SUPPLEMENTARY MATERIAL

Absolute fluorescence and absorption measurements over a dynamic range of $10^6$ with cavity-enhanced laser-induced fluorescence

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INTRODUCTION

The principles of the data and error analysis described in the main body of the paper are discussed here in greater detail. For most of the data presented in the paper, ring-down times and integrated transients were determined ‘on-the-fly’ during the measurements. While all the pre-processed data has been recorded, due to acquisition times and computing demands, only a part of the transients were saved. In the first part of the supplementary material we present a rigorous analysis of individual transients to demonstrate the strong correlation between the cavity ring-down (CRD) and the cavity-enhanced laser-induced fluorescence (CELIF) measurements. We then discuss and compare the statistical distributions observed in the CRD and CELIF measurements. In the final part of the supplementary material the procedure to derive the absorption coefficient, $\alpha$, from a CELIF measurement including background subtraction, normalisation and calibration is explained in greater detail.

S1. ANALYSIS OF INDIVIDUAL MEASUREMENTS

In a CELIF measurement three quantities are extracted from the LIF and CRD transients: the time-integrated LIF transient, $S_{\text{LIF}}$, time-integrated CRD transient, $S_{\text{CRD}}$, and the ring-down time, $\tau$ or $\tau_0$. For the data presented in the main paper, the ring-down times were determined via non-linear least-squares fits and the integrated transients via numerical integration. In the following we demonstrate the quality and error of the fitting and we assess the error of the numerical integration due to the noise in the LIF and CRD transients.

Fitting of transients

Fig. S1 shows a pair of simultaneously recorded LIF and CRD transients. This is the same data as presented in Fig. 2 of the main paper although shown at the original sampling rate of 2.5 GS/s of the digital oscilloscope used (LeCroy, Waverunner 104Xi, 8 bit, 1 GHz). We will first discuss the analysis of the CRD transient. The non-zero offset of the PMT signal was determined via the average of the sampled data points before the trigger (in Fig. S1, 1200 points, from $-0.53\mu s$ to $-0.05\mu s$). This offset was subtracted from the transient before
FIG. S1. Raw-data of simultaneously recorded (a) LIF and (b) CRD transients of jet-cooled BPEB on the vibronic transition at 319.44 nm. The data is the same as depicted in Fig. 2, panels (a) and (b). Note that the transients in Fig. 2 were smoothed to a time bin of $\Delta t = 4.8$ ns for clarity whereas the raw data was recorded at $\Delta t = 0.4$ ns. The exponential fits (red) and residuals (blue) are superimposed.

Performing a non-linear least-squares fit using the exponential function

$$I_{\text{fit}}(t) = I_0 \exp \left(-\frac{t}{\tau}\right)$$

(S1)

in which $I_0$ is the amplitude at time $t = 0$. The resulting fit and residual are superimposed on Fig. S1(b). The flat residual demonstrates the high quality of the ring-down decay and the fitting.

Integration of transients

The error in the numerically integrated ring-down transient cannot be determined directly as the magnitude of the noise of the transient is not known beforehand and may change with signal levels. However, if we assume that the exponential fit to the transient represents the true decay, we can compare the numerical integral of the noisy data to the analytical integral of the “noiseless” fitting function.

The integrals of the ring-down transient, based on the fit and on the numerical integration
FIG. S2. Shot-to-shot correlation between the integrated ring-down transients, determined by fitting the ring-down transient, $S_{\text{CRD}}^{\text{fit}}$ (x axis), and by numerical integration via the trapezium rule, $S_{\text{CRD}}^{\text{trapz}}$ (y axis). The Pearson correlation coefficient is 1.000, demonstrating the quality of the ring-down transients as well as the robustness of the data analysis. The propagated fitting error in $S_{\text{fit}}^{\text{CRD}}$ is similar to the width of each data point in the graph.

Using the trapezium rule, are given by

$$S_{\text{fit}}^{\text{CRD}} = I_0 \int_{t_1}^{t_2} \exp(-t/\tau) \, dt = I_0 \tau \cdot \left[ \exp \left( -\frac{t_1}{\tau} \right) - \exp \left( -\frac{t_2}{\tau} \right) \right]$$

and

$$S_{\text{trapz}}^{\text{CRD}} = \sum_{i=i_1}^{i_2-1} \frac{I_i + I_{i+1}}{2} \Delta t,$$

respectively, in which $t_1$ and $t_2$ are the limits of the integration (cf. Fig. 2 of the main paper), $i_1$ and $i_2$ are the corresponding indices of the digitised intensities, $I_i$, and $\Delta t$ is the time resolution (bin width) of the digitizer.

