

# Translational versus Rotational Energy Flow in Water Solvation Dynamics

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Early molecular dynamics simulations discovered an important asymmetry in the speed of water solvation dynamics for charge extinction and charge creation for an immersed solute, a feature representing a first demonstration of the breakdown of linear response theory. The molecular level mechanism of this asymmetry is examined here via a novel energy flux theoretical approach coupled to geometric probes. The results identify the effect as arising from the translational motions of the solute-hydrating water molecules rather than their rotational/librational motions, even though the latter are more rapid and dominate the energy flow.

## I. INTRODUCTION

Water solvation dynamics induced by a sudden change in the charge distribution of a solute within it has been the object of much research over the years, including both experiment<sup>1–12</sup>—primarily via dynamic Stokes shifts in time-dependent fluorescence—and theory—including both analytic modeling<sup>13–19</sup> and computations<sup>20–30</sup> (see Ref. 31 for a recent review). An especially intriguing case was discovered in the pioneering molecular dynamics (MD) simulations by Maroncelli and Fleming<sup>20</sup> (MF). These authors found for a small solute, in non-equilibrium simulations, significantly different time scales for water’s relaxation to equilibrium for a full unit charge creation and the extinction of such a full charge. This disparity—which is absent in the commonly employed equilibrium time correlation function approach to solvation dynamics—appears to be one of the first demonstrations of the breakdown of linear response, and was not observed for other charge changes and for larger solutes by MF. (We adhere to the definition of MF, and e. g. Ref. 22, that there is a breakdown if there is not a single relaxation function describing the normalized dynamical response independent of the solute charge change.)

MF attributed their observation to important water molecular rotational and translational motion induced by the sudden extinction of the solute’s charge. We would express their argument as follows: important water-water repulsive torques and forces would no longer be compensated by the attractive interactions of these waters with the (now vanished) solute charge, thus inducing the motions mentioned; this effect would be absent for the case of charge creation, and also absent for large ionic solutes due to the repulsive force/torque reduction.

As will be seen within molecular level investigation of this apparently reasonable explanation proves not to be at all straightforward. The non-equilibrium response functions  $S(t)$  for the charge extinction and creation cases for the solute and water solvent model we have used<sup>29</sup> shown in Fig.1 display a disparity similar to

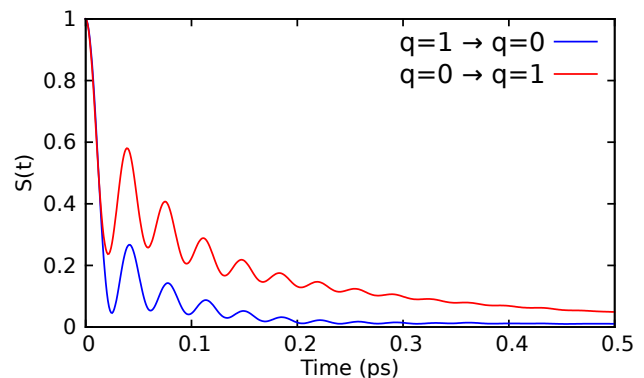


FIG. 1: Nonequilibrium response function  $S(t)$  for solute charge extinction and creation in water solvent after Ref. 28–30. Blue:  $q = 1 \rightarrow q = 0$ ; red:  $q = 0 \rightarrow q = 1$ . As in Ref. 20, there is more rapid decay for charge extinction compared to creation, both at short times which is our own focus, and as measured by the integrated response functions (here 0.03 ps for charge extinction vs. 0.1 ps for charge creation).

that found by MF for a similar but somewhat different model, but—as discussed further below—are mute on the molecular interpretation. The importance of obtaining an appropriate molecular interpretation is emphasized not only by the non-linear response aspect mentioned above, but also, and more generally, by the key role in hydrogen-bonded water molecular dynamics in a host of charge transfer chemical reactions and related phenomena<sup>32–45</sup>.

