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Coincidence angular correlation in electron impact single or double ionisation of atoms and molecules

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Abstract. Experimental results obtained with our multi-parameter multi-coincidence spectrometer are presented for the (e,3e) double ionisation of Ar and (e,2e) single ionisation of small molecules. The (e,3e) measurements are discussed in terms of competition between the two double ionisation processes present under the chosen kinematics, and qualitative conclusions are given. The results for the ionisation of H_2 and the outer orbital of N_2 are compared with the predictions of the most elaborate available theoretical models for description of the molecular ionisation process. Overall reasonable agreement is observed and tentative interpretations for the discrepancies are discussed.

1. Introduction

The coincidence study of angle and energy resolved multiply differential cross sections for electron impact single ionisation (SI) or double ionisation (DI), so called (e,2e), (e,3e) and (e,3-1e) experiments, provides a detailed image of the three- or four-body Coulomb scattering dynamics [1]. We have recently achieved new developments aimed to extend the capabilities and the sensitivity of the (e,2e)/(e,3e) multi-coincidence spectrometer at Orsay University [2]. The present system is unique in that it is the only system which combines three toroidal analysers all equipped with position sensitive detectors, thus allowing, for example, the *triple* coincidence detection of the *three* electrons present in the final state of an electron impact DI process. With this technical improvement, it has become possible to perform a whole class of new experiments which otherwise revealed to be difficult if not impossible to realize, due to the small cross sections of the involved processes. In this report, selected new results of (e,2e) SI and (e,3e) DI of atoms and small molecules will be presented and discussed in the light of state-of-the-art theoretical models, where they exist.

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2. Inner shell ionisation of atoms

In these measurements we discuss (e,3e) cross section for the DI of Ar under chosen kinematical conditions which allow either a direct DI from the outer 3p-shell, or an indirect DI with a 2p-inner shell hole creation followed by an Auger electron emission. A complete discussion of these results was published in ref [3]. From the (e,3e) results we extract useful information on the competition and/or the interference between the two DI processes, direct and indirect. In earlier works, the study of these processes under the above defined kinematics was hampered by their small cross sections. This is made possible here by the recently achieved increase in collection efficiency of our multidetection (e,2e)-(e,3e) spectrometer.

2.1. Description

The description of the spectrometer and method are given elsewhere [2] and need not be repeated here. Peculiar kinematics are used in this work, where the fast (500 eV) scattered electron is collected in coincidence with a second electron whose kinetic energy exactly matches that of the Auger electron (205 eV). Under these circumstances, the 'ejected' and the 'Auger' electrons cannot anymore be specified, being fully indistinguishable. In these completely new (e,3e) results the three final electrons (scattered – ejected – Auger) are simultaneously resolved in energy and angle, with the ultimate objective of contributing to the understanding of the role of the various inner shell DI mechanisms.

In the indirect (Auger) DI process, the primary ionisation process involves the 2p inner orbital of Ar, followed by the Auger decay, as follows :

$$e_0\ (E_0) + Ar(3p^6) \rightarrow Ar^+(2p^{-1})^* + e_a\ (E_a = E_0 - E_b - E_{SI,2p}) + e_b\ (E_b) \quad (1)$$
$$Ar^+(2p^{-1})^* \rightarrow Ar(3p^{-2}) + e_{Aug}\ (E_{Aug}=205eV)$$

where $E_{SI,2p}$ = 248eV is the ionisation energy of the 2p-shell of argon, and where the indexes 0, a and b refer to the incident, scattered (fastest) and ejected (slowest) electron from the 2p-orbital, respectively, while the index Aug refers to the Auger electron emitted consecutive to the electronic rearrangement. However, the same final state can also be reached by *direct* DI where two electrons are emitted from the 3p outer-shell (DI energy $E_{DI,3p}$ = 43eV), that is :

$$e_0\ (E_0) + Ar(3p^6) \rightarrow Ar^{++}(3p^4) + e_a(E_a = E_0 - E_b - E_c - E_{DI,3p}) + e_b\ (E_b=205eV) + e_c\ (E_c=205eV) \quad (2)$$

where now the two ejected electrons are indexed b and c. Both processes (1) and (2) contribute to our measured intensities, and may interfere. In the following, these processes are referred to as the 2p-SI, the Auger process and the 3p-DDI, respectively.

