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Experimental and theoretical study of electron-impact ionization plus excitation of aligned H₂

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Abstract

We report quadruple differential cross sections for electron-impact ionization of H₂ with simultaneous excitation of the H₂⁺ ion which will immediately dissociate. The alignment of the molecule is determined by detecting the emitted proton. The first measurements of this type were recently reported (2013 *Phys. Rev. A* **88** 062705). Here we report measurements with much better angular resolution using the COLTRIMS method. Experimental results are compared with molecular 4-body distorted wave calculations and reasonably good agreement between experiment and theory is found.

Keywords: ionization excitation, electron impact, differential cross sections, 4 body

(Some figures may appear in colour only in the online journal)

Introduction

Studying ionization cross section of atoms and molecules by electron impact provides important information about the mechanisms contributing to the collision process. The most detailed information for single ionization of atoms is contained in the triply differential cross section (TDCS) which determines the full kinematical information about the collision particles both initially and finally. For ionization of atomic hydrogen and helium, close coupling methods such as the convergent close-coupling method [1], the complex exterior scaling technique [2], or the time-dependent close coupling (TDCC) method [3, 4] provide essentially exact numerical results for the TDCS. However, equally accurate methods do not exist for larger atoms and molecules. Single ionization of atoms or molecules with the residual ion being left in the ground state can be treated as a 3-body problem and the distorted wave Born approximation or one of its variants typically yields reasonably good agreement with experiment.

For molecular targets, the orientation of the molecule provides a new variable so the TDCS is not a fully differential cross section. Most experimental measurements do not determine the orientation of the molecule so all possible orientations must be averaged in any theoretical calculation. If the orientation is also determined, the cross sections will be quadruple differential cross section (QDCS). TDCS are actually 5-fold differential (4 angles and 1 energy) so the QDCS is 7-fold differential.

The orientation of a molecule such as H₂ can be determined if it dissociates since the fragments will leave in opposite directions along a straight line path parallel to the orientation. Consequently, detecting the proton, for example, will determine the direction of orientation. Both the ground and excited states of H₂⁺ will dissociate and the first experiments were performed for dissociation of the ground state of H₂ [5–9]. These works revealed that both the TDCC method and the molecular 3-body distorted wave approximation gave reasonably good agreement with experimental data. The

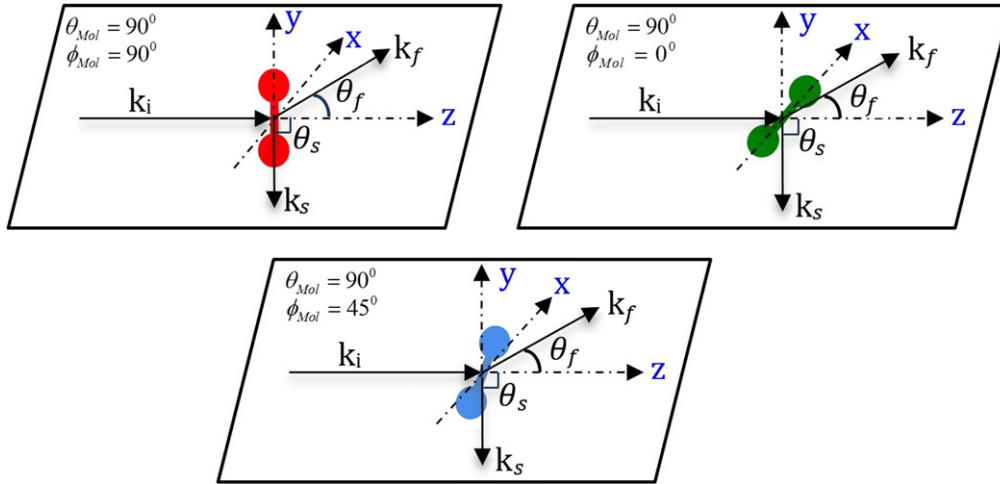


Figure 1. Different molecular alignments. The incident electron momentum is k_i along the z -axis, the scattered and ejected electron momenta are k_f , k_s respectively, k_f is in the scattering plane (xz) and the ejected electron momentum k_s is in the perpendicular plane (xy).

problem with looking at the ground state is that the dissociation probability is very small whereas the excited states will immediately dissociate.

