Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics


# Absolute density measurement of SD radicals in a supersonic jet at the quantum-noise-limit

## Supplementary information

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### I. DATA AND ERROR ANALYSIS

The number of photon counts on the LIF PMT $S^{\rm LIF}_{{\rm tot},i}$ for each $i$th shot was recorded for $n$ laser shots to give the "total" signal counts originating from SD molecules and from background sources. Simultaneously, the cavity ring-down (CRD) transient was recorded for each $i$th laser shot. Each CRD transient was fitted with an exponential to obtain the amplitude $A^{\rm CRD}_{0,i}$ and the ring-down time $\tau_i$ and the integrated CRD intensity calculated

$$I^{\rm CRD}_{{\rm tot},i} = A^{\rm CRD}_{0,i}\tau_i. \tag{1}$$

The total CELIF signal for each laser shot

$$S^{\rm CELIF}_{{\rm tot},i} = \frac{S^{\rm LIF}_{\rm tot,i}}{I^{\rm CRD}_{{\rm tot},i}} \tag{2}$$

was then calculated and averaged over all laser shots to give the average total CELIF signal per shot $S^{\rm CELIF}_{\rm tot}$. This procedure was found to give the same result as using

$$S^{\rm CELIF}_{\rm tot} = \frac{S^{\rm LIF}_{\rm tot}}{I^{\rm CRD}_{\rm tot}}, \tag{3}$$

where the subscript $i$ has been dropped because $S^{\rm LIF}_{\rm tot}$ is the average number of photon counts per laser shot and $I^{\rm CRD}_{\rm tot}$ is the average integrated CRD intensity per shot.

Immediately following $n$ laser shots, the dissociation laser was blocked and the same procedure above was repeated for another $n$ laser shots to arrive at the average CELIF signal per shot from background sources $S^{\rm CELIF}_{\rm bg}$. The average CELIF signal per shot originating from SD molecules was thus determined by the background subtraction

$$S^{\rm CELIF}_{\rm SD} = S^{\rm CELIF}_{\rm tot} - S^{\rm CELIF}_{\rm bg} \tag{4}$$

and is plotted in Fig. 3. The CELIF normalisation of the background is justified when one considers the sources of the background signal. Even though the cavity is an effective discriminator of scattered light compared to a standard LIF setup, 99% of $S^{\rm LIF}_{\rm bg}$ originated from scattered light from the probe laser, most likely from UV fluorescence of the UV grade fused silica substrate of the cavity entrance mirror. $S^{\rm LIF}_{\rm bg}$ was found to be proportional to $I^{\rm CRD}_{\rm bg}$.

The error bars in Fig. 3 for $S^{\rm CELIF}_{\rm SD}$ were determined as follows. The relative fitting error on $A^{\rm CRD}_{0,i}$ and $\tau_i$, was

$$\beta(A_{0,i}) = \frac{\delta A^{\rm CRD}_{0,i}}{A^{\rm CRD}_{0,i}} = 0.1\% \qquad \text{and} \qquad \beta(\tau_i) = \frac{\delta\tau_i}{\tau_i} = 1\%, \tag{5}$$

respectively. The relative fitting errors, $\beta(A_{0,i})$ and $\beta(\tau_i)$, were found on analysis to vary insignificantly over all laser shots because the cavity was set up such that the ring-down transients were good quality single exponential decays with electronic noise that did not vary significantly shot-to-shot. Thus, $\beta(A_{0,i})$ and $\beta(\tau_i)$ are treated as constants, $\beta(A_0)$ and $\beta(\tau)$, where $\beta(A_0) \ll \beta(\tau)$. The resulting relative error $\beta(I)$ on the *determination* of each $I^{\rm CRD}_{{\rm tot},i}$ only depends on the fitting errors and is, therefore

$$\beta(I) = \sqrt{\beta(A)^2 + \beta(\tau)^2} \approx \beta(\tau), \tag{6}$$

$\beta(I)$ is the only relevant error with respect to $I^{\mathrm{CRD}}_{\mathrm{tot},i}$ because an important point of CELIF is to remove noise caused by shot-to-shot fluctuations in laser intensity. The quantum noise from counting LIF photons over $n$ laser shots was

$$\delta S^{\mathrm{LIF}}_{\mathrm{tot}} = \left(\frac{S^{\mathrm{LIF}}_{\mathrm{tot}}}{n}\right)^{1/2}, \tag{7}$$

and comes from Poisson statistics. Therefore, the combined noise in $S^{\mathrm{CELIF}}_{\mathrm{tot}}$ is

$$\delta S^{\mathrm{CELIF}}_{\mathrm{tot}} = \left[\frac{1}{nS^{\mathrm{LIF}}_{\mathrm{tot}}} + \beta(\tau)^2\right]^{1/2} S^{\mathrm{CELIF}}_{\mathrm{tot}}. \tag{8}$$

