Supplementary Information to 'The electronic structure of the aqueous permanganate ion: aqueous-phase energetics and molecular bonding studied using liquid jet photoelectron spectroscopy'

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This supplement provides further details regarding the results presented in the main text and the analysis of additional, complementary data sets. Particularly, we address specific points concerning the $MnO_{4^-(aq)}$ UV-visible and partial electron yield X-ray absorption spectroscopy (PEY-XAS) spectra, multi-peak fitting analysis applied to the non-resonant X-ray photoelectron spectroscopy (XPS) data, surface-sensitive NaMnO_{4(aq.)} non-resonant XPS spectra and non-resonant surface- and resonant bulk-sensitive KMnO_{4(aq.)} spectra. Similarly, we expand on our report of the resonant photoelectron spectroscopy experiments by presenting results associated with Resonances III and IV. Furthermore, we present our multi-peak fitting analysis of the NaMnO_{4(aq.)} RPES data discussed throughout the main text and of the KMnO_{4(aq.)} data presented in this supplement.

UV-visible and PEY-XAS spectra

Figure S1 A shows UV-visible absorption spectra recorded from NaMnO_{4(aq.)} (upper panel) and KMnO_{4(aq.)} (lower panel) solutions at 0.25 M concentrations. The electronic state and associated predominant molecular orbital transitions are labelled in accordance with Reference 1. At such concentrations, the spectra show similar optical transitions despite the presence of different cations. The NaMnO_{4(aq.)} and KMnO_{4(aq.)} spectra were fit using a set of Gaussian functions in order to extract the energies associated with different spectral bands – particularly of those attributed to transitions between the HOMO (1t₁), LUMO (2e), and LUMO+1 (5t₂) molecular orbitals. Considering our experimentally determined BE for the $1t_1^{-1}$ ionizing transition (see Table 1 in the main text), and the excitation energies extracted from fits to the first (2.337 ± 0.001 eV) and third (4.070 ± 0.009 eV) dominant bands in the NaMnO_{4(aq.)} UV-visible spectrum, electron binding energies of 5.15 ± 0.08 eV and 6.88 ± 0.08 eV were respectively estimated for the 5t₂ and 2e virtual valence orbitals, neglecting electron correlation effects.

Panels B and C show (baseline-corrected) Mn L- and O K-pre-edge PEY-XAS spectra recorded from 0.2 M NaMnO_{4(aq.)} solutions, respectively. Cumulative Gaussian fits were applied to both spectra to determine resonant photon energies corresponding to $MnO_{4^{-}(aq.)} 1t_2 (Mn 2p_{3/2}) \rightarrow 2e$, $1t_2 (Mn 2p_{3/2}) \rightarrow 5t_2$, $1t_2 (Mn 2p_{1/2}) \rightarrow 2e$, $1t_2 (Mn 2p_{1/2}) \rightarrow 5t_2$, $3a_1 (O 1s) \rightarrow 2e$ and $3a_1 \rightarrow 5t_2$ transitions. The fit results are shown in purple. These transitions respectively correspond to Resonances I – VI discussed in the main text. In this case we can (erroneously) neglect electron correlation effects to extract significantly higher average electron binding energies of 5.7 ± 0.4 eV and 7.6 ± 0.1 eV for the associated $5t_2$ and 2e virtual valence orbitals. (Note that a greater variance is observed for the $5t_2$ feature energies extracted at Resonances II, IV, and VI in comparison to the 2e feature energies extracted at Resonances I, III, and V. This leads to a greater uncertainty in the former value). The difference between these values and those more reliably extracted from the UV-visible data (where the electron correlation effects partially cancel due to the electron hole being (predominantly) centred in the $1t_1$ orbital within all of the considered states), reflect the eV-scale energy level shifts associated with accommodation of an additional valence electron and an inner shell hole following resonant X-ray excitation.



Fig. S1: (A) NaMnO_{4(aq.)} and KMnO_{4(aq.)} solution UV/Visible absorption spectra and cumulative Gaussian fits to the electronic absorption bands: (1) ${}^{1}A_{1} \rightarrow$ (1) ${}^{1}T_{2}$, ${}^{1}A_{1} \rightarrow$ (2) ${}^{1}T_{2}$, and (1) ${}^{1}A_{1} \rightarrow$ (1) ${}^{1}T_{2}$, labelled according to Reference 1. The lower-intensity band at ~1.9 eV is associated with spin- and / or orbital-forbidden transitions to the ${}^{3}T_{2}$ and ${}^{1}T_{1}$ states ². (B) Mn L_{II,III}-pre-edge PEY-XAS spectra from a 0.2 M NaMnO_{4(aq.)} solution and associated fits. The broad Gaussian feature spanning the 652 – 661 eV range was added to account for the remaining background after the baseline correction procedure mentioned in the main text. (C) O K-pre-edge PEY-XAS spectra from 0.2 M NaMnO_{4(aq.)} solutions. Fits corresponding to MnO_{4 (aq.)} core-to-virtual-valence transitions are shown in purple. The light blue curves close to 534 eV and 535 eV respectively correspond to the O 1s – 4a₁ transitions from gas-phase ³ and liquid-phase ⁴ water molecules. The value associated with the latter was used to calibrate the photon energy scale in panel B.