From a theoretical viewpoint, the problem of ionizing plus exciting the target is much more difficult to treat since collisions in which two target electrons change state requires a 4-body treatment. One such problem on the atomic level is electron-impact ionization of helium with simultaneous excitation of the remaining target electron [10, 11]. While agreement between experiment and theory for this case is not good for perturbation approaches [10, 11], good agreement was achieved within a close-coupling approximation [12]. Here we study the four-body problem of electron impact excitation-ionization of the hydrogen molecule. The possible excited states of H_2^+ are ($2s\sigma_g$, $2p\sigma_u$, $2p\pi_u$) all of which immediately dissociate and the alignment of the molecule can be determined by detecting one of the fragments.

An experiment of this type was recently performed in Canberra, Australia [13–15]. In that experiment, the energy resolution was good enough to resolve the $2p\sigma_u$ state but not the individual $2s\sigma_g$ and $2p\pi_u$ states. In the Canberra experiment, the experimental angular width was 2° FWHM. However, to have sufficient statistics, the ejected electron detector was integrated over the angular range of 40° – 80° and the scattered electron was integrated over a 10° angular range. Measurements were made for four different scattered projectile angles for each molecular orientation (i.e. four data points for each orientation). The experimental results were compared with molecular 4-body distorted wave (M4DW) calculations and reasonably good agreement between experiment and theory was found for the shape of the data and relative magnitudes for different orientations. However, experiment found the magnitude of the $2p\sigma_u$ state relative to the $2s\sigma_g + 2p\pi_u$ to be a factor of 200 larger than theory. The energy of the incident electron was 176 eV for these measurements, the scattered electron energy was 100 eV, and the scattered and ejected electrons were measured in the scattering plane.

Here we compare experiment and theory for a similar QDCS for electron ejection in the perpendicular plane measured using the reaction microscope technique. With this method, we can access almost the full solid angle and we have good statistics for a much better angular resolution for the ejected electron than the Canberra experiment. In this experiment, the ejected electron is integrated over a 12° angular range (as opposed to 40°) and the angular acceptance of the scattered electron is 4° (as opposed to 10°) whereas the Canberra measurement was for one ejected electron angle, four projectile scattering angles and one energy, we have results for 25 ejected electron angles, two projectile scattering angles and three different energies. Whereas the Canberra measurements had 4 data points for each molecular orientation, here we report 150 measured points for each molecular orientation. Consequently, the present measurement represents a much more stringent test of theory. However, our energy resolution is not as good as Canberra and we cannot distinguish which of the three possible states has been excited so our measurements represent a sum over the three possible excited states ($2s\sigma_g$, $2p\sigma_u$, $2p\pi_u$). The experimental measurements were performed for an incident electron energy of 126 eV and ejected electron energies of 4, 10, and 25 eV.

Results are presented for three different alignments of the molecule as shown in figure 1. The scattering plane is xz and the orientations of interest are in the xy -plane which is perpendicular to the incident beam direction. Measurements were performed for alignments along the y -axis, x -axis, and 45° between the x - and y -axes. Here, we present a comparison of theoretical M4DW QDCS results with experimental data for electron impact ionization of H_2 with simultaneous excitation of the H_2^+ ion summed over the three possible ($2s\sigma_g$, $2p\sigma_u$, $2p\pi_u$) excited states with the ejected electron also being detected in the perpendicular plane. However the $2s\sigma_g$ state completely dominates theoretically so the other two states can be ignored.

