

Triple Differential Cross Section Measurements for Double Photoionization of D₂

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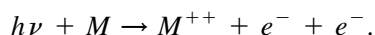
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Angular distributions of the two ejected electrons following photodouble ionization of molecular deuterium have been measured using a toroidal photoelectron-photoelectron coincidence spectrometer in conjunction with synchrotron radiation. Six ($\gamma, 2e$) triple differential cross sections (TDCS) were measured in the plane orthogonal to the photon beam direction with $E_1 = E_2 = 10$ eV. The angular distributions are similar to those of helium, but with differences which we highlight by comparing the D₂ TDCS with helium TDCS measured under nearly identical conditions. [S0031-9007(97)04143-4]

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In photodouble ionization (PDI) a single photon is absorbed by an atom or a molecule, followed by the ejection of two electrons. PDI is simplest for the fundamental two-electron systems, helium and molecular hydrogen, as there is only one possible ion state and there are no intermediate states above it:



It is not possible for direct PDI to be described within the familiar independent particle model as the photon cannot interact with more than one electron. Consequently, PDI is a manifestation of electron-electron interactions and so is a sensitive test for electron correlation theories.

The angular distribution—or triple differential cross section (TDCS)—of the ejected electrons is a particularly sensitive measure of the electron correlation. These measurements [e.g., 1–6] have only been possible during the last few years due to improvements in synchrotron radiation sources and in the necessary photoelectron-photoelectron coincidence (PEPECO) techniques. Recently, a complementary technique has been applied to helium which determines the momentum of the recoiling ion in coincidence with one of the photoelectrons, providing similar information but in momentum space [7]. To date, TDCS has been investigated only for rare gases, and the progress in this area has benefited greatly from a close relationship between experiment and theory (e.g., [8–16]). However, such studies have yet to be applied to molecules. In this Letter we present the first measurements of molecular TDCS, having performed them in the most fundamental system: hydrogen.

The photodouble ionization of helium results in the classic three-particle Coulomb continuum problem, whose solution determines the correlation factor in the expression for the TDCS [8]. The situation in hydrogen is not unrelated, but is further complicated by the inevitable dissociation of the molecule during double ionization. Therefore, PDI in hydrogen results in four unbound particles, albeit with two types of particles having different charges, masses, and velocities. However, it is perhaps not unreasonable to expect similarities in the angular

distributions with helium (final state electronic symmetry $^1P^0$) if the experimental conditions are chosen such that the electrons' speeds are much greater than those of the protons. The nuclear motion could then be considered as a perturbation which increases as the electron energies decrease.

Previous experimental studies of H₂, using photoion-photoion coincidence (PIPICO) techniques, investigated both the total double ionization cross section and the proton energy and angle distributions [17,18]. Kossmann *et al.* [18] describe the photon operator as providing two transition amplitudes, D_Σ and D_Π , from the molecular ground state to the double ionization continuum, which are associated with photoionization with the D₂ molecular axis along (Σ) or perpendicular (Π) to the electric vector of radiation. Although their PIPICO studies have shown that the D_Π component dominates at photon energies of less than 120 eV, causing a pronounced asymmetry in the protons double differential cross section (with $\beta = -0.75$ in the threshold region), there have been no theoretical studies to indicate how the TDCS will depend on the D_Σ and D_Π amplitudes. There has been, however, a semiclassical study of the Wannier-type threshold breakup in a system of two electrons and two protons, resulting in four free particles of zero energy [19]. This requires protons to lead in the escape, with electrons following in a plane normal to the protons direction and all four particles maintaining a dynamically unstable equilibrium configuration. If, despite obvious differences in the particle dynamics, the proposed orthogonality between the planes in which the proton and electron motion takes place applies to the near threshold photodouble ionization of H₂, the detection of the electron-proton interactions in TDCS spectra may prove elusive even for energies much smaller than in the present experiment.