We recently made a first attempt<sup>29,30</sup> to examine this question via a different approach; we employed a work/power or energy flow perspective for solvation dynamics following electronic excitation of a solute<sup>28</sup>, which is an extension to this arena of the corresponding perspective to energy flows to the solvent following solute vibrational excitation<sup>46,47</sup>. The attraction of this perspective is the possibility of provision of a detailed molecular picture for the process.

But a straightforward application of this approach was

in fact thwarted; while the response function  $S(t)$  for the solute charge creation case  $q = 0 \rightarrow q = +1$  could be related to a real coulombic energy flow,  $S(t)$  for the charge extinct ion case  $q = +1 \rightarrow q = 0$  could not be so related, due to a mismatch of the electronic state for the dynamics and the solute charge. We resolved this problem by focusing on the real, total energy fluxes<sup>29</sup>, the relevant results of which are employed here, and whose conclusions are supported by the molecular level configuration calculations that we present within.

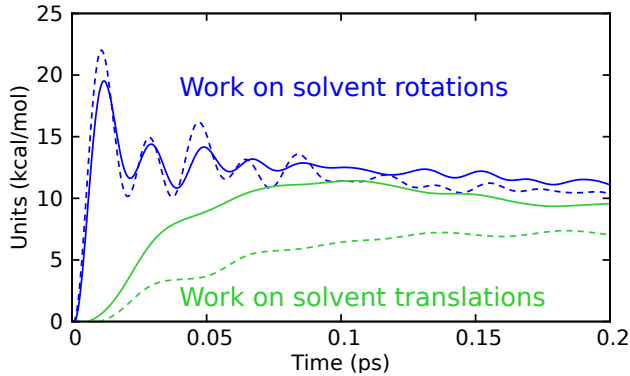


FIG. 2: Total work on, i.e., energy flow to, the water solvent molecular rotations (librations) and translations, for the solute charge extinction and creation cases (after Ref. 29). Solid  $1 \rightarrow 0$ , dashed  $0 \rightarrow 1$ . (Similar patterns are found for the corresponding anionic cases<sup>29</sup>, but are not discussed here, since these nonequilibrium cases were not addressed by MF).

The essential results for our present purposes are shown in Fig. 2, where we have focused on the short timescales which capture the essence of the issue. The work results displayed there (and in Ref. 29) indicate that the charge creation/extinction asymmetry can be associated with the flow of translational energy to the water solvent; but perhaps surprisingly there is no clear evidence of an important role for rotational energy flow in that asymmetry, despite the fact that it is the more rapid and dominant energy flow mechanism. In particular, the (blue) curves for the rotational energy flow for the two solute charge change cases in Fig. 2 differ little, especially for short times, compared to the much larger difference for the (green) translation energy flow curves there. Thus, while the rotational energy flow is more important than the translational energy flow in each case for short times, it is the latter flow that is significantly different for the charge extinction and creation cases. (For an early general discussion of the role of translational modes in solvation dynamics, see Ref. 48.)

In the present work we aim to provide some understanding of these dynamics results from a more molecular level perspective, with a particular emphasis on the insight provided by a water spatial configurational viewpoint. We begin with water molecular translation and then turn to rotation.

## II. METHODS

The same basic models as in our initial contribution<sup>28</sup> are used here, with the limitation (as in Ref. 29) that, given the negligible role of internal solvent vibrations<sup>28</sup>, we consider only the (rigid) SPC/E model<sup>49</sup> for the solvent water molecules. For the solute, the model is taken (as in our previous contributions<sup>28-30</sup>) from the work of Tran and Schwartz,<sup>26</sup> where the water-solute interaction consists of a Lennard-Jones interaction identical to the water-water LJ interaction, plus Coulomb interactions which depend on the solute charge. All simulations have been run with an in-house code for one solute and 199 water molecules, with a cut-off distance of half the box length, and with the Ewald sum correction implemented for Coulomb forces. Equilibrium and nonequilibrium simulations have been run depending on the topic under discussion. Most of the results correspond to nonequilibrium simulations, which consist of a long trajectory from which initial configurations are sampled. These configurations are used for 10,000 independent separate nonequilibrium runs, where the solute charge is changed at  $t = 0$ , and along which the quantities of interest are calculated. Temperature control is maintained<sup>50</sup> during the generation of initial configurations, and turned off at the start of each non-equilibrium trajectory.

