

Electronic Supplementary Information for: Mode-specific Excited-state Dynamics of *N*-Methylpyrrole

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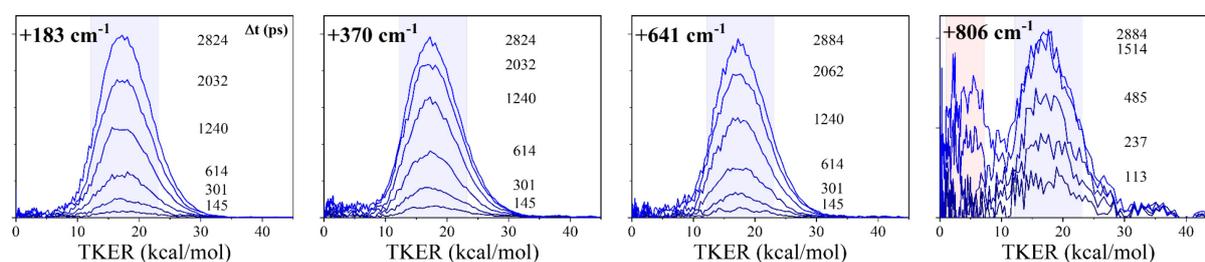


Fig. S1. Total kinetic energy release (TKER) distributions at few selected delay times (among total 31 time steps) after the state-selective excitation at the indicated S_1 vibronic levels. In order to exclude the influence of undesired multiphoton contributions, distributions measured at time-zero have been subtracted (see Figure 1(c) in the main text).

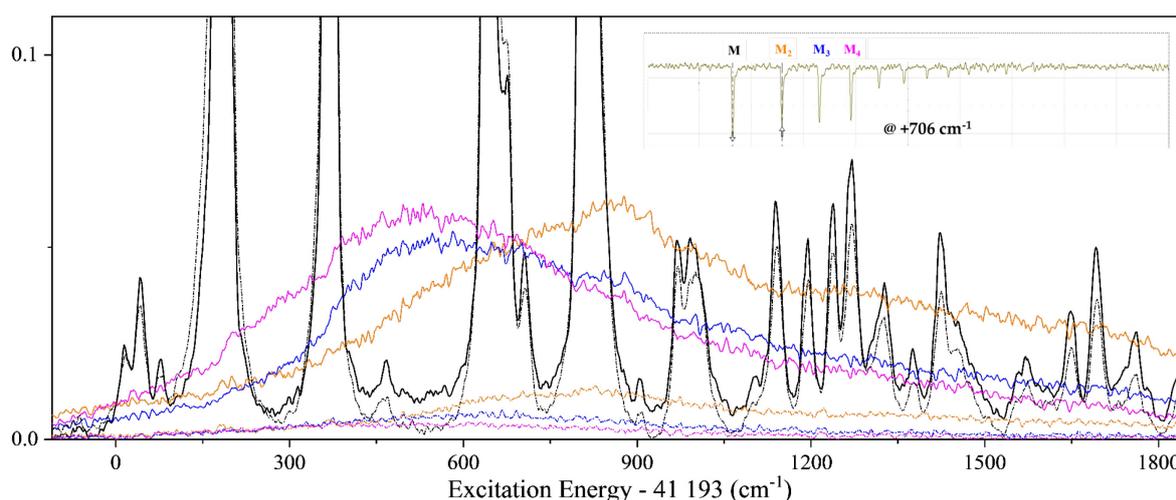


Fig. S2. Expanded view of picosecond (1+1') R2PI (solid black). Relative contributions of higher mass clusters including dimer (orange), trimer (blue), and tetramer (magenta) can be optimally reduced by controlling the nozzle-laser delay by 50 μ s with hotter rotational temperature (dashed lines). Inset: representative time-of-flight mass spectrum showing higher mass clusters (before reduction) at +706 cm^{-1} band near the time-zero.

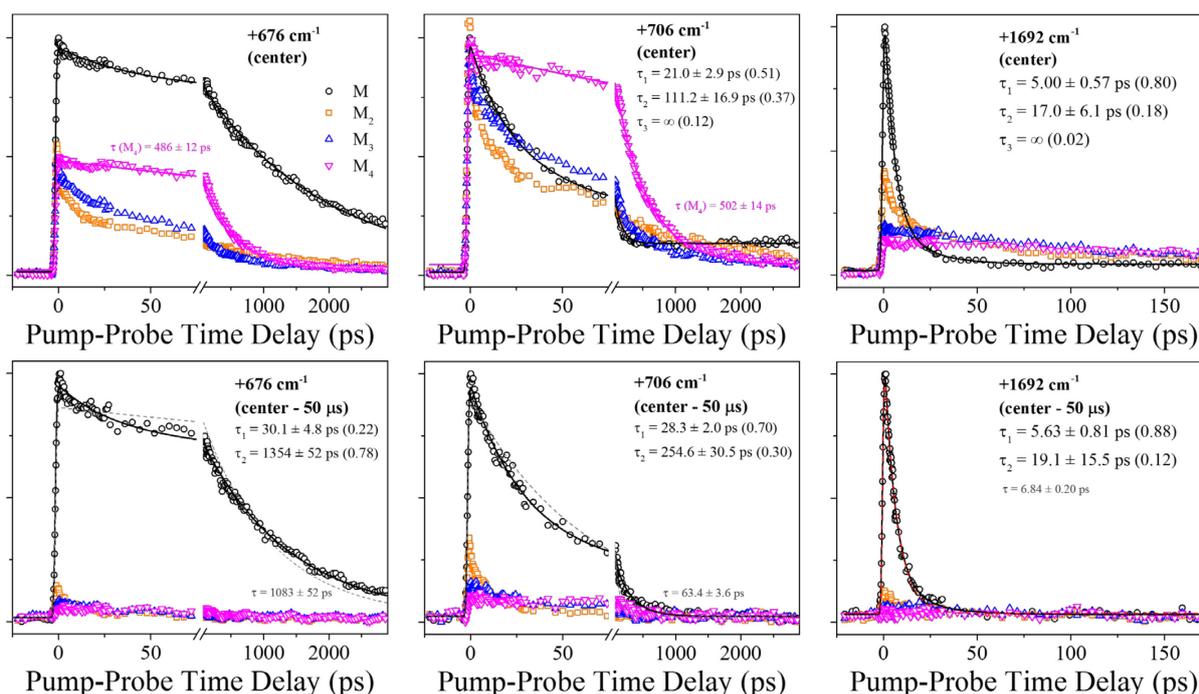


Fig. S3. TR-IY of NMP monomer and higher mass clusters compared at different experimental conditions of nozzle-laser delay at center of maximum signal (upper row) and at 50 μs shifted delay (lower row). Residual-like flat function should be included when the cluster contribution is large. Special photostability of tetramer (inverse triangles) could be identified by the longest decay among higher mass clusters.

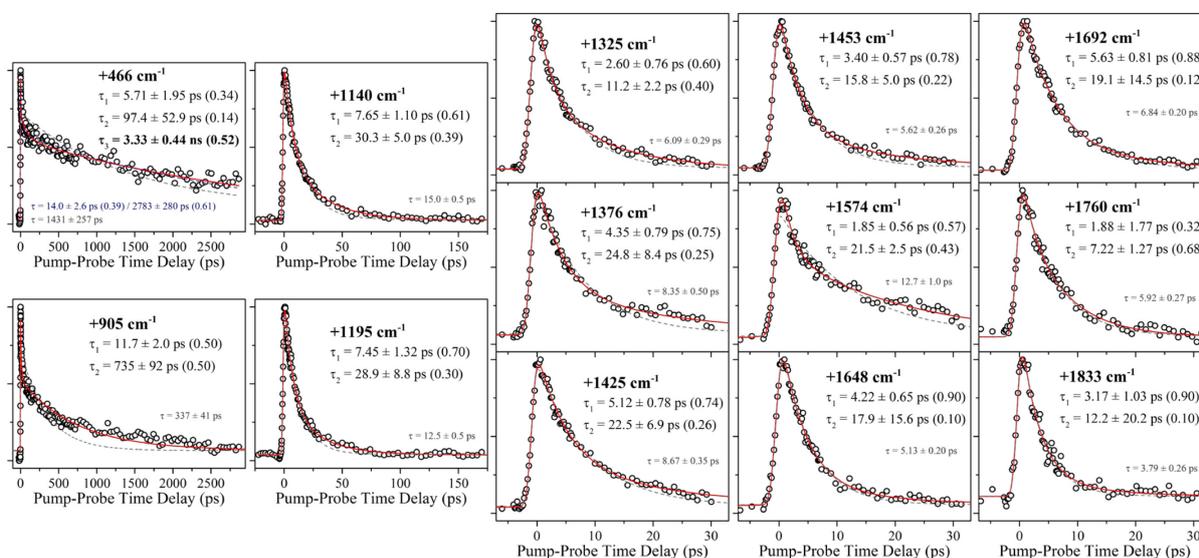


Fig. S4. Rest of parent decay transients at other vibronic bands not presented in the main text.

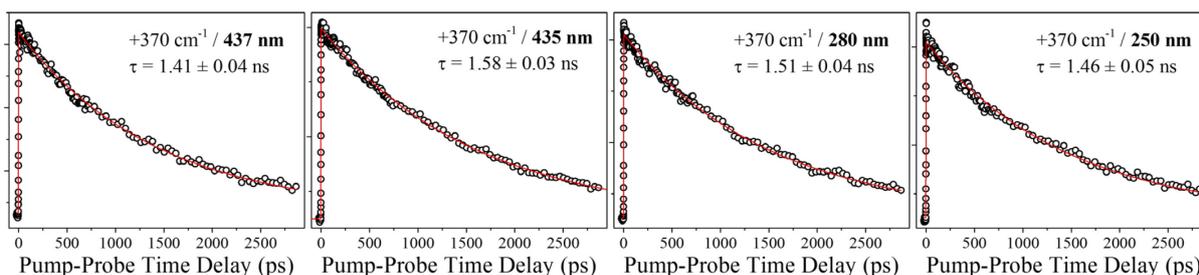


Fig. S5. Parent decay transients at +370 cm⁻¹ band with various probe wavelengths.

Table S1. Summary of S₁ vibronic state-specific decay rate measurement derived from the multicomponent kinetic fits of parent ion transients. Time constants (τ_i) are units in ps, and relative fractions (f_i) are defined as $f_i = \frac{c_i}{\sum c}$. Error bars are from the kinetic fit with the 95% confidence level. Tentative assignments are given based on the frequency calculation of the S₁ state (not scaled) by the time-dependent density functional theory (TD-DFT) with the B3LYP functional and the aug-cc-pVDZ basis set.

Energy (cm ⁻¹) ^[a]	Single Exp τ	Biexponential		Triexponential			Assignment ^[b]	TD-DFT ^[c]
		τ_1 (f ₁)	τ_2 (f ₂)	τ_1 (f ₁)	τ_2 (f ₂)	τ_3 (f ₃)		
0 (41193)	8150 ± 370						0 ⁰	
15		52.9 ± 10.1 (0.28)	5100 ± 470 (0.72)				m ₁ ^{2 [b]}	
43		96.3 ± 35.4 (0.12)	6430 ± 500 (0.88)				m ₀ ^{3+/3- [b]}	
77		17.1 ± 3.5 (0.23)	6010 ± 430 (0.77)				m ₁ ^{4 [b]}	
183	5130 ± 100						v ₂₂ ^[b]	217 (133)
370	1490 ± 30						v ₂₁ ^[b]	491 (376)
466		14.0 ± 2.6 (0.39)	2783 ± 280 (0.61)	5.71 ± 1.95 (0.34)	97.4 ± 52.9 (0.14)	3330 ± 440 (0.52)	v ₁₄	520 (463)
632		19.1 ± 4.2 (0.17)	2695 ± 84 (0.83)	2.14 ± 0.64 (0.22)	118.2 ± 32.5 (0.10)	2947 ± 114 (0.68)	v ₁₁	635 (606)
641		16.9 ± 3.6 (0.10)	2510 ± 40 (0.90)				v ₂₀	718 (742)
676		30.1 ± 4.8 (0.22)	1354 ± 52 (0.78)				641 + m	
706		28.3 ± 2.0 (0.70)	254.6 ± 30.5 (0.30)				v ₃₂	687 (730)
806		51.1 ± 5.2 (0.43)	236.8 ± 13.9 (0.57)	6.42 ± 1.89 (0.10)	94.7 ± 9.3 (0.62)	349.1 ± 55.1 (0.28)	v ₁₉	891 (878)
824		45.3 ± 4.2 (0.44)	411 ± 21 (0.56)	7.78 ± 2.04 (0.14)	96.7 ± 10.7 (0.48)	554 ± 57 (0.38)	v ₁₃ / 183 + 632	877 (801)
905		11.7 ± 2.0 (0.50)	735 ± 92 (0.50)				v ₁₂	931 (931)
969		8.59 ± 1.67 (0.36)	92.8 ± 5.8 (0.64)				v ₃₀	988 (935)
999		3.51 ± 0.32 (0.64)	30.5 ± 2.7 (0.36)				v ₃₁ / 370 + 632 / 969 + m	1042 (1114)
1048		28.0 ± 3.3 (0.45)	261.6 ± 18.3 (0.55)	2.83 ± 0.74 (0.21)	63.9 ± 8.2 (0.48)	371.9 ± 48.5 (0.31)	v ₈	1091 (1162)
1140		7.65 ± 1.10 (0.61)	30.3 ± 5.0 (0.39)				v ₁₈	1138 (1219)
1195		7.45 ± 1.32 (0.70)	28.9 ± 8.8 (0.30)				v ₂₈	1220 (1236)
1237		13.0 ± 3.1 (0.57)	50.8 ± 10.7 (0.43)				183 + 1048	
1271		5.04 ± 0.73 (0.77)	18.3 ± 6.3 (0.23)				v ₂₉ / 632 + 641	1301 (1388)
1325		2.60 ± 0.76 (0.60)	11.2 ± 2.2 (0.40)				v ₂₆	1397 (1484)
1376		4.35 ± 0.79 (0.75)	24.8 ± 8.4 (0.25)				v ₂₇	1419 (1569)
1394		4.42 ± 0.85 (0.36)	50.8 ± 3.5 (0.64)				v ₅	1405 (1489)
1425		5.12 ± 0.78 (0.74)	22.5 ± 6.9 (0.26)				v ₁₇ / 370 + 1048	1449 (1609)
1453		3.40 ± 0.57 (0.78)	15.8 ± 5.0 (0.22)				641 + 806 / 1425 + m	

1473	5.70 ± 0.29	3.13 ± 1.49 (0.61)	9.74 ± 3.97 (0.39)	v_6	1510 (1622)
1574		1.85 ± 0.56 (0.57)	21.5 ± 2.5 (0.43)		183 + 1394
1648	5.13 ± 0.20	4.22 ± 0.65 (0.90)	17.9 ± 15.6 (0.10)		183 + 1473
1692	6.84 ± 0.20	5.63 ± 0.81 (0.88)	19.1 ± 14.5 (0.12)		641 + 1048
1696	6.91 ± 0.38	1.28 ± 0.87 (0.35)	8.52 ± 0.97 (0.65)		632 + 1048
1760	5.92 ± 0.27	1.88 ± 1.77 (0.32)	7.22 ± 1.27 (0.68)		370 + 1394
1833	3.79 ± 0.26	3.17 ± 1.03 (0.90)	12.2 ± 20.2 (0.10)		370 + 1473

[a] Text in bold are two-photon-accessed vibronic levels, which are assigned as a_1 symmetry vibrations.

[b] First few assignments and the mode numberings are based on Biswas *et al.* (2003).¹ Few high intensity bands are assigned as b_1 symmetry vibrations ($v_{19} - v_{22}$).

[c] Values in parentheses are from the CIS calculation by Kanamaru (2004).²

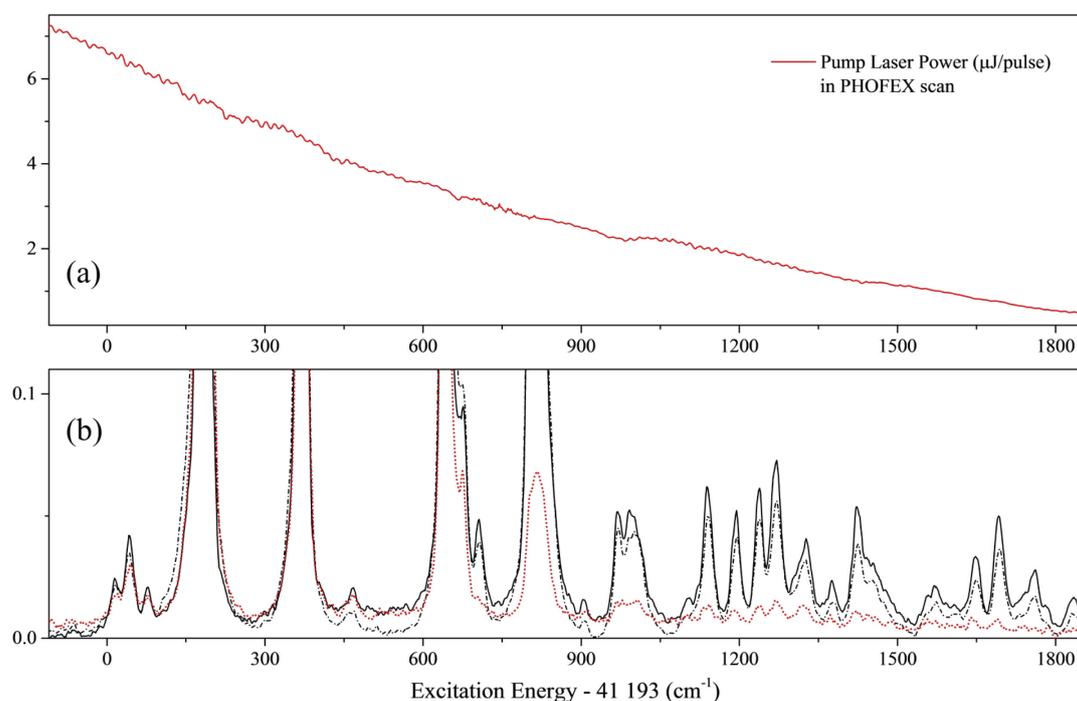


Fig. S6. (a) Pump laser power was monitored and recorded while scanning the wavelength of the optical parametric amplifier (OPA) unit. Since the 230 nm wavelength range is approaching the threshold of the second harmonic of sum-frequency with the OPA signal beam, the power drops constantly as with higher excitation energies. (b) Picosecond spectroscopic results reproduced from Fig. 2 in the main text, where the power correction is not applied.

Supplementary References

1. N. Biswas, S. Wategaonkar and J. G. Philis, *Chem. Phys.*, 2003, **293**, 99-109.
2. N. Kanamaru, *J. Mol. Struct.*, 2004, **686**, 15-23.