A new apparatus for the study of electron impact fragmentation of molecular clusters

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Abstract. This paper reports on the development of a new experiment for the study of electron-impact induced dissociation and fragmentation of molecular clusters and biomolecules and other species solvated in water clusters. The purpose is to look at clusters that are of interest to biophysics, atmospheric physics, and other fields. The experiment consists of a differentially pumped vacuum system, with an expansion chamber to generate a pulsed supersonic beam of clusters, and a collision chamber where the cluster beam intersects with an electron beam. Water clusters can be seeded with biomolecules emerging from a resistively heated oven. Investigation will be possible into both ion yields and long-lived neutral metastable yields produced by electron-impact fragmentation of relevant clusters and biomolecules.

1. Introduction

For most molecules the total cross sections for electron-impact excitation and ionisation vary smoothly with electron energy and reach maxima at around 70 - 100 eV. In contrast, cross sections for electron attachment typically peak at electron energies of a few eV and decrease at higher energy. Low-energy negative-ion resonances greatly enhance the cross sections for electron attachment to most molecules [1, 2], and recent research has demonstrated the relevance of resonances in electron attachment to biomolecules [e.g. 3, 4].

An important pathway of evolution of the transient negative-ion state formed in electron attachment involves the dissociation into fragments consisting of one ion and one or more neutrals, a process known as dissociative electron attachment. Other reaction pathways also exist. Autodetachment may leave the molecule in an excited state with the electron slowly receding. Relaxation into a stable negative ion state may occur, if such a state exists, but this is very unlikely in the gas phase and is orders of magnitude slower compared to autodetachment and dissociation.

The situation becomes much more complex for a molecule solvated in a water cluster. When a transient negative ion is formed in the cluster, various new mechanisms may occur depending on the way the extra energy is dissipated in the cluster [1]. In the case of reactions where charged particles are involved, the solvent represents a dissipative environment which can considerably modify the transfer of energy into the various reaction channels.

As stated by Gohlke and Illenberger (2002) [5]: *"The question then is to which degree these intrinsic properties (as revealed by gas phase studies) can be transferred to their analogue in solution. This problem has been a longstanding issue in many areas of Physical Chemistry. One has to be*

aware that the solvent represents a dissipative environment and in the case of reactions where charged particles are involved, solvation can considerably modify the energy profile along the reaction coordinate." Two current areas of research where this problem is particularly relevant are briefly discussed here.

1.1. Electron-impact induced damage of biomolecules

Many of the mutagenic or lethal effects of ionising radiation on biological organisms can be traced to structural and chemical modifications in cellular DNA. These are often linked to localisation of either positive or negative charges on the DNA bases caused by the large amounts of low-energy secondary electrons created in very short times along the radiation tracks and spurs. In water, by far the largest amount of secondary electrons is produced at early times by the radiation and this amount greatly exceeds the amount of electrons with higher energies. Even though the electrons have energies below the ionisation energies of the molecules, they very efficiently dissociate organic molecules in either the gas phase or the condensed phase. These secondary electrons are therefore of great relevance in relation to radiation damage in biological organisms. The strong electron energy dependence of the DNA strand breaks has been attributed to electron attachment and rapid decay of transient negative-ion resonances localised on the DNA's basic components, followed by bond rupture and subsequent reactions of the fragmentation products (see the review by Sanche 2005 [6]).

The experiments that have led to the current understanding of mechanisms giving rise to DNA damage have been performed under dry high-vacuum conditions, with biomolecules in the gas phase or in thin films on a substrate [6]. These conditions do not take into consideration the hydrated and aerobic environment of the cell, and it is therefore crucial to understand how these fundamental mechanisms are affected and modified in the presence of vital cellular components, particularly H_2O, O_2 and the histone proteins which are in contact with DNA. For this reason a number of groups studying radiation damage are currently working towards the realisation of experiments with biomolecules solvated in water clusters. A recent study [7] using hydrated single DNA strands in a thin film has found that DNA damage via dissociative electron attachment induced by low-energy electron impact increased by a factor of about 1.6 owing to the presence of water.

