



UNIVERSITY OF LEEDS

This is a repository copy of *An instrument to measure fast gas phase radical kinetics at high temperatures and pressures*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/99591/>

Version: Accepted Version

Article:

Stone, D, Blitz, M orcid.org/0000-0001-6710-4021, Ingham, T et al. (3 more authors) (2016) An instrument to measure fast gas phase radical kinetics at high temperatures and pressures. *Review of Scientific Instruments*, 87. 054102. ISSN 0034-6748

<https://doi.org/10.1063/1.4950906>

Reuse

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

1 **An instrument to measure fast gas phase radical kinetics**
2 **at high temperatures and pressures**

3
4 **Daniel Stone,¹ Mark Blitz,^{1,2} Trevor Ingham,^{1,2} Lavinia Onel,¹ Diogo J. Medeiros¹**

5 **and Paul W. Seakins^{1,2}**

6 ¹ School of Chemistry, University of Leeds, Leeds, UK

7 ² National Centre for Atmospheric Science, University of Leeds, Leeds, UK

8
9 **Abstract**

10 **Fast radical reactions are central to the chemistry of planetary atmospheres and combustion**
11 **systems. Laser-induced fluorescence is a highly sensitive and selective technique that can be used to**
12 **monitor a number of radical species in kinetics experiments, but is typically limited to low pressure**
13 **systems owing to quenching of fluorescent states at higher pressures. The design and characterisation**
14 **of an instrument is reported using laser-induced fluorescence detection to monitor fast radical kinetics**
15 **(up to 25,000 s⁻¹) at high temperatures and pressures by sampling from a high pressure reaction region**
16 **to a low pressure detection region. Kinetics have been characterised at temperatures reaching 740 K**
17 **and pressures up to 2 atm, with expected maximum operational conditions of up to ~ 900 K and ~ 5**
18 **atm. The distance between the point of sampling from the high pressure region and the point of**
19 **probing within the low pressure region is critical to the measurement of fast kinetics. The**
20 **instrumentation described in this work can be applied to the measurement of kinetics relevant to**
21 **atmospheric and combustion chemistry.**

25 Introduction

26 The kinetics of gas phase reactions involving free radicals are central to the chemistry of planetary
27 atmospheres (1), interstellar space (2,3) and combustion systems (4). A variety of experimental approaches
28 exist for the extraction of rate coefficients; for radical reactions, real-time measurements monitoring the
29 removal of reagents or generation of products following the production of radicals by laser flash photolysis
30 (LFP) is a successful approach (5). Laser-induced fluorescence (LIF) spectroscopy is commonly employed in
31 flash photolysis experiments to monitor changes in radical concentrations throughout the course of a reaction
32 in real-time, thus enabling determination of kinetic parameters. LIF is a highly sensitive and selective
33 technique, with the sensitivity to measure OH radical concentrations in the atmosphere at concentrations of
34 less than 10^6 cm^{-3} (6) and the selectivity to distinguish between isotopic species such as ^{16}OH and ^{18}OH (7).
35 The nature of LFP-LIF, where the reaction is monitored only where the photolysis and probe lasers intersect,
36 significantly reduces the potential for the influence of heterogeneous chemistry compared to flow methods.
37 However, LIF spectroscopy is typically limited to low pressure regimes (typically $< 0.5 \text{ atm}$) owing to
38 collisional quenching of fluorescent states at higher pressures. Whilst many bimolecular rate coefficients are
39 pressure independent, and hence results determined at low pressures can be used in chemical models (e.g.
40 combustion simulations) at higher pressures, association and dissociation reactions are pressure dependent
41 (8). Although it is sometimes possible to determine the high pressure limiting rate using isotopic (9) or proxy
42 (10) methods, determination of rate coefficients over a wide range of temperature and pressure is important
43 to verify theories of reactions (11) and provide kinetic input into models. Pressures in the 1 – 10 atm range
44 are particularly relevant in elucidating autoignition processes (4,12), a subject of topical interest due to the
45 role of autoignition in homogenous charge compression ignition (HCCI) and related engines (13,14).

46 Saturated laser-induced fluorescence (SLIF) spectroscopy has been successfully used to minimise the
47 influence of collisional quenching on observed fluorescence signals at high pressures (15-18), and thus to
48 enable determination reaction kinetics of reactive species at high pressures (up to 150 bar in He (15)).
49 However, the technique requires sufficiently strong laser powers to ensure stimulated emission dominates
50 over spontaneous emission and collisional quenching and can be affected by non-uniform saturation (15). In

51 addition, consideration of rotational energy transfer (RET) schemes are required which can complicate data
52 analysis (15-17).

53 Absorption methods do not suffer from quenching and have the added advantage of providing
54 absolute measurements if cross-sections are known. However, simple absorption methods are significantly
55 less sensitive than LIF, although modulation methods can enhance sensitivity (19). Cavity ring down
56 spectroscopy (CRDS) generally provides a significant enhancement in sensitivity (20-22), but as with other
57 absorption techniques there are practical issues in maintaining uniform temperatures over the absorption
58 region, determining the region of overlap with photolysis, avoiding surface effects and additionally keeping
59 cavity mirrors aligned over wide pressure and temperature ranges. Thus, whilst other detection methods exist
60 (and indeed, using a variety of methods is important to identify systematic errors), LIF has significant
61 advantages in sensitivity, selectivity and minimising heterogeneous interferences.

62 In this work, we describe the use of LIF at low pressures (~ 1 Torr) in the Fluorescence Assay by Gas
63 Expansion (FAGE) technique (23) to determine reaction kinetics of reactive species at higher pressures (> 1
64 atm). The FAGE technique is used by several groups worldwide (6,24-31) to measure OH radical
65 concentrations in the atmosphere, and relies on sampling gas from a region of high pressure through a
66 pinhole nozzle to a region of low pressure, resulting in a supersonic expansion to form a free jet. Expansion
67 of the gas significantly reduces the rate of collisional quenching of fluorescent states, thus permitting LIF
68 spectroscopy within the low pressure region.

69 Field instruments to measure the total loss rate of OH in the atmosphere (k'_{OH} , the OH reactivity) are
70 currently in operation which use LFP in conjunction with LIF-FAGE to make real-time measurements of OH
71 radical kinetics with ambient concentrations of trace gases at atmospheric pressure (31-38). These
72 instruments rely on flash photolysis of O_3 (followed by the subsequent reaction of $\text{O}(^1\text{D})$ with water vapour)
73 to produce relatively high concentrations of OH radicals in a reaction cell containing a flow of ambient air at
74 atmospheric pressure. The subsequent OH decay, owing to reactions with trace gases in the ambient air, is
75 monitored by sampling from the atmospheric pressure reaction cell to the low pressure (~ 1 -2 Torr) FAGE
76 cell for detection by LIF.

77 However, ambient OH reactivity is typically low compared to reaction rates used in laboratory
78 experiments, maximum reported values of k'_{OH} reaching $\sim 100\text{-}120\text{ s}^{-1}$ even in polluted environments
79 (37,39,40). Calibrations of OH reactivity instruments using known reactant concentrations report deviations
80 from expected kinetics at higher reactivities, with non-exponential behaviour reported for some instruments
81 at reactivities $> 60\text{ s}^{-1}$ (33). Such conditions correspond to a very small dynamic range for laboratory
82 experiments.

83 In this work we present the design and characterisation of an instrument to determine fast radical
84 kinetics at high pressure and temperatures up to 740 K by coupling flash photolysis in a high pressure
85 reaction cell to LIF in a low pressure detection cell using the FAGE technique. The use of flash photolysis to
86 initiate the chemistry significantly lowers the potential for interference from heterogeneous chemistry. In
87 addition to applications in combustion chemistry, we discuss the kinetic limitations of OH reactivity
88 instruments employing similar designs, with suggestions for potential improvements. While the focus in this
89 work is on OH kinetics, results are widely applicable to other species observable by LIF.

91 **Experimental**

92 Figure 1 displays a schematic of the instrument. The high pressure reaction cell consists of a stainless
93 steel tube (304L grade) of 19 mm I.D., and length of 1 m to ensure sufficient preheating of the gas, if
94 necessary, prior to the region near the pinhole. Gases, prepared at known concentrations and pre-mixed at
95 known flow rates, as determined by calibrated flowmeters, are passed in to the reaction cell at one end
96 through a T-piece which also houses a window to enable propagation of the photolysis laser beam (Lambda
97 Physik, Compex 200 operating on either ArF at 193 nm or KrF at 248 nm, beam dimensions of 24 mm \times 12
98 mm expanded to fill the diameter of the cell) through the cell to initiate chemistry and produce a uniform
99 distribution of radicals throughout the cell. Precursor concentrations in the cell are maintained sufficiently
100 low such that attenuation of the photolysis laser beam along the length of the reaction cell is negligible,
101 leading to uniform radical concentrations along the length of the cell. The repetition rate of the photolysis

laser was varied between 1 and 10 Hz, with no impact on the observed kinetics. Gas flows in the cell are maintained under laminar conditions (Reynold's number, $R_e < 2300$ for laminar conditions).

