

Chapter 3

Normalisation Methods

3.1 Introduction

An absolute DCS, measured in a crossed electron-target beam experiment, is determined by measuring the count rate (\dot{N}^e) of electrons scattered, at a given angle and energy loss, by a collimated beam of the atom/molecule under study. The relationship between the measured scattered electron count rate and the absolute DCS for the scattering process under study is given by:

$$\dot{N}^e = F^e \eta DCS \int_V \int_E \rho \Delta\Omega dE dV, \quad (3.1.1)$$

where F^e is the incident electron flux, η is the detector efficiency function, ρ is the density of the target beam, $\Delta\Omega$ is the solid angle subtended by the scattered electron detector, V is the volume of intersection between the electron and molecular beams and E is the range of electron energies [55].

In practice, explicit characterisation of all the terms in equation (3.1.1) is not feasible. Some reasons for this are: (i) crossed beam experiments typically involve extended interaction volumes with non-uniform target and electron densities; (ii) the effective scattering volume usually depends on the angle of the detector; and (iii) the detector efficiency usually changes with the detected electron energy. Hence, a method of obtaining an absolute normalisation of the DCS was sought.

3.2 Skimmed Supersonic Relative Density Method (SSRDM)

The main idea underpinning the present method is to compare the scattered electron count rate from a target with an unknown (U) DCS, to the count rate from a reference (R) species, whose DCS can be considered as defined. A diagram of the scattering geometry for a crossed beam experiment featuring a skimmed, supersonic gas beam is given in Figure 3.2.1. According to equation (3.1.1), the unknown DCS is expressed in terms of the DCS of the reference species by:

$$DCS_U = DCS_R \frac{\dot{N}_U^e \int \rho_R \Delta\Omega dV dE}{\dot{N}_R^e \int \rho_U \Delta\Omega dV dE}. \quad (3.2.1)$$

The beam density at the intersection of the electron and target beam is expressed as:

$$\rho = \frac{I(\phi)}{v_\infty R^2}, \quad (3.2.2)$$

where $I(\phi)$ is the target beam intensity at the scattering centre, v_∞ is the terminal beam velocity and R is the distance to the gas source [55]. The intensity of the gas beam is factored as $I_0 J(\phi)$, with I_0 the centreline intensity and $J(\phi)$ the relative density distribution [55]. Downstream of the skimmer, $J(\phi)$ is defined as:

$$J(\phi) = \frac{1}{2\pi} \int_0^{2\pi} [\exp(-S_\infty^2 \sin^2(\phi_1))]_{\phi_{1max}(\theta, \phi)}^{\phi_{1min}(\theta, \phi)} d\theta, \quad (3.2.3)$$

where θ is an angle of rotation about the jet axis, ϕ is the angle between the beam centreline and a ray drawn from an off axis point in the scattering volume, back to the nozzle [44]. Explicit evaluation of equation (3.2.3) is not required, provided that the gas jet is in free molecular flow upon reaching the skimmer. Given free flow prevails at the skimmer, ϕ_{1max} and ϕ_{1min} are described solely by the terminal speed ratio of the gas jet and the apparatus geometry [44]. The terminal speed ratio, $S_\infty = v_\infty/v_{therm}$, is defined as the ratio of translational (v_∞) to thermal velocity (v_{therm}) once the gas jet reaches free molecular flow. Since S_∞ is the only species dependent term, the density distribution of the two gas jets can be matched if the speed ratios of the two gas beams are matched and free molecular flow occurs prior to the skimmer. The distance from the nozzle

