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Low energy (e, 2e) differential cross-section measurements on the $3\sigma_g$ and $1\pi_u$ molecular orbitals of N_2

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Abstract
Experimental results are reported for the (e, 2e) differential ionization cross-section from the $3\sigma_g$ and $1\pi_u$ valence molecular orbitals of molecular nitrogen N_2 at incident electron energies between 25.6 and 76.7 eV. The measurements have been conducted in a coplanar symmetric geometry in an energy regime where ionization is sensitive to contributions from shape resonances and autoionizing doubly excited states. The results suggest that these additional channels may contribute to the measured cross-section. The measurements also display trends qualitatively similar to previous results at higher incident electron energies using the same geometry.

1. Introduction

Understanding electron impact ionization of atoms and molecules remains one of the most interesting and challenging problems facing atomic and molecular physics in recent years. The greatest detail is yielded when angular correlations are measured between 'scattered' and 'ejected' electrons following ionization by an incident electron. One such technique is the electron–electron coincidence experiment, commonly referred to as an (e, 2e) experiment. In principle, selection of different momenta for the outgoing electrons allows a complete description of the ionization process to be obtained, particularly when studied at incident electron energies from a few eV to approximately 100 eV above the ionization potential. In this range ionization mechanisms are highly sensitive to processes such as post-collision interactions, polarization of the target, interference effects between the two outgoing channels and multiple collisions (see, for example, Murray and Read (1992, 1993a, 1993b), Roder *et al* (1996), Whelan *et al* (1993)).

The (e, 2e) process may be represented by the reaction

$$e_0(E_0, \boldsymbol{k}_0) + \mathrm{A} \rightarrow \mathrm{A}^+ + e_a(E_a, \boldsymbol{k}_a) + e_b(E_b, \boldsymbol{k}_b),$$

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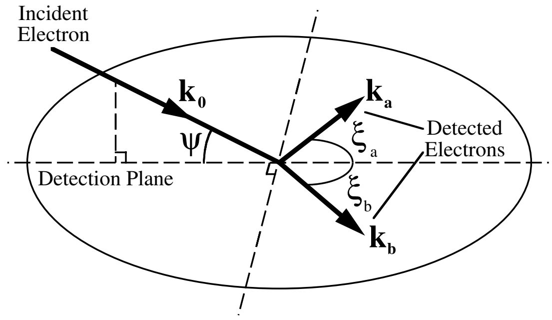

Figure 1. The kinematic geometry used in (e, 2e) coincidence experiments at Manchester. The electron gun angle ψ is the angle between the incident electron momentum and the detection plane. The scattered and ejected electrons are detected at angles ξ_a and ξ_b with respect to the projection of the incident electron momentum onto the detection plane.

where e_0 represents the incident electron with energy E_0 and momentum $\boldsymbol{k}_0$, A and A^+ correspond to the target atom or molecule before and after ionization respectively and e_a and e_b denote the scattered and ejected electrons with energies E_a and E_b, and momenta $\boldsymbol{k}_a$ and $\boldsymbol{k}_b$ respectively. Quantum mechanically the two outgoing electrons are indistinguishable, therefore the terms 'scattered' and 'ejected' are equivalent. In the experiments reported here, the spin of the particles is not measured and therefore the only constraints to the kinematics of the reaction are energy and momentum conservation. This permits the outgoing electrons to have a range of different directions and a range of different energies. Thus, to fully describe the ionization process for a given incident energy, E_0, a differential cross-section (DCS) is required,

$$\mathrm{DCS} = \frac{\mathrm{d}^3\sigma}{\mathrm{d}E_a\,\mathrm{d}\Omega_a\,\mathrm{d}\Omega_b},$$

where $\mathrm{d}\Omega_a$ and $\mathrm{d}\Omega_b$ correspond to solid angles defined by the direction of the outgoing electrons and E_a represents the energy of one of the outgoing electrons. It is only necessary for one energy to be defined since the energies of the two outgoing electrons are related by energy conservation.

Experimentally, to measure the cross-section it is necessary to restrict the number of independent variables by holding one or more parameters constant and allowing the remaining parameters to vary. This results in a number of different kinematic regimes under which the experiment can be conducted. Figure 1 shows the geometry of the reaction, where ξ_a and ξ_b represent the angles of the outgoing electrons e_a and e_b with respect to the projection of the incident electron onto the detection plane (defined as the plane containing the two electron detectors). The angle of the incident electron beam to the detection plane is ψ. Measurements are usually conducted in one of three geometries, defined as coplanar symmetric, coplanar asymmetric and non-coplanar symmetric.