Direct (non-resonant) NaMnO_{4(aq.)} **photoemission spectra**: *bulk-sensitive spectra, multi-peak fitting analysis*



Fig. S2: Bulk-sensitive 0.2 M NaMnO_{4(aq.)} solution XPS spectra recorded at a 635 eV photon energy with associated cumulative Gaussian fits to the solute anion (purple), solute cation (grey), and solvent (blue) signals. MnO₄ (aq.) features are labelled with numbers in accordance with Table 1 in the main text. Solvent and counter-ion ionization features are labelled with lower-case Roman numerals in accordance with Table 2 in the main text. The fit associated with peak 4 was coloured with purple and striped to indicate an overlap between photoelectron signals corresponding to the solute $5a_1^{-1}$ ionizing transition and electron energy-loss peaks associated with water $1b_1^{-1}$ and $3a_1^{-1}$ photoelectrons. The additional striped signals at nominal BEs of 33 eV and 51 eV are similar energy-loss peaks primarily associated with water $1b_2^{-1}$ and $2a_1^{-1}$ photoelectrons, respectively.

Fig. S2 shows the results of a cumulative Gaussian multi-peak fit to a Shirley-background-corrected 0.2 M NaMnO_{4(aq.)} spectrum recorded at a 635 eV photon energy. The $MnO_{4^{-}(aq.)} 1t_1^{-1}$ (peak 1) and $2t_2^{-1}$ (peak 5), and $Na_{4^{+}(aq)}^+ 2s^{-1}$ (peak vi) BEs were determined from the fit results and are consistent with those extracted from difference spectra and the results presented in Table 1 in the main text. The fit results associated with the water orbitals were used to report the average values shown in Table 2 in the main text. The $MnO_{4^{-}(aq.)} 5a_{1}^{-1}$ (peak 4) and $Na_{(aq)}^{+} 2p^{-1}$ (peak v) features overlap with secondary electron energy-loss background signals associated with ionization from the water outer valence orbitals (1b1 ¹, $3a_1^{-1}$, $1b_2^{-1}$) ⁵ and could not be isolated using this data treatment. Accordingly, we relied on the solution-solvent different spectra, like those shown in red in Fig. 2 in the main text, to extract these binding energies (BEs, see Fig. 2 in the main text). Similarly, the broad peak centred at a nominal BE of 51 eV is primarily associated with energy-loss background signals from the water 2a₁-1 ionization feature ⁵.



50

0.0

0.20 M NaMnO

0.50 M NaCl(ag)

Difference spectru

Direct (non-resonant) NaMnO_{4(aq.)} photoemission spectra: surface-sensitive spectra

60

3a₁ / O 1s _{vii}

vii-g

0.5 0.0 70

signal 0.8

в 1.0

0.04 Normalized † 0.6 0.6 zed 0.02 0 00 0.4 538 536 53 Binding energy / eV 0.3 0 2 7 0.0 0.0 542 541 540 539 538 537 536 535 534 665 660 655 650 645 Binding energy / eV Binding energy / eV Fig. S3: As Fig. 2 in the main text but for the surface-sensitive NaMnO_{4(aq.)} solution data. (A) Outer and inner valence spectrum recorded at a 150 eV photon energy.

40

Binding energy / eV

12 11 10 9 8 Binding energy / eV

iii

10

0

20

0.20 M NaMnO

8

iv

30

1t₂ / Mn 2p

С

(B) O 1s permanganate and water reference spectra recorded at a 688 eV photon energy. (C) Mn 2p spectrum recorded at a 800 eV photon energy. The † peak label in the inset of panel B denotes an apparent solute signal that exclusively arises in the surface-sensitive direct XPS data and is ascribed to the slight increase of the liquid water O 1s peak (peak vii) width in the solution versus the aqueous-solvent reference spectra. The spectra shown in panels A and B were recorded at the U49/2 PGM-1 beamline at BESSY II under ambient temperature conditions, while the spectrum shown in panel C was recorded at the PO4 beamline at PETRA III at a regulated liquid jet temperature of 4°C. Comparison between data sets recorded at temperatures in the ~ 2 – 20°C range confirmed that variations in sample temperature have no detectable effect on the extracted BEs under our experimental conditions.

Fig. S3 shows inner and outer valence (panel A), O 1s (panel B), and Mn 2p (panel C) gas-liquid interface-sensitive spectra recorded from 0.2 M NaMnO_{4(ac.)} solutions with 150 eV, 688 eV, and 800 eV photon energies, respectively. In comparison to the bulk-sensitive data, the drop in the spectrometer transmission efficiency at low kinetic energies (<100 eV) and the relatively high secondary electron background prevents resolution of peaks 4 and 5 in the 150 eV photon energy data. Hence, as shown in Fig. S4, outer and inner valence spectra were additionally recorded at a photon energy of 225 eV, achieving more appropriate analyser conditions (more uniform collection efficiency over the spectrum) that allowed us to extract the MnO_{4⁻(aq)} $5a_1^{-1}$ (peak 4) and $2t_2^{-1}$ (peak 5) BEs. It was not possible, however, to extract the MnO₄- $_{(aq)}$ 4a₁⁻¹ (peak 6) BE from any of the surface-sensitive XPS measurements.