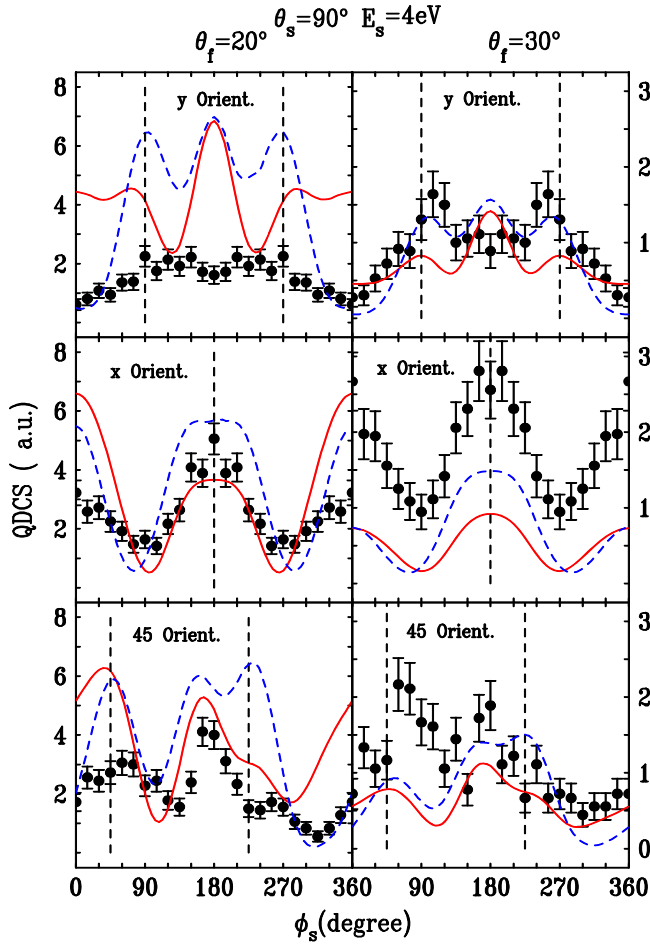


Figure 2. Experimental and Theoretical QDCS for electron-impact ionization of orientated H_2 in the perpendicular plane. The orientation of the molecule is indicated in each part of the figure and the energy of the ejected electrons is 4 eV. The black circles are the present experimental measurements. The M4DW calculations are: solid (red) line results using Rosen [17] ground state wavefunction; and dashed (blue) line results using Dyson ground state wavefunction. Vertical dashed lines indicate the molecular alignment direction.

Experiment

The experiment was performed using a dedicated reaction microscope [16]. Details about the molecular frame (e, 2e) experiment have been described elsewhere [8]. Briefly, a pulsed electron beam crosses a cold H_2 gas jet. Using uniform electric and magnetic fields, the final state fragments, electrons, and ions are projected (with almost 4π solid angle) onto two position- and time-sensitive multi-hit detectors. From the positions of the hits and the fragment times of flight, the momentum vectors of the detected particles can be calculated. Triple-coincidence detection of both outgoing electrons and the proton was achieved. In the present experiment, H_2 was chosen as a target gas instead of D_2 , which was used in previous studies. There, the lower fragment velocity of D^+ give more time for ramping up their electric extraction field. In our experiment, we use constant electric field. The fragment trajectories for both species (H^+ and D^+) are identical and using D_2 is not advantageous.

