Low Energy Electron Scattering from Fuels

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Abstract. In order to understand and optimize processes occurring during the ignition of plasma and its consequences in post-discharge for an internal combustion engine, especially considering the spark plug, we have produced in this work some basic information necessary to modeling spark ignition in alcohol-fuelled engines. Total cross sections of electron scattering by methanol and ethanol molecules in the energy range from 60 to 500 eV are reported, using the linear transmission method based on the Beer-Lambert law to first approximation. Additionally to that, measurements and calculations of differential cross sections for elastic low-energy (rotationally unresolved) electron scattering were also discussed, for impact energies of 1, 2, 5, 10, 15, 20, 30, 50, and 100 eV and for scattering angles of 5°–130°. The measurements were obtained using the relative flow method with an aperture source, and calculations using two different implementations of the Schwinger multichannel method, one that takes all electrons into account and is adapted for parallel computers, and another that uses pseudopotentials and considers only the valence electrons.

1. Introduction
The replacement of automotive fuels by alternative fuels, not from oil, which are cleaner than gasoline and diesel, is a strategy that is gaining more attention in order to reduce the emission of toxic gases in the air. Bio-ethanol is inherently cleaner than gasoline because it does not contain toxic substances such as benzene, which is highly carcinogenic, and butadiene which is proven teratogen. In addition, by having a simpler composition, this compound releases lower levels of complex substances into the atmosphere during its combustion. In order to efficiently use ethanol as fuel, increase fuel economy and reduce
emissions, the automotive industry has worked toward improving the designs of engines and related systems. In turn, to meet the demands of this market, research must find answers in new technologies to make methanol combustion more efficient, to reduce the emission of pollutants and to reduce consumption. This implies the development of engines with better performance, better ignition and application of new fuels. The engines with spark discharge (internal combustion engines) are governed by their combustion mechanisms that occur in the initial electric discharge [1]. For a fuel-air mixture ignited in a combustion chamber of the engine it is needs a spark between the electrodes of the spark candle providing as much energy as possible, so that all the mixture is completely burned in order to obtain maximum horsepower. This relevance, which has attracted much attention, has been one of the subjects of a recent collaboration between experimental and theoretical groups in the USA and Brazil.

This work is part of our investigation of processes that occur during the ignition of the plasma and its consequences in post-discharge time for an internal combustion engine, in order to find the appropriate parameters to be used in cars that operate with lean mixtures air-fuel. That research aims to point more suitable methods and materials to be used in order to provide an analysis of the processes occurring in plasma and combustion. We have carried out experimental measurements of absolute total cross section (TCS) electron scattering at intermediate energies by methanol and ethanol [2], and also, measurements and calculations of differential cross sections (DCS) for elastic low-energy (rotationally unresolved) electron scattering by several primary alcohols; namely methanol, ethanol, propanol and butanol [3,4] in order begin to elucidate the different kinetic mechanisms, producing new information to optimize ignition process.

TCS measurements of electron scattering from methanol have been made by Schmieder et al [5], Sueoka et al [6] and by Szmytkowski and Krzysztofowicz [7] who covered a broad energy range of incident electron energies (0.8 eV to 250 eV). Sugohara et al [8] have reported recently differential (DCS), integral (ICS), and momentum-transfer (MTCS) cross sections for methanol in the 100 to 1000 eV energy range, using the conventional relative flow technique. They [8] also have reported TCS for electron-methanol collisions obtained by summing up their experimental Integral Cross Section (ICS) and the Total Inelastic Cross Section (TICS) obtained Rejoub et al. [9]. The results of all these groups reveal essentially the same energy dependence for TCS. The electron scattering by methanol was also studied by Mathur and Hasted [10] who observed broad resonances, using electron transmission spectrum. There are also, measurements of resonant dissociative electron attachment to methanol reported by von Trepka and Neuert [11], by Kühn et al [12], by Curtis and Walker [13], by Prabhudesai et al [14], by Skalicky and Allan [15] and, recently in the condensed phase, by Parenteau and Sanche [16]. Skalicky and Allan [15] additionally assigned several grandparent states to resonances observed in their electron attachment spectra using He I photoelectron spectroscopy to observe the binding energies of these negative ion species. Ibañescu et al. [17] extended the work of Skalicky and Allan [15], observing a new peak at 2.99 eV in the CH\textsubscript{3}O\textsuperscript{-} yield which they assigned to an O–H σ* resonance. Wen et al. [18] have measured electron-impact vibrational excitation cross sections for condensed-phase methanol and observed several broad resonances. More recently, Tan and Wang [19] have reported calculations of total cross sections for electron scattering using a revised additivity rule and Vinodkumar et al. [20] reported various total cross sections namely total elastic, total (complete) cross sections and grand total cross sections for the impact of electrons on methanol at energies from circa threshold to 2000 eV, using the ‘Spherical Complex Optical Potential’ (SCOP) formalism. In contrast with methanol, ethanol was much less studied up date. The only available experimental data of TCS have been reported by Schmieder et al [5] covering the energy range from 1.5 to 50 eV. Tan and Wang [19], have also reported recently calculations of TCS for ethanol, covering the energy range from 10 to 1000 eV. Dissociative attachment spectra, revealing a variety of resonance peaks, were reported by Prabhudesai et al [14], Ibañescu et al. [17], and Orzol et al [21]; the second group also measured vibrational excitation cross sections and photoelectron spectra. The latter two groups observed a low energy peak in the yield of C\textsubscript{2}H\textsubscript{5}O\textsuperscript{-} similar to the CH\textsubscript{3}O\textsuperscript{-} peak earlier seen in methanol [17], albeit the spectrum of Orzol et al [21] appears shifted to lower incident electron energies relative to that of
Ibănescu et al. [17]. Bouchiha et al. [22] have investigated low-energy electron scattering from ethanol and performed ab initio R-matrix calculations within the fixed-nuclei approximation for incident electron energies from 0 to 12 eV. In their work, their elastic and electronic excitation cross section calculations have shown the presence of three core-excited resonances in the range of 6 – 12 eV.

