Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for publication:

Reactivity of Zn^{+}_{aq} in high-temperature water radiolysis

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Contents:

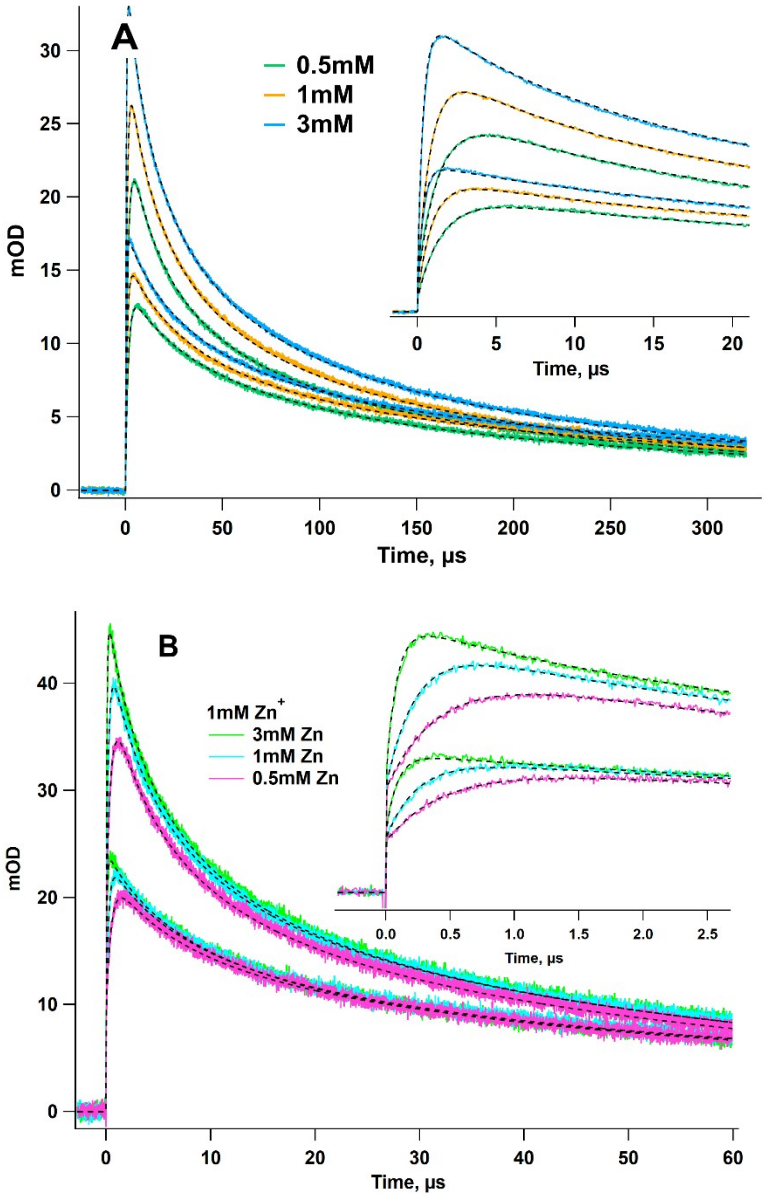

Figure S1. Decay kinetics of Zn^+ at 311nm observed after 4ns- and 9-ns pulse radiolysis in Ar-saturated solutions **(A)** $ZnCl_2$, pH 5.6-6 and **(B)** $Zn(ClO_4)_2$, pH 3.5-4 (9.6 & 4.6 Gy) solutions at room temperature (9.6 & 4.6 Gy). When fitting the kinetic curves for $Zn(ClO_4)_2$, we took into account the pH of the medium.