Fig. S2 shows the correlation between the integrated ring-down transients from fitting and numerical integration (Eqs S2 and S3, respectively) based on the same 101 CRD transients used to derive the ring-down times with sample as shown in Fig. S3 (left). The ratios $S_{\text{trapz}}^{\text{CRD}} / S_{\text{fit}}^{\text{CRD}}$ determined from the individual transients are virtually one, i.e. identical, with a statistical $1\sigma$ spread of only $2 \cdot 10^{-4}$. The Pearson correlation coefficient of the two data
sets is $r > 1 - (6 \cdot 10^{-7})$, showing that both methods determine the same integral. This means that, as expected, the numerical integration virtually eliminates the noise of the transient from $S_{\text{CRD}}$. Based on this comparison, we conclude that $S_{\text{CRD}}$ can be determined with a relative error of $\pm 0.02\%$ in our measurements. This value is consistent throughout the whole series of measurements shown in Fig. 5 of the main paper.

We employ the same procedure to determine the integrals of the LIF transients, see the fitted example in Fig. S1(a). The noise on the LIF transient seems more erratic than that on the CRD transient. For high BPEB sample densities (corresponding to the 350 ppm data point in Fig. 5), where the LIF transient is a well defined exponential, the typical relative error in $S_{\text{LIF}}$ is in the order of $\pm 0.03\%$, i.e. comparable to the error for the integrated ring-down transient. As the LIF signal diminishes with decreasing sample density, the noise of the LIF transient becomes more significant. At low BPEB concentrations, the gain of the LIF PMT had to be increased to such an extent that the transients were affected by quantum noise and were too noisy to be fitted individually. In order to derive a meaningful fits, the 101 individual transients were averaged to determine a common decay time. The individual transients were then fitted using a floating amplitude but keeping the decay time fixed, cf. Eq. S1. At the lowest BPEB density used (0.5 ppm data point in Fig. 5), the relative error in the determination of $S_{\text{LIF}}$ increased to about 2%.

The above analysis shows that the determination of $S_{\text{LIF}}$ and $S_{\text{CRD}}$ via numerical integration is very robust and justifies the normalization procedure to determine the CELIF signal, as described in Section II.A (Eqn. 14) of the main paper:

$$S_{\text{CELIF}} = \frac{S_{\text{LIF}}}{S_{\text{CRD}}}$$  \hspace{1cm} (S4)

S2. DISTRIBUTIONS

Distributions of ring-down times

The data set used to demonstrate the superior signal-to-noise ratio of the CELIF technique compared to traditional pulsed CRDS, Fig. 5 of the main paper, was analysed in more detail. In particular, the first 101 simultaneously recorded LIF and CRD transients were saved for post-analysis and fitted according to Eq. S1. Note that this data set was recorded with a digitizer (AlazarTech ATS460, 14-bit, 125 MS/s, 65 MHz).
FIG. S3. Histograms and normal distributions of cavity ring-down times based on 101 samples of a cavity under vacuum (right) and with an absorber (left). The laser wavelength coincides with the strongest absorption of BPEB in Fig. 4 (319.69 nm). The distribution with absorber corresponds to the highest sample density as shown in Fig. 5 of the main paper. The limits for the exponential fit, from 0.12 µs to 2.68 µs with respect to the start of the decay, are the same as seen in Fig. 2 of the main paper. The respective ring-down times and 1σ spreads are 2.174 ± 0.016 µs and 1.675 ± 0.051 µs.

The right-hand side of Fig. S3 shows the distribution of fitted ring-down times for an empty (in vacuo) cavity. The average ring-down time is $\bar{\tau}_0 = 2.1738 \pm 0.0162$ µs (1σ spread, ±0.75%). In comparison, the average of the 101 individual fitting errors of $\tau_0$ is 0.0183 µs with a small spread of ±0.0013 µs. The fitting errors may be dominated by the electrical noise of the detection system (photomultiplier, cables and digitizer). Lehmann and Huang give a detailed account on how electronic (or mathematical) filters can be used to improve the quality of the extracted ring-down times from CRD transients.\textsuperscript{S1} Here, we apply a simple Gaussian filter (full-width at half maximum of 80 ns, 8 ns time bin of digitizer) to suppress the electrical noise without distorting the decay. Refitting the smoothed transients reduces the fitting errors by about a factor of six (average 0.0030 ± 0.0006 µs) whereas the ring-down times are unchanged within their respective fitting errors ($\bar{\tau}_0 = 2.1732 \pm 0.0159$ µs). This demonstrates that the transients are high-quality exponential decays and the consistency of the fitting. We conclude that the spread of the empty-cavity ring-down times is not caused...
by electronic noise but is due to shot-to-shot variations of the dye laser beam (spectral composition, spatial profile) as well as random mechanical motions of the cavity mirrors (mode coupling into the cavity).

