Marcus Theory of Ion-Pairing

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Supporting Information

ABSTRACT: We present a theory for ion pair dissociation and association, motivated by the concepts of Marcus theory of electron transfer. Despite the extensive research on ionpairing in many chemical and biological processes, much can be learned from the exploration of collective reaction coordinates. To this end, we explore two reaction coordinates, ion pair distance and coordination number. The study of the correlation between these reaction coordinates provides a new insight into the mechanism and kinetics of ion pair dissociation



and association in water. The potential of mean force on these 2D surfaces computed from molecular dynamics simulations of different monovalent ion pairs reveal a Marcus-like mechanism for ion-pairing: Water molecules rearrange forming an activated coordination state prior to ion pair dissociation or association, followed by relaxation of the coordination state due to further water rearrangement. Like Marcus theory, we find the existence of an inverted region where the transition rates are slower with increasing exergonicity. This study provides a new perspective for the future investigations of ion-pairing and transport.

INTRODUCTION

Ion-pairing can occur in molecular systems ranging from simple salts dissolved in bulk solvents to complex interfaces between different molecular species and is at the heart of many fundamental chemical and biological processes.^{1,2} For example, it plays crucial roles in the phase behavior of polyelectrolytes at bulk and interfaces,^{3–5} specific ion effects in biomolecules such as proteins and DNA,^{6,7} salt bridge formation in proteins,⁸ protein-DNA interactions,9 and protein translocation across cell membranes via ion-pair-driven pore formation.¹⁰ Furthermore, for designing and developing novel energy materials such as Nafion fuel cells membranes^{11,12} and batteries based on metal ions and ionic liquids,¹³ fundamental understanding of ionpairing in the presence of matierial interfaces is a critical step. Herein, we present a new theory in analogy with the Marcus theory of electron transfer^{14,15} to unravel a generalized principle of ion-pair dissociation and association mechanisms and their rates in bulk water.

Numerous experimental studies such as X-ray scattering and absorption,¹⁶ nuclear magnetic resonance (NMR),^{17,18} surface enhanced Raman,¹⁹ dielectric relaxation,²⁰ infrared (IR), and 2DIR spectroscopies²¹⁻²³ have examined ion pairs at bulk and interfaces in different environments. These studies have revealed the presence of contact ion pairs (CIPs) and solvent shared/ separated ion pair (SSIPs) and have elucidated solvent dynamics around them. For example, dielectric relaxation measurements²⁰ and anisotropy decay measurements using polarization-resolved mid-IR spectroscopy^{21,24,25} have shown that solvent molecules that are bound to ion pairs exhibit extremely slow rotational dynamics as compared to bulk solvent molecules. Due to the important competition between ion-water and ion-ion interaction strengths, the dynamics of solvation in the CIP state should be different than in the SSIP state that is again

different than isolated ions in solutions. Solvent dynamics will influence the mechanisms and rates for ion pair dissociation and association. An improved understanding of the kinetics and the equilibrium between CIPs and SSIPs will lead to a more complete picture of ion-pairing events.

Computer simulations complement experiments by allowing one to identify reactants, products, and the pathways connecting them with molecular level details. This has the potential to identify the critical processes associated with ion-pairing and solvent exchange dynamics.^{26–38} Reaction rates can be determined employing reaction rate theory (RRT) in computer simulations, revealing the dependency of these rates on the choice of reaction coordinates and their couplings to the surrounding environment.³⁹ The transition state theory (TST),^{40–43} which is an integral part of RRT, is frequently used to determine the transition rates (k) between reactants and products at temperature *T*:

$$k = \kappa k_{\rm TST} = \frac{\kappa}{\beta h} \exp(-\beta \Delta G^{\dagger}) \tag{1}$$

Here, $\beta = 1/k_{\rm B}T$ with $k_{\rm B}$ as the Boltzmann constant and h is the Planck constant; ΔG^{\dagger} is the free energy difference between the transition state and the reactants that is required to activate reactions. Also, κ is the transmission coefficient which is unity when TST is exact (implying $k = k_{TST}$), namely, the trajectories located initially at the equilibrium reactant state arrive at the dividing surface and proceed to the product state without recrossing; $\kappa < 1$ indicates barrier-recrossing due to the coupling of the reaction coordinate to solvent fluctuations.^{44–4}

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Figure 1. W(q) (a), $W(q_1,n)$ (b and d), and Marcus parabolas (c and e; solid lines fitted to dotted lines representing $W(q_1,n)$ and $W(q_2,n)$) demonstrating dissociation mechanisms for the Li⁺-F⁻ ion pair in bulk water. Contours are placed between 0 kcal/mol (blue) and 10 kcal/mol (red) with a spacing of 0.5 kcal/mol between two neighboring contours (left panel). Solvation structures of the Li⁺-F⁻ ion pair indicating the reactant (CIP), activated (CIP* and SSIP*), and product (SSIP) states in the dissociation process (right panel).