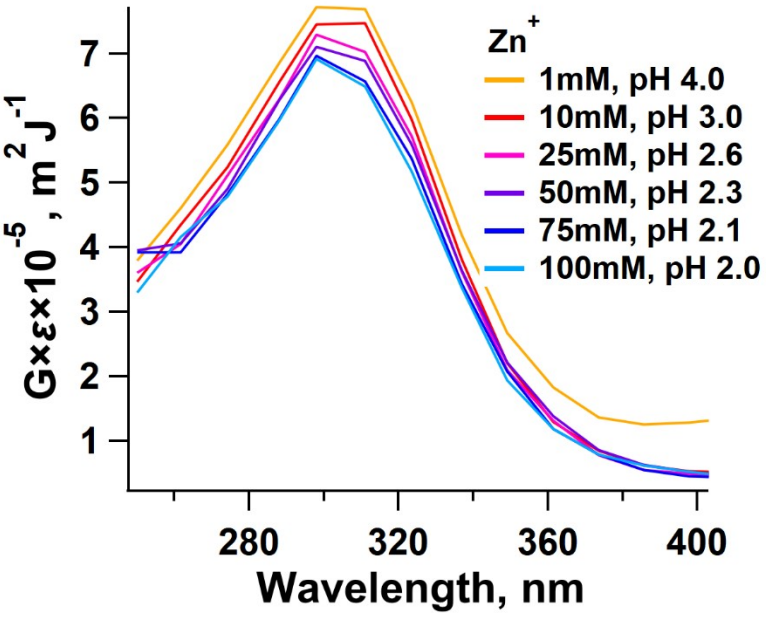

Figure S2. Transient absorption spectra observed 2 μs after 15-ns pulse radiolysis in Ar-saturated solutions with 1-100 mM $Zn(ClO_4)_2$ solutions at room temperature (15 Gy).

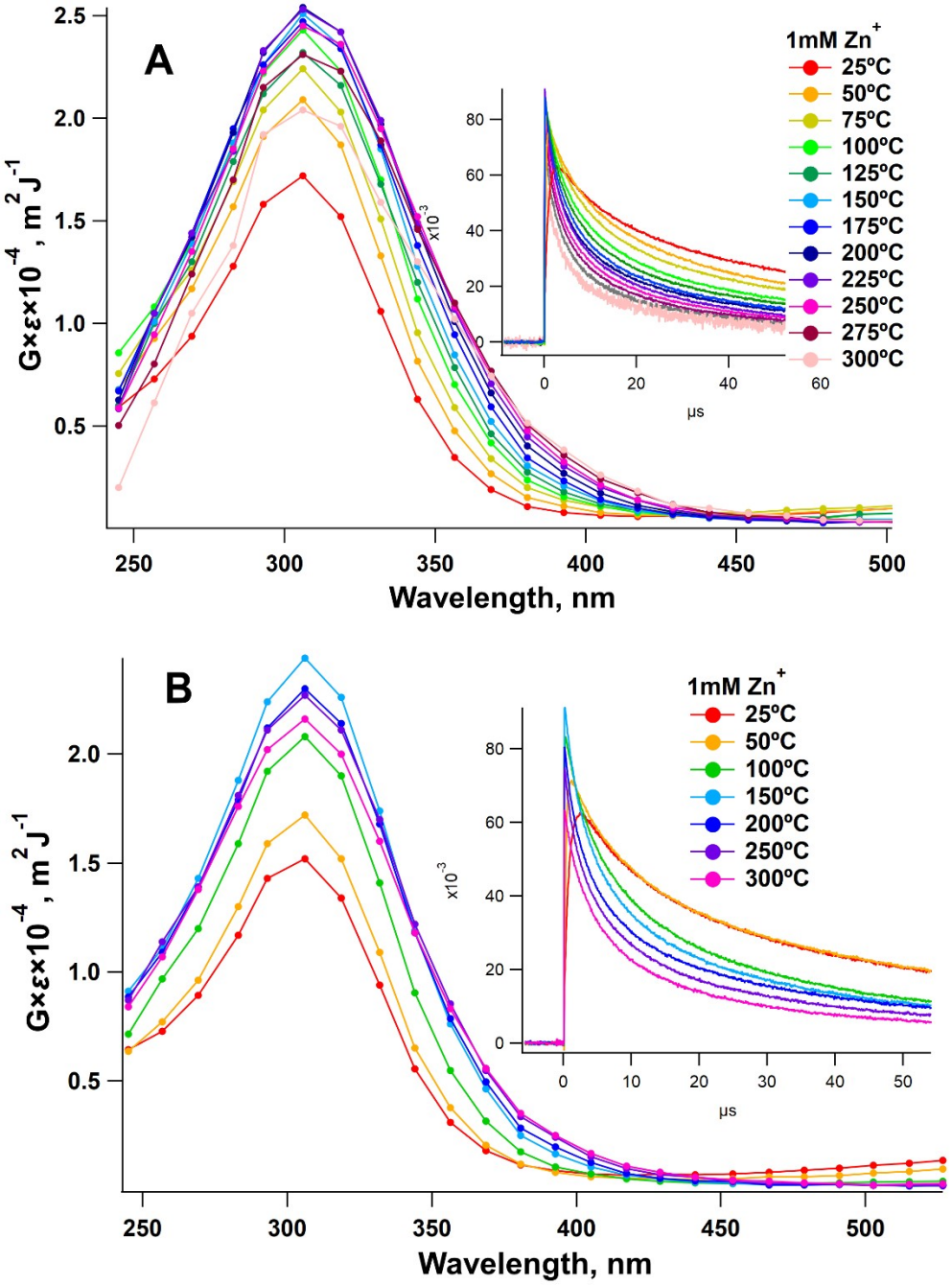

Figure S3. Transient absorption spectra and decay kinetics (insert) at 306 nm observed after 9-ns pulse radiolysis in Ar-saturated solutions with 1 mM $ZnCl_2$ and $Zn(ClO_4)_2$ at a temperature range from 25 to 300 °C (~14Gy).