Notably, the increased gas-phase signals at 150 eV with respect to 635 eV photon energies and the differential sample charging that occurs between the solution and solvent jet samples lead to numerous gas-phase background subtraction



Fig. S4: 0.2 M NaMnO_{4(aq.)} surface-sensitive valence spectra recorded at 225 eV photon energy at the U49/2 PGM-1 beamline at BESSY II at a regulated liquid jet temperature of 5°C. (A) Inner valence spectrum. The inset on the right highlights the solute $1t_1^{-1}$ (peak 1) and $4t_2^{-1}$ (peak 2) features. The inset on the left highlights the solute $5a_1^{-1}$ (peak 4) ionizing transition. (B) Outer valence spectrum, displaying the $2t_2^{-2}$ solute ionizing transition (peak 5). The $4a_1^{-1}$ signal (peak 6 in Fig. 3 in the main text) could not be isolated in the surface-sensitive spectra. The signal at ~87 eV is present in both the solution and solvent spectra and appears to be an artefact associated with the analyser lens table. Notably, this feature could not be reproduced at other photon energies.

artefacts in the 150 eV photon energy difference spectra. This, for example, prevented us from extracting a peak **3** BE (as shown in Fig. 2 in the main text) from the 150 eV photon energy data.

In the O 1s solution-solvent difference spectrum shown in panel B, an additional peak arises with respect to the bulksensitive data at a BE of $538.3 \pm 0.2 \text{ eV}$ (peak marked by a ⁺ in the inset of Fig. S3 B). In contrast to the results obtained by fitting the surface-sensitive difference spectra, cumulative Voigt profile fits to the solution $3a_1^{-1}$ / O 1s spectra produce a single, albeit broadened, contribution to the solute O 1s feature (peak 7). As explained in the main text, the additional ionisation feature in the surface-sensitive difference spectra either originates from a slightly larger liquid water peak vii (O 1s) width in the MnO₄ (aq) spectrum with respect to the corresponding water reference (50 mM NaCl_(aq.)) spectrum or is a genuine additional solute peak that arises at the solution-gas interface. With the data currently available to us, we cannot distinguish between these two possibilities.

The cumulative fit results extracted from the surface-sensitive data shown in Figs. S3 and S4 are summarised in Table S1. Importantly, similar BEs are extracted from our surface-sensitive data, for example that shown in Figs. S3 and S4, and our bulk-sensitive data, for example that shown in Fig. 2 in the main text.

Table S1: Summary of the MnO_{4 (aq)} BEs extracted from Gaussian (top) and Voigt profile (bottom) fits to the surface-sensitive spectra shown in Figs. S3 and S4. The top panel summarizes the inner and outer valence BEs extracted from data sets recorded at 150 eV and 225 eV photon energies. The bottom panel displays the $3a_1^{-1}$ and $1t_2^{-1}$ solute BEs extracted from spectra recorded at 688 eV and 800 eV photon energies, respectively.

Label	Peak Origin –	ħω = 150 eV		ħω = 225 eV	
		BE / eV	FWHM _G / eV	BE / eV	FWHM _G / eV
1	(1t ₁) ⁻¹	9.27 ± 0.04	0.69 ± 0.06	9.22 ± 0.08	0.6 ± 0.2
2	(4t ₂) ⁻¹	10.59 ± 0.04	1.34 ± 0.05	10.71 ± 0.06	1.5 ± 0.2
4	(2a ₁) ⁻¹	-	-	26.9 ± 0.1	3.6 ± 0.3
5	(2t ₂) ⁻¹	-	-	59.7 ± 0.3	2.0 ± 0.3
Label	Peak Origin —	ħω = 0	588 eV	ħω = 3	800 eV
		BE / eV	FWHM _G / eV	BE / eV	FWHM _G / eV
7	(3a ₁) ⁻¹	536.2 ± 0.1	1.59 ± 0.01	-	-
+	?	538.3 ± 0.2	1.0 ± 0.1	-	-
8	(1t ₂)-1	-	-	650.8 ± 0.1	1.11 ± 0.04

KMnO_{4(aq)} photoemission spectra: surface-sensitive and bulk-sensitive spectra



Fig. S5: Surface-sensitive spectra from ~0.2 M KMnO_{4(aq.)} solutions recorded at the U49/2 PGM-1 beamline at BESSY II. The solute anion and cation (peak viii) signals are illustrated by brown and green fills, respectively. (A) Outer valence spectrum recorded at a 150 eV photon energy. Given the relatively low solubility limit of KMnO₄ ⁶, the liquid jet temperature needed to be set to 30°C in order to achieve stable liquid jet conditions over the acquisition time required to achieve sufficient signal-to-noise ratio over a 5 – 45 eV BE range. (B) O 1s permanganate and water reference spectra recorded at 688 eV photon energy and a liquid jet temperature of 18°C. (C) Mn 2p spectrum recorded at 793 eV photon energy and a liquid jet temperature of 14°C. The † peak label in the inset of panel B denotes an apparent solute signal that exclusively arises in the surface-sensitive direct XPS data and is ascribed to the slight increase of the liquid water O 1s peak (peak vii) width in the solution versus the aqueous-solvent reference spectra.