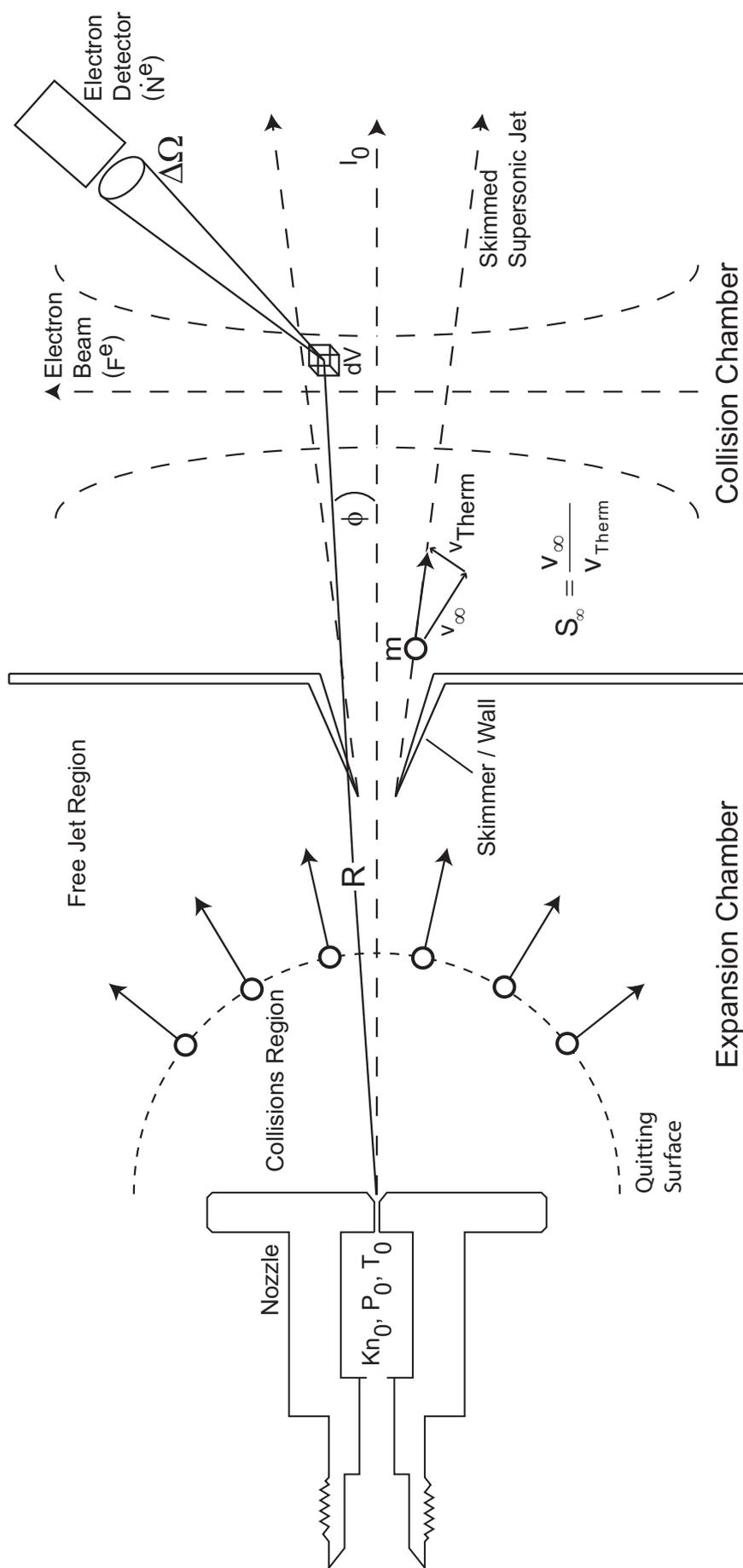


Figure 3.2.1: A schematic diagram of the scattering geometry with a skimmed supersonic gas jet source.

at which free molecular flow is achieved is referred to as the *quitting surface*, x_q , calculated as:

$$x_q \approx d \left(\frac{S_\infty}{C_1} \sqrt{\frac{2}{\gamma}} \right)^{\frac{1}{\gamma-1}} \quad (3.2.4)$$

where C_1 is a gas dependent factor [42], given for several different gases in Table 3.1. Once the relative density profiles of the unknown and reference beams are matched, the integrals in equation (3.2.1) cancel and the unknown DCS is expressed in terms of the reference DCS by:

$$DCS_U = DCS_R \left(\frac{I_0}{\dot{N}^e v_\infty} \right)_R \left(\frac{\dot{N}^e v_\infty}{I_0} \right)_U. \quad (3.2.5)$$