Using the (e, 2e) technique it is possible to study either the electronic structure of the target or the dynamics of the ionization process. The former is known as electron momentum spectroscopy (EMS) and yields information such as the binding energy and electron momentum distributions of the ionized orbitals. EMS experiments are mostly performed at electron impact energies of approximately 1–2 keV using a symmetric geometry in both outgoing electron energy and angle (Weigold and McCarthy 1978, Coplan *et al* 1994, Brion *et al* 2001). Experiments performed using an asymmetric geometry in both energy and detection angle over a range of incident electron energies are conventionally used to study the ionization process

(Ehrhardt *et al* 1986). A large body of data exists for both EMS and ionization dynamic studies of atomic targets (see for example Lahmam-Bennani (1991), McCarthy and Weigold (1991), Coplan *et al* (1994)), whereas the majority of existing studies on molecules adopt the EMS technique (see for example Brion *et al* (2001) and references within).

Studies of the ionization dynamics of molecular targets are less common, and include those by Jung *et al* (1975) and Chérid *et al* (1989) for H_2; Jung *et al* (1975), Avaldi *et al* (1992), Doering and Yang (1996), Rioual *et al* (1996) for N_2; Rioual *et al* (1996) for CO; Doering and Yang (2001) for O_2; Cavanagh and Lohmann (1999) for N_2O and Avaldi and Camilloni (1990) for C_2H_2. As far as we are aware, Rioual *et al* (1996) present the only results collected using a coplanar symmetric geometry for ionization of the two outer valence orbitals of N_2. The remaining studies are all conducted under coplanar asymmetric kinematics. A comparison of results between the two geometries is difficult as it is common for experiments conducted with asymmetric kinematics to refer to the momentum transfer vector, $\boldsymbol{K} = \boldsymbol{k}_0 - \boldsymbol{k}_a$, which has a constant direction when the scattered electron energy E_a and angle ξ_a are fixed. By contrast, in coplanar symmetric kinematics the angles of both scattered and ejected electrons are varied, resulting in $\boldsymbol{K}$ also varying. The results presented here are collected using a coplanar symmetric geometry and therefore can be principally compared with the results of Rioual *et al* (1996). However, to place previous studies in context, the results of experiments conducted using asymmetric kinematics are also briefly discussed.

Jung *et al* (1975) and Chérid *et al* (1989) measured the DCS for ionization of the valence orbital of H_2 in coplanar asymmetric geometry. Jung *et al* (1975) used incident electron energies of 250 and 100 eV with scattered electron angles ξ_a ranging between 4° and 25°. The ejected electron energies were 4.5 and 9 eV. Chérid *et al* (1989) used incident electron energies of 4087 and 4168 eV, with scattered electron angles ξ_a between 1° and 9.6° and ejected electron energies E_b of 20 and 100 eV respectively. The cross-sections for both experiments were characterized by a binary peak centred around the momentum transfer direction $\boldsymbol{K}$, and a recoil peak aligned approximately along the $-\boldsymbol{K}$ direction. The lower incident energy results of Jung *et al* (1975) also displayed an angular shift of the binary peak towards larger angles with respect to the $\boldsymbol{K}$ direction.

Previous experiments conducted on N_2 all used a coplanar asymmetric geometry (Jung *et al* 1975, Avaldi *et al* 1992, Doering and Yang 1996) with the exception of Rioual *et al* (1996) who adopted a coplanar symmetric geometry. Jung *et al* (1975), Avaldi *et al* (1992) and Doering and Yang (1996) all used incident electron energies between 100 and 300 eV with momentum transfer $\boldsymbol{K} \sim 0.36$ au. The relative results of Doering and Yang (1996) on the $3\sigma_g$ orbital of N_2 show good agreement with the absolute measurements of Avaldi *et al* (1992) in both shape and magnitude. Both display an angular shift of the recoil peak to smaller angles and a shift of the binary peak to larger angles, with respect to the momentum transfer vector $\boldsymbol{K}$. Doering and Yang (1996) also measured the angular distribution of ejected electrons from the $1\pi_u$ valence molecular orbital of N_2 under the same kinematic conditions as for the $3\sigma_g$ orbital. These results show a shift in the maximum of the binary lobe to larger angles compared to that of ionization from the $3\sigma_g$ orbital. The maxima of the recoil lobes are at approximately the same angle for both valence states, again shifted to smaller angles compared to the momentum transfer vector $-\boldsymbol{K}$. Similar structures are seen in the results of Avaldi *et al* (1992) from the carbon σ1s orbital of C_2H_2 at incident electron energies $E_0 \sim 1500$ eV and for the measurements of Doering and Yang (2001) on the three outer valence states of O_2 at an incident energy of 100 eV. In each experiment a shift in the maximum of the binary lobe to larger angles is observed.

