On the vibrational spectra of the ground and the singlet excited ππ* state of 6,7-dimethyl-8-ribityllumazine

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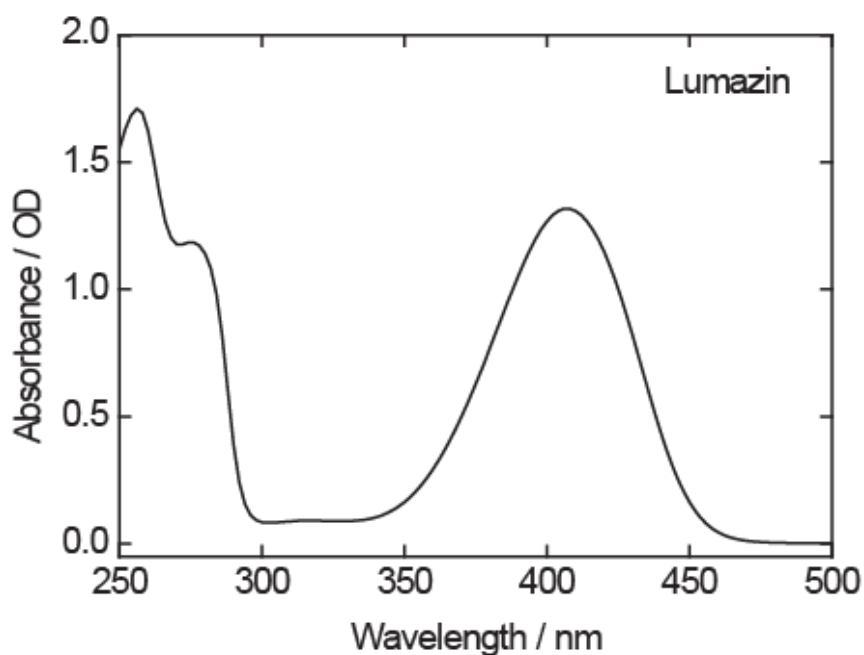
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1. UV/Vis absorption spectrum of 6,7-dimethyl-8-ribityl-lumazine

Figure S1. Absorption spectrum of 6,7-dimethyl-8-ribityl-lumazine in D_2O containing 40 mM potassium phosphate (pD ~ 7).