The velocities of the respective molecular beams are given by:

$$v_\infty = \sqrt{\frac{2k_B T_0}{m} \left(\frac{\gamma}{\gamma-1} \right)}, \quad (3.2.6)$$

where T_0 is the stagnation temperature and γ is the adiabatic constant, defined as:

$$\gamma = \frac{f+2}{f}, \quad (3.2.7)$$

where f is the number of degrees of freedom of the gas molecules (translational+vibrational+rotational). When evaluating v_∞ for polyatomic molecules, the value of γ used is an important consideration. The number of vibrational degrees of freedom (V) for an arbitrary non-linear molecule consisting of N atoms is normally evaluated as $V = 3N - 6$ [15]. However, the higher energy excited vibrational modes of molecules at room temperature typically have a very low occupation and may be considered inactive for the purposes of evaluating γ . In the experiments reported in this thesis, excited vibrational modes with energies in excess of 150 meV were considered to be inactive when evaluating γ .

Two final factors need to be determined to produce absolute DCSs according to equation (3.2.5), one is a method to determine the centreline intensity of a skimmed gas beam and the other is a method for matching the speed ratios. Methods for evaluating these factors are subsequently given in Sections 3.2.1 and 3.2.2.

3.2.1 Pressure Rise Method

The first method presented for evaluating the centreline intensity of a skimmed supersonic gas jet is referred to as the pressure rise SSRDM (p-SSRDM). When the relevant gas was admitted to the collision chamber by activating the pulsed nozzle, I_0 downstream of the skimmer was related to the collision chamber's pressure rise, ΔP , by the expression:

$$I_0 = \frac{\Delta P S_P R^2}{\alpha k_B T_c}, \quad (3.2.8)$$

where S_P is the pumping speed in the collision chamber for the gas under study, α is the cross sectional area of the molecular beam in the scattering plane and T_c is the temperature of the collision chamber ($T_c = 298^\circ\text{K}$) [36]. The cross sectional area of the molecular beam at the scattering centre is:

$$\alpha = \pi \left(\frac{x_d - x_s}{S_\infty} + r_s \right)^2 \quad (3.2.9)$$

where x_d is the distance to the scattering centre, x_s is the distance to the skimmer (both distances are relative to the nozzle) and r_s is the skimmer radius. For polyatomic molecules, the terminal speed ratio was approximated to within 10% by:

$$S_\infty \approx 5.4 (P_0 d)^{0.32}, \quad (3.2.10)$$

with $P_0 d$ in units of Torr·cm [56]. The terminal speed ratio for a monatomic or diatomic species is defined in Section 3.2.2.

As the pressure in the collision chamber was measured using an ionisation gauge, the sensitivity of the ion gauge to different gas species needed to be considered. The 150 eV total electron impact ionisation cross section (Q^{ion}) for a particular species was used to correct the pressure reading from the gauge (ΔP^*) by:

$$\Delta P = \Delta P^* \frac{Q_{N_2}^{ion}}{Q^{ion}} \quad (3.2.11)$$

where $Q_{N_2}^{ion}$ is the 150 eV total ionisation cross section for molecular nitrogen [57]. Nitrogen was used as the reference since this gas was originally used to calibrate the gauge. The DCS of the unknown species is now given as:

$$DCS_U = DCS_R \left(\frac{\Delta P^* S_P}{Q^{ion} v_\infty \dot{N}^e} \right)_R \left(\frac{Q^{ion} v_\infty \dot{N}^e}{\Delta P^* S_P} \right)_U. \quad (3.2.12)$$

The total uncertainty in this normalisation procedure, excluding counting statistics and the uncertainty in the reference DCS, was typically between 15-25%. This figure was calculated as the quadrature sum of a 2.5% uncertainty in the pressure rise due to the gauge resolution, a 2.5% uncertainty in the pump speeds, a 10% uncertainty in the each of the speed ratios and the uncertainty in the ionisation cross sections, which was typically between 5-20%. The total uncertainty in the final DCS once statistical uncertainties and the reference DCS uncertainty are included typically ranged between 15-35%, with the exact figure depending on the target.

