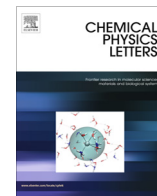




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Research paper

Solvation dynamics in water confined within layered manganese dioxide

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ABSTRACT

The confined environment presented by layered transition metal oxides is conducive to a variety of chemical reactions. Despite intense interest in these materials, little is known regarding the microscopic details relevant to their catalytic activity. We characterize aspects of the dynamics governing a redox reaction in the interlayer environment between manganese dioxide sheets. The nonequilibrium solvation dynamics surrounding charge transfer between an ion and the surface are highly non-linear and exhibit long-time relaxation that is governed by collective dynamics. These dynamics are rationalized in terms of structural rearrangements, allowing connections to be made to more complex reactions in these materials.

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1. Introduction

Layered manganese dioxides, known as birnessites, hold promise as water oxidation catalysts [1–4]. Between the two-dimensional MnO₂ layers of birnessite is a highly confined, single layer of water and cations [5–7], and this unique confined environment is conducive to redox chemistry. However, little information is known about the microscopic structure and dynamics surrounding reactivity in the highly confined interlayer region, illustrated in Fig. 1.

We recently reported an investigation of the structure in the interlayer solution [8]. In particular, we uncovered unique ion hydration structures resulting from a competition between water–water, water–surface, and water–ion interactions. The confined water acts as a two-dimensional fluid of dipoles, and cations typically share hydration shells due to a high concentration of ions in the interlayer (roughly 3:1 water:cation), qualitatively evidenced by the snapshot shown in Fig. 1. Water molecules shared between cations are frustrated, in the classic sense that they cannot adopt a unique orientation that minimizes their energy.

The appearance of frustrated hydration in two-dimensional confinement has a profound effect on the thermodynamics of charge transfer between ions and the surface [8]. Frustration enhances fluctuations of water molecules that are relevant to charge transfer, leading to non-Gaussian free energy landscapes. This non-Gaussian nature lowers the free energetic barrier for

charge transfer beyond expectations from Marcus theory, which predicts parabolic free energy landscapes [9]. An increase in charge transfer rates accompanies the lowering of this barrier.

In order to understand chemical reactions like electron transfer, especially in unique environments like that presented by confinement within layered manganese dioxides, one needs to move beyond the static, equilibrium picture provided by thermodynamic calculations. In particular, solvent dynamics can significantly impact the nature of chemical reactivity [10–15]. Moreover, such dynamics can also significantly impact our understanding of multi-step chemical processes involving electron transfer reactions.

In this work we examine the dynamics of solvation surrounding electron transfer reactions involving hydrated cations confined between layered manganese dioxide sheets. Solvation dynamics can be significantly influenced by confinement effects [16–20] and nearby interfaces [17,21–28]. The existence of an underlying non-Gaussian free energy landscape [8] leads to violations of linear response theory in the non-equilibrium relaxation following a charge transfer event. These non-linear features originate in frustrated ion hydration structures, and the complex relaxation process can be rationalized in terms of local structural relaxation of water molecules in the hydration shell of the charge transfer site. We also detail the existence of long relaxation times – on the order of ns – which are governed by collective dynamics that control translational diffusion within the interlayer. We then conclude with a discussion of how understanding the origins of such long relaxation times may impact the study of step-wise reaction mechanisms involving charge transfer in similar environments.

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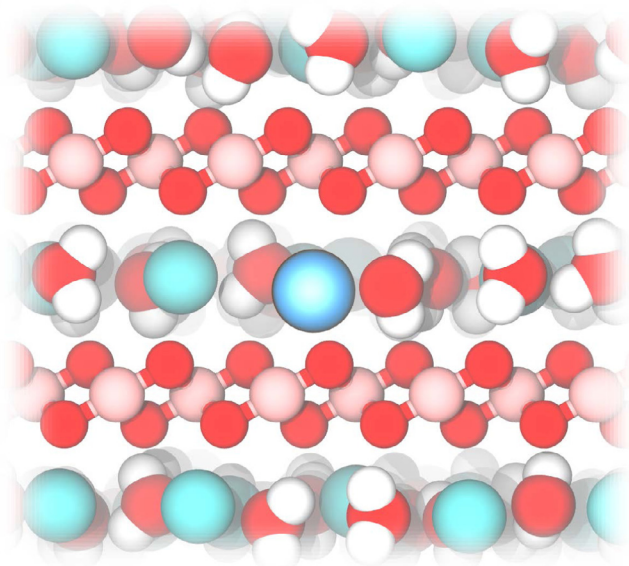


Fig. 1. Snapshot of the aqueous solution confined between the layered MnO₂ sheets of birnessite. Oxygen atoms are colored red, hydrogen atoms are white, manganese are colored pink, and potassium ions are green. The redox active ion undergoing a change in charge state (M) is indicated by the blue sphere near the center of the figure. Some molecules have been omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Non-equilibrium relaxation dynamics in response to charge transfer are non-linear