For studying ion-pairing, the ion-pair distance (q) has been historically the choice of reaction coordinate. The TST formulation for q utilizes the potential of mean force (PMF) W(q) exerted by solvent molecules along q:^{49,50}

$$k_{\rm TST}^{q} = \frac{1}{\sqrt{2\pi\mu\beta}} \frac{q^{\dagger 2} \exp(-W(q^{\dagger}))}{\int_{0}^{q^{\dagger}} q^{2} \exp(-W(q)) dq}$$
(2)

where μ is the reduced mass of the ion-pair and q^{\dagger} is the location of the top of the barrier between reactant and product states. Studies^{28,38,49,51–53} showed that the consideration of this barrier top as the transition state could result in extremely small transmission coefficient ($\kappa \ll 1$), implying significant barrierrecrossing. This is a direct consequence of strong coupling between solvent fluctuations and the reaction coordinate *q*. This suggests that *q* alone is not a good reaction coordinate to describe ion-pairing; explicit inclusion of solvent effects on *q* is necessary.

Herein, we study ion-pairing by utilizing a two-dimensional reaction coordinate, $\mathbf{Q} \equiv (q,n)$, where *n* is the coordination number,^{34,54} i.e., the number of water molecules bound to an ion in the first solvation shell; n is introduced to account for solvent fluctuations coupled to q. By computing W(q,n) using molecular dynamics (MD) simulations in conjunction with classical force fields, we show how solvent rearrangement activates ion pair dissociation and association. We explore and highlight the connection with Marcus theory of electron transfer, ^{14,15} wherein environment rearrangement is necessary to create a favorable geometry before electron transfer can take place between molecules. Thus, we are able to determine the rates and mechanisms of ion-pairing with a Marcus-like theory of charge transfer⁵⁵ that accounts for explicit *q*-solvent couplings. We examine this theory for the systems of ion pairs including Li⁺-F⁻ (small-small), Li⁺-I⁻ (small-large), Rb⁺-F⁻ (large-small), and Rb⁺-I⁻ (large-large) in the infinitely dilute water solutions, which are expected to pose distinct W(q,n) surfaces as a result of their different solvation structures.

TWO-DIMENSIONAL PMFS

In order to construct the Hamiltonian in terms of the coordinate $\mathbf{Q} \equiv (q,n)$ for our ion pair systems, we perform coordinate transformation as follows. The set of Cartesian coordinates **X** of 3*N* components (*N* is the number molecules including ions) is transformed to generalized coordinates (**Q**, **S**). The **S** coordinate has 3N - 2 components. The new conjugate momenta, which are transformed from the set of Cartesian momenta **P** of 3*N* components, are $p_{qp} p_{np}$ and **P**_S, where **P**_S has 3N - 2 components. Following the work by Darve and Pohorille, ⁵⁶ for a given $\mathbf{Q} \equiv (q,n)$ and the basis **S**, we can express the Hamiltonian with no cross-terms involving p_a and p_n with **P**_S as

$$H = \frac{1}{2} Z_{q} p_{q}^{2} + \frac{1}{2} Z_{n} p_{n}^{2} + Z_{qn} p_{q} p_{n} + \frac{1}{2} \mathbf{P}_{S}^{T} \mathbf{Z}_{S} \mathbf{P}_{S} + V(q, n, \mathbf{S})$$
(3)

Here, the first four terms represent kinetic energy terms, and the last one is potential energy. Also, Z_q is $\mu_{\text{ion-ion}}^{-1}$, where $\mu_{\text{ion-ion}}$ is the reduced mass of an ion pair; Z_n is related to the ion-water reduced mass $\mu_{\text{ion-water}}$:

$$Z_n = \frac{\Lambda}{\mu_{\rm ion-water}} \tag{4}$$

Reference 34 shows that Λ depends on the number of water molecules near the boundary between the first and second solvation shells of an ion and governs fluctuations in coordination number. The derivation for Z_{qn} (demonstrated in the Supporting Information (SI)), links Z_{qn} to the mass of the ion (m_{ion}) for which the coordination number *n* is considered:

$$Z_{qn} = \frac{1}{m_{\rm ion}} \left[\sum_{i=1}^{N_{\rm wat}} f'_i \hat{r}_i \cdot \hat{q} \right] \tag{5}$$

Here, \hat{r}_i and \hat{q} are the unit vectors pointing from an ion, say a cation, to the *i*th of N_{wat} water molecules and to an anion, respectively. Also, f'_i is derivative of the functional form of *n* given in eq 6 with respect to the ion-water distance r_i .³⁴ It is obvious from eq 5 that $Z_{qn} \rightarrow 0$ for the isotropic solvation structure around the ion.

