Electron momentum spectroscopy in the study of intermolecular interactions

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Abstract. This paper describes progress towards developing a new electron momentum spectrometer specifically designed for the purpose of studying weak, non-covalent intermolecular interactions. Electron momentum spectroscopy will be employed to measure the electronic wavefunction, with particular attention being paid to the electrons involved in the intermolecular interactions present within the target. This work requires a triple coincidence experiment; namely the detection of an (e,2e+ion) event. Results of characterisation experiments conducted with noble gases are given in order to demonstrate the performance of this new apparatus.

1. Introduction
Non-covalent intermolecular interactions, also known as van der Waals forces, are integral to the behaviour and properties of the condensed phases. As such, knowledge about these forces is essential to our understanding of the many phenomena that they control. Fundamental physical properties such as condensation, boiling point, viscosity and surface tension result from the intermolecular interactions acting between the molecules of the liquid. Non-covalent forces also dictate the complicated folding patterns of biological polymers to give them their active shape, such as proteins and enzymes. Finally, and perhaps of most interest to us, these intermolecular interactions also govern the dynamics of chemical reactions occurring in solutions. In many cases the behaviour of the reactants is dependant on the solvent, which can modify the pathway and outcome of reactions in solutions. In order to develop accurate models of these phenomena precise computation of the intermolecular interactions between the reactant and solvent molecules is required. The ultimate evaluation of the accuracy of such calculations is by direct comparison with experimental data.

The study of intermolecular interactions in the gas phase offers the opportunity to use the precision of gas phase experimental techniques to probe these ubiquitous forces. van der Waals clusters are comprised of two or more atoms or molecules held together by the weak non-covalent forces that are present in the condensed phase. These clusters are produced in a supersonic free jet expansion. As such, van der Waals molecules provide the means to investigate intermolecular interactions in the gas phase. Optical spectroscopy has employed van der Waals clusters for this purpose, but results from such experiments are predominantly concerned with the motion of the nuclei. However, it is the behaviour of the electrons forming the intermolecular interactions that give these non-covalent forces their properties and therefore the electronic structure of the target is of particular interest.
Electron momentum spectroscopy (EMS) measures the modulus squared of the wavefunction for the electrons within a target. This technique is particularly sensitive to electrons with low momentum, corresponding to those far from the nuclei. As the presence of intermolecular interactions increases the electron density between the molecules, i.e. in the region far from the nuclei, EMS represents an ideal technique to be applied to a detailed study of such electronic behaviour.

2. Experimental Design
Electron momentum spectroscopy uses kinematically complete electron impact ionisations to probe the target [1]. A collimated beam of incident electrons with a known energy is used to collide with, and knock out, an electron from within the target. Both of the out-going electrons, the scattered incident electron and the ejected target electron, are detected in coincidence with known energies and at known angles. This ionising collision can be represented by the following equation:

$$e_0^+(k_0, E_0) + T_n^0 \rightarrow T_i^{\text{scatt.}} + e_{\text{scatt.}}^-(k_{\text{scatt.}}, E_{\text{scatt.}}^0) + e_{\text{ject.}}^+(k_{\text{ject.}}, E_{\text{ject.}}^0)$$

where $E$ and $k$ are the energies and momenta of the incident (0), scattered (scatt.) and ejected (ject.) electrons. $T_n^0$ represents an $n$ electron target, which after ionisation is left in the electronic state, $i$, denoted by $T_i^{\text{scatt.}}$. The conservation of energy and momentum laws can hence be used to calculate the binding energy ($\varepsilon$) and momentum (q) of the target electron [1].

Employing a supersonic expansion to generate the van der Waals clusters results in a target beam composed of many species of which the carrier gas and target monomer molecule are dominant. Data collected from this target beam will therefore also have contributions from all of the species present in the beam. The desired signal from higher order clusters, dimers, trimers, etc., can be extracted from the measured data if the scattering target is also known. Identification of the scattering target can be made from the analysis of the resultant ions created in the interaction region using mass spectrometry. The apparatus has been designed with a time of flight mass spectrometer (ToFMS) because such devices have, in principle, 100% collection and transmission efficiency. Therefore, in order to obtain data regarding intermolecular interactions both of the out-going electrons and the resultant ions need to be collected, rendering this as an (e,2e+ion) experiment. Two such triple coincidence apparatus are operational [2,3] highlighting the success of such triple coincidence experiments. The objective of these previous two experiments is to obtain ‘molecular frame’ (e,2e) data, which is quite different to the aim of our apparatus.

