Fully Differential Molecular-Frame Electron Impact Ionization Measurements

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Abstract. (e,2e) measurements in the molecular frame using a new spectrometer are described. This work requires a triple coincidence experiment in which (e,2e+ion) events are detected. Preliminary results are presented for a nitrogen target, which illustrate the performance of the apparatus. The nitrogen data clearly shows that the (e,2e) cross section depends sensitively on the orientation of the molecule relative to the incident direction.

1. Introduction

(e,2e) experiments are a powerful tool for providing information on the electronic structure of atoms and molecules and on the mechanisms underlying electron impact ionization. However, until recently the information that could be obtained from these kinds of experiments for molecular targets has been limited because measurements have been averaged over the molecular orientations. The orientation of a molecule can be inferred from the momenta of ion fragments produced following dissociative ionization. The method relies on fragmentation occurring within the axial recoil approximation, that is that the molecule fragments in a time interval considerably faster than its rotational period [1], i.e. that the energy of dissociation is much greater than the rotational energies.

While numerous molecular-frame experiments have been reported for photoionization [2], only two studies have been reported for electron-impact ionization [3, 4], and these have been severely limited by poor statistics. These experiments are more difficult for electron-impact induced ionization than for the analogous photoionization measurements because an extra charged particle must be detected in coincidence and its kinematics fully determined. The photoionization experiments frequently employ charged particle imaging techniques such as cold target recoil ion momentum spectroscopy COLTRIMS [5] and velocity map imaging (VMI) [6], which can provide detailed kinetic energy and angular distributions of fragment ions. Again these techniques are simpler to implement for photoionization measurements as the electric and magnetic fields required for imaging can be used without interfering with the ionizing projectile.

Takahashi and co-workers performed the first (e,2e) measurement for H₂ molecules fixed in space [3]. Our group also performed a preliminary study to assess the feasibility of obtaining orientation

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resolved data [4]. While these measurements showed that obtaining orientation-resolved data was indeed possible, they also showed large improvements in count rate would be required to develop a dependable technique. We have recently modified our high efficiency electron spectrometer to considerably improve both electron and ion detection efficiencies. In our preliminary study only ions emitted within an approximately 30 degree emission-cone were detected on a position-sensitive detector located above the reaction plane, corresponding to measurement of about 10% of the total solid angle. We have since introduced a pulsed ion extraction scheme so that all ions emitted over the full 4π solid angle are detected and their momenta determined.

Theory predicts very strong orientation dependent effects should be observed. Calculations performed on both \( \text{N}_2 \) and \( \text{H}_2 \) targets show that the cross sections are expected to be quite different for different molecular orientations [7, 8, 9]. To date there is no experimental data to test these predictions. In order to test the theoretical models and to shed new light on the process of electron impact dissociative ionization, we have developed an apparatus and the associated techniques to enable fully differential (e,2e+ion) cross sections to be measured in the molecular frame.

2. Experiment

2.1. Overview

As the electron analyzers have been described in detail in a previous publication [10] only an overview will be given here which will focus on details relevant to the incorporation of the new ion spectrometer into this apparatus. The electron analyzers and ion spectrometer are shown schematically in figure 1.

![Figure 1. Schematic of the apparatus.](image_url)

A primary beam of spin polarized electrons is produced from a strained GaAs photocathode by illuminating it with circularly polarized laser light. The light at 850 nm is produced from a laser diode and first passed through an acousto-optic modulator, which periodically switches the light on and off and accordingly turns the electron beam on and off. The electron beam is deflected through 90 degrees...
and transported at high energy through a differential pumping stage to the main collision chamber where it is decelerated to the collision energy of interest. Deceleration from the transport energy of around 700 eV occurs in two stages using a 7-element electrostatic lens system.

The electron beam then intersects a molecular target beam which is formed by the effusion of the target gas through a 0.5 mm internal diameter titanium capillary, mounted orthogonal to the electron beam. Both the electron beam and molecular target beam are oriented such that they are parallel to the face of the ion detector and lie within the scattering plane, which is defined by the momentum vectors of the incident and measured emitted electrons. Electrons emitted within the scattering plane are momentum and energy analysed in two separate toroidal sector electrostatic energy analysers. Each analyser consists of an entrance lens system, double toroidal sector electrodes and a time- and position-sensitive delay line detector [11].