Journal of Chemical Theory and Computation

$$n = \sum_{i} \frac{1 - (r_i/r^{\dagger})^a}{1 - (r_i/r^{\dagger})^{2a}} = \sum_{i} f(r_i)$$
(6)

With $a \ (= 12)$ as an integer in eq 6, we define coordination number of an ion in terms of the smooth function f. Here, r^{\dagger} can be determined from the ion–water radial distribution function (RDF); the first and the second peaks in the RDF correspond to the first and second solvation shells, respectively, and the location of the minimum between these peaks is r^{\dagger} representing the boundary between these shells. We showed in our previous work³⁴ that the size of the solvation shells of ions depends on the size and charge of ions; e.g., for a given ionic charge the size of the first solvation shell increases with increasing ionic size, which is understood from the increasing value of r^{\dagger} and coordination number. The derivative f' in eq 5 is vanishingly small for all water molecules except those near r^{\dagger} contributing the most to Z_{an} .

To calculate the PMF W(q,n), we are required to determine the probability distribution function $\rho(q,n)$ associated with the generalized coordinates q' and n' having values q and n, respectively, by the phase space integration of the Hamiltonian:⁵⁶

$$\rho(q, n) = \frac{1}{C} \int d\mathbf{x} d\mathbf{p} \delta(q' - q) \delta(n' - n) \exp(-\beta H)$$
(7)

Here, *C* is the normalization constant. Now, the PMF can be expressed utilizing $\rho(q,n)$ as follows:

$$W(q, n) = -k_{\rm B}T \ln \rho(q, n) + k_{\rm B}T \ln(q^2 dq) + dW$$
(8)

where dW is a constant introduced to make sure the global minimum of W(q,n) is adjusted to zero. The term involving dq (a small increment in q) is the radial correction.

RESULTS AND DISCUSSION

Discovery of Marcus Behavior. We employed umbrella sampling⁵⁷ and the WHAM method⁵⁸ for obtaining the PMFs from the OPLS-TIP4P force field-based^{59–62} MD simulations (see SI for the detailed description). The PMFs for Li^+ -F⁻ are presented in Figure 1, while the PMFs for other ion pairs can be found in the SI (Figures S1 and S2). We separately computed W(q,n) for $n = n_{1,i}$ (coordination number of Li⁺ ion) and for n = $n_{\rm F}$ (coordination number of F⁻ ion). Here, W(q), which can be determined from the equation $\exp(-\beta W(q)) = \int dn_{\text{Li}} \exp(-\beta W(q)) dn_{\text{Li}}$ $\left[-\beta W(q,n_{\rm Li})\right] = \int dn_{\rm F} \exp\left[-\beta W(q,n_{\rm F})\right]$, is also presented in Figure 1a. From W(q), it is clear that the Li⁺-F⁻ pair prefers to stay in the CIP state $(q = q_1)$ than in the SSIP state $(q = q_2)$, and the CIP \rightarrow SSIP transition along *q* will require crossing the barrier of 7 kcal/mol. On the other hand, W(q,n) provides an alternative pathway of the CIP \rightarrow SSIP transition, where coordination number rearrangement activates the ion pair separation similar to what Marcus proposed for the solvent rearrangement induced electron transfer between molecules. To elucidate, we have presented in Figure 1c and e the slices through W(q,n) for $q = q_1$ and $q = q_2$ (dotted lines), respectively. We assume that these slices can be fitted with parabolas (solid lines):

$$W_i(n) = W_i^0 + \frac{1}{2}K_i(n - n_i)^2, \ i = 1, 2$$
(9)

The quadratic form of eq 9 represents "Marcus Parabolas" with same force constants ($K_1 = K_2$, as assumed by Marcus). If the minima of these parabolas are W_1^0 at $n = n_1$ and W_2^0 at $n = n_2$, respectively, the difference in PMFs from CIP to SSIP is

$$\Delta W = W_2(n_2) - W_1(n_1)$$

= $W_2^0 - W_1^0$ (10)