Pump Speed Determination

The simplest method for determining the relative pumping speed was to apply a scaling law based on the mass of the molecule in the system. For a system evacuated by a turbo pump, the pump speed scales approximately as $m^{1/2}$ [36], while for a diffusion pumped system an $m^{-1/2}$ scaling is a better approximation [58]. However, during the course of this thesis work, these approximations were found to be accurate only to within 30%. Explicit measurement of the pumping speed is therefore recommended in general.

To measure the pumping speed, gas was admitted into the vacuum system by opening the pulsed nozzle while the collision chamber pressure was logged by the control PC. The pulsed nozzle was then closed to allow the pressure in the collision chamber to decay. The pressure in the vacuum chamber decayed with the following time dependence:

$$P(t) = P(0)e^{-t\frac{SP}{V}}, \quad (3.2.13)$$

where t is the elapsed time, $P(0)$ is the pressure when the pulsed valve was closed and V is the volume of the collision chamber. A typical plot of the natural log of the chamber pressure versus time (Figure 3.2.2) is shown. This procedure was conducted for both the unknown and reference gases, with the ratio of the pump speeds then being taken as the ratio of the slopes of each data set. The

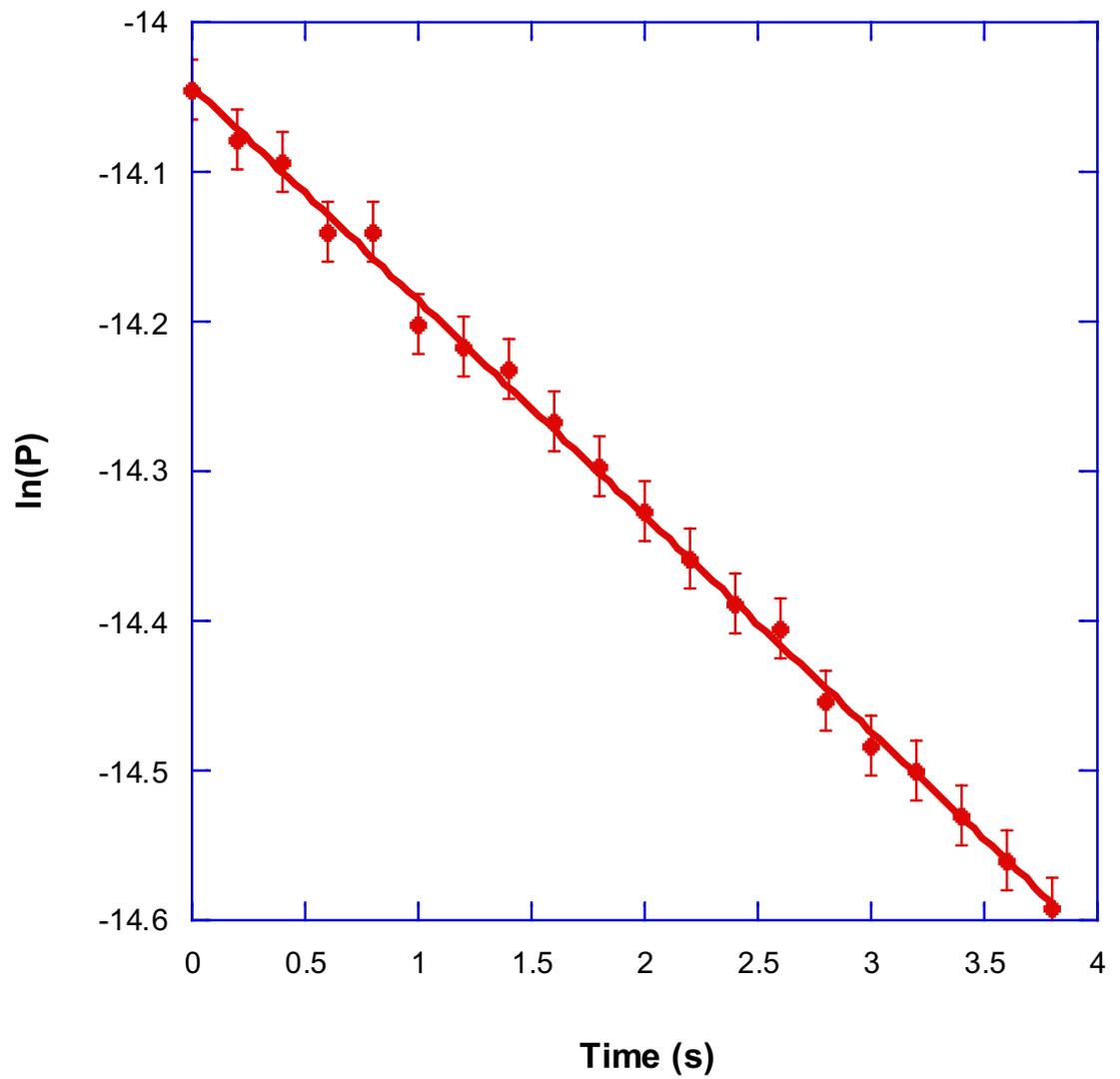


Figure 3.2.2: A plot showing the natural log of the collision chamber pressure, P , (\bullet) as a function of time, once the pulsed nozzle was closed. A linear function has been fitted to the data. The error bars represent the gauge resolution.

uncertainty in each slope was typically $\sim 2.5\%$, resulting in a total uncertainty in the pump speed ratio of $\sim 4\%$.

3.2.2 Transmission Method

