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NO_2 quantum yields from ultraviolet photodissociation of methyl and isopropyl nitrate

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Analysis of CRDS data to obtain quantum yields

The UV laser used to photolyse $RONO_2$ has an elliptical Gaussian intensity profile. If we take the laser to be propagating along the *z* axis, with total power I_0, the intensity profile $i(x,y)$ at any *z* is given by:

$$i(x,y) = \frac{2I_0}{\pi w_x w_y} exp\left(-\frac{2x^2}{w_x^2}\right) exp\left(-\frac{2y^2}{w_y^2}\right) \tag{1}$$

where w_x and w_y are the Gaussian beam waists along two orthogonal axes of the elliptical profile, and the intensity is normalized so that the integral over all *x* and *y* gives the total power.

Consider a single pass of the UV laser pulse through a sample of $RONO_2$ with concentration $[RONO_2]$ and sample length ℓ. From the Beer-Lambert law, the number of photons absorbed (N_{abs}) by the $RONO_2$ sample is related to the total number of photons in the laser pulse (N_{ph}) via:

$$N_{abs} = N_{ph}\{1 - exp(-\sigma_{RONO_2}[RONO_2]\ell)\} \tag{2}$$

The number of NO_2 molecules formed photolytically is

$$N_{NO_2} = N_{abs}\Phi_{NO_2} \tag{3}$$

If we assume that the distribution of the NO_2 molecules mirrors the intensity distribution of the UV laser pulse, we can express the 3-D probability density function of NO_2 as:

$$n(x,y,z) = \frac{N_{NO_2}}{V_{UV}} exp\left(-\frac{2x^2}{w_x^2}\right) exp\left(-\frac{2y^2}{w_y^2}\right) \tag{4}$$

Here, V_{UV} is the volume swept out by the laser pulse passing through the sample, and can be calculated by integration of (1) over *x* and *y* and multiplication by ℓ. The absorption by the sample is assumed to be sufficiently weak that the change in intensity over the 3-cm pathlength is negligible, so $n(x,y,z)$ is independent of *z*. The resultant expression for the photolysis laser volume is:

$$V_{UV} = \frac{\pi}{2}\,\ell\, w_x w_y \qquad (5)$$

Substitution of equations (2), (3) and (5) into (4) gives an expression for the probability density function for the photolytically generated NO_2 in terms of known experimental parameters and the required quantum yield.

The CRDS experiment measures absorption by NO_2 along a line of sight that we choose to be the *y* axis. If we approximate the CRDS beam waist as being very small compared to the cross sectional dimensions of the UV photolysis beam, the absorbance measured in the CRDS experiments at the probe laser wavelength λ is (at any *x*, and independent of *z*):

$$A_x(\lambda) = \sigma_{NO_2}(\lambda)\int_{-\infty}^{\infty} n(x,y,z)\,dy \qquad (6)$$

The resultant function is evaluated at $x = 0$ to represent the CRDS beam passing through the centre of the UV photolysis beam: $A(\lambda) = A_{x=0}(\lambda)$. The absorbance at a probe laser wavelength λ is related to the change in the ring-down rate coefficient in the presence of NO_2 by:

$$\Delta k(\lambda) = \frac{A(\lambda)c}{L} \qquad (7)$$

where *c* is the speed of light and *L* the length of the ring-down cavity. Carrying out the integration in equation (6) and substitution into (7) gives the result:

$$\Delta k = \frac{c\,N_{ph}\,\Phi_{NO_2}\sigma_{NO_2}}{L w_x \ell}\sqrt{\frac{2}{\pi}}\left\{1 - exp\left(-\sigma_{RONO_2}[RONO_2]\ell\right)\right\} \qquad (8)$$

The explicit dependence on wavelength has been dropped from the notation, but Δk, Φ_{NO_2} and σ_{RONO_2} will all depend on the photolysis wavelength. The right hand side of equation (8) can be doubled to allow for the double-pass of the UV laser through the sample, giving equation (5) of the main text, or evaluated separately for each pass of the laser beam, with correction for attenuation of the laser beam on the second pass by windows and optics, and summation of the two values of Δk.

Under the experimental conditions employed, the beam waist of the CRDS probe beam at the centre of the ring-down cavity is calculated to be w_0 = 0.26 mm if the cavity TEM_{00} mode is excited. This is a factor of 2.8 smaller than the UV laser beam waist along the x direction. The assumption that the probe beam waist is negligible must therefore be examined more carefully. The absorbance calculation of equation (6) can be modified to include integration over the CRDS beam in the x dimension. For simplicity, an approximation is made of uniform probe beam intensity:

$$A(\lambda) = \int_{-w_0}^{w_0} A_x(\lambda)\, dx \qquad (9)$$

The resulting expression for the change in ring-down rate is:

$$\Delta k = \frac{c\, N_{ph} \Phi_{NO_2} \sigma_{NO_2}}{L w_0 \ell \sqrt{\pi}}\, erf\left(\frac{\sqrt{2} w_0}{w_x}\right)\left\{1 - exp\left(-\sigma_{RONO_2}[RONO_2]\ell\right)\right\} \qquad (10)$$

This alternative equation, incorporating an error function, can be evaluated in the same spreadsheet as used for the analysis of ring-down data by equation (8), with account taken for the double pass of the photolysis laser beam. If, as in our experiments, the UV laser is partially attenuated by passage out of the flow tube, through a turning prism, and return through the flow tube window, the second pass is best treated using a second calculation of Δk by equation (8) or (10) in which the parameter N_{ph} is appropriately reduced in magnitude. The inclusion in the data analysis of the non-negligible waist for the CRDS intra-cavity laser beam makes less than a 3% difference in the finally derived Φ_{NO_2} values under the conditions of our experiment.

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