

Supplementary Information

Ultrafast Vibrational Wave Packet Dynamics of the Aqueous Tyrosyl Radical Anion Induced by Photodetachment

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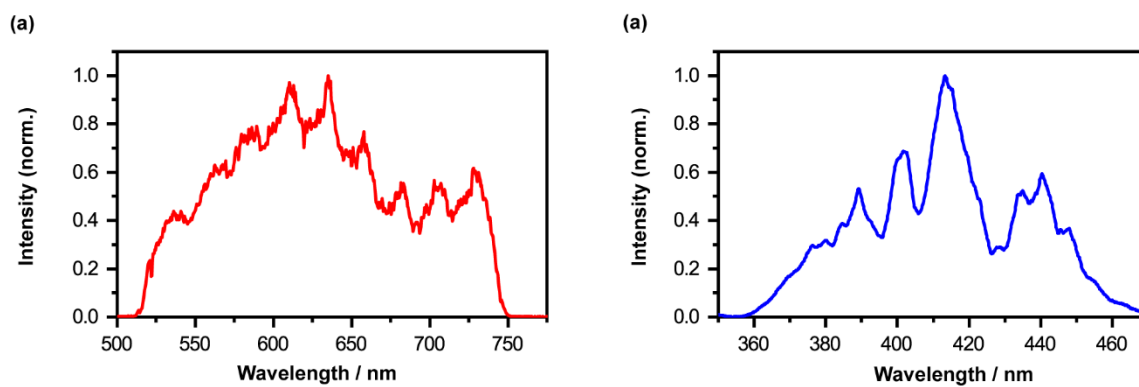


Fig. S1 (a) The visible-NIR ionizing pump spectrum ranges from 520 nm to 750 nm, with a central wavelength of 630 nm. **(b)** The UV probe spectrum ranges from 360 nm to 470 nm.

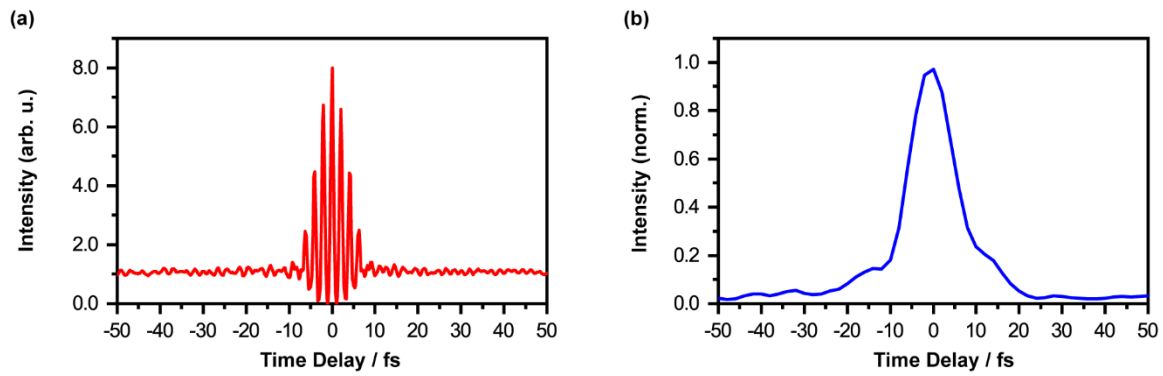


Fig. S2 (a) A second-order interferometric auto-correlation trace of the visible-NIR ionizing pump spectrum, measured in a 10- μm -thick, $\theta = 37.0$ deg Type I BBO crystal, reveals a pulse duration with full-width-half-maximum (FWHM) of 5.2 fs. **(b)** The pump-probe cross-correlation, measured *via* difference frequency mixing in a 10- μm -thick, $\theta = 29.2$ deg Type I BBO crystal, reveals a FWHM of 12 fs.

Section S1. Photon-Order Measurements for Strong-Field Photodetachment of the Tyrosinate Dianion in Aqueous Solution

A power dependence measurement is performed to determine the photon order of the strong-field photodetachment process of the tyrosinate dianion in aqueous solution. For an N -photon photodetachment process, the differential absorption signal, ΔA , scales with intensity, I , i.e. $\Delta A \propto I^N$. The photon-order measurements are performed by using a visible-NIR probe, which measures the absorption of the ground-state hydrated electron at a pump-probe time delay of 5 ps. The photon-order measurements are performed in the visible region due to the strong absorption of the ground-state hydrated electron at 720 nm. Since the hydrated electron is produced alongside upon the photodetachment of tyrosinate dianion and hydroxide ion, the hydrated electron absorption signal is proportional to the extent of the photodetachment process.

Several factors are taken into consideration in order to determine the photon order accurately of the photodetachment. During the photodetachment of aqueous solution of the tyrosinate dianion, there is a possibility that electrons are produced from both the tyrosinate dianion and hydroxide ion, even though the ionization of the solute is more likely to occur due to its vertical ionization potential (~ 7.1 eV)^{1,2} being significantly lower than that of the hydroxide ion (9.2 eV).³ In our study, the ΔA against ionizing pump intensity is recorded for both the aqueous tyrosinate dianion and aqueous sodium hydroxide under similar experimental conditions. A difference ΔA signal ($\Delta\Delta A$) is then obtained, which in principle corresponds to solely the ΔA signal from the photodetachment of tyrosinate dianion, shown in Fig. 3 of the main text. The $\Delta\Delta A$ signal is then fit to the following function:

$$\Delta\Delta A = \alpha I^N / [1 + (I/I_{\text{sat}})^N], \quad (1)$$

where α is the amplitude, N is the photon order and I_{sat} is the saturation intensity. The best fit when $N = 3$ yields $\alpha = (6.90 \pm 0.06) \times 10^{-42} \text{ cm}^6 \cdot \text{W}^{-3}$ and $I_{\text{sat}} = (1.67 \pm 0.01) \times 10^{13} \text{ W} \cdot \text{cm}^{-2}$. The value of N indicates that the photodetachment of tyrosinate dianion in aqueous environment occurs via a three-photon process.

Section S2. Calculation of the Initial Concentration of the Hydrated Electron

The $\Delta A_1(\lambda)$ values obtain from the global fitting of the time traces track the formation of the hydrated electron, and thus should follow the absorption spectrum of the hydrated electron. By plotting a graph of ΔA_1 as a function of the molar extinction coefficient of the hydrated electron, ϵ_e , (Fig. S3) we would obtain the initial concentration of hydrated electron, c_e . Using the relation in Eq. 2 of the main text, the gradient obtained from the linear fit is $c_e L = (3.08 \pm 0.02) \times 10^{-5} \text{ M} \cdot \text{cm}$, where L is the sample path length. Since $L = 7 \pm 1 \mu\text{m}$, we obtain $c_e = 44 \pm 6 \text{ mM}$.

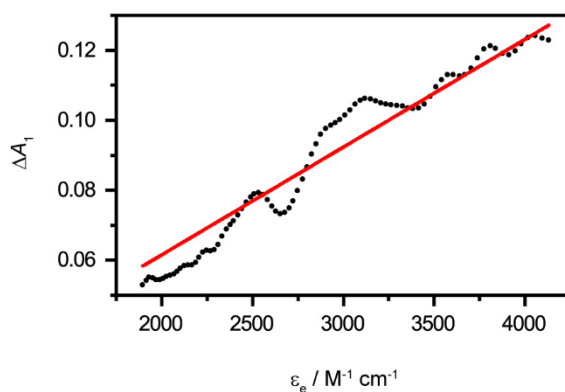


Fig. S3 Plot of ΔA_1 as a function of molar extinction coefficient of hydrated electron, and the linear fit function, in red. The gradient of the linear fit function corresponds to the product of the concentration of hydrated electron, c_e and the sample path length, L .

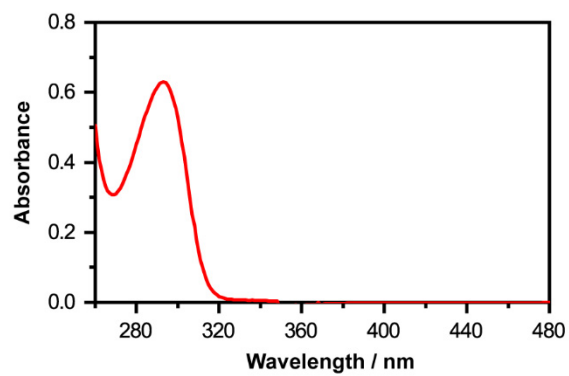


Fig. S4 Static UV-visible absorption spectrum of 3 mM tyrosinate dianion in aqueous sodium hydroxide solution (pH 14), measured with a 1-mm path length quartz cuvette. The absorption maximum is at 290 nm.

Section S3. Cartesian Coordinates of Optimized Geometries

(a) Isolated tyrosinate dianion, with PCM

Symbol	X	Y	Z
C	2.599337	1.209646	0.305402
C	1.242395	1.241094	0.004854
C	0.561584	0.122887	-0.50693
C	1.327072	-1.03654	-0.70349
C	2.688369	-1.08917	-0.40954
C	3.401032	0.035416	0.115602
H	3.08837	2.099893	0.693507
H	0.691421	2.165623	0.167722
H	0.843872	-1.92354	-1.10864
H	3.243851	-2.00749	-0.58362
O	4.664436	0.000981	0.390765
C	-0.92178	0.166489	-0.80029
H	-1.17541	1.093511	-1.3269
H	-1.18859	-0.66369	-1.46505
C	-1.82693	0.080548	0.464895
H	-1.59866	0.946802	1.093746
C	-3.31047	0.202032	0.028464
N	-1.62646	-1.14188	1.25608
H	-2.17608	-1.8788	0.819401
H	-0.64918	-1.42155	1.219466
O	-3.74705	1.369068	-0.16158
O	-3.94965	-0.87155	-0.14119

(b) Microhydrated tyrosinate dianionin, with PCM

Symbol	X	Y	Z
C	-1.18363	-1.17986	0.026498
C	0.188757	-1.21373	-0.20042
C	0.897782	-0.07979	-0.62578
C	0.157984	1.094995	-0.81397
C	-1.21796	1.145659	-0.58966
C	-1.93519	0.006364	-0.15976
H	-1.70362	-2.07619	0.350913
H	0.723003	-2.14829	-0.0481
H	0.667363	1.992918	-1.15419
H	-1.7602	2.07217	-0.74973
O	-3.24575	0.038641	0.056501
C	2.393732	-0.12571	-0.84382
H	2.664276	-1.04286	-1.37758
H	2.699465	0.717792	-1.47302
C	3.229368	-0.07954	0.469625
H	2.951449	-0.95156	1.069477

C	4.730607	-0.2268	0.102784
N	3.016656	1.131467	1.273156
H	3.589301	1.870348	0.871222
H	2.045077	1.426117	1.217236
O	5.14826	-1.40016	-0.08754
O	5.399202	0.834915	-0.01612
O	-4.73656	2.205891	-0.49993
H	-4.15954	1.416362	-0.31332
H	-5.44359	1.873671	-1.062
O	-4.74969	-1.80544	-1.21333
H	-4.70132	-2.62088	-0.70453
H	-4.17263	-1.16096	-0.72567
O	-4.09066	-0.539	2.552424
H	-4.12074	0.303572	3.016469
H	-3.76208	-0.3208	1.641515

(c) Isolated tyrosyl radical anion, with PCM

Symbol	X	Y	Z
C	2.560098	1.259945	0.271345
C	1.226778	1.271038	-0.04037
C	0.568657	0.107561	-0.52145
C	1.323195	-1.08147	-0.67351
C	2.660864	-1.12294	-0.3673
C	3.352685	0.052652	0.12559
H	3.063907	2.149652	0.631757
H	0.653506	2.185329	0.073111
H	0.828113	-1.97014	-1.05018
H	3.239709	-2.03152	-0.48844
O	4.577978	0.027405	0.408755
C	-0.89599	0.136851	-0.81415
H	-1.15589	1.085892	-1.29221
H	-1.1671	-0.67749	-1.49122
C	-1.7845	0.015776	0.480214
H	-1.50566	0.835312	1.14698
C	-3.26303	0.240041	0.039295
N	-1.66052	-1.24672	1.199263
H	-2.17251	-1.9623	0.690292
H	-0.69402	-1.54264	1.29251
O	-3.63999	1.435914	-0.04853
O	-3.93286	-0.79104	-0.22341

(d) Microhydrated tyrosyl radical anion, with PCM

Symbol	X	Y	Z
C	-1.12195	-1.19601	-0.12384
C	0.22706	-1.21409	-0.35121
C	0.942702	-0.02459	-0.66252
C	0.226296	1.198326	-0.72347
C	-1.12528	1.244732	-0.49788
C	-1.8627	0.042708	-0.18506
H	-1.66888	-2.10321	0.104379
H	0.769389	-2.15221	-0.30363
H	0.76329	2.108278	-0.96682
H	-1.67444	2.17715	-0.55274
O	-3.11746	0.075168	0.025779
C	2.413712	-0.06462	-0.86516
H	2.694806	-0.98936	-1.37618
H	2.750238	0.786521	-1.46131
C	3.217458	-0.04517	0.504579
H	2.860664	-0.88627	1.102216
C	4.713116	-0.30578	0.133714
N	3.102356	1.175377	1.278386
H	3.623075	1.918404	0.821617
H	2.141822	1.471544	1.414074
O	5.061951	-1.50967	0.062872
O	5.413208	0.712373	-0.0895
O	-4.69478	2.430342	-0.11709
H	-4.14983	1.620321	-0.0922
H	-5.36709	2.257794	-0.78453
O	-4.92461	-1.64825	-1.42967
H	-5.09288	-2.44698	-0.91853
H	-4.3063	-1.1304	-0.88582
O	-4.28991	-1.02853	2.425212
H	-4.53471	-0.25427	2.943039
H	-3.89527	-0.66952	1.611907

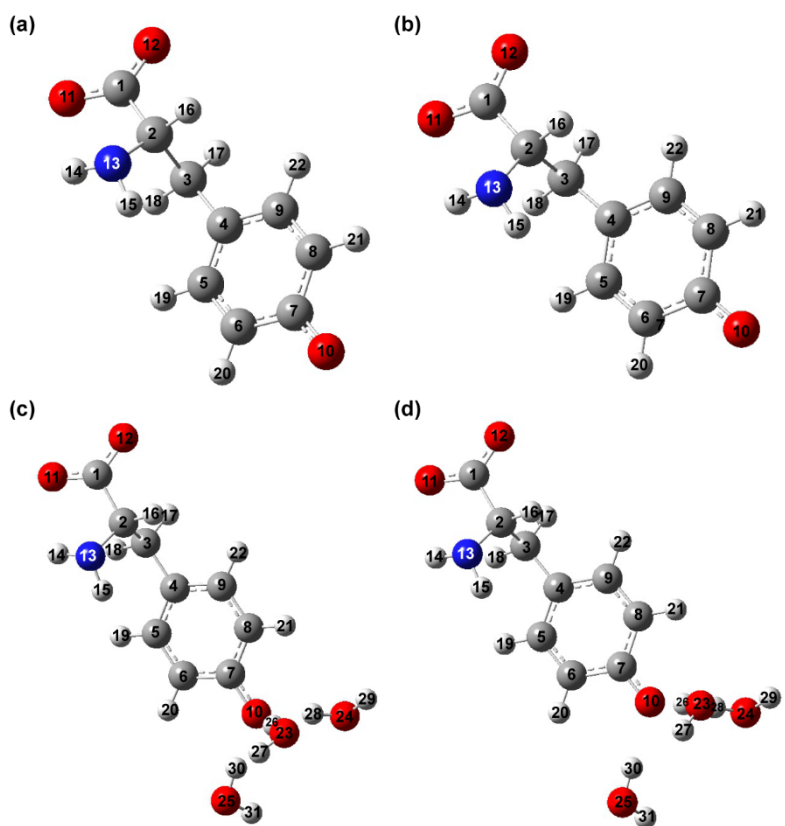


Fig. S5 Equilibrium molecular geometries of the (a) tyrosinate dianion, (b) tyrosyl radical anion, (c) microhydrated tyrosinate dianion and (d) microhydrated tyrosyl radical anion. The microhydrated species includes three water molecules hydrogen-bonded directly to the phenoxide oxygen atom. The carbon atoms are in gray, the hydrogen atoms are in white, oxygen atoms are in red, and the nitrogen atom is in blue.

Table S1 Calculated vibrational frequencies of the tyrosyl radical anion and the microhydrated tyrosyl radical in aqueous environment. The assignment of atoms is based on the equilibrium molecular geometries of the tyrosyl radical anion and the microhydrated tyrosyl radical anion, shown in Figs. S5(b) and S5(d), respectively. Numbered assignments denote benzene ring modes in the Wilson notation.⁵

Calculated Vibrational Frequency (cm ⁻¹)			
	Tyrosyl Radical Anion	Microhydrated Tyrosyl Radical Anion	Assignment
1	38	42	Benzyl Ring Torsion / COO ⁻ Twist
2	52	53	Chain Torsion
3	59	61	Benzyl Ring Torsion
4	80	77	COO ⁻ Twist / Chain CH ₂ Rock
5	157	176	11
6	176	186	Chain Bend
7	241	252	NH ₂ Rock
8	294	295	10b
9	322	337	15
10	351	356	Chain CH ₂ Rock / NH ₂ Twist
11	383	386	16a
12	389	388	Chain Bend
13	458	469	3
14	483	482	6a
15	519	522	16b
16	556	558	16b
17	622	622	6b
18	679	676	4
19	715	715	4
20	763	768	4
21	792	795	10a

22	805	816	12
23	825	832	1
24	841	789	17b
25	862	850	NH ₂ Wag
26	884	886	17b
27	893	876	Benzene Out-of-plane CH Bend
28	968	938	Chain CH ₂ Rock
29	988	992	5
30	990	994	19a
31	996	1000	17a
32	1076	1074	19b
33	1123	1127	14
34	1158	1155	Chain CH ₂ Twist / NH ₂ Wag
35	1175	1185	8a
36	1219	1221	Chain CH ₂ Twist / Chain CH Wag
37	1231	1240	13
38	1271	1264	Chain CH ₂ Wag / Chain CH Wag
39	1275	1293	9b
40	1316	1304	Chain CH Wag / Chain CH ₂ Wag
41	1343	1350	Chain CH ₂ Wag
42	1355	1340	COO ⁻ Bend / Chain CH Wag / Chain CH ₂ Twist
43	1401	1400	Chain CH Wag / NH ₂ Twist
44	1429	1420	20a
45	1452	1462	18b
46	1483	1485	Chain CH ₂ Bend
47	1506	1508	18b
48	1515	1520	20a
49	1580	1586	NH ₂ Bend / COO ⁻ Asymmetric Stretch
50	1605	1626	9a
51	1620	1622	NH ₂ Bend

52	3035	3042	Chain CH ₂ Symmetric Stretch
53	3054	3067	Chain CH Stretch
54	3089	3089	Chain CH ₂ Asymmetric Stretch
55	3166	3173	7b
56	3169	3177	7b
57	3188	3195	20b
58	3190	3197	2
59	3485	3494	NH ₂ Symmetric Stretch
60	3569	3582	NH ₂ Asymmetric Stretch

Table S2 Calculated low-frequency vibrational modes of the microhydrated tyrosyl radical anion.

Microhydrated Tyrosyl Radical Anion Low Frequency / cm⁻¹		Assignment
1	16	Intermolecular bending
2	22	Intermolecular bending
3	26	Intermolecular bending
4	31	Intermolecular bending
5	34	Intermolecular bending
6	38	Intermolecular bending
7	62	Intermolecular bending
8	70	Intermolecular bending
9	74	Intermolecular bending
10	130	Translation
11	134	Translation
12	158	Translation

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