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1 **Complementarity of neutron reflectometry and ellipsometry for the study** 2 **of atmospheric reactions at the air–water interface.**

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8 **Abstract**

9 The combined application of neutron reflectometry (NR) and ellipsometry to determine the
10 oxidation kinetics of organic monolayers at the air–water interface is described for the first
11 time. This advance was possible thanks to a new miniaturised reaction chamber that is
12 compatible with the two techniques and has controlled gas delivery. The rate coefficient for
13 the oxidation of methyl oleate monolayers by gas-phase O₃ determined using NR is $(5.4 \pm$
14 $0.6) \times 10^{-10} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$, which is consistent with the value reported in the literature
15 but is now better constrained. This highlights the potential for the study of faster atmospheric
16 reactions in future studies. The rate coefficient determined using ellipsometry is $(5.0 \pm 0.9) \times$
17 $10^{-10} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$, which indicates the potential of this more economical, laboratory-
18 based technique to be employed in parallel with NR. In this case, temporal fluctuations in the
19 optical signal are attributed to the mobility of islands of reaction products. We outline how
20 such information may provide critical missing information in the identification of transient
21 reaction products in a range of atmospheric surface reactions in the future.

22 *Keywords:* aerosol surface, kinetics, atmospheric reactions, air–water interface, methyl oleate,
23 ozone, oxidation, neutron reflectometry, ellipsometry.

25 **1. Introduction**

26 Organic monolayers at the air–water interface have been widely studied because of their
27 natural abundance,^{1,2} and their relevance for modification of the physical properties of
28 formulations in common use.^{3,4} Our interest is the reaction kinetics of atmospheric relevance
29 occurring at the surface of aerosol droplets. The reaction involves an insoluble organic
30 monolayer and gas-phase oxidants. In the atmosphere, organic compounds are mainly
31 oxidized by nitrate radicals, NO₃, hydroxyl radicals, OH and ozone, O₃. Knowledge of the
32 kinetic parameters for monolayer oxidation is necessary for model studies aiming to de-
33 convolute surface and bulk processes of atmospheric aerosols.^{5,6}

34 A powerful technique used to study organic monolayers at the air–water interface is neutron
35 reflectometry (NR).⁷ Neutrons are non-destructive for soft and biological materials, and by
36 exploiting the method of isotopic substitution, i.e. deuteration of the monolayer as well as
37 partial deuteration of the aqueous subphase to match its scattering properties to that of air, the
38 technique can be used to quantify directly the surface excess during oxidation reactions. For
39 example, a decrease in the surface excess during the reaction occurs when double bonds in
40 unsaturated molecules are cleaved by the oxidant resulting in smaller reaction products with
41 higher solubility and/or volatility.^{e.g.8} As such, it is the rate of loss of material, which
42 determines the evaporation rate of the subphase of key atmospheric relevance, which is
43 measured.

44 NR has been applied previously to the atmospheric oxidation of organic monolayers in large
45 custom-built reaction chambers with gas volumes on the order of 25 l that contained a

1 commercial Langmuir trough.^{8–11} The macroscopic air–water interface acted as a proxy for
2 the surface of aerosol droplets. The large volume of the chamber placed an upper limit on the
3 fastest reaction rates that could be measured due to uncertainties both in the time between
4 introducing the oxidant flow and reaching steady state concentrations and in the non-
5 homogeneous gas diffusion. These issues did not limit the experiments because the time
6 resolution of the technique used was typically on the order of several minutes.^{8,9} However,
7 with the advent of new instrumentation, quantitative measurements of the surface excess of
8 organic monolayers at the air–water interface can now be carried out with a time resolution as
9 short as 1 s.^{10,11} The limitation in the efficiency of the experiments thus became the reaction
10 chamber. There was therefore scope for significant improvements in the design of the
11 chamber if its size could be reduced considerably without compromising the gas diffusion
12 conditions as a result of physical perturbations to the free liquid surface.

13 Ellipsometry is a precise and sensitive optical reflectometry technique.¹² It can, in principle,
14 be used also to measure the surface excess during oxidation reactions at the air–water
15 interface, but to our knowledge such measurements have not been published to date. The
16 technique has the advantage that it is more accessible than NR as it can be carried out in a
17 laboratory rather than a large-scale facility. Such an approach for the characterisation of
18 single-component systems has the advantage that precious neutron beam time may be
19 conserved for experiments which exploit selective deuteration of specific components in
20 mixtures to determine relative reaction rates or partial deuteration of portions of a molecule to
21 determine the reaction mechanism. Also, there is the potential to gain additional information
22 concerning the lateral homogeneity of the interface during reactions given that temporal
23 fluctuations in the optical signal reveal macroscopic domains of material present in a different
24 phase.^{13,14} Possible limitations, however, are that ellipsometry does not provide a direct
25 quantification of the surface excess as the data need to be calibrated independently, and the
26 measured optical signal would be affected by any changes in anisotropy in the interfacial
27 layer during the reactions. To see if such complications could be overcome, the shapes of
28 surface excess decays measured using the two techniques during the reactions would need to
29 be compared. Such work would clearly be best carried out using the same reaction chamber to
30 minimize uncertainties related to different gas mixing conditions. However, a reaction
31 chamber compatible with both techniques has not been previously available.