In the presence of an absorbing sample, here 1,4-bis(phenylethynyl)benzene (BPEB) seeded in a pulsed molecular beam, the observed distribution of ring-down times is widened, see left-hand side of Fig. S3. The average ring-down time of the 101 individual transients with its $1\sigma$ spread is $\bar{\tau} = 1.6746 \pm 0.0509 \text{ } \mu$s ($\pm3.0\%$) and the average fitting error is $0.0123 \pm 0.0006 \text{ } \mu$s. The notably larger spread of the ring-down times compared to the empty-cavity measurement is due to density fluctuations in the molecular beam caused by the pulsed source. In the measurements presented in this paper, these fluctuations in sample density are the largest source of uncertainty in the determination of absorption coefficients from both the ring-down time (CRDS) and CELIF measurements.

**Standard deviations in CRD and CELIF measurements**

The statistics of the pulsed molecular-beam measurements of BPEB discussed in this work are affected by the large fluctuation in sample density on a shot-to-shot basis, cf. Fig. S3. In contrast, the $\text{N}_2$ Rayleigh-scattering measurement of a filled cavity presented in Fig. 3(b) of the main paper is devoid of these shot-to-shot density fluctuations. This data was recorded over the course of more than two hours starting from vacuum, increasing the pressure to 1 bar and then evacuating the cavity again. The flow and pumping speeds were not held constant, leading to a different number of laser shots per pressure interval. The empty-cavity ring-down time and the background CELIF signal were determined from a linear fit to all data points extrapolated to a pressure of zero. The background-subtracted CELIF fractional “absorption” (Rayleigh-scattering loss) was calibrated via the slopes of the linear fits to the CRD and CELIF data with pressures above the lower trusted limit of the capacitance manometer of 1.4 mbar. Both linear fits used a floating intercept, both of which are zero within their fitting errors.

Fig. 3(b) compares the variations in the CRD and CELIF measurements as a function of sample density (pressure). For visualisation, we grouped the laser shots in pressure intervals of 10 mbar per data point. The minimum number of laser shots per interval was 311, hence, this number of data points was randomly selected from the shots in each pressure interval.
TABLE S1. Reference to Fig. 3(b) of main paper. Comparison of the fractional Rayleigh-scattering losses per pass, $\mathcal{L}$, their standard deviations, $\sigma_{\mathcal{L}}$, and standard errors, $\sigma_{\mathcal{L}}/\sqrt{n}$, determined from the simultaneous CRD and CELIF measurements of N$_2$ Rayleigh scattering in a filled cavity. Data points are grouped within a 2 mbar pressure interval centred at the listed pressures. The fit represents the linear fit to all CRD data points used in the calibration, see text.

<table>
<thead>
<tr>
<th>Pressure (mbar)</th>
<th>Shots, $n$</th>
<th>Fit</th>
<th>CRD</th>
<th>CELIF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\mathcal{L}$</td>
<td>$\sigma_{\mathcal{L}}$</td>
<td>$\mathcal{L}$</td>
</tr>
<tr>
<td>10</td>
<td>715</td>
<td>0.074 ppm</td>
<td>0.033 ppm</td>
<td>0.420 ppm</td>
</tr>
<tr>
<td>50</td>
<td>369</td>
<td>0.369 ppm</td>
<td>0.374 ppm</td>
<td>0.470 ppm</td>
</tr>
<tr>
<td>124</td>
<td>314</td>
<td>0.915 ppm</td>
<td>1.118 ppm</td>
<td>0.456 ppm</td>
</tr>
<tr>
<td>220</td>
<td>262</td>
<td>1.624 ppm</td>
<td>1.602 ppm</td>
<td>0.441 ppm</td>
</tr>
<tr>
<td>508</td>
<td>183</td>
<td>3.750 ppm</td>
<td>3.599 ppm</td>
<td>0.435 ppm</td>
</tr>
<tr>
<td>998</td>
<td>625</td>
<td>7.366 ppm</td>
<td>7.480 ppm</td>
<td>0.422 ppm</td>
</tr>
</tbody>
</table>

The standard deviations of the CRD measurements in Fig. 3(b) show no pressure dependence. Over the range of N$_2$ pressures (0.1 − 1000 mbar) the ring-down time does not change significantly (averages 20.6 − 19.5 $\mu$s) such that this observation is not surprising. In contrast, the standard deviation in the CELIF measurement increases with pressure, i.e. with the amount of fluorescence detected, consistent with the statistical fluctuations caused by the amplification of electron current in the photomultiplier.

