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Ultra-fast Charge Migration Competes with Proton Transfer in the Early Chemistry of $H_2O^{\bullet+}$

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SUPPLEMENTARY INFORMATION

Figure S1. *Franck-Condon density-of-states for the electron transfer from HSO_4^-* toward $H_2O^{\bullet+}$**.**

Figure S2: *Electron transfer rates calculated by the Jortner-Bixon formalism for the electron transfer from HSO_4^-* toward $H_2O^{\bullet+}$

Theoretical estimates of electron transfer rates

Non-adiabatic rate expression

For an electron-transfer reaction taking place in the electronic perturbative regime, the rate may be calculated with the Jortner-Bixon formulation of ET theory which is derived from the Fermi Golden Rule[1]

$$k_{JB} = \frac{2\pi}{\hbar}\frac{1}{\sqrt{4\pi\lambda_o k_B T}}\langle H_{DA}{}^2\rangle \sum_{b\,\in\,inner} \langle \chi_0^i \,|\, \chi_b^f\rangle^2 \exp\left(-\frac{(\Delta G° + \Delta E_{vib} + \lambda_o)^2}{4\lambda_o k_B T}\right) \quad (1)$$

k_B is the Boltzmann constant, T is the temperature and $\hbar$ is Planck's reduced constant. H_{DA} is the electronic coupling between the $\{H_2O^{\bullet+};HSO_4^-\}$ and $\{H_2O;HSO_4^{\bullet}\}$ electronic states. $\langle \chi_0^i \,|\, \chi_b^f\rangle^2$ is the Franck-Condon factor between the initial ground vibronic state and the final vibronic state. In the Jortner-Bixon theory the quantum description of the nuclear reorganization upon ET is preserved only for a subset of vibrational modes (the so-called inner-sphere).[2] These modes are those belonging to the redox partners *i.e.* $H_2O^{\bullet+}$ and HSO_4^-. The outer-sphere reorganization is estimated by the standard Marcus theory[3] *via* the introduction of the outer-sphere reorganization energy λ_o. $-\Delta G°$ is the ET driving force and ΔE_{vib} is the difference of vibrational energy associated with each pair of initial and final vibronic states. The key parameters $\Delta G°$, λ_o, H_{DA}, ΔE_{vib} and $\langle \chi_0^i \,|\, \chi_b^f\rangle^2$ have been calculated with Density Functional theory. The calculations were carried out for a concentration of sulfuric acid of 14 mol.L^{-1} which is close to the concentration for which the production of $HSO_4^{\bullet}$ is maximum (see Fig.2 of the main text).

- $\Delta G°$ was estimated as $\Delta G_{ox}(HSO_4^-) + \Delta G_{red}(H_2O^+) + 1/R$ where $\Delta G_{ox}(HSO_4^-)$ and $\Delta G_{red}(H_2O^+)$ are the free energy of oxidation and reduction of HSO_4^- and $H_2O^{\bullet+}$ respectively, and R is the center-to-center distance between the reactants. The first two terms were calculated at the DFT level with the Gaussian09 program[4]. The environment of redox partners was simulated with an implicit continuum model of static

dielectric constant (ε_s) of 102.3. ε_s was determined by a linear interpolation between pure water and neat sulfuric acid, the static dielectric constant of which amounts to 78.6 and 110.0 at room temperature[5]. In DFT calculation the BHandHLYP functional[6] and the 6-311G** basis set[7,8] were used. This functional was chosen because of recent benchmark calculations showing that this functional compared well with reference wave-function methods.[9] We found a redox potential of 2.7 V/NHE for the $HSO_4^{\bullet}$/ HSO_4^- couple. This is in excellent agreement with the experimental value of 2.5 V/NHE [10]. For the water radical cation we remark that no stable geometry in which $H_2O^{\bullet+}$ hydrogen bonded to another water molecule could be obtained. Such a finding was previously described in the literature.[9] The notion of redox potential for $H_2O^{\bullet+}$ in water is therefore not well defined. To circumvent this difficulty geometry optimizations were first performed for $H_2O^{\bullet+}$ and H_2O in the gas phase and single point calculations with the implicit continuum model were subsequently carried out. This procedure leads to a redox potential of 4.45 V/NHE for the $H_2O^{\bullet+}$/ H_2O couple. In Ref. [11] the redox potential of $H_2O^{\bullet+}$ was estimated to 4 V/NHE based on thermodynamic cycle, a value which is close to our theoretical estimate. The last term ($1/R$) entering the calculation of the driving force reflects the direct interaction between the reactants.

