] concluded with the following remark: “But perhaps the greatest challenge for the experimenter is an accurate determination of the dissociative recombination coefficient of H\textsubscript{3}, since it is this ion which offers the best possibility for a quantitative \textit{ab initio} calculation to which the measurement can be compared.” It is quite remarkable that after twenty years of research into dissociative recombination, there was a lack of experiments with the simplest of all molecular ions. This was to change during the 1970s and 1980s, and on the experimental side this was due to the development of beam techniques.

The technique of merged beams was developed in the 1960s [2,3] and has recently been comprehensively reviewed [4]. The first beam studies of dissociative recombination were performed by Dolder and Peart using an inclined beam technique, i.e. the two beams cross at a small but finite angle [5]. The merged-beam technique was applied to dissociative recombination in the mid 1970s [6]. Many of the results emerging from this effort have been reviewed [7]. In the 1990s, ion storage rings dominated beam experiments on dissociative recombination [8,9].
In this article I will briefly discuss the advantages and disadvantages with merged beams, followed by a detailed discussion of experiments on the simplest of molecular ions, H$_2^+$. The final part of the article will discuss new goals and open questions.

2. Merged-beam methods

When a beam of electrons with speed $v_e$ in the laboratory frame and a beam of ions with speed $v_i$ in the same frame intersect at an angle $\theta$, the relative speed of the two beams is given by

$$v_r = (v_e^2 + v_i^2 - 2v_e v_i \cos \theta)^{1/2}.$$  \hfill (1)

The total kinetic energy in the centre-of-mass frame (i.e. the interaction energy) is given by

$$E = \frac{1}{2} \mu v_r^2 = \mu \left[ \frac{E_e}{m_e} + \frac{E_i}{m_i} - 2 \left( \frac{E_e E_i}{m_e m_i} \right)^{1/2} \cos \theta \right].$$ \hfill (2)

where $m_e$ and $m_i$ are the electron and ion mass, respectively, and $\mu$ is the reduced mass. When the two beams are merged, $\theta$ becomes zero and Equation (2) is simplified to

$$E = \mu \left[ \left( \frac{E_e}{m_e} \right)^{1/2} - \left( \frac{E_i}{m_i} \right)^{1/2} \right]^2.$$ \hfill (3)

For molecular ions $m_i \gg m_e$, which means the reduced mass is in practice equal to the electron mass; the centre-of-mass frame is essentially the same as the frame in which the ions are at rest. When $(E_e/m_e) = (E_i/m_i)$, $E$ becomes zero, implying that collisions at zero energy are possible under ideal conditions. In practice, the resolution is finite and the ions collide with electrons having a finite energy distribution. This distribution can either be due to the fact that the two beams may not be perfectly aligned, and that the beams have a slight divergence. It can also be related to the finite electron velocity distribution in the electron beam.

Figure 1 shows a generic single-pass merged-beam apparatus. It contains an ion source, an analyser magnet, an electron gun, a section where crossed electric and magnetic fields are used to merge electrons and ions, an interaction region, a demerger region, and detectors for measuring the electron current, the ion current and the number of reaction products. Uncertainties in the beam currents, the length of the interaction region, and the neutral particle detector efficiency are sources of error.
The resolution analysis given for the single-pass merged-beam apparatus \[6,10\] used at The University of Western Ontario, London, Ontario, Canada, was based on the assumption that the energy spread in the two beams was vanishing in the longitudinal direction. This gave as result that the main contribution to a degraded resolution came from the electron beam angular spread and the misalignment of the two beams. At an ion beam energy of 440 keV and an electron beam energy of 120 eV, the resolution was found to be 20 meV near zero interaction energy. Later an improved resolution of 5 meV was reported \[11\]. A better collimation of the electron beam is probably one explanation for the improved resolution. Dittner et al. \[12\] introduced a different type of analysis for their merged-beam apparatus at the Oak Ridge National Laboratory, which was used for studies of dielectronic recombination of atomic ions. They took into account the electron velocity spread in the electron beam arising from the emission of electrons from a thermionic cathode. Dittner et al. \[12\] obtained a resolution of \(kT_\perp = 1\) eV, where \(kT_\perp\) is the transverse electron temperature.

