Low Energy Electron Scattering from Polyatomic Targets

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Abstract. Low energy elastic electron scattering cross-sections from water and several alcohols are presented. This paper addresses accurately measuring quantitative differential elastic scattering cross-sections, using the relative flow method with an aperture source, and focuses on the long range dipole interaction of the scattering electron with these polar targets. The electron-dipole interaction dominates the scattering for these molecules and contributes significantly to their integral elastic cross-sections.

1. Introduction
Electron scattering from molecules plays an important role in the physical chemistry of many environments. A recent review of scattering measurements can be found in Brunger and Buckman [1]. Differential elastic cross-sections for low energy electrons scattering from polyatomic molecules has been of interest recently, because it is possible with present-day computer technology to be able to model these processes, and also because these collisions play key roles in plasmas [2, 3], astrophysics [4] and in DNA break-up [5]. Elastic electron scattering is a dominant process in the transport of low energy electrons through gaseous media and condensed matter, and is thus important in our understanding of the transport of electrons in media such as biological tissue [6], planetary atmospheres and interstellar media [4], lasers and fusion plasmas [7].

Recently, at California State University Fullerton (CSUF) we successfully modified the relative flow method with an aperture source [8] to make differential elastic scattering measurements of electrons from atoms and molecules. The aim was to be able to apply the relative flow method without the usual restriction that the pressures behind the source be in the ratio of the gas kinetic molecular diameter squared. This restriction is removed since an aperture source’s gas profile is not dependent on the source pressure as long as the mean free path of the gas behind the source is long
compared to the thickness of the aperture. This method is therefore useful for large molecules whose molecular diameters are not accurately known. The elastic electron scattering results are supported by new large theoretical calculations using the variational Schwinger multichannel (SMC) many-electron model of the Caltech group and a variant incorporating core pseudopotentials used by several groups in Brazil. Both implementations of the SMC method provide accurate descriptions of the low energy scattering physics, including exchange and polarization effects [9]. The testing of these theoretical methods by the present experiments has been central to recent collaboration between experimental and theoretical groups in the USA and Brazil [10].

In this paper we focus on recent work undertaken to study electron scattering from H₂O, which is both a key biological molecule and an especially clear example of the importance of the long-range charge-dipole interaction on both the differential and integral scattering cross-sections of highly polar molecules.

2. Experimental
The most successful and popular method used for measuring differential elastic electron scattering from relatively light atomic and molecular targets has been the relative flow method, which was first formulated by Srivastava et al. [11] and has been applied extensively in the last 30 years to determine elastic electron scattering differential cross-sections (DCS) for many (mostly light, hard-sphere) targets. The reader is referred to the extensive review of Brunger and Buckman [1] for the most recent summary of this work. The present experimental apparatus (spectrometer, vacuum chamber, control equipment) has been described in detail in previous papers, e.g. Khakoo et al. [8]. In this experiment the conventional gas tube source was replaced by a thin-walled aperture. This target aperture of 0.3mm diameter was located centrally in a thin-walled disc of 0.025mm thickness which was counter-flushed centrally at the end of a 6.35mm o.d. and 4.3mm i.d. brass tube [8]. The tube-and-aperture assembly was incorporated into a moveable source [12] arrangement, another method developed at CSUF, which enables background scattering rates to be accurately and repeatedly measured.

We followed the recipe given in [13] to calibrate our relative flow rate (RFR) vs. the pressure behind the source Pₚ. A second-order polynomial in Pₚ (at low pressure) expresses RFR usefully as a function of Pₚ in the form RFR = aPₚ(1+εPₚ). The coefficient ε is proportional to the molecular diameters of the gases [14, 15], whereas the a coefficient is proportional to the inverse square root of the mass for non-reactive gases. For reactive gases, it is affected by the stickiness of the gas [16]. These coefficients are given in Table 1 for all gases used in our aperture gas system to date. As can be seen the gas kinetic molecular diameters determined from ε values from our flow measurements for water and even the smaller alcohols are large, typifying the long-range dipole forces these molecules must exert on each other as compared to hard-sphere molecules.