32 To examine the complementary use of NR and ellipsometry in the study of atmospheric
33 reactions at the air–water interface, we have developed a miniaturised reaction chamber with
34 optimised conditions, i.e. a low volume for controlled gas injection and compatibility for
35 equivalent measurements using the two techniques. To validate the performance of the
36 chamber, we have studied the oxidation of methyl oleate monolayers by gas-phase ozone.
37 Reasons for this choice of system are related to its high interest given that methyl oleate is
38 both a key component of biodiesels¹⁵ and a food lipid that contributes to meat cooking
39 emissions.¹⁶ An additional reason is that recently we reported a second order rate coefficient
40 for methyl oleate ozonolysis of $(5.7 \pm 0.9) \times 10^{-10} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$ for the loss of material
41 from the interface using NR on a large reaction chamber,¹⁰ thus providing a suitable
42 reference. The scope of this study is to describe the design of the new chamber, to examine
43 the potential resulting from the advanced instrumentation and new chamber to study faster
44 oxidation reactions than were previously possible, and to explore the prospects of using
45 ellipsometry in the study of single-component systems in the future to focus the use of
46 neutrons in more studies of more complex systems.

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1 2. Materials and Methods

2 2.1. Materials

3 The organic monolayer comprised either deuterated methyl oleate (*d*MO, Oxford Deuteration
4 Facility, ~ 95%; see Pfrang *et al.* for sample characterisation)¹⁰ for NR or hydrogenous
5 methyl oleate (*h*MO, Sigma-Aldrich, ≥ 99%) for ellipsometry. The subphase was either a
6 mixture of 8.1% by volume D₂O (Eur-isotop, France) in pure H₂O (generated using a
7 Millipore purification unit, 18.2 MΩ cm), known as air contrast matched water (ACMW), for
8 NR or pure H₂O for ellipsometry. Chloroform (Sigma-Aldrich, > 99.8%) and O₂ (Air
9 Liquide, France, > 99.9%) were used as supplied.

10 2.2. Gas setup

11 O₃ was produced by flowing pure O₂ through a commercial ozoniser (UVP Pen-Ray
12 continuous flow generator, UK). The O₃ concentration was regulated by changing the flow
13 rate and the exposure to the UV lamp. A flow of O₃ in O₂ was then admitted to the reaction
14 chamber and the organic monolayer was oxidised at a rate that was determined by the O₃
15 concentration. Measurements of O₃ absorption at 253.7 nm were carried out using UV-visible
16 spectroscopy to establish the volume concentration, [O₃]_v (in molecule cm⁻³), and its
17 uncertainty.¹⁷ The surface concentration, [O₃]_s (in molecule cm⁻²), of ozone that dissolves
18 into the organic layer at the air–water interface is calculated from [O₃]_v assuming that the
19 surface concentration is constant in time and is equal to Henry's Law solubility following the
20 approach of Smith *et al.*¹⁸ (compare Pfrang *et al.*).¹⁰

21 2.3. Neutron reflectometry

22 A brief description of the physical basis of NR with reference to its application here can be
23 found in part 1 and an example of the raw data can be found in part 2 of the Electronic
24 Supporting Information. NR measurements of the oxidation of *d*MO monolayers by O₃ in the
25 new reaction chamber were carried out on FIGARO at the Institut Laue-Langevin (Grenoble,
26 France).¹¹ High neutron flux settings were used to maximise the data acquisition rate
27 involving an incident angle of 0.62°, a wavelength range of 2 – 20 Å (data reduction was
28 carried out over the range of 3.4 – 20 Å), and a constant resolution in momentum transfer of
29 11%. Normalisation of the reflectivity data was carried out with respect to the total reflection
30 of an air–D₂O measurement. The sample stage was equipped with passive and active anti-
31 vibration control. The new reaction chamber was mounted on the sample stage, it was
32 interfaced with the gas setup, and the custom-made miniature PTFE trough was filled with 80
33 ml of D₂O for the optimisation of the gas mixing conditions (section 3.2) or of ACMW for the
34 kinetic experiments (section 3.3). In the latter case, a monolayer with a surface concentration
35 of 2.7 × 10¹⁸ molecule m⁻² was spread using 31.5 μl of 1.13 mg ml⁻¹ *d*MO in chloroform.
36 Data were recorded for a few minutes before O₃ was admitted into the chamber at a flow rate
37 of 5 l min⁻¹, leading to [O₃]_s ranging from (2.2 ± 0.6) × 10⁶ to (4.0 ± 0.9) × 10⁷ molecule
38 cm⁻². The time resolution was 2 s except for an O₂ blank recorded with a time resolution of
39 10 s. The alignment of the interface was maintained using an optical sensor (LKG-152,
40 Keyence, Japan), which operated through the laser alignment window. Data were analysed
41 using the program MOTOFIT.¹⁹

