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Rossend Rey† and James T Hynes‡

† Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Campus Nord B4-B5, Barcelona 08034, Spain
‡ Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA

Abstract. Molecular dynamics is applied to the title problem. It is shown how the methodology for solution reactions easily allows for a detailed study of the interchange, which has a rather complex character with unexpected dynamical features. The methodology can be applied with equal ease to cases with very different lifetimes including those with strongly bound shells.

1. Introduction

Despite the obvious interest [1, 2] of solvent exchange between the first and second solvation shells of anions, simulation evidently has not been much exploited in this connection, in contrast to the extensive work devoted to the problem of equilibrium hydration. After the pioneering work of Impey *et al* [3], there are relatively few contributions on the topic of which we are aware [4–7]. Nevertheless, simulation is crucial in discovering interesting phenomena that occur in this process [8].

Exchange times have up to now been mainly computed [3–7] in a type of mean first-passage-time approach: during an equilibrium simulation of the hydrated ion, the survival time is monitored for the molecules inside the shell defined by the first minimum of the radial distribution function ($g(r)$). It is obvious that the computation time critically depends on the ion charge (and size), so sufficient statistics can easily become unattainable for higher-charge-density ions. In addition, one has to somehow define the time span within which a molecule can temporarily leave the first shell without in fact constituting a real exchange [3, 7].

The general reactive flux method for rate constant determination [9] is specifically devised for slow activated processes such as the one addressed here, and should be the method of choice. As developed [8] for the exchange process (in a manner similar to that for ion pair conversion [10]), it does not involve *ad hoc* parameters, and if a well-defined exchange time exists, it shows up as a plateau in the reactive flux function. In principle, it should roughly require the same amount of computation independent of the ion. Finally, both methods are equivalent in the case [8] in which the former is still feasible thanks to the short exchange time.

Here we focus on the dynamical features of the exchange process, complementing our previous work [8] on the quantitative kinetic results. We show how the methodology for rate constant computations provides the possibility of sampling just the events that one is interested in, and discuss some sample trajectories that provide insight into the nature of the process.

In section 2 we briefly describe the simulations carried out and summarize the theoretical basis. In section 3 we discuss in some detail some sample trajectories, addressing the problem from the perspective of bimolecular (S_N2) versus unimolecular (S_N1) exchange mechanisms [11]. Finally, in section 4 we summarize the main conclusions.

2. Molecular dynamics simulations

The method we apply starts [8] with the computation of the potential of mean force ($W(r)$) between the ion and a surrounding water molecule. This can be accomplished by direct equilibrium calculation of an orientationally averaged $g(r)$ [2, 8] ($W(r) = -\beta^{-1}\ln(g(r))$) or with any of the methods that exploit constrained simulations [9](e), [12] (the two approaches could be combined so that the latter might only be required to accurately determine the behaviour at the first minimum of $g(r)$). The quantity that defines the one-dimensional probability density is the effective potential $W_{eff}(r) = W(r) - (2/\beta)\ln(r/r^{\ddagger})$, where $r^{\ddagger}$ is the distance corresponding to the maximum of $W_{eff}(r)$. This distance slightly differs from the one corresponding to the first minimum of $g(r)$, although in practice it is not a significant difference.

It is worth mentioning in passing that with the equilibrium calculation just described, we can use the transition state theory (TST) approximation for the rate to directly estimate a *rigorous lower bound* for the exchange time. Therefore, this may provide a novel and useful straightforward probe of interaction potentials. This lower (classical) bound is given by the expression

$$\tau_{min}^{-1} = \sqrt{\frac{k_B T}{2\pi\mu}}\,\mathrm{e}^{-\beta W_{eff}(r^{\ddagger})}\Big/\int_0^{r^{\ddagger}} \mathrm{d}r\ \mathrm{e}^{-\beta W_{eff}(r)} \tag{1}$$

with μ being the reduced mass of the ion–water molecule pair. This time should always be smaller than the experimental value, if the force field used is to be a realistic one.

The details of the simulations have been summarized elsewhere [8]. In short, configurations with one solvent molecule held at a distance $r^{\ddagger}$ from the ion centre are generated during an equilibrium constrained simulation [8] of a single sodium ion plus 107 SPC [13] water molecules, with the ion–water interaction represented by the potential proposed in reference [14]. These configurations are the starting points for the trajectories during which the reactive flux function is computed, providing the dynamical correction to equation (1). This same set of trajectories, which are not biased in any sense and thus are truly representative of equilibrium exchanges [9](b), is the one that can be exploited to understand in detail the interchange process.

3. Simulation results and analysis

We have chosen [8] the distance from the sodium ion to the water centre of mass as the coordinate monitoring the exchange process, viewing the process for computational purposes in a unimolecular dissociation perspective. Integration up to the first minimum of the corresponding $g(r)$ results in a coordination number of six water molecules and, thus, an octahedral hydration structure. The value of $r^{\ddagger}$ is approximately 3.18 Å, with a barrier for dissociation of approximately $4k_BT$, so that the process is activated.