## III. TRANSLATIONAL ENERGY FLOW

Figure 2 indicates that the flow of translational energy to the water solvent is distinctly faster for the  $1 \rightarrow 0$  (compared to the  $0 \rightarrow 1$ ) solute electronic transition. The simplest route to a molecular perspective for the acquired translational motion of the solvent waters is via the time-dependent radial distribution function (rdf); this details the evolution of the spatial distributions of the water molecules' oxygen atoms with respect to the center of the solute. These rdfs are computed and averaged over the non-equilibrium trajectories generated, as detailed in Ref. 30 for the charge extinction and creation cases, and they are shown in Fig. 3.

For the charge extinction case  $1 \rightarrow 0$ , Fig. 3(a) shows that even after 20 fs (see the caption re this time choice) the first rdf peak is already shifted to the right, reflecting the rapid Coulomb repulsion of the water molecules away from the newly neutral solute. In contrast, Fig. 3(b) for the charge creation case  $0 \rightarrow 1$  shows that on that same 20 fs time scale, there is no change in the distribution of the water molecules' positions; there is no short time Coulomb repulsion effect here.

A further representation which better isolates the distinctly different water molecular translational response to the solute charge extinction and creation is shown in Fig. 4, which plots

$$\Delta g(r; t = 20 \text{ fs}) \equiv g(r; t = 20 \text{ fs}) - g(r; t = 0), \quad (1)$$

the rdf difference at 20 fs. The strong water solvent

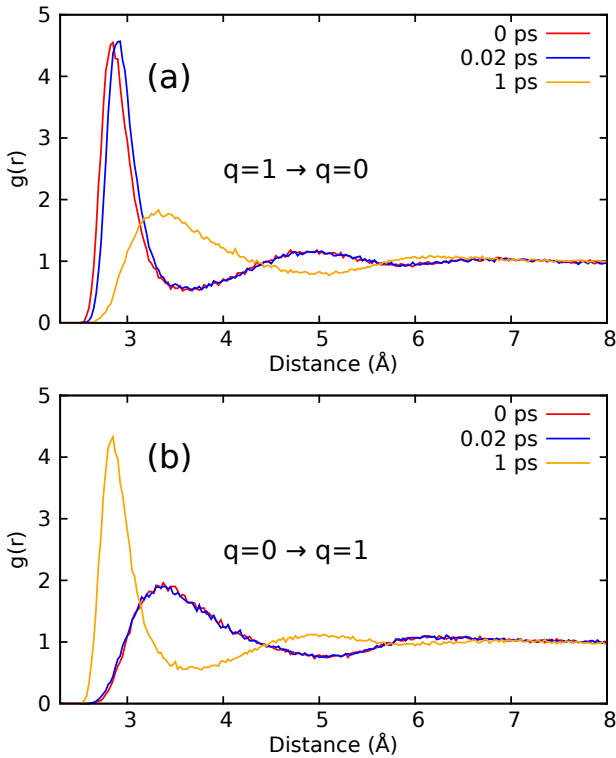


FIG. 3: Time-dependent water molecule radial distribution functions (rdfs), evaluated at different times, for the solute charge (a) extinction and (b) creation cases with the origin of coordinates at the center of the solute. The choice of 20 fs, the time on which the text discussion is focused, is indicated by the first minimum in Fig.1 and the first rotational maximum in Fig. 2, both distinguishing the two cases, and avoiding complications due to oscillations.