An alternative method of normalisation that is more reliant on the theoretical dynamics of supersonic beams than the p-SSRDM is also possible, with this method referred here to as the transmission SSRDM (t-SSRDM). The uncertainty limits in a DCS normalised by t-SSRDM are typically smaller than those obtained using p-SSRDM normalisation, since experimental uncertainties on the measured/estimated parameters (ΔP , S_∞ and Q^{ion}) are not introduced. However, the theoretical description of the interaction between the gas jet and the skimmer-wall system only gives reliable results for monatomic gases [42, 43]. Hence, the t-SSRDM technique is applied here only to monatomic species.

Without the skimmer-wall system in place, the ideal centreline intensity, \mathcal{I}_0 , at the scattering centre [42, 44] is:

$$\mathcal{I}_0 = \frac{\kappa \dot{N}}{\pi} = \frac{\kappa F(\gamma) \rho_0 d^2}{4} \sqrt{\frac{2k_B T_0}{m}}, \quad (3.2.14)$$

where κ is the peaking factor, \dot{N} is the flow rate, ρ_0 is the stagnation density and:

$$F(\gamma) = \left(\frac{\gamma}{\gamma - 1} \right)^{1/2} \left(\frac{2}{\gamma + 1} \right)^{1/(\gamma - 1)}. \quad (3.2.15)$$

The value of κ in equation (3.2.14) is given in Table 3.1 for a given γ . With the skimmer-wall system in place the centreline intensity at the scattering centre, I_0 , is reduced from the ideal value \mathcal{I}_0 . There are three causes of reduction in the centreline intensity (Figure 3.2.3). First, jet molecules leaving the quiting surface with sufficient thermal velocity to cross the centreline at the scattering centre are blocked by the skimmer-wall system. Second, jet molecules scattered by the skimmer-wall may reflect back into the beam centreline upstream of the skimmer resulting in attenuation. Finally, jet molecules scattered by background molecules further reduce the centreline beam intensity below the ideal value.