We find that a common type of interchange is similar to a S_N2 chemical reaction mechanism, that is, one molecule would leave the first shell while another would enter it simultaneously, or in a novel variant, after a short period of time. We stress that we are not
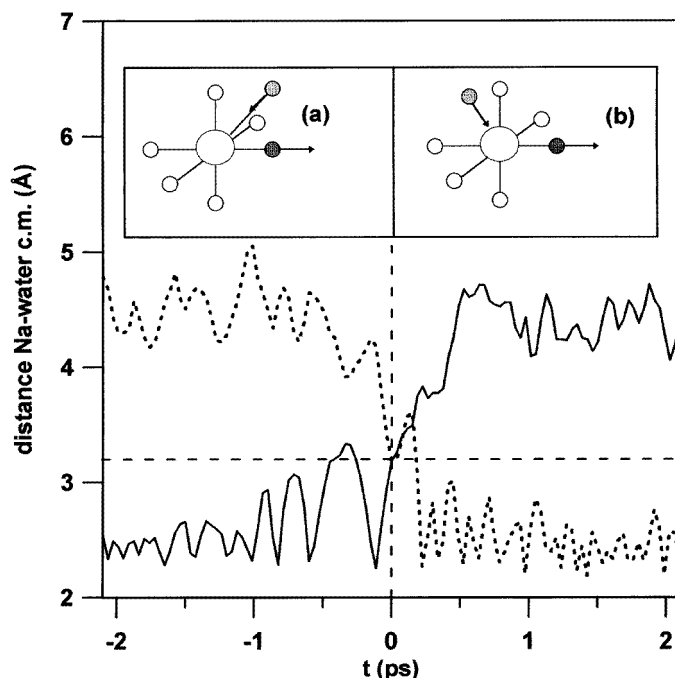
Figure 1. Na$^+$–water centre-of-mass distance for water molecules that cross the TS for a S_N2-type exchange. Inset: sketches of possible processes leading to similar trajectories.

here suggesting that this is the only pathway for exchange: the process can be extremely varied, as we shall point out below. Nevertheless, we believe that the unimolecular S_N1 and bimolecular S_N2 paradigms are valuable starting points for interpretation; probably they will be even more so for more strongly associated shells [11], a topic that merits future investigation.

Figure 1 displays an almost simultaneous S_N2 interchange of solvent molecules. We have carried out an analysis (for a limited number of cases) of the relative angle between the two water molecules. In the inset of figure 1 we sketch a simple representation of the octahedral hydration structure, together with the two types of process found to occur in this type of interchange. One possibility (figure 1(a)) consists of the interchange of two water molecules that are in direct contact. The second-shell water molecule would enter the first hydration shell in the direction defined by a line forming equal angles with all the coordinates axes. Thus, the incoming molecule would displace a molecule with which there is direct contact. From the diagram, one would expect an angle of about 55 degrees, which is indeed very similar to those found in the case-by-case analysis. In a second possibility (figure 1(b)), a second-shell water molecule would enter the first shell, and displace a distant first-shell molecule. From the diagram, the relative angle in this process is about 125 degrees, which again compares well with the simulation results.

The exchange shown in figure 2 also looks like a S_N2 process, but some delay exists between one molecule leaving and another entering. While it is certainly difficult to draw a general pattern, we have found that this process can mainly be explained by the sequence of events depicted in the inset. The exchange would start with a molecule leaving the first shell. The vacancy so created would then be nearly immediately filled by a close
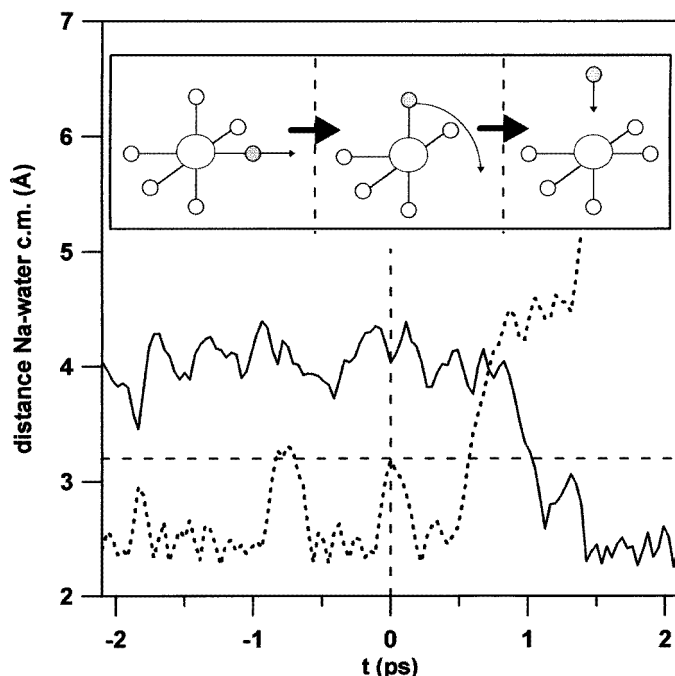
Figure 2. Na^+–water centre-of-mass distance for water molecules that cross the TS for a delayed S_N2-type exchange. Inset: a sketch of a probable sequence of events leading to this sort of slightly delayed exchange.

first-shell hydration molecule and, in turn, its vacancy would be occupied by a second-shell water molecule. Therefore, while the process may seem initially to be a S_N1 dissociation immediately followed by a recombination (with a different solvent molecule), the very short time elapsed would be indicative that these are correlated events, and that the process would be better viewed as a S_N2 exchange. In fact, in the cases studied it is found that the second-shell incoming molecule enters at almost a right angle with respect to the outgoing molecule, which is indicative of the correlation just mentioned.