Fig. S5 shows surface-sensitive 0.22 ± 0.02 M KMnO_{4(aq.)} solution XPS spectra spanning the outer valence, O 1s, and Mn 2p BE ranges. The spectra are comparable to the surface-sensitive NaMnO_{4(aq.)} solution spectra shown in Figs. S3 and S4 and highlight that a change in counter-ion has no discernible effect on the extracted electron BEs. The lone extractable K⁺ counter-ion feature, $3p^{-1}$, is highlighted in the left inset of panel A, labelled as peak **viii**, and is identified by a green Gaussian profile associated with a fit to the solution-solvent difference spectrum. The fit results associated with Fig. S5 are summarized in Table S2 (top). Comparing the results from the KMnO_{4(aq.)} (Table S2) and NaMnO_{4(aq.)} (Table S1) solutions, all anion BEs were found to be in agreement and cation independent. Accordingly, we conclude that the MnO₄^{-(aq.)} and Na⁺ or K⁺ counter-ions similarly (and likely fully) dissociate in ~0.2 M aqueous solutions and that the anions and cations are, on average, similarly well-separated at the aqueous-gas phase interface.

As discussed in the main text, the high photon energies associated with the core-to-virtual valence energy gaps in our Mn 2p and O 1s RPES experiments ensure bulk-solution sensitivity. Hence, bulk-sensitive RPES results from 0.15 M KMnO_{4(aq.)} solutions can be compared to the NaMnO_{4(aq.)} results presented in the main text (Fig. 2) to assess the effects of the counter-ion on the bulk electron energetics. Fig. S6 panels A and D respectively show Mn L_{III}- and O K-pre-edge RPES maps (left) and associated PEY-XAS spectra (right). High signal-to-noise-ratio spectra recorded at the 1t₂ (Mn 2p_{3/2}) \rightarrow 2e (Resonance I), 1t₂ (Mn 2p_{3/2}) \rightarrow 5t₂ (Resonance II), 3a₁ (O 1s) \rightarrow 2e (Resonance V), and 3a₁ \rightarrow 5t₂ (Resonance VI) resonances are also respectively shown in panels B, C, E, and F. The participator BEs were exclusively extracted from difference spectra associated with Resonances I, II and VI and are shown in the bottom panel of Table S2. The fit results and additional assignments of spectator Auger and ICD features are reported in detail in the *Resonant photoemission spectra* section of this supplement (see Table S5). Similarly to the surface-sensitive non-resonant XPS experiments, our bulk-sensitive RPES results yield equivalent results for ~0.2 M KMnO_{4(aq.)} and 0.2 M NaMnO_{4(aq.)} solutions. Accordingly, we conclude that the MnO₄⁻_(aq.) and counter-cations fully dissociate in bulk ~0.2 M aqueous solutions and that the anions and cations are on average well-separated in the aqueous-bulk.

Fig. S6: RPES spectra from 0.15 M KMnO_{4(aq.)} solutions recorded at the U49/2 PGM-1 beamline at BESSY II. (A) 1t₂/Mn 2p_{3/2} to virtual valence RPES map (left) and PEY-XAS spectrum (right). (B) $1t_2/Mn 2p_{3/2} \rightarrow 2e$ resonant spectrum recorded at Resonance I. (C) $1t_2/Mn 2p_{3/2} \rightarrow 5t_2$ resonant spectrum recorded at Resonance II. (D) $3a_1/O$ 1s to virtual valence RPES map (left) and PEY-XAS spectrum (right). (E) $3a_1/O$ 1s \rightarrow 2e resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonant spectrum recorded at Resonance V. (F) $3a_1/O$ 1s \rightarrow 5t₂ resonance V. (F) $3a_1/O$ recorded at Resonance VI. Off-resonant spectra are shown as reference signals (i.e. spectra without resonant-enhancement, black curves) in panels B, C, E, and F. As in the main text, participator Auger signals are labelled with numbers (see the bottom panel of Table S2) while spectator Auger and potential ICD signals are labelled with letters (see Table S5 at the end of this document). The asterisks highlight an artefact signal associated with ionisation of H₂O₍₁₎ 1a₁/O 1s electrons by the second harmonic of the beam line.

Table S2: Summary of the MnO _{4 (aq.)} solute BEs and associated Gaussian peak width components, FWHMG, extracted from KMnO _{4(aq.)} surface-sensitive direct P	۶E
experiments (top panel) and bulk-sensitive RPES experiments (bottom panel). The values associated with features 7, 8, and 3-a were extracted from Voigt profile fi	its,

Label	Peak Origin	BE / eV	FWHM _G / eV
		MnO ₄ -(aq.) – XPS	
1	(1t ₁) ⁻¹	9.29 ± 0.07	0.75 ± 0.06
7	(3a ₁) ⁻¹	536.2 ± 0.1	1.59 ± 0.01
8	(1t ₂) ⁻¹	650.8 ± 0.1	1.11 ± 0.04
	MnO ₄ -(a	_{q.)} – RPES Participator Auger	
2-a	(4t ₂) ⁻¹	9.6 ± 0.1	0.73 ± 0.03
3-a	(1e or 3t ₂) ⁻¹	12.8 ± 0.1	0.83 ± 0.05
5	(2t ₂) ⁻¹	59.7 ± 0.4	2.5 ± 0.1

Resonant photoemission spectra: $Mn 2p_{1/2} RPES$ spectra (Resonances III and IV)

Fig. S7 shows Mn $2p_{1/2}$ RPES data similar to that shown in Fig. 3 panels A, B, and C in the main text for the Mn $2p_{3/2}$ coreto-virtual-valence transitions. A Mn $2p_{1/2}$ RPES map (left) and PEY-XAS spectrum (right) are shown in panel A. Panels B and C show spectra recorded at Resonances III and IV, respectively. An off-resonant spectrum recorded at a lower photon energy of 638 eV is plotted in each panel as a non-resonant reference spectrum (*i.e.* a spectrum devoid of resonant signal enhancements). The associated Resonance III and IV difference spectra are shown in Figure S8.