- The outer-sphere reorganization energy λ_o was calculated with the expression derived by Marcus: $\lambda_o = \left({}^{1}\!\left/ {}_{2a_{H_2O^+}} + {}^{1}\!\left/ {}_{2a_{HSO_4^-}} - 1/R \right.\right.\right)\left(1/D_{op} - 1/\varepsilon_s\right)$ where a_x is the radius of reactant x and D_{op} is the optical constant of the medium[3]. D_{op} was taken as the square of the experimental refractive index of an sulfuric acid solution concentrated at 75%[12].The radii were obtained from the "Volume" module of the program Gaussian09 that maps the space occupied by a molecule based on the spread of the electron density calculated at the DFT level. $a_{H_2O^+}$ and $a_{HSO_4^-}$ were evaluated at 2.53 and 3.53

Å respectively. We verified that the non-adiabatic rates are not sensitive to few percent variations of the reactant radii.

- The Franck-Condon factors were calculated under the harmonic approximation with the molFC program[13]. molFC reads the frequency analysis output files produced by Gaussian09. It determines the displacements and mixing of normal modes upon ET.

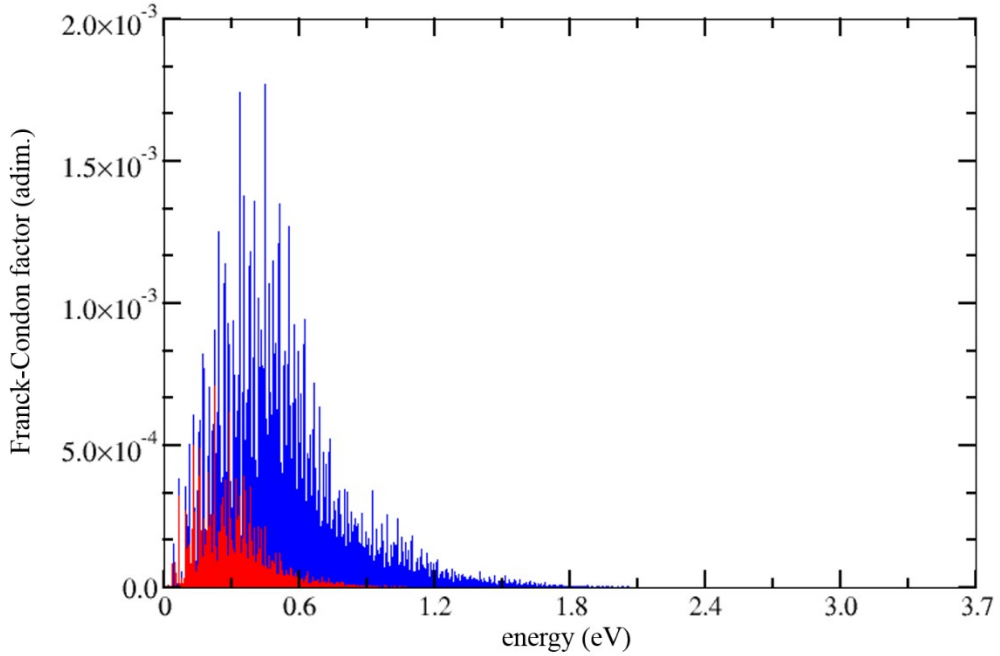

Figure S1 | *Franck-Condon density-of-states arising from the inner-sphere: blue for HSO_4^- and $H_2O^{\bullet+}$ and red for DSO_4^- to $D_2O^{\bullet+}$. The former allows a much wider range of energy to serve as reactive channel in the electron transfer process, hence faster rates in hydrogenated solutions*.

- The electronic coupling H_{DA} was calculated for a model of the $H_2O^{\bullet+}$---HSO_4^- ion pair at the constrained DFT level with the software deMon2k[14,15].A series of geometries obtained by elongating the $H_2O^{\bullet+}$---HSO_4^- hydrogen bond was constructed. As expected the electronic coupling decays exponentially with the hydrogen bond length (R_{hb}). The relationship relating the two quantities is:

$H_{DA} = H_{DA}^{eq} \exp\left[-1.1811\left(R_{hb} - R_{hb}^{eq}\right)\right]$ with $H_{DA}^{eq} = 0.3249eV$ with a linear regression coefficient of 0.991.