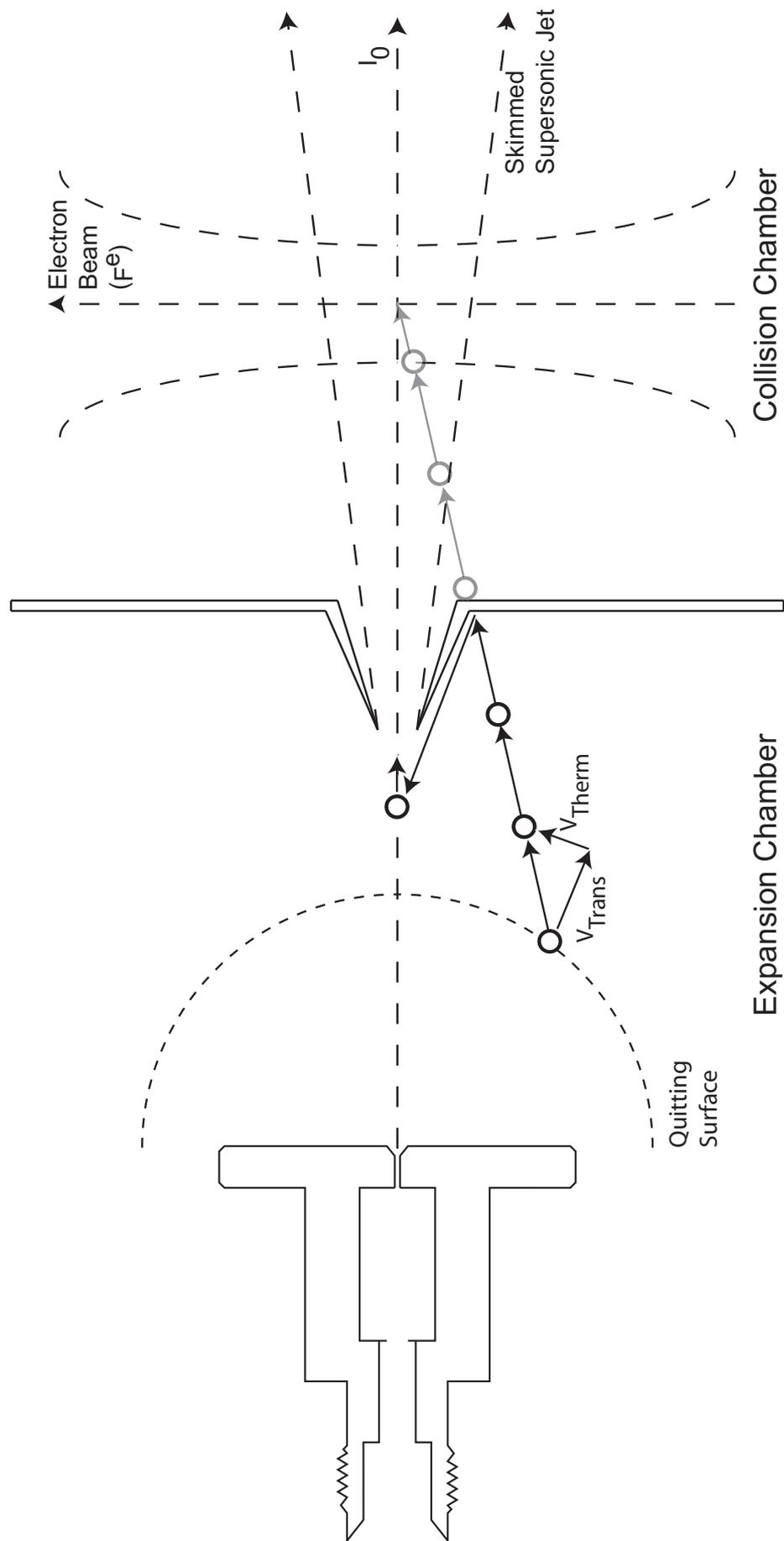


Figure 3.2.3: A schematic diagram illustrating skimmer/wall attenuation of a supersonic jet.

