Supplementary information for

**Picosecond activation of the DEACM photocage unravelled**

by VIS-pump-IR-probe spectroscopy

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1. Assignment of protonated azide (hydrazoic acid)

Two alternative explanations and mechanisms besides formation of HN₃ have been suggested which could result in a feature around 2139 cm⁻¹, i.e. carbon monoxide or a ketene. The central wavenumber of HN₃ in neat acetonitrile matches that of CO. CO formation has been reported to occur from a light-induced decarbonylation reaction of matrix-isolated coumarin. Consequently, the release of CO leaves a benzofuran after a ring-opening reaction of the lactone. However, the CO/water complex should lead to an upshift of about 11 cm⁻¹ for νCO (12 cm⁻¹ in D₂O), while we see a downshift upon addition of water in the FTIR spectra, ruling out the presence of CO from a decarbonylation reaction. A second observed reaction path in matrix-isolated coumarin experiments involves the formation of a conjugated aldehyde-ketene after ring-opening. Such a compound has a C≡C=O moiety with an absorption around 2140 cm⁻¹ that is assigned to νC=O. DFT computations on ketene (H₂C=O) predict νC=O at 2229 cm⁻¹ (unscaled wavenumber), downshifting only 3 cm⁻¹-5 cm⁻¹ upon hydrogen bonding with 1 H₂O molecule (the shift depends on its orientation relative to the ketene), and a total 12 cm⁻¹ downshift if complexed with 2 water molecules. Comparing to our data, we observe a 3 cm⁻¹ - 5 cm⁻¹ downshift when increasing the D₂O content from 5% to 50%, therefore corresponding to the wavenumber shift calculated for the situation where no water molecule is hydrogen bound to that with only one molecule bound. Considering that there are many more water molecules than coumarin molecules available at 50% water concentration it is not likely that a ketene is hydrogen bound to a single water molecule in that situation. Although the presence of a ketene cannot be excluded based on the IR spectra, an equilibration reaction (as discussed in the main paper) between the azide anion and its protonated form is favoured because of the good match with experimental FTIR and literature data.

2. Assignment of CO₂

In neat acetonitrile and in 5% water a small feature is observed at 2342 cm⁻¹ (see the bottom panel of Figure S1), which can be either assigned to a nitrilium cation (CM-N’≡C-CH₃) or to CO₂. A nitrilium cation can be formed by solvent/carbocation interaction, and is reported to be stable in the presence of weakly nucleophilic anions. We consider a reaction with the solvent unlikely, because a separate control experiment of CM-N₃ in neat DMSO also produces a peak at 2337 cm⁻¹ after illumination, matching an earlier observation. On the other hand, CO₂ could be formed via a decarboxylation reaction which has been proposed as an additional photolytic pathway. Note that in 5% water a small feature at 2295 cm⁻¹ is seen, but this band is assigned to acetonitrile (a remainder of imperfect subtraction of the solvent spectrum).

3. Light-induced infrared difference spectra and full table of assignments

The observed wavenumbers of the features in the light-induced infrared and their assignments are given in Table S1.
Table S1. Extended version of Table 1. Vibrational assignments and observed frequencies (in cm\(^{-1}\)) in different solvent mixtures based on the FTIR difference experiments (light-minus-dark spectra). The sign of each feature is symbolized by +/-.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile/D(_2)O (%)</td>
<td>vC=O</td>
</tr>
<tr>
<td>100/0</td>
<td>1605/1621</td>
</tr>
<tr>
<td>95/5</td>
<td>1605/1620(^+)</td>
</tr>
<tr>
<td>50/50</td>
<td>1603/1616(^-)</td>
</tr>
</tbody>
</table>

\(^a\) In neat acetonitrile it is HN\(_3\).
\(^b\) Not measurable due to solvent absorption, see Figure S1.

The complete wavenumber region of the solvent-subtracted FTIR spectra are shown in Figure S1.

Figure S1. Infrared spectra of coumarin-azide in neat acetonitrile and in acetonitrile water mixtures (see the legend in the top panel; given in volume percent). Steady-state absorption spectra are collected using 24 mM with 50 \(\mu\)m pathlength. Light-minus-dark difference spectra (after illumination with a 365 nm LED) are shown in the bottom panel with each spectrum shifted for clarity. This panel also shows the product assignments. The spectra of 50% v/v water is cut above 2320 cm\(^{-1}\) due to water absorption. Both panels share the same legend and all spectra are corrected for solvent absorption and normalized to the band around 1620 cm\(^{-1}\) (as in panels B and D of Figure 1).
4. Vibrational mode computations