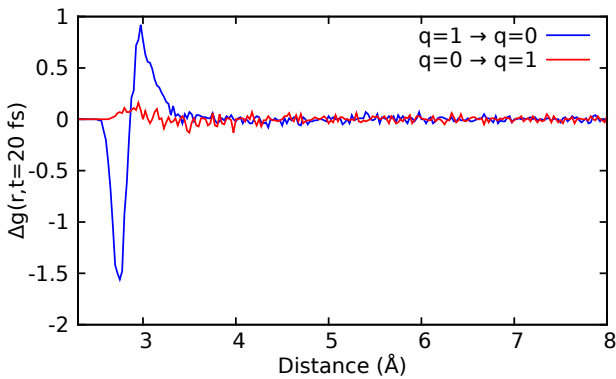


FIG. 4: The non-equilibrium trajectory-averaged difference Eq. 1 of the radial distribution function at times 20 fs and 0 fs for the solute charge extinction and creation cases.

translational response to the charge extinction sharply contrasts to the negligible response to the charge creation; in the former case, the probability density closest to the solute decreases as water molecules are repelled away from the solute, while the larger distance peak reflects the resulting increase by the arrival of those same

water molecules.

These results have shown explicitly for the first time that indeed there is a very rapid translational repulsion effect for the solute charge extinction, absent for the charge creation case. These support our previous results<sup>29</sup>, here illustrated by Fig. 2, and the original remarks of MF.

#### IV. ROTATIONAL ENERGY FLOW

We now turn to the rotational response of the solvent waters to the solute charge change. The water rotations are of course hindered, i.e. are librations, and we will often use the terms libration and librational in our discussion. As we remarked in the Introduction and as shown in Fig. 2, our previous analysis in terms of energy flow and work indicated a lack of a substantially faster water solvent rotational response for the solute charge extinction  $1 \rightarrow 0$  compared to charge creation  $0 \rightarrow 1$ , in strong contrast to the solvent translational response just discussed. This result is at variance with the expectations from the original MF discussion, and we now probe the issue at a more molecular level.

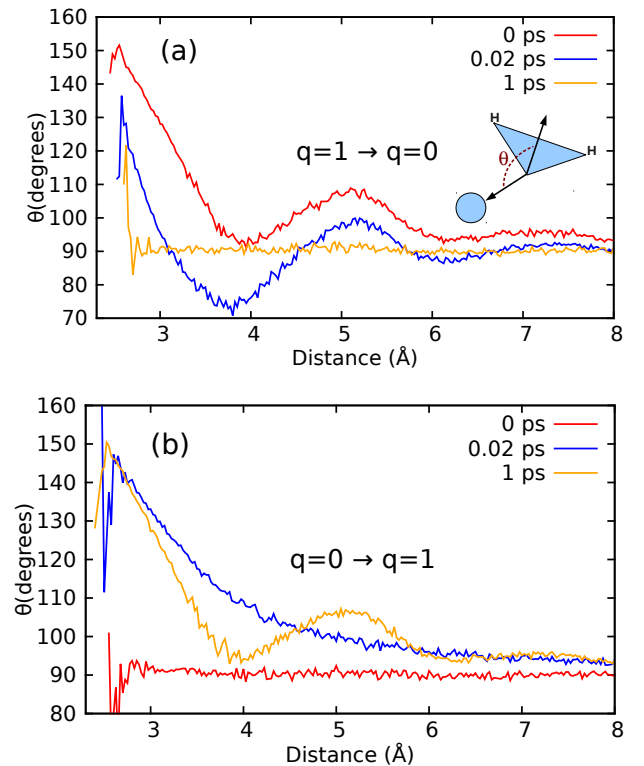


FIG. 5: The nonequilibrium trajectory-averaged angle, defined in the inset in panel (a), of water molecules at various distances from the solute, at several times, for the two solute charge change cases. Here, and in the following figures, noise is dominant at the shortest separations since these are hardly visited for the limited number of trajectories run, specially for the neutral solute (see Fig. 8).

In order to examine this issue in a molecular perspective, we have calculated, and Fig. 5 displays, the average angle between a solute-water separation axis and the water dipolar axis (see panel (a) insert) for the nonequilibrium trajectories generated for Ref. 30, and averaged the results. The two Fig. 5 panels reflect the obvious feature that the initial water solvent conditions for the two solute charge change cases are quite different, and this can easily lead to confusion in comparing these cases. In order to avoid this, it will prove convenient to introduce the absolute magnitude of the angle change