An expression for the beam centreline intensity downstream of a skimmer, under the conditions of $x_q < x_s$ and $S_\infty > 5$ [44], is:

$$I_0 = \mathcal{I}_0 \left(1 - \exp \left[- \left(\frac{S_\infty r_s x_d}{x_q (x_d - x_s)} \right)^2 \right] \right), \quad (3.2.16)$$

where the terminal speed ratio for a monatomic gas is:

$$S_\infty = A (Kn_0)^B. \quad (3.2.17)$$

Here Kn_0 is the source Knudsen number, and the parameters A and B are given in Table 3.1 for different gases [42]. Equation (3.2.16) accounts for the first two causes of attenuation of the centreline intensity for a monatomic gas. In principle, equation (3.2.17) can be used to calculate terminal speed ratios for diatomic or polyatomic expansions. Nonetheless, the results should be considered less reliable [42] as internal relaxations in a molecule release energy into the expansion, increasing v_{therm} and lowering the speed ratio. Equation (3.2.17) is expected to give adequate results for diatomic molecules [42], since the occupation of excited vibrational modes is typically low at room temperature. However, as the number of atoms is increased beyond two, equation (3.2.17) will become an increasingly poor approximation.

The third cause of attenuation, background scattering on the centreline intensity, was quantified by including a Beer's attenuation term into the t-SSRDM normalisation:

$$\frac{I_0}{\mathcal{I}_0} \propto \exp(-bP_0). \quad (3.2.18)$$

Table 3.1: Terminal Speed Ratio Constants. Alternate experimental values are indicated in parentheses. This table has been reproduced from Miller [42].

γ	κ	A	B	C_1
5/3(monatomic)	1.98(2.0)	0.527(0.778)	0.545(0.495)	3.232
7/5(diatomic)	1.38(1.47)	0.783	0.353	3.606
9/7(polyatomic)	1.11(1.18)	1.022	2.610	3.971