1.2. Electron impact on atmospheric species

Electron-induced excitation and fragmentation processes play an important role in the Earth's atmosphere [8, 9]. High-energy electrons from the solar wind interact with atoms and molecules to produce ions and lower-energy electrons. These secondary electrons can excite atoms and molecules to excited states, which then radiatively decay, producing auroral emissions. Direct sunlight produces photoelectrons which lead to atomic and molecular emissions responsible for the dayglow. Other processes, such as predissociation, dissociative electron attachment, quenching, and chemical reactions reduce the population density of excited states, but the products produced in dissociations may induce further reactions.

These dissociative and fragmentation processes are initiated by electron or photon impact, and result in fragment ions, atoms, and/or molecules, which may be electronically, vibrationally and/or rotationally excited. An important aspect of fragmentation processes is the release of kinetic energy from the incident electron or photon into heat, leading to the production of kinetically and excitationally energetic fragments whose chemical reactivity may be substantially enhanced. The surplus kinetic energy released also results in the emission of radiation with highly Doppler-broadened linewidths, a factor that complicates the analysis of the role of fragmentation processes in astrophysical and planetary environments [10].

In recent years weakly bound complexes containing water have increasingly been the topic of scientific research [11, 12, 13]. Protonated water cluster ions ($H^+(H_2O)_n$) are a dominant ionic species in the D region of the ionosphere (50-90km) [8]. Water dimers ($(H_2O)_2$) were recently detected (difficult) in the troposphere [14], and the existence of larger water clusters has been predicted [15]. Water clusters and complexes with other atmospheric species may play an important

role in the radiative balance [13], in the oxidation of trace gases, and other atmospheric processes [11]. It is therefore important to study electron-driven processes involving these species.

Studies of electron impact on water clusters and complexes are particularly relevant, not only because of the importance of electron-driven processes in the upper atmosphere, but also because electron scattering is an important alternative spectroscopic tool for the study of molecules and clusters. In contrast to optical spectroscopy there are no transitions forbidden by selection rules, and all the electronic states of the target may be excited by electron impact.

1.3. Research in Maynooth

A new experiment is being set up, incorporating a source of molecular clusters (water or methanol) containing relevant biological or atmospheric molecules, to research electron-induced fragmentation of these clusters by detection of the neutral metastable fragments and the ionised fragments using time-of-flight techniques.

The purpose of the experiment is to:

- Identify new products (ions, neutral metastables, and radicals) and new breakage pathways and mechanisms resulting from low-energy electron impact of molecules solvated in molecular clusters.

- Extend the information obtained from electron-impact studies on dry and gas phase DNA components by using a solvated environment. This is important as a significant amount of damage occurring *in vivo* may not result directly from the impact of electrons with the DNA, but from interactions with particles produced as the consequence of the radiolysis of water.

- Study the electron-impact fragmentation of small neutral water clusters and water complexes containing molecules such as SO_2, NO, O_2, Ar, CO_2, which are of relevance in processes such as the absorption of solar radiation, the formation of sulphuric acid in cloud droplets, and the oxidation of trace gases. Study of dissociative electron attachment to neutral water complexes, leading to negative ion products, is of relevance to the physics and chemistry of the D region of the ionosphere.

The remainder of this paper is organised as follows. The next chapter will give a brief overview of time-of-flight techniques, in particular the techniques used for neutral metastable fragments. Chapter 3 will give an overview of the experimental apparatus, and some of the experimental techniques used will be discussed in more detail. Because this paper is very much a report of work in progress, chapter 4 will present preliminary results and a synopsis of plans for the future.

2. Time of flight techniques

2.1. Time-of-flight mass spectrometry

Time-of-flight mass spectrometry is a very well established technique that has been reviewed in many books and articles (eg. [16]). Important new developments in time-of-flight techniques are velocity slice imaging [17] and cold target recoil ion momentum spectroscopy (COLTRIMS) [18]. Velocity slice imaging has been applied to many gas phase molecular reactions [19].