Theory

The details of the M4DW approach were presented in [14] and [15] so only a brief overview will be presented here. Since the collision time is much shorter than the vibrational or rotational times, we make the usual assumption of stationary nuclei. For the 4-body problem, the T -matrix is a nine dimensional integral which we evaluate numerically. The T -matrix is given by

$$T_{fi} = \left\langle \chi_f^-(\mathbf{k}_f, \mathbf{r}_0) \chi_s^-(\mathbf{k}_s, \mathbf{r}_1) \phi_{\text{ion}}(\mathbf{r}_2) C(\mathbf{r}_{01}) \right| \times V_i - U_i \left| \psi_{\text{target}}(\mathbf{r}_1, \mathbf{r}_2) \chi_i^+(\mathbf{k}_i, \mathbf{r}_0) \right\rangle. \quad (1)$$

Here $\chi_i^+(\mathbf{k}_i, \mathbf{r}_0)$ is a continuum initial state distorted wave for wave number \mathbf{k}_i and the + indicates outgoing wave boundary conditions, $\chi_f^-(\mathbf{k}_f, \mathbf{r}_0)[\chi_s^-(\mathbf{k}_s, \mathbf{r}_1)]$ is a continuum distorted wave for the faster (slower) final state electron with wave number \mathbf{k}_f [\mathbf{k}_s] and the minus indicates incoming wave boundary conditions, $\psi_{\text{target}}(\mathbf{r}_1, \mathbf{r}_2)$ is the initial state target wavefunction, $\phi_{\text{ion}}(\mathbf{r}_2)$ is the final state ion wavefunction, $C(\mathbf{r}_{01})$ is the Coulomb interaction between the two final state continuum electrons, V_i is the initial state interaction between the projectile electron and the target, and U_i is an initial state spherically symmetric approximation for V_i .

In our previous work, we have used two different approximations for the ground state wavefunction for the target $\psi_{\text{target}}(\mathbf{r}_1, \mathbf{r}_2)$; (1) a product of two Dyson 1s-type orbitals and (2) a variational wavefunction of Rosen [17] which contains both s- and p-state contributions. For this wave function, the dissociation energy was within 10% of the experimental value which represents a significant improvement over the product of Dyson orbitals. There are better wavefunctions for H_2 which give even better energies but we found that, in the evaluation of a 9D integral, the time required to evaluate the ground state wavefunction was crucial to the feasibility of evaluating the integral. For example, we tried a 30 term and a 50 term Hartree–Fock (HF) ground state wavefunction and quickly learned that it was not feasible to use these wavefunctions. The calculations presented here using the Rosen wavefunction required three million SU on the NSF XSEDE cluster (Kraken) while we estimated that the HF wavefunctions would require several hundred million SU on the same cluster which is obviously not feasible. The time required to run results for the Dyson wavefunction was essentially the same as the Rosen wavefunction so about six million SU were used to obtain the results presented in this paper.

Results

Experimental results were measured for the three orientations shown in figure 1, for three different ejected electron energies (4 eV, 10 eV, and 25 eV), and for each energy two different fixed scattering angles for the scattered projectile (18 different cases). (Obviously we do not know which final state electron is the projectile and which one is the ejected electron but we

