Appendix A

Photolytic Radical Source

A.1   Introduction

As well as the pyrolytic radical source described in this thesis, the feasibility of producing radicals by 193 nm photolysis of the precursor molecules at the nozzle orifice was also investigated, although ultimately photolysis was abandoned in favour of pyrolysis. In this appendix the photolytic source which was developed is described and characterisation characterisation data presented, in order to give a full appreciation of the scope of the work undertaken in this study. Based on these characterisation results the reasons for discounting photolysis as a viable radical production method, for the present experiment, are discussed.

Photodissociation of a precursor molecule, coupled with supersonic expansion of the molecular beam, has been used extensively for spectroscopic studies of several radicals [83–89]. Radicals are formed by the absorption of photons from a laser beam passed in front of the supersonic nozzle, where the molecular density is at its maximum. Photolysis presents one distinct advantage over pyrolysis, which is the temperature of gas is initially room temperature, so that the radicals can be cooled to low vibrational temperatures in the supersonic expansion.

Experimental Configuration

Radicals were formed by passing 193 nm radiation from a 2 W ArF excimer laser (Lambda Physik LPX 200i) in front of the nozzle as the gas jet exited. The excimer laser was pulsed at a frequency of 10 Hz and the individual pulses were 10 ns in duration. To minimise the production of ozone in the laboratory, the excimer beam was passed through PVC tubes (OD 10 cm) filled with nitrogen gas. The tubes were evacuated by the Alcatel rotary pump prior to nitrogen filling.

The diameter of the laser beam was narrowed using a converging lens (CVI Laser BICX-50.0-308.5-UV) paired with a diverging lens (CVI Laser BICC-25.4-51.8-UV), with the focal lengths coincident. The diameter of the narrowed laser beam was about 4 mm. The excimer beam was not passed through a focus at the photodissociation region, to ensure that the photon flux was low enough to prevent multiphoton absorption events, and also to prevent damage to the excimer optics.

The excimer beam entered the expansion chamber through a fused silica window (CVI Laser PW-2025-UV), and was directed along a path that passed in front of the nozzle and back outside the chamber by a series of coated fused silica mirrors (CVI Laser ARF-1025-45-UP). The beam then exited the vacuum chamber via a second, identical, fused silica window and was collected by an aluminium beam dump which was manufactured in-house.

Thermalisation Adaptor

The process of excimer laser photolysis deposits some of the excess photon energy into the internal degrees of freedom of the dissociated radicals [89], so that the radicals' initial vibrational temperatures are $\sim$1000°C. Even the subsequent vibrational cooling by supersonic expansion is incapable of removing all of the excess energy from these hot radicals.

As well as heating the radical products, the excess laser energy which is not deposited into the internal degrees of freedom of the photolysed radicals will be deposited into the translational degrees of freedom. The resulting recoil momentum is then sufficiently large to remove the photolysed radicals out of the beam before they reach the skimmer. As an example, the required energy for C_2F_4 to dissociate into CF_2 radicals is $2.95\,eV$ [88], leaving an excess energy of $3.47\,eV$ from a single $193\,nm$ photon ($6.41\,eV$). Even assuming that the CF_2 radicals were heated to a vibrational temperature of 10,000°C (a high value), the resulting recoil velocity is still $1440\,ms^{-1}$, compared with a translational velocity of $918\,ms^{-1}$. Thus, the excess laser energy would cause the radicals would fly out of the molecular beam and be undetectable in the TOFMS, $\sim400\,mm$ downstream of the nozzle.

To form a long range beam of radicals a thermalisation adapter [89] was fitted at the front of the nozzle (Figure A.1.1). The thermaliser was a $5\,mm$ thick disc of solid PTFE, with a $2\,mm$ central bore to allow the gas to exit the nozzle. A second $2\,mm$ bore was drilled at right angles through the first, to allow the passage of the excimer laser.