2.2. Time-of-flight detection of neutral fragments

Neutral atoms, radicals and molecular/cluster fragments in metastable or high-lying Rydberg states can be detected when they hit a metal surface, de-excite, and release an electron from the conduction band of the surface. The technique is suitable for states with comparatively long lifetimes ($\tau > 1\mu s$), and with excitation energies larger than 8 eV or 5 eV with specially prepared surfaces [20]. Because the neutral fragments cannot be accelerated, their arrival time at the detector is proportional to their velocity and therefore to the kinetic energy they have acquired in the fragmentation process.

Contrary to the detection of ions or the detection of luminescence, there are few experimental studies of excited neutral cluster fragments or atoms produced by electron-impact on clusters. However, the technique has been applied with great success in electron and photon impact dissociation

of many molecules, such as N_2, H_2O, CO_2, CH_4, etc. [10, 21]. The observed kinetic energies of the metastable fragments typically range from zero to a few eV and higher. As compared to mass spectrometry, the yields of neutral metastable fragments are in general lower and therefore require longer data acquisition times.

Neutral metastable fragments can provide very specific information about repulsive excited-state potential curves and of the fragmentation processes [10, 21]. With a simple transformation kinetic energy distributions of the metastable fragments can be obtained from the measured time-of-flight distributions. In determining the kinetic energy of a fragment, a correction needs to be made for the forward velocity of the parent molecule/cluster, as described in [22]. These kinetic energy distributions are measured as a function of electron impact energy. The following information is obtained. Fragmentation processes produce onsets in the yield of metastables as a function of electron energy, and the fragmentation processes involved can often be deduced from the location of these onsets. The shape of a kinetic energy spectrum indicates whether the fragmentation occurred from a purely repulsive excited state or from the repulsive wall of a bound excited state (see figure 1). Kinetic energy distributions can in a number of cases provide sufficient information to determine repulsive potential curves.
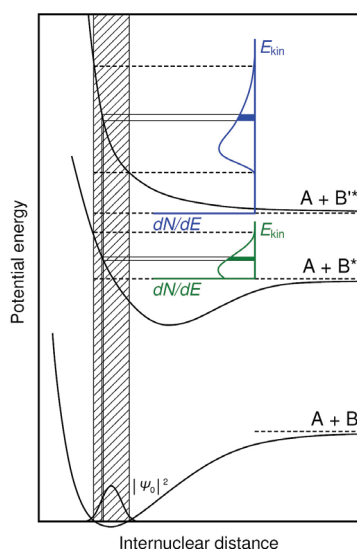

Figure 1. Illustration of two types of dissociation processes and the associated kinetic-energy distributions of the metastable fragments. The shaded area represents the Franck-Condon region. The illustration is for a diatomic molecule AB, and B* indicates an atom in a metastable or high-Rydberg state (adapted from figure 1 in [10]).

3. Experimental set-up

3.1. Overview of the apparatus

The experiment consists of a differentially pumped vacuum system, with an expansion chamber to generate a pulsed supersonic beam of molecules or clusters, and a collision chamber where the molecules or clusters are fragmented. In the collision chamber the supersonic beam is crossed with an electron beam or a laser beam (or both) and the reaction products (ions and neutral metastable atoms) are detected. Both chambers are separated by a top hat which contains the skimmer, and onto which the holder for the pulsed valve and the electron gun are mounted.

The electron beam is pulsed with a typical pulse width of 1 μs, so that both ions and neutral metastable fragments can be detected using time-of-flight techniques. This pulse width is sufficient to achieve very high mass resolution and good resolution in the kinetic-energy spectra of the neutrals.
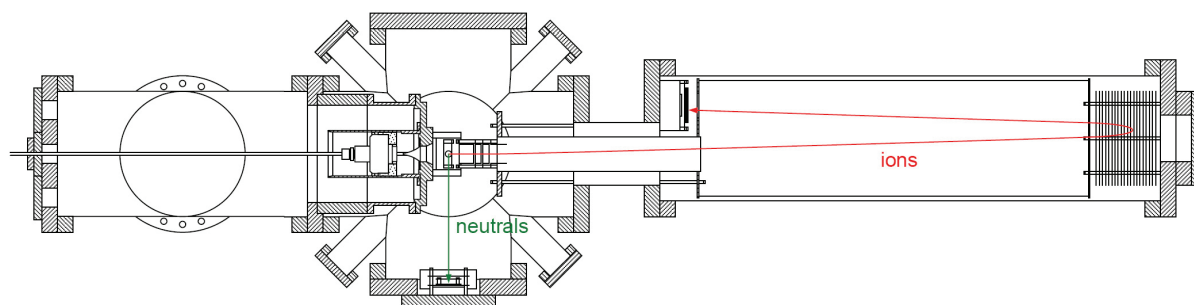
Figure 2. Overview of the supersonic beam experiment (the total length is 2 m). The left chamber contains the supersonic expansion. The middle chamber is a 6-way cross containing the electron gun and the metastable detector (the electron beam is pointing out of the paper). The right chamber is the flight tube of the reflectron mass spectrometer. Trajectories of a neutral metastable fragment and an ionised fragment are indicated.

