Progress towards the measurement of absolute elastic
electron-molecular radical scattering cross sections

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Abstract. We report on our progress in developing a dedicated crossed beam apparatus, for the
measurement of absolute cross sections for elastic scattering of electrons from molecular
radicals. Features which are original to this apparatus will be highlighted, and a discussion of
its current status and future developments provided.

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1. Introduction
It is well known that the control of plasma processing methodology can only be achieved through a
detailed understanding of the properties of plasmas at the nanoscale. Part of this requires a knowledge
of what is usually referred to as plasma chemistry [1], while another relates to the interactions in
plasmas of electrons with neutral species [2]. Note that by neutral species we are not only referring to
the primary feedstock gas of the plasma, we are also considering those secondary species produced in
the plasma (e.g. radicals).

While Christophorou and colleagues [3] have written several reviews on data sets for the most
commonly used semiconductor gases, data on many of the radical species produced in the plasma are
lacking. In addition, as environmental concerns drive industry to explore the use of alternative
feedstock gases, the need for an expanded database has become more pressing. Until now these new
challenges to the ATMOP community have largely been addressed by theorists, with important R-
matrix calculations on CF₃ (x=1,2,3) species being reported by Tennyson and co-workers [4–7] and
some Schwinger variational results for CH₃ (x=1,2,3) and CF₃ being given by Lee and colleagues
[8,9]. Work on CHₓ (x=1,2,3) and NHₓ (x=1,2), as well as an extensive series of fluorocarbons and
their radicals, has also been published by Joshipura and his group [2,10]. We also note the Binary
Encounter-Bethe total ionisation cross sections from Kim et al. [see e.g.11] and a modified form of
this approach, to account for the strong electronegativity of fluorine atoms, from Huo [12].

To the best of our knowledge the only experimental data available in the literature, for electron-
radical scattering, are the total ionisation cross section measurements from Becker and colleagues [12–
15]. As a consequence, we are developing an apparatus to measure absolute elastic differential and
integral cross sections for electron scattering from molecular radicals. Such data, if realised, will
provide a very sensitive test for the validity of the existing theoretical calculations [2,4–10] as well as
expanding the database needed to model plasma behaviour. In the next section we therefore briefly describe the apparatus we are developing, as well as presenting some preliminary results. Finally, in section 3, some conclusions and future directions are described.

2. Experiment

Only a cursory description of the apparatus we are developing to measure absolute cross sections is given now, as full details will be reported elsewhere [16]. The apparatus (figure 1) is a crossed-beam electron scattering experiment comprising three differentially-pumped chambers. The expansion chamber houses the nozzle, the pulsed solenoid valve and the skimmer. The nozzle diameter is 0.8 mm, and the skimmer orifice is 1 mm in diameter. Beams containing molecular radicals are generated by excimer laser photolysis with the addition of a PTFE thermalisation adapter [17]. This adapter, made from solid PTFE and mounted to the nozzle flange, provides a region of high collision rate in order to thermalise the fragmentation products prior to expansion. The nozzle-skimmer separation is variable, but is typically set to 50 mm. The valve is pulsed at 10 Hz and individual gas pulses have 3–5 ms duration. Gas is introduced to the expansion chamber at stagnation pressures in the range of 50–500 mbar, with due care being taken to ensure that the operational stagnation pressure minimises the potential for cluster formation.

![Schematic diagram of the present crossed beam spectrometer.](image)

Figure 1. Schematic diagram of the present crossed beam spectrometer.

The collision chamber houses a differentially pumped hemispherical electron monochromator, which produces a collimated electron beam of well-defined energy in the range 0.5–50 eV and with good energy resolution. The gas pulse enters the collision chamber through the skimmer and crosses the electron beam at 90°. The angular distribution of the scattered electrons is measured simultaneously using a fixed-position multi-detector array containing up to 13 individual detectors. Each detector unit incorporates one channel electron multiplier (CEM), with a retarding potential
analyzer (RPA) mounted before each CEM to prevent detection of inelastically scattered electrons. The combined energy resolution of the spectrometer and RPAs is ~ 1.5 eV [16]. Note that in practice this configuration has a significant advantage over those employed in typical electron-scattering spectrometers. It enables the elastic scattering data to be collected simultaneously, as opposed to the usual case where a lone detector makes a measurement at a single scattering angle (θ) before its rotation to the next θ of interest.