Radicals were produced within the thermaliser, prior to undergoing supersonic expansion. Inside the thermaliser the gas was still effectively at stagnation conditions (P_0, T_0 and with negligible beam velocity). The advantage of adding this thermaliser to the front of the nozzle is that by creating the radicals in this region of high pressure (ie. high collision rate), hot radicals were allowed to relax to a room temperature vibrational distribution before expansion. This meant the radicals would be at low vibrational temperature for the scattering. The collisions inside the thermaliser also served to reduce the thermal motion (recoil momentum) of the radicals back to a room temperature distribution, thus preventing them from recoiling out of the molecular beam.
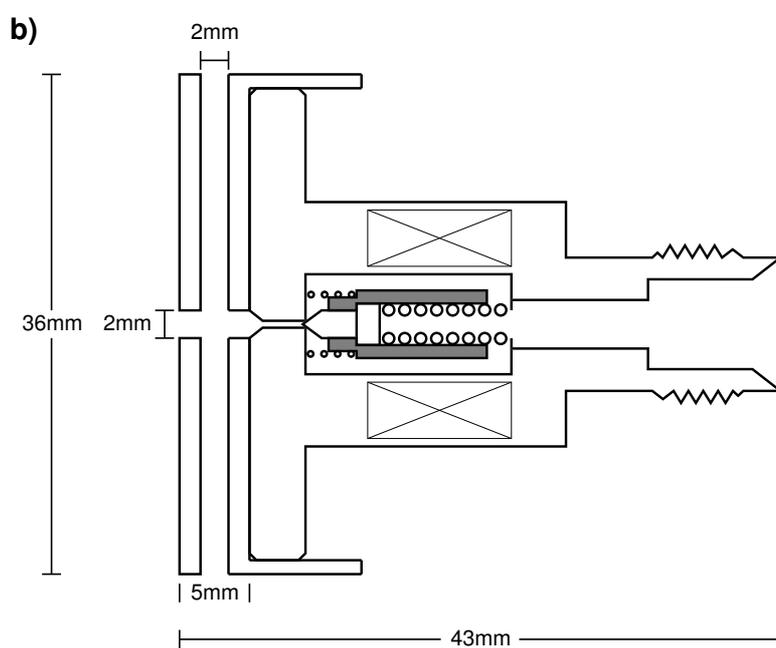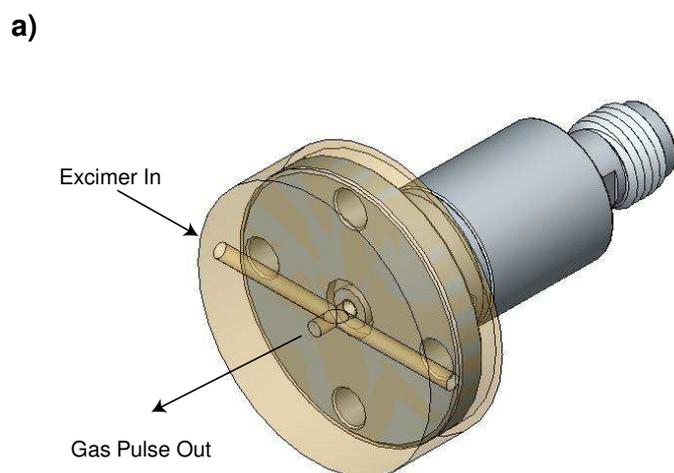
Figure A.1.1: Pictorial representation (a) and schematic diagram (b) of the pulsed nozzle with the thermalisation adaptor fitted.

