Low Energy Elastic Differential Electron Scattering from H_2O

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Normalized differential cross sections for elastic (rotationally averaged) electron scattering from gaseous water (H_2O) are obtained using the relative flow method against helium with a thin aperture collimating source of gas instead of a tube. This method obviates the use of gas kinetic molecular diameters for helium or water. Our measurements are found to be largely in quantitative disagreement with past differential elastic electron scattering measurements and suggest that present recommended electron scattering total cross sections for water be revised.

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Water is not only the third most abundant molecule in the Universe after H_2 and CO, it plays the major role in the existence of terrestrial life and weather [1]. In terms of electron-water interactions, elastic scattering is a dominant process, especially at low energy below 100 eV. Differential elastic electron scattering from H_2O has been studied experimentally as early as 1982 by Jung *et al.* [2] to as late as 2004 [3]. These measurements are in good agreement with each other and are supported by theoretical values of these differential cross sections (DCSs), but there remains a puzzling disagreement of these DCSs with absolute total cross section measurements, when these DCSs are angle integrated to yield integral cross sections (ICSs).

Accuracy in these DCSs is required for modeling electron collisions in biological tissues, especially when modeling DNA breakup by low energy electrons [4], knowing that DNA in tissue is hydrated [5]; water makes up about 60% of human tissue. Elastic scattering is the most probable process affecting the transport of slow electrons in organic tissue, needing accurate scattering cross sections for modeling this. In addition, tetrahertz absorption of radiation by tissues, much used in investigations of the structure of condensed matter, is sensitively dependent on electron-water cross sections [6].

We have recently conducted elastic electron scattering measurements using a significant modification of the "conventional" relative flow method [7] with an aperture replacing a conventional tube source of gas [8]. This modification obviates the need to know the molecular diameters of the gases used. In the popular relative flow method, the DCS for scattering of the unknown gas is determined by comparing scattering signals from a standard target (usually helium) with that of the unknown gas under identical collision region geometry conditions. To obtain the same profiles for both gas beams, when using a tube collimating source, the gases must be operated at pressures behind the collimating tube so that their mean-free paths are the same [9]. For a thin aperture source, the profile of the gas beam is invariant of the gas pressure, provided the mean-free path of the gas is greater than the

thickness of the aperture. Conventional relative flow methods using collimating tubes have several systematic limitations. First, the pressures of the unknown and calibrating gases must be accurately operated to obtain equal mean-free paths for both gases. Second, to calculate accurate mean-free paths, one must know accurate gas kinetic diameters (cross sections). For molecules which have permanent dipoles general viscosity measurements (see, e.g., Guthrie [10]) measure essentially the hard-sphere diameter (surface-molecule collisions) rather than dipole-dipole extensions of the molecular diameter (molecule-molecule collisions). For example, the quoted molecular diameter of water vapor from viscosity measurements is 4.60×10^{-8} cm, comparable to CO_2 4.59×10^{-8} cm [10] which has no dipole moment. One would expect the dipole-dipole interactions in water to increase its gas kinetic diameter substantially and affect the results of the conventional relative flow experiment.

In our present setup, described in detail in [8], we made a series of elastic scattering DCS measurements for several primary alcohols [11], which were not available then, because their molecular diameters were not published. Initially we decided not to measure elastic DCSs for H_2O because of the already numerous DCS measurements [3,12–14], which were in reasonable agreement with each other. However, we later decided to measure DCSs for H_2O as an added test of our system, which had performed well for the alcohols. Preliminary measurements using H_2O at $E_0 = 20$ eV revealed that our apparatus (which is free from molecular diameter constraints [8]) provided measurements that were from 30% to 100% greater than the available measured DCSs, causing us to extend our e-H_2O DCS measurements to other incident electron energy (E_0) values.