Article

The reorganization energy, which is the amount of energy required to change equilibrium coordination number in the CIP state to equilibrium coordination number in the SSIP state, is

$$\lambda = W_1(n_2) - W_1(n_1)$$
(11)

Now, the free energy of activation can be determined using λ and ΔW :

$$\Delta W^{\dagger} = \frac{(\lambda + \Delta W)^2}{4\lambda} \tag{12}$$

which leads to the Marcus' expression of rate equation:⁵⁵

$$k = \kappa k_{\text{Marcus}}$$

$$= \frac{\kappa}{\beta h} \exp(-\beta \Delta W^{\dagger})$$

$$= \frac{\kappa}{\beta h} \exp\left[-\beta \frac{(\lambda + \Delta W)^2}{4\lambda}\right]$$
(13)

Marcus parabolas are diabatic states, i.e., they cross at a point that can be treated as the activated complex. Figure 1 shows that Marcus parabolas have a crossing point (n^*) for $W(q,n_{\text{Li}})$ (Figure 1c) but not for $W(q,n_{\text{F}})$ (Figure 1e). Hence, the Marcus theory can only be applied utilizing the former.

Like TST, this Marcus-like theory is exact when the transmission coefficient κ is unity. Utilizing this exact theory, we can then describe a possible ion pair separation mechanism that requires adiabatic traversal of n^* , in which the ion pair system switches from the CIP diabat to the SSIP diabat. The proposed mechanism for the Li⁺-F⁻ pair separation is schematically presented in Figure 1f. Starting in the CIP state, solvent fluctuations change the number of water molecules in the first solvation shell of Li^+ from n_1 to n^* , forming the activated CIP*. While this coordination state of Li⁺ persists, F⁻ separates from Li⁺ and transfers to the SSIP* state where both ions have distinguishable solvation shells. Finally, additional solvent fluctuations drive the rearrangement of the Li⁺-water coordination, relaxing the ion pair system to the SSIP equilibrium. We can treat this pathway as reversible and demonstrate that ion pair association (SSIP \rightarrow CIP transition) occurs by reversing the dissociation pathway. Note that λ and ΔW will be different, given that the reactant and product will be interchanged. This proposed ion-pairing mechanism can be validated by the quantitative determination of the transmission coefficient, which we elucidate later in the paper.

Upon examining the PMFs for other ion pairs, Li⁺-I⁻, Rb⁺-F⁻, and Rb⁺-I⁻ (Figures S1 and S2, SI), we find that their dissociation and association mechanisms also follow a Marcus-like theory. We have showcased the ion-specific difference by examining the crossing region of the Marcus parabolas. Although the Marcus picture holds only for Li⁺ in Li⁺-I⁻, in the case of Rb⁺-F⁻ and Rb⁺-I⁻ pairs, both the cation and anion exhibit Marcus behavior. For these situations, one can make the case that the physical process is triggered by faster dissociation and association. Our research suggests that the activation of the coordination state of F⁻ for the Rb⁺-F⁻ pair and the activation of the coordination state of Rb⁺ for the Rb⁺-I⁻ pair produce the faster rates.

Along the Marcus pathway, the ion pair separation becomes spontaneous when the activated coordination state is achieved. However, one can argue that such separation may still require overcoming a barrier along the q coordinate. In that case, the exact TST rate of ion pair separation is proportional to the product of the factor for the activation along n and the factor for overcoming the barrier along q, which is given by

$$k_{\text{TST}}^{q,n} = \frac{1}{\beta h} \exp[-\beta \Delta W_{q_1}^{n^*}] \exp[-\beta \Delta W_{n^*}^{q^{\dagger}}]$$
(14)

Here, $\Delta W_{q_1}^{n*}$ and $\Delta W_{n^*}^{q^{\mathsf{T}}}$ are the free energies of activation associated with *n* and *q* coordinates, respectively. In Figure 2, we



Figure 2. Dissociation (red) and association (blue) rate constants as a function of free energy difference between reactants and products, constituting the Marcus inverted region.

have presented both the dissociation and association rates calculated using the exact TST (eq 14) and Marcus methods (k_{Marcus} in eq 13) for a variety of ion pairs as a function of their reactant—product free energy differences (ΔW). For $\Delta W > 0$, the anion transfer rate increases with the decrease in ΔW . For $\Delta W <$

0, the rate increases then decreases with the increase in ΔW . This is analogous to the inverted region that Marcus discovered for electron transfer. We also find that the association rates are faster than dissociation rates for all ion pairs except for Rb⁺-F⁻, where the SSIP state is more stable. Although the Marcus rates and the TST rates have a very similar trend, the former is significantly faster than the latter in the case of Li⁺-F⁻ because of the large $\Delta W^{2^{\dagger}}$ that the Marcus method does not account for

 $\Delta W^{q^{\prime}}_{n^{*}}$ that the Marcus method does not account for.