42 2.4. Ellipsometry

43 A brief description of the physical basis of ellipsometry with reference to its application here
44 can be found in part 3 and examples of the raw data with error bars can be found in part 4 of
45 the Electronic Supporting Information. Ellipsometry measurements of the oxidation of *h*MO
46 monolayers by O₃ in the new reaction chamber were carried out using a phase modulated
47 ellipsometer (Picometer Light Ellipsometer, Beaglehole Instruments, Wellington, NZ). The

1 machine was equipped with a HeNe laser with a wavelength of 632.8 nm and the angle of
2 incidence was 50°. The sample stage was equipped with active anti-vibration control. The
3 new reaction chamber was mounted on the sample stage, it was interfaced with the gas setup,
4 and the trough was filled with 80 ml of H₂O. For the kinetic experiments (section 3.4),
5 monolayers of *h*MO were prepared using an equivalent approach to that described above.
6 Data were recorded for 250 s before O₃ was admitted into the chamber at a flow rate of 1.8 l
7 min⁻¹, leading to [O₃]_s in the ranging from (9.0 ± 0.6) × 10⁶ to (7.2 ± 0.4) × 10⁷ molecule
8 cm⁻². The time resolution was 5 s. Adjustment of the liquid height during reactions was not
9 required because the error introduced by evaporation was negligible.

10 The calibration between the measured optical phase shift, Δ, and the surface excess, Γ, can be
11 found in part 5 of the Electronic Supporting Information. In short, both for linear²⁰ and
12 empirical quadratic²¹ relations have been used in the literature for Gibb's monolayers. To our
13 knowledge such a calibration has not been determined to date for Langmuir monolayers.
14 Recently the importance of calibrating the relation on a case-by-case basis was emphasized.²²
15 As such, we measured Δ using ellipsometry and Γ using NR for equivalent spread amounts of
16 *d*MO at the air–water interface and a linear relationship was determined.

17 3. Results and Discussion

18 3.1. Chamber design

19 A schematic cross section of the new reaction chamber is shown in Figure 1.a with a
20 photograph of its exterior in Figure 1.b. The chamber is made of single blocks of aluminium
21 due to its high strength, low neutron activation and low density. It weighs just 1.6 kg, which is
22 suitable for use on a range of active anti-vibration tables. A custom-made o-ring (omitted in
23 Figure 1.a for clarity) between the top and bottom parts ensures efficient sealing. The internal
24 volume of 0.9 l is ~ 30 times lower than that of chambers used in previous related studies. A
25 custom-made PTFE trough (13 wide × 10 long cm²) is fixed at the bottom of the chamber by
26 nylon screws. Sapphire windows for the neutron beam are rectangular (90 wide × 40 high × 3
27 thick mm³) and are positioned vertically. Quartz windows for the ellipsometry beam are
28 circular (25 mm diameter) and are positioned in a tilted part of the lid at 50° to the horizontal.
29 Two o-rings for each window, one on each side, ensure gas-tight sealing as a result of their
30 clamping by window frames fixed by stainless steel screws. The inlet and outlet ports for the
31 gas flow are placed diametrically opposite on the short walls of the bottom part; the relative
32 positions of inlet and outlet was chosen to optimise the homogeneity of the gas diffusion. The
33 custom-made stainless steel gas connectors consist of a thin-walled stainless steel tube (1/8
34 inch outer diameter), and were inserted in and welded to a drilled hexagonal stainless steel
35 screw. On the outer wall a 1/4 inch tube is welded to the small tube, and on the inner part it is
36 connected to a detachable PTFE tube (inner diameter 1/8 inch), which is closed at the end and
37 contains 11 holes drilled with a separation of 1 cm along the major axis.