In the case of the $1\pi_g$ outer valence state of O_2 this shift is particularly pronounced with the maximum of the binary lobe at 90° compared to the momentum transfer vector $\boldsymbol{K}$ at 34°.

Doering and Yang (2001) attribute this to an effect of the long range force between one of the unpaired electrons in the $1\pi_g$ orbital and the incident electron. The results for the $1\pi_u$ and $3\sigma_g$ orbitals of O_2 also show a shift of the binary lobe; however, the maximum of the recoil lobe appears to be aligned with the momentum transfer vector $-\boldsymbol{K}$ in contrast to the results for N_2. Doering and Yang (2001) note that the second and third valence orbitals of O_2 are the same as the outer two orbitals of N_2, but are reversed in energy. Furthermore, these authors propose that the similarity of the measurements for the analogous orbitals of both molecules suggests that the symmetry of the orbital is more important in determining the cross-section than the order of the orbitals in terms of binding energy.

A shift in the recoil lobe has also been observed in the measurements of Cavanagh and Lohmann (1999) on the valence state of N_2O at an incident energy $E_0 \sim 900$ eV (coplanar asymmetric geometry). However, in this study the binary lobe is symmetrical about the momentum transfer direction $\boldsymbol{K}$. Cavanagh and Lohmann also draw a comparison between molecular valence ionization and atomic inner shell ionization, in that a shift in the recoil lobe to smaller angles is seen in both cases.

The disparity between ionization studies on atomic targets and those of molecules is more evident from a theoretical aspect. At intermediate to high incident energies (400 eV to ~7 keV) the reaction mechanisms for closed shell atomic systems are reasonably well understood (see for example Ehrhardt *et al* (1986), Lahmam-Bennani *et al* (1988)), whereas there are still discrepancies between theory and experiment for ionization of molecules, particularly at lower incident electron energies. Chérid *et al* (1989) compare coplanar asymmetric experimental results for ionization of H_2 at incident electron energies $E_0 \sim 4$ keV with several theoretical models. Good agreement was found between the first Born Coulomb wave approximation and the experimental results. Agreement was also found between the plane wave impulse approximation (PWIA) and experimental results for ionization corresponding to an ejected electron initially at rest. At lower incident electron energies (Jung *et al* 1975), first Born type calculations fail to reproduce the angular shifts in the binary and recoil lobes for asymmetric kinematics. Weck *et al* (1999) have calculated fivefold DCSs for ionization of H_2, D_2 and T_2 from the molecular ground state to different vibrational levels of the ground state of the ion. The kinematic geometry of Chérid *et al* (1989) was used in this study; however, no comparison was drawn between theory and experiment.

Rioual *et al* (1996) investigated the validity of the PWIA for ionization of the valence states of N_2 at incident electron energies $E_0 = 400$ eV in a coplanar symmetric geometry in the vicinity of the binary peak. The agreement between experiment and calculation was poor for scattered and ejected electron angles smaller than the binary peak, both in magnitude and position. At angles above the binary peak this agreement was better. Rioual *et al* attribute this to recoil processes from the multi-centred molecular system together with post-collision interactions between electrons and the residual ion. At low incident electron energies ($E_0 <$ 400 eV) and for coplanar symmetric kinematics where experiments focus on the ionization dynamics rather than EMS, there exist no accurate models to describe the ionization process.

As discussed earlier, the majority of experimental (e, 2e) investigations on the ionization dynamics of molecules have been conducted at energies above 400 eV using a coplanar asymmetric geometry. By contrast, in this paper (e, 2e) DCS measurements are presented for ionization from $3\sigma_g$ and $1\pi_u$ valence molecular orbitals of N_2 at incident electron energies between 25.6 and 76.7 eV. The motivation for these experiments was partly to fill the gap in the study of low energy ionization dynamics on molecules and thus encourage more rigorous theories to be developed, and partly as a precursor to the study of dissociative ionization of molecules, where DCS measurements on the outgoing electrons are collected for each fragment ion channel. The latter technique is currently in the final stages of development and implementation.