A.2 Photolysis Characterisations

The characteristics of the photolytic configuration were investigated by studying the 193 nm decomposition of allene (C_3H_4). Allene was chosen as the precursor as all of the photodissociation products, plus allene, can be ionised by 118 nm radiation and so are detectable in the TOFMS. Photolytic decomposition of allene at 193 mn has been previously studied [86, 90] with both studies finding that, in the absence of multiphoton events, the two major dissociation products were propargyl radicals (C_3H_3) and propadienylidene radicals (C_3H_2). The quantum yields of C_3H_3 and C_3H_2 were found to be 0.89 and 0.11, respectively, by both studies. The absolute photoabsorption cross section (σ_{abs}) for allene at 193 nm has also been previously measured as σ_{abs}=0.0150 Å^2 [91]. The absolute partial dissociation cross section is now calculated as the product of the photoabsorption cross section and the quantum yield, yielding cross sections of 0.0134 Å^2 for C_3H_3 production and 0.0017 Å^2 for C_3H_2 production.

Allene was photolysed by the excimer with the thermaliser in place, and the products were detected in the TOFMS. In this initial investigation allene was admitted to the vacuum chamber at a stagnation pressure of 60 mbar and the excimer laser power was set to 20 mJ/pulse. The resulting TOF spectrum is shown in Figure A.2.1.