Eigen State Picture and Transmission Coefficient. To determine the transmission coefficient, κ , we must consider the adiabatic or nonadiabatic nature of ion pair dissociation. If the diabatic states represented by Marcus parabolas are strongly coupled, the ion pair dissociation can be treated as an adiabatic process. Following Hush's work on the adiabatic theory of electron transfer in infinitely dilute solutions, $^{63}\kappa$ may be assigned to unity. However, the four different ion pairs studied here are expected to exhibit different coupling strengths between the diabatic states, which may result in different transmission coefficients. To discern between these couplings (see SI for details), we approximately determine the coupling strength as $C(n) = \sqrt{[W_1(n) - W_1(n_1)][W_2(n) - W_2(n_2)]}$. The inclusion of the coupling C(n) between the two states $W_1(n)$ and $W_2(n)$ straightforwardly leads to the eigen state picture of ion pairing; the dynamics in coordination number space that governs ionpairing is restricted on the lower eigen free energy surface in the adiabatic case, while the higher eigen free energy surface is accessed from the lower one in the nonadiabatic case.

In Figure 3a, we elucidate the eigen state picture of ion-pairing. The crossing region for $\text{Li}^+\text{-}\text{F}^-$ is located in the "abnormal region" (it is at the same side of the two parabolas and $|\Delta W| \gg \lambda$), and due to the large coupling strength the lower eigen free



Figure 3. (a) Eigen free energy surfaces (red and blue) originated due to coupling between Marcus parabolas (black); dynamics is restricted on the lower surfaces (red) within adiabatic approximation. For all ion pairs but Li⁺-F⁻, n'_1 and n'_2 are the higher energy species that are not accessed in this approximation. It forbids Li⁺-F⁻ separation because of the surface exchange between n'_2 and n_2 , i.e., n'_2 is on the lower surface and n_2 is on the higher surface. For Rb⁺-I⁻, the zoomed in crossing region is indicated with an arrow. (b) Ion-pairing pathways: The pathway involving the "normal region" describes dissociation of Li⁺-F⁻, and Rb⁺-I⁻, and the pathway involving the "abnormal region" describes dissociation of Li⁺-F⁻. Reversing these pathways can also describe association of ion pairs. Within adiabatic approximation, the dashed arrows are nonreactive, supporting the persistence of the Li⁺-F⁻ paired state. (c) Curvature of the lower eigen free energy surfaces in the neighborhood of the crossing regions.

energy surface, it tends to avoid the higher one and remains well separated. The only pathway that allows Li⁺-F⁻ dissociation must involve nonadiabatic hopping between these surfaces across the "abnormal region"; that is unlikely to occur due to their couplinginduced large free energy gap. Our finding is supported by the fact that Li⁺-F⁻ always prefers to stay in the paired state and is insoluble in water.⁶⁴ In the case of Li⁺-I⁻ and Rb⁺-F⁻, and Rb⁺-I⁻, the crossing region is located in the "normal region" (crossing region at the opposite sides of the two parabolas). Since the eigen free energy surfaces are well separated for Li⁺-I⁻ and Rb⁺-F⁻ due to strong couplings, the idea of adiabatic traversal of the crossing region for the CIP-SSIP transition is valid. The coupling is small for Rb⁺-I⁻ and both the nonadiabatic and adiabatic pathways may describe the dissociation mechanism. However, we propose in our classical description of ion-pairing that the adiabatic pathway is reactive.

Landau^{65,66} and Zener⁶⁷ introduced a semiclassical approach to determine the transmission coefficient (κ_{LZ}) for electron transfer. We map their idea to our classical description of a negative charge (anion) transferring from the CIP state to the SSIP state and show that $\kappa_{LZ} \rightarrow 1$ in the strong coupling limit and $\kappa_{LZ} \ll 1$ in the weak coupling limit. In this theory, we need to determine the probability (*P*) of the ion pair systems actually undergoing the reactive transitions through the crossing region. Different passages involving different states or species (n_1^*, n_2^*, n_1' , and n_2') near the crossing region on the eigen free energy surfaces are depicted in Figure 3b. Now, following Landau–Zener theory, $^{65-68}$ we can obtain *P* that will depend on the coupling strength and the traversal velocity in coordination number (v_n) space:

$$P = 1 - \exp\left[-\frac{2\pi C^2}{\hbar v_n |S_2 - S_1|}\right]$$
(15)