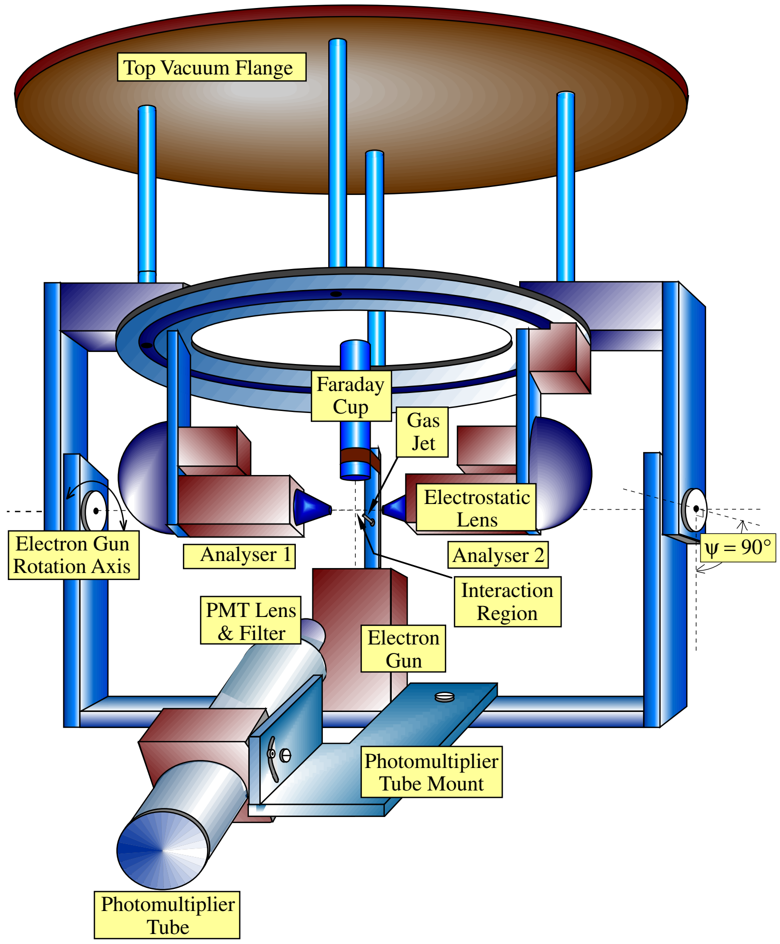

Figure 2. The Manchester (e, 2e) spectrometer setup in the perpendicular plane ($\psi = 90°$). For details, see text.

(This figure is in colour only in the electronic version)

2. Experiment

A complete description of the fully computer controlled (e, 2e) coincidence spectrometer used for the experiments reported in this paper is given in Murray *et al* (1992). Figure 2 is a schematic of the apparatus showing the spectrometer configured in the perpendicular plane geometry. The spectrometer is mounted beneath a 25 mm thick 310 grade stainless steel top flange supported by a 1500 mm high vacuum chamber. A vacuum pressure of approximately 1.0×10^{-7} Torr is achieved by a Balzers TPU-510 500 ls^{-1} turbomolecular pump attached to the underside of the chamber. The spectrometer is shielded from magnetic fields by 3 mm thick μ-metal cylinders both internal and external to the vacuum chamber.

The electron gun, photomultiplier tube and effusive target beam source are mounted on an arm so as to rotate from the perpendicular plane to the coplanar geometry. The electron gun consists of a tungsten filament, two triple-element electrostatic aperture lenses and three sets of x–y electrostatic deflectors allowing the electron beam to be focused onto the 1 mm diameter interaction region. The incident electron energy can be varied from 20 to 300 eV with an energy resolution of around 600 meV. The target beam effuses from a 20 mm long, 0.5 mm internal diameter hypodermic needle and intersects the electron beam at 45°. The interaction region is focused onto an EMI 9789QB photomultiplier tube through a 35 mm f 1.2 glass lens, 2 mm aperture and a 450 nm filter, so as to allow the electron beam to be focused onto the interaction region independent of the electron analysers.

Scattered and ejected electrons are detected by two electrostatic hemispherical analysers that rotate in the horizontal plane via internal gears. Each analyser consists of a three-element electrostatic cylinder lens, a pair of x–y deflectors, a hemispherical deflector analyser with 25.4 mm mean radius and a Photonis X919BL channeltron. The energy resolution of the analysers, operated at a pass energy of 15 eV, is approximately 500 meV, and the angular acceptance angle is around ±2°. Further details can be found in Murray *et al* (1992).