Fig. S7: RPES spectra recorded from 0.2 M NaMnO_{4(aq.)} solutions at the U49/2 PGM-1 beamline at BESSY II. (A) $1t_2$ /Mn $2p_{1/2}$ to virtual valence RPES map (left) and PEY-XAS spectrum (right). (B) $1t_2$ /Mn $2p_{1/2} \rightarrow 2e$ resonant spectrum recorded at Resonance III. (C) $1t_2$ /Mn $2p_{1/2} \rightarrow 5t_2$ resonant spectrum recorded at Resonance IV. Participator Auger signals are labelled with numbers and spectator Auger signals are labelled with letters.

The resonantly-enhanced signal strengths at Resonance III and IV are significantly less intense than those occurring at Resonance II, for example (see Fig. S1 B). This is particularly apparent in the RPES difference spectra shown in Fig. S8 and the spectral regions where valence participator signals might be expected, the 640-650 eV electron kinetic energy (KE) region. The signals in this region are highlighted in yellow in Fig. S8 and were found to be highly sensitive to the experimental conditions, subtleties of the implemented baseline subtraction method, and resonant-non-resonant difference spectra procedures. The resulting spectral differences were generally found to oscillate around zero, with peak positions differing between comparable data sets. Hence, it has not been possible to reliably assign any participator Auger channels to the Resonance III and IV difference data or extract any associated binding energies (BEs).

Despite the challenges in assigning participator Auger signatures in the data recorded at Resonance III and IV, spectator Auger signatures have been reproducibly extracted. Similar spectator Auger features to those observed at Resonances I and II (see Fig. 5 in the main text) are present in the Resonance III and IV spectra shown in Fig. S8. Feature 'a' is notably narrower in the Resonance I and II cases ($2p_{3/2}$ core-hole) in comparison to the Resonance III and IV data ($2p_{1/2}$ corehole), as expected based on the shorter average core-hole lifetimes of the latter (~1.8 fs versus ~0.7 fs, respectively ⁷). Furthermore, additional Coster-Kronig ⁸ L_{II}-L_{III}V spectator Auger processes (lower KE relaxation channels) notably become accessible following higher-energy excitation to Resonances III and IV. These processes lead to spectrally broadened, lower KE tails of feature 'a' in the Resonance III and IV data sets, which are spectrally shifted to lower KEs by the $1t_2$ spin-orbit splitting energy, ~10.9 eV (see Table 1 in the main text). These assignments and the considerable span of feature 'a' (15 - 30 eV) suggests a significant delocalization of the virtual valence electrons occurs within the sub-fs core-hole lifetime following photoexcitation at Resonance III and IV.

Feature '**b**' in Fig. S8 displays similar behaviour to feature '**a**' in moving from Resonances I and II to III and IV. Additional, lower KE spectator Auger features occur following excitation to Resonances III and IV. We ascribe these features to Coster-Kronig L_{II}-L_{III}, 2t₂ spectator Auger processes. This assignment attests to the hybridised nature of the Mn 2p (2t₂) atomic (inner valence molecular) orbital. The spectator Auger peak assignments associated with Figs. S7 and S8 are summarised in Table S3 below.

Fig. S8. Resonance III (Mn $2p_{1/2} \rightarrow 2e$) and IV (Mn $2p_{1/2} \rightarrow 5t_2$) RPES difference spectra. The participator Auger signal associated with the MnO₄⁻_(aq) $2t_2^{-1}$ ionizing transition is labelled as peak **5**, as in the main text. Spectator Auger signals are similarly labelled with letters ('a' and 'b'). The yellow overlay (640 – 650 eV KE) indicates the spectral region where over- and under-subtraction of the off-resonant spectrum from the resonant spectra resulted in sharp features that oscillate around zero in intensity, thus preventing the isolation of resonantly-enhanced MnO₄⁻_(aq). Auger features over this KE range.

Peak	Assignment 1	Assignment 2	KE / eV
а	L _{II} -V,V	-	636.6 ± 0.2
	L ₁₁ -L ₁₁₁ ,V	-	631.0 ± 0.4
	L _{II} -5a ₁ ,V	-	622.6 ± 0.2
b	L _{II} -2t ₂ ,V	-	585.2 ± 0.3
	L ₁₁ -L ₁₁₁ ,2t ₂	L _{II} -2t ₂ , 5a ₁	576.5 ± 0.2

Table S3: Assignments of the RPES spectator Auger signals associated with the data shown in Figs. S7 and S8.