Here, $S_{1,2}$ are the slopes of the Marcus parabolas at n^* $(\frac{dW(n)}{dn}|_{n=n^*})$. Also, v_n at n^* can be obtained from phase space trajectories (v_n vs n, see Figure S3 in SI for example trajectories). According to Newton and Sutin,⁶⁸ the relation between the transmission coefficient and P depends on whether Marcus parabolas cross at the "normal region" or "abnormal region" as follows:

$$\kappa_{\rm LZ} = \begin{cases} 2P/(P+1) \text{ for "normal region"} \\ 2P(1-P) \text{ for "abnormal region"} \end{cases}$$
(16)

The values of *C* at the crossing point and κ_{LZ} are listed in Table 1. As gleaned from the case of the "abnormal region" in Figure 3b and eq 15, $P \sim 1$ for going from n_1 to n'_2 through n_1^* for Li⁺-F⁻ due to the large value of *C*. Therefore, the improbable event (1 - P) of hopping to higher energy states $(n'_1, n^*_2, \text{ or } n_2)$ causes $\kappa_{LZ} \sim 0$ (eq 16), and thus, the paired state of Li⁺-F⁻ persists. In the case of Li⁺-I⁻ and Rb⁺-F⁻, the couplings are large enough to cause the adiabatic transitions between n_1 and n_2 through the "normal region" with a probability close to 1, resulting in $\kappa_{LZ} \ll 1$.

The semiclassical transmission coefficient is justifiable from the perspective of classical adiabatic dynamics on a lower eigen free energy surface in terms of the kinetic energy, $\text{KE}_n = \frac{1}{2Z_n} v_n^2$, and the approximate mass-weighted-curvature of the surface, $\Omega \sim \sqrt{Z_n} \frac{\partial}{\partial n} \left[\sqrt{Z_n} \frac{\partial W(n)}{\partial n} \right]$. Here, the values of Z_n should be extracted from the plateau of Z_n vs q profile in Figure S4 of the SI.

Table 1. Coupling Strength (C) at Crossing Point (<i>n</i> *) of
Marcus Parabolas and Corresponding Landau–Zener
Transmission Coefficient along with Barrier ΔW_a^{n*a}

Ion pair	$\Delta W^{n*}_{q_1} \ (ext{kcal/mol})$	$\Delta W^{n_1^*}_{q_1} \ (ext{kcal/mol})$	$\Delta W^{q^{\dagger}}_{n^{st}} \ (ext{kcal/mol})$	C (kcal/mol)	$\kappa_{\rm LZ}$
Li ⁺ -F ⁻	6.20	2.50	5.00	3.50	0.000
Li^+-I^-	2.90	1.55	2.00	1.90	0.990
Rb^+-F^-	0.25	0.04	0.07	0.50	0.990
Rb^+-I^-	1.39	1.39	0.58	0.01	0.002
^{<i>a</i>} The cou	pling between	n these parab	olas generates	s a lower ei	igen free

energy surface with a reduced barrier $(\Delta W_{q_1}^{n_1^{\pi}})$ on which the adiabatic dynamics take place. A spontaneous dissociation of ion pairs after activation of the coordination number may require overcoming an additional barrier $(\Delta W_{n^*}^{q^{\dagger}})$ along the *q*.

The classic works of Marcus,⁶⁹ Miller,⁷⁰ Levine,⁷¹ and Truhlar⁷² addressed the utility of KE_n and Ω . Especially, the reaction pathway curvature at the transition state (crossing region) is crucial because it dictates whether the transmission coefficient is unity (zero curvature) or much less than unity (large curvature).

For Li⁺-F⁻, KE_n is 3.5 kcal/mol and Ω is extremely small at the crossing region as shown in Figure 3c. This allows to cross the barrier on the lower free energy surface (Table 1) but forbids access to the higher surface (>4.5 kcal/mol). Therefore, $\kappa_{LZ} \sim 0$ for the CIP-SSIP transition. For Li⁺-I⁻ and Rb⁺-F⁻, $\kappa_{LZ} \sim 1$ because of much greater KE_n (25.9 and 0.2 kcal/mol, respectively) than the barriers and vanishingly small Ω . Finally, although KE_n (5.5 kcal/mol) is greater than the barrier for Rb⁺-I⁻, the extremely small κ_{LZ} arises due to the large curvature-induced barrier recrossing. The link between the semiclassical Landau–Zener method and this classical approach is feasible through the relation between the coupling strength *C* and the curvature Ω ; a large (small) value of *C* causes extremely small (large) Ω , directly governing the transmission coefficient.