38 3.2. Gas injection

39 Fluid dynamics simulations were performed to optimise the positioning of the gas connectors
40 prior to the construction of the new reaction chamber. We used the ANSYS-CFX package
41 (commercially available) based on finite volume analysis. In the simulation, O₂ with a
42 dynamic viscosity of 20.459 μPa s and a density of 1.2917 kg m⁻³ was used at 25 °C. The
43 inlet tube had an inner diameter of 3.27 mm and the linear speed was 10 m s⁻¹, hence the flow
44 rate was 5 l min⁻¹. These conditions resulted in a Reynolds number of 2064 at the entry of the
45 inlet tube, which suggests that the model is close to the upper limit of laminar flow conditions
46 at the max. flow of 5 l min⁻¹. We performed both laminar and turbulent calculations and
47 observed negligible differences in the obtained velocities. The NR studies were performed at

1 5 l min⁻¹ while the ellipsometry experiments were performed at a flow rate of 1.8 l min⁻¹ i.e.
2 well into the laminar flow regime. The line of holes is oriented in order to have initially a gas
3 flow direction at 45° with respect to the horizontal. Figure 2.a shows an example of a ray
4 tracing image of the velocity resulting from the simulations under the optimum conditions: the
5 O₂ flow reaches the water surface with a low speed (< 0.5 m s⁻¹) and a pressure gradient of
6 about 2 × 10⁻³ mbar, hence the surface is only minimally affected by the gas flow.

7 Only fairly slow oxidation reactions of organic monolayers at the air–water interface
8 involving the relatively mild oxidant O₃ have been studied using NR to date.^{8–11} It would be
9 useful also to be able to study faster reactions such as oxidation initiated by nitrate radicals,
10 NO₃ (typically ~ 3 orders of magnitude faster than equivalent reactions with O₃) as well as
11 hydroxyl radicals, OH (generally ~ 3 orders of magnitude more reactive than NO₃).²³ As such,
12 we tested the maximum flow rates accessible in the new reaction chamber by examining the
13 degree of perturbation on the liquid surface resulting from the gas flow. The tests were carried
14 out by measuring the width of the specular peak of neutron reflection of an air–D₂O
15 measurement with respect to the flow rate, where broadening of the peak indicates the
16 presence of surface waves. Figure 2.b shows the results for two different pieces of tubing,
17 each 13-cm long, used to diffuse the gas inside the chamber: tubing A had 11 holes of 1-mm
18 diameter and delivers the gas more homogeneously at low flow rates and tubing B had 11
19 holes of 2-mm diameter which delivers the gas less turbulently at high flow rates. At low gas
20 flow rates the detected full width half maximum peak width remains at its minimum value of
21 2.8 mm, which shows that the gas flow does not produce measurable surface waves. This
22 minimum value, determined by the collimating slit openings and the intrinsic detector
23 resolution, is maintained to within a maximum broadening of 30% until the flow rate exceeds
24 ~ 5 l min⁻¹. This result is in keeping with the simulations discussed above.

25 A flow rate of ~ 5 l min⁻¹ in the new reaction chamber leads to a significant reduction in the
26 minimum mixing time: ~ 10 s compared to at least ~ 90 s previously.¹⁰ This improvement
27 demonstrates the capability of the new chamber to be used to study faster reactions, e.g. more
28 highly oxidised organic species with multiple functional groups and/or more potent oxidants
29 such as NO₃ uptake on organic surfaces.²⁴ Information on the kinetics of such systems has not
30 previously been accessible from NR studies at the air–water interface.

31 3.3. Neutron reflectometry

32 Recently we reported the second order rate coefficient for the oxidation of methyl oleate
33 monolayers at the air–water interface by O₃ as (5.7 ± 0.9) × 10⁻¹⁰ cm² molecule⁻¹ s⁻¹.¹⁰ The
34 measurements were carried out also using NR but in a much larger reaction chamber where it
35 was more challenging to control and characterise the gas injection. In order to demonstrate the
36 performance of the new reaction chamber, we recorded four surface excess decays with [O₃]_s
37 ranging from 2.2 × 10⁶ to 4.0 × 10⁷ molecule cm⁻², while maintaining an optimum O₂ flow
38 rate of 5 l min⁻¹. Figure 3 shows the first order rate coefficients, $k_1 = k [O_3]_s$, as a function of
39 [O₃]_s for data recorded in the new chamber in comparison with those reported previously from
40 the old chamber.¹⁰ The new data are compatible with those previously reported as they fall
41 well within the confidence limits. Furthermore, there are new data points at higher values of
42 [O₃]_s and they have statistically significantly smaller error bars. The solid line in Figure 3
43 corresponds to an orthogonal distance regression fit weighted by the uncertainties both in k_1
44 and [O₃]_s using only the four runs performed with the new miniature reaction chamber. The
45 resulting second order rate coefficient, (5.4 ± 0.6) × 10⁻¹⁰ cm² molecule⁻¹ s⁻¹, not only agrees
46 with the recently determined value but is better constrained despite having used only 4 rather
47 than 11 experimental runs. We have therefore demonstrated the potential to measure second

1 order rate coefficients of atmospheric reactions of organic monolayers at the air–water
2 interface (i) more precisely and (ii) involving faster reactions than was previously possible.

