

The effect of bonding on the fragmentation of small systems

R D Thomas,¹ A Ehlerding,¹ W Geppert,¹ F Hellberg,¹ M Larsson,¹
V Zhaunerchyk,¹ E Bahati,² M E Bannister,² C R Vane,² A Petrigiani,³
W J van der Zande,^{3,4} P Andersson⁵ and J B C Pettersson⁵

¹ Department of Physics, Albanova, Stockholm University, S106 91 Stockholm, Sweden

² Physics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6377, USA

³ FOM Instituut for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

⁴ Molecule and Laser Physics, IMM, Radboud University Nijmegen, 6525 ED Nijmegen, The Netherlands

⁵ Department of Chemistry, Göteborg University, SE-412 96 Göteborg, Sweden

E-mail: rdt@physto.se

Abstract. In several recent dissociative recombination (DR) experiments, the observed DR products depend on the structure, bonding and charge center of the molecular ion. For examples, the dominant product channel observed in the DR of $N_2O_2^+$, D_5^+ , and $D_5O_2^+$ suggests that the former two ions have the form $NO^+ \cdot NO$, and $D_3^+ \cdot D_2$, respectively, whilst the latter is known to have the form $D_2O \cdot D^+ \cdot D_2O$. We compare and contrast these observations by investigating the DR of one of the simplest such systems, $Li^+ \cdot H_2$. This system, a weakly bound cluster with the charge center located on the lithium atom, will provide us with an excellent opportunity for investigating the role played by the type of bonds and charge center in the DR process.

1. Introduction

Dissociative recombination (DR) is a process in which a molecular ion recombines with a free electron and subsequently dissociates into neutral fragments. For plasmas containing molecular ions, DR is the most important neutralizing process and is therefore of great importance to the chemistry occurring in such diverse regions as interstellar clouds, planetary atmospheres and in semi-conductor etching.

Many recent DR studies have focussed on the break-up of polyatomic ions. This has been driven, to some extent, by the fact that given the apparent simplicity of the DR process, developing a general theory to predict product branching ratios for even the simplest polyatomic ions, e.g. XH_2^+ , has proven to be difficult. The earliest models suggested that the reaction would predominantly proceed via the least amount of internal rearrangement, i.e. the fracture of the weakest X-H bond, producing $H + XH$. However, all recent storage ring studies on the DR of such ions show a propensity for three-body break-up, i.e. $X + H + H$ (see [1] for a comprehensive list).

To understand the dynamics occurring in such simple systems, the effect of the structure, bonding, and charge center of the molecular ion needs to be investigated. Small molecular cluster ions represent good toy models and several systems have recently been investigated, for examples $N_2O_2^+$, D_5^+ , and $D_5O_2^+$. These systems are small enough to allow complete detection of the product fragments and represent systems for which there are several different bond types, i.e. dative, covalent, hydrogen, and dipole, and either localized or delocalized charge centers, and the combination of these will influence how the neutral

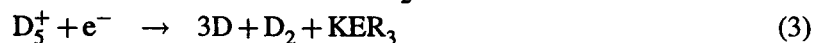
molecular system dissociates. Based on the experimental data obtained on the DR of these systems, the simplest model system which combines all of the features just discussed was chosen for investigation, i.e. $\text{Li}^+\cdot\text{H}_2$.

2. Dissociative recombination in storage rings

All the experiments discussed in this paper were carried out at the heavy ion storage ring CRYRING, located at the Manne Siegbahn Laboratory, Stockholm University. The use of such facilities for the study of DR is due to several experimentally desirable aspects. The high ion-beam energies used, usually a few MeV, have several experimental advantages. The electron capture cross section in collisions between the stored ion beam and residual gas molecules is small at high beam energy, which significantly reduces the contribution of background signals to the true data. For zero eV relative collisions between the electrons and the ions, it is much easier to create and control a stable and dense electron beam if the beam velocity is high, and this requires MeV ion beams. The good vacuum $< 10^{-11}$ Torr in the ring indicates that the number of residual gas molecules is extremely low, further decreasing the background contributions as well as enabling a long storage lifetime of the ion beam. This time, which can be tens of seconds, allows metastable and vibrationally excited components in the ion beam to decay to the ground state. A recent review on the use of merged-beams in atomic and molecular physics can be found in the literature [2].

3. Experimental results and discussion

In the collisions of N_2O_2^+ , D_3^+ , and D_5O_2^+ with 0 eV electrons, the following reaction channels, with their associated kinetic energy release (KER_n), are observed to be the most dominant:



It is noted that the available KER is a maximum for ground state fragments and the production of internally excited products reduces this. These results were obtained with the standard detection techniques used for obtaining chemical branching from DR, and these techniques are discussed in [3].