At the other end of the reaction cell, the 19 mm I.D. tube is open and housed within a pressure-sealed chamber (70 mm I.D. and 200 mm in length) which couples the reaction cell to the low pressure FAGE detection cell. The open end of the reaction cell is 5 mm from the 0.5 mm pinhole nozzle which is mounted on a flat plate and enables sampling of the gas from the high pressure reaction cell into the detection cell. The flow rate of gas through the detection cell is ~ 1.2 slm (for a detection cell pressure of ~ 1 Torr), with any excess gas in the reaction cell passed out through the pressure-sealed chamber, which is connected to a rotary pump (Edwards 210 ED660). Control of the total pressure within the reaction cell is achieved by throttling the exit valve to the pump.

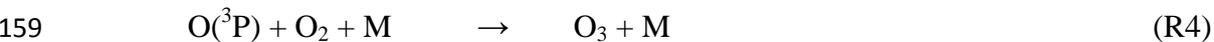
The temperature of the gas in the reaction cell is controlled by varying the voltage applied to a heating coil (Watlow, WATROD tubular heater) surrounding the reaction cell within the pressure-sealed chamber. Pre-heating of the gas to achieve a longer residence time in the heated region can be achieved using a ceramic heater (Watlow, ceramic fiber heater, VS102A18S) situated around the reaction cell prior to the heating coil within the pressure-sealed chamber. Three K-type thermocouples (Omega) are situated along the length of the heated region of the reaction cell to monitor the temperature.

Pressure in the detection cell is maintained at ~ 1 Torr by a rotary pump (Edwards 210 ED660) backed supercharger pump (EUROSERV). OH radicals in the gas flow are monitored by off-resonance laser-induced fluorescence following excitation at 282 nm ($A^2\Sigma(v'=1) \leftarrow X^2\Pi(v''=0)$, $Q_1(1)$), generated using the 532 nm output of an Nd:YAG (Spectron Laser Systems) to pump a dye laser (Spectron Laser Systems) operating on Rhodamine-6-G dye. While 308 nm laser light offers the potential for higher sensitivity (41,42), temporal gating would be required to discriminate the fluorescence emission from scattered laser light. The 282 nm probe laser beam is passed through the detection cell perpendicular to the direction of gas flow at a variable distance (between 5 and 200 mm) from the sampling point of the gas from the reaction cell (i.e. from the position of the pinhole). The off-resonant OH fluorescence at ~ 308 nm is passed through an interference filter (Barr Associates, 308 ± 5 nm) and detected by a channel photomultiplier (CPM, Perkin-Elmer C1943P) mounted perpendicular to the plane of the gas flow and probe laser beam.

129 The time delay between photolysis and probe laser pulses is controlled by a digital delay generator
130 (BNC DG535) and varied to enable monitoring of the OH profile as a function of time following photolysis
131 of the gas mixture. Kinetic traces typically consist of 200 data points, with each data point typically averaged
132 5-10 times. OH signals are monitored before, during and after the photolysis laser pulse at several known
133 reactant concentrations. The pseudo-first-order rate coefficient (k' , where $k' = k_{\text{OH+X}}[\text{X}]$) is determined by
134 fitting an exponential decay to the observed OH signal. The bimolecular rate coefficient (i.e. $k_{\text{OH+X}}$) is
135 obtained from the gradient of the bimolecular plot (i.e. the plot of the pseudo-first-order rate coefficient
136 against $[\text{X}]$, the known concentration of reactant X).

138 **Instrument characterisation at room temperature**

139 Initial experiments to characterise the instrument and optimise experimental parameters were
140 performed at a temperature of 298 K, total pressure of 1000 Torr, and a total flow rate of 18 slm to measure
141 the well-known kinetics of $\text{OH} + \text{CH}_3\text{OCH}_3$ (dimethyl ether, DME) (18,43) by flash photolysis of
142 $\text{O}_3/\text{H}_2\text{O}/\text{DME}/\text{O}_2/\text{N}_2$ gas mixtures. O_3 was generated from O_2 by a commercial ozone generator (EASELEC,
143 Ozone Technology, ELO-3G), diluted in N_2 to $\sim 1\%$ by volume and stored in an aluminium cylinder (Luxfer
144 Gas Cylinders M4141) at a total pressure of ~ 6000 Torr. DME (Sigma-Aldrich, $\geq 99\%$) was diluted to a
145 known concentration in N_2 and also stored in an aluminium cylinder. Cylinders were stored overnight prior
146 to use to ensure complete mixing, and were used within one week of preparation. No significant differences
147 were observed between experiments using cylinders stored for different periods of time. Water vapour was
148 introduced to the gas flow by passing the carrier gas (N_2) through a bubbler containing distilled water. N_2
149 (BOC, 99.99%) and O_2 (BOC, 99.999%) were used as supplied. OH radicals were produced in the reaction
150 cell by the photolysis of O_3 ($\lambda = 248$ nm), followed by the subsequent reaction of $\text{O}(^1\text{D})$ with water vapour
151 (R1-R2). Concentrations of O_2 were sufficient to ensure that any $\text{O}(^3\text{P})$ formed was rapidly converted back
152 to O_3 (R3-R4). Initial OH radical concentrations were $\sim 1 \times 10^{12} \text{ cm}^{-3}$, estimated from the laser fluence and
153 ozone absorption cross-section at $\lambda = 248$ nm. DME concentrations were sufficient to ensure pseudo-first-
154 order conditions for reaction with OH (R5). While there is the potential for some regeneration of OH
155 through reaction of CH_3OCH_2 with O_2 , the extent of this was small at the pressures used here (44).



161 Figures 2 and 3 show the observed temporal behaviour of OH and corresponding bimolecular plots
162 for the reaction of OH with DME. At a probe distance (i.e. the distance from the pinhole, where gas is
163 sampled from the high pressure reaction cell, to the probe laser, as shown in Figure 1) of 5 mm, the observed
164 OH decay was well-described by pseudo-first-order kinetics and the bimolecular rate coefficient obtained for
165 OH + DME, $k_{OH+DME} = (2.6 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, is in good agreement with recent determinations of
166 $k_{OH+DME} = (2.7 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (18) and $k_{OH+DME} = (2.9 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (43) and literature
167 recommendations of $k_{OH+DME} = (2.8 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (45) at 298 K. The signal-to-noise ratio of the OH
168 measurements is estimated at ~50:1 (Figure 2), and can be improved through use of alternative OH radical
169 precursors not requiring the presence of large amounts of water vapour, which efficiently quenches the OH
170 fluorescent state. The sensitivity of the instrument described in this work is approximately a factor of ten
171 lower than that achieved in a standard time-resolved LIF experiment conducted at pressures up to ~100 Torr
172 ((43), for example). Although the number density of OH is reduced on expansion into the FAGE detection
173 cell, the reduction in temperature associated with the expansion results in significantly increased population
174 of the $X^2\Pi (v''=0)$, $Q_1(1)$ state probed in the experiment, reducing the impact of the decreased number
175 density in the FAGE cell.

176 Measurements of the rate coefficients of reactions of OH with methane (CH_4) (see below and
177 supplementary information for further information (46)) and isoprene (2-methyl-1,3-butadiene, C_5H_8) (see
178 supplementary information for further information (46)) have also been obtained at probe distances of < 5
179 mm in agreement with literature values (45), with pseudo-first-order rate coefficients of up to ~25,000 s^{-1}
180 measured in this work.

181 When probing the OH signal further away from the pinhole a significant rise time was noted for the
182 OH signal (Figure 2b, Figures S1 and S3 in supplementary information (46)) and the resulting bimolecular
183 plots (Figure 3b, Figures S2 and S4 in supplementary information (46)) produced a bimolecular rate
184 coefficient that was approximately a factor two lower than the literature values. This is discussed further
185 below.