We also find that a S_N1 perspective is useful in describing another substantial set of events in the exchange process [8]. Two different scenarios would also be possible. The first of these would correspond to the limit of the case just considered, with one of the molecules having left the first shell, and with its vacancy only being filled several picoseconds later (see figure 3(a) in reference [8]). The direction of the incoming molecule would be uncorrelated with that of the outgoing one, and therefore we should consider the two events as essentially independent and constituting a unimolecular dissociation, followed by a bimolecular recombination. In the second scenario (figure 3(a)), there is a sort of frustrated exchange, in which one molecule is able to leave the first shell, while the incoming molecule fails to get stabilized. Again the net balance corresponds to a S_N1 process.

Finally, we note that even the processes just described do not constitute a full description for this system. There are more complex processes, though less common, like the dramatic exchange displayed in figure 3(b), where four water molecules are interchanged in a quite short time span, leaving the overall hydration number intact.
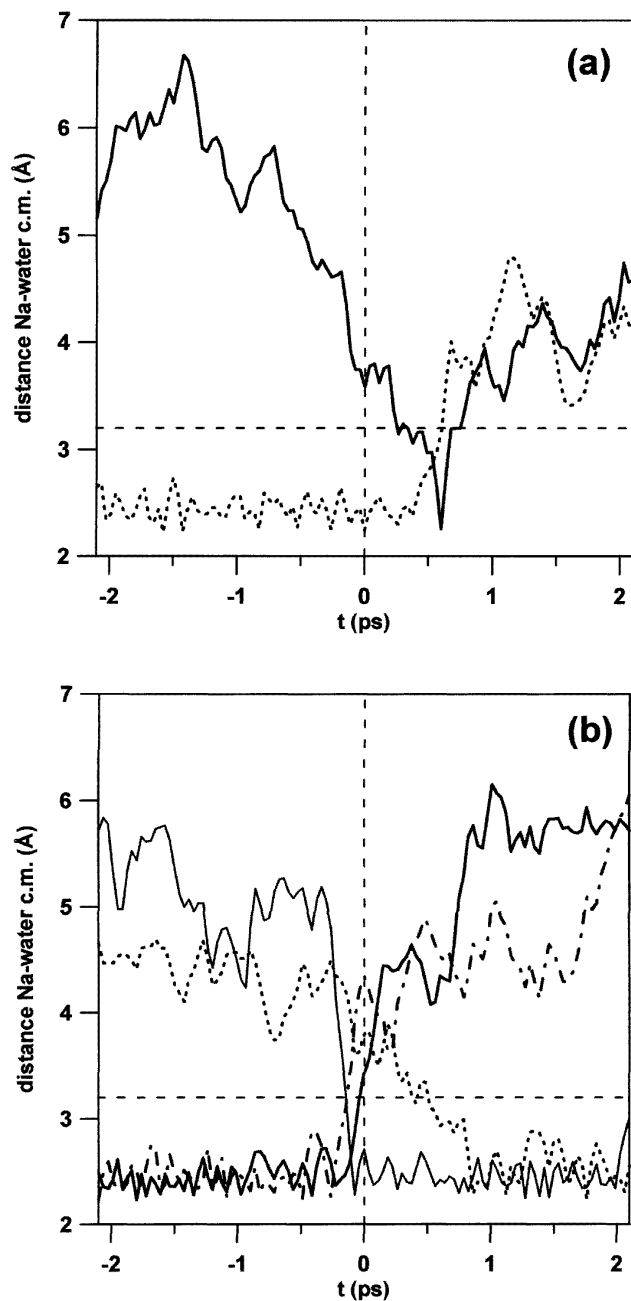
Figure 3. Na$^+$–water centre-of-mass distance for water molecules that cross the TS. (a) S$_N$1 type from frustrated S$_N$2 exchange; (b) massive simultaneous exchange of molecules.

4. Concluding remarks

We have performed a detailed analysis of the hydration shell exchange dynamics for Na$^+$ in water. Although the process can be extremely complex, a very substantial portion of the

exchanges can be understood via simple and well-known reaction categories. We believe that the methodology proposed should be of great help for the study of similar (and other [15]) systems, especially those with multiply charged ions, where we might expect that the exchange might be fully described by a subset of the possibilities described within.

Acknowledgments

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