Our experimental apparatus has been detailed before, e.g., Khakoo *et al.* [15]. Cylindrical electrostatic optics and double hemispherical energy selectors were utilized in the spectrometer. Energy loss spectra of the elastic peak were collected at fixed (E_0) values and scattering angles (θ) by multichannel scaling. The target gas beam was formed by

effusing the gas through a 0.3 mm diameter aperture in a 0.025 mm thick brass disk which was centrally flush mounted at the end of a 6.35 mm outside diameter and 4.3 mm inside diameter brass tube. The aperture was sooted to reduce secondary electrons, and was 6 mm below the axis of the electron beam. The tube was incorporated into a movable source arrangement [16] for the determination of accurate background scattering rates [17,18]. Temperatures in the gas flow system were at 74 °C, and >120 °C in the spectrometer and collision region areas. As a check, we repeated our measurements with the gas flow system at room temperature and found no difference in our DCS values for H_2O. We used doubly distilled water in a vacuum flask and repeatedly freeze-pump-thaw cycled it to remove dissolved gases.

Monitoring the energy position of the $He^-(2^2S)$ resonance, with the movable gas source in and out of place, revealed a >0.03 V variation. We also observed a small yet noticeable nonlinear drop of scattered signal (at $E_0 =$ 20 eV and $\theta = 30°$) vs relative flow rate, in contrast to the linear behavior observed in earlier tests with ethylene, N_2, H_2, and methanol and ethanol [11], with a variation from the linear curve by about 5% at high pressures around 0.5 Torr indicating a possibility of dimer formation at these pressures, which would result in a reduced signal if the cross section between $(H_2O)_2$ and H_2O would increase proportional to the square of their respective dipole moments (3.2D and 1.84D), but the density of the dimer would be less than the monomer by the root-mass ratio. Hence the presence of dimers would lead to an overall upward increase in signal versus flow rate by ≈ 2. Calculations based on binding energy of HNO_3-H_2O dimer complex formation by Tao *et al.* [19], applying the Boltzmann partition function for the HNO_3-H_2O and $(H_2O)_2$ dimer (binding energies of ≈ 0.4 and ≈ 0.2 eV, respectively), suggest that the fraction of dimers in our gas beam (at ≈ 0.6 Torr)

should be $<10^{-5}$. The recent partition function calculations of Goldman *et al.* [20] show this to be significantly higher, i.e., $\approx 3 \times 10^{-3}$, when their graph is extrapolated to low pressures of around 0.6 Torr. This is relevant to the work of [12], since, using an ionization mass spectrometer, they did not observe $(H_2O)_2$ from a multicapillary tube source operating with a high 2 Torr pressure behind it, but it is possible that their ionization mass spectrometer could fragment the dimers to the level of an unobserved signal.

The DCS for water (DCS_{Wr}) is related to the DCS for He by

$$DCS_{Wr}(E_0, \theta) = DCS_{He}(E_0, \theta) \frac{RFR_{He}\ Is_{Wr}}{RFR_{Wr}\ Is_H} \sqrt{\frac{M_{He}}{M_{Wr}}}, \quad (1)$$

involving the relative flow rates (RFR, s^{-1}) of helium and water, the incident electron beam fluence (Is, s^{-1}) for helium and water and the molecular masses (M, kg) of helium and water, appropriately subscripted. The elastic DCSs for helium used are well established [21,22]. Is did not vary by more than 10% for a run comprising of the different gases. DCS were determined at E_0 values of 1, 2, 4, 6, 8, 10, 15, 20, 30, 50, and 100 eV for θ ranging from 5° to 130°. Because of limited space, a small selection of our DCSs will be discussed here. These DCSs were integrated over angle to obtain ICSs.