Figure S2. DFT computations of CM-N₃. Panels A-B show the FTIR data and the unscaled (note the unequal abscissa) DFT computations using the M06/6-31+G(d,p) functional/basis set with acetonitrile as solvent modelled by a polarized continuum model, respectively. Panels C-F depict the vibrational modes given by the black arrows (generated in Jmol www.jmol.org). The calculated and observed (in neat acetonitrile) frequencies are also listed.
Figure S3. Reproduction of the spectral slices in Figure 2, but here the full spectral range is shown, consisting of four different spectral windows that are collected separately. All panels contain three axis breaks (from 1132 cm⁻¹ to 1610 cm⁻¹, from 1830 cm⁻¹ to 1990 cm⁻¹ and from 2182 cm⁻¹ to 2303 cm⁻¹) and the wavenumber ticks are equally spaced over the full range. The absorptions in the low and high wavenumber ranges are multiplied with a depicted factor for better visibility. The dashed lines serve as guides-to-the-eye by using the spectral features in the top panel as reference. All panels share the same colour legend (panel C).
Figure S4. Reproduction of Figure 3, but here the ordinate is plotted on a linear scale and all collected spectral windows are shown.
Figure S5. Averaged sum of the residuals of the applied global analysis in wavenumber (panels A-C) and time (panels D-F), respectively, for all used solvent mixtures. The data consist of 69 timepoints and 105 pixels (but 79 pixels for the 50% D2O data). The maximum error in fit for 0% and 5% D2O is found around time zero (partially clipped vertically to show the later more relevant time points more clearly) and correlated mainly with an error-of-fit in the carbonyl wavenumber range, while the error in fit for 50% D2O is rather random in time but correlated spectrally with the azide wavenumber region. The results using 4 as well as 5 components to fit the data are shown. The total sum-of-squared errors (SSE): 0% water: SSE(4 components) = 83, SSE(5 components) = 81; 5% water: SSE(4 components) = 144, SSE(5 components) = 136; 50% water: SSE(4 components) = 1.14, SSE(5 components) = 1.01.

Figure S6. Water influences the ground state recovery of the photo-excited loaded cage. ESA of coumarin’s C=O group (the band’s maximum signal around 1650 cm⁻¹ is plotted for each solvent mixture, represented by the different symbols) is plotted as function of time and solvent composition. The signals (symbols) and corresponding fits (continuous lines; resulting from the global analysis shown in Figure 3) are normalized to the maximum of the data (disregarding the sub-ps spike). The time axis is linear up to 10 ps and logarithmic thereafter.
Figure S7. Ultrafast laser data of the azide region only. Each solvent composition exhibits an underlying dynamic baseline that is larger than the signals from the azide (panels A-C). A baseline correction is applied that consists of a line connecting the extreme wavenumbers for each time point (and each solvent), resulting in panels D-F. To highlight the azide bands the colour scale is adapted and identical for the plots corresponding to the same solvent composition (with signals larger than the depicted extremes coloured grey, those at zero coloured white). For comparison the (scaled) FTIR difference spectra from Figure 1D are also shown in panels G-I. Note that the two products around 2125 cm$^{-1}$ in panel H correspond to HN$_3$ and DN$_3$ (see main text).
Figure S8. Zoom of the species-associated difference spectra in the carbonyl region, highlighting the coumarin dimer (appearing at the dashed vertical line in neat acetonitrile). The legend shows the fitted lifetimes with the error in the last significant digit in brackets. Note that the full wavenumber region is globally analysed and that here only a region of the SADS is shown. The scaled light-induced FTIR difference spectra are shown for comparison.
6. Steady state spectra of coumarin alcohol and assignment of the red-shifted UV/Vis product band

Figure S9. Comparison of FTIR and UV/Vis spectra of potential photoproducts. Panel A shows the comparison of the FTIR spectrum of unilluminated CM-N3 to that of CM-OH under the same conditions as Figure 1B (at 25 mM and using a 50 μm spacer). The labelled arrows highlight the presence of major spectral differences in the spectrum of CM-OH. Note also the absence of the N3 band above 2000 cm⁻¹ in CM-OH. Panel B shows the UV/Vis spectra of different CM compounds (the azide, alcohol and aldehyde forms; all concentrations are 0.5 mM and the used optical pathlength was 1 mm) before and after illumination under the same conditions as used for Figure 1C. All spectra have the solvent (mixture) subtracted.