In this work we report absolute TCS for electrons scattering by methanol and ethanol over the incident electron energy range of 60-500 eV compared with recent data published in the literature [19]. These data were obtained in a new apparatus constructed at laboratory at Universidade Federal de Juiz de Fora in Brazil, based on the well-known linear transmission technique. To our knowledge, these are the first measurements reported for electron scattering TCSs from ethanol in the energy range of this work. Additionally, we discuss our experimental and calculated data on elastic electron scattering (differential) cross-sections for methanol and ethanol taken at incident electron energies of 1, 2, 5, 10, 15, 20, 30, 50, and 100 eV and for scattering angles of 5°–130°, whose to our knowledge are also the first data on literature up to 50 eV. The only data available for comparison with those data is for methanol at 100 eV, from Sugohara et al. [8]. These methanol and ethanol DCS measurements have been carried out at California State University Fullerton, using a new relative flow method [23], which does not necessitate the use of gas kinetic molecular diameters. The results are supported by the theoretical calculations using the variational multi-channel Schwinger method with polarization effects included.

2. Method

The experimental arrangement to determine the absolute TCS for electron scattering using the linear transmission technique, has been discussed in detail in reference [2]. Briefly, it is based on the measurement of the attenuation of a collimated electron beam through a gas cell containing the molecules to be studied at a given pressure. It consists of an electron gun, a gas cell, and an electron energy analyzer composed of decelerating electrostatic lenses, a cylindrical dispersive 127º analyzer (CDA 127º) and a Faraday cup. The low energy limit of that apparatus is determined by that gun optics which provides a low intensity of the beam at below 60 eV. The collimated electron beam passes through the scattering cell and the electrons that succeed in leaving it are discriminated by the energy analyzer, which prevents electrons inelastically scattered in the forward direction, being collected by the Faraday cup. The angular acceptance of the analyzer, defined by the solid angle formed by the analyzer aperture as seen from the center of the scattering cell, is 8.26 x10^{-55} sr. The temperature of the sample was taken as the room temperature as was discussed in detail in [2]. The pressure inside the scattering cell is measured using a capacitance manometer Baratron MKS 627B. All measurements were performed for incident beam current of 10^{-10} A, where no dependence of TCS upon current was found. The TCS has been evaluated using the Beer-Lambert law:

$$I(E) = I_0(E) e^{-n\sigma(E)}$$

where $I_0(E)$ is the initial intensity of the electron beam, $I(E)$ the intensity of the beam after traveling the scattering gas medium, whose average particle number density is $n$. $L$ is the path length of the electron beam through the gas cell; $\sigma(E)$ is determined by measuring the transmitted intensities with and without gas in the cell; $n$ is taken to be equal to $P/kT$, using the ideal gas law, where $P$ is pressure of the target measured with a Baratron, $k$ is the Boltzmann constant and $T$ the absolute gas temperature. The pressure range of the target in the scattering cell was maintained between 1 and 4 mTorr, so that double scattering was negligible. The variation of $\ln(I/I_0)$ with the pressure $P$ in Torr is a straight line whose slope is a measure of the total scattering cross section. An averaging procedure was applied to determine the total cross section at a particular energy. The electron energy resolution in all our measurements was typically 0.7 eV (FWHM). The systematic error that is the quadratic sum of all contributions was evaluated as 5%. An extended discussion about the contribution of different error sources can be found in [2]. Methanol and ethanol vapor was obtained from pure liquid degassed using at least six freeze-pump-thaw cycles. The purities of methanol (Nuclear - Caq-Casa da Quimica Indústria e
comércio Ltda) and ethanol (F. Maia Indústria e Comércio Ltda) were 99.8% and 99.3%, respectively. Although we expect some condensation of methanol and ethanol in our gas lines, gas cell and other elements of the spectrometer, the experiment was conducted without any heating, and consequently at a room temperature of around 25°C.