The UV/vis absorption spectrum of 6,7-dimethyl-8-ribityl-lumazine has been discussed in the literature before [1-3]. Lumazine exhibits an unstructured absorption band around 400 nm with its peak centered at 408 nm. It is generally assumed that this absorption is due to the lowest singlet $\pi\pi^*$ transition. In the short wavelength range a band at 256 nm with a shoulder at 280 nm appears.
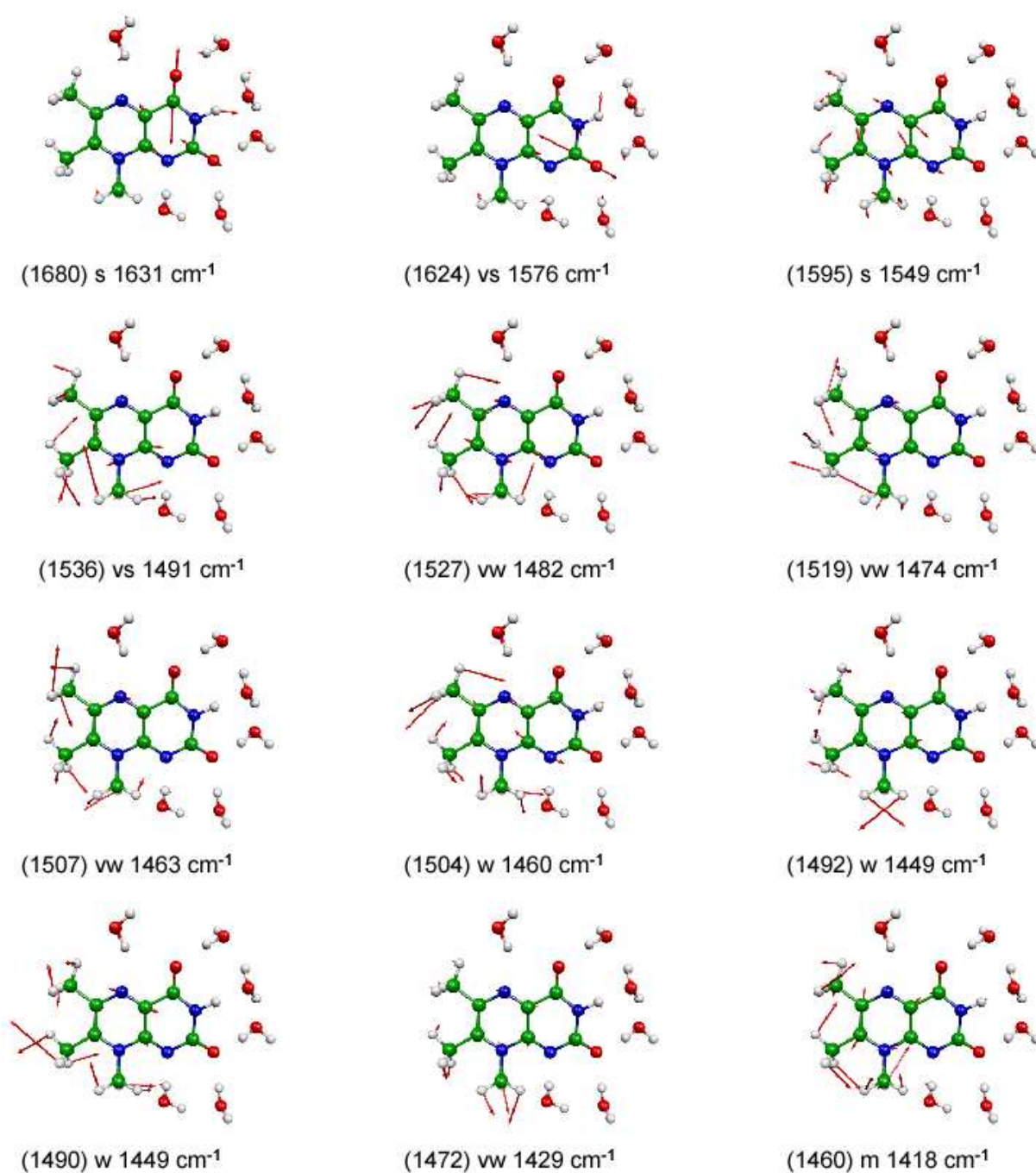
2. Results of global data-analysis

Table S1. Relaxation times of 6,7-dimethyl-8-ribityl-lumazine (RiboLu) and its isotopologues in D_2O buffered solution after photoexcitation as determined by time resolved infrared spectroscopy in a global data analysis.

sample	τ_1 / ps	τ_2 / ps	τ_3 / ns
RiboLu	2.7	88	3.2*
[U-^{15}N$_4$]	1.9	81	4.9*
[2-^{13}C$_1$]	2.1	91	5.2*
[4-^{18}O$_1$]	2.2	84	6.1*