The eigen state picture and the transmission coefficients have now clarified that the solvent rearrangement-based Marcus-like mechanism of ion pairing, which were originally proposed for Li⁺-F⁻ (Figure 1f), is transferable to ion pairs that are separable in water. The CIP-SSIP transition rates can be obtained by correcting the Marcus rates with the Landau–Zener transmission coefficient. Additionally, a correction may be required if the solvent rearrangement-induced activation in coordination number does not trigger a spontaneous separation or association of ion pairs due to an existing barrier along q ($\Delta W_{n^*}^{q^{\dagger}}$ in eq 14, Table 1, and Figure 2). Thus, based on eqs 13 and 14, the

$$k_{\text{actual}} = \kappa_{\text{LZ}} k_{\text{Marcus}} \exp[-\beta \Delta W_{n^*}^{q^{\dagger}}]$$

= $\frac{\kappa_{\text{LZ}}}{\beta h} \exp\left[-\beta \frac{(\lambda + \Delta W)^2}{4\lambda}\right] \exp[-\beta \Delta W_{n^*}^{q^{\dagger}}]$ (17)

prescription for an actual ion-pairing rate calculation is given by

Structure and Switching Dynamics of the Solvent. Solvent rearrangement not only triggers ion-pairing but also encodes the ion-specific nature of the pairing process. This is due to the unique solvation structures and dynamics around different ions that result in different PMFs. When two ions are far from each other and their solvation shells are well separated, one may expect the solvation shells to be isotropic. In the SSIP environment or beyond, the solvent exchange dynamics involves a smooth change in coordination state driven by thermal fluctuations. This picture breaks down when two ions are in the close proximity of each other. Here, the overlapping solvation shells and the underlying dynamics of the change in coordination state lead to anisotropic water distribution around the paired state.

One of the advantages in casting the multidimensional rate problem into the form of eq 3 is that it allows us to analyze the effect of solvation structure on ion pairs formation that is encoded in Z_{qn} (eq 5). Here, Z_{qn} is a measure of the degree of isotropic solvation of ions in ion pair systems. Figure 4 displays



Figure 4. Collective mass element Z_{qn} as a function of ion-pair distance. Red corresponds the reaction coordinate involving q and coordination number of cation, while blue corresponds the same involving q and coordination number of anion.

that Z_{qn} approaches zero in the solvent separated state for all ion pairs, indicating isotropic solvation. If both the cation and anion are small (e.g., Li⁺-F⁻), the CIP state results in large anisotropic values of Z_{qn} due to a frustrated overlapping solvation shells. For the combinations of small/large cations/anions or vice versa, (e.g., Li⁺-I⁻ and Rb⁺-F⁻), the CIP state is significantly less perturbed yielding smaller values of Z_{qn} . Finally, Z_{qn} is vanishingly small when both the cation and anion are large (e.g., Rb⁺-I⁻) and is nearly independent of q. Note that Z_n (eq 4) is also affected in a similar fashion due to ion-pairing (Figure S4, SI), but it has a nonvanishing limit for isotropic solvation.

Thermal fluctuations of the positions of water molecules projected along the ion pair distance introduces fluctuations in Z_{qn} . Since the water molecules near the boundary between the first and second solvation shells contributes the most to Z_{qn} , their switching dynamics across the boundary control the timedependent behavior of Z_{qn} . To illustrate this further, we have presented the time correlation function $C_{Z_{qn}}(t)$ in Figure 5 (left panel) for the Li⁺-F⁻ pair defined as

$$C_{Z_{qn}}(t) = \langle \delta Z_{qn}(t) \delta Z_{qn}(0) \rangle / \langle \delta Z_{qn}(0) \delta Z_{qn}(0) \rangle$$
(18)

We calculate $C_{Z_{qn}}(t)$ in the CIP or the SSIP state where $\delta Z_{qn}(t) = Z_{qn}(t) - \langle Z_{qn} \rangle$. A biexponential behavior of $C_{Z_{qn}}(t)$ is observed for both Li⁺ and F⁻ in the left panel of Figure 5. There is a rapid drop on femtosecond time scale followed by a slower decay on picosecond time scale. A simple fit with a biexponential function shows that the fast time scale dominates the correlation function (~70%). Mechanistic insight can be achieved by identifing the location of water molecules that contribute to the observed dynamics in $C_{Z_{qn}}(t)$. To this end, we construct the distribution, $P(\theta)$, where θ is the angle between the center of mass location of water molecules with the largest f' and the vector pointing