Elastic scattering cross sections were measured for CH$_3$OH and C$_2$H$_5$OH at 1, 2, 5, 10, 15, 20, 30, 50, and 100 eV at scattering angles from 5° to 130°, with a coarser interval 20° at large scattering angles than at small scattering angles 10°. These data were obtained using a new implementation of the relative flow method [23], in which gas-kinetic molecular diameters are not needed. This method is a simple modification of the conventional relative flow method in which a collimating tube source is replaced by an aperture source using He as a calibration standard [23]. The apparatus and these measurements were discussed in details in [3] and only a brief description will be given here. Cylindrical electrostatic optics and double hemispherical energy selectors were utilized both in the electron gun and in the detector. Energy loss spectra of the elastic peak were collected at fixed incident energies and scattering angles by repetitive, multichannel-scaling techniques. The target gas beam was formed by effusing the gas through a brass aperture of 0.3 mm diameter, located centrally at the end of a tube. The tube was incorporated into a moveable source [24] arrangement which allow determining background scattering rates expediently and accurately. The methanol and ethanol were housed in a flask vacuum coupled to the leak valves used to send the vapor into the gas feed line. American Chemical Society ACS grade (99.94%) purity CH$_3$OH and C$_2$H$_5$OH and high purity He (99.995%) purity were used. Once DCSs were recorded in much lower energy range than TCS measurements, here the feed gas lines were held at 320 K to prevent condensation. It was observed no condensation in these lines was established by reproducing flow rates with increasing and decreasing source drive pressures. To prevent the vapor from condensing in the spectrometer, the spectrometer was heated to about 393 K. This heating stabilized the spectrometer and made scattering rates reproducible, whereas at lower temperatures the analyzer surfaces were affected by the vapor. The calibration of relative flow rate (RFR) vs. the pressure behind the source $P_s$ it was followed the procedure given in [3, 23].

In addition to the experimental data, calculations were performed of elastic DCS for methanol and ethanol using two different implementations of Schwinger multichannel (SMC). The first one, that takes all electrons into account and is adapted to parallel computers, was carried out by the Caltech group of Winstead and McKoy and the other that uses pseudopotentials to replace the core electrons and explicitly includes only the valence electrons, was carried out by Brazilians group of Bettega and Lima. Details of these calculations have been described in detail in reference [3].

3. Results
The present results of TCS for electron scattering by methanol in the energy range from 70 to 500 eV is shown in figure 1, and numerically displayed in table 1 where it is compared to data from others authors [5,7,19,20]. Szmytkowski and Krzysztofowicz [7] reported data were obtained using the same technique in our laboratory, however covering the energy range from 5–250 eV, whilst Vinodkumar et al [20] and Tan and Wang [19] calculated their TCSs using a SCOP method [25] in the incident electron energy region of 5–500eV and revised additivity rule in the energy range from 10 to 1000 eV, respectively. An excellent agreement between our results and the results of Szmytkowski and Krzysztofowicz [7] is verified while the data of Vinodkumar et al. [20] and Tan and Wang [19] are slightly higher for the energies below 90 eV and 200 eV, respectively. This discrepancy increases at lower electron energies, due to forward dipole scattering of the electrons by the target which affects the resultant TCSs. Schmieder et al [5] data are about 15% lower than ours.

TCSs for electrons scattering by ethanol obtained in the energy region of 60 - 500eV are shown in figure 1 and listed in table 2. There are no experimental data of TCSs for ethanol for energies above 50 eV. The only experimental available data published in the literature was published by Schmieder et al [5] covering the energy range from 9 to 49 eV, which are about 25% lower than our results over all studied energy range. We also compared our data to the TCS calculated by Tan and Wang [19]. Their results compared to ours are slightly higher for the energies below 400 eV.
The measured and calculated values of elastic DCS for methanol and ethanol produced was published in reference [3] and will not be shown and discussed in details in this paper, although we should emphasize its importance in the context of this work. The agreement between the measured and calculated values for CH$_3$OH is qualitatively excellent at all energies, although from 1 to 5 eV the calculated results are generally about a factor of 2 smaller than the measured DCS. From 10 to 20 eV, the calculated and measured DCS values agree within the experimental uncertainty at almost all angles. The SMCPP results for methanol include polarization effects up to 10 eV, while the results above 10 eV were obtained in the static exchange (SE) approximation. The results at 50 eV and 100 eV were obtained only with the SMCPP method. The largest differences between experiment and theory occur at lower impact energies, where the differences between the two calculations are also largest; this may reflect limitations in the treatment of polarization but may also be due to differences in the partial-wave cutoff for the Born-dipole corrections.