An equivalent to eqn (8) for the background CELIF signal can be derived in the same way except the error is dominated by the quantum noise because $S^{\mathrm{LIF}}_{\mathrm{bg}}$ is very small, *i.e.*

$$\delta S^{\mathrm{CELIF}}_{\mathrm{bg}} \approx \left(\frac{1}{nS^{\mathrm{LIF}}_{\mathrm{bg}}}\right)^{1/2} S^{\mathrm{CELIF}}_{\mathrm{bg}}. \tag{9}$$

The noise in $S^{\mathrm{CELIF}}_{\mathrm{SD}}$ from eqn (4) is

$$\delta S^{\mathrm{CELIF}}_{\mathrm{SD}} = \left[\left(\delta S^{\mathrm{CELIF}}_{\mathrm{tot}}\right)^2 + 2\left(\delta S^{\mathrm{CELIF}}_{\mathrm{bg}}\right)^2\right]^{1/2}, \tag{10}$$

where the factor 2 comes from the fact that $S^{\mathrm{CELIF}}_{\mathrm{tot}}$ contains $S^{\mathrm{CELIF}}_{\mathrm{bg}}$.

## II. LIMIT OF DETECTION DERIVATION

To derive an expression for the limit of detection (LOD) of $S^{\mathrm{CELIF}}_{\mathrm{SD}}$, which is the horizontal line in Fig. 3, the approximation that $I^{\mathrm{CRD}}_{\mathrm{tot}} = I^{\mathrm{CRD}}_{\mathrm{bg}} = I^{\mathrm{CRD}}$ is made such that

$$S^{\mathrm{LIF}}_{\mathrm{SD}} = S^{\mathrm{LIF}}_{\mathrm{tot}} - S^{\mathrm{LIF}}_{\mathrm{bg}}, \tag{11}$$

so the noise in $S^{\mathrm{LIF}}_{\mathrm{SD}}$ is

$$\left(\delta S^{\mathrm{LIF}}_{\mathrm{SD}}\right)^2 = \left(\delta S^{\mathrm{LIF}}_{\mathrm{tot}}\right)^2 + 2\left(\delta S^{\mathrm{LIF}}_{\mathrm{bg}}\right)^2 = \frac{1}{n}\left(S^{\mathrm{LIF}}_{\mathrm{SD}} + 2S^{\mathrm{LIF}}_{\mathrm{bg}}\right). \tag{12}$$

At the LOD, $S^{\mathrm{LIF}}_{\mathrm{SD}} = S^{\mathrm{LIF,LOD}}_{\mathrm{SD}} = \delta S^{\mathrm{LIF}}_{\mathrm{SD}}$, therefore

$$n\left(S^{\mathrm{LIF,LOD}}_{\mathrm{SD}}\right)^2 = S^{\mathrm{LIF,LOD}}_{\mathrm{SD}} + 2S^{\mathrm{LIF}}_{\mathrm{bg}}. \tag{13}$$

Solving for $S^{\mathrm{LIF,LOD}}_{\mathrm{SD}}$ gives

$$S^{\mathrm{LIF,LOD}}_{\mathrm{SD}} = \frac{1}{2n} + \left(\frac{1}{4n^2} + \frac{2S^{\mathrm{LIF}}_{\mathrm{bg}}}{n}\right)^{1/2}, \tag{14}$$

which, in the limit of large $n$, gives

$$S^{\mathrm{LIF,LOD}}_{\mathrm{SD}} \approx \left(\frac{2S^{\mathrm{LIF}}_{\mathrm{bg}}}{n}\right)^{1/2}. \tag{15}$$

The CELIF signal at the LOD is therefore

$$S^{\mathrm{CELIF,LOD}}_{\mathrm{SD}} \approx \left(\frac{2S^{\mathrm{LIF}}_{\mathrm{bg}}}{n\left(I^{\mathrm{CRD}}\right)^2}\right)^{1/2}, \tag{16}$$

which, when compared to eqn (9), reveals that

$$S^{\mathrm{CELIF,LOD}}_{\mathrm{SD}} \approx \sqrt{2}\delta S^{\mathrm{CELIF}}_{\mathrm{bg}}. \tag{17}$$