Polyatomic ions, branching ratios and hot molecules

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Abstract. A discussion is given of the reason for the sharp fall-off observed in Dissociative Recombination (DR) cross sections above about 0.1 eV and of the need for accurate branching ratios being used in complex models of molecular ion chemistry. New measurements from TSR have shown that stored ions are not as cold as they were once thought to be and a new experiment facility is presented.

1. Introduction
Dissociative recombination is a process whereby molecular ions can be rapidly neutralized in collision with free electrons, with the recombination energy being converted into product kinetic energy. Rate coefficients for this process are generally large and for polyatomic ions, a wide variety of exit channels can occur leading to many atomic and radical species as well as stable neutral molecules. The process is normally important below 1 eV and much work has been devoted to studies relevant to astrochemistry where temperatures in the range of 10 – 100K are encountered. In particular, in this application, molecular ions are usually in there ro-vibrational ground state and there has been much interest over the last 20 years in using heavy ion storage rings to cool ions vibrationally and then to study their recombination down to sub-milli-electronvolt energies. The high signal count rates found in these experiments have allowed measurements to be performed over a wide energy range and in several cases, these experiments have revealed the presence of peaks in the cross sections above a few eV due to direct transitions from the ion ground state to a dissociative neutral excited state, a process not dissimilar to dissociative excitation where in that case both ions and neutral products are formed. These observations have particular significance to thermonuclear plasma research where electrons with tens and hundreds of electron-volts are to be found in the near edge and diverter regions of tokamaks. Recent general reviews of DR measurements and of the theoretical background to the subject have been given by Florescu-Mitchell and Mitchell [1], Larsson and Orel [2] and a detailed review of afterglow based measurements by Adams et al. [3]. Another source of information concerning DR is the series of books published from the conference series Dissociative Recombination: Theory, Experiment and Applications. (See list in the Appendix.)

2. Medium energy DR
The first systematic investigations of DR over a wide electron temperature (energy) range were performed using inclined beam [4] and merged beam experiments [5]. These initially concentrated on hydrogenic species (H₂⁺, H₃⁺ and their isotopomers) and it was found that the measured cross sections decreased linearly for diatomic species but not for polyatomic ions which generally displayed a sharp change of regime in the vicinity of 0.1 eV [6]. This is illustrated in Figure 1a and 1b that shows an example of this phenomenon with DR cross sections for H₃O⁺ [7-9] measured using the single pass and multiple pass techniques respectively. Other examples are given graphically in [10]. The reason
for this abrupt regime change was not however obvious. With the advent of heavy ion storage rings and the application of the merged beams technique at these facilities, the improved signal to noise thus achievable allowed measurements to be made for up to tens of electron volts of electron energy. This yielded further surprises with the appearance of peaks in some case that could be attributable to direct transitions from the ion ground state to repulsive excited, autoionising, neutral states that could dissociate through neutral daughter channels. Again in these studies, a sharp drop-off was observed in the vicinity of 0.1 eV.

![Fig. 2a. Single pass merged beam measurements of the DR of H$_3$O$^+$ (solid circles) and D$_3$O$^+$ (solid squares) (From [7] with permission)](image)

![Fig. 2b. DR cross sections for H$_3$O$^+$ measured at ASTRID [8] and CRYRING [9] (From [10] with permission)](image)

While theoretical studies of simple ions have addressed the low energy and “high energy” (few eV) portions of the cross section spectrum, and have shown sharp fall-offs in the 0.1 eV region, a clear reason for this was not given. Recently though, a new article by Jungen and Pratt [10] has addressed this particular issue directly. These authors have been very active in the experimental and theoretical study of the competition between different decay channels (ionization, dissociation, radiation) for autoionising neutral Rydberg states formed by excitation from ground state neutral molecules. In this process, it has been well recognized that there is a propensity rule whereby autoionisation can occur via a transfer of vibrational energy from a bound state to the electronic energy (thus liberating the electron) that is most likely to occur for a change of one vibrational quantum number i.e. $\Delta v = -1$.