In the first experiments using an electron cooler beam \[13−15\], in single-pass experiments on dielectronic recombination, electron temperatures of \(kT_\perp = 0.135\) eV and \(kT_\parallel = 1−2\) meV were found. Similar resolutions were to begin with obtained in the ion storage ring experiments as well, but this changed radically with the adiabatic expansion technique invented by Danared et al. \[16\]. Figure 2 shows the rate coefficient for dissociative recombination of \(^3\)HeH \(^+\) measured in CRYRING with electron beams of three different transverse temperatures \[17\]. The rate coefficient is defined as

\[
\alpha(v_d) = \langle \sigma, v \rangle = \int \sigma(v_e, v_d, f(v_e, v_d)) d^3v_e
\]

(4)

where \(v_d\) is the detuning velocity, equal to the difference between the electron and ion speeds in the longitudinal direction, and \(f(v_e, v_d)\) is

\[
f(v_e, v_d) = \frac{m_e}{2\pi k T_\perp} \exp \left( -\frac{m_e v_d^2}{2k T_\perp} \right) \sqrt{\frac{m_e}{2\pi k T_\perp}} \exp \left( -\frac{m_e (v_e - v_d)^2}{2k T_\parallel} \right)
\]

(5)

Figure 2. Rate coefficient for dissociative recombination of \(^3\)HeH measured in storage-ring merged beams experiments, where the transverse electron temperature amounted to 1 meV (filled circles), 10 meV (open diamonds) and 100 meV (open triangles), respectively (reproduced from \[17\]). The detuning energy is defined as \((m/2)v_d\). The data for 100 meV and 10 meV were originally published in \[18\] and \[19\].
It is important to note that the rate coefficient in Equation (4) is valid for the conditions in the electron cooler, where the electron-velocity distribution is far from isotropic. The effect of lowering the transverse electron temperature is clearly visible in figure 2.

The advantages and disadvantages with the merged-beam technique to study dissociative recombination were discussed by McGowan and Mitchell in a review article in 1984 [20]. Advantages: very wide energy range; high energy resolution; absolute cross sections measured; product branching ratios measured; long interaction path gives high signal count rate. Disadvantages: up to now, reactant-ion excitation states have not been well determined; in present form, limited to molecular weights less than 32. The two disadvantages have been addressed by the implementation of ion storage rings, and the list of advantages has been made longer. The MeV ion beams used in storage rings have allowed the upper mass limit to be increased to somewhere around 100, although this is not a fixed upper limit. The high ion beam energy used in storage rings has also been advantageous for the measurements of product branching ratios [21]. A further advantage with the high beam energy is that electron capture from residual gas molecules, a process which gives a background that cannot be separated from the dissociative recombination signal, is much reduced at high energies. The circulation of the ion beam increases the effective current and allows excited ions to relax to the point where they reach a rovibrational temperature equal to that of the blackbody radiation. The reactant-ion excitation state is much better determined in ion storage rings as compared with earlier single-pass experiments, although there are situations when one has to be careful [22].

The present situation concerning merged-beam studies of dissociative recombination is that the single-pass merged-beam apparatus in London, Ontario [6,10] has been decommissioned, as has the TARN II ion storage ring [23]. The ion storage rings ASTRID at Aarhus University in Denmark, CRYRING, Manne Siegbahn Laboratory at Stockholm University, Sweden, and TSR at the Max-Planck-Institute for Nuclear Physics, Heidelberg, Germany (see [8] for ring parameters) are still used for recombination experiments, but the Manne Siegbahn Laboratory, which operates CRYRING, recently lost its status as Swedish national facility. This has resulted in reduced funding and an unclear long-term future for CRYRING. A new single-pass experiment is under development at the University of California at San Diego [24], and a merged electron-ion beam is used in a new electrostatic storage ring in Tsukuba, Japan [25].