2.2. Results and discussion

From symmetry configuration of our setup, the (e,3e) cross section measured at positive scattering angle $+\theta_a$ must be identical to the one measured at negative angle $-\theta_a$ with an exchange of the role of θ_b and θ_c, i.e. $\sigma_{e3e}(+\theta_a, \theta_b, \theta_c) = \sigma_{e3e}(-\theta_a, -\theta_c, -\theta_b)$. Our data are indeed found to fulfil this requirement (to within statistical uncertainties). As a consequence, the final angular distribution with improved statistics is constructed by adequately summing up the two sets of data corresponding to $+\theta_a$ and $-\theta_a$ angles. The result is displayed in Fig. 1 as a grey (colour) 2D representation of the (e,3e) cross section distribution. To our best knowledge, such an angular correlation diagram constitutes the first (e,3e) experiments on inner shells and the first one involving an Auger process. It is to be noted that in order to increase their statistical significance, the raw data from the position sensitive detectors were binned using overlapping sectors with a width $\Delta\theta_{b,c}$ = 8° and a center-to-center distance of 4°. In the following, we comment on some experimental observations that can be extracted from these results.

(i) The bi-dimensional distribution of the emitted electrons displays several peaks on top of a somewhat uniform contribution. Some of them labelled B, F, R, L for convenience can be discussed in terms of angular directions of the correlated electrons. These particular emission diagrams are shown at the bottom of the figure.

A large probability is found for a symmetrical emission both in the forward (peak F) and backward (peak B) directions. Such highly symmetric situation tends to minimize the final state Coulomb repulsion between the three electrons (more so for peak B). These two peaks can be related to our (e,2e) experiments on the ionisation of the 2p-shell of Ar [3] since the angular positions of the binary and recoil peaks associated to a 2p shell single ionisation coincide with those of the peaks F and B. It is thus legitimate to assign these two peaks to a two-step DI mechanism, where the single ionisation of the 2p-shell is independently followed by an Auger emission of the second electron from the target.
The intensity distribution in Fig. 1 is however more complex as there are other (unlabelled) peaks present, most notably the one at angles ~ (310°,160°), or the smaller one at ~ (215°,140°). No simple interpretation in terms of known DI mechanisms could be given. Speculatively, they might be related to the interference of ionisation processes leading to the same final state, which could give rise to 'new' maxima and minima not expected from simple kinematical considerations. This is the well known shake-off (SO) process.

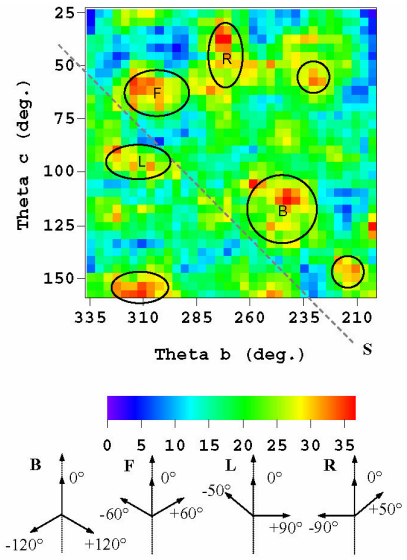

Figure 1. (Color online): (e,3e) measured angular correlation diagram for two electrons emitted from an Ar target with identical kinetic energy 205 eV, at an impact energy E_0 = 953 eV and a scattering angle θ_a = -6°. The bar gives the relative scale of the cross section. The diagrams at the bottom illustrate the emission directions of the three electrons, for the peaks labeled B, F, R and L, respectively, see text.