Jungen and Pratt have combined their experience in vibrational autoionization with the concept of indirect DR and they have argued that indeed, for polyatomic systems, the process is dominated by the indirect process, proceeding via transitions involving $\Delta v = +1$. The energy required for a transition to the first vibrationally excited state is typically on the order of 0.1 eV and so when the electron energy exceeds this, DR would have to involve a transition of $\Delta v > +1$ which is much less likely than the $\Delta v = +1$ transition and the result is that the probability of indirect DR drops and hence the cross section drops dramatically. This is illustrated in Figure 3. This explanation presupposes that indirect DR is the main driving force for the recombination of such species and indeed this is supported by the observation that generally polyatomic ions have rate coefficients that do not differ one from another by much more than an order of magnitude [1]. This is to be contrasted with the similar process of dissociative electron attachment that can only proceed via a direct transition from a molecule to a negative ion state, there being no comparable indirect process. In this case it is observed that rates can vary by 5 orders of magnitude from one molecule to another [11]. This argues in favor of the dominance of the indirect process for DR.
Fig. 3: Electron capture from the continuum of the ion into a bound neutral Rydberg state. At low electron energy the transition passes by $\Delta v=+1$, but at higher energy the transition would have to be by $\Delta v=+2$ (From [10, with permission].

3. Branching Ratios for DR

For many years, Branching Ratios, that is the ratio of the importance of respective dissociation channels for polyatomic ion recombination, was the Holy Grail of recombination research. These were of particular interest to astrophysicists since DR is one of the main mechanisms for the formation of interstellar molecules. While there were methods for determining the production of particular excited fragments using spectroscopic and chemical techniques, these methods were not sufficiently general to yield complete branching ratios and in particular were not able to determine the comparative likelihoods of the different channels that would lead to the formation of stable molecules. A notable advance in the measurement of branching ratios for polyatomic molecules was that of Mitchell et al. [12] for $\text{H}_3^+$ using a method that involved the merged beam technique coupled with a detection system in which some products were inhibited from reaching the energy sensitive surface barrier detector by placing a grid in front of it. This early measurement was fraught with background noise problems but with the development of high energy heavy particle storage rings, this limitation was largely removed and since then a wide variety of polyatomic ions have had their branching ratios determined at least with respect to fragment species of differing atomic masses [1,2,13]. However, complete branching ratios for hydrocarbon molecular ions with more than 2 or 3 carbon atoms are still beyond the reach of current experimental capabilities.

The importance of having accurate information concerning branching ratios has been highlighted recently by a modeling study by Pernot and associates [14] of the ionosphere of Titan where the atmosphere consists mainly of nitrogen and methane, yielding a rich chemistry. These authors have analysed the influence of the accuracy of known and speculated branching ratios on the final number densities of the products of polyatomic recombination reactions involving hydrocarbon species. In the astrophysical literature and other studies of Titan modeling [15], it has been generally assumed that
when a polyatomic hydrocarbon molecular ion undergoes recombination, this leads to the ejection of a single hydrogen atom leaving behind the remaining dehydrogenated neutral partner:

\[ e + C_nH_m^+ \rightarrow C_nH_{m-1} + H \quad \ldots \ldots \ldots (I) \]

While this is the main decay channel for \( CH_m^+ \) and \( C_2H_m^+ \) ions \([1,2,13]\), Mitchell et al. \([16]\) showed using the Astrid storage ring in Aarhus, Denmark, that for \( C_4H_m^+ \) ions, this was no longer necessarily the case and indeed when \( m \) is large, scission of the C-C bonds dominates. This was subsequently confirmed by other experiments involving \( C_3H_m^+ \) and \( C_4H_m^+ \) ions \([17,18]\) at Astrid and at CRYRING in Stockholm \([19]\).