3 3.4 Ellipsometry

4 We recorded eight decays of the oxidation of *h*MO monolayers by O₃ using ellipsometry with
5 values of [O₃]_s ranging from 0.9 to 7.2×10^7 molecule cm⁻² while maintaining an O₂ flow rate
6 of 1.8 l min⁻¹. Figure 4 displays the resulting surface excess profiles with the error bars
7 omitted for clarity (errors are given in Figure S2 in the supplementary information). The mean
8 values of the ozone concentrations are reported in the legend of Fig. 4 and their uncertainties
9 are in the range of 3.5 – 10%.

10 The two slowest decays exhibit temporal fluctuations in the measured surface excess values.
11 Such a feature in the data was also observed in refs 13 and 18 where it was attributed to the
12 presence of macroscopic polymer/surfactant aggregates embedded in Gibb's monolayers. In
13 the present case, however, the fluctuations are likely to originate instead from the presence of
14 macroscopic islands of reaction products that are segregated from the reactant in the
15 Langmuir monolayer due to de-mixing, and that have different optical properties. The optical
16 signal fluctuates with time because the islands are transported in and out of the area probed by
17 the laser (~ 1 mm²) by Brownian motion and probably also Marangoni flow. (The question is
18 raised of whether this process affects the NR data analysis but the change in scattering length
19 density between the deuterated reactant and deuterated reaction products will be minimal.)
20 The surface excess values fall to zero with time, which shows that these products are present
21 only transiently at the interface before they evaporate or dissolve. The size of the islands
22 remains unresolved because to date we have not managed to couple the new reaction chamber
23 with a Brewster angle microscope during oxidation reactions (given the short focal distance of
24 the microscope objective together with the required protection of the objective from the
25 highly oxidising gas-phase environment) but it follows that they have a length scale up to the
26 millimetre range. Incorporation of a protected Brewster angle microscope into a larger
27 reaction chamber would benefit future studies even though the lateral morphologies observed
28 would not be directly comparable with the kinetic data recorded using NR and ellipsometry in
29 the miniaturised chamber due to the different gas mixing conditions. Brewster angle
30 microscopy of *h*MO monolayers prior to the decay reactions has been carried out on an open
31 trough, and the resulting images recorded at different surface pressures are presented in part 6
32 of the Electronic Supporting Information. Such fluctuations have not been revealed using NR
33 which can be explained in terms of the much larger probed area of the interface (several cm²).
34 The complementarity of using ellipsometry and NR to provide additional information for the
35 identification of reaction products, which is not trivial due to the small quantities produced
36 combined with the lack of stability at the interface, is therefore demonstrated. Also, X-ray
37 reflectometry may be used as an alternative complementary technique that is compatible with
38 our miniaturised reaction chamber (this would require only changes of the vertical windows
39 of the chamber from sapphire to, e.g., kapton), and additional structural information (e.g.
40 tilting angle)²⁵ may then be accessible thanks to the larger range of momentum transfer values
41 accessible.

42 Figure 5 shows the values of k_1 from each fitted $\Gamma(t)$ profile as a function of [O₃]_s. The linear
43 fit leads to the determination of a rate coefficient of $(5.0 \pm 0.9) \times 10^{-10}$ cm² molecule⁻¹ s⁻¹;
44 the error reported is at 95% confidence limits. The fit was performed taking into account
45 uncertainties in the k_1 values from ellipsometry and in the ozone concentrations. The negative
46 intercept lies well within the uncertainty of the fit. It should be noted that the ellipsometry
47 experiments were performed with *h*MO on pure water while the NR work was performed with
48 *d*MO on ACMW (*i.e.* 8.1% D₂O in H₂O). Ozonolysis is known to involve radical species that

1 could display a kinetic isotope effect, but our results suggest that there is no significant
2 isotope effect on the kinetics of the methyl oleate ozonolysis. The rate coefficient determined
3 here is in agreement with the values discussed above that were measured using NR.
4 Ellipsometry has therefore proved to be an adequate substitute for NR in the study of the
5 oxidation of methyl oleate monolayers by O₃. Such a positive result must be reported with a
6 degree of caution, however, as it is possible that different reaction products that have different
7 optical properties to the reactant may be retained at the interface for longer in other systems,
8 which could render the surface excess calibration and therefore the kinetic analysis inaccurate.
9 We advise therefore that new systems are validated on a case-by-case basis, i.e. a limited
10 number of measurements should be carried out using both techniques prior to the acquisition
11 of a complete data set using only ellipsometry. Nevertheless the indication is promising that
12 neutron beam time may be focussed more efficiently in the future towards studies of more
13 complex systems.