Figure S3 shows the evolution of the rate constant as a function of the hydrogen bond length (R_{hb}). The origin corresponds to a close contact between the reactants, namely when a hydrogen bond of length 1.81 Å, as calculated by DFT, is formed between H_2O and HSO_4^-. The center-to-center distance R between reactants is defined as $R = \left(R_{hb} - R_{hb}^{eq}\right) + a_{H_2O^+} + a_{HSO_4^-}$. The evolution is non-monotonic and exhibits a maximum after 3 Å. This is easily understandable since each of the three parameters $\Delta G°$, λ_o and H_{DA} are sensitive to the separating distance. At very short distance the free energy of the reaction is positive because of the $1/R$ term and a significant barrier to ET exists on the potential energy surface. As the distance between the partners increases $\Delta G°$ becomes more favorable and one reaches a point where $-\Delta G° \approx \lambda_o$. However, at these distances the electronic coupling H_{DA} is weak and doesn't show ET in the sub-picosecond time domain. The rates are found to be slightly smaller in deuterated systems. The DFT-based estimate of $\Delta G_{ox}\left(HSO_4^-\right) + \Delta G_{red}\left(H_2O^+\right)$ is -1.7eV. We repeated the calculations with the smaller value of -1.1eV that arise from the experimental[10] $\Delta G_{ox}\left(HSO_4^-\right)$ (2.5eV) and the estimate $\Delta G_{red}\left(H_2O^+\right)$ of - 4eV proposed in Ref. [11]. We also find again that non-adiabatic ET cannot compete with a proton transfer taking place on the tens of femtoseconds time scale.