When an electron pair is detected in coincidence, the extraction electrodes are switched on immediately and ions are extracted and imaged onto the ion detector. This is a third time- and position-sensitive detector, again consisting of an 80 mm active area microchannel plate pair and delay line anode [11]. It takes ~165 ns from the moment of ionization for the extraction field to be turned on. This delay is comprised of the time for an electron to travel through the spectrometer, the time to process the signal in the detection electronics and the time required to switch the extraction voltage from 0 to ~210 V. The momenta of the ions are reconstructed from their arrival times and positions on the detector by matching these to simulated arrival times and positions which are calculated using SIMION software [12].

2.2. Modifications to electron analysers
As a means of increasing the (e,2e) count rate for these molecular frame ionization experiments, the electron analysers have been reconfigured to allow for more asymmetric kinematics to be measured. For a molecular nitrogen target, Avaldi et al [13] demonstrated that a factor of 10 increase in data collection speed can be achieved if asymmetric rather than symmetric kinematics are employed. One analyser presently covers the range \( \theta_1 = -10^\circ \) to \(-50^\circ\) and the other \( \theta_2 = 30^\circ \) to \(130^\circ\), where \( \theta_1 \) and \( \theta_2 \) are measured in the scattering plane with respect to the primary electron beam.

The electron analyzer entrance optics for both analyzers had to be modified to allow the ion extraction electrodes to be inserted around the interaction region. In addition, to help maximize the triple coincidence count rate, the electron analyzer lenses have been adapted to enable a greater electron transmission through the analyzers whilst still maintaining good energy resolution. With the modified lens system, electrons emitted with angles of up to +/-3\(^\circ\) out of the scattering plane are detected.

2.3. Ion Spectrometer
The ion spectrometer is shown in detail in figure 2. The spectrometer consists of a series of titanium rings which are electrically isolated from each other. The first seven rings have an outer diameter of 78 mm and an inner diameter of 50 mm with the exception of the 4\(^{th}\) ring which has a smaller inner diameter of 40 mm and is designed to block and therefore to reduce the number of background ions that reach the detector. The remaining rings have an outer diameter of 120 mm, the first few of these have an inner diameter of 80 mm and the next rings, which form a drift region, have a larger inner diameter of 100 mm.

The first ten rings are joined together with resistors which form a voltage divider chain and which are used to create a two-stage electric field. The fast pulsed extraction voltage of 212 V is applied to the first electrode. The gas capillary located midway between the 3\(^{rd}\) an 4\(^{th}\) rings has a separate pulsed voltage applied, which is set to match the potential at the interaction region when the ion extraction field is turned on. The high transmission mesh (~90% transmission) labeled M1 is held at ground potential. The rings between M2 and the ion detector are joined together and held at a constant potential of 81 V creating a drift region. Two more high transmission meshes are located immediately in front of the ion detector. These meshes are also both held at 81 V and are to shield the drift region.
from the high potential applied to the front of the ion detector. The first two rings at the end of the spectrometer are both filled with a high transmission copper mesh to allow the interaction region to be pumped more efficiently and the purpose of the double mesh is to prevent electric field penetration from outside the spectrometer so as to ensure a uniform extraction field at the interaction region.

A possible complication in performing these measurements can arise from the buildup of low-energy ions in the interaction region which will all be extracted when an (e,2e) event is identified and may result in false triple coincidence events being detected. To reduce this buildup we have introduced a cleaning and measuring cycle which is repeated every 10 microseconds. During the cleaning time a potential of 178 V is applied to the gas capillary to sweep all the positively charged ions from the interaction region and the electron beam is turned off to prevent the production of further ions. At the commencement of the measurement time the potential on the needle is reduced to 0 V and the electron beam is switched on for 2 microseconds. The electron beam current, which affects the number of ionization events, is set at a level such that the ratio of ions detected to (e,2e) events is independent of beam current and only true triple coincidence events are measured.

Also shown in figure 2 are N$^+$ ion trajectories modeled using the program SIMION. The N$^+$ ions, all with the same energy of 10 eV, are started from five different positions separated by 1 mm. Twelve ions are started at each position with different initial angles which are stepped in $30^\circ$ intervals. In the simulation the ions are allowed to drift field free for 165 ns before potentials are applied to the extraction electrodes and the ions are imaged onto the detector.

![Figure 2. Simion simulation showing a cross section through the centre of the ion spectrometer. The ion trajectories are for 10 eV N$^+$ ions. See text for details.](image)

Ions with different initial spatial positions but the same initial energy and angle of emission are focused together on the detector.

Experiments to test the spectrometer were performed with a nitrogen target at an incident electron energy of 178 eV. At this energy around 20% of ionization events lead to dissociation [14]. The
scattered projectile (fast) and ejected target (slow) electrons were detected with mean energies of $E_1=100$ eV and $E_2=40$ eV respectively and in the angular range $\theta_1 = -10^\circ$ to $-50^\circ$ degrees and $\theta_2 = 30^\circ$ to $70^\circ$. Fragment ions emitted with energies up to 10 eV and over $4\pi$ solid angle are detected.