Since the radicals were created by a 10 ns laser burst, and the gas pulse was in excess of 2.5 ms, then one might assume that radicals were only present within a small section of the total gas pulse. However, since scattered electrons would in principle be detected from the entire gas pulse, the spatial distribution of the radicals within the gas pulse also had to be characterised to determine their total abundance. The distribution of radicals was therefore investigated by varying the time between the YAG and pulser triggers, and recording the C_3H_3 and allene intensity at each time step (Figure A.2.2). This data indicates that C_3H_3 radicals were distributed completely throughout the allene pulse.
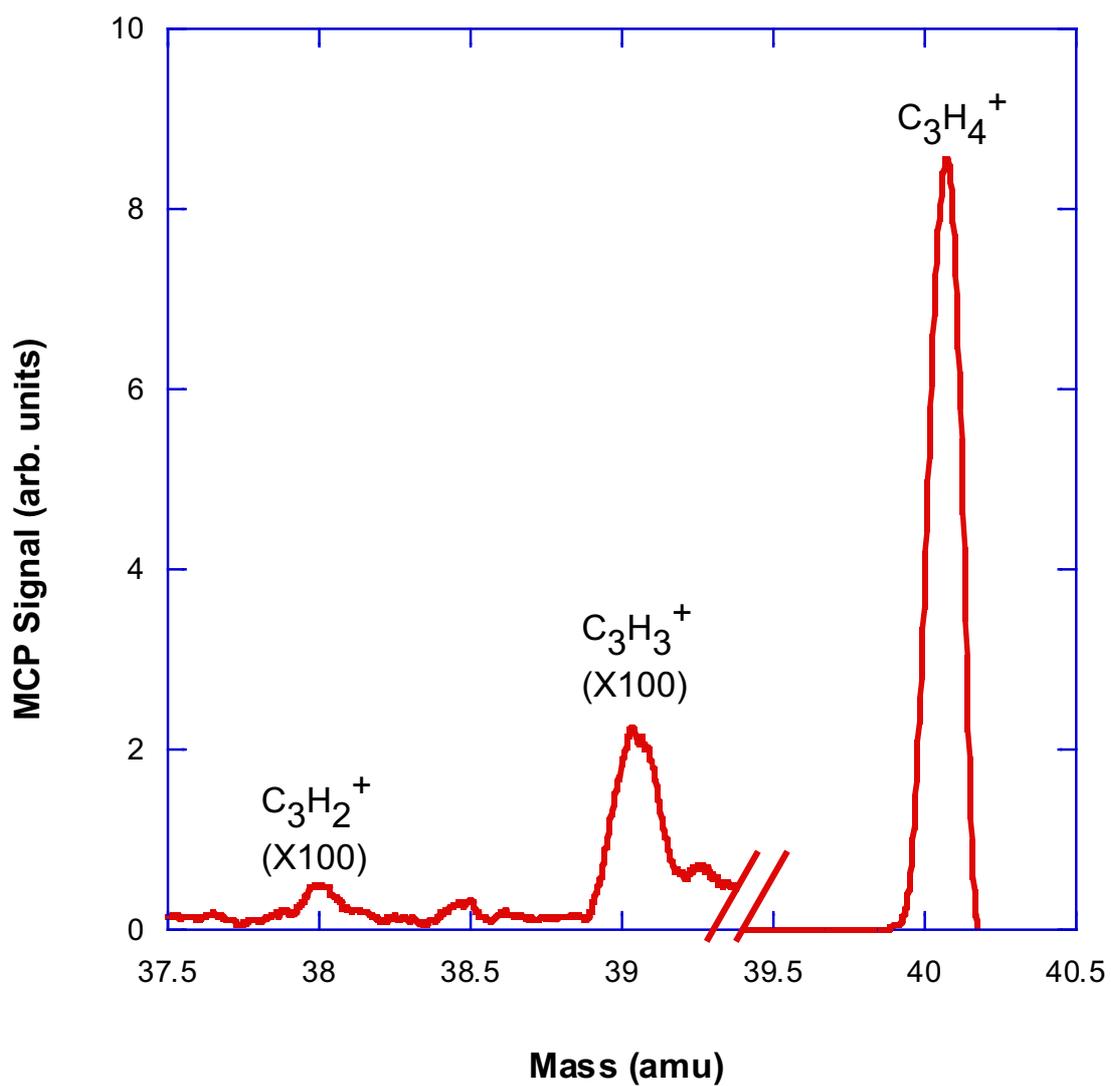
Figure A.2.1: A typical TOF spectrum of the photofragments of allene and the allene precursor. The signal of the photofragments has been multiplied by 100.
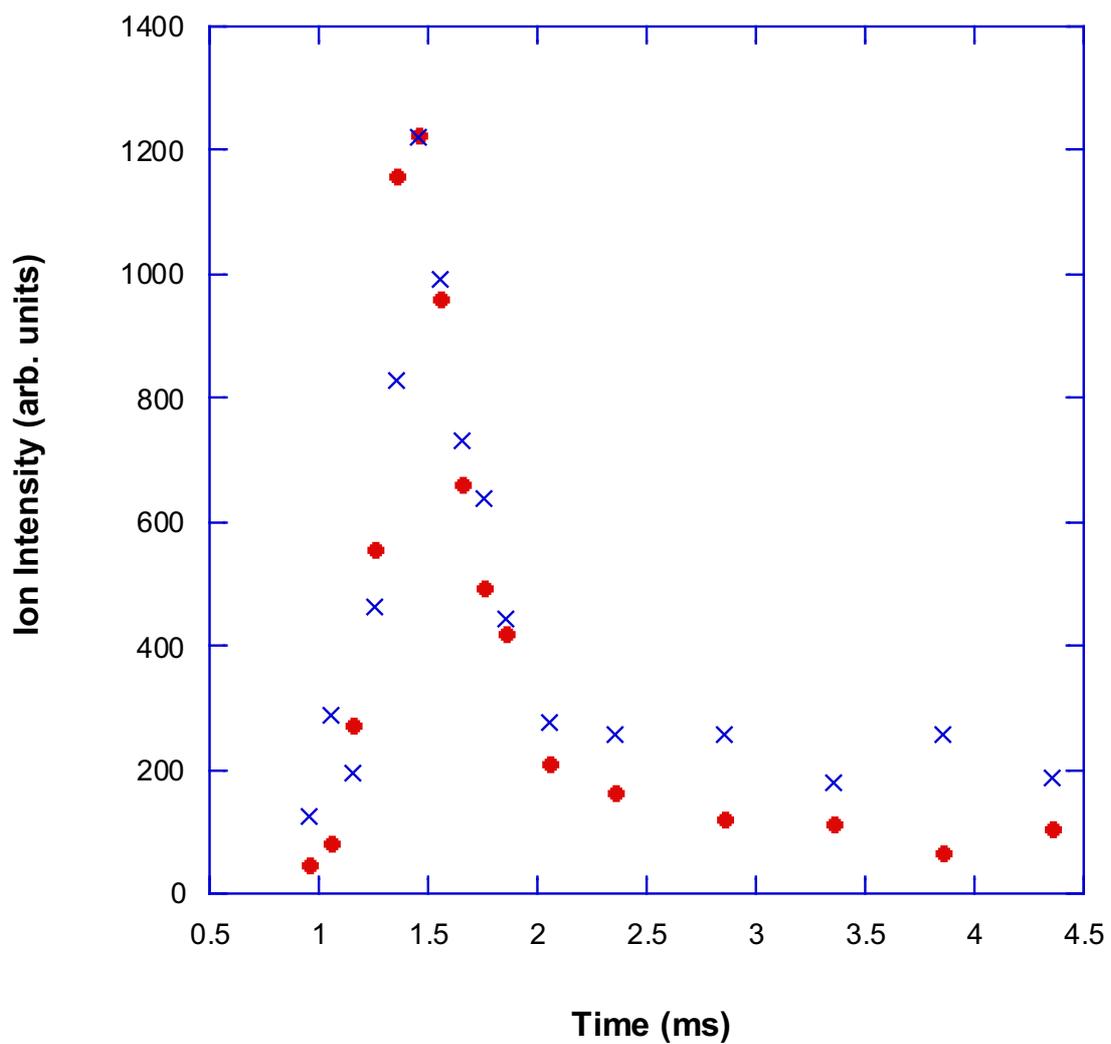
Figure A.2.2: Graph of the intensity of allene molecules (●) and propargyl radicals (×) detected in the TOFMS, as a function of time from the pulser fire. The intensity of propargyl radicals has been multiplied by 624 for clarity.