The origin of the red-shifted product band seen in the steady-state UV/Vis spectra (see Figure 1C) is unclear. We exclude that it is caused by dimers because they generally have a blue-shifted absorption spectrum. Interestingly, we found that the UV/Vis spectrum of CM-aldehyde shows a high degree of similarity with that of illuminated CM-LG (see Figure S9B). A rough estimate implies that about 25% CM-aldehyde could explain the red-shifted CM-LG photoproduct, but the FTIR spectra (compare Figure 1D to Figure S10) do not reveal two carbonyl modes (the aldehyde moiety in addition to the ring carbonyl). If the rough estimate of 25% CM-aldehyde is correct the corresponding IR intensities would be obscured by the much larger single-peaked absorption of CM-N3 for instance. It is however observed that the steady-state UV/Vis and FTIR spectra continuously change with longer illumination times, until eventually the absorption above 350 nm has disappeared (indicating the loss of coumarin’s ring system). Both C=O modes of the aldehyde form absorb at wavenumbers that are significantly lower than the dimer-assigned 1769 cm⁻¹ band. To check if the aldehyde form is susceptible to photoconversion, we excited it at 365 nm (to mimic the experimental conditions of the steady-state experiments shown in Figure 1). Such experiments only showed small changes in the UV/Vis spectra (see Figure S9B), but essentially no detectable changes in the FTIR spectra.
7. Sample synthesis

**General experimental Procedures.** Solvents and reagents were purchased from commercial sources and used as received. TLC was performed using Macherey-Nagel precoated TLC-sheets ALUGRAM Xtra SIL G/UV254 and visualization was done under UV light (254 and 365 nm). For column chromatography a Macherey-Nagel silica gel 60 (particle size 0.04-0.06 mm) was used. NMR spectra were measured in CDCl₃ and referenced to the solvent peak (¹H 7.26 ppm, ¹³C 77.16 ppm). ¹H and ¹³H spectra were measured at a Bruker AV 300 or AV 500 MHz devices. Chemical shifts (δ) are reported on a ppm scale. Following abbreviations (or combinations thereof) were used to describe multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (J) are reported in Hertz (Hz). High-Resolution Mass Spectrometry (HRMS) data were recorded on a Thermo Scientific LTQ Orbitrap XL using MALDI ionization.

**Experimental Procedures and Characterization Data.** A general reaction scheme is shown in Figure S11.

![Figure S11. Synthesis scheme of CM-N₃ (3).](image)
methanesulfonyl chloride (504 mg, 4.4 mmol, 1.5 eq). After stirring for 1.5 h the mixture was diluted with DCM, washed with saturated NaHCO₃ solution and brine, dried over Na₂SO₄ and concentrated under reduced pressure to yield mesylated product (**CM-OMs**). ¹H NMR (CDCl₃, 250 MHz): δ 7.32 (d, 1H, J = 9.0 Hz), 6.60 (dd, 1H, J = 9.0, 2.6 Hz), 6.52 (d, 1H, J = 2.6 Hz), 6.18-6.15 (m, 1H), 5.29 (d, 2H, J = 1.0 Hz), 3.41 (q, 4H, J = 7.1 Hz), 3.10 (s, 3H), 1.21 (t, 6H, J = 7.1 Hz). The crude **CM-OMs** (362 mg, 1.4 mmol) was dissolved in DMF (7 mL), NaN₃ (381 mg, 5.8 mmol, 4 eq) was added and the mixture was stirred overnight at room temperature. Upon completion the mixture was diluted with EtOAc, 3 x 30 mL was extracted with half-saturated NaCl solution followed by brine, dried over Na₂SO₄ and concentrated under reduced pressure. The product was purified via a column on silicagel, using CH:EE (3:1) as eluent to yield 290 mg (93%) of yellow powder. ¹H NMR (CDCl₃, 500 MHz): δ 7.32 (d, 1H, J = 9.0 Hz), 6.59 (dd, 1H, J = 9.0, 2.6 Hz), 6.51 (d, 1H, J = 2.6 Hz), 6.13 (t, 1H, J = 1.0 Hz), 4.43 (d, 2H, J = 1.0 Hz), 3.41 (q, 4H, J = 7.1 Hz), 1.21 (t, 6H, J = 7.1 Hz). ¹³C NMR (CDCl₃, 125 MHz): δ 161.8, 156.6, 150.9, 148.9, 124.9, 108.8, 108.2, 106.4, 98.0, 51.0, 44.9, 12.6. HRMS (MALDI) m/z: [M+H]⁺ Found 273.13457, Calc. for C₁₄H₁₇N₄O₂ 273.13460.
Figure S12. $^1$H (upper) and $^{13}$C (lower) NMR spectra of CM-N$_3$ (3) in CDCl$_3$. 