In their paper, Pernot and colleagues have determined the difference in the final predicted number densities of products if one considers only reactions of type I or if one uses actually measured branching ratios where C-C bond scission is included. The results are shown in Figure 4 and it can be seen that the differences can be dramatic, up to 5 orders of magnitude in some cases.

\[ \text{Fig. 4. Comparison of the ratio of the production rates for neutral species } (\nu^{\text{Full}}/\nu^{\text{H-Loss}}) \text{ assuming that (a) the process passes by reaction I } (\nu^{\text{H-Loss}}) \text{ (Brown boxes along the centre-line) or (b) by a full set of possible evaluated branching ratios } (\nu^{\text{Full}}) \text{ (Blue boxes). (From [14] with permission).} \]

This study highlights the need for continuing explorations of polyatomic ion recombination branching ratios. Given the problems related to the lack of experimental facilities capable of yielding such data, other approaches must be employed to address this problem. The work of Chabot and collaborators \([19,20]\) perhaps points the way to new methods of determining branching ratios using sophisticated detector technology with the analysis of event timing. While this has not been directly used for DR research, the information concerning the dissociation of highly excited species can provide valuable information concerning fragmentation processes.
4. Ion cooling

Ion beams contain ions that are generally formed through violent processes such as electron impact and as such usually begin life in a variety of ro-vibrational and even electronically excited states. One of the major features of heavy ion storage rings is their ability to store ions for time longer than the typical relaxation times for vibrationally excited states (provided the ions possess a dipole moment) and so they were able to offer measurements involving vibrationally cold species. Rotational excitation is much longer lived and so it was perhaps not surprising that experimental measurements at the TSR ring in Heidelberg [21] found that $\text{H}_3^+$ ions used for their DR studies were indeed rotationally excited. What was surprising was how excited the ions really were (3000K). In other words they had as much internal energy as if they had been vibrationally excited. This observation prompted other techniques to be used to form the ions prior to their injection into the storage rings. In particular a supersonic expansion source was developed for this purpose [22]. It is well known that efficient rotational cooling can be achieved in the supersonic expansion of a gas through a nozzle, passing from a high to a low pressure environment. Supersonic expansion is much less efficient in producing vibrational cooling but this was not considered important given the radiative cooling achieved in the storage ring. In another approach, a cryogenically cooled (15K), multipole radiofrequency ion storage trap was used to produce the ions and this allowed them to be cooled via collisions with the background gas in the trap [23]. This approach [24,25] had originally been used in the single pass experiments of Mitchell et al. for $\text{H}_3^+$ [26], $\text{H}_2^+$ [27], $\text{HeH}^+$ [28] and $\text{N}_2^+$ [29] though in these experiments the trap was not cryogenically cooled. These different methods have been compared recently at TSR [30].

Again the results are quite surprising. Firstly it is found that the supersonic expansion source produced ions that were hotter ($450 \pm 100$ K) that those in test-bed studies that did not involve ion storage in a ring. This points to a fundamental problem and that is that the electron cooler used to produce the high quality ion beam in the ring, can have an effect on the internal excitation state of the ions through both exciting and de-exciting collisions. Cross sections for electron induced rotational state change are in fact enormous at low electron energies [31]. Secondly it was found that the ion trap source was capable of producing relative cool ions provided the extraction voltage on the source was kept low. This in fact had been found in early merged beam studies of $\text{H}_3^+$ recombination performed using a trap source with the single pass experiment of Mitchell et al. [26]. When the ions are to leave the trap which is at a relatively high pressure (up to 1 Torr), they must be accelerated to extract them and then to form them into a beam and during this process, they pass through the gas cloud downstream of the extraction region where they can undergo exciting collisions. Thus the need to reduce this effect as much as possible by reducing the extraction voltage while sacrificing beam intensity. The final temperatures obtained in these experiments ($150 \pm 50$K) are certainly not as low as originally thought but the high temperatures obtained with conventional sources are a cause for concern perhaps. This will probably not have a great influence on branching ratios but in some cases may play on the total rates measured with these machines.