| Gas | T (°C) | a (s⁻¹) | ε (Torr⁻¹) | δ (x10⁸ cm) | M | a√M/ε | ε/δ² | x |
|-----|--------|---------|------------|-------------|---|----------|------|---|
| H₂  | 25     | 0.218   | 1.050      | 2.74        | 2.046 | 0.310    | 1.40 | 1 |
| He  | 25     | 0.155   | 0.739      | 2.18        | 4.002 | 0.310    | 1.56 | 1 |
| N₂  | 25     | 0.0596  | 2.115      | 3.75        | 28.02 | 0.316    | 1.50 | 1 |
| C₃H₆| 25     | 0.0566  | 4.070      | 4.95        | 28.03 | 0.300    | 1.66 | 1 |
| H₂O | 74     | 0.0242  | 7.792      | 7.25        | 18.02 | 0.313    | 1.48 | 0.33 |
| CH₃OH| 47    | 0.0387  | 5.722      | 6.30        | 32.04 | 0.313    | 1.44 | 0.70 |
| C₄H₈OH| 47   | 0.0352  | 7.346      | 7.15        | 46.07 | 0.313    | 1.44 | 0.76 |
| n-C₃H₇OH| 74 | 0.0288  | 8.095      | 7.49        | 60.11 | 0.313    | 1.44 | 0.71 |
| n-C₄H₉OH| 74 | 0.0212  | 9.754      | 8.23        | 74.12 | 0.313    | 1.44 | 0.58 |
| C₆H₆O| 23     | 0.0291  | 8.677      | 7.75        | 72.11 | 0.313    | 1.44 | 0.79 |

Table 1: a and ε coefficients derived from the second-order fits to the relative flow-rate vs. pressure Pₚ behind the gas source for several hard sphere gases (above middle line) and (below line) water, methanol, ethanol,
propanol, and most recently ethyl vinyl ether (C\textsubscript{4}H\textsubscript{8}O). The molecular diameter \(\delta\) is determined from the \(\varepsilon\) coefficient after comparison with He. The \(\alpha\) coefficient is proportional to \(1/\sqrt{M}\) (molecular mass) and a transmission (Clausing) factor \(\kappa\) \cite{16} which is related inversely to the stickiness of the gas with the walls of the gas handling system, i.e. \(\kappa=1\) is completely un-sticky. Note that our estimate of \(\delta\) (7.25\(\pm\)0.45 x10\textsuperscript{-8} cm) for water, at 74°C, is significantly larger than the literature value of 4.2x10\textsuperscript{-8} cm \cite{22}. Note too that the \(\kappa\) factor for water is the lowest in group of molecules used, i.e. that water is the stickiest.

We measured elastic scattering from CH\textsubscript{3}OH, C\textsubscript{2}H\textsubscript{5}OH, n-C\textsubscript{3}H\textsubscript{7}OH, n-C\textsubscript{4}H\textsubscript{9}OH and H\textsubscript{2}O at incident electron energies \(E_0\) from 1 eV to 100 eV and at scattering angles (\(\theta\)) of 5° to 130°, over a coarser interval (20°) at large scattering angles than at small scattering angles (10°). Our DCS were normalized via the relative flow method to the established He elastic electron scattering DCS values from \cite{17} and \cite{18}. These measurements and corresponding SMC calculations have been published earlier \cite{10,19-21}. Here we summarize the overall results with a focus on H\textsubscript{2}O and compare the experimental cross-sections both to the SMC results and, at low energies, to the simple Born-dipole approximation.

1. Theory

The H\textsubscript{2}O calculations were carried out by the Caltech group of Winstead and McKoy using the all-electron SMC method \cite{9,23} implemented for parallel computers and discussed in \cite{21}. The long-range dipole interaction is included using a closure procedure based on the first Born approximation to electron scattering from a point dipole. This procedure is also discussed in \cite{21}. Under the approximations made, the SMC results are most reliable at energies above about 3 eV and below the ionization threshold, although results were computed for all energies presented here. The dipole moment of the Hartree-Fock target wave function used for the SMC calculations was 0.787 a. u., which is fairly close to the standard value in the literature of 0.730 a. u.