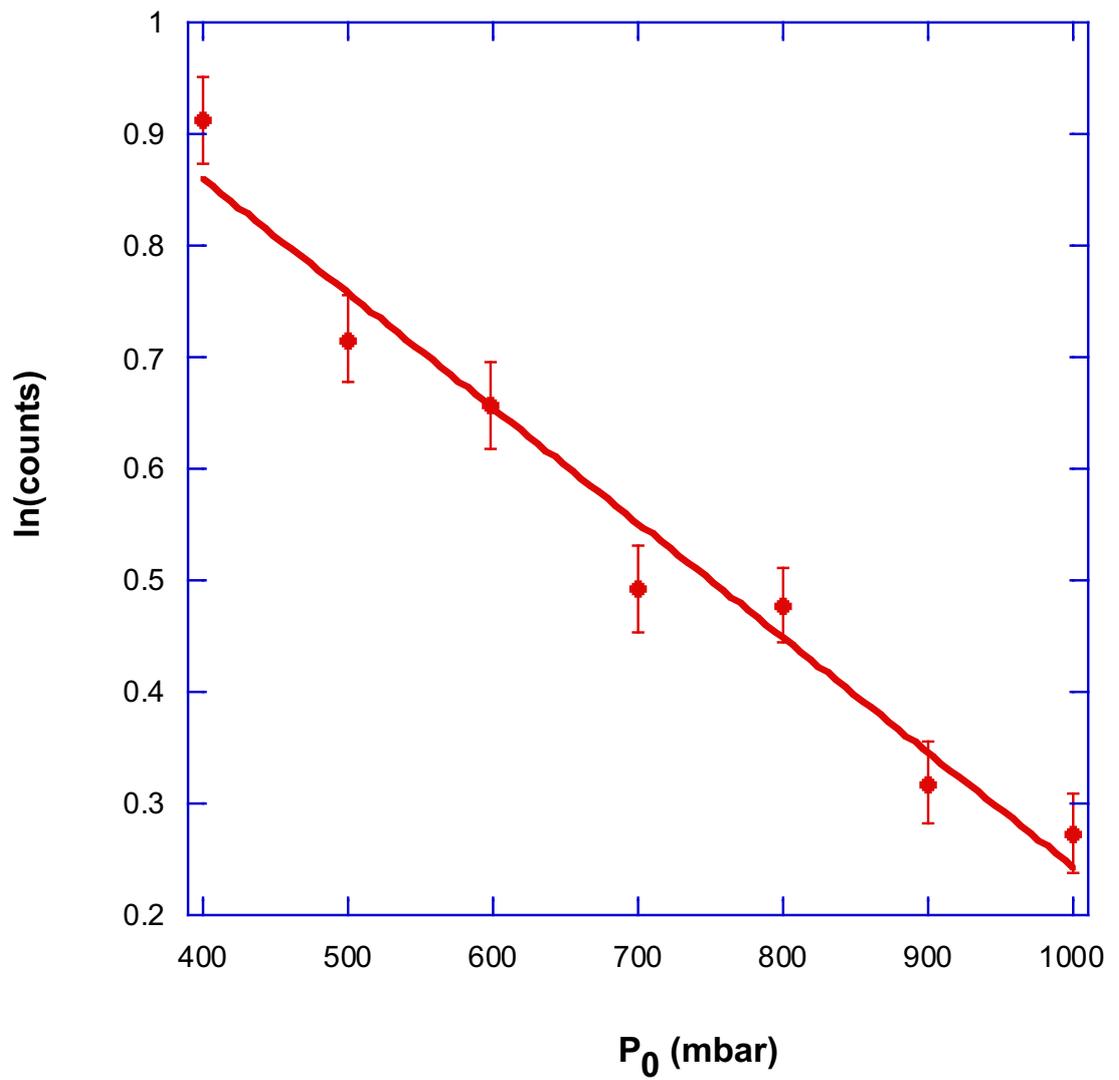


Figure 3.2.4: A typical result for Beers attenuation, shown here in the 120° elastic scattering of electrons from Ar. The error bars represent the variation in the electron counts due to statistical and pulse-by-pulse density variations.

The Beer's parameter, b , was determined by opening the pulsed nozzle to introduce gas into the apparatus at a given driving pressure and then measuring the elastically scattered electron count rate, which was normalised by the skimmer attenuation term (equation 3.2.16). This process was repeated at a series of different driving pressures, the natural log of the normalised counts was then plotted against the driving pressure, and b determined as the slope of a linear fit to the data. A typical result from such an experiment is shown in Figure 3.2.4. Beer's parameters for both the unknown and reference gases were determined using this procedure, with the uncertainty in each parameter being typically $\sim 5\%$.

Once Beer's attenuation constants were determined for both the unknown, b_U , and reference, b_R , gases and included into the t-SSRDM equation, the absolute DCS of the unknown molecule was determined as:

$$DCS_U = DCS_R \left(\frac{P_0 \exp(-b_R P_0)}{\dot{N}^e v_\infty m^{1/2}} \right)_R \left(\frac{\dot{N}^e v_\infty m^{1/2}}{P_0 \exp(-b_U P_0)} \right)_U. \quad (3.2.19)$$

The uncertainty in the t-SSRDM normalised DCS were evaluated as the quadrature sum of 1% statistical variations, 5% uncertainty in each of the Beer's constants, 2% uncertainty in the stagnation pressure due to gauge resolution and the uncertainty in the reference DCS, which for He was 7%. The total uncertainty in the final DCS was therefore typically about 10%.