187 **Characterisation of temperature and pressure**

188 Subsequent experiments were performed to characterise the instrument as a function of temperature.
189 Figure 4 shows the temperature profiles along the reaction cell, measured by a K-type thermocouple (Omega)
190 situated in the centre of the gas flow in the reaction cell at varying distances from the point at which gas is
191 sampled. Temperature profiles were found to be constant in the region of the reaction cell immediately prior
192 to the sampling point for at least 10 cm (the total heating region using the heating coil alone is ~ 18 cm in
193 length). For a gas flow of ~ 5 slm, a distance of 1 cm in the reaction cell corresponds to a residence time of ~
194 18 ms. Temperatures are monitored throughout experiments by three K-type thermocouples situated along
195 the length of the heated region.

196 Kinetics of the reaction between OH and methane, CH₄, were obtained at various temperatures and
197 pressures to characterise the instrument as a function of temperature and pressure. OH was generated by the
198 photolysis of H₂O ($\lambda = 193$ nm) and detected at a probe distance of 5 mm from the sampling point in all
199 cases. The OH + methane reaction was chosen for validation as it is well characterised (45,47), has a strong
200 temperature dependence (hence a sensitive probe of the reaction temperature) and at low temperatures is a
201 slow reaction ($k_{298\text{ K}} = 6.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$) (45); reproducing literature rate coefficients at low temperatures
202 therefore suggests an absence of interfering radical-radical reactions (47). Concentrations of CH₄ (BOC, 100
203 %, CP Grade, used as supplied) were sufficient to ensure pseudo-first-order conditions for OH + CH₄ at all
204 temperatures. Total flow rates in the reaction cell were varied between 5 slm and 18 slm, with no significant
205 effect on the observed kinetics.

Figure 5 shows the bimolecular rate coefficients ($k_{\text{OH}+\text{CH}_4}$) determined in this work at temperatures in the range 298 to 740 K and pressures up to 2 atm. Results obtained with this experimental approach are in good agreement with those reported previously in the literature (48-50), and those currently recommended for use in atmospheric (45) and combustion models (51).

The maximum temperatures and pressures reported in this work are primarily a result of current safety constraints. To achieve the maximum temperature of 740 K reported in this work, the coil heater is operating at ~75 % of its maximum power, with an expected maximum achievable temperature of ~ 900 K, while current gas fittings and components within the system are specified to operate up to ~ 5 atm. It is thus expected that higher temperatures and pressures could be readily achieved with this instrument than are reported in this work.

Effects of probe distance

Measurements of $k_{\text{OH}+\text{DME}}$ and $k_{\text{OH}+\text{CH}_4}$ obtained using the experimental approach described above compare favourably with previous measurements for experiments conducted here using a short (≤ 5 mm) probe distance (i.e. the distance from the point of sampling from the high pressure reaction cell at the pinhole nozzle to the point at which the probe laser intersects the gas flow in the low pressure detection cell). However, the probe distance has been shown to be critical to accurate kinetic measurements, as described above and shown in Figures 2 and 3.

At longer probe distances (> 10 mm) and low reactant concentrations (i.e. with low pseudo-first-order rate coefficients, $< \sim 500 \text{ s}^{-1}$), the observed OH kinetics were broadly similar to literature values (Figure 3b, reaction of OH with DME). However, as the reactant concentration was increased, significant deviations from expected behaviour were observed when probing at longer distances. The observed OH decays at higher reactant concentrations and longer probe distances appeared to display biexponential behaviour (Figure 2b, reaction of OH with DME), with bimolecular rate coefficients obtained from these data significantly lower than expected values (Figures 3b, reaction of OH with DME). In addition, OH signals took significantly longer to appear than in experiments probing at a distance of 5 mm.

232 The differences observed between experiments probing at short distances from the sampling point and
233 those probing at longer distances can be rationalised in terms of the behaviour of the gas sampled in to the
234 low pressure detection region. When sampling from a high pressure region to a low pressure region,
235 expansion of the sampled gas into the low pressure region results in the generation of a supersonic jet.
236 Species within the jet can be characterised by low rotational temperatures, and have a narrow and well-
237 defined velocity distribution around a relatively high mean velocity. The length of the jet can be
238 approximated by the position of the Mach disk:

$$x_m = 0.67d \sqrt{p_0/p_b}$$

239 where x_m is the position of the Mach disk (i.e. the length of the jet), d is the diameter of the pinhole nozzle
240 and p_0 and p_b are the pressures in the high pressure region and the background pressure in the low pressure
241 region, respectively. At the Mach disk, the supersonic jet breaks down and plug flow conditions dominate.
242 Under plug flow conditions, species have higher rotational temperatures, the mean gas velocity is much
243 lower, and the velocity distribution is much broader and can be described by a Maxwell-Boltzmann
244 distribution.

245 Thus, when the distance between the sampling point (i.e. the position of the pinhole) and the detection
246 point (i.e. the point at which the probe laser passes across the gas flow) is short (< 10 mm), the arrival time of
247 species travelling from the sampling point to the detection point will be relatively short, with a relatively
248 narrow distribution. The impact of this spread in arrival times on observed first-order kinetics has been
249 described for experiments sampling from high pressure reaction regions to low pressure detection regions
250 using mass spectrometry, and solutions enabling exact determinations of kinetics have been reported (52).

251 In contrast, when the distance between the sampling point and the detection point is longer ($> \sim 10$
252 mm for a transition from 760 Torr to 1 Torr for a 0.5 mm pinhole), species will be probed from the plug flow
253 region. Subsequently, arrival times at the detection point will not only be much longer, but there will also be
254 a much more significant spread of arrival times at the detection point from species which were sampled at the
255 pinhole at the same time. The impact of this spread in arrival times will therefore be much greater if species
256 are probed in the plug flow region than if species are probed within the jet. Deconvolution of kinetics from

transport within the detection region thus becomes more problematic under plug flow conditions, and it is not possible to obtain an exact solution to enable extraction of kinetic parameters.

Creasey et al.(53) demonstrated that the rotational temperature determined by LIF increases sharply at the expected location of the Mach disk. Figure 6 shows the LIF excitation spectra recorded for OH probed at 5 mm and 200 mm from the sampling point, indicating a transition from a low rotational temperature (~ 40 K when compared to simulations using LIFBASE (54)) at a probe distance of 5 mm to a much higher rotational temperature (~ 200 K) at a probe distance of 200 mm. Measurements of the OH LIF spectra in the detection region thus indicate that probing at a distance of 5 mm from the sampling point (where the observed kinetics indicate reliable measurements up to $k' \sim 20,000$ s⁻¹) probes species within the supersonic jet, while probing at a distance of 200 mm from the sampling point (where the observed kinetics deviate significantly from expected behaviour) probes species outside of the supersonic jet and within the plug flow regime.

Figure 7 shows the expected distributions of arrival times, and impacts on temporal profiles for identical pseudo-first-order reaction conditions, of species at probe regions of 5 mm from the sampling point (i.e. within the supersonic jet, simulated using the exact solution described by Taatjes (55)) and 200 mm from the sampling point (i.e. in the plug flow region, simulated using a Maxwell-Boltzmann distribution at the temperature indicated by the LIF spectra in the plug flow region). There is a clear difference in both the mean arrival time and the spread in arrival times between species probed at 5 mm and those probed at 200 mm (Figure 7a), leading to significant impacts on observed temporal profiles (Figures 2 and 5) and consequences for extraction of kinetic parameters.

Applications

Ambient OH reactivity

Deviations from the expected pseudo-first-order behaviour at high reactivities have been reported for a number of field instruments used to measure ambient OH reactivity using laser flash photolysis coupled to FAGE detection (LFP-FAGE), which typically probe OH at distances of 120-200 mm from the sampling point (31,33,36,38,56). For some instruments, such deviations from the expected exponential behaviour are

283 observed at reactivities above 60 s^{-1} , potentially leading to underestimations of ambient OH reactivity in
284 polluted environments (33,34). The use of FP-FAGE to measure ambient OH reactivity does, however, offer
285 advantages over other techniques to measure OH reactivity, particularly in high NO_x environments owing to
286 the ability to produce OH in isolation from HO_2 which significantly reduces the impact of OH production
287 from $\text{HO}_2 + \text{NO}$ on the timescale of the experiment.

288 The observed deviations from expected behaviour at high ambient reactivities can be explained by the
289 long probe distances typically employed in field instruments. Increased dynamic ranges for measurements of
290 OH reactivity can thus be achieved by reducing the probe distance such that radicals are detected within the
291 supersonic jet of the gas expansion.