Fig. S9: Cumulative fits to the difference spectra produced by subtracting the off-resonant spectrum from the resonant data. (A) Resonance I difference spectrum. (B) Resonance II difference spectrum. The inset on the right shows the results of a cumulative Voigt fit to the lower BE range in the spectra. The inset on the left shows the spectator signal involving the $MnO_{4^{'}(aq)}$, $4a_1$ (Mn 3s) molecular orbital. (C) Resonance III difference spectrum. (D) Resonance IV difference spectrum. (E) Resonance V difference spectrum. (F) Resonance VI difference spectrum. The inset shows the participator Auger signal associated with the $MnO_{4^{'}(aq)}$, $4t_2^{-1}$ ionizing transition. Participator Auger signals are labelled with numbers and spectator Auger / ICD signals are labelled with letters. The asterisk in panels E and F indicates a signal resulting from ionization with the unfiltered second harmonic of the beamline.

Figs. S9 and S10 respectively show cumulative fits to the resonant-non-resonant difference spectra respectively recorded from 0.2 M NaMnO_{4(aq.)} and 0.15 M KMnO_{4(aq.)} solutions. For the 0.2 M NaMnO_{4(aq.)} data, the results obtained from these fits were used to report the KEs in Table 4 in the main text. The fitting results and peak assignments associated with the NaMnO_{4(aq.)} and KMnO_{4(aq.)} solutions are summarized in Table S4 and Table S5, respectively.

Fig. S10: Cumulative fits to the KMnO_{4(aq)} solution resonant – off-resonant difference spectra. (A) Resonance I difference spectrum. (B) Resonance II difference spectrum. (C) Resonance V difference spectrum. (D) Resonance VI difference spectrum. The inset shows the participator Auger signal associated with the $MnO_{4(aq)} 4t_2^{-1}$ ionizing transition. Participator Auger signals are labelled with numbers and spectator Auger / ICD signals are labelled with letters. The asterisk in panels E and F indicates a signal resulting from ionization with the unfiltered second harmonic of the beamline.

A comparison between the participator BEs and spectator KEs reported in Tables S4 and S5 reveals that the results associated with Fig. S9 and Fig. S10 are generally equivalent. Hence, at ~0.2 M concentration, intramolecular Auger relaxation mechanisms and non-local autoionization processes in MnO₄-(aq.) solutions are similar both in the presence of $Na^{+}_{(aq.)}$ or $K^{+}_{(aq.)}$ counter ions. For example, regarding peak 3-a, a BE of 12.66 ± 0.04 eV was determined from $NaMnO_{4(aq.)}$ solutions, while a consistent BE of $12.80 \pm 0.1 \text{ eV}$ was extracted from KMnO_{4(ac.)}. We note, however, that while the Gaussian component of the width (FWHM_G) is equivalent between $NaMnO_{4(aq.)}$ and $KMnO_{4(aq.)}$ samples, the Lorentzian component, 1.20 ± 0.04 eV at FWHM, is slightly larger in the latter case. (The total Voigt feature FWHM was determined to be $1.64 \pm 0.02 \text{ eV}$). We attribute this discrepancy to resonant excitation at slightly different photon energies, resulting in differing core-hole lifetime extractions, between the measurements. Notably, for peak 2-a, BEs of 9.85 ± 0.08 eV and $9.61 \pm 0.1 \text{ eV}$ were respectively extracted from the NaMnO_{4(ac.)} and KMnO_{4(ac.)} samples. We attribute the observed nominal BE difference to uncertainties associated with the photon energy calibration procedure and, particularly for peak 2-a, to a differential effect of the over-subtraction on the fitting procedure used to determine the BE (as explained in the main text). Finally, two additional BEs – $12.87 \pm 0.04 \text{ eV}$ and $10.57 \pm 0.08 \text{ eV}$ – could be extracted from the Resonance I KMnO_{4(aq.)} data with respect to similar data from NaMnO_{4(aq.)} (see panels A in Figs. S10 and S9, respectively). The 12.87 ± 0.04 eV BE feature corresponds to the resonantly-enhanced signal labelled peak 3-a (similar to that observed in the Resonance II spectrum in panel B, and for the NaMnO₄ data shown in Fig. 5 in the main text). The second extracted BE may be a signature of a L_{III}-6a1,2e process. A similar ~10.5 \pm 0.1 eV feature was observed in some of the NaMnO_{4(aq.)} Resonance I, III, and IV data sets but could not be reproducibly extracted. Hence, the latter assignment cannot be confirmed without further experimental investigation.

Table S4: 0.2 M NaMnO _{4(aq.)} fit results and assignments for the participator and spectator Auger and solute-solvent ICD signals from the spectra shown in Fig. S9. Where
single FWHM _G values were reported, results were extracted from Gaussian fits. Where Voigt fits were implemented, both the Gaussian (FWHM _G) and Lorentzian
(FWHM _L) widths are reported. The KE associated with the dominant feature is highlighted in bold font. The (w) subscripts associated with some of the peak assignments
highlight solute-water ICD core-hole relaxation mechanisms following excitation to Resonances V and VI.