Two mechanisms were deduced to explain the large radical distribution. The difference in the time taken for the gas pulse to reach the TOFMS, with the thermaliser in and out, indicated that the velocity of the gas pulse inside the thermaliser was $\sim 10\,\mathrm{ms}^{-1}$, compared with $500\,\mathrm{ms}^{-1}$ through the experiment. As the nozzle was opened with a $200\,\mu$s electrical pulse, the gas pulse inside the thermaliser was estimated to be $2\,\mathrm{mm}$ in length. Since the diameter of the laser passage bore in the thermaliser was also $2\,\mathrm{mm}$, the entire gas pulse was potentially irradiated by the excimer laser. Another contributing factor may be that inside the thermaliser, the radicals were collisionally mixed throughout the gas pulse. In any event, based on the result in Figure A.2.2, scanning the entire gas pulse in the TOFMS for every experiment was concluded to be unnecessary as the profiles of the precursor and radicals were largely identical and therefore the concentration could be evaluated at any single point within the gas pulse.

The abundance of radicals within the beam was calculated using the results from Figure A.2.1, using the $118\,\mathrm{nm}$ photoionisation cross sections of $0.190\,\mathrm{\mathring{A}}^{2}$ for allene [92] and $0.088\,\mathrm{\mathring{A}}^{2}$ for the C_3H_2 radicals [93]. Absolute $118\,\mathrm{nm}$ photoionisation cross sections for C_3H_2 radicals are unknown, however, a previous study [86] did show the cross sections for C_3H_3 and C_3H_2 radicals to be approximately equal. The quantum yield of C_3H_3 and C_3H_2 radicals was thus determined to be 0.91 and 0.09, respectively, a result consistent with previous studies [86, 90]. In addition, the data in Figure A.2.1 also yields that the overall abundance of C_3H_3 radicals in the beam is $\approx 0.7\%$.