292

293 **Low temperature combustion**

294 Real-time measurements of reactive species involved in low temperature combustion are key to the
295 elucidation of reaction mechanisms involved in autoignition processes in homogeneous charge compression
296 ignition (HCCI) engines (57). There is, however, a gap between techniques appropriate to measurements of
297 oxidation processes at temperatures and pressures relevant to the atmosphere, and those appropriate to
298 measurements of high temperature combustion processes in traditional spark ignition or diesel engines,
299 limiting experimental capabilities in the temperature range $\sim 500\text{-}900 \text{ K}$ (57). The lack of appropriate
300 experimental techniques for studies of low temperature combustion and the chemistry controlling
301 autoignition has thus hindered the full exploitation of biofuels and novel fuels to improve fuel security and to
302 reduce emissions of CO_2 , NO_x and soot (4,57).

303 The instrumentation described in this work will bridge the gap between techniques currently
304 described in the literature to enable more detailed investigations of the processes controlling autoignition and
305 low temperature combustion in real-time. Dimethyl ether (DME) is a potentially promising biofuel (58), and
306 several groups have recently reported measurements of key markers in the low temperature combustion of
307 DME (43,59-64). However, the mechanism of DME combustion remains unclear, and the processes leading
308 to radical chain branching have yet to be experimentally determined. Application of the techniques described

309 in this work to such systems will enable greater understanding of the gas phase radical chemistry involved in
310 autoignition and low temperature combustion, and will be explored further in future work.

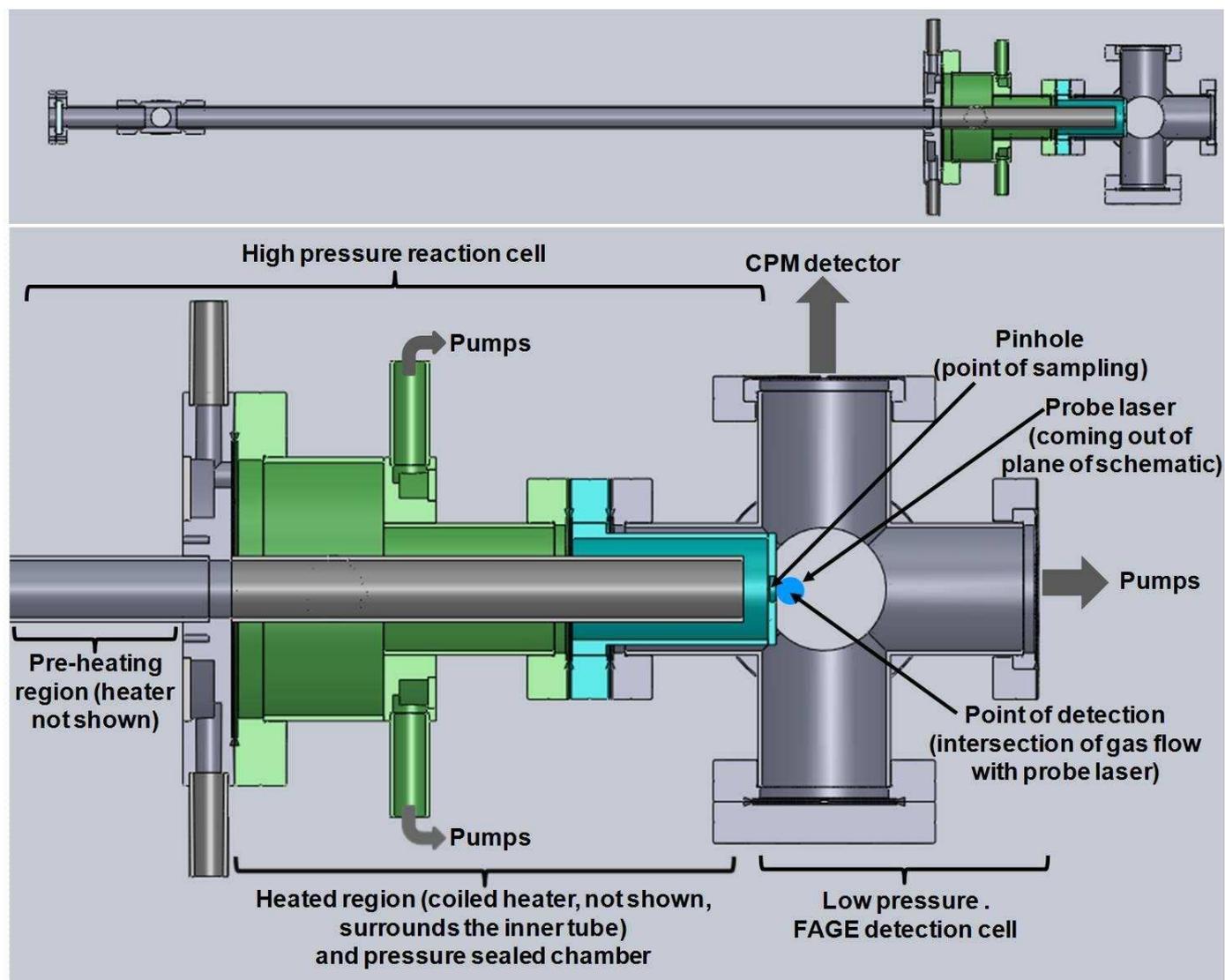
312 **Summary**

313 The design and characterisation of an instrument to measure fast gas phase kinetics in real-time at
314 high temperatures and pressures by sampling from a high pressure reaction region to a low pressure detection
315 region using the FAGE technique has been described. Radical generation in the high pressure reaction region
316 is achieved by laser flash photolysis, thus minimising the potential for heterogeneous chemistry. We have
317 demonstrated successful accurate measurements of kinetics over a range of temperatures and pressures.
318 However, the distance between the sampling point and the probe region is critical for accurate measurements
319 of reaction kinetics, with measurement accuracy requiring probing within the supersonic jet formed on
320 sampling from the high pressure region to the low pressure region.

321 The experimental approach described in this work can be applied to measurements of fast gas phase
322 kinetics relevant to atmospheric and combustion chemistry, and is applicable to any species exhibiting laser-
323 induced fluorescence.

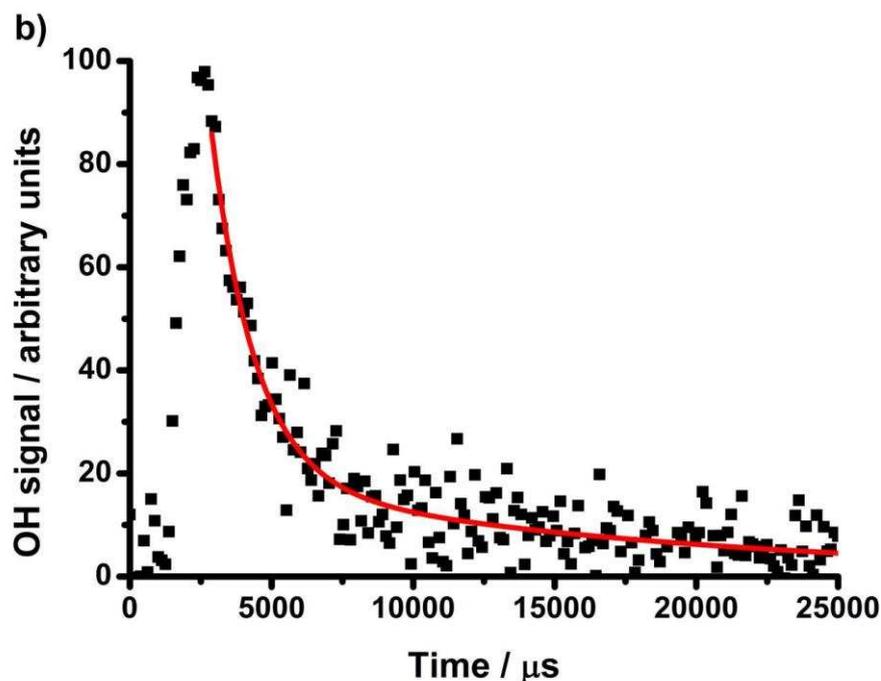
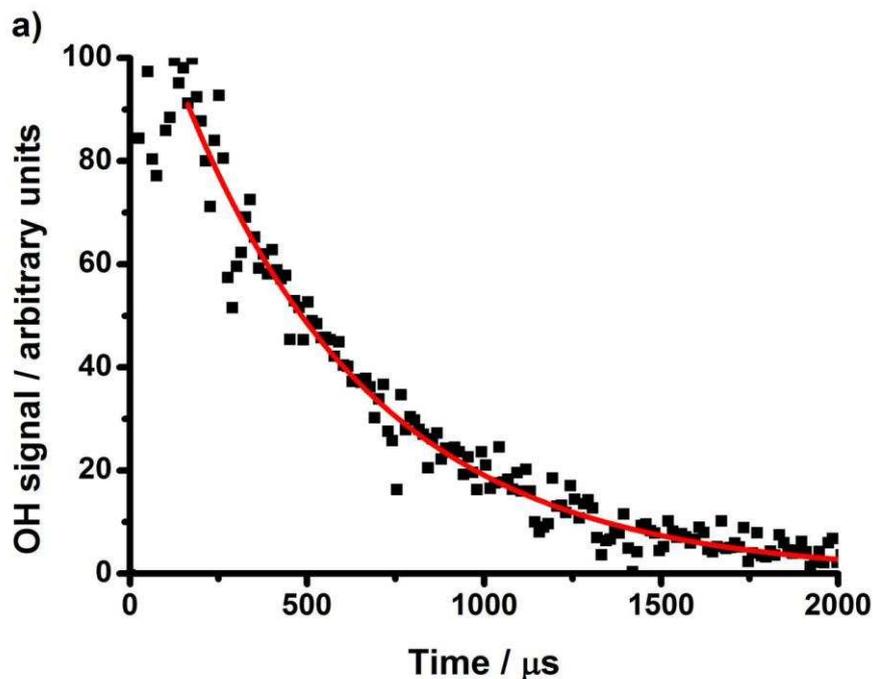
325 **Acknowledgements**