Peak	Assignment	KE / eV	(Nominal) BE / eV	FWHM _G / eV	FWHM _L / eV
		Resona	ance I		
а	L _{III} -V,V / L _{III} -5a ₁ ,V	626.8 ± 0.3	16.6 ± 0.3	2.4 ± 0.4	-
		624.3 ± 0.2	19.1 ± 0.2	3.2 ± 0.3	-
5	L ₁₁₁ -2t ₂ 2e	583.9 ± 0.1	59.5 ± 0.1	2.2 ± 0.3	-
b	L _{III} -2t ₂ ,V	578.8 ± 0.4	64.8 ± 0.5	5.3 ± 0.8	-
		575.2 ± 0.3	68.3 ± 0.3	3.6 ± 0.4	-
C	L _{III} -2t ₂ ,5a ₁	566.3 ± 0.1	79.4 ± 0.1	2.3 ± 0.3	-
		Resona	nce II		
3-a	L_{III} -1e5 t_2/L_{III} -3 t_2 5 t_2	633.0 ± 0.1	12.66 ± 0.04	0.83 ± 0.04	0.77 ± 0.03
а	L _{III} -V,V / L _{III} -5a ₁ ,V	627.4 ± 0.3	18.3 ± 0.3	3.3 ± 0.3	-
		625.1 ± 0.3	20.6 ± 0.3	3.0 ± 0.3	-
5	L_{III} -2 t_2 5 t_2	585.6 ± 0.1	60.05 ± 0.04	3.02 ± 0.05	-
b	L _{III} -2t ₂ ,V	580.7 ± 0.1	65.15 ± 0.08	4.2 ± 0.1	-
		576.6 ± 0.1	69.23 ± 0.05	4.45 ± 0.06	-
С	L _{III} -2t ₂ ,5a ₁	565.1 ± 0.1	80.6 ± 0.1	3.0 ± 0.2	-
d	L _{III} -4a ₁ ,V	544.6 ± 0.1	101.1 ± 0.1	2.8 ± 0.2	-
		Resona	nce III		
а	L _{II} -V,V	636.7 ± 0.2	17.5 ± 0.2	3.1 ± 0.4	-
	L ₁₁ -L ₁₁₁ ,V	631.2 ± 0.4	23.0 ± 0.3	10.4 ± 0.9	-
	L _{II} -5a ₁ ,V	622.6 ± 0.2	31.6 ± 0.2	4.8 ± 0.6	-
b	L ₁₁ -2t ₂ ,V	585.0 ± 0.2	69.2 ± 0.2	10.0 ± 0.5	-
	L _{II} -L _{III} ,2t ₂ / L _{II} -2t ₂ , 5a ₁	576.5 ± 0.2	77.7 ± 0.2	6.2 ± 0.4	-
		Resonal	nce IV		
а	L _{II} -V,V	636.5 ± 0.2	19.5 ± 0.2	4.3 ± 0.2	-
	L ₁₁ -L ₁₁₁ ,V	630.7 ± 0.2	25.3 ± 0.2	6.4 ± 0.6	-
	L _{II} -5a ₁ ,V	622.6 ± 0.2	33.4 ± 0.2	5.1 ± 0.3	-
5		596.1 ± 0.2	59.9 ± 0.2	4.1 ± 0.4	-
b	L ₁₁ -2t ₂ ,V	585.4 ± 0.2	70.6 ± 0.2	8.6 ± 0.3	-
	L _{II} -L _{III} ,2t ₂ / L _{II} -2t ₂ , 5a ₁	576.5 ± 0.2	79.5 ± 0.2	7.5 ± 0.2	-
		Resona	nce V		
e	K-V,V	516.3 ± 0.1	12.18 ± 0.05	1.23 ± 0.09	-
		514.3 ± 0.2	14.2 ± 0.2	2.2 ± 0.4	-
		512.1 ± 0.1	16.39 ± 0.05	2.2 ± 0.2	-
		510.0 ± 0.1	18.51 ± 0.04	2.2 ± 0.1	-
		507.9 ± 0.1	20.6 ± 0.1	2.2 ± 0.1	-
f	K-5a ₁ ,1b _{1(w)} / K-5a ₁ ,V	498.4 ± 0.4	30.1 ± 0.4	3.8 ± 0.7	-
g	K-5a ₁ ,3a _{1(w)} / K-5a ₁ ,V	496 ± 1	33 ± 1	6 ± 3	-
h	K-5a ₁ ,1b _{2(w)} / K-5a ₁ ,V	489.9 ± 0.1	38.6 ± 0.1	3.9 ± 0.1	-
i	K-5a ₁ ,2a _{1(w)} / K-5a ₁ ,V	475.5 ± 0.1	53.04 ± 0.05	4.9 ± 0.1	-
		Resonal	nce VI		
2-a	K-4t ₂ ,5t ₂	520.1 ± 0.1	9.85 ± 0.08	0.7 ± 0.2	-
е	K-V,V	514.4 ± 0.1	15.6 ± 0.1	2.2 ± 0.1	-
		512.2 ± 0.1	17.8 ± 0.1	2.2 ± 0.3	-
		510.3 ± 0.1	19.73 ± 0.09	2.2 ± 0.2	-
		508.1 ± 0.2	21.9 ± 0.2	2.2 ± 0.2	-
f	K-5a ₁ ,1b _{1(w)} / K-5a ₁ ,V	498.1 ± 0.3	31.9 ± 0.3	4.3 ± 0.3	-
g	K-5a ₁ ,3a _{1(w)} / K-5a ₁ ,V	494.1 ± 0.3	35.9 ± 0.3	4 ± 1	-
h	K-5a ₁ ,1b _{2(w)} / K-5a ₁ ,V	490.2 ± 0.1	39.8 ± 0.1	3.8 ± 0.1	-
i	K-5a ₁ ,2a _{1(w)} / K-5a ₁ ,V	475.8 ± 0.1	54.19 ± 0.06	5.0 ± 0.1	-