3. Experimental Characterisations
A preliminary description of the apparatus has been given elsewhere [4] and only details in addition to those are discussed within this paper. Typical EMS results obtained with the apparatus configured in a coplanar geometry ($E_0 = \sim 830\text{eV}$, $E_{\text{scattered}} = 720\text{eV}$, $E_{\text{ejected}} = 95\text{eV}$ and $\theta_{\text{scattered}}=20.5^\circ$) utilizing the usual cylindrical optics and an effusive target source from a single capillary are shown in figures 1-3. Figure 1 gives a typical timing spectrum from helium. The coincidence peak has a FWHM of 8ns, and a coincidence count rate of $\sim 4$ counts per minute was achieved. The binding energy spectrum in figure 2, also of the 1s$^{-1}$ transition of helium, illustrates that a coincidence energy resolution of 0.9eV (FWHM) is typical. With the 40mm active area position sensitive detectors employed within this apparatus, a binding energy range of 15eV can be sampled simultaneously. This is advantageous when working with molecules which possess many orbitals spread over a range of binding energies.

Momentum distributions for the Ar 3p and He 1s states, again using the cylindrical optics, are shown in figure 3. The momentum resolution of the apparatus in this configuration is estimated to be $\sim 0.3\text{a.u.}$ (FWHM) from the Ar 3p data. An improvement in this resolution can be achieved by employing a more collimated target source, such as that from a capillary array. However the current result is satisfactory for the characterisation purposes until the supersonic expansion source is implemented. The agreement between this argon experimental data and a distorted wave impulse approximation (DWIA) is clearly good. A convergent close coupling (CCC) calculation [5] of the...
momentum distributions for helium is also shown in figure 3. The theoretical data are well correlated with the experimental data only when a sufficient number of partial waves (l) are used to describe the ejected electron. Note that as the experimental data are relative, a one point normalization to the theory has been made in each case.

The characterisation results described above established the successful implementation of the (e,2e) component of this apparatus.

Figure 1: A typical timing spectrum from helium obtained for the coplanar geometry. See text for kinematical details.

Figure 2: The binding energy spectrum for the 1s\(^1\) transition of helium showing an energy resolution of 0.9eV FWHM.

The characterisation results described above established the successful implementation of the (e,2e) component of this apparatus.

Figure 3: Momentum distributions for the Ar 3p (left) and He 1s (right) orbitals. The theoretical curves in both plots have been convoluted with a momentum resolution of ~ 0.3a.u.. In both cases the agreement with the theoretical calculations shown is excellent. See text for further details.
4. Experimental Developments

The above results demonstrate that this apparatus has been successfully applied to gain EMS results from atomic targets. The triple coincidence experiment is expected to have a much lower coincidence count rate given the pulsed nature of the free jet supersonic expansion and the relatively small percentage of the desired clusters within the target source beam. Strategies to partially offset this significant decrease in count rate, and corresponding increase in data collection times, were therefore implemented. Utilising parallel detection capabilities within an apparatus has previously resulted in increases in coincidence count rates by two [6] or three [7] orders of magnitude. Note that the parallel detection of a range of electron energies was already employed within this apparatus [4] with the cylindrical optics. The position sensitive detectors within this apparatus have 2-D capabilities and therefore the simultaneous detection of a range of momentum is also possible when non-coplanar electrons are also detected. Hence, a second generation set of deceleration electron optics for the outgoing electrons was developed and installed such that the azimuthal angular scattering information is preserved. The design of these optics were based on the slit optics employed within the existing solid state EMS spectrometers [8,9]. They each consist of six elements. Each lens is 80mm high and curved in such a way that the differences in flight paths from the interaction region to the lens are minimized for electrons of different azimuthal angles. Ideally, this would result in spherical lens elements with the centre of the sphere located at the interaction region. For ease of construction, however, this curve was only followed in the vertical, azimuthal, direction. The maximum vertical angular range sampled by the slit optics is $\phi = \pm 7^\circ$, given the geometric limitation on the lens element height within the apparatus. Figure 4 shows a vertical section through these new optics with the simulated electron trajectory through them as modeled in SIMION [10].