14 **4. Conclusions & Outlook**

15 We have discussed the strengths and limitations of the combined application of NR and
16 ellipsometry in the study of atmospherically-relevant chemical reactions at the air–water
17 interface. For this work we commissioned a miniaturised reaction chamber, the main features
18 of which are a low volume for controlled gas injection and compatibility for equivalent
19 measurements using the two techniques. The motivation behind this development was to keep
20 abreast with advances in NR instrumentation so that more precise determinations of rate
21 coefficients can be carried out and faster reactions can be studied. The rate coefficient of the
22 oxidation of methyl oleate monolayers by O₃ recorded using NR in the new chamber is
23 consistent with that reported previously from samples measured in a large reaction chamber
24 and is better constrained in spite of the fact that the analysis is based on fewer data points.
25 This general improvement in performance opens up in the future the possibility to access the
26 kinetics of chemical reactions that involve more reactive organic materials and/or more potent
27 gas-phase oxidants.

28 Ellipsometry was also applied to measurements of the same system in the new chamber and a
29 consistent rate coefficient was determined. The agreement between the data recorded using
30 the two techniques validates our original hypothesis concerning the use ellipsometry to
31 replace NR in the determination of the rate coefficient of the oxidation of single-component
32 monolayers. Our results also suggest that there is no significant kinetic isotope effect for the
33 ozonolysis of methyl oleate at the air–water interface. Nevertheless, for the slowest reactions
34 studied ellipsometry revealed temporal fluctuations in the optical signal, which we attribute to
35 the transient presence of segregated islands of reaction products with different optical
36 properties. On the one hand, we believe that this complementary information may be useful in
37 the future as a mean to help with the tricky identification of the reaction products, e.g. by tests
38 of the mixing of the reactant with different possible products using Brewster angle
39 microscopy. On the other hand, the results prompt us to apply a degree of caution in our
40 conclusion about the use of ellipsometry as a substitute for NR in the stated application: if
41 products with different optical properties were to remain at the interface for longer in different
42 systems, and the calibration of the optical signal to the surface excess is different for the
43 reactant and products, then the kinetic analysis may no longer be valid. Even though each new
44 system needs to be validated on a case-by-case basis, we demonstrate the potential for neutron
45 beam time to be conserved for more sophisticated studies such as those involving mixed
46 monolayers (with selective isotopic substitution) and the determination of reaction
47 mechanisms (with partial isotopic substitution).

48 **Acknowledgements**

1 We thank Alessio Laloni for the support with the design and construction of the new reaction
2 chamber, Fredric Thomas for performing the fluid dynamics simulations, Bob Thomas and
3 the Oxford Deuteration Facility for the provision of the deuterated methyl oleate, Kunal
4 Rastogi and Francesco Piscitelli for help during neutron experiments, the Partnership for Soft
5 Condensed Matter for access to the ellipsometer and the Brewster angle microscope, and the
6 ILL (Grenoble, France) for funding the construction of the chamber and allocations of beam
7 time on FIGARO. FS is grateful for support from the ILL and the University of Reading in
8 the framework of the NEATNO_x studentship. CP thanks NERC (grant number
9 NE/G000883/1) for support.

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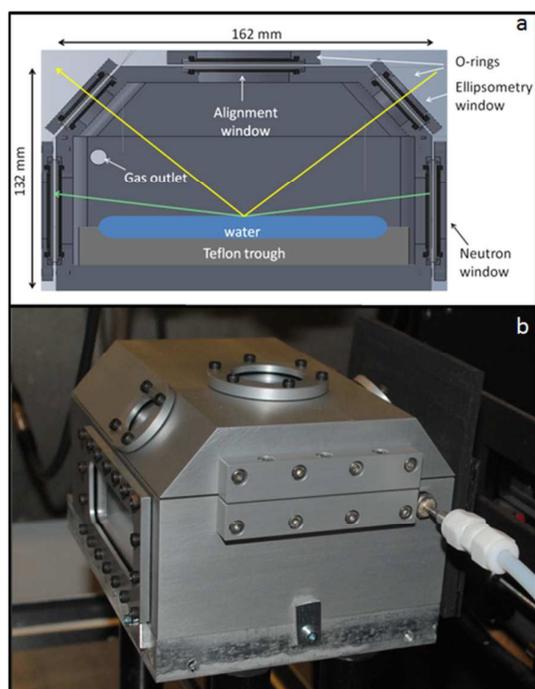
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1 Figures