As we employ a skimmed supersonic expansion (SSE) in this apparatus, the theory behind the effusive-beam relative flow method [18], to set the absolute cross section scale, is not applicable here. Hence a new procedure, known as the pressure-rise skimmed supersonic relative density method (p-SSRDM) [19], was developed as a part of this work. Full details of the p-SSRDM can be found in Hargreaves et al. [19] and so we do not repeat that detail again here. Briefly, however, the elastic differential cross section (DCS) of the unknown (U) species is given in terms of that of a reference (R) species by:

\[
\text{DCS}_U = \text{DCS}_R \left( \frac{\Delta P_d^*}{Q_{v\infty} m^{1/2} N_e} \right) \left( \frac{Q_{v\infty} m^{1/2} N_e}{\Delta P_d^*} \right)_R
\]

where \( \Delta P_d^* \) is the corrected measured pressure-rise reading, \( Q \) is the total ionisation cross section for the species of interest at 150 eV, \( v_{\infty} \) is the terminal velocity of the ideal gas molecules in a SSE, \( m \) is the molecular mass and \( N_e \) the measured elastic count rate [19]. As an example of how we tested the applicability of the p-SSRDM, consider the results we obtained for CF\(_4\) employing He as the reference gas (see figure 2). In that work the helium cross sections from [20] were used for the normalisation, while the following 150 eV ionisation cross sections: \( Q_{\text{CF}_2} = 5.71 \text{Å}^2 \) [1] and \( Q_{\text{He}} = 0.33 \text{Å}^2 \) [21] were also employed. The relevant stagnation pressures for CF\(_4\) and He were 120 mbar and 83 mbar, respectively. Note that at these pressures the dimer formation was calculated [19] to be less than 1% in both cases.

Considering figure 2 in more detail, we see that the present p-SSRDM elastic DCSs are in very good agreement, to within the errors on the respective data sets, with the earlier effusive relative flow method results from Boesten et al. [22]. This statement holds at each of the energies considered (15 eV, 20 eV, 30 eV and 50 eV). In addition, at 15 eV, 20 eV and 30 eV, the present results are in excellent agreement with the calculations from Varella et al. [23]. This level of agreement, and a similar level of agreement with elastic DCS for other species [19], gives us confidence in the validity of our p-SSRDM procedure. It is interesting to note that as our apparatus uses a SSE, thereby cooling the incident molecular beam to being predominantly in its lowest rovibrational state, our data mimics the fixed-nuclei approximation of the calculation better than that using a normal effusive source. This point also appears to be supported by figure 2, where the present data is in better agreement with the calculations [23] than the earlier work [22].
Figure 2. Absolute elastic DCS (Å²/sr) for CF₄ at various energies. Present results obtained by the p-SSRDM are shown (○). The effusive beam experiments of Boesten et al. [22] (×) and the Schwinger multichannel calculation of Varella et al. [23] (—) are also shown.

The final stage of the apparatus (see figure 1) is the time-of-flight (TOF) chamber. This chamber contains a linear, Wiley-McLaren type [24], orthogonal-acceleration time-of-flight mass spectrometer (oa-TOFMS). The oa-TOFMS features 380 mm of field-free flight, two ion-acceleration stages producing second-order space focus, and a 118 nm VUV photoinisation source [16]. Full details on the design and performance of this part of the apparatus can be found elsewhere [16], at this time we simply show the results from the oa-TOFMS for a photolysed allene (C₃H₄) beam (see figure 3). It is clear from figure 3 that our oa-TOFMS is capable of unit mass resolution. It is also clear that while propargyl radicals (C₃H₃) and C₃H₂ radicals were produced (in an ~ 10:1 ratio), the overall percentage of the propargyl radical (0.2%) was very low (see figure 3). While such an abundance would have been sufficient for optical spectroscopy studies [25], our preliminary experiments suggest that it is not sufficient for performing statistically meaningful electron-scattering DCS measurements.
Figure 3. A typical TOF Mass Spectrum showing the products from 193 nm photolysis of allene.

3. Conclusions and Future Developments.
We have reported on the development of an apparatus to measure absolute cross sections for electron scattering from molecules and molecular radicals. Our preliminary experiments suggest that further improvement in radical yield from photolysis will be needed, before viable electron scattering experiments will be feasible. As an alternative, using a pyrolysis source might prove to be a more efficient means of radical production in the future. Finally, the present 118 nm photoionisation source restricts us to probing species in the oa-TOFMS with ionisation energies below about 10.5 eV. This limitation might therefore necessitate the development of an in situ electron-beam ionisation source.

4. References
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