The double ionization of hydrogen can be represented by a vertical transition from the $^1\Sigma_g^+(v=0)$ ground state to the Coulomb repulsive curve of H₂⁺⁺ of which the dissociation limit corresponds to the formation of H⁺ + H⁺. During double ionization, the ground state

wave function is projected onto the Coulomb repulsive curve, resulting in a double ionization region, rather than a specific threshold, that is spread over several electron volts [20]. This significant feature has important experimental consequences and is different from helium and from other diatomic molecules which have quasibound doubly ionized states supporting vibrational progressions [21,22]. Ideally, one would measure over all the available phase space. While this has been done effectively for the protons using time-of-flight PIPICO methods [17,18], it is generally more difficult to achieve this using conventional photoelectron spectrometers. This is because such spectrometers have restricted angular acceptances and are generally designed for high energy resolution which cannot be easily degraded to the extent required for this experiment. In the present study the coincident energy resolution was ~ 0.75 eV (FWHM), and the true coincidence count rates integrated over all the detectable emission angles were 1 s^{-1} (He) and $\sim 1/80 \text{ s}^{-1}$ (D_2) for two 10 eV electrons. An excess energy of 20 eV was chosen, as this corresponds to the maximum in the H_2 (also D_2) double ionization cross section [17,18]. We measured the TDCS of D_2 , rather than H_2 , as it has the same mass as helium, and so the effusive gas beam profiles and pumping speeds will be identical for the same throughput of gas. This allows for an accurate comparison of the D_2 results with similar measurements of helium made under as nearly identical experimental conditions as is possible to achieve.

This study was performed using a toroidal grating monochromator on a bending magnet (beam line 3.3) at the Daresbury Synchrotron Radiation Source. The angular distributions were measured using a novel multicoincidence spectrometer [23] consisting of two independent electron analyzers, both based on a toroidal geometry [24]. Electrons emitted in the plane orthogonal to the photon beam, over the range of angles indicated in Fig. 1, are energy analyzed and focused onto separate two-dimensional position-sensitive detectors while preserving the initial angles of emission. The multicoincidence capability can be realized, as electrons arriving anywhere on one detector can be correlated with electrons detected simultaneously anywhere on the other detector. This enables independent TDCS to be measured concurrently and allows the flexibility to later choose the size of the angular sectors over which one integrates the yield. Although the relative orientation of the two partial toroidal analyzers is fixed (see Fig. 1), the spectrometer can rotate about the photon beam direction and so sample a different aspect of the differential cross section. This is because the TDCS depends on the electron emission angles with respect to the polarization direction, which is essentially horizontal in these synchrotron studies.

Each part of the angle-dispersed image can be thought of as independent, as the electron trajectories responsible for that part are unique. Therefore variations in the

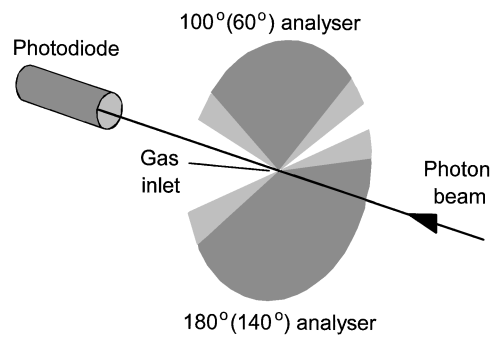


FIG. 1. A schematic diagram showing the fields of view of the two electron analyzers. The central interaction region is defined by the intersection of the gas and photon beams, and the photon flux is monitored by an aluminum photodiode. The mechanical acceptance angles within the perpendicular plane are 100° and 180° , but these are reduced to 60° and 140° , respectively, due to electric field termination effects within the electron optics. The acceptance angle out of the perpendicular plane is $\pm 6^\circ$.

yield as a function of angle, including microchannel plate gain nonuniformities, could occur and have to be corrected. The angular distribution for the $\text{He}^+ n = 1$ state is a convenient standard as it has an asymmetry parameter $\beta = 2$ for all photoelectron energies (i.e., $\cos^2 \theta$ distribution). The $\text{He}^+ n = 2$ level can also be used, as its asymmetry parameter is reasonably well known as a function of energy [25] and this acts as an important consistency check. A full description of the angular normalization procedure, its justification, and its effects has been published elsewhere [23]. However, deformations in the coincident angular distributions due to coincidence volume irregularities cannot be corrected by the above normalization procedure. This problem, inherent in all such coincidence experiments, can be minimized by precise alignment and careful tuning of the spectrometer.