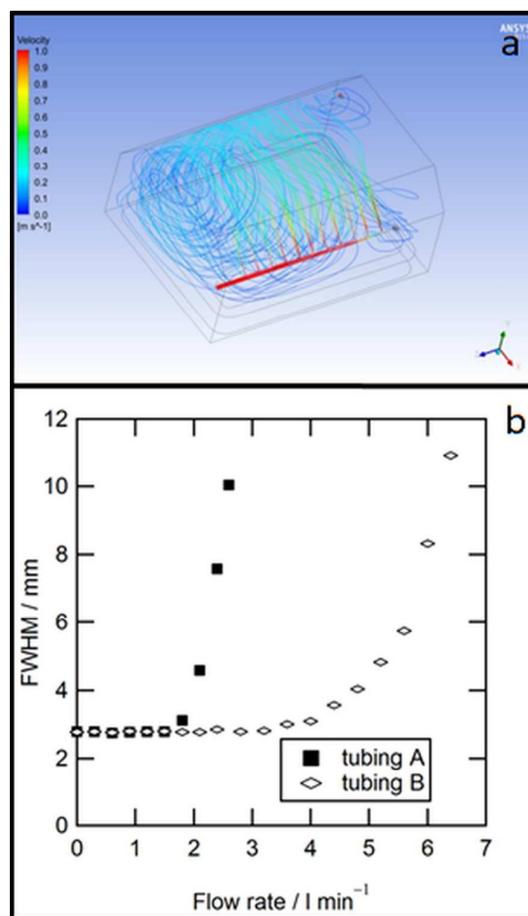
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3 **Figure 1:** a. Schematic cross section of the
 4 reaction chamber. The green arrow
 5 indicates the path of the neutron beam and
 6 the yellow arrow indicates the path of the
 7 laser beam for ellipsometry. The angle of
 8 incidence of the neutrons has been
 9 exaggerated for clarity. b. Photograph of the
 10 reaction chamber installed on the FIGARO
 11 sample stage. The neutron exit window, the
 12 laser alignment window (top), the
 13 ellipsometry windows and the gas inlet can
 14 be seen.

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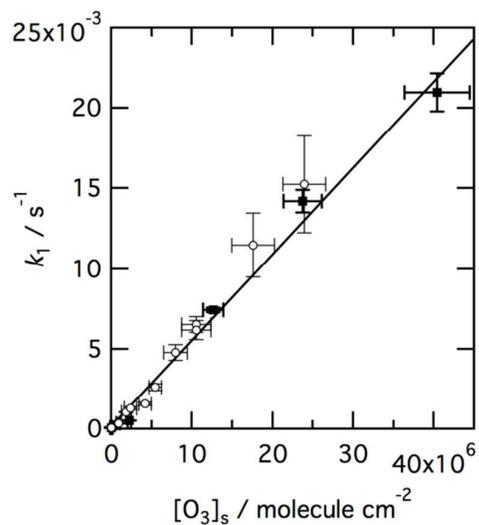
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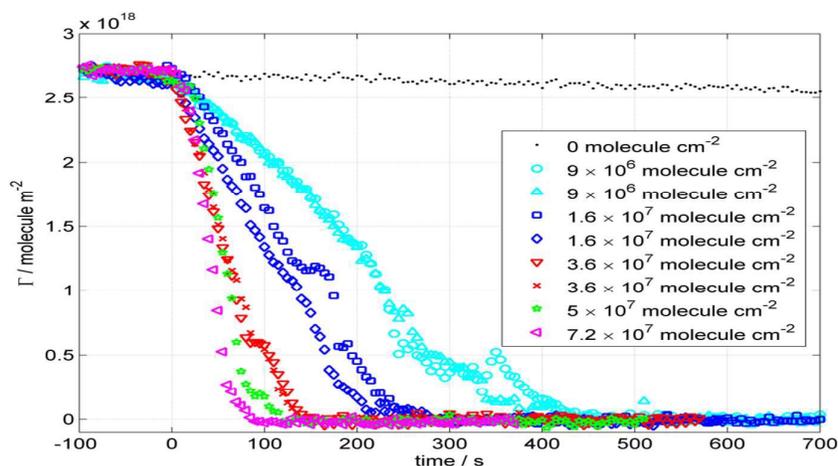


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19 **Figure 2:** a. Ray tracing image of the
 20 velocity profile in the reaction chamber
 21 when simulating a flow of pure O₂ at 25 °C
 22 and 5 l min⁻¹. b. Width of the peak
 23 corresponding to the specular reflection of
 24 neutrons at a clean air-D₂O interface with
 25 respect to the flow rate through the reaction
 26 chamber. Two different inlet systems were
 27 employed: tubing A with 11 holes of 1-mm
 28 diameter (black squares) and tubing B with
 29 11 holes at 2-mm diameter (white
 30 diamonds). Tubing A was used at a flow
 31 rate of 1.8 l min⁻¹ for all the ellipsometry
 32 studies while tubing B was used at the max.
 33 flow rate of 5 l min⁻¹ for NR.