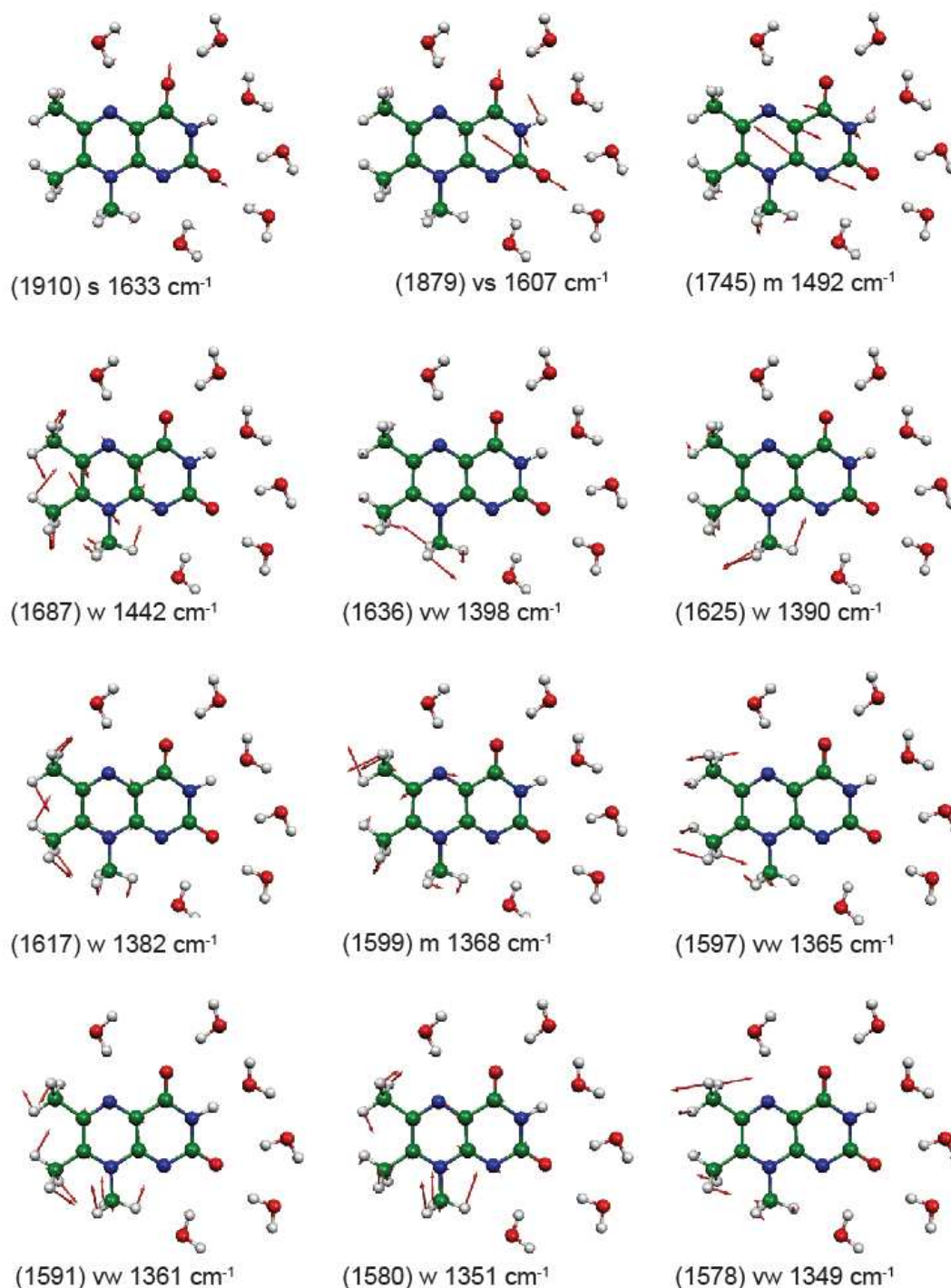In the global data analysis the signals were modeled as sums of exponentials analytically convoluted with a Gaussian that represents the instrument response function (~ 250 fs) of the ultrafast IR spectrometer. As the time resolved experiments are limited to a maximum delay time of ~ 3 ns the values marked with * are subject to substantial uncertainty and have to be regarded as order of magnitude approximation.

3. Calculated vibrational modes of MeLu in the electronic ground state

(1680) s 1631 cm⁻¹   (1624) vs 1576 cm⁻¹   (1595) s 1549 cm⁻¹

(1536) vs 1491 cm⁻¹   (1527) vw 1482 cm⁻¹   (1519) vw 1474 cm⁻¹

(1507) vw 1463 cm⁻¹   (1504) w 1460 cm⁻¹   (1492) w 1449 cm⁻¹

(1490) w 1449 cm⁻¹   (1472) vw 1429 cm⁻¹   (1460) m 1418 cm⁻¹

Figure S2. Calculated vibrational modes of N-deuterated 6,7,8–trimethyl-lumazine (BLYP/TZVP) solvated by 6 D_2O molecules. The intensities of the vibrational modes are categorized as: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. Scaled frequency values (scaling of factor 1.03) are given in brackets.

4. Computed vibrational modes of MeLu in its electronic singlet excited ππ* state

(1910) s 1633 cm⁻¹   (1879) vs 1607 cm⁻¹   (1745) m 1492 cm⁻¹

(1687) w 1442 cm⁻¹   (1636) vw 1398 cm⁻¹   (1625) w 1390 cm⁻¹

(1617) w 1382 cm⁻¹   (1599) m 1368 cm⁻¹   (1597) vw 1365 cm⁻¹

(1591) vw 1361 cm⁻¹   (1580) w 1351 cm⁻¹   (1578) vw 1349 cm⁻¹

Figure S3. Calculated singlet ππ* excited state vibrational modes of N-deuterated 6,7,8 – trimethyl-lumazine (CIS / 6-311G**) solvated by 6 molecules of deuterated water. The intensities of the vibrational modes are categorized as: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. Scaled frequency values (scaling factor of 0.855) are given in brackets.

