Is OH produced from NO_2^* + H_2O or NO_3^* + H_2O?

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Li *et al*. (1) identified a new source of atmospheric radicals, whereby electronically excited NO_2 (A^2B_2 or B^2B_1, together denoted NO_2^*, produced via photoexcitation, R1), reacts with H_2O to generate OH (R2b):

$NO_2 + h\nu$ (vis.)	$\rightarrow$	NO_2^*	(R1)
$NO_2^* + H_2O$	$\rightarrow$	$NO_2 + H_2O$	(R2a)
	$\rightarrow$	$OH + HONO$	(R2b)

Despite the reportedly low product yield, $k_{2b} / k_2 = 0.001$, this process may still represent a significant source of OH due to the large solar flux in the visible region of the spectrum. Wennberg et al. (2) calculated enhancements in modeled OH of up to 40 % upon including (R1-R2) in polluted-air scenarios. Large uncertainties remain however, as several groups (3,4,5) have found little or no evidence for OH production following excitation at certain discrete visible wavelengths.

Accordingly, experiments were conducted using pulsed laser excitation at five suitable visible wavelengths (532 – 647 nm) to prepare NO_2^*. Despite the presence of a large excess of H_2O, no evidence for OH formation (R1b) was found. Calibration of the LIF detection system allowed upper-limits of $k_{2b} / k_2 < 0.0002$ to be assigned at all wavelengths tested, indicating that this reaction is of no atmospheric interest.

The experimental setup was extended to facilitate generation of NO_3 radicals by pulsed laser photolysis. Pulsed laser excitation (R3, 612 – 662 nm) was used to generate excited-state radicals NO_3^* ($A^2\Sigma$); calibrated LIF to monitor any OH production from (R4).

$NO_3 + h\nu$ (vis.)	$\rightarrow$	NO_3^*	(R3)
$NO_3^* + H_2O$	$\rightarrow$	$NO_3 + H_2O$	(R4a)
	$\rightarrow$	$OH + HONO_2$	(R4b)

References

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