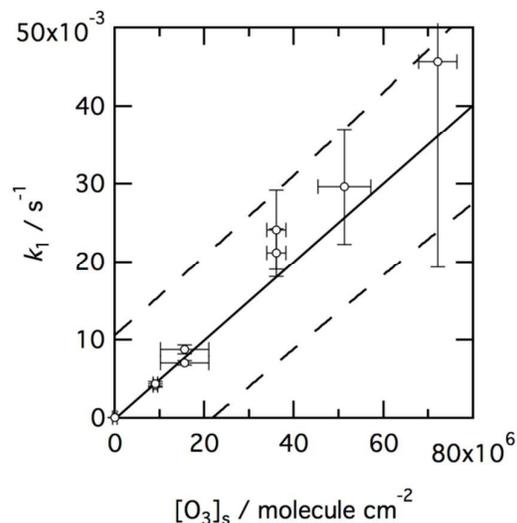
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 2 **Figure 3:** Pseudo-first order rate
 3 coefficients, k_1 , as a function of the ozone
 4 surface concentration, $[O_3]_s$, for methyl
 5 oleate monolayers measured using NR in
 6 the new reaction chamber (black squares)
 7 and those reported previously in a large
 8 chamber (white circles).¹⁰ The error bars
 9 represent the associated uncertainties at one
 10 standard deviation. The solid line
 11 corresponds to an orthogonal distance
 12 regression fit weighted by the uncertainties
 13 both in k_1 and $[O_3]_s$ using only the four new
 14 data points. The small positive intercept lies
 15 well within the uncertainty of the fit ($(2 \pm$
 16 $7) \times 10^{-4} \text{ s}^{-1}$).



1

2 **Figure 4:** Surface excess decays as a function of time for *h*MO monolayers oxidised by O₃
 3 measured using ellipsometry. The O₂ flow rate was fixed to 1.8 l min⁻¹ and the setting of the
 4 ozoniser was varied. The legend displays the mean values of the ozone surface concentration,
 5 [O₃]_s. The error bars are omitted for visual clarity; the errors range between 3.5 and 10% (the
 6 errors increase as the surface excess decreases in each experimental run). The equivalent plot
 7 with error bars can be found in part 4 of the Electronic Supporting Information.

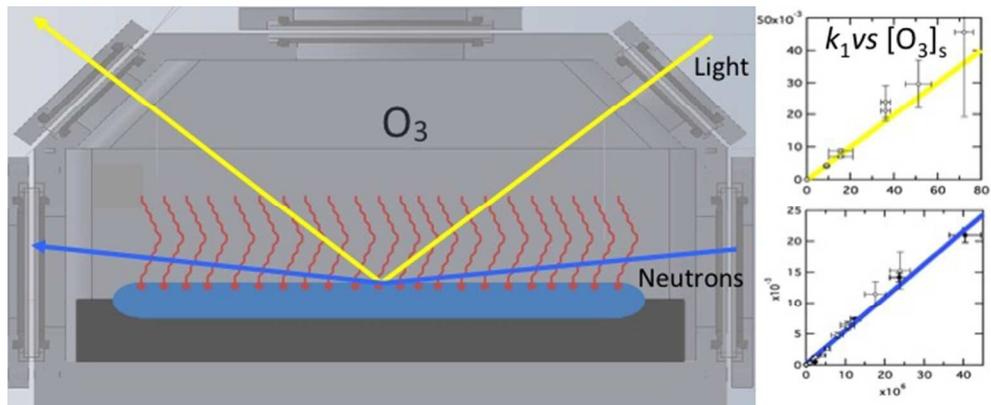
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10 **Figure 5:** Pseudo-first order rate coefficients, k_1 , as a function of the ozone surface
 11 concentration, [O₃]_s, for methyl oleate monolayers measured using ellipsometry in the new
 12 reaction chamber (white circles). The error bars represent the associated uncertainties at one
 13 standard deviation. The solid line corresponds to an orthogonal distance regression fit
 14 weighted by the uncertainties both in k_1 and [O₃]_s. The small negative intercept lies well
 15 within the uncertainty of the fit ($-(1 \pm 6) \times 10^{-4} \text{ s}^{-1}$). The dashed lines represent the 95%
 16 prediction bands.

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