In the course of extensive investigations of the helium TDCS with excess energies of 10, 20, and 40 eV under equal-energy sharing conditions [26], we have found this normalization procedure to result in TDCS, which compare well with other theoretical and experimental studies [1,4–6,8,9,14,16]. In particular, we confirm the full applicability of Huetz *et al.*'s parametrization [8] in terms of a Gaussian correlation factor for equal-energy sharing conditions in our perpendicular plane geometry, i.e.,

$$\text{TDCS} \propto \exp[-4 \ln 2 (180^\circ - \theta_{12})^2 / \theta_{1/2}^2] \times (\cos \theta_1 + \cos \theta_2)^2, \quad (1)$$

where θ_{12} is the angle between the two electrons, and θ_1 , θ_2 are their emission angles with respect to the polarization axis. This is in agreement with the recent investigations of the shape of the angular correlation factor in helium using an expansion in terms of the electrons' angular momenta [27]. Consequently, this simple formula with a single energy-dependent parameter $[\theta_{1/2}(E)]$ provides a

convenient means of evaluating and comparing measured helium TDCS.

Our measurements were performed at two spectrometer orientations, with the smaller analyzer centered at 90° and 160° , in the following manner: Calibration spectra of the single ionization angular distributions for the He^+ $n = 1, 2$ levels were measured for 10 eV electrons on both analysers. The degree of linear polarization was found to be 0.67 ± 0.03 . Coincidence measurements were obtained for $E_1 = E_2 = 10$ eV electrons in helium ($h\nu = 99.0$ eV), then D_2 , ($h\nu = 71.1$ eV), and finally again in helium, with no change in the spectrometer tuning conditions. The helium- D_2 gas loads were judged to be the same from the indicators on the turbomolecular pump controllers and the ionization gauge readings (corrected for sensitivity). As the D_2 measurements took several days of continuous data collection, the repeated helium data were used to check for consistency. The two sets of helium data were equivalent, indicating that no change in spectrometer sensitivity was discernible over that time interval. The normalization of the analysers efficiencies on the He^+ $n = 2$ state was applied to the coincidence data and the results fitted with Eq. (1). Our value for the correlation function half-width ($\theta_{1/2}$) of $91^\circ \pm 3^\circ$ is entirely consistent with the value obtained earlier [6] for the same kinematic conditions. These normalization functions from helium are then applied to the D_2 data to give the measurements presented in Fig. 2.

The TDCS in Fig. 2 are for a 16° wide sector for one electron, centered at the indicated α angle, and for 15° wide angular sectors for the other electron. The dashed curve represents the TDCS [Eq. (1)] for helium for the corresponding α angle. It can be seen at first glance that there is an overall similarity between the measured TDCS of the two gases, which could have been expected because the single-center expansion of the ground state molecular wave function would be dominated by $1S^e$ character [28,29], and due to averaging over molecular orientations. At these energy conditions, where the final speeds of the electrons are ~ 60 times higher than those of the nuclei, the asymptotic wave function will be even more like that of helium. But we also observe differences which can be summarized as follows: (i) different angular widths and positions of the large lobe as a function of α and (ii) a general "filling in" of the characteristic node at the mutual angle (θ_{12}) of 180° for all α . Incidentally, the main features in the shape variation of the large D_2 lobe can be modeled with the helium formalism (1) if the Gaussian angular half-width is reduced from 91° to 78° , as shown by the solid curves. The apparent narrowing of the lobes could result from interference effects arising from the higher complexity of the initial state. Such a situation has already been encountered in neon [30].

To highlight the observed differences between D_2 and He, Fig. 3 shows the ratios of the coincidence yields for the spectra shown in Figs. 2(a)–2(c) and the correspond-