The results for ionization from the $3\sigma_g$ and $1\pi_u$ orbitals of N_2 presented in this paper were collected in a coplanar symmetric geometry, where the scattered and ejected electrons have equal angles and equal energies. The angular range of the spectrometer in this geometry ($\psi = 0°$) is limited to between $\xi = 35°$ and 125° due to physical restrictions from the Faraday cup and the electron gun. A vacuum of approximately 1.0×10^{-5} Torr was used during these measurements. Incident electron currents between 50 and 200 nA were adopted with data collection times between 1000 and 3000 s per angle depending on the coincidence cross-section. Drift in the spectrometer is eliminated by the use of the computer control and optimization technique. The results for any given energy are averaged over a number of angular sweeps of the detection plane, the associated error for each data point being the standard deviation of this average. True coincidence count rates ranged between 0.5 and 2 Hz, hence the collection time for a particular valence orbital and incident energy ranged between 1 and 2 weeks. The incident energy was determined by measuring the signal from helium as a calibration standard.

3. Results and discussion

As discussed in section 1, no accurate model exists to describe electron impact ionization of molecules at incident electron energies below 100 eV, particularly in a coplanar symmetric geometry. The following discussion is therefore limited to a qualitative comparison with previous low energy coplanar symmetric studies of N_2 and for atomic targets.

The ground state electronic configuration of N_2 is given by

$$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^4(3\sigma_g)^2\ {}^1\Sigma_g^+$$

with the ionization potentials of the $3\sigma_g$ and $1\pi_u$ orbitals at 15.6 and 16.7 eV respectively. Removal of an electron from the $3\sigma_g$ orbital results in the X $^2\Sigma_g^+$ state of the ion whereas ionization from the $1\pi_u$ orbital produces the A $^2\Pi_u$ ionic state.

Figure 3 shows the results obtained from the $3\sigma_g$ molecular orbital of nitrogen at incident electron energies of 25.6, 35.6, 55.6 and 75.6 eV. This corresponds to scattered and ejected electron energies of 5, 10, 20 and 30 eV respectively. The detection angles $\xi = \xi_a = \xi_b$ were restricted to the range from 35° to 125°. All measurements have been normalized to unity at the angle $\xi = 45°$, to allow comparison for each incident electron energy.

With reference to figure 3, two peaks are seen in the DCS at each electron energy. The first, between 40° and 60°, can be explained by a binary collision between the scattered incident electron and the ejected electron. This is the dominant process at all electron energies. The second peak in the backward direction at $\xi \approx 125°$ may be explained by a recoil process, sometimes referred to as ante-collision backscattering (Rioual *et al* 1996). A simple model of