Figure 1 shows our DCSs at E_0 values of 4, 6, and 20 eV. At $E_0 = 4$ eV, we observe best agreement with the theory of Varella *et al.* [23] using the successful Schwinger multichannel model, especially at $\theta \le 60°$, and observe good agreement with Cho *et al.* [3] and Shyn and Cho [13]. Our DCSs are in excellent shape agreement, but consistently higher than other experiments. At $E_0 = 6$ eV we note that our DCSs are in reasonable quantitative agreement only with Shyn and Cho [13] at $\theta < 60°$, being higher by about 40% on average with other measurements. Agreement with
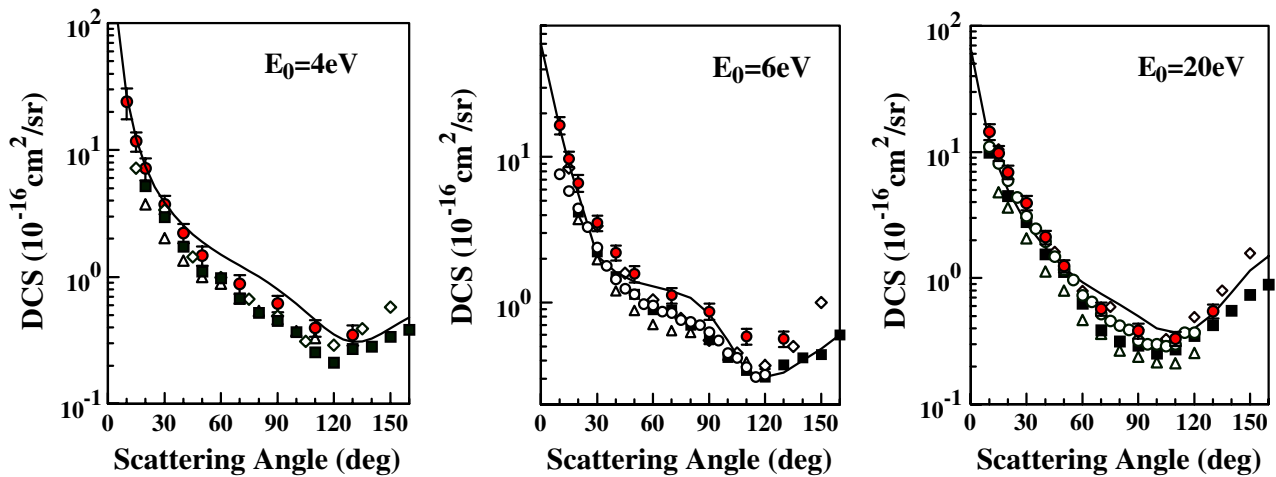

FIG. 1 (color online). Elastic electron scattering DCSs for H_2O at $E_0 = 4$, 6, and 20 eV. Legend: experiments: ● present experiment, △ Danjo and Nishimura [12], ◇ Shyn and Cho [13], ○ Johnstone and Newell [14], ■ Cho *et al.* [3]. Theory: (solid line) Schwinger multichannel method with polarized pseudostates and with Born closure, Varella *et al.* [23]. See text for discussion.
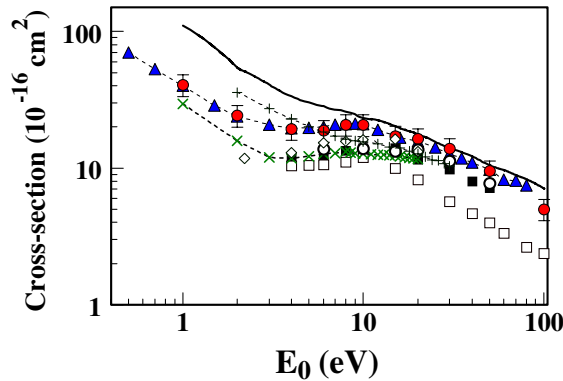
FIG. 2 (color online). Low energy total and integral elastic electron scattering cross sections for H_2O. Legend: Experiments: ● Present experiment (ICS), □ Danjo and Nishimura [12] (ICS), ◇ Shyn and Cho [13] (ICS), ○ Johnstone and Newell [14] (ICS), ■ Cho *et al.* [3] (ICS); × Sueoka *et al.* [27] (TCS), — Kimura *et al.* [26] (TCS), and ▲ Szmytkowski [28] (TCS). Theory: + Varella *et al.* [23].