2. Observations and Discussion

Figure 1 shows a summary of our low energy results for water taken at 6 eV and below. At 1 eV, we note that the Born-dipole approximation, using the dipole moment of 0.730 a.u. for water \cite{21}, is in excellent quantitative agreement with the experimental results. The Born-dipole DCS is given by

\[
DCS = \frac{4}{3} \mu^2 \frac{k_f}{k_i} \frac{1}{K^2},
\]

where \(\mu\) is the dipole moment (a.u.), \(k_f\) and \(k_i\) are the scattered electron momenta (a.u.) and \(K^2\) is the momentum transfer squared \(= k_f^2+k_i^2-2k_fk_i \cos \theta\). In terms of energies, \(|k_f|=\sqrt{2(E_0-E)}\) and \(|k_i|=\sqrt{2E_0}\), where \(E_0\) is the incident electron energy (a.u.) and \(E\) is the final energy. In the limit \(K^2\rightarrow 0\) (zero \(\theta\)), the Born-dipole approximation DCS will go to infinity unless the energy loss \(E_0-E\) is nonzero. Thus some realistic (rotational) inelasticity is included. In our case we used \(E_0-E=4.6\) meV, which is equal to the \(J=0_{oo} \rightarrow 1_{11}\) rotational transition in H\textsubscript{2}O. Importantly, the assumed energy loss does not significantly affect the Born-dipole DCS. For example changing the energy loss from 4.6 meV to 0 affects the DCS by no more than 8% at \(\theta >10^\circ\) and \(E_0 \geq 1\) eV, and this variation rapidly decreases with increasing \(\theta\). The Born-dipole DCS curve progressively separates from our experimental DCS as \(E_0\) is increased from 1 eV to 6 eV.

Agreement with the calculations improves as \(E_0\) increases, with overall quantitative agreement being very good, although the calculated DCS tend to be below the present measurements. At \(E_0=2\) eV, the complex Kohn DCS of Rescigno and Lengfeld \cite{28} show excellent agreement with our results, but they deviate more as \(E_0\) increases. The agreement with the Born-dipole cross-section at very low energy reinforces the conclusion that the quantitative accuracy of the present work supersedes that of earlier work, in which the relative flow method was used with tube sources, requiring the invocation of the equal mean free path condition \cite{21}. Our method is free of this
condition and yields DCS significantly higher (by 20-40%) than those obtained in earlier work, as is
clearly observed in Figure 1. Note that a 20% drop in our elastic scattering DCS at, e.g., 1 eV would
result in a marked disagreement with the Born-dipole approximation.

Figure 2 shows the importance of the dipole interaction for the OH containing molecules
addressed here. We note that, systematically, the DCS of the largest of these molecules (n-butanol)
deviates from the Born-dipole curve at smallest $\theta$, followed in size sequence by the lighter alcohols,
viz. n-propanol, ethanol and methanol. Water, being the smallest in size, deviates the least. What is
also interesting is that the DCS for n-butanol show increasing structure at larger $\theta$, indicating an
important contribution to the scattering from higher partial waves that can most easily penetrate to the
vicinity of the molecule for this, the largest target. The Born-dipole approximation also works well for
the alcohols presented here because their dipole moments do not vary by more than 11% from that of
water, and thus the dipole moment squared, which determines the Born cross-section, differs by 23% at
most. One must also, of course, consider the effect of dipole polarizability, which increases with
molecular size and thus will likely be largest for n-butanol.

![Figure 1: DCS for elastic scattering of low energy electrons from H2O. Experiments: Red filled circles, Khakoo et al.[21]; black squares, Cho et al [22]; open triangles, Danjo and Nishimura [24]; open diamonds, Shyn and
Cho [25]; open circles, Johnston and Newell [26]. Theory: solid line, Khakoo et al. [21]; dash-dots, Varella et al. [27]; short dashes, Rescigno and Lengfield [28]; dots, Faure et al. [29]; line and dots, Born-dipole approximation [30].](image-url)
As a final note regarding the DCS, we find excellent agreement with the shape of the results of Cho et al. [22], who have conducted the most thorough investigation of the H$_2$O DCS to date. Their measurements were taken using a magnetic angle changer and cover the full range of backward scattering angles and were useful in guiding our DCS extrapolations into the backward angle region $\theta \geq 130^\circ$, improving the accuracy of the experimental ICS determined from this work, which we will discuss next.