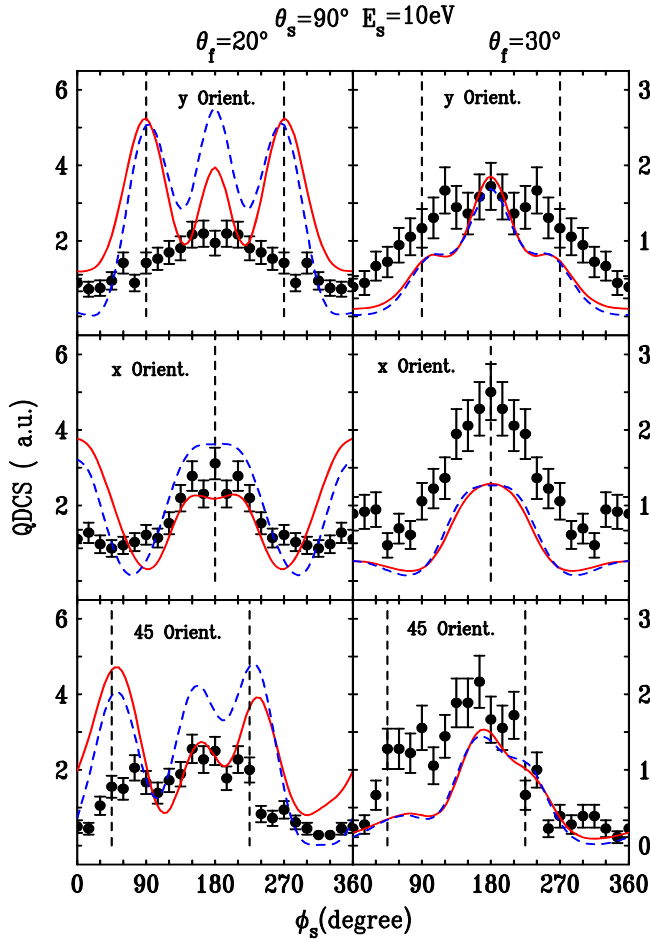


Figure 3. Same as figure 2, except that the energy of the ejected electrons is 10 eV.

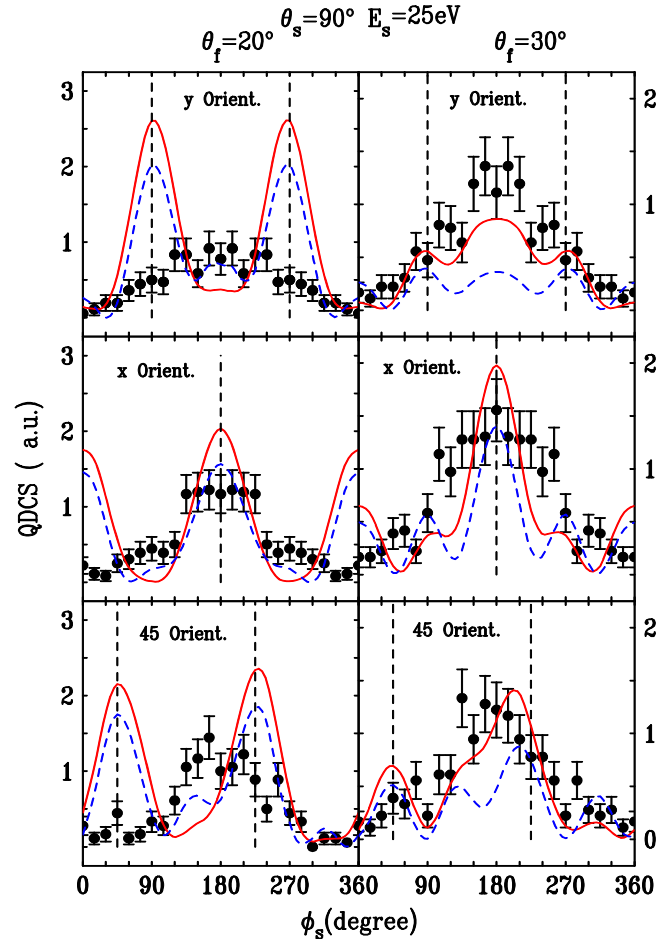


Figure 4. Same as figure 2, except that the energy of the ejected electrons is 25 eV.

refer to the faster final state electron as the projectile and the slower one as the ejected electron for convenience.) Recall that the experiment represents a sum over the three possible unresolved excited states ($2s\sigma_g$, $2p\sigma_u$, $2p\pi_u$) while theory predicts that the only important state is the $2s\sigma_g$ so this is effectively a comparison with excitation of the $2s\sigma_g$ state only. Although the experimental measurements are not absolute, they are ‘relatively absolute’ which means that the ratio of any two cross sections is absolute. Consequently, only one normalization is required to put the entire data set (18 angular distributions) on an absolute basis and we have normalized the data to the Rosen calculation. The results of the Dyson wavefunction calculation were uniformly larger than Rosen so we normalized the Dyson results to the Rosen for the case of 10 eV, and $\theta_f = 30^\circ$ since the shape of the two calculations were almost the same for this case (and this case only!). This normalization was achieved by multiplying all the Dyson results by $\frac{2}{3}$. It seems odd that the two calculations have identical shapes for this case only but we have checked for errors and could not find any.