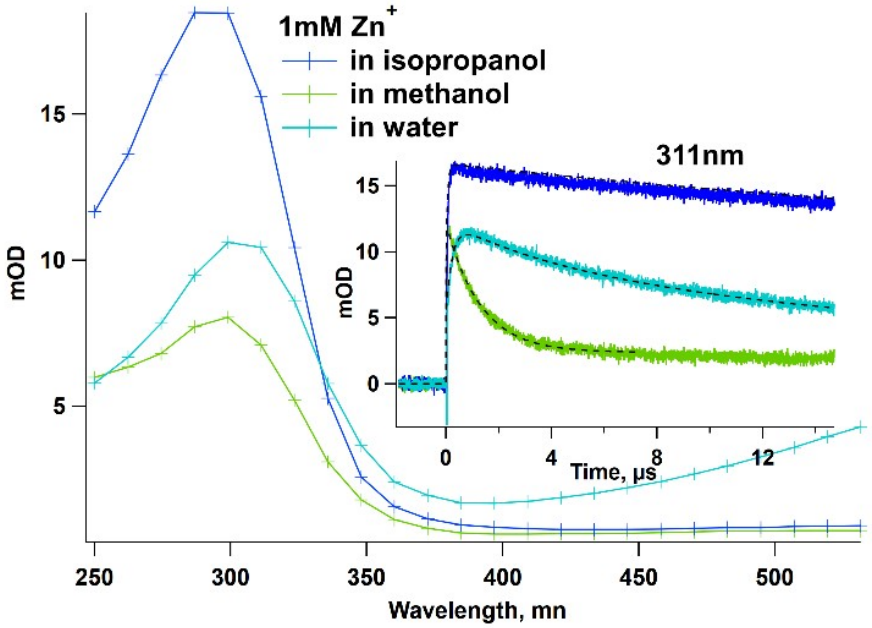

Figure S4. Transient absorption spectra and decay kinetics (insert) observed 2 μs after 6-ns pulse radiolysis (~14Gy) in 1 mM $Zn(ClO_4)_2$ solutions in water, methanol and isopropanol saturated with Ar at room temperature.