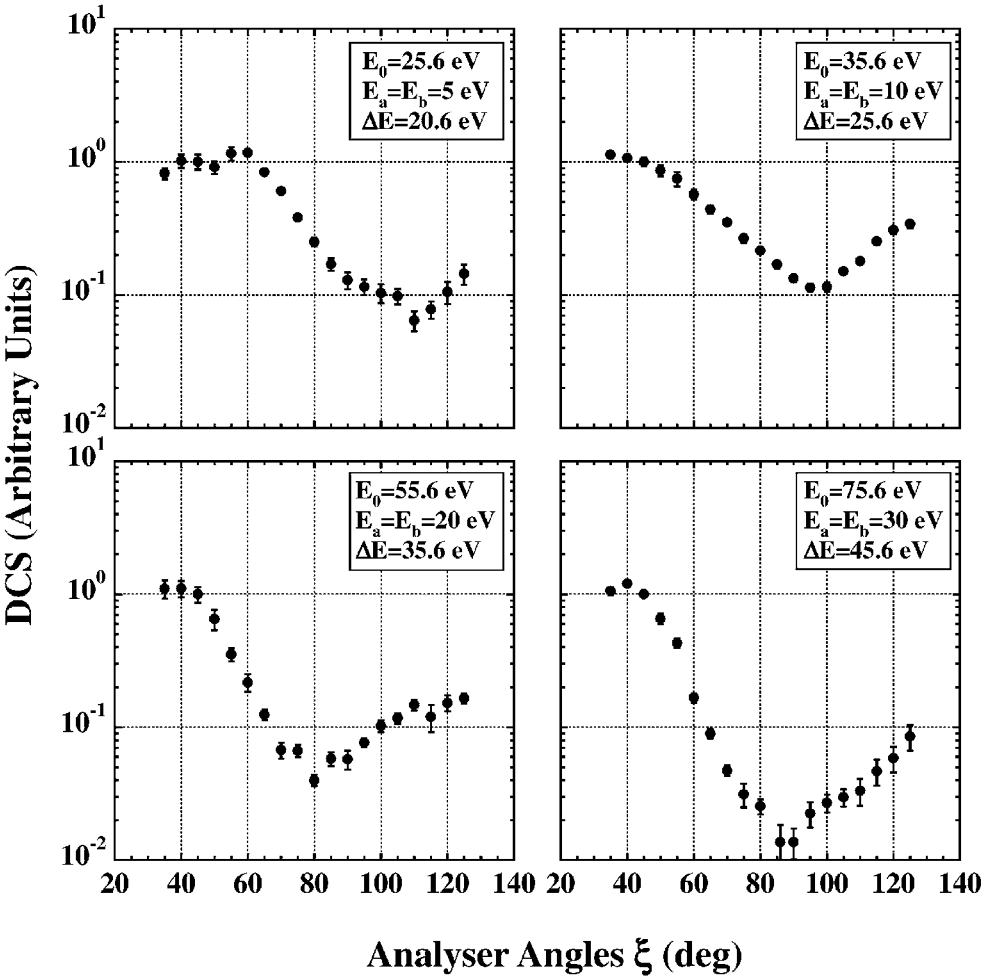

Figure 3. DCS measurements for ionization from the $3\sigma_g$ molecular orbital of N_2 at incident electron energies $E_0 = 25.6$, 35.6, 55.6 and 75.6 eV. The results were collected in a coplanar symmetric geometry where the outgoing electrons were detected at equal angles $\xi_a = \xi_b$ and equal energies $E_a = E_b$, corresponding to 5, 10, 20 and 30 eV respectively. All results are normalized to unity at $\xi = 45°$.

this process is that the incident electron scatters from one of the nuclei, followed by a binary collision with the bound electron. When the electron energy decreases the backscattering process becomes more dominant, while the minimum observed at $\xi \approx 100°$ reduces in depth with respect to the binary peak. The binary peak is also seen to move towards lower angles together with a flattening of the peak with decreasing energy, as seen for incident electron energies of 75.6, 55.6 and 35.6 eV (this trend does not apply at $E_0 = 25.6$ eV). These features are similar to those seen by Rioual *et al* (1996) who measured ionization from the $3\sigma_g$ molecular orbital of N_2 at incident electron energies of 100, 200 and 400 eV in a coplanar symmetric geometry. However, the shift in the minima towards lower angles with decreasing energy as seen by Rioual *et al* (1996) is not observed at these lower energies. It is also noted that the DCS for ionization from the $3\sigma_g$ molecular orbital displays a similar trend to that for ionization from a helium 1s atomic orbital (see for example Murray and Read (2000)).

Electron impact ionization of molecules is further complicated by the possibility of shape resonances and autoionizing doubly excited states that compete with the direct ionization process. Photo-ionization studies of the $3\sigma_g$ orbital of N_2 resulting in the X $^2\Sigma_g^+$ state of the ion have shown that the presence of a σ_u shape resonance at approximately 13 eV above the ionization threshold significantly alters the expected branching ratios of the final vibrational levels. Dehmer *et al* (1979) showed that this resonance exhibits substantial changes in position and width as a function of inter-nuclear separation, which results in significant deviation of the vibrational branching ratios compared to that expected from the Frank–Condon principle. West *et al* (1980) found that the deviation of the $(\upsilon = 1)/(\upsilon = 0)$ branching ratio for the $3\sigma_g$ photoionization channel is greatest at approximately 35 eV photon energy, equivalent to 19.4 eV in photoelectron energy. Iga *et al* (1989) also found that the photoelectron angular distributions are strongly perturbed in the energy region dominated by this resonance. In terms of (e, 2e) experiments, Avaldi *et al* (1992) investigated the effect of the σ_u resonance on the cross-section in coplanar asymmetric kinematics at an incident electron energy $E_0 \sim 300$ eV. Data were collected at two values of electron energy loss, $\Delta E = 34$ and 25.6 eV (where $\Delta E = E_0 - E_a$), corresponding to an energy where the effects of the resonance are observed to be greatest and at an energy where these effects are negligible. At $\Delta E = 34$ eV these authors tentatively attribute a shift in the recoil lobe and the symmetry and shape of the binary lobe as effects due to this resonance. Fortuitously, the results presented here for ionization of the $3\sigma_g$ orbital also span the energy range of the σ_u resonance. From figure 3 it is difficult to see any significant effect of this resonance. At an energy loss $\Delta E = 35.6$ eV, where the influence of the resonance is expected to be greatest, a shift in the minimum to smaller angles and a slight broadening of the recoil peak is observed, compared to the other results. These results do not provide definitive evidence that the resonance perturbs the cross-section. However, as noted by Avaldi *et al* (1992), if the photoelectron angular distribution is affected in this energy region it is likely that the (e, 2e) cross-section will also be affected.