For a more quantitative discussion, we analysed the same data more specifically. Table S1 lists the fractional Rayleigh-scattering losses and their variations at selected pressures, grouped within 2 mbar pressure intervals. We have confirmed that the variation in pressure over the 2 mbar intervals does not change the standard deviations. The table shows the same trends as discussed above. Although the CELIF probe volume is only about 0.4% of that of the simultaneous CRD measurement, the variations in the CELIF measurements are notably better, particularly at low pressures. While CRD measurements at constant sample densities typically yield a small spread in ring-down time (cf. Fig. S3 (right)), sample densities derived from CRD measurements rely on the small change on a comparatively large
signal, here the ring-down time. Given our modest CRD setup, which was not designed or optimized for high sensitivity, the improvement in sensitivity by the upgrade to a CELIF setup is striking and is a consequence of the “background-free” fluorescence measurement and the robust normalization procedure.

**Mechanical stability of the cavity**

In CRDS, the mechanical stability of the cavity throughout the measurement—background and sample—is crucial to avoid errors in sample densities. The mechanical stability of cavities can be affected by slow drifts, *e.g.* temperature, short-time effects such as vibrations or pressure gradients across the mirrors. The study and compensation of these effects have been discussed extensively in the literature.\(^{S2,S3}\)

Here we want to demonstrate and discuss why such cavity instabilities do not (or at least to a much lesser extend) affect CELIF measurements. The pressure-dependent N\(_2\) Rayleigh-scattering measurements, see Fig. 3(b), show that both the CRD and CELIF measurements follow the same linear trend. However, the CRD measurement shows much larger deviations from the linear trend with pressure than the CELIF measurement also evident in the ratio of the \(\chi^2\) values of the linear fits to the binned data, \((\chi^{\text{CRD}}/\chi^{\text{CELIF}})^2 = 8\). Likewise, at the selected pressures listed in Table S1, the deviation from linearity is large for CRD (often more than five times the standard error) compared to the CELIF data set (typically one standard error based on smaller spreads).

In our fairly basic setup, the cavity is sealed by the mirrors via O-rings. The flexibility of the O-rings also accommodates the mirror alignment through compression. While this basic setup provides a mechanically stable cavity in the context of the pulsed UV measurement, *i.e.* if the pressure inside the cavity is constant, this is no longer the case if the pressure inside the cavity changes. The pressure difference across the mirrors leads to small changes in the mirror alignment.

While this effect may compromise a CRD measurement, it can be seen from Fig. 3(b) and Table S1 that it does not affect the CELIF measurement. A change in cavity alignment changes the amount of light coupled into the cavity as well as the ring-down time. From Eq. S4 it is clear that an increase in light inside the cavity will also lead to increased fluorescence and therefore \(S^{\text{CELIF}} = \text{const}\). However, the CRD measurement depends on \(\tau_0\)
which will change with cavity (mis-)alignment.

Different groups using cavity-enhanced absorption spectroscopy have demonstrated that these effects can be mitigated, e.g. mirrors glued into position\textsuperscript{S3} or mirrors moved inside the cell which is sealed by fixed windows,\textsuperscript{S4} which lead to other issues regarding cavity alignment or cleaning of the mirrors. We have demonstrated that CELIF is robust against such changes in cavity alignment greatly simplifying the setup without compromising the quality of the measurements.

**S3. BACKGROUND, CALIBRATION AND CELIF ABSORBANCES**

While introducing the CELIF method in the main body of the paper, we made the following two assumptions that do not compromise the generality:

1. The cavity is either empty (no losses in addition to mirror losses, $\tau_0$) or contains an absorber ($\tau$). No additional losses are considered.

2. The LIF measurement is considered to be background-free, *i.e.* for an empty cavity the LIF signal is zero.

The following discussion does not make these two assumptions and all data presented in the main body of the paper has been analysed by the procedure that follows.