3.2. Cluster source

A pulsed supersonic beam is generated using either a solenoid valve (General Valve Series 9; 0.5 mm conical nozzle, 1 ms pulse width) or a piezo-electric valve (Lasertechnics LPV; 0.3 mm conical nozzle, 200 µs pulse width). The typical repetition rate is several Hertz.

A source of biomolecules (DNA bases and uracil) soluted in water clusters is currently being built. Water clusters will be generated in a pulsed supersonic expansion of water vapour into a vacuum chamber. The water clusters are seeded with biomolecules emerging from a resistively heated oven at temperatures well below the decomposition temperature of the molecules [23, 24]. This technique can also be used for producing clusters with relevant atmospheric species [25]. The design of the oven mounted in front of the piezo-electric valve is shown in figure 3.
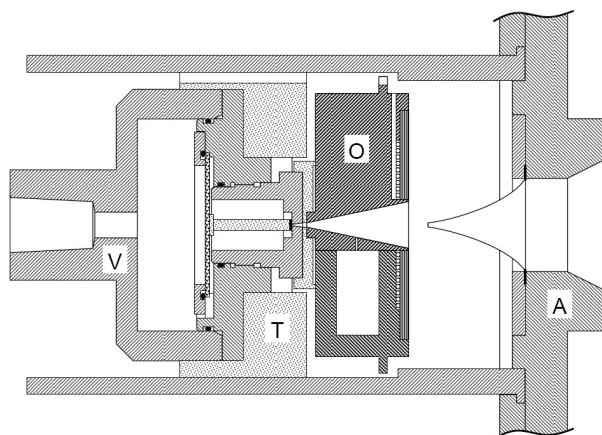

Figure 3. The piezo-electric valve (Lasertechnics LPV) with the resistively heated oven mounted in front of the skimmer. The gas inlet to the valve is not shown. Legend: V = valve, T = teflon holder, O = oven with reservoir, A = aluminium bracket and (part of) the front of the top hat separating the expansion chamber from the collision chamber.

3.3. Electron gun

The pulsed electron beam presently used in the experiment is generated with a 7-element electrostatically-focussed electron gun. The electron impact energy is computer controlled. This gun

is able to generate dc currents of a few μA with a resolution slightly less than 1 eV over an energy range of 12 - 300 eV. This is sufficient for the initial studies, but for further work an electron gun capable of generating beams at energies lower than 12 eV is needed. Plans are to build a trochoidal electron gun [26], which will enable electron impact studies with electrons of very low energy.

3.4. Detection of ions

A reflectron time-of-flight mass spectrometer (Jordan TOF Products) with a microchannel plate detector is used for the detection of ions. Depending on the voltages applied to the instrument, the reflectron can resolve both positive and negative ions. Mass spectra can be taken as a function of electron impact energy (see §3.6), so that excitation functions (ion yield curves) can be obtained for each of the ions in the mass spectrum.

3.5. Detection of neutral fragments

Metastable atoms, molecules or radicals incident on a surface may eject electrons, if their internal energy exceeds the workfunction of the surface (see §2.2). Detectors based on secondary electron ejection are easy to construct and operate at typical overall efficiencies of up to 0.5. Two different metastable detectors have been constructed, both mounted on 6" conflat flanges. The first detector uses a channeltron and the second detector uses a set of microchannel plates. Both detectors have appropriately biased meshes mounted at the front to avoid detection of charged particles.