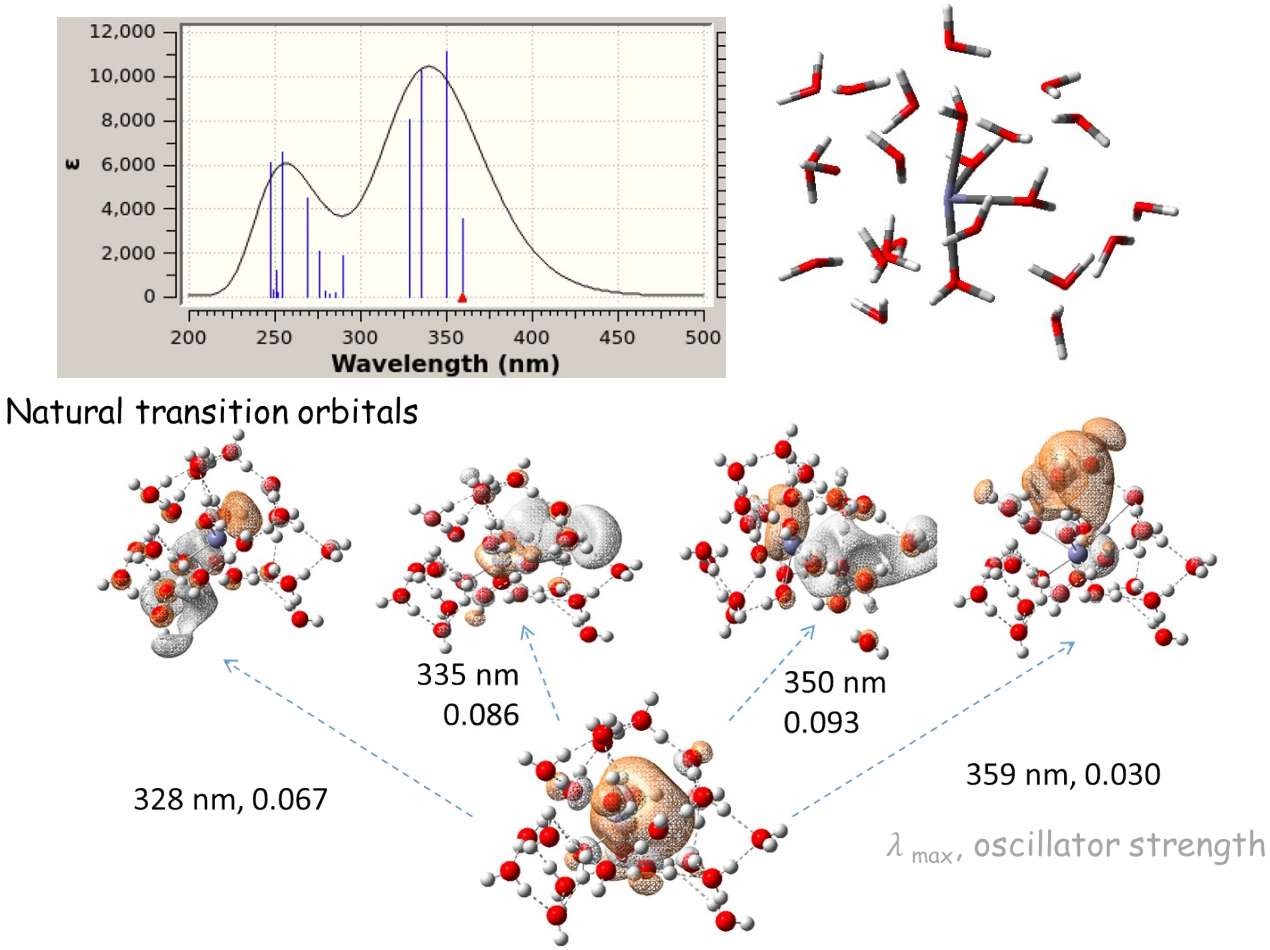

Figure S5. TD-DFT calculated absorption spectra of Zn^{+} coordinated by 24 water molecules. We used color code to show positive (gold) and negative (silver) lobes of the natural transitions of orbitals. The structures were optimized using the iefpcm(SAS)ωb97xD/pc-1 procedure and the vertical excitation spectra were obtained with the same method but including diffuse function in the basis set (apc-1).

Table S1. Rate constants ($k \times 10^9 \pm 6\%$ $M^{-1}s^{-1}$) of the main reactions (1-4) applied in the kinetics model for Zn^+ decay at temperatures up to 300°C in $ZnSO_4$ and $ZnCl_2$ solutions

№	25°C	50°C	75°C	100°C	125°C	150°C	175°C	200°C	225°C	250°C	275°C	300°C
1	1.3	4.6	14.4	27.7	83.9	149	289	328	438	425	488	361
2	11.8	15.5	20.1	25.3	29.4	30.6	34.4	36.3	36.8	38.4	39.0	42.0
3	2.10	2.71	34.4	4.42	5.72	5.85	6.15	7.22	7.8	8.28	8.31	8.41
4	1.40	2.71	3.50	4.42	5.71	5.80	6.21	7.17±	7.32	8.24	8.30	8.46

*The given values are corrected for ionic strengths. When fitting the data obtained, the dose distribution in a 2.5 cm cell was taken into account.

Table S2. Optimized Quantum Mechanical Geometries of Zn^+ transients

$Zn^+(H_2O)_3$

Zn	0.102072	-0.033664	0.80147
O	0.113345	-1.58793	-0.871252
O	-1.623637	0.653736	-0.601653
O	1.211002	1.028871	-0.891351
H	-0.769923	-1.529794	-1.248481
H	0.218274	-2.493843	-0.569533
H	-1.252047	1.37654	-1.116326
H	-2.395261	1.008618	-0.153789
H	1.95489	1.563325	-0.602605
H	1.576229	0.327663	-1.439308

$Zn^+(H_2O)_2(OH^-)$

Zn	-1.039825	-0.011728	-0.129208
O	0.178767	1.378049	0.425981
O	0.527713	-1.583277	0.369748
O	2.445592	0.251993	-0.173161
H	-0.092545	2.237261	0.102269
H	1.347342	-1.088828	0.141038
H	0.477743	-2.321383	-0.241282
H	2.591665	0.316942	-1.118035
H	1.653981	0.833743	0.0117