(ii) The b- and c- electrons' emission may also occur according to the intermediate cases of peaks L and R with the angles ~ (-50°,+90°) or ~ (-90°,+50°), respectively. This configuration is remarkable for the fact that one emitted electron is emerging at right angles to the scattered one, evoking a binary electron-electron collision, hence the tentative assignment of these peaks to an (e,3e) 3p-DDI *via* a so-called two step 2 (TS2) mechanism, as follows: the incident projectile with energy 953 eV is first scattered towards a small (positive or negative) angle in an electron-electron collision with an outer-shell 3p-target electron, transferring to it the kinetic energy 205 eV (in addition to losing 15.6 eV outer-shell binding energy). As a result of this e-e collision, the knocked 'atomic' electron is ejected at right angle from the scattered one (hence the angle ± 90°). The intermediate scattered, 'fast' electron (with energy 732 eV) in turn hits a second 3p-target electron, ejecting it (with kinetic energy 205 eV) in a kind of (e,2e) binary peak at ± 50° while it is scattered through the observation angle of 6° with energy 500 eV. This is the well known TS2 process.
(iii) It is well-established [1] that if the direct DI process is the result of one single projectile-target interaction (e.g. in the SO 'first-order' model) then the cross section distribution must exhibit a symmetry axis (labelled S in Fig.1) whose existence corresponds to both electrons being ejected symmetrically with respect to the momentum transfer direction: $\theta_b - \theta_K = -(\theta_c - \theta_K)$. Clearly, the

experimental data strongly violate this reflection symmetry. Therefore, higher order mechanisms such as the two step 2 (TS2) must play a role in the pattern of Fig. 1, as suggested above.
To our knowledge, there is, to date, no satisfactory theoretical model whose results could be used either for comparison with our (e,3e) data, or as a help to fully understand these data.

3. Single ionisation of molecules

In this section we discuss measurements of the (e,2e) triply differential cross sections (TDCS) for the ionisation of the nitrogen and hydrogen molecules, N_2 and H_2, in coplanar asymmetric geometry at an incident energy of about 600 eV and a large energy transfer to the target, about 90 eV. This kinematical regime, which remained rather unexplored to date, is characterised by a large momentum of the recoiling ion, implying an active participation of the ion in the collision process. The results are discussed in comparison with the predictions of the most sophisticated available theoretical models for treating differential electron impact ionisation of molecules.

3.1. Description

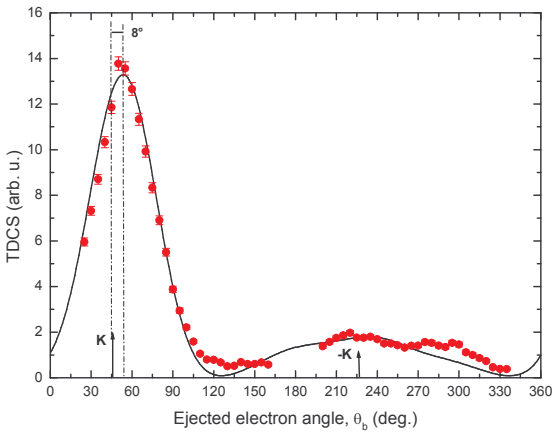

Figure 2 (Color online): Relative TDCS for ionisation of He, at an incident electron energy of 598.6 eV. The scattered electron with energy 500 eV is detected at an angle $\theta_a = -6°$ in coincidence with an emitted electron with energy 74 eV. The arrows indicate the momentum transfer direction and its opposite. Full circles are the experimental data, with one standard deviation statistical error bar. Solid curve is the theoretical prediction from the CCC model. The relative experimental data are normalised to theory for the best visual fit.

Before discussing the molecular data, we first describe how our experimental procedure was validated. To this purpose, an (e,2e) experiment was performed on He *under exactly the same experimental conditions* as those used for N_2 and H_2 (except for a slight change in incident energy). The objective is as follows: ionisation of a helium target has been the subject of extensive investigations, and it is nowadays well established that at high and intermediate impact energy the ionisation process is very well described, for instance, by the convergent close coupling method (CCC) [4]. Our measurements are obtained on a relative scale (no attempt was made to determine the absolute value of the cross section), and are compared in figure 2 with the results of CCC calculations kindly furnished by Igor Bray. The agreement between experiments and theory is excellent, both in the shape of the distribution and the position of the binary lobe. The CCC results show a shift of the binary lobe of about +8 deg from the momentum transfer direction (θ_K), and so do our data. This is consistent with known trends for He [5,6], where peak shifts away from θ_K-direction are to be expected whenever the first Born approximation is not sufficiently accurate. We thus believe that the experiments are free from any significant error or artifact.
We now discuss the molecular (e,2e) data. The measured TDCS distribution for ionisation of H_2 and of the outermost orbital $3\sigma_g$ of N_2, shown in Figures 3 and 4, respectively, are obtained for the first time to our knowledge under these kinematics. Due to the modest energy resolution of the