the theory of Varella *et al.* [23] is reasonable for $\theta \le 90°$, but with qualitative differences at larger θ. For $E_0 = 20$ eV, very good agreement with Shyn and Cho [13] and Johnstone and Newell [14] is found, but noticeable disagreement with theory [23] exists. At both energies, we see excellent qualitative agreement with the most recent DCSs of Cho *et al.* [3], but quantitative difference by about 40%–50%. The DCSs of Cho *et al.* [3] are important as they cover essentially the full θ range, using a magnetic angle changing system [24]. The fact that our results are larger can be hypothesized to a too-small molecular diameter used in previous experiments. From our flow measurements (see Ref. [8] for details) we estimate the molecular diameter (δ) with $\approx 10\%$ accuracy from gas kinetic cross sections related to the flow of gas in our experiment. The value of δ used by the previous measurements was 4.2×10^{-8} cm (see, e.g., [3]). However, our flow measurements provide a δ value for water $7.4 \pm 0.7 \times 10^{-8}$ cm, different by a factor of ≈ 1.8. H_2O has a permanent dipole (1.84D) that would increase its effective δ from that of a pure hard sphere to include soft-sphere (long range) scattering. An estimate using data from [25] of gas beam profile angular widths versus mean free paths, assuming Gaussian profile beams and that the electron beam scatters off the forward gas beam gives the result that using a lowered δ value in a relative flow experiment results in DCSs that are lower by the ratios of δ, i.e., ≈ 1.75.

Figure 2 shows our electron-H_2O ICSs, which are compared to both total cross sections (TCS) and other ICS values. The TCS values of Kimura *et al.* [26] are recommended TCSs in the recent review of Itikawa and Mason [1], after they revised the TCSs of Sueoka *et al.* [1,27]. Szmytkowski and co-workers have repeated TCS measurements in H_2O [28] as well as D_2O [29], but found at most a 2%–3% variation in their initial [30] TCSs for H_2O and no

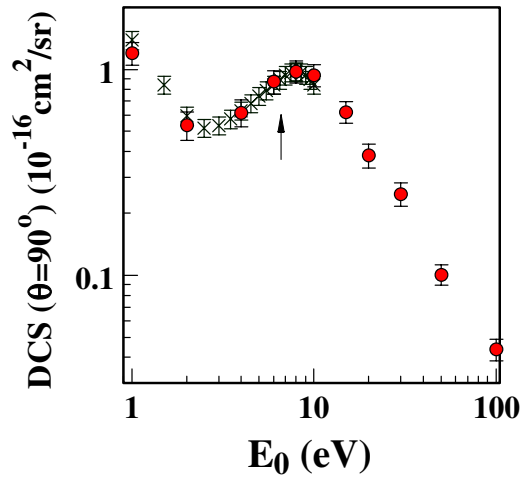FIG. 3 (color online). Comparison of the present, ●, elastic scattering DCSs at $\theta = 90°$ with the relative DCSs of Seng and Linder [33], ×, normalized to present DCSs at $E_0 = 8$ eV (arrowed). See text for discussion.

isotope effect in their D_2O TCSs [29] relative to H_2O. Our ICSs agree best with Shyn and Cho, but generally all ICSs remain significantly lower than ours. Our ICSs show excellent quantitative agreement at low E_0 with the TCSs of Szmytkowski [30] only, falling significantly below their TCS at $E_0 = 100$ eV. This level of agreement with different experimental techniques is significant. The disagreement at large E_0 is where the sum of excitation [31] and ionization [32] cross sections become significant (in the range of 10%–30%). Clearly, the recommended values of TCS for H_2O by [1] should be revised to the Szmytkowski values with which we agree excellently at low E_0 values. We also note that the theoretical ICSs of Varella *et al.* [23] produce results close to our values, but their shape differs from measurements.

There are no available experimental quantitative DCSs measured for $E_0 \le 2$ eV. Hence, we compared our DCSs with the early, pioneering low energy relative DCS measurements of Seng and Linder [33], who carefully calibrated their spectrometer for different E_0 at $\theta = 90°$. Figure 3 compares our $\theta = 90°$ DCSs across the full E_0 range of 1 to 100 eV with the "excitation function" of Seng and Linder [33] which ranges from $E_0 = 1$ to 10 eV. Clearly, the agreement is excellent supporting the reliability of our DCSs.

We have measured accurate DCSs for elastic scattering from H_2O, using a thin aperture gas source [8], in a movable source setup [16]. This work improves our knowledge of recommended cross sections for electron scattering from H_2O, by accurately extending the elastic scattering DCSs to $E_0 = 1$ eV. These DCSs impact the modeling of low energy electron transport in water-containing systems of interest in biomedical fields and in astrophysics and plasma physics and will be published in full in a longer paper.

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