$$\Delta\theta(r, t) = |\theta(r, t) - \theta(r, t = 0)|. \quad (2)$$

This definition—which we will apply presently—is designed to place the different initial water solvent conditions for the two charge cases in a perspective allowing their simple comparison. In order to indicate how this functions, we first consider the two cases in Fig. 5 in more detail. In Fig. 5(a) for the solute charge extinction, the water solvent is initially equilibrated to the charge  $q = 1$  (red curve) and evolves to (near) equilibrium with the final neutral charge  $q = 0$  (orange curve) at 1 ps. In contrast, in the charge creation Fig. 5(b), the solvent evolves from initial equilibrium with the neutral solute  $q = 0$  (red curve) to reach (near) equilibrium with the new charge  $q = 1$  at 1 ps (orange curve). Now we can see that the absolute value definition Eq. 2 exploits the reversed symmetry of these evolutions to allow an effective comparison of the time scales, as shown in Fig. 6. Here panel (a) of the final angle difference  $\Delta\theta(r, t = 1 \text{ ps}) = \theta(r, t = 1 \text{ ps}) - \theta(r, t = 0)$  (note the lack of absolute value bars) reflects the reversed symmetry, while the magnitude of this difference Eq. 2 (i.e. absolute value) shows that a useful comparison of the two is achieved, as in panel (b).

We now exploit the magnitude of the average angle increment, Eq. 2, evaluated at the end 20 fs of the key time period, displayed in Fig. 7 versus the distance from the solute center, for the solute charge extinction and creation cases. These results can be regarded as surprising from the point of view of the original MF explanation. While the librational behavior is the same for most of the distances shown, there is a difference for small distances ( $< 3.2 \text{ \AA}$ , as indicated by the vertical dashed line), where it is the charge creation  $0 \rightarrow 1$  case with the more rapid evolution, and not the expected  $1 \rightarrow 0$  case. In fact, this is consistent with the rotational work/energy flux result from Ref. 29 shown in Fig. 2, where the charge creation response is slightly faster than is the charge extinction response.

Examination of the water solvent structure around the differently charged solutes, shown in Fig. 8, sheds some light on this behavior. Both panels of this Figure convey the same message, perhaps most clear in panel (b): this shows that for distances less than  $3.2 \text{ \AA}$ , the hydration number for the neutral solute (red curve) is (roughly) only 2. Even though water rotational dynamics is faster

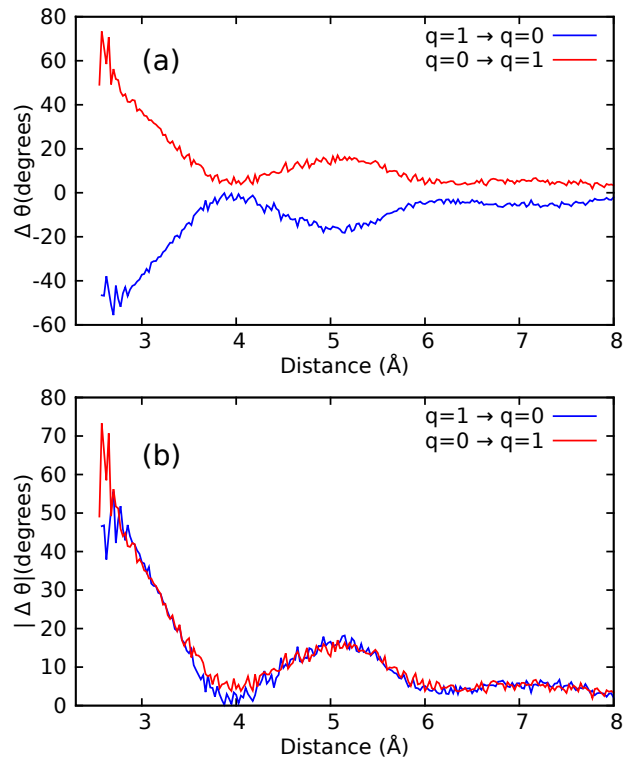


FIG. 6: (a) The nonequilibrium trajectory-averaged angle difference  $\theta(r; t = 1 \text{ ps}) - \theta(r; t = 0)$  and (b) its absolute magnitude Eq. 2, for the two different solute charge cases, versus the water molecules distance from the solute