3.6. Data acquisition

The data acquisition techniques for measuring time-of-flight spectra are the same for the ions and for the metastables. The moment of fragmentation is determined by the electron beam pulse (or the laser beam pulse) passing through the supersonic beam. The pulse used to trigger the electron beam is also used to start a fast multichannel scaler (FastComtec 7886S, 1 ns per channel). Standard pulse counting techniques are used to detect both ions and metastable neutral particles. A time-of-flight spectrum is obtained by accumulating the signals for many electron pulses.

A digital delay generator (Stanford DG535) is used to accurately time the valve pulse, the electron pulse, the extraction pulse to extract the ions into the reflectron, and the trigger of the multichannel scaler.

A LabView program has been written, controlling the electron impact energy and the data acquisition with the multichannel scaler. Time-of-flight spectra are accumulated as a function of electron impact, from which excitation functions can be extracted (depending on the detector used: for individual masses, or for neutral fragments with specific kinetic energy).
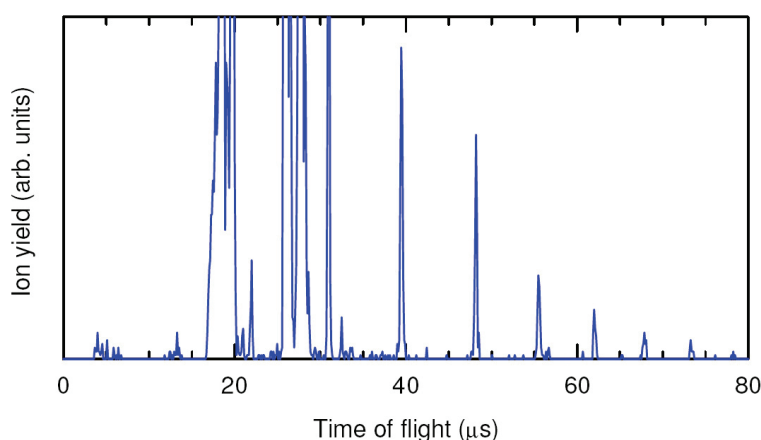

Figure 4. Mass spectrum of methanol obtained using the reflectron time-of-flight mass spectrometer. The electron impact energy is 100 eV. Positive cluster ions of sizes up to n = 8 are observed.

4. Preliminary results and future plans

The focus to date has been on optimising the supersonic expansion, implementing enhancements in data acquisition, and testing the functionality of the system. Preliminary tests of the apparatus involve generation of argon clusters and molecular clusters such as methanol in an argon-based (1.5-2 bar) supersonic expansion. Methanol cluster ions, $(CH_3OH)_n^+$, have been observed up to n = 8 (see figure 4). Based on these tests, work is currently focused on further enhancement of the cluster yields by replacement of the solenoid valve with a piezoelectric valve, which has a smaller nozzle and a shorter pulse width. Once clustering has been optimized, plans are to seed a supersonic beam of water clusters with DNA bases and uracils, and to study these through low-energy electron impact.

Future plans involve the construction of a trochoidal electron gun to enable electron impact studies in the range 0 - 12 eV. Pending funding, dissociative ionisation and dissociative electron attachment will be studied using a velocity slice imaging technique. The technique was recently applied to the study of dissociative electron attachment by Nandi et al (2005) [27]. In the Maynooth experiment a position sensitive detector consisting of twin microchannel plates, a phosphor screen and a CCD camera can be mounted behind the reflector of the reflectron mass spectrometer [28]. Electron impact on some atmospherically relevant molecules have been studied recently by other groups using velocity slice imaging, but little information is available on small clusters.

5. Conclusions

A new experiment for the study of electron-impact induced dissociation and fragmentation of molecular clusters has been described. The goal is to study electron-impact on biomolecules and other species solvated in water clusters which are relevant to biophysics and atmospheric physics. Versatility is provided by the detection of both ions and long-lived neutral metastables produced by electron-impact fragmentation of these clusters. Initial tests demonstrate the functionality of the experiment, and work is now in progress to implement a source of water clusters with biomolecules in solvation. A possible future expansion of the experiment is the implementation of a velocity slice imaging technique.

Acknowledgements

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