3. Merged-beam studies of \( \text{H}_2^+ \) and its isotopomers

The very first merged-beam experiment on dissociative recombination concerned the simplest of all molecules, \( \text{H}_2^+ \) [6]. This was a natural choice because \( \text{H}_2^+ \) is the obvious benchmark system for comparison of experiment and theory, it is an ion inaccessible to afterglow techniques, and there are no problems in producing strong beams of \( \text{H}_2^+ \). What did pose a problem, however, was to produce \( \text{H}_2^+ \) with a known distribution of vibrational levels. In the first reported experiment [6], resonances in the cross section were observed, but apparently these resonances were difficult to reproduce. A significant step forward was taken when a radio-frequency trap source [26] was used to produce vibrationally relaxed \( \text{H}_2^+ \) ions [27]. This allowed for the first time a detailed comparison with theory. Figure 3 shows the experimental data [27] and theoretical multichannel quantum defect (MQDT) results [28]. The agreement between experiment and theory is extremely good, in particular regarding the minima in the cross section at \( \sim 15 \), 40 and 60 meV; from this alone it would seem that by the early 1990s, dissociative recombination of \( \text{H}_2^+ \) was a closed case. But this is not so. The MQDT results were obtained assuming non-rotating molecule. Takagi [29] showed that rotation influences the positions of the resonances, which means that a cross section averaged over several rotational levels would have less distinct structure.
Several investigations were undertaken at ion storage rings, where HD$^+$ is preferred because its rovibrational motion is associated with a time-varying dipole moment and hence relaxes fairly rapidly by spontaneous emission. The experimental data were compared with theoretical calculations for individual $(v = 0, J)$ levels. This was done by calculating $\alpha(v_d)$ in Equation (4) using an electron temperature equal to the one of the storage ring for which the comparison was made; in addition, rotational temperatures of 300–800 K were assumed. The first attempt, a combined Japanese effort, seemed convincing [30], but the catch was that the experimental cross section was relative. The structures in the experimental cross section were quite well reproduced, but a comparison of the absolute levels was not possible. Absolute data for the rate coefficient (i.e., $\alpha(v_d)$ in Equation (4)) from CRYRING were compared with results from MQDT calculations [31], and although a quite good agreement was found, it was not as good as the one shown in figure 3. The CRYRING data were obtained at an electron temperature similar to the one at TARN II [30], and for the first time it was possible to compare structures in the cross section obtained in two different merged-beam experiments. The agreement was very good, with the caveat that a comparison on the absolute level was not possible. A comparison on the absolute level was possible with results from ASTRID [32] and the agreement was found to be very good at low electron energies. In 1999, at the Nässlingen DR conference, Tanabe et al. [33] and Takagi [34] presented an absolute comparison of experimental TARN II results and results from MQDT. This time the new ultracold electron beam at TARN II was used, which had a transverse temperature of 1 meV. The experimental cross section (rate coefficient) was clearly lower than the theoretical one, and the structure in the theoretical result was more pronounced. One could speculate that the reason for this could be that the electron temperature was a bit larger than 1 meV, in which case the theoretical results should have been convoluted (see Equation (4)) with a broader electron-velocity distribution.

A dedicated effort was made to compare experimental results for HD$^+$ $(v = 0)$ from three different storage rings, ASTRID, CRYRING and TSR [35]. The absolute cross sections agree within the experimental errors of 20%, and structures in the rate coefficient are well reproduced (figure 4). Calculations by MQDT [30,31,34] exceed the experimental results by more than the 20% estimated experimental uncertainty. Takagi is addressing this question in his contribution to this volume [36].