The ionic structure, charge center and bond type of these ions is of relevance when analyzing the dominant fragmentation channels. The weakly bound NO dimer ion has the form $\text{NO}^+\cdot\text{NO}$ [4] while D_3^+ has the form $\text{D}_3^+\cdot\text{D}_2$ [5], i.e. it is a weakly hydrogen-bonded cluster. Finally, D_5O_2^+ has a proton-bridge structure, and has an almost linear geometry given by $\text{D}_2\text{O}\cdot\text{D}^+\cdot\text{D}_2\text{O}$ [3]. In each case, the dominant product channels observed in the DR reaction are similar to those which would be expected if the "solvent" neutrals played little or no role in the reaction, i.e. the dominant channels in the DR of $\text{D}_3^+\cdot\text{D}_2$ are similar to those from the DR of D_3^+ or H_3^+ [6], and the completely dominant production ($> 90\%$ [3]) of $2\text{D}_2\text{O} + \text{D}$ from the DR of $\text{D}_2\text{O}\cdot\text{D}^+\cdot\text{D}_2\text{O}$ would also be expected. For $\text{NO}^+\cdot\text{NO}$ the only other significantly populated channel is $\text{NO} + \text{NO}$.

The question that arises from these results is then how much of the available reaction energy has been used in excitation of the molecular fragments. This is an important aspect in the case of both $\text{NO}^+\cdot\text{NO}$ and $\text{D}_3^+\cdot\text{D}_2$ as this would indicate the importance of the role played in the DR reaction by the solvent molecule. A technique is needed which can measure the kinetic energy given to the reaction fragments, and such a technique has been developed and used with great success in studying the DR of both diatomic and triatomic molecular ions. Using a position-sensitive detector (briefly, a stack of multi-channel plates (MCPs), a phosphor screen and a photo-multiplier tube (PMT) [7, 8]) monitoring the position of the fragments from the DR reaction allows the kinetic energy given to the fragments to be determined.

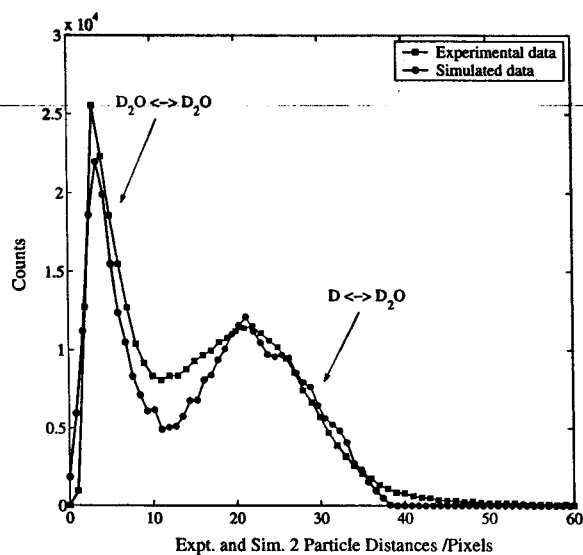
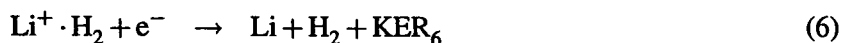


Figure 1. Distance distributions obtained from the DR of $D_5O_2^+$.

An example of the power of this technique is given in the following example, where the kinetic energy given to the D and D_2O fragments from the DR of $D_5O_2^+$ has been determined. The preliminary results are shown in figure 1, together with a simulation of the experimental data. The simulation, described in some detail in [7], indicates that from the available reaction energy of 5.1 eV, up to 3 eV is used in exciting the molecular D_2O fragments, i.e. $KER_5 = 2.1$ eV for 3 eV of molecular excitation. It is obvious that the D_2O molecules solvating the D^+ play a significant role in the reaction after the ion attaches the electron. The corresponding data obtained from the DR of the $NO^+ \cdot NO$ and $D_3^+ \cdot D_2$ are under analysis.

It is clear, even from such preliminary analysis, that the dynamics occurring in the dissociation step immediately following the attachment of the electron are very important for an understanding of the DR process. To help further understand the analysis for such toy-model systems, a much simpler system was selected for analysis. The cluster ion $Li^+ \cdot H_2$ represents an ideal model. The charge center of the ion is extremely localized on the lithium atom. The bonding between the Li^+ and the H_2 molecule is controlled by the charge on the Li atom and is thus a weak dipole-induced bond. The dative bond in the H_2 molecule is extremely strong in comparison. The neutral system, i.e. $Li \cdot H_2$, is even more weakly bound than the ionic system, being Van der Waal's in nature. An initial prediction for the DR reaction would be that only the channel producing $Li + H_2$ would be populated and any deviation from this would be illustrative of the post attachment interactions happening in a very weakly bound system.