Sannes and Veseth (1997) have also predicted the existence of doubly excited states that can autoionize to the X $^2\Sigma_g^+$ state of $N_2{}^+$. In particular they predict a doubly excited state of $^1\Sigma_u^+$ symmetry at a photon energy of 21.62 eV produced by a mixture of doubly excited configurations $(2\sigma_u)^1(3\sigma_g)^1(1\pi_g)^2$ and $(3\sigma_g)^{-2}(1\pi_g)^1(2\pi_u)^1$. It is possible that these autoionizing states may also contribute to the anomalous shape of the cross-section for the incident energy of 25.6 eV.

In figure 4, DCS measurements are shown for ionization from the $1\pi_u$ molecular orbital of N_2 for incident electron energies of 26.7, 36.7, 56.7 and 76.7 eV. This again corresponds to outgoing electron energies of 5, 10, 20 and 30 eV respectively. As with ionization from the $3\sigma_g$ orbital, a binary peak occurs at $\xi \approx 40°$, with a minimum at $\xi \approx 80°$ and a recoil peak beyond $\xi = 125°$. At an incident electron energy of 76.7 eV the ionization process is dominated by the binary peak at $\xi = 40°$. As the detection angle ξ increases, the DCS rapidly decreases to a minimum at $\xi = 90°$, after which the recoil process becomes significant towards $\xi > 125°$. With decreasing electron energy the cross-section follows a similar pattern to that for the $3\sigma_g$ orbital; however, the change between 76.7 and 65.7 eV is more rapid. Further, the minimum in the cross-section becomes less pronounced while the binary peak flattens off and the recoil peak increases in magnitude. Since the maximum of the recoil peak lies outside the measurable range of the spectrometer ($\xi > 125°$), it is not possible to quantify which peak is larger.

In comparison to the measurements for the $3\sigma_g$ orbital, the recoil peak for the $1\pi_u$ orbital also becomes larger as the energy is decreased. Again this is qualitatively similar to the results of Rioual *et al* (1996) who investigated ionization from the $1\pi_u$ state at incident electron energies of 100, 200 and 400 eV using a coplanar symmetric geometry. Rioual *et al* (1996)