If the molecular beam contains multiple species, then the DCS which is measured (DCS_{mix}) is a convolution of all the cross sections within the beam. The DCS of a unique radical can then determined by subtracting all contributions from other species to the scattering signal. Using this procedure, the lower bound to the uncertainty, δ_r, of the DCS of a radical r, is then given by δ_{mix}/I_r, where δ_{mix} is the total uncertainty of the mixed beam measurement and I_r is the total abundance of radical r. Therefore, an abundance of 0.7% radicals is unlikely to be sufficient to perform statistically meaningful elastic electron scattering studies.

To investigate whether the concentration of radicals in the beam could be increased, the 193 nm laser power was increased to 60 mJ/pulse. However, the intensity of C_3H_3 radicals was actually seen to reduce, rather than increase (Figure A.2.3). This reduction in C_3H_3 intensity with increased laser power was attributed to multiphoton absorption. No particles at mass 37 amu (C_3H) or 36 amu (C_3) were observed in this spectrum, however, the ionisation energy of C_3 (13.0 eV [94]) is in excess of 10.48 eV, and is unknown for C_3H. In all likelihood then, C_3 and C_3H were not detectable using the current photoionisation source. Ultimately, increasing the excimer power was concluded to create a higher number of side species within the beam by multiphoton absorption, instead of simply increasing the abundance of any one radical.

In another attempt to increase the radical concentration, the excimer power was set at 20 mJ/pulse and the concentration of C_3H_3 radicals measured as the stagnation pressure behind the nozzle was varied (Figure A.2.4). This data shows the concentration of C_3H_3 radicals in the beam decreasing as the stagnation pressure was increased. This result is probably best understood as C_3H_3 radicals being increasingly lost to recombination inside the thermaliser as the gas pressure was raised. At a stagnation pressure of 60 mbar, the elastic electron signal was only just resolved from the background, so further reductions to the stagnation pressure to try and further increase the radical abundance from 0.7% were considered unfeasible.

Photolysis Summary

A photolytic radical source was developed and has been described and characterised using allene as a test system. Experiments were undertaken to optimise the relative concentration of radicals in the molecular beam, but the overall concentration at the optimal conditions remained at <1% abundance.