326 The authors are grateful to the Engineering and Physical Sciences Research Council (EPSRC, grant
327 reference EP/J010871/1), the Natural Environment Research Council (NERC, grant reference
328 NE/L010798/1), the National Centre for Atmospheric Science (NCAS), and the Brazilian National Council
329 for Scientific and Technological Development (CNPq, grant reference 206527/2014-4) for funding.



331

332 Figure 1: Schematic of the instrument. Upper panel shows the full instrument, with the lower panel
 333 displaying the region connecting the high pressure reaction cell and the low pressure detection cell in detail.
 334 The pinhole is incorporated within the section shown in blue, and this section is readily interchangeable if a
 335 change in pinhole diameter is required.



336

337

338

339

340

341

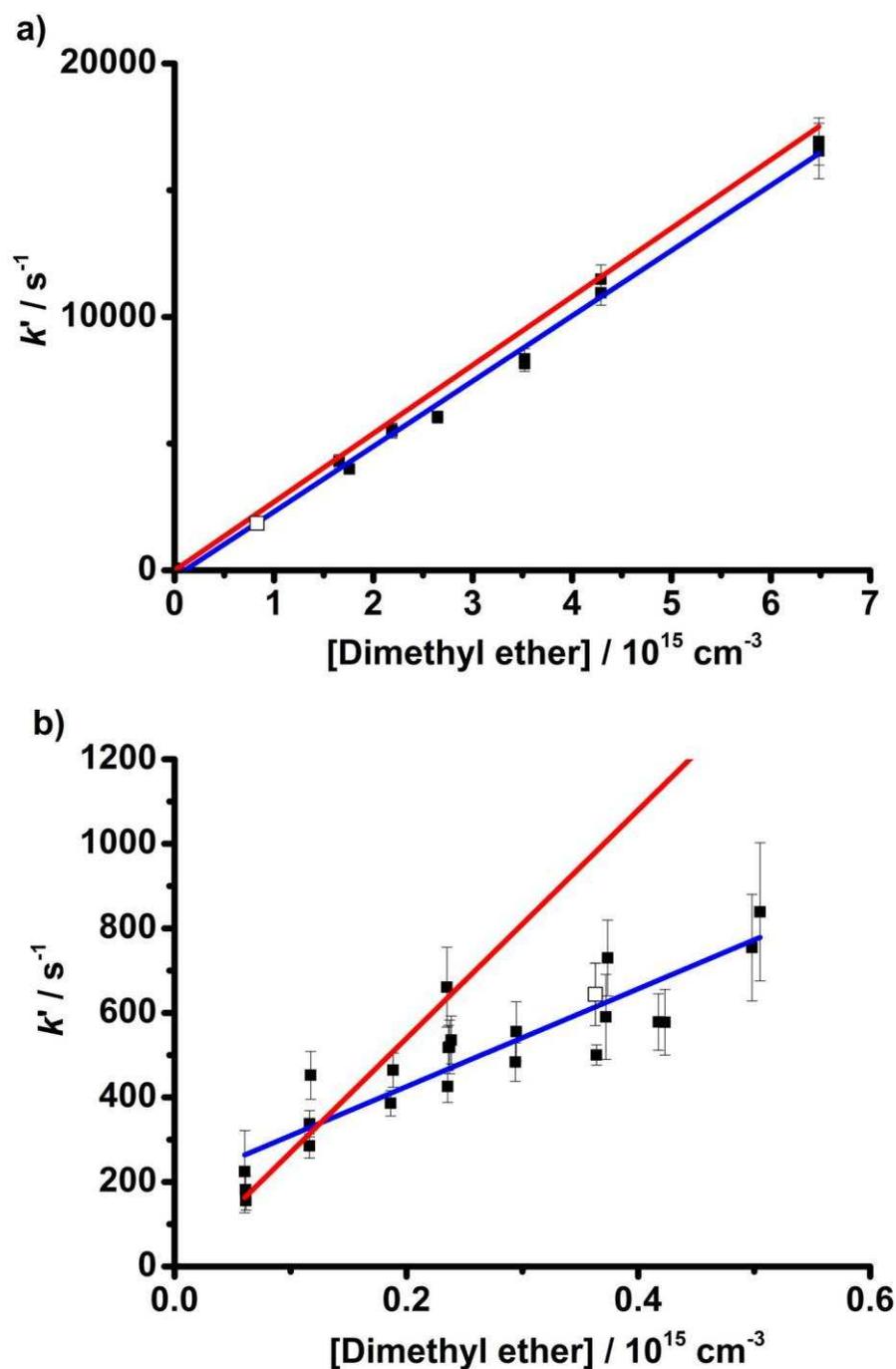
342

343

344

345

Figure 2: Temporal behaviour of OH signals for reaction of OH + CH₃OCH₃ (dimethyl ether, DME) at probe distances of a) 5 mm and b) 200 mm from the sampling point. For both plots, the reaction cell was at 298 K, 1000 Torr and the detection cell at 0.8 Torr. Fits to the data are shown in red. Data collected at a probe distance of 5 mm (panel a, [DME] = $8.3 \times 10^{14} \text{ cm}^{-3}$) were fitted to a single exponential decay ($k_{\text{obs}} = (1850 \pm 58) \text{ s}^{-1}$), while those collected at a probe distance of 200 mm (panel b, [DME] = $3.6 \times 10^{14} \text{ cm}^{-3}$) were fitted to a biexponential decay ($k_{\text{obs,fast}} = (644 \pm 74) \text{ s}^{-1}$; $k_{\text{obs,slow}} = (64 \pm 14) \text{ s}^{-1}$), with only the fast component of the decay observed to display any dependence on [DME] and used in the bimolecular plots in Figure 3. Additional kinetic results obtained for OH + CH₄ at probe distances of < 5 mm and 50 mm, and for OH + C₅H₈ at a probe distance < 5 mm, are shown in the supplementary information.



346

347

348

349

350

351

352

353

354

355

356

357

Figure 3: Bimolecular plots of observed OH decay kinetics at 298 K and 1000 Torr, with the detection cell at a pressure of 0.8 Torr, for sampling distances of a) 5 mm and b) 200 mm for reactions of OH with CH_3OCH_3 (dimethyl ether, DME). Best fit lines are shown in blue; ($k = (2.6 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ when probing at 5 mm from the sampling point (panel a, analysed using a single exponential decay); $k = (1.2 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ when probing at 200 mm from the sampling point (panel b, analysed using a biexponential decay)). The data points shown by the open symbols correspond to the kinetic traces shown in Figure 2. Literature recommendations shown in red ($k = 2.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$) (45). Note that at longer probe distances (200 mm in panel b) and low reactant concentrations, the observed OH kinetics are similar to those expected from literature values, with higher reactant concentrations leading to deviation from expected kinetics. Additional kinetic results obtained for OH + CH_4 at probe distances of < 5 mm and 50 mm, and for OH + C_5H_8 at a probe distance < 5 mm, are shown in the supplementary information.