Detailed comparisons for H$_2^+$ have been more difficult to achieve, the reason being that it has taken time to sort out how to do storage ring experiments on this ion populating primarily its lowest vibrational level [37,38]. Basically the procedure is to let the electron beam reduce rovibrational excitations in the H$_2^+$ by making use of super-elastic collisions (SEC), in which internal energy of the ions is transferred to electrons colliding at nominally zero energy. The electrons gain kinetic energy in this type of collisions, but the electron beam is continuously renewed with cold electrons. It is now
possible to compare the single-pass merged-beam results [27] for H$_2^+$ (see figure 3) with storage-ring merged-beam data from the TSR [39]. Figure 5 shows this comparison. It is obvious that below 0.1 eV the TSR data [39] have a much smaller variation amplitude than the single-pass data [27], although the internal state distributions of the H$_2^+$ ions in the two experiments should be similar. If an average of the single-pass data is taken, the agreement is satisfactory on an absolute level. However, the single-pass data cannot possibly give such large variation if the ions populate a reasonable number of rotational levels. It seems that the data either were taken with H$_2^+$ ions populating a single rovibrational level, which is hard to understand the reason for, or that there are some errors with the data or their interpretation. The error bars shown in figures 3 and 5 suggest that the statistics is poor at the electron energies where the minima in the experimental cross section appear. Thus, their association with the minima predicted theoretically [28], as suggested by figure 3, may be premature. Experiments on HeH$^+$ performed with the single-pass machine some ten years ago [40] also turned out to be incompatible with later storage ring results. Since the single-pass apparatus has been decommissioned,

**Figure 4.** Dissociative recombination rate coefficient for HD$^+$ (v = 0) ions measured [35] at the three storage ring facilities ASTRID, CRYRING and TSR. The electron coolers used have different transverse electron temperatures amounting to 20 meV (ASTRID), 4.5 meV (TSR) and 2 meV (CRYRING).

**Figure 5.** A comparison of dissociative recombination results for H$_2^+$ (v = 0) from the TSR (black solid line with filled circles) [39] and from the single-pass experiment at The University of Western Ontario [27] (gray line with filled circles).
this will never be sorted out, but one may speculate that measured cross sections became unreliable when the cross section dropped below some level. It should be noted that the luminosity is much higher and the background much lower in storage rings, which allow much smaller cross sections to be measured.

To summarize, data for HD+ obtained with merged beams in four different storage rings are entirely consistent, indicating that the systematic errors in these type of experiments are well under control. The agreement with theory is satisfactory, but one would wish for a better agreement for this benchmark system. Single-pass data for H2+ are difficult to reconcile with result from the TSR, unless one averages the single-pass data. The apparent agreement between experiment and theory as of 1993 is not at all well understood. The long struggle to come to grips with the dissociative recombination of H2+ and its isotopomers illustrates well the complexity of this process. It should finally be noted that there is much more experimental and theoretical work on other aspects of dissociative recombination of H2+ and its isotopomers which for space limitations could not be discussed here (see, e.g., [9]).

4. New goals and open questions

The Mosbach conference made it clear that the field of dissociative recombination is moving in different and exciting directions. It was also clear that there are open questions. Merged beams will continue to make important contributions to the field. In the near future (say next five years; but is always dangerous to make predictions, and your predictions are always best remembered if you are wrong) the magnetic storage ring will continue to make important contributions. The electrostatic storage rings have already demonstrated their versatility in studies of dissociative recombination (electron capture dissociation) of biomolecular ions [25,41], and by the research programmes at ELISA in Aarhus [42]. New electrostatic storage rings are about to be commissioned [43] or have been proposed [44,45], and one can anticipate that they will finally replace the magnetic rings.

The molecule receiving the most talks during the Mosbach meeting was H3+, and there is no question that there are still open questions regarding the dissociative recombination of this species. At the same time, there has been tremendous progress since the last DR meeting in Chicago [46]. If one were to single out one H3+ talk in Mosbach it would be Johnsen’s critical review [47] of dissociative recombination experiments during the last 30 years. Maybe a consistent explanation of all the conflicting experiments is within reach. On the other hand, H3+ has surprised us many time before and may very well do so also in the future.

A challenging problem will be the unravelling of the mechanism for electron capture dissociation, the “DR” of biomolecular ions. Is the mechanism of DR type, or is it a “hot atom” effect [48]? Experiments on model systems have started [49], but much work remains.

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