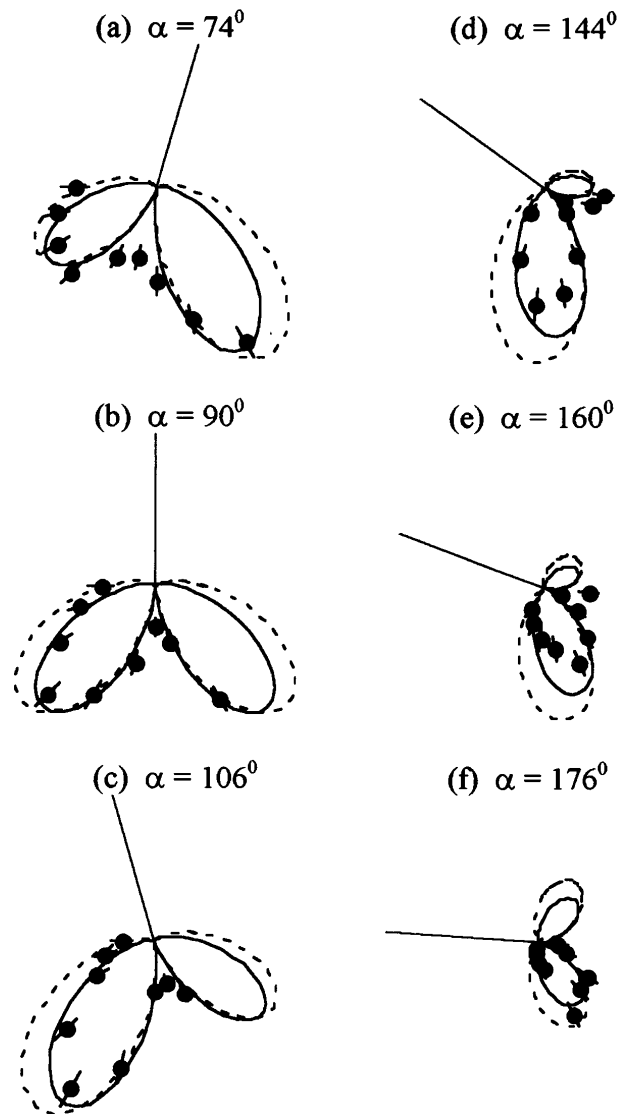


FIG. 2. $(\gamma, 2e)$ triple differential cross sections for D_2 for two 10 eV electrons. The mean ejection angle (α) for one electron with respect to the polarization axis is indicated. The angular distributions show the coincident yield of the second electron in polar form, with error bars indicating the statistical error of $\pm\sigma$. Three measurements at the same orientation of the spectrometer, which have been obtained simultaneously, are aligned vertically. The TDCS have a single normalization value with respect to the curves, which are of the form (1), with $\theta_{1/2} = 91^\circ$ (dashed curves) and 78° (solid curves)—as discussed in the text.

ing He distributions (not shown), compared with the ratios between the parametrizations (1) for $\theta_{1/2} = 78^\circ$ and 91° , respectively. The remaining differences between the measurements and the calculated ratio are in the node region (case ii) and at smaller mutual angles. As the apparatus solid angle effects should have been equal for the two gases, these statistically significant differences are surprising. However, as they occur in angular regions where the expected cross section is extremely small, one should treat

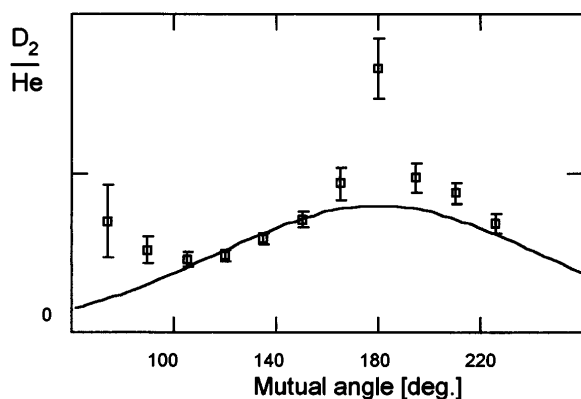


FIG. 3. Ratios of the measured coincident signals in D_2 and He. Points: weighted means corresponding to the orientations shown in Figs. 2(a)–2(c) and the related He data. Curve: ratio between the correlation factors (1) for $\theta_{1/2} = 78^\circ$ and 91° , respectively.

the result (ii) with some caution until further experiments become available.

It is hoped that these new results will stimulate further theoretical studies in molecular photodouble ionization. Further experimental studies are also needed for H_2/D_2 under a wide range of kinematic conditions and especially for smaller mutual angles.

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