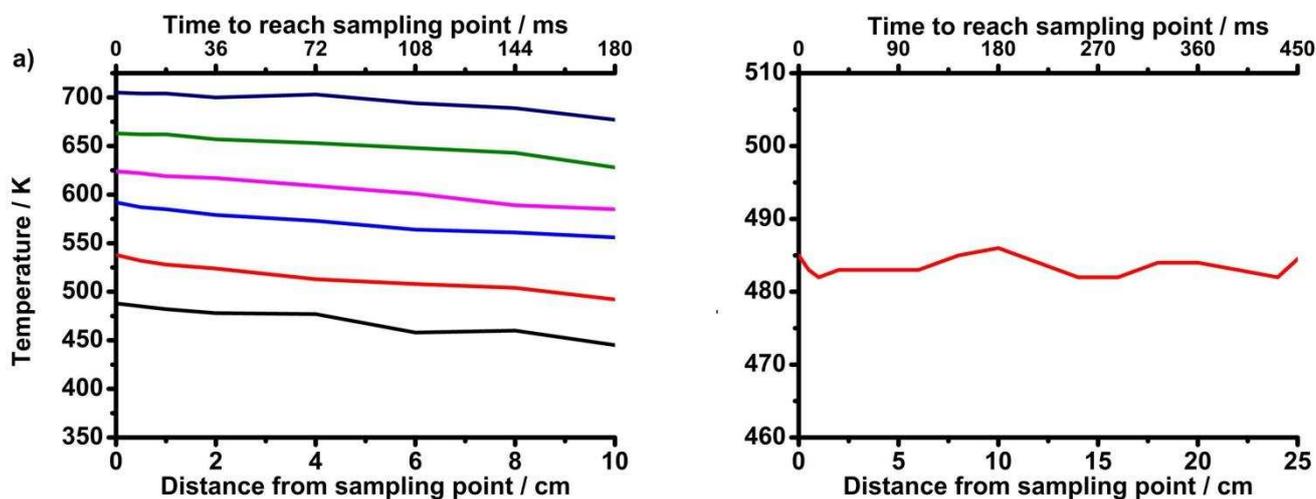


Figure 4: Temperature profiles along the length of the high pressure reaction cell (measured from the sampling point, such that the pinhole nozzle is at 0 cm). Temperatures were measured in the centre of the gas flow for flow rates of ~ 5 slm, corresponding to a residence time of ~ 18 ms in each 1 cm length of the reaction cell (times taken to reach the sampling point from the corresponding distance at a flow rate of 5 slm are shown in the upper x-axes). Pressures in the reaction cell were maintained at 1000 Torr. Panel (a) shows the temperature profiles obtained using the single heating coil only (18 cm in total length, of which only the section with stable temperature profile is shown); panel (b) shows an example temperature profile obtained using the ceramic pre-heater in addition to the coil heater.

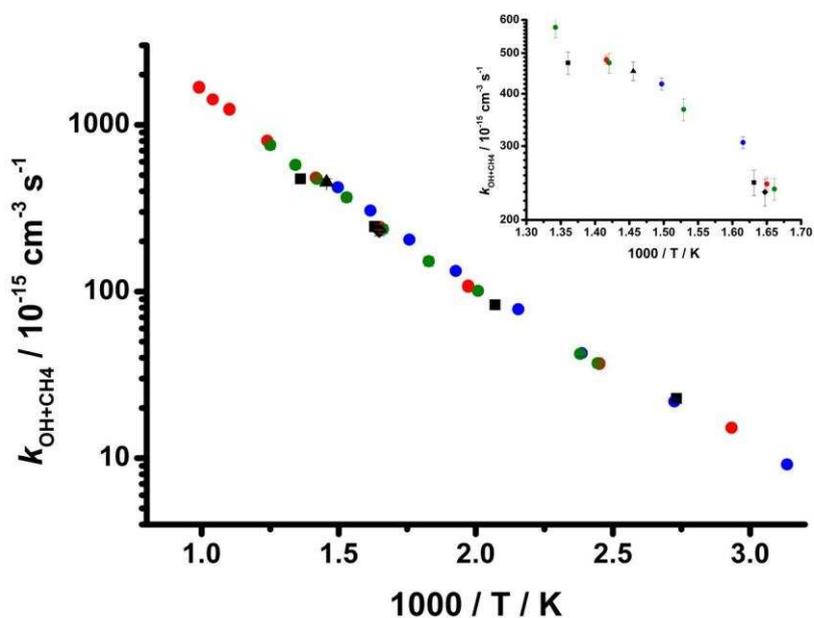
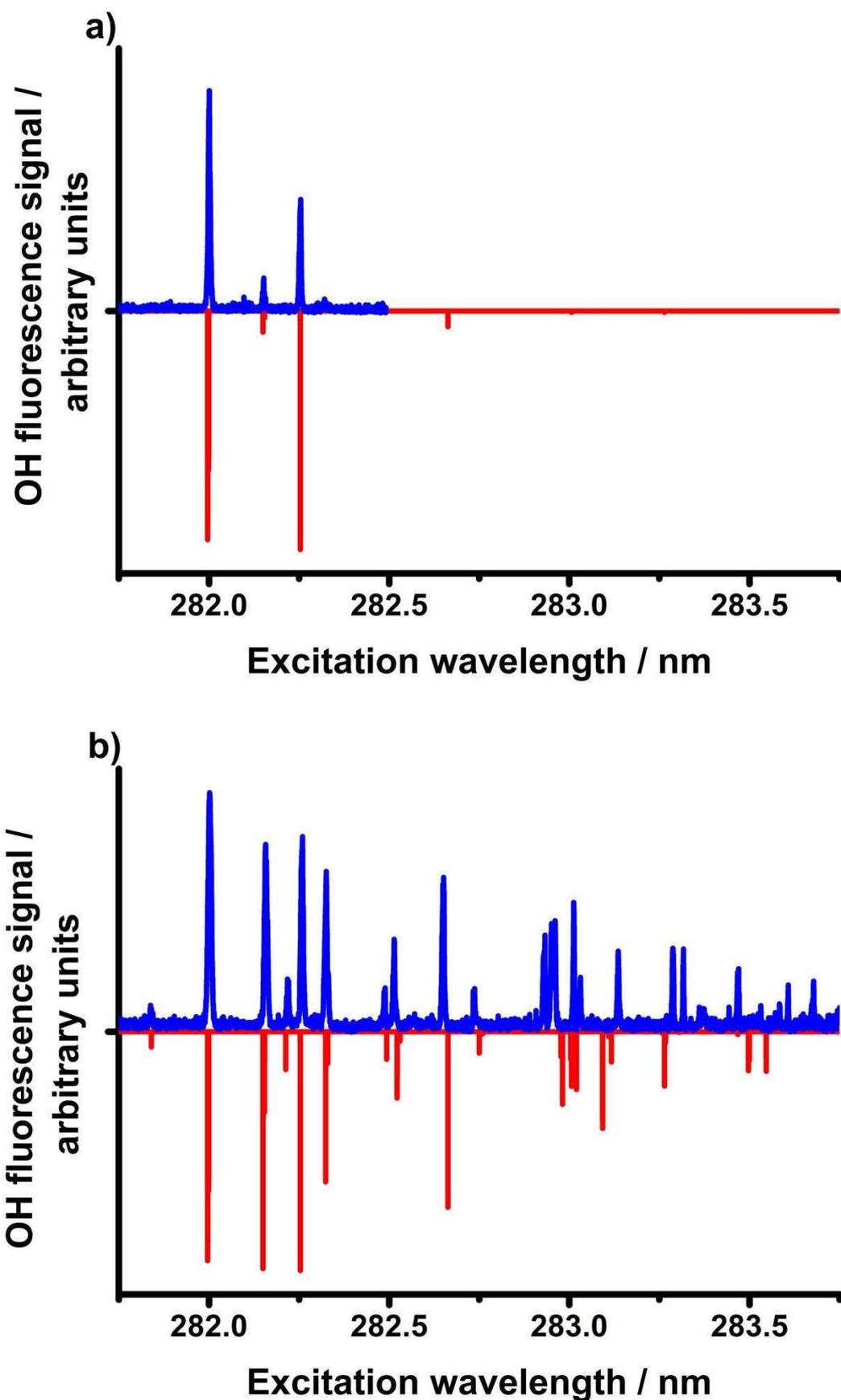
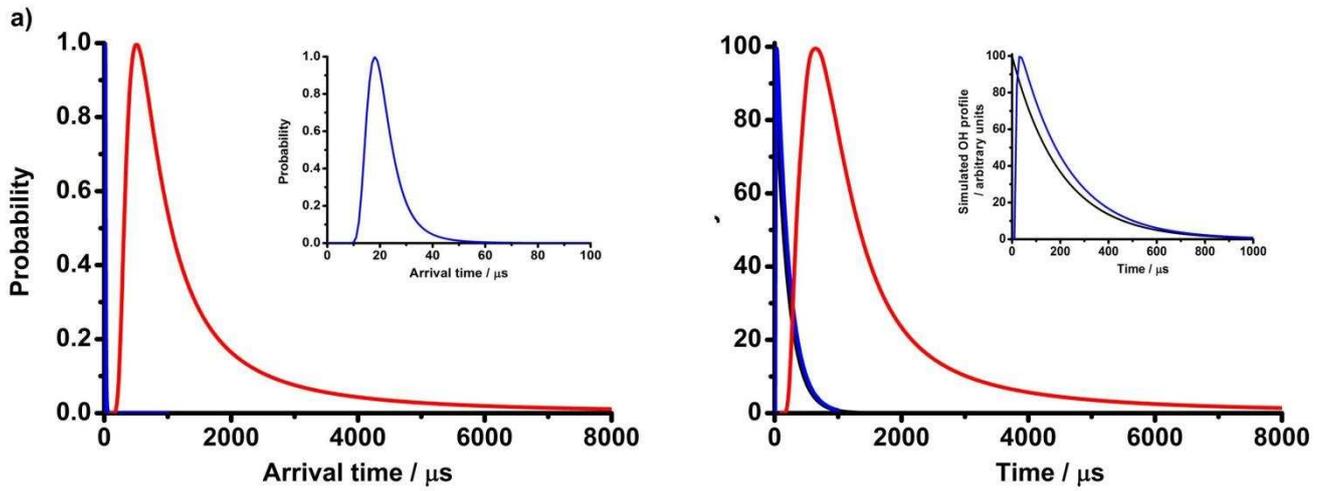