3. Results

An N$^+$ ion time of flight spectrum for nitrogen measured using the apparatus is presented in figure 3. The velocity component of the ion’s momentum perpendicular to the extraction direction (i.e. in the scattering plane) determines the position it arrives at on the two dimensional detector, zero energy ions arriving in the centre of the detector. The ion spectrometer has been designed so that information about the ions’ velocity component parallel to the ion extraction direction is preserved, which enables the full $4\pi$ angular and momentum distribution of fragment ions to be determined. This is in contrast to the velocity map imaging technique [6], in which the mass resolution is maximized by time focusing so that ions with the same mass arrive in a narrow time interval and information about the momenta of the ions along the spectrometer axis is lost. There is a narrow peak occurring at 4.8 microseconds in the time-of-flight spectrum corresponding to N$^+$ fragment ions with essentially zero kinetic energy and also to very low energy N$_2^{2+}$ ions. N$_2^{2+}$ ions all arrive at a later time due to their higher mass to charge ratio and can therefore be easily eliminated.

Figure 4 shows the ion kinetic energy distribution of N$^+$ fragment ions reconstructed from their arrival times and positions on the detector. Only the momenta of ions with energies between 0.2 eV and 10 eV are reconstructed, as the very low energy ions may include contributions from N$_2^{2+}$ ions.

![Figure 3](image1.png) **Figure 3.** A typical ion time of flight spectrum from nitrogen. See text for details.

![Figure 4](image2.png) **Figure 4.** Ion kinetic energy distribution of N$^+$ ions emitted over all angles. See text for details.

Figure 5 shows the correlation between N$^+$ ion kinetic energy and electron binding energy. The intensity lies along lines with slope 0.5 corresponding to different dissociation channels where the N$^+$ and N fragments are formed in different internal energy states. Approximately 2200 triple coincidence events per day are obtained with a nitrogen target.

The orientation dependence of fragmentation of molecular nitrogen measured using the new spectrometer is shown in figure 6. Summed ejected (slow) electron counts measured between 30$^\circ$ and 70$^\circ$ are plotted as a function of the scattering angle of the fast electron for ions in the two bands in figure 5. Two orientations of the molecules perpendicular to the incident electron beam have been chosen by selecting triple coincidence events in which the ion fragments were emitted within 30$^\circ$
emission cones oriented either perpendicular to the scattering plane or lying within the scattering plane.

Figure 5. Ion kinetic energy as a function of electron binding energy.

Figure 6. Orientation dependence of dissociative fragmentation for molecular nitrogen resulting from an (e, 2e) ionization event. Ejected electron counts are plotted as a function of the projectile scattering angle. The curves shown are for different orientations of the nitrogen molecules. Solid circles: molecules lying within the scattering plane, but perpendicular to the incident electron beam direction. Open squares: molecules oriented perpendicular to scattering plane.
When the molecule is oriented perpendicular to the scattering plane the cross section is significantly larger than when the molecule lies within the scattering plane. There are currently no calculations available for comparison with our measurements. The calculations of Gao et al [9] for nitrogen are for transitions to the ground state of \( \text{N}_2^* \), which does not dissociate.

The present data has only undergone preliminary analysis. Further analysis of the data, including investigating the dissociative fragmentation of different excited states and additional molecular orientations, will appear in a future publication.

4. Conclusion
Here we have described progress in the development of a new (e,2e+ion) spectrometer for use in studies of the electron-impact-induced dissociative ionization of molecules. We have shown that the apparatus can be used to provide the angular dependencies of molecular fragmentation processes and

![Figure 7](image_url)

**Figure 7.** Experimental [16] and calculated (SCF) spherically averaged orbital momentum densities (left hand panels) and momentum and position densities for molecular nitrogen.
thus enables (e,2e) measurements to be performed within the molecular frame. The technique promises to provide a greater understanding of electron-impact-induced molecular fragmentation processes.

The work reported here also opens up the possibility of measuring the momentum distributions of molecular orbitals in the molecular frame using electron momentum spectroscopy (EMS) [15]. In the past EMS has been limited to measuring spherically averaged orbital momentum distributions. Figure 7 shows EMS data [16] for the valence orbitals of nitrogen compared with calculated spherically averaged orbital momentum densities as well as contour maps of corresponding position and momentum densities. This indicates the extra information that can be obtained for measurements in the molecular frame.

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