**Background subtraction**

The molecule studied here, BPEB, possesses a broad background absorption in the measurement range, possibly caused by a broad absorption to another electronic state or by resonance-enhanced scattering. In order to determine the absorption coefficient, $\alpha$, we need to perform four individual measurements:

**B+A, on:** Measurement performed on the absorption resonance (A), wavelength $\lambda^{B+A}$, in the presence of the broad background (B) with the sample present (on), meaning the molecular beam pulse coincides with the laser pulse.

**B+A, off:** Measurement performed on the absorption resonance (A), wavelength $\lambda^{B+A}$, in the presence of the broad background (B) with no sample (off). In this case, the nozzle
is mis-timed to the laser. This allows for the measurement of background gas present in the cavity determined by the pumping speed of the vacuum system.

**B, on:** Measurement performed away from any absorption resonance, wavelength $\lambda^B$, in order to capture the broad background signal (B) only with the sample present (on), meaning the molecular beam pulse coincides with the laser pulse.

**B, off:** Measurement performed away from any absorption resonance, wavelength $\lambda^B$, in order to capture the broad background signal (B) only with no sample (off).

Based on the absorption coefficients of each of the four measurements above, the absorption coefficient of the sample, $\alpha_A$, is determined by

$$\alpha_A = (\alpha_{\text{on}}^{B+A} - \alpha_{\text{off}}^{B+A}) - (\alpha_{\text{on}}^B - \alpha_{\text{off}}^B). \quad (S5)$$

In the case of a CRD measurement we replace Eq. 2 from the main text by

$$\alpha^{\text{CRD}} = \frac{1}{c} \times \frac{d}{s} \times \left[ \left( \frac{1}{\tau_{\text{on}}^{B+A}} - \frac{1}{\tau_{\text{off}}^{B+A}} \right) - \left( \frac{1}{\tau_{\text{on}}^B} - \frac{1}{\tau_{\text{off}}^B} \right) \right]. \quad (S6)$$

Here, we reflect that the molecular beam is of spatial width, $s$, in comparison to the cavity length, $d$. The measurements of the broad background signal (B, on and B, off) are performed at a wavelength different to the absorption. We assumed the broad background absorption to be wavelength-independent in the absence of further information of its nature. The spectra, Fig. 4 in the main paper, illustrate that any wavelength-dependence of the broad background is small.

The same procedure is performed in order to determine the background-subtracted CELIF signal

$$S^{\text{CELIF}} = (S_{B+A, \text{ on}}^{\text{CELIF}} - S_{B+A, \text{ off}}^{\text{CELIF}}) - (S_{B, \text{ on}}^{\text{CELIF}} - S_{B, \text{ off}}^{\text{CELIF}}) \quad (S7)$$

and subsequently the absorption coefficient of the CELIF measurement

$$\alpha^{\text{CELIF}} = \frac{1}{\mathcal{K}} \times S^{\text{CELIF}}. \quad (S8)$$

The calibration factor, $\mathcal{K}$, is determined as described in the body of the main paper based on a simultaneous measurement of ring-down times and CELIF signal.

For molecules that do not possess a broad background absorption, the second terms in Eqs S5, S6 and S7 can be omitted.
FIG. S4. Shot-to-shot correlation between the measured absorption coefficients (plotted as fractional absorptions, $\alpha \cdot s$) based on the ring-down times (x axis) and CELIF (y axis, plotted after calibration). The two error bars reflect the uncertainties in the fitted ring-down times. Red solid line: linear least-squares fit (the fitting error is about the thickness of the line).

Calibration

The measurement with the highest sample density (350 ppm in Fig. 5 of the main paper) was used to demonstrate the robustness of the calibration. Four sets of 101 simultaneously recorded LIF and CRD transients were measured comprised of the set with sample present and the three background data sets. These sets were analysed as described above to determine $\tau$ and $S_{\text{CELIF}}$ for each laser shot. By necessity, the background values (B+A,off; B,off; B,off) were used as averages in order to extract $\alpha_{\text{CRD}}$ and $S_{\text{CELIF}}$ as per Eqs S6 and S7, respectively. The shot-to-shot correlation of $S_{\text{CELIF}}$ and $\alpha_{\text{CRD}}$ is shown in Fig. S4. The Pearson correlation coefficient of this data set is 0.967, demonstrating the strong, positive linear relationship between the CRD and CELIF measurements. The calibration factor, $K$, was determined via a linear least-squares fit of $S_{\text{CELIF}}$ over $\alpha_{\text{CRD}}$ with a relative error of 0.4%.
REFERENCES