Figure 2 compares experiment and theory for 4 eV ejected electrons (largest cross section), figure 3 for 10 eV ejected electrons (next largest cross sections) and figure 4 compares experiment and theory for 25 eV ejected electrons

(smallest cross sections). Both the molecular alignment and ejected electrons are in the perpendicular plane (perpendicular to the incident beam and perpendicular to the scattering plane). For the coordinate system we are using, the beam direction is the z -axis, the xz plane is the scattering plane, and the xy plane is the perpendicular plane. The projectile is scattered in the $+x$ -direction so the final-state scattering angle for the faster projectile θ_f is in the $(+x, +z)$ plane. Since the slower electron is in the perpendicular plane, $\theta_s = 90^\circ$ and the azimuthal angle of the slow electron ϕ_s is measured counterclockwise in the xy plane starting from the x -axis ($\phi_s = 0^\circ$), y -axis ($\phi_s = 90^\circ$), negative x -axis ($\phi_s = 180^\circ$), etc. The cross sections are symmetric about the scattering plane for molecules oriented along the x -axis and y -axis but they are not symmetric for orientation at 45° in the xy plane. This means that the x -orient and y -orient cross sections should be symmetric about $\phi_s = 180^\circ$, while the differential cross sections should not be symmetric for orientation at 45° in the xy plane. This symmetry (and lack thereof) can be seen in both the theoretical and experimental results.

Interestingly a large part of the cross section patterns can be assigned to intuitively accessible mechanisms. Firstly, there is a binary peak in the cross section originating from the direct knock out of the target electron by the projectile.

Accordingly it lies in the scattering plane on the opposite side of the z -axis from the scattered projectile (i.e. negative x -axis). The perpendicular plane cuts through this binary lobe such that a maximum can be found at $\phi_s = 180^\circ$ for almost all kinematics of the figures 2–4. Secondly, in a previous study of (e, 2e) on hydrogen leaving the ion in the ground state, cross section peaks were found for electron emission along the direction of the molecular axis [9]. These maxima were prominent for large projectile scattering angle and low energy of the ejected electron. These maxima can be found also in the present data for ionization–excitation. In the figures, vertical lines are drawn at the angles corresponding to the direction of the molecular orientation and significant maxima can be seen for the larger angle $\theta_f = 30^\circ$ and the lowest energy $E_s = 4$ eV (figure 2). If the ejection energy is increased to 10 eV (figure 3), and 25 eV (figure 4), these maxima decrease relative to the central binary peak. In these cases there is rather good agreement between experiment and theory. If the scattering angle is decreased to $\theta_f = 20^\circ$, the peaks essentially disappear in the experimental data. Theory in contrast shows increasing peak magnitude causing strong discrepancy to the experimental data in all top-left panels of figure 2. To find an intuitive explanation for this behavior is not straight forward. In the earlier publication [9] for ionization into the H_2^+ ground state, it was argued that the maxima for electron emission along the molecular axis are stronger for larger projectile scattering angle since then the projectile classically undergoes a close collision. For close collisions with classical impact parameters in the order of the H_2 internuclear distance, the target structure and orientation can become relevant. For small scattering angle and, thus, distant collisions the cross section should become less sensitive to the target structure and orientation. In this sense apparently theory overestimates the target wave function anisotropy at large distance.

In the middle row panels the binary peak and molecular axis directions coincide at 180° giving rise to a dominating central maximum. Finally, in the bottom row panels the molecular axis maxima are at $\phi_s = 45^\circ$ and $\phi_s = 225^\circ$. It is a somewhat surprising finding that the main dynamical features in the QDCS are the same for single ionization (a one electron transition) and the much more involved and complex ionization and excitation reaction (a two electron transition).