We characterize the nonequilibrium relaxation dynamics of the system through the response function [29,30]

$$S(t) = \frac{\overline{\Delta E}(t) - \overline{\Delta E}(\infty)}{\overline{\Delta E}(0) - \overline{\Delta E}(\infty)}, \quad (1)$$

where $\overline{F}(t)$ indicates a nonequilibrium average of an observable $F(t)$ over trajectories propagated with the solute in its excited (oxidized) state, but prepared with initial states sampled from the Boltzmann distribution corresponding to the ground (reduced) state. Here, the ground state of the model redox ion (blue in Fig. 1) corresponds to a charge of $q = +1$, such that the ion is equivalent to all others in the system. The excited state is obtained when $q = +2$, where the negative charge has transferred to the nearest Mn site, following previous work [8]. The nonequilibrium averages were computed over 70 initial configurations with 20 trajectories per configuration, each initialized with randomized velocity distributions. Here, $\Delta E(t) \equiv \Delta E(\overline{\mathbf{R}}(t))$ is the energy gap between the ground and excited states [9,13,29–32], defined as the difference between the respective Hamiltonians \mathcal{H}_0 and \mathcal{H}_1 in configuration $\overline{\mathbf{R}}(t)$ at time t ,

$$\Delta E(\overline{\mathbf{R}}(t)) = \mathcal{H}_1(\overline{\mathbf{R}}(t)) - \mathcal{H}_0(\overline{\mathbf{R}}(t)), \quad (2)$$

where \mathcal{H}_λ is in general the Hamiltonian of state λ .

If the system responds linearly, the nonequilibrium correlation function $S(t)$ is equal to the equilibrium time correlation function of the energy gap [29,30],

$$C_\lambda(t) = \frac{\langle \delta \Delta E(t) \delta \Delta E(0) \rangle_\lambda}{\langle (\delta \Delta E(0))^2 \rangle_\lambda}, \quad (3)$$

where $\langle F \rangle_\lambda$ indicates an equilibrium ensemble average of F over configurations sampled under the Hamiltonian \mathcal{H}_λ , and $\delta \Delta E(t) = \Delta E(t) - \langle \Delta E \rangle$. $C_\lambda(t)$ was computed by averaging over the results obtained from 16 trajectories with independent initial conditions

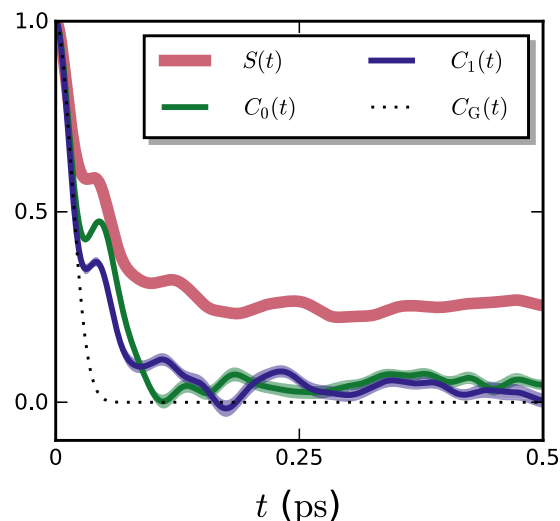


Fig. 2. The nonequilibrium response function does not equal its equilibrium counterparts even approximately, $S(t) \neq C_\lambda(t)$, respectively. Shaded regions indicate one standard error.

taken from an equilibrium simulation 100 ns in duration. Each trajectory in the $\lambda = 1$ state was equilibrated for at least an additional 10 ns before computing $C_1(t)$. This averaging over initial conditions is necessary because of the slow dynamics in this system.

The above response functions are shown in Fig. 2 and illustrate that $S(t) \neq C_\lambda(t)$, although $C_1(t)$ more closely mimics the general features of $S(t)$. This is not surprising since both $S(t)$ and $C_1(t)$ are evolving in time under the same Hamiltonian, \mathcal{H}_1 ; similar conclusions have been drawn in simpler systems [33]. The violation of linear response theory illustrated in Fig. 2 is largely a result of a non-Gaussian free energy landscape underlying the charge transfer process. We note that non-stationarity of even Gaussian free energy landscapes under time evolution also contribute to violations of linear response theory [34].

We find that multiple timescales are involved in the decay of $S(t)$, the features of which can be traced to their molecular origins. This is now detailed below.

3. Molecular origins of non-linear relaxation

3.1. Relaxation dynamics are Gaussian at very short times

Despite the differences in the three correlation functions shown in Fig. 2, the initial rapid decay of $S(t)$ is captured equally well by both $C_0(t)$ and $C_1(t)$, suggesting Gaussian time character at short times governed by the inertial motion of solvent molecules [33,35–39], despite the total nonequilibrium response being non-Gaussian. Indeed, the Gaussian approximation to the dynamics $C_G(t)$ accurately captures the short-time relaxation behavior, as evidenced in Fig. 2, where

$$C_G(t) = e^{-\omega_\lambda^2 t^2 / 2} \quad (4)$$

and

$$\omega_\lambda^2 = \frac{\langle (\delta \dot{\Delta E})^2 \rangle_\lambda}{\langle (\delta \Delta E)^2 \rangle_\lambda}, \quad (5)$$

such that the dot indicates a time derivative and the ensemble averages can be performed over either end point. We find $\omega_0 = 62 \pm 15 \text{ ps}^{-1}$ and $\omega_1 = 68 \pm 17 \text{ ps}^{-1}$, where the error bars represent the standard error between the trajectories averaged to

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