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Electronic Supplementary Information

Site and bond-specific dynamics of reactions at the gas-liquid interface

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Calculation of OH translational energy

The average values of OH translational energy in Table 3 have been obtained by fitting the experimental appearance profiles to Monte Carlo simulated profiles with a thermal distribution of recoil speeds. The Monte Carlo simulation accounts for parameters such as the beam-to-surface distance, the O(^{3}P) velocity distribution resulting from 355 nm NO_2 photolysis, the diameter of the laser beams and the dimensions of the liquid surface, and the geometry of the detection volume. Appearance profiles are simulated by calculation of a large number of individual OH trajectories using Monte-Carlo sampling over the experimental parameters. First, the initial position of the NO_2 molecule in the photolysis beam is selected from a uniform distribution. The velocity of the resulting O(^{3}P) atom is sampled from the known distribution produced in the photolysis of NO_2 at 355 nm. If the resulting trajectory intersects the liquid surface, the flight-time to the surface is recorded and the impact point is calculated, and used as the starting point for an OH recoil trajectory. The speed of the recoiling OH is selected from a Maxwell-Boltzmann distribution defined by a temperature, *T*, and the OH recoil direction is sampled from a cosine-weighted distribution about the surface normal. If the returning OH trajectory intersects the detection volume, the range of delays at which the OH is within the volume is calculated, and the relevant times in the simulated appearance profile are incremented. A comparison between experimental and simulated profiles is presented in Fig. S1, along with the values of *T* employed in each simulation. Each simulated profile is the result of sampling typically 2.5×10^6 trajectories, of which approximately 2×10^5 were successful. Experimental appearance profiles for the $Q_1(1)$ transition have been taken as representative of all of the scattered OH. Temperatures, *T*, have been chosen to match the simulated profiles to the experimental ones. The average speeds as a function of delay in Fig. S1 are the result of averaging the recoil speeds of all successful trajectories that contribute to a particular delay.

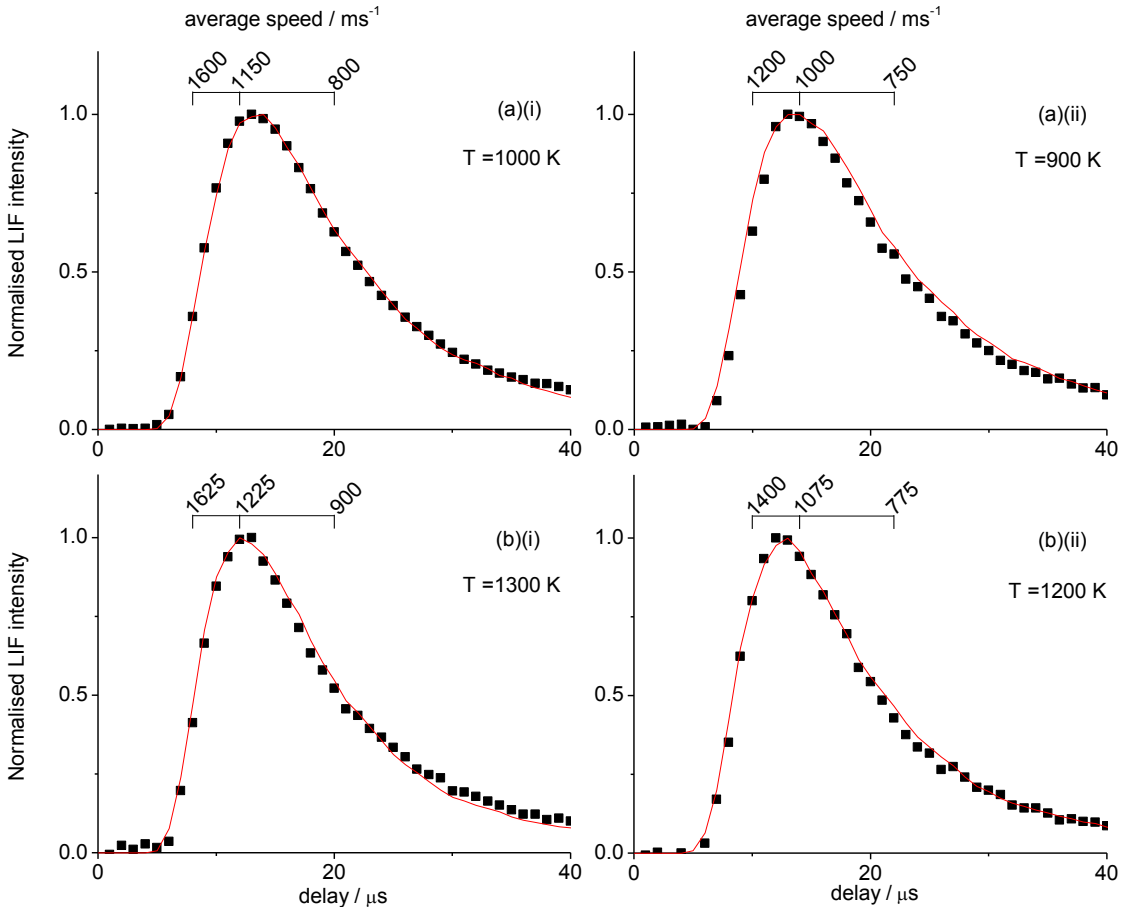

Figure S1. Experimental (black squares) and simulated (red lines) OH appearance profiles for the $Q_1(1)$ transition, as described in the text. (a)(i) Squalane v'=0, (a)(ii) squalane v'=1, (b)(i) squalene v'=0, (b)(ii) squalene v'=1. Values of T employed in the simulated profiles are indicated in each of the panels. Average OH speeds as a function of delay derived from the Monte-Carlo simulation are also shown.