![Graph](image)

Figure 2: Experimental DCS for elastic scattering of low energy electrons from several alcohols and water compared to the Born-dipole approximation for water. See text for discussion. Red filled circles, H$_2$O; open circles, CH$_3$OH; open triangles, C$_2$H$_5$OH; open diamonds, n-C$_3$H$_7$OH; and open squares, n-C$_4$H$_9$OH. Dotted line is the Born-dipole approximation.

In Figure 3 we observe the significant contribution of forward scattering to the total or integral cross-section as was discussed by Itikawa and coworkers [30,32]. We encountered this problem in our first paper on H$_2$O [20], where we used the visually extrapolated DCS to determine ICS. After the importance of the Born-dipole forward scattering was brought to our attention [30], we corrected our experimental ICS by accounting for dipolar scattering in the forward extrapolation of our DCS using the Born-dipole formula and found almost a factor of 2 increase in the ICS at our lowest energy of $E_0=1$ eV. Whereas our previous visual extrapolation gave ICS in excellent agreement with the total cross-sections of Szmytkowski [35], Born-dipole extrapolation raises our ICS well above their TCS measurements. This illustrates the difficulty in TCS experiments of correcting the transmitted current for the strong forward scattering signal of a polar target at very low energy. Nevertheless, the results of Szmytkowski are in very good agreement with our ICS at $E_0=10$ eV and above. Our ICS are also in good agreement with those recommended by Itikawa and Mason [32] (not shown) at low $E_0$, but their values fall significantly below ours at higher $E_0$ values (see [21] for a complete picture).

3. Conclusions

have presented low energy elastic scattering results obtained with a novel experimental method combining the relative flow technique with an aperture source. Good agreement with theoretical values is observed, though there is room for improvement. At the lowest energies, excellent agreement with the DCS we computed within the Born-dipole approximation is found, while comparison among the alcohols and H$_2$O reveals a consistent pattern, whereby the DCS at a given energy depart from the Born-dipole curve in order of decreasing size as the scattering angle increases. Accurate elastic DCS for H$_2$O are important in applications such as radiation track modeling on account of water's central role in biological systems, while accurate DCS for the primary alcohols are relevant to combustion studies and may thus may prove useful developing in bio-alcohols as fuels in motor engines.
Figure 3: Integral elastic cross sections (ICS) and total scattering cross sections (TCS) for low-energy electron collisions with H₂O.

ICS measurements: red filled circles, Khakoo et al. [20], obtained with a visual extrapolation; brown filled squares results of Khakoo et al. [21], obtained with the Born-dipole extrapolation to 0° below 20 eV with a 4.6 meV inelasticity assumed (increased error bars); open squares, Danjo and Nishimura [24]; open diamonds, Shyn and Cho [25] from 5 eV to 20 eV and Shyn and Grafe [31] at 30 eV and above; open circles, Johnstone and Newell [26]; black filled squares, Cho et al. [22]. ICS calculations: long black dashes, Khakoo et al. [21], with a 10 meV inelasticity assumed; dotted line with +’s, Varella et al. [27]. The rotationally summed result of Faure et al. [29] is in almost exact agreement with Khakoo et al. [21] and is not shown.

TCS measurements: solid line, recommended TCS of Itikawa and Mason [32] based on data of Kimura et al. [33] and Zecca et al. [34]; blue filled triangles, measurements of Szmytkowski [35]. See text for discussion.

4. Acknowledgements

This work was sponsored by the U.S. National Science Foundation through Grants No. PHY-0653452 and No. PHY-0653396 and by the Brazilian Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) under a collaborative program. We acknowledge important discussions with Dr. Yukikazu Itikawa (Institute of Space and Aeronautical Science, Japan). We very much thank Dr. M. H. F. Bettega (Universidade Federal do Paraná, Brazil) for sending us tabulated elastic scattering DCS of Refs. [27]. The work of C. Winstead and V. McKoy was also supported by the Chemical Sciences, Biosciences, and Geosciences Division, Office of Basic Energy Science, Office of Science, U.S. Department of Energy, and made use of the Jet Propulsion Laboratory’s Supercomputing and Visualization Facility. M. C. A. Lopes and H. Silva acknowledge support from CNPq, from Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), and from Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG). CSUF undergraduate students John Muse and Colin Campbell were funded under NSF grant No. RUI-PHY-0653450.
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