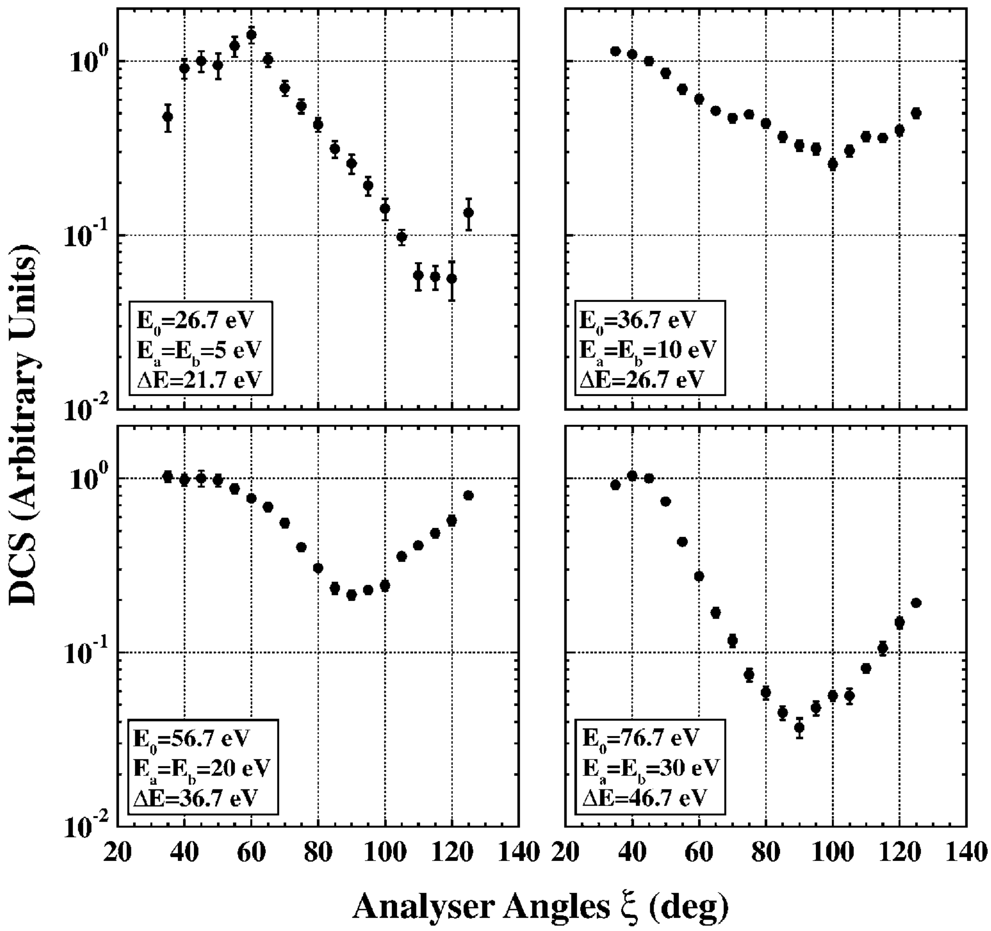

Figure 4. DCS measurements for ionization from the $1\pi_u$ molecular orbital of N_2 at incident electron energies $E_0 = 26.7$, 36.7, 56.7 and 76.7 eV. The results were collected in a coplanar symmetric geometry where the outgoing electrons were detected at equal angles $\xi_a = \xi_b$ and equal energies $E_a = E_b$, corresponding to 5, 10, 20 and 30 eV respectively. All results are normalized to unity at $\xi = 45°$.

draw comparisons between the influence of the recoil peak for the $1\pi_u$ orbital of N_2 and that of the atomic $2p^6$ orbital of neon (Rosel *et al* 1991, Rioual *et al* 1995). A similar comparison can also be made for the results presented here at 36.7 eV with those for the $2p^6$ orbital of neon at 41.6 eV (Murray and Read 2000), where the cross-section is observed to have a similar shape. A small peak seen in the cross-section for the $1\pi_u$ orbital of N_2 at $\xi \approx 75°$ is also seen for the $2p^6$ orbital of neon at 41.6 eV incident energy. These similarities suggest that the atomic 2p origin of the $1\pi_u$ orbital of nitrogen, sometimes referred to as the $2p\pi_u$ orbital, is an important factor in determining the ionization cross-section.

Rioual *et al* (1996) also measured the DCS for ionization of the $1\pi_u$ molecular orbital between 30° and 60° at intervals of 2.5°. The results for an incident electron energy of 400 eV displayed a local minimum characteristic of a bound p electron. In the non-coplanar symmetric EMS studies of Weigold *et al* (1977) and Cook *et al* (1990) this minimum is much deeper. Rioual *et al* partly attribute the less pronounced minimum which they observe to the coplanar geometry which is adopted, and to the sensitivity to the incident electron momentum direction. It is interesting to note that the results presented in figure 3 show no evidence of this minimum. This absence may be due either to the lower incident electron energy, or to the larger angular step size which is used here.

As with ionization of the $3\sigma_g$ orbital, ionization from the $1\pi_u$ molecular orbital is also complicated by the presence of indirect processes. Photoionization studies of the $1\pi_u$ orbital of N_2 (Rius i Riu *et al* 2001) have demonstrated non Frank–Condon effects in the vibrational branching ratios of the A $^2\Pi_u$ ion state due to the existence of autoionizing doubly excited Rydberg states between 20 and 30 eV photon energy. In particular there is a pronounced feature in the vibrational branching ratio between 21 and 24 eV that these authors attribute to autoionizing doubly excited Rydberg states of configuration $(1\pi_u)^3(3\sigma_g)^1(1\pi_g)^1(ns\sigma)^1$. The existence of these states in this energy range may explain the difference in the cross-section at $E_0 = 26.7$ eV compared to the other results shown in figure 4.

4. Conclusions

A set of new low energy (e, 2e) DCS measurements for ionization of the $3\sigma_g$ and $1\pi_u$ molecular orbitals of N_2 has been presented. To our knowledge this is only the second study of the ionization dynamics of molecules conducted in the coplanar symmetric regime. Further, the results constitute the only coplanar symmetric ionization study of molecules below 100 eV incident electron energy, where the cross-section is sensitive to post-collision interactions and contributions from indirect processes. The absence of an accurate theoretical model at these energies only permits a qualitative description of the data. Comparison with previous higher energy studies of the ionization dynamics of N_2 in this geometry shows similar trends as a function of incident electron energy for both valence states.

A number of features observed in the $3\sigma_g$ cross-section presented here are at variance with the higher incident energy results. These are tentatively attributed to the presence of resonances in this energy regime. The anomalous shape of the cross-section at $E_0 = 25.6$ eV remains uncertain, and further measurements are to be performed to elucidate the cause of this anomaly. The results for ionization of the $1\pi_u$ orbital also show features unlike those at higher energies, and these may also be explained by the presence of indirect processes contributing to ionization in this range.

Acknowledgments

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