From the data presented here, a photolytic radical source was concluded to be inappropriate for an elastic scattering experiment with C_3H_3 as the target, since
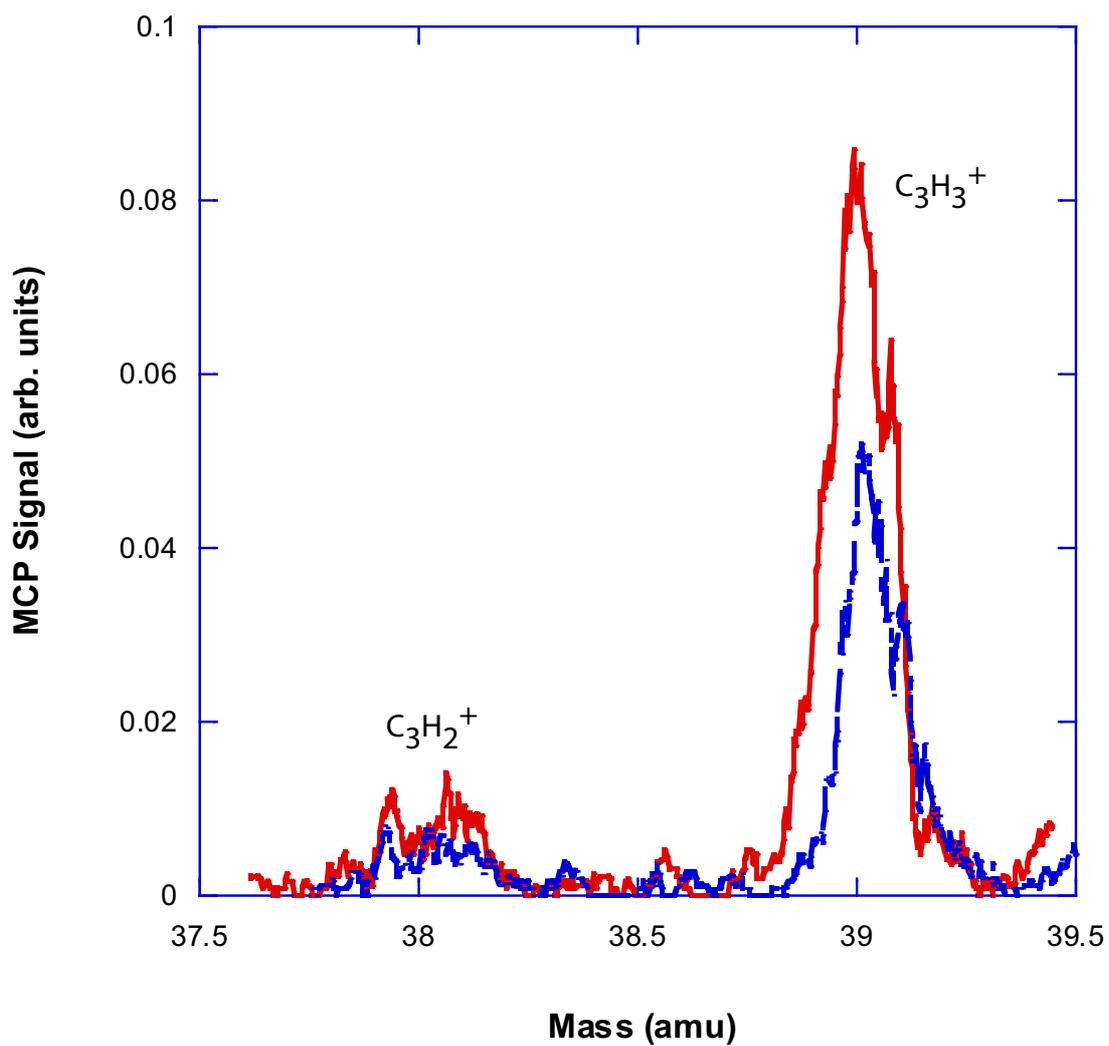
Figure A.2.3: TOF spectrum of the photofragments of allene, at excimer laser powers of 20 mJ/pulse (solid curve) and 60 mJ/pulse (dashed curve).
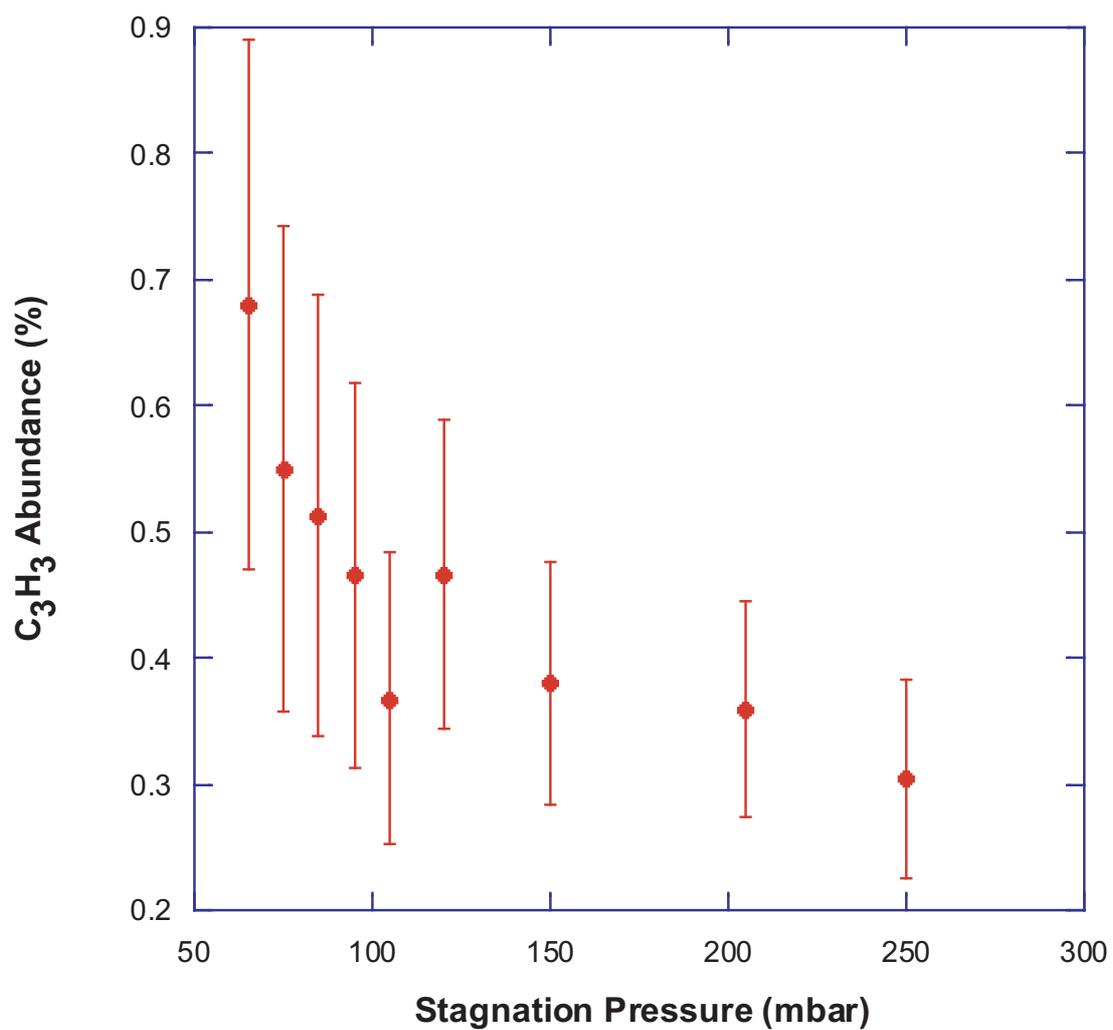
Figure A.2.4: Measured concentration of C_3H_3 radicals ($\bullet$) as a function of stagnation pressure. The error bars represent a quadrature sum of the statistical variations in the C_3H_3 and allene intensities.