In 0eV collisions the following reaction channels, with their associated kinetic energy release (KER_n), are possible:



Data obtained on the population of these possible channels will be sufficient for an initial handle on the intra-cluster dynamics occurring post electron attachment. Preliminary data are shown in figure 2, where the peaks in the spectrum correspond to the various combinations of products possible in the reaction. Details on the data analysis techniques are discussed in [3]. The results from this analysis show that although the dominant channel populated in the DR reaction is that producing $Li + H_2$, i.e. channel (6), it is not the only channel. Just over a fifth of the DR reactions lead to the production of both $LiH + H$, and $Li + 2H$. These results indicate that the post-attachment interaction is sufficiently strong, leading both to the fracture of the strongest bond in the system, the molecular hydrogen bond, and the formation of a much weaker-bonded molecular system, LiH .

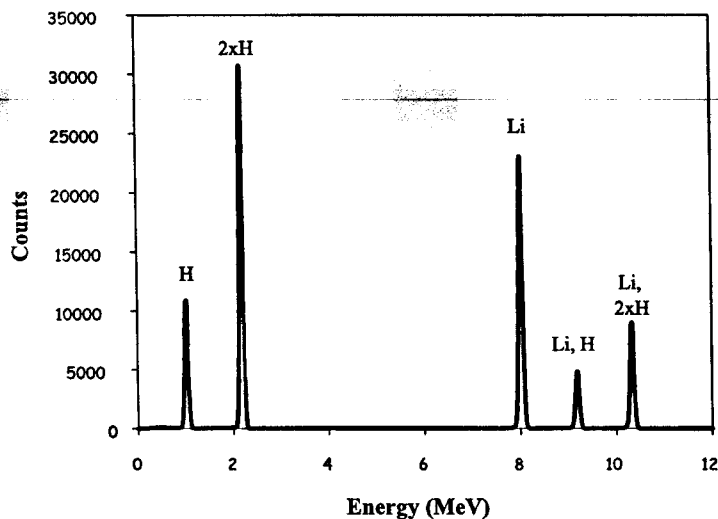


Figure 2. Multi-channel analyzer data of the fragments produced from the DR of $\text{Li}^+\cdot\text{H}_2$.

4. Conclusions

In the light of experimental observations, the development of a simple model to describe the DR process for even a small polyatomic ion does not seem to be a trivial matter. The preliminary results presented here for the DR of some model systems show that the products depend on the structure, bonding and charge center of the molecular ion, and that the transition of the molecular system in moving from a single ionic state to an ensemble of highly-excited neutral states induces a dynamical interaction between the molecular and atomic constituents of the system. More work is needed to understand which types of interactions are the most dominant, and this could lead to the development of at least semi-empirical models.

Acknowledgments

We would like to thank the CRYRING staff at the Manne Siegbahn Laboratory for their tireless work and excellent support. This work was supported by the Swedish Research Council, the Swedish Foundation for International Cooperation in Research and Higher Education. RT is funded under the IHP Programme of the EC under contract HPRN-CT-2000-00142. The work of WJvdZ is part of the research of the 'Stichting voor Fundamenteel Onderzoek der Materie', made possible by financial support by the Stichting voor Wetenschappelijk Onderzoek. The Oak Ridge collaboration is sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.

References

- [1] Larsson M and Thomas R 2001 *Phys. Chem. Chem. Phys.* **3** 4471
- [2] Phaneuf R A, Havener C C, Dunn G H and Müller A 1999 *Rep. Progr. Phys.* **62** 1143
- [3] Någård M *et al.* 2002 *J. Chem. Phys.* **117** 5264
- [4] Petrigani A *et al.* 2003 in *Proceedings of the XXIII ICPEAC, Stockholm, Abstracts* ed Anton J *et al.* (ICPEAC CDROM) Contribution Mo108
- [5] Andersson P *et al.* 2003 in *Proceedings of the XXIII ICPEAC, Stockholm, Abstracts* ed Anton J *et al.* (ICPEAC CDROM) Contribution Mo109
- [6] Datz S, Sundström G, Biedermann Ch, Broström L, Danared H, Mannervik S, Mowat J R and Larsson M 1995 *Phys. Rev. Lett.* **74** 896
- [7] Thomas R, Rosén S, Hellberg F, Derkatch A, Larsson M, Datz S, Dixon R and van der Zande W J 2002 *Phys. Rev. A* **66** 032715
- [8] Amitay Z and Zajfman D 1997 *Rev. Sci. Instrum.* **68** 1387