Figure 5: Bimolecular rate coefficients obtained for the reaction of OH with CH_4 as a function of temperature. Data obtained in this work are shown in the black points (squares represent data in 2 atm of N_2 ; diamonds represent data in 2 atm of Ar; triangles represent data in 1 atm of N_2). Previous measurements are shown for Bonard et al. (48) (blue circles), Bryukov et al. (49) (red circles) and Dunlop and Tully (50) (green circles). Errors are 2σ (although masked by the data points on the scale). The inset shows an expanded region to that the data can be seen in greater detail.



374
375
376
377
378

Figure 6: LIF excitation spectra for OH at sampling distances of a) 5 mm and b) 200 mm. Observed spectra are shown in blue (positive values), with LIFBASE simulations shown in red (negative values) for rotational temperatures of a) 40 K and b) 200 K. There is a sharp change in the observed spectrum at the expected location of the Mach disk (~ 12 mm in these experiments).



379
 380 Figure 7: Simulations showing impacts of velocity distributions at probe regions of 5 mm (blue; shown more
 381 clearly in the inset plots) and 200 mm (red) on a) the normalised probabilities of arrival times at the probe
 382 region (i.e. for species leaving the sampling point at $t = 0$) and b) the apparent OH signal at the probe region
 383 for identical pseudo-first-order reaction conditions ($k^{\prime} = 5000 \text{ s}^{-1}$, shown by the black line for a simulation not
 384 including any transport). Note that Creasey et al. (53), using a combination of experimental data and
 385 computational fluid dynamics calculations, demonstrated that the mean bulk gas velocity in the plug flow
 386 region was $\sim 65 \text{ m s}^{-1}$. The impact of this slow mean bulk gas flow in our experiments is apparent from the
 387 difference in the arrival times simulated here to those observed experimentally (Figure 2b), but has not been
 388 included in these simulations since it is not possible to determine the mean bulk velocity in the plug flow
 389 region for our experimental configuration a priori with any certainty.

References

- (1) M. A. Blitz, P. W. Seakins, *Chemical Society Reviews* **41**, 6318 (2012).
- (2) A. Canosa, F. Goulay, I.R. Sims, B.R. Rowe, in: I.W.M. Smith (Ed.), *Low Temperatures and Cold Molecules*, World Scientific, Singapore, 55 (2008).
- (3) I.W.M. Smith, in: S.M. Faber, E. VanDishoeck (Eds.), *Annual Review of Astronomy and Astrophysics* **49**, Annual Reviews, 29 (2011).
- (4) J. Zador, C.A. Taatjes, R.X. Fernandes, *Progress in Energy and Combustion Science* **37**, 371 (2011).
- (5) P.W. Seakins, *Annual Reports on the Progress of Chemistry, Section C: Physical Chemistry* **103** (2007).
- (6) D.E. Heard, M.J. Pilling, *Chemical Reviews* **103**, 5163 (2003).
- (7) L. D'Ottone, D. Bauer, P. Campuzano-Jost, M. Fardy, A.J. Hynes, *Faraday Discussions* **130**, 111 (2005).
- (8) K.A. Holbrook, M.J. Pilling, S.H. Robertson, *Unimolecular Reactions*, Wiley, Chichester, 1996.
- (9) P.W. Seakins, S.H. Robertson, M.J. Pilling, D.M. Wardlaw, F.L. Nesbitt, R.P. Thorn, W.A. Payne, L.J. Stief, *Journal of Physical Chemistry* **101**, 9974 (1997).
- (10) I.W.M. Smith, *Journal of the Chemical Society-Faraday Transactions* **93**, 3741 (1997).
- (11) M.A. Blitz, N.J.B. Green, R.J. Shannon, M.J. Pilling, P.W. Seakins, C.M. Western, S.H. Robertson, *Journal of Physical Chemistry A* **119**, 7668 (2015).
- (12) M.J. Pilling, S.H. Robertson, P.W. Seakins, *Journal of the Chemical Society-Faraday Transactions* **91**, 4179 (1995).
- (13) C.K. Westbrook, W.J. Pitz, H.J. Curran, in: H. Zhao (Ed.), *HCCI and CAI engines for the automotive industry*, CRC Press, Boca Raton, (2007).
- (14) M.F. Yao, Z.L. Zheng, H.F. Liu, *Progress in Energy and Combustion Science* **35**, 398 (2009).
- (15) R. Forster, M. Frost, D. Fulle, H.F. Hamann, H. Hippler, A. Schlegel, J. Troe, *Journal of Chemical Physics* **103**, 2949 (1995).
- (16) R.V. Ravikrishna, C.S. Cooper, N.M. Laurendeau, *Combustion and Flame* **117**, 810 (1999).
- (17) K. Kohse-Hoinghaus, W. Perc, T. Just, *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics* **87**, 1052 (1983).
- (18) C. Bansch, J. Kiecherer, M. Szori, M. Olzmann, *Journal of Physical Chemistry A* **117**, 8343 (2013).
- (19) A.M. Knepp, G. Meloni, L.E. Jusinski, C.A. Taatjes, C. Cavallotti, S.J. Klippenstein, *Physical Chemistry Chemical Physics* **9**, 4315 (2007).
- (20) A. Bossolasco, E.P. Farago, C. Schoemaeker, C. Fittschen, *Chemical Physics Letters*, **593**, 7 (2014).
- (21) A.E. Parker, C. Jain, C. Schoemaeker, P. Szufrtger, O. Votava, C. Fittschen, *Applied Physics B-Lasers and Optics* **103**, 725 (2011).
- (22) M.D. Wheeler, S.M. Newman, A.J. Orr-Ewing, M.N.R. Ashfold, *Journal of the Chemical Society-Faraday Transactions* **94**, 337 (1998).
- (23) T.M. Hard, R.J. O'Brien, C.Y. Chan, A.A. Mehrabzadeh, *Environmental Science & Technology* **18**, 768 (1984).
- (24) D. Stone, L.K. Whalley, D.E. Heard, *Chemical Society Reviews* **41**, 6348 (2012).
- (25) D.J. Creasey, P.A. Halford-Maw, D.E. Heard, M.J. Pilling, B.J. Whitaker, *Journal of the Chemical Society-Faraday Transactions* **93**, 2907 (1997).
- (26) D. Tan, I. Faloon, J.B. Simpas, W. Brune, J. Olson, J. Crawford, M. Avery, G. Sachse, S. Vay, S. Sandholm, H.W. Guan, T. Vaughn, J. Mastromarino, B. Heikes, J. Snow, J. Podolske, H. Singh, *Journal of Geophysical Research-Atmospheres* **106**, 32667 (2001).
- (27) F. Holland, M. Hessling, A. Hofzumahaus, *Journal of the Atmospheric Sciences* **52**, 3393 (1995).
- (28) M. Martinez, H. Harder, D. Kubistin, M. Rudolf, H. Bozem, G. Eerdeken, H. Fischer, T. Klupfel, C. Gurk, R. Konigstedt, U. Parchatka, C.L. Schiller, A. Stickler, J. Williams, J. Lelieveld, *Atmospheric Chemistry and Physics* **10**, 3759 (2010).
- (29) S. Dusanter, D. Vimal, P.S. Stevens, *Atmos. Chem. Phys.* **8**, 321 (2008).
- (30) Y. Kanaya, H. Akimoto, *The Chemical Record* **2**, 199 (2002).
- (31) D. Amedro, K. Miyazaki, A. Parker, C. Schoemaeker, C. Fittschen, *Journal of Environmental Sciences-China* **24**, 78 (2012).
- (32) Y. Sadanaga, A. Yoshino, K. Shungo, K. Yoshizumi, *Environmental Science & Technology* **39**, 8847 (2005).