realistically the radicals needed to constitute the predominant fraction of the target beam for an experiment to be viable. However, the possibility that a different chemical system with a significantly higher photolysis efficiency might exist, which in principle could form a viable target for an elastic scattering experiment, could not be totally discounted. For example, the photodissociation cross section for C_2F_4 into CF_2 radicals is $0.0521\,\text{Å}^2$ ($\sigma_{abs} = 0.0521\,\text{Å}^2$ [88], quantum yield of 1), an increase of a factor of 3.5 over an allene precursor. As well as a higher absorption cross section than allene, each dissociation in this system yields two CF_2 radicals, thus further increasing the yield. Given equivalent stagnation conditions to the allene experiment, the concentration of CF_2 radicals from C_2F_4 should be approximately 5%. However, even this significant improvement would still be insufficient for CF_2 to form the predominant fraction of the molecular beam.

A study of C_2F_4 photolysis into CF_2 radicals was conducted, to confirm whether or not C_2F_4 was a viable precursor. Since CF_2 radicals could not be detected in the TOFMS, the dissociation was characterised by monitoring the loss of C_2F_4 in the TOF spectra when the excimer was turned on. However, even with the C_2F_4 intensity within the TOFMS determined to better than 1% uncertainty for both the laser on and laser off spectra, no statistically significant difference was seen between the two spectra. The literature was further surveyed in an attempt to identify a target with a significantly higher dissociation cross section than C_2F_4, however this survey failed to yield a chemical system for which an elastic electron scattering experiment seemed likely to be viable.