Figure 5. Time correlation function for the collective mass element Z_{qn} in the CIP and SSIP states of the Li⁺-F⁻ ion pair (left panel). Distribution of water molecules that govern the switching dynamics (middle panel). Free energy associated with the orientation distribution of such water molecules with respect to \vec{q} (indicated by green for Li⁺) and $-\vec{q}$ (indicated by magenta for F⁻) (right panel).

between the cation and anion, namely, \vec{q} and $-\vec{q}$, respectively. In Figure 5 (middle panel), $P(\theta)$ is shown. Here, the region of the solvent where water molecules are shared between Li⁺ and F⁻ is more densely populated than the region where water molecules are not shared. From $P(\theta)$, we can construct the relative free energy profiles $W(\theta) = -k_{\rm B}T \ln (P(\theta)/\sin \theta)$ that identifies the precise location of the water molecules that exhibit the fast and slow dynamics (right panel, Figure 5). Here, $W(\theta)$ confirms that the water molecules shared by Li⁺ and F⁻ are in the most likely state and thus dominate the switching dynamics. The salient picture is that water molecules at this minimum $W(\theta)$ are bound to Li⁺ and can rapidly switch to the state where they are bound to F^- and vice versa. In the unshared region ($\theta > 45^\circ$), water molecules switch across the boundary between the first and second solvation shells at a slower rate. In the SSIP state, significantly more water molecules populate the neighborhood of the boundary than in the CIP state (middle panel, Figure 5), increasing the availability of partner water molecules that participate in the switching dynamics. Thereby, $C_{Z_{uv}}(t)$ decays faster in the SSIP state than in the CIP state. These findings about $C_{Z_{an}}(t)$ for Li⁺ and F⁻ are consistent with those for the larger ions Rb⁺ and I⁻ (Figure S5, SI).

CONCLUSIONS

In conclusion, we have shown that we can map the process of ionpairing to a Marcus-like picture where the solvent rearrangement around ion pairs leads to an activated coordination state. Once in this activated state, ion pair separation or association is triggered followed by further rearrangement of the solvent to the final state. Our research found important dynamical corrections to the spontaneous dissociation of the activated state that were found to be ion specific. Specifically, the transmission coefficient was shown to depend directly on the coupling between the Marcus parabolas representing the CIP and SSIP states and is related to the reaction path curvature. Strong couplings lead to a vanishingly small curvature of the reaction path and provide $\kappa_{\rm LZ} \sim 1$, while weak couplings that lead to a large curvature provide $\kappa_{\rm LZ} \ll 1$.

Our analysis is general enough to describe the limits of strongly associating (insoluble) and dissociating ion pairs, namely, that Li^+ -F⁻ is predicted to persist in the CIP state. Moreover, significant dynamical corrections are also assigned to

Journal of Chemical Theory and Computation

soluble salts, such as RbI, that is attributed to the reaction path curvature of solvent reorganization. This is consistent with Peters and co-workers' finding⁵³ that dynamical recrossing may never be eliminated for certain ion pairs, especially for the large cationlarge anion combination. However, we expect to find many examples of salts with intermediate ionic size that will obey a perfect Marcus-like mechanism with $\kappa_{LZ} \sim 1$. In addition, we predict that the rates of association and dissociation follow a picture that is consistent with the inverted region of Marcus theory. Having reduced the multidimensional rate problem to two-dimensions allows us to easily ascertain mechanistic insight through studying the correlations of the mass element associated with the collective q-n motion. Future research will focus on detailed studies of comparing between other formulations of rate theory that utilize the full 3N degrees of freedom to maximize reactive flux for model electrolytes. Furthermore, investigating special cases where Morse-type free energy surfaces are expected instead of parabolic ones will be pursued, which may require developing new kinetic models.^{73,74} We are also interested to employ our self-consistent theory to explore the utilities of other reaction coordinates such as dipole moment rearrangement because dipole fluctuations can potentially be a good representation of solvent fluctuations. These future investigations will complement our current findings and will further ascertain the accuracy of our simple reduced picture of the complex ion-pairing dynamics.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.7b00332.

Details of the mass element Z_{qn} , coupled Marcus parabolas, and MD simulations. PMFs and values of Z_n for all ions pairs, $C_{Z_{qn}}(t)$ for Rb⁺ and I⁻, and phase space trajectories for the Li⁺-F⁻ pair. (PDF)

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Notes

The authors declare no competing financial interest.

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