Peak	Assignment	KE / eV	Nominal BE / eV	FWHM _G / eV	FWHM _L / eV
		Reson	ance I		
а	L _{III} -V,V / L _{III} -5a ₁ ,V	626.8 ± 0.1	16.7 ± 0.2	2.9 ± 0.3	-
		624.4 ± 0.1	19.1 ± 0.2	2.9 ± 0.2	-
5	L _{III} -2t ₂ 2e	584.0 ± 0.1	59.5 ± 0.1	2.5 ± 0.1	-
b	L _{III} -2t ₂ ,V	579.7 ± 0.1	63.8 ± 0.1	4.0 ± 0.2	-
		576.1 ± 0.1	67.4 ± 0.1	4.3 ± 0.1	-
с	L_{III} -2t ₂ ,5a ₁	564.4 ± 0.1	79.1 ± 0.1	3.5 ± 0.2	-
		Resona	ance II		
3-a	L _{III} -1e,5t ₂ / L _{III} -3t ₂ ,5t ₂	633.0 ± 0.1	12.8 ± 0.1	0.83 ± 0.05	1.20 ± 0.04
а	L _{III} -V,V / L _{III} -5a ₁ ,V	627.0 ± 0.1	18.8 ± 0.1	4.7 ± 0.2	-
		624.3 ± 0.1	21.5 ± 0.1	2.0 ± 0.3	-
5	$L_{111}-2t_25t_2$	585.8 ± 0.1	60.0 ± 0.1	2.52 ± 0.07	-
b	L _{III} -2t ₂ ,V	578.6 ± 0.1	67.2 ± 0.1	7.81 ± 0.05	-
		576.1 ± 0.1	69 . 8 ± 0.1	3.39 ± 0.06	-
С	L _{III} -2t ₂ ,5a ₁	564.8 ± 0.1	81.0 ± 0.2	3.5 ± 0.5	-
		Resona	ance V		
е	K-V,V	516.1 ± 0.2	12.1 ± 0.1	1.06 ± 0.05	-
		514.2 ± 0.2	14.0 ± 0.2	2.3 ± 0.2	-
		511.9 ± 0.2	16.3 ± 0.1	2.3 ± 0.2	-
		509.8 ± 0.1	18.4 ± 0.1	2.3 ± 0.1	-
		507.7 ± 0.1	20.6 ± 0.1	2.34 ± 0.07	-
f	K-5a ₁ ,1b _{1(w)} / K-5a ₁ ,V	498.5 ± 0.2	29.7 ± 0.2	3.7 ± 0.2	-
g	K-5a1,3a1(w) / K-5a1,V	494.9 ± 0.3	33.3 ± 0.3	5.2 ± 0.8	-
h	K-5a ₁ ,1b _{2(w)} / K-5a ₁ ,V	489.8 ± 0.2	38.4 ± 0.1	4.13 ± 0.06	-
i	K-5a1,2a1(w) / K-5a1,V	475.4 ± 0.2	52.8 ± 0.1	4.97 ± 0.06	-
		Resona	ince VI		
2-a	K-4t ₂ ,5t ₂	520.1 ± 0.2	9.6 ± 0.1	0.73 ± 0.03	-
e	K-V,V	516.0 ± 0.2	13.7 ± 0.1	1.20 ± 0.08	-
		514.1 ± 0.2	15.6 ± 0.2	2.4 ± 0.3	-
		512.0 ± 0.2	17.8 ± 0.1	2.4 ± 0.4	-
		509.9 ± 0.2	19.8 ± 0.2	2.4 ± 0.2	-
		507.7 ± 0.2	22.0 ± 0.2	2.4 ± 0.1	-
f	K-5a ₁ ,1b _{1(w)} / K-5a ₁ ,V	497.7 ± 0.2	31.8 ± 0.2	3.4 ± 0.4	-
g	K-5a ₁ ,3a _{1(w)} / K-5a ₁ ,V	494.7 ± 0.4	35.0 ± 0.4	5 ± 1	-
h	K-5a ₁ ,1b _{2(w)} / K-5a ₁ ,V	489.9 ± 0.2	39.8 ± 0.1	4 ± 1	-
i	K-5a, 2a, / K-5a, V	475.5 ± 0.2	54.2 ± 0.1	4.9 ± 0.3	-

Table S5: 0.15 M KMnO_{4(aq.)} fit results and assignments for the participator and spectator Auger and solute-solvent ICD signals from the spectra shown in Fig. S9. Where single FWHM_G values were reported, results were extracted from Gaussian fits. Where Voigt fits were implemented, both the Gaussian (FWHM_G) and Lorentzian (FWHM_L) widths are reported. The KE associated with the dominant feature is highlighted in bold font. The (w) subscripts associated with some of the peak assignments highlight solute-water ICD core-hole relaxation mechanisms following excitation to Resonances V and VI.

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