![Figure 1: Absolute Total Cross Section for electron scattering by methanol and ethanol. The bars correspond to standard deviation absolute uncertainties. Legend: (●) present work; (—) Tan and Wang [19]; (---) Vinodkumar et al. [20] (■) Szmytkowski and Krzysztofowicz [7] and (V) Schmieder et al. [5].](image)
Table 1: TCS obtained in this work for methanol compared to results of Schmieder *et al.* [5], Szmytkowski and Krzysztofowicz [7], Vinodkumar *et al.* [20], and Tan and Wang [19] in units of $10^{-30} \text{m}^2$.

| Energy (eV) | this work | Ref.[5] | Ref.[7] | Ref.[20] | Ref.[19] |
|------------|-----------|---------|---------|---------|---------|
| 10         | 26.40     | 26.05   |         |         | 45.77   |
| 20         | 21.00     | 21.80   | 31.78   | 26.22   |
| 25         | 20.00     | 28.23   |         |         |         |
| 30         | 17.50     | 18.40   | 25.56   | 22.57   |
| 35         | 17.50     | 23.5    |         |         |         |
| 40         | 15.50     | 16.70   | 21.65   | 20.77   |
| 45         |           |         |         |         |         |
| 50         | 14.00     | 15.70   | 18.75   | 19.12   |
| 60         |           |         | 16.82   | 17.64   |
| 70         | 14.26     | 14.30   | 15.34   | 16.40   |
| 80         | 13.58     | 13.50   | 14.23   | 15.36   |
| 90         | 13.05     | 12.90   | 13.35   | 14.46   |
| 100        | 12.36     | 12.40   | 12.59   | 13.67   |
| 110        |           |         | 11.90   |         |
| 120        |           |         | 11.40   |         |
| 140        |           |         | 10.70   |         |
| 150        | 9.97      |         |         |         |
| 160        |           |         | 10.10   |         |
| 180        |           |         | 9.40    |         |
| 200        | 8.50      | 8.81    | 8.58    | 9.04    |
| 220        |           |         | 8.28    |         |
| 250        | 7.45      | 7.55    |         |         |
| 300        | 6.61      | 6.74    | 6.91    |         |
| 350        | 6.29      |         |         |         |
| 400        | 5.74      | 5.65    | 5.59    |         |
| 450        | 5.60      |         |         |         |
| 500        | 5.37      | 4.91    | 4.68    |         |
Conclusions
In this work we have reported TCSs for methanol and ethanol in the electron-impact energy ranges 70 - 500eV and 60 - 500eV, respectively. Our TCS data for methanol are found to be in excellent agreement with experimental TCSs obtained by Szmytkowski and Krzysztofowicz [7] and reasonable agreement with theoretical TCSs of Vinodkumar et al. [20] and Tan and Wang [19]. Our TCS for ethanol are found also to be in reasonable agreement with the only TCS available in the literature, calculated by and Tan and Wang [19] using a revised additivity rule. We applied the relative flow technique with an aperture source [23] coupled with a moveable gas target method [24], to carry out the first measurements of DCSs for methanol and ethanol. Comparison of these measured cross sections with results of calculations is encouraging.

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Table 2: TCS obtained in this work for ethanol compared to results of Schmieder et al [5], and Tan and Wang [19] in units of 10⁻²⁰m².

| Energy (eV) | this work | Ref. [5] | Ref. [19] |
|------------|-----------|-----------|-----------|
| 9          | 36.40     |           |           |
| 10         | 33.88     | 45.77     |           |
| 12         | 33.04     |           |           |
| 16         | 31.22     |           |           |
| 20         | 29.40     | 26.22     |           |
| 25         | 27.72     |           |           |
| 30         | 26.18     | 22.57     |           |
| 36         | 24.92     |           |           |
| 40         | 23.10     | 20.77     |           |
| 42         | 22.12     |           |           |
| 49         |           |           |           |
| 50         | 19.12     |           |           |
| 60         | 25.43     | 17.64     |           |
| 70         | 23.47     | 16.40     |           |
| 80         | 21.81     | 15.36     |           |
| 90         | 20.53     | 14.46     |           |
| 100        | 18.71     | 13.67     |           |
| 150        | 14.52     |           |           |
| 200        | 12.86     | 9.04      |           |
| 250        | 10.60     |           |           |
| 300        | 9.14      | 6.91      |           |
| 350        | 7.93      |           |           |
| 400        | 7.67      | 5.59      |           |
| 450        | 7.40      |           |           |
| 500        | 7.24      | 4.68      |           |
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