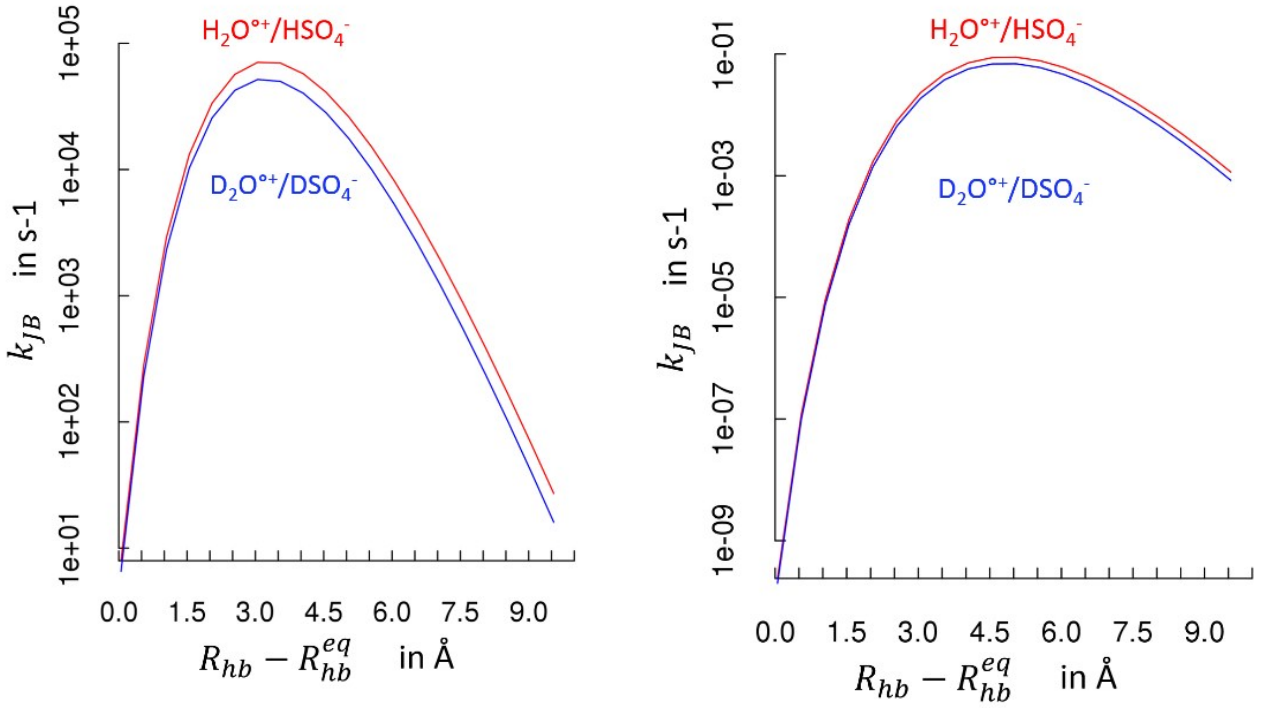

Figure S2 | *Electron transfer rates calculated by eq. 1. for the electron transfer from HSO_4- to H_2O^+ using either the DFT (Left) or experimental (Right) estimates of* $\Delta G_{ox}\left(HSO_4^-\right) + \Delta G_{red}\left(H_2O^+\right)$.

Excess of energy in the electron cloud

The excess of energy present within the electron cloud after sudden ionization has been estimated as follow. We first determined the stationary electronic density of the {H_2O;HSO_4^-} system. The resulting Kohn-Sham determinant was subsequently used as a guess for the calculation of the {$H_2O^{\bullet+}$;HSO_4^-} system, *i.e*. after ionization. Molecular orbital permutations was operated to depopulate the highest MO localized on water and created a hole on water. The excess energy was then identified as the difference between the energies obtained from the KS determinant corresponding to the stationary electronic state of {$H_2O^{\bullet+}$;HSO_4^-} and with the KS determinant corresponding to the stationary electronic state of {H_2O;HSO_4^-}. Various exchange correlation energy functionals have been tested. The 6-311G** basis set was used for all these calculations.[7,8] Excess energies of the order

of 7 eV were obtained with range-separated functionals (CAM-B3LYP[16]: 6.84 eV, M11[17]: 7.70 eV; ωB97XD[18]: 7.12 eV). With the purely local BLYP[19,20] functional we obtained a value of 7.43 eV, while with global hybrids values of 6.76 eV and 8.10 eV were obtained with BHandHLYP[6] and B3LYP[21] respectively.

Simulation of ultrafast charge migration

The electronic coupling between the { $H_2O^{\bullet+}$;HSO_4^- } and {H_2O;$HSO_4^{\bullet}$} diabatic electronic states was found to amount to 0.36 eV, which is a very large value for which the non-adiabatic regime considered above is not applicable. Actually, given the strength of the interaction between the diabatic states, they should mix heavily. To simulate electronic dynamics at fixed nuclear positions real-time propagations of the electronic density was conducted at the DFT level with the NWCHEM module[22,23]. Two geometries were considered for which the hydrogen bond length was set to 1.81 Å (the equilibrium position of the pair H_2O/HSO_4^- before ionization) or 2.40 Å. We used the 6-311G** basis set and the range separated CAM-B3LYP functional.[16] To assess the potential importance of diffuse functions, we compared the electronic spectra obtained by linear response TD-DFT with either the 6-311G** or the 6-311++G** basis sets. The difference of energy excitations with the two basis sets are well below 0.1eV, apart a few exceptions, for the fifteenth first excited states. The 6-311G** thus offers a good quality/computation cost ration to describe the system. The DFT equations-of-motion were propagated with the Magnus scheme combined with a self-consistent extrapolation scheme[23]. An integration time-step of 3.6 as chosen. We verified that the total number of electrons was strictly conserved during the propagation. The initial electronic state was defined as follows. We first carried out an SCF calculation for the H_2O/HSO_4^- system. *i.e*. before ionization. Then an electron was removed from a valence molecular orbital of the water molecule and the TDDFT propagation was launched from this out-of-equilibrium electronic state.

Table 1: Excited state energies, in eV calculated by Linear Response TD-DFT) with two basis sets. The electronic ground state is taken as energy reference.

Excited state number	E (eV) 6-311++G**	E (eV) 6-311G**	ΔE (eV)
1	0.6195	0.5452	0.0743
2	0.9081	0.641	0.2671
3	1.0555	1.0434	0.0121
4	1.8074	1.8005	0.0069
5	1.9077	1.8683	0.0394
6	1.9487	1.9614	0.0127
7	2.7281	2.6711	0.057
8	2.9888	2.7018	0.287
9	4.7835	4.7475	0.036
10	5.6253	5.6168	0.0085
11	5.7888	5.6588	0.13
12	6.009	6.0766	0.0676
13	6.5827	6.5227	0.06
14	6.6827	6.7099	0.0272
15	6.7524	6.8187	0.0663

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