experiments, some contribution of the neighbouring orbitals $2\pi_u$ and $2\sigma_u$ of N_2 is included in the measured signal. The data are compared with calculated results obtained using two state-of-the-art approaches for molecular targets. The first theoretical model uses a first Born framework (FBA) in which the two centre continuum (TCC) approximation with correct boundary conditions in the entrance and exit channels [7] is applied. The second one is the molecular three body distorted wave (M3DW) approximation coupled with an orientation-averaged molecular orbital approximation (OAMO) [8,9]. Note that the relative experimental data have been normalised to the absolute scale given by TCC theory.

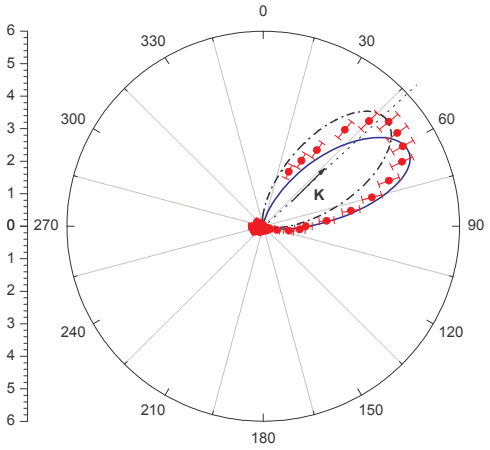

Figure 3. (Color online): TDCS for ionisation of H_2. Incident, scattered and ejected electrons energies are E_0 = 589.4 eV, E_a = 500 eV, E_b = 74 eV. Scattering angle is θ_a = – 6°. The arrow indicates the momentum transfer direction (θ_K = 49°). Full dots : experimental data, with one standard deviation statistical error bar. Dash-dotted curve: theoretical predictions from the FBA-TCC model. Solid curve: theoretical predictions from the M3DW-OAMO model. Experiment and theories are all normalised for the best visual fit at the maximum of the binary lobe.

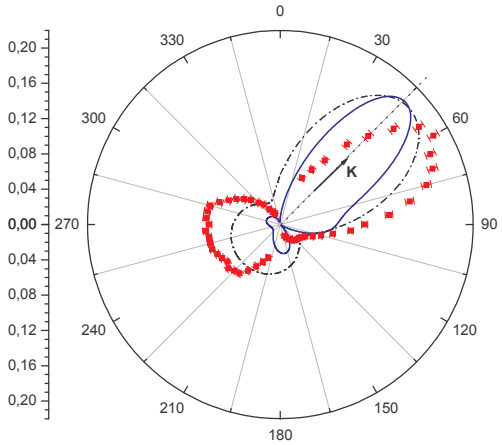

Figure 4. (Color online): As in fig. 3, but for the weighted sum (see text) of the TDCS for ionisation of N_2 from the $3\sigma_g$, the $1\pi_u$ and the $2\sigma_u$ 'outer' orbitals. Dash-dotted curve: theoretical predictions from the FBA-TCC model. Solid curve: theoretical predictions from the M3DW-OAMO model. The absolute scale shown for the cross sections (in atomic units) is that of the TCC model, while the M3DW results have been multiplied by a factor 4.6.

For hydrogen, both models yield an overall satisfactory description of the experiments as to the relative intensities of the binary and recoil peaks. A noticeable difference can be seen between the theoretical and experimental results for the position of the binary peak. The TCC distribution is symmetrical about **K**, as expected from any first-order model, whereas the experimental distribution shows a shift with respect to this direction. The M3DW includes final state PCI between the two continuum electrons, whose effect is usually to rotate the binary lobe towards large angles. This is indeed the case, but the rotation of the lobes is overestimated in the present conditions.