5. New experimental developments

With the shutdown of the CRYRING and TSR facilities, the pursuit of heavy ion storage ring experiments has been curtailed. There are however, new developments on the horizon. There are two new electrostatic storage rings in development at Stockholm and Heidelberg that will be used for some recombination studies and these are discussed elsewhere in this issue [32] and in the proceedings of the 8th and 9th DR Conference. A third electrostatic storage ring is under construction in Saudi Arabia [33] and DR and DE measurements of light ions will be studied at this facility. This machine will have an injection energy of 20 keV and it is planned to build a merged beams setup into the ring that can be used for single and multiple pass experiments. Particular emphasis will be given to the examination of how these cross sections depend upon the electronic and ro-vibrational excitation of the ions.

A large heavy ion storage ring MIRFL has been designed in Langzhou China [34] and if built, this machine would offer a much higher magnetic rigidity that previously available in the three European
rings. This would allow (a) much heavier ions to be studied and (b) higher ion energy to be used that would permit branching ratios to be measured for more complex species than previously possible. Some of the latter measurements use an energy sensitive surface barrier detector technology that when coupled with the grid technique mentioned earlier, allow products to be separated according to their mass. The higher the ion energy, the easier it is to perform this separation. At the present time, the schedule for the construction is uncertain [35].

While the heavy ion storage ring measurements have been designed to treat cold ions, those found in fusion wall and diverter plasmas are more likely to be excited and so future experiments will be needed to characterize the ions produced in low pressure ion sources and to perform single pass experiments to make prompt measurements of such excited ions. In previous studies, it has been found that excited ions can have cross sections that can differ by a factor of 3 or 4 from ground state species [36]. DR is such a complicated process and the position of the states implicated is so critical in some cases that it is not easy to predict a priori what the effects of an excitation will be. Hence the need for continuing experimental and theoretical efforts in a field that continues to surprise and for which there is a continual demand for data.

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Appendix: The Dissociative Recombination Conferences
1988: Dissociative Recombination: Theory, Experiment and Applications, Lake Louise, Canada, (Editors: J.B.A. Mitchell and S. L. Guberman), World Scientific, Singapore, 1989.
1992: Dissociative Recombination: Theory, Experiment and Applications, St. Jacut de la Mer, France, (Editors: B. R. Rowe, J.B.A. Mitchell and A. Canosa), NATO ASI Series, Plenum Press, New York, World Scientific, 1993.
1995: Dissociative Recombination: Theory, Experiment and Applications, Ein Gedi, Israel, (Editors: D. Zajfman, J.B.A. Mitchell, D. Schwalm and B.R. Rowe), World Scientific, Singapore, 1996.
1999: Dissociative Recombination: Theory, Experiment and Applications IV, Stockholm, Sweden, (Editors: M. Larsson, J.B.A. Mitchell, I.F. Schneider), World Scientific, Singapore, 2000.
2001: Dissociative Recombination of Molecular Ions with Electrons (Chicago, USA) (Editor: S.L. Guberman), Kluwer Academic/Plenum Publishers, New York, 2003.
2005: Sixth International Conference on Dissociative Recombination: Theory, Experiment and Applications (DR2004), Mosbach, Germany (Editors: A. Wolf, L. Lammich and P. Schmelcher), J. Phys Conference 4, 2005.
2007: Seventh International Conference on Dissociative Recombination: Theory, Experiment and Applications (DR2007), Ameland, The Netherlands (Editor: W.J. van de Zande), J. Phys Conference 192, 2009.
2010: Eighth International Conference on Dissociative Recombination: Theory, Experiment and Applications (DR2010), Lake Tahoe, USA (Editors: S.L. Guberman and A.E. Orel), J. Phys. Conference 300, 2011.
2013: Ninth International Conference on Dissociative Recombination: Theory, Experiment and Applications (DR2013), Paris, France (Editors: I. Schneider, O. Dulieu, J. Robert) EPJ Web of Conferences (to be published).

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