Overall, the agreement between experiment and the M4DW theory is reasonably good—certainly much better than was found earlier for excitation–ionization of helium [10, 11] and the Canberra measurement of excitation–ionization for D_2 . Comparing the two different theoretical calculations, sometimes the Rosen results look better and sometimes the Dyson results look better. Overall the Rosen results are a little better. The more important point is that the theoretical results are quite sensitive to the initial state wavefunction and theory would presumably be in even better agreement with data if a better ground state wavefunction were used. The worst agreement between experiment and theory was found for $\theta_f = 20^\circ$ and the molecule aligned along the y -axis (which is the smallest cross section for the three different orientations). There is at least a qualitative

agreement between experiment and theory for all the other cases. In most cases, the shape agreement between experiment and theory is quite good even when the relative magnitude is not that good. For example, looking at ($E_s = 4$ eV, $\theta_f = 30^\circ$, x – Orient), the theory is about a factor of 2 lower than the data but the shape of the theory is in very good agreement with experiment.

Conclusion

In conclusion, we present a comparison between experiment and theory for the 4-body QDCS problem of electron-impact ionization of molecular H_2 with simultaneous excitation of the final state ion. Similar measurements have been recently reported by Lower *et al* [14, 15]. However, in that work the cross sections were integrated over a 40° angular range for the ejected electron and a 10° angular range for the scattered electron to achieve acceptable statistics. Our detector angular resolution is 12° for the ejected electron and 4° for the scattered electron, and we access the full angular range in the perpendicular plane. Because of the extremely long data acquisition times, the earlier measurements reported 4 data points per molecular alignment whereas we have measured 150 so the present work represents a much more stringent of theory.

This is a particularly important 4-body problem since the excited state ion will immediately dissociate and detection of the proton fragment determines the orientation of the molecule at the time of the collision. Over the last 2–3 decades, there have been numerous studies of electron-impact ionization of molecules which do not determine the orientation of the molecule so this possibility is a very recent development. We have measured relatively absolute QDCS which means that one normalization factor places the entire data set on an absolute scale (i.e. one normalization factor for the 18 different panels in figures 2–4). The observed cross section pattern can be understood as originating primarily from binary knock-out of the target electron plus preferential electron emission along the molecular axis.

The experimental results were compared with the results of the M4DW calculation and reasonably good agreement with experiment was found—much better than was found for the much smaller data set [14, 15] and very much better than was found for the equivalent atomic scattering problem of electron-impact excitation–ionization of helium [10, 11]. Two different ground state wavefunctions were used in the calculation and a significant wavefunction dependence was found. Since the better wavefunction gave the best agreement with experiment, it was postulated that an even better wavefunction would give improved agreement with experiment. This calculation will have to wait for a new generation of computers (for this calculation we have used 5000 processors at a time whereas a calculation with a much better ground state wavefunction would require at least 500 000 processors to finish in a comparable time).

It is somewhat surprising that the agreement between experiment and theory is as good as it is. The experiment cannot distinguish between different excited states so it represents a sum over the three possible ($2s\sigma_g$, $2p\sigma_u$, $2p\pi_u$) excited states of the H_2^+ ion. The theory, on the other hand predicts that the $2s\sigma_g$ totally dominates so that the comparison in figures 2–4 represents a comparison with this state only. The earlier Canberra measurements had a better energy resolution and they could distinguish the $2p\sigma_u$ state from the unresolved ($2s\sigma_g$, $2p\pi_u$) states and they found the relative magnitude of the $2p\sigma_u$ state to be 200 times larger than theory predicted which means that $2s\sigma_g$ and $2p\sigma_u$ should be of comparable magnitude. Consequently, one would expect the summed cross sections to be substantially different from the cross section for the $2s\sigma_g$ state alone. It would be very interesting to have an independent determination of the relative sizes of these cross sections.

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