The comparison is more contrasted for the nitrogen molecule. We first note that the TCC results include a sum of contributions from the three outermost molecular orbitals, weighted by the experimental resolution function, whereas the M3DW only includes the $3\sigma_g$ contribution. Both theories do essentially reproduce the shape of the binary lobe structure. The agreement with experiments is overall better with the TCC results especially for the description of the recoil lobe. As

in He and H_2, the measured binary lobe is shifted to large angles, here by about 12° while this shift is not reproduced by theories. In the M3DW model the PCI effect does not produce any sensible deviation from the momentum transfer direction. One possible explanation for this behaviour can be found in the final state description, as already noticed in a previous work on H_2 [10]. The most noticeable difference with the experimental results reside in the recoil intensity distribution. Concerning the TCC model, the recoil distribution is not asymmetrically distributed as it is in the experiments, while its magnitude (relative to that of the binary lobe) is underestimated. We stress here that the TCC model behaved very well [7] in describing high energy (~ 4.1 keV) (e,2e) processes on H_2 [11], so that its deficiencies here must be attributed on the one hand to the different impact energy regime and on the other hand to the more active participation of the residual target ion. As to the M3DW-OAMO model, the recoil intensity yielded by this model is much smaller than experiment. We believe the breakdown of this model in the recoil region to be due to an inadequacy of the orientation average method used. Indeed, Gao *et al* [12] showed analytically that the OAMO approximation is valid for gerade orbitals providing the momentum transferred to the ion (defined by $\mathbf{q} = \mathbf{K} - \mathbf{k_b}$) is small – preferably less than 1 au. For the kinematics of this experiment, q ranges between 1.5 and 3.2 au, so the OAMO approximation is of questionable validity. Hence, the present measurements represent a severe test of the OAMO approximation, and this is precisely one of the reasons why they were undertaken. However, the smallest (respectively largest) momentum transferred to the residual ion occurs when the ejected electron is emitted parallel (anti-parallel) to the direction of momentum transfer, **K**, i.e. near the binary peak (its opposite). Hence, the OAMO approximation is expected to be best at the binary peak and worst for the recoil peak, and this is indeed what we observe in Fig. 4. Although some of the M3DW-OAMO underestimation of the recoil peak probably comes from the fact that the ungerade orbitals are not included in the M3DW-OAMO results, a significant part stems from the breakdown of the OAMO approximation.

Clearly, the inability of both calculations to fully reproduce the experimental distribution, and in particular to account for the substantial recoil intensity demonstrates the need for further refinement of the theory in order to correctly model such a fundamental process as the single ionisation of the nitrogen molecule.

4. Conclusion

(e,3e) fully differential cross sections for double ionisation of the argon atom at ~ 950 eV incident energy are reported, involving for the first time the coincidence detection of the scattered- ejected – Auger electrons. Competition and/or interference between the two DI processes, direct and indirect, were shown to play an essential role. Some of the observed structures in the measured (e,3e) angular distribution could be assigned to given ionisation mechanisms. The development of new theoretical model whose results could be used either for comparison with our (e,3e) data, or as a help to fully understand these data, is urgently needed.

(e,2e) TDCS for ionisation of the H_2 and N_2 molecules at ~ 600 eV incident energy are reported. Similar data obtained for the ionisation of He provided a validation of our experimental procedure. The results are compared with the most elaborate available molecular calculations. Encouraging similarities are found between measured and calculated distributions in the binary region, especially for the hydrogen case. However, clear discrepancies are observed between theories and experiments, and also between the two theories, in particular for the intensity distribution in the recoil region, the discrepancies being more pronounced for the more complex nitrogen target. The origin of these discrepancies is partly due to the chosen kinematics for the experiments, which constitute a stringent test for theory as they imply an active participation of the residual ion in the collision process. These discrepancies demonstrate the need for further development of the theoretical models in order to accurately model the ionisation process for molecular targets. To this end, we are considering several issues, such as improving in the TCC the final state description and/or the bound state functions, or else introducing second order effects, and also developing a better averaging method for the M3DW model, which would allow, in particular, to account for ungerade orbitals. On the experimental side,

more data with better resolution and varied kinematics and targets are also desirable, and an effort should be made towards determining the absolute scale for the cross section.

5. References

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Acknowledgments

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