- 440 (33) S. Lou, F. Holland, F. Rohrer, K. Lu, B. Bohn, T. Brauers, C.C. Chang, H. Fuchs, R. Haseler, K. Kita, Y. Kondo, X. Li,
441 M. Shao, L. Zeng, A. Wahner, Y. Zhang, W. Wang, A. Hofzumahaus, *Atmospheric Chemistry and Physics* **10**,
442 11243 (2010).
- 443 (34) K. Lu, F. Rohrer, F. Holland, H. Fuchs, B. Bohn, T. Brauers, C.C. Chang, R. Haseler, M. Hu, K. Kita, Y. Kondo, X.
444 Li, S. Lou, S. Nehr, M. Shao, L. Zeng, A. Wahner, Y. Zhang, A. Hofzumahaus, *Atmos Chem Phys* **12**, 1541 (2012).
- 445 (35) K.D. Lu, A. Hofzumahaus, F. Holland, B. Bohn, T. Brauers, H. Fuchs, M. Hu, R. Haseler, K. Kita, Y. Kondo, X. Li,
446 S.R. Lou, A. Oebel, M. Shao, L.M. Zeng, A. Wahner, T. Zhu, Y.H. Zhang, F. Rohrer, *Atmospheric Chemistry and*
447 *Physics* **13**, 1057 (2013).
- 448 (36) A.E. Parker, D. Amedro, C. Schoemaeker, C. Fittschen, *Environmental Engineering and Management Journal*
449 **10**, 107 (2011).
- 450 (37) L.K. Whalley, D. Stone, R. Dunmore, J.F. Hamilton, J. Hopkins, J.D. Lee, B. Bandy, D.E. Heard, *Atmospheric*
451 *Chemistry and Physics* **16**, 2109 (2016).
- 452 (38) D. Stone, L.K. Whalley, T. Ingham, P.M. Edwards, D. Cryer, C. Brumby, P.W. Seakins, D.E. Heard, *Atmospheric*
453 *Measurement Techniques Discussions*, doi:10.5194/amt-2016-51, in review (2016).
- 454 (39) T.R. Shirley, W.H. Brune, X. Ren, J. Mao, R. Leshner, B. Cardenas, R. Volkamer, L.T. Molina, M.J. Molina, B.
455 Lamb, E. Velasco, T. Jobson, M. Alexander, *Atmospheric Chemistry and Physics* **6**, 2753 (2006).
- 456 (40) V.G.C. Dolgorouky, R. Sarda-Esteve, V. Sinha, J. Williams, N. Marchand, S. Sauvage, L. Poulain, J. Sciare, B.
457 Bonsang, *Atmospheric Chemistry and Physics* **12**, 9593 (2012).
- 458 (41) C.Y. Chan, T.M. Hard, A.A. Mehrabzadeh, L.A. George, R.J. O'Brien, *Journal of Geophysical Research* **95**, 18569
459 (1990).
- 460 (42) P.S. Stevens, J.H. Mather, W.H. Brune, *Journal of Geophysical Research-Atmospheres* **99**, 3543 (1994).
- 461 (43) S.A. Carr, T.J. Still, M.A. Blitz, A.J. Eskola, M.J. Pilling, P.W. Seakins, R.J. Shannon, B. Wang, S.H. Robertson,
462 *Journal of Physical Chemistry A* **117**, 11142 (2013).
- 463 (44) A.J. Eskola, S.A. Carr, R.J. Shannon, B. Wang, M.A. Blitz, M.J. Pilling, P.W. Seakins, S.H. Robertson, *Journal of*
464 *Physical Chemistry A* **118**, 6773 (2014).
- 465 (45) R. Atkinson, D.L. Baulch, R.A. Cox, J.N. Crowley, R.F. Hampson, R.G. Hynes, M.E. Jenkin, M.J. Rossi, J. Troe,
466 *Atmospheric Chemistry and Physics* **6**, 3625 (2006).
- 467 (46) See supplemental information for further details of kinetic measurements of reactions of OH with methane
468 and isoprene as a function of the probe distance.
- 469 (47) G.L. Vaghjiani, A.R. Ravishankara, *Nature* **350**, 406 (1991).
- 470 (48) A. Bonard, V. Daele, J.L. Delfau, C. Vovelle, *Journal of Physical Chemistry A* **106**, 4384 (2002).
- 471 (49) M.G. Bryukov, V.D. Knyazev, S.M. Lomnicki, C.A. McFerrin, B. Dellinger, *Journal of Physical Chemistry A* **108**,
472 10464 (2004).
- 473 (50) J.R. Dunlop, F.P. Tully, *Journal of Physical Chemistry* **97**, 11148 (1993).
- 474 (51) D.L. Baulch, C.T. Bowman, C.J. Cobos, R.A. Cox, T. Just, J.A. Kerr, M.J. Pilling, D. Stocker, J. Troe, W. Tsang,
475 R.W. Walker, J. Warnatz, *Journal of Physical and Chemical Reference Data* **34**, 757 (2005).
- 476 (52) M.T. Baeza-Romero, M.A. Blitz, A. Goddard, P.W. Seakins, *International Journal of Chemical Kinetics* **44**, 532
477 (2012).
- 478 (53) D.J. Creasey, D.E. Heard, M.J. Pilling, B.J. Whitaker, M. Berzins, R. Fairlie, *Applied Physics B-Lasers and Optics*
479 **65**, 375 (1997).
- 480 (54) J. Luque, D.R. Crosley, LIFBASE: Database and Spectral Simulation Program, SRI International (1995).
- 481 (55) C.A. Taatjes, *International Journal of Chemical Kinetics* **39**, 565 (2007).
- 482 (56) Y. Sadanaga, A. Yoshino, K. Watanabe, A. Yoshioka, Y. Wakazono, Y. Kanaya, Y. Kajii, *Review of Scientific*
483 *Instruments* **75**, 2648 (2004).
- 484 (57) D.K. Manley, A. McIlroy, C.A. Taatjes, *Physics Today* **61**, 47 (2008).
- 485 (58) T.A. Semelsberger, R.L. Borup, H.L. Greene, *Journal of Power Sources* **156**, 497 (2006).
- 486 (59) H. Guo, W. Sun, F.M. Haas, T. Farouk, F.L. Dryer, Y. Ju, *Proceedings of the Combustion Institute* **34**, 573
487 (2013).
- 488 (60) F. Herrmann, B. Jochim, P. Oswald, L. Cai, H. Pitsch, K. Kohse-Hoinghaus, *Combustion and Flame* **161**, 384
489 (2014).

- 490 (61) N. Kurimoto, B. Brumfield, X. Yang, T. Wada, P. Dievart, G. Wysocki, Y. Ju, Proceedings of the Combustion
491 Institute **35**, 457 (2015).
- 492 (62) K. Moshhammer, A.W. Jasper, D.M. Popolan-Vaida, A. Lucassen, P. Dievarti, H. Selim, A.J. Eskola, C.A. Taatjes,
493 S.R. Leone, S.M. Sarathy, Y. Ju, P. Dagaut, K. Kohse-Hoeinghaus, N. Hansen, Journal of Physical Chemistry A
494 **119**, 7361 (2015).
- 495 (63) T. Ngoc Linh Le, M. Djehiche, C.D. Jain, P. Dagaut, G. Dayma, Fuel **158**, 248 (2015).
- 496 (64) A. Rodriguez, O. Frottier, O. Herbinet, R. Fournet, R. Bounaceur, C. Fittschen, F. Battin-Leclerc, Journal of
497 Physical Chemistry A **119**, 7905 (2015).

498