The experimental characterisation of these optics is shown in figure 5, in which elastically scattered electrons were detected. For the data in this figure a mask was placed at the entrance of the optics, consisting of evenly spaced, 0.1mm diameter, holes along the height of the entrance aperture. Figure 5 demonstrates that electrons scattering from the interaction region with various azimuthal angles can be detected and distinguished. Elastic scattering experiments such as these are used to accurately map the arrival position of an electron to the conditions with which it left the interaction region, i.e. the energy and azimuthal angle.
Typical timing and binding energy spectra measured with these slit optics are given in figures 6 and 7. Comparison of figure 6 with figure 1 shows the improvement in the signal to background ratio obtained with these new optics. Furthermore, an increase in the coincidence count rate of ~1000 times is also observed. The binding energy spectrum displayed in figure 7 indicates that the coincidence energy resolution for this experimental configuration is 1.2eV (FWHM), slightly higher than that for the cylindrical lenses. This increase in the energy resolution can, however, be offset by lowering the mean analysing potential of the hemispherical deflectors. Indeed, measurement of the LMM Auger lines of argon indicate that an energy resolution of 0.2-0.3eV is readily achievable with the analysers within this apparatus, as shown in figure 8.

Figure 5: Image of the electron impact positions on the position sensitive detector for elastically scattered electrons through the calibration mask. The horizontal and vertical separations of each position of intensity corresponds to 2eV and 2° respectively. These data are for the ejected electron analyser.

Figure 6: A typical timing spectrum from helium obtained for the non-coplanar geometry. The coincidence count rate in this configuration is typically 100 counts/minute utilising an incident beam current 30 times smaller than that used for the cylindrical optics.

Figure 7: The binding energy spectrum for the $3p^{-1}$ transition within argon. The FWHM is slightly higher (1.2eV FWHM) using these optics than for the cylindrical optics. Wings on each side of the binding energy peak are also evident.

In order to maximise the energy resolution obtainable with this apparatus, and thus further separate the many, closely spaced orbitals within molecules, a combination of lowering the mean analysing
potential of the analysers and decreasing the energy spread within the incident electron beam is required. The energy spread in the incident electron beam is predominantly due to the thermal spread from the tungsten filament. Therefore, replacing this electron source with a low temperature electron emitter, such as a barium oxide cathode, is currently being implemented. Coincidence energy resolutions of ~ 0.4eV (FWHM) are anticipated to be achieved with this configuration.

The momentum distribution for the argon 3p state collected with the new slit lenses is shown in figure 9. The data within this figure were collected when the out-going electrons were restricted to a coplanar configuration by small apertures placed at the entrance to the optics. Again, the agreement between the experimental and theoretical data is quite good, indicating the successful operation of the apparatus. However, data simultaneously collected using the full azimuthal range of the slit lenses still exhibits an unsatisfactory correlation to the theoretical curve. The non-coplanar data simultaneously collected with the slit deceleration optics cannot simply be plotted as a function of the ejected electron analyser angle; it requires a transform to elucidate the target electron momentum. A successful method of manipulating the measured data to obtain the momentum distribution for this configuration requires further development.

Figure 8: Experimental measurement of the argon LMM Auger lines with the mean analysing potential of the hemispherical deflector reduced to 20eV. Gaussian fits to the Auger transitions all have the same width of 0.3eV.

Figure 9: Measured and calculated momentum distributions for the Ar 3p\(^{-1}\) transition. The theoretical curve has been convoluted with a momentum resolution of ~ 0.2a.u. which is slightly better than that obtained with the cylindrical optics. Quite good agreement is seen with the DWIA calculation result.
5. Conclusions and Future Work

This paper has described the current operational stage of a new electron momentum spectrometer being constructed specifically to probe the electrons involved in intermolecular interactions. The (e,2e) spectrometer has been shown to be functional and the components relating to the cluster source and ion detection are soon to be integrated into the experiment.

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