5. Optimized structures of 6,7,8-trimethyl-lumazine (MeLu) solvated by various numbers of D$_2$O molecules
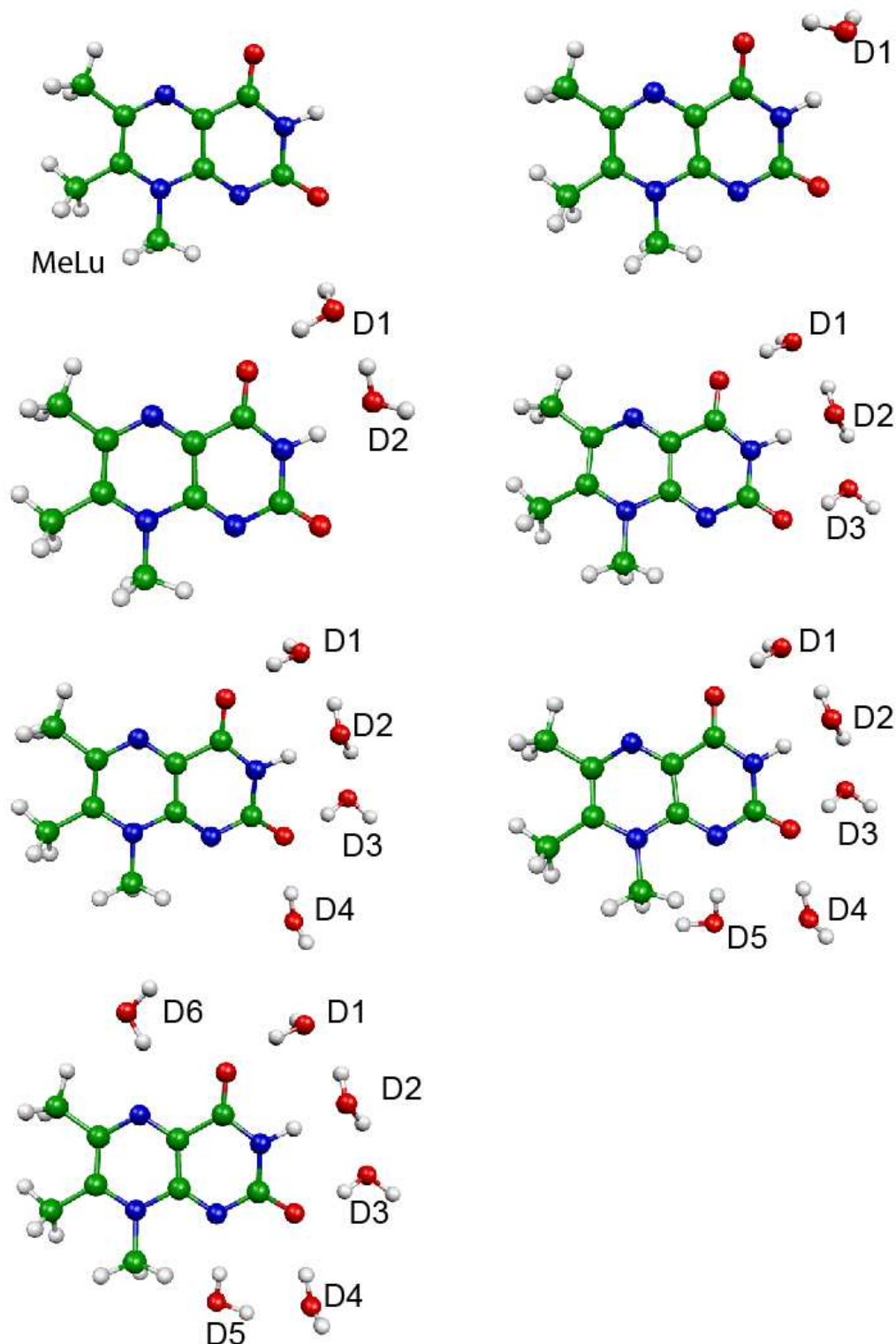
Figure S4. Fully optimized models of N-deuterated 6,7,8-trimethyl-lumazine (MeLu)
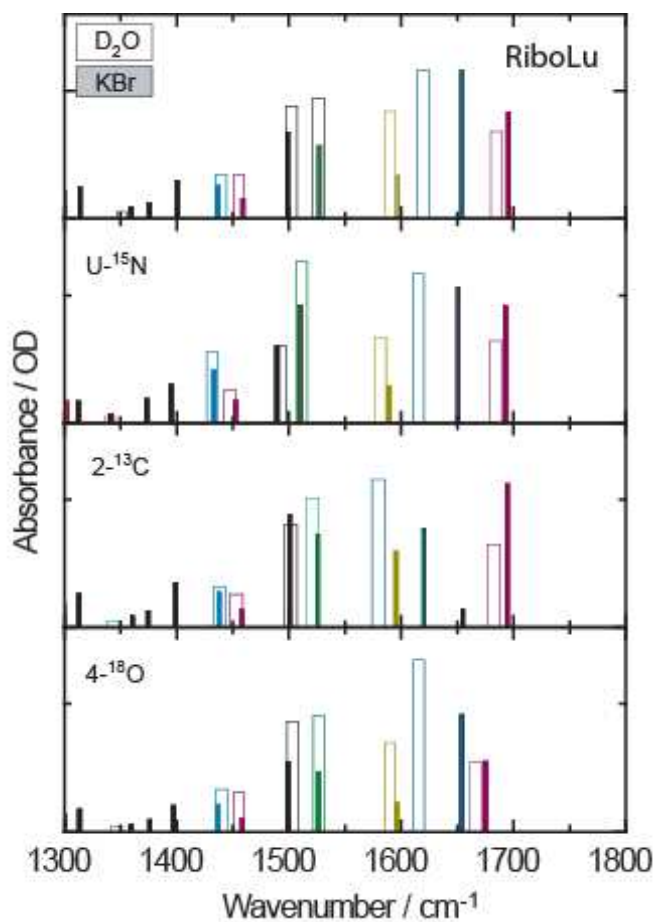
solvated by various numbers of D$_2$O molecules.

6. Optimized structure of the 6,7-dimethyl-8-ribityl-lumazine solvated by six D_2O molecules
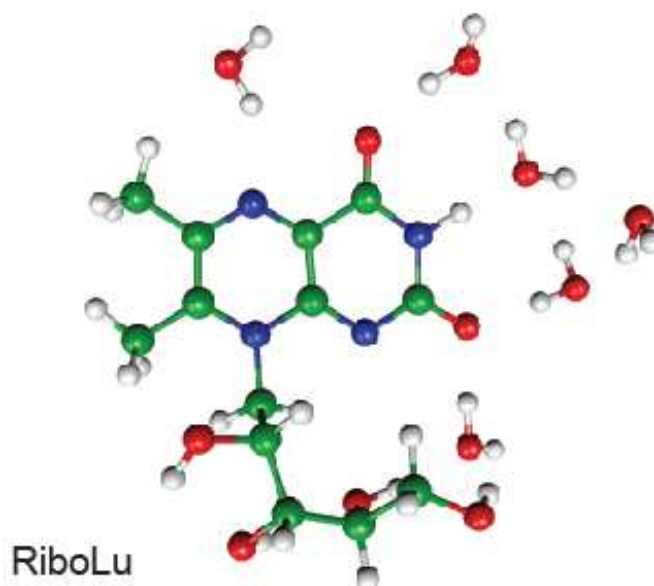
Figure S5. Fully optimized structure of N-deuterated 6,7-dimethyl-8-ribityl-lumazine

(RiboLu) solvated by six D_2O molecules.

7. Comparison between KBr and solvent surrounding

Figure S6: Comparison of the peak positions of the infrared absorption spectra of 6,7-dimethyl-8-ribityl-lumazine in D_2O solution (open bars) and KBr-matrix (filled bars). The solvent leads to a significant downshift of the C(2)O(2) carbonyl band compared to the matrix. The positions of the other visible bands are hardly affected by the different surrounding conditions.

8. List of all authors for Reference 34

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