

# Molecular-beam scattering of OH radicals from atmospherically relevant liquid surfaces

K.G. McKendrick, \* R.H. Bianchini, M. A. Tesa-Serrate and M. L. Costen

Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot Watt University, Edinburgh, UK.

\* Corresponding author: [K.G.McKendrick@hw.ac.uk](mailto:K.G.McKendrick@hw.ac.uk)

The aim of the work is to study the inelastic scattering of rotationally cold OH radicals from a series of continuously refreshed liquid surfaces, of interest in atmospheric chemistry, using a newly developed molecular-beam source. For technical reasons, it is more convenient to study OD radicals, which are produced by a pulsed DC electrical discharge of D<sub>2</sub>O seeded in a carrier gas. The radicals are detected via laser-induced fluorescence (LIF) at a fixed point above the liquid surface. This probes the internal energy distribution of the pre-collision and scattered species and the initial and final translational energies via time-of-flight. The liquid surfaces studied so far have been the potentially reactive surfaces squalane (C<sub>30</sub>H<sub>62</sub>, 2,6,10,15,19,23-hexamethyltetracosane) and squalene (C<sub>30</sub>H<sub>50</sub>, trans-2,6,10,15,19,23-hexamethyltetracos-2,6,10,14,18,22-hexaene), with a perfluorinated polyether (PFPE, Krytox<sup>®</sup> 1506) used as an inert reference.

The collision energy of the incoming radicals can be modified by changing the carrier gas. In experiments so far, the incoming beam was scattered at normal incidence from the liquid surfaces. Ne and He carriers give lab-frame collision energies of 6.1 kJ mol<sup>-1</sup> and 26 kJ mol<sup>-1</sup>, respectively. Integrated OD survival probabilities from the potentially reactive surfaces were obtained, assuming 100% of OD scatters from PFPE, and taking into account the rotational distribution of the scattered species. The results can be compared with previous measurements in our group using alternative photolytic sources of translationally hot OH at a higher lab-frame collision energy (54 kJ mol<sup>-1</sup>).<sup>1-3</sup> For squalene, the survival probability increases with increased collision energies, which is consistent with more thermally accommodated OD preferentially reacting via an addition mechanism at the vinyl sites on the surface. Surprisingly, the survival probabilities for squalane are relatively insensitive to collision energy over the measured range. This may be because OD at lower collision energies is more thermally accommodated at the surface, giving it more chance to react via secondary interactions, counteracting the expected higher reactivity in primary abstraction reactions at higher energies. Other subtle differences in the appearance profiles and rotational distributions of the scattered species will be discussed. Further insights into the properties of the scattered species are obtained from realistic Monte Carlo simulations of product angular and translational energy distributions.

## References

1. P. A. J. Bagot, C. Waring, M. L. Costen and K. G. McKendrick, *Journal of Physical Chemistry C*, 2008, **112**, 10868-10877.
2. C. Waring, K. L. King, P. A. J. Bagot, M. L. Costen and K. G. McKendrick, *Physical Chemistry Chemical Physics*, 2011, **13**, 8457-8469.
3. K. L. King, G. Paterson, G. E. Rossi, M. Iljina, R. E. Westacott, M. L. Costen and K. G. McKendrick, *Physical Chemistry Chemical Physics*, 2013, **15**, 12852-12863.