$Zn^+(H_2O)(OH^-)_2$

Zn	-0.684829	-0.318138	0.283245
O	0.867033	-0.940498	-0.732252
O	-1.435269	1.240804	-0.531337
O	2.69243	0.803492	0.138885
H	1.133936	-1.794819	-0.390071
H	-2.14874	1.562186	0.020931
H	2.521515	0.806693	1.081196
H	2.044619	0.13969	-0.21179

$Zn^+(OH^-)_3$

Zn	0.006961	-0.004556	0.218693
O	-1.359919	-1.325364	-0.345636
O	-0.442952	1.844576	-0.349072
O	1.825128	-0.553065	-0.349529
H	-1.67581	-1.63871	0.504094
H	-0.564623	2.273208	0.500363
H	2.293633	-0.565492	0.487241

$Zn^+(H_2O)_{24}$

O	-0.081262	-2.507724	-1.439002
H	0.275791	-2.468669	-0.524059
H	0.396907	-3.313133	-1.766885
O	1.139606	-3.379299	0.946358
H	1.874334	-2.92383	1.403501
H	0.405615	-3.407462	1.602500
O	-3.19999	-0.578551	-2.945507
H	-2.240898	-0.297804	-2.920155
H	-3.204649	-1.347132	-2.318864
O	-2.848935	-2.720338	-1.248008
H	-1.861765	-2.72624	-1.298356
H	-3.045107	-2.536512	-0.304184
O	2.71211	3.046698	-1.931653
H	2.028537	2.635542	-2.521429
H	2.228636	3.49255	-1.203332
O	-3.289027	-2.324063	1.526988
H	-3.484896	-1.393433	1.834025
H	-4.044434	-2.860561	1.817241
O	0.945847	1.893601	-3.683082
H	0.296536	2.569389	-3.933107
H	0.385976	1.156623	-3.284898
O	-5.454438	1.105579	0.538868
H	-6.040177	0.346574	0.389914
H	-5.025549	1.267441 -	0.351418
O	1.559602	-4.678856	-1.555467
H	1.489978	-4.51996	-0.5906
H	2.372119	-4.166369	-1.799542
O	-0.631271	0.110201	-2.517472
H	-0.251137	-0.772938	-2.323247
O	-0.909239	3.554065	1.176989
H	-1.089608	2.888688	0.451948
H	-1.63359	4.20061	1.098301
O	0.273871	-0.471745	2.693929
H	-0.255686	-1.302157	2.791879
H	-0.299714	0.290729	2.997613
O	-0.943683	-2.913337	2.699797

H	-1.086617	-3.350093	3.554178
H	-1.84559	-2.791276	2.292516
O	4.427453	1.211787	-1.012246
H	4.965529	1.005603	-1.792712
H	3.773744	1.900452	-1.336636
O	3.705668	-3.028517	-2.066155
H	3.415358	-2.26111	-1.508657
H	4.466886	-3.391712	-1.586894
O	1.623629	4.302702	0.357562
H	1.803089	5.249633	0.468267
H	0.684452	4.167514	0.639752
O	2.910618	-0.923663	-0.485489
H	3.530012	-0.152581	-0.66126
H	3.024482	-1.162932	0.47129
O	2.372819	2.152705	1.931887
H	2.360715	3.023021	1.477031
H	1.84603	1.586685	1.329205
O	2.84932	-1.448242	2.22299
H	2.021139	-1.020246	2.539164
H	3.565711	-0.809157	2.488295
O	-3.734691	0.20881	2.347081
H	-4.3574	0.605551	1.659088
H	-4.26058	0.166898	3.163367
O	-1.413114	1.564142	3.215673
H	-1.204466	2.295095	2.593736
H	-2.24992	1.176383	2.870136
O	0.762759	0.434567	0.28494
H	0.502989	-0.03092	1.141647
H	1.476386	-0.12015	-0.153213
O	-4.290354	1.566827	-1.830438
H	-3.916781	0.722102	-2.237054
H	-4.949885	1.881454	-2.468884
O	4.495152	0.649022	2.703842
H	4.538089	0.820868	3.657848
H	3.808097	1.290467	2.375251
Zn	-0.834943	0.992519	-0.856047

Zn^+H_2O

Zn	-0.000002	-0.540696	0.000000
O	-0.000002	1.509056	0.000000
H	0.000036	2.074215	0.780526
H	0.000036	2.074215	-0.780526

$Zn^+(H_2O)_2$

Zn	-0.003053	-0.613768	0.000372
O	1.511937	0.866406	-0.021917
O	-1.506081	0.872616	0.021549
H	2.403274	0.66664	-0.325357
H	1.587896	1.55195	0.649543
H	-2.415638	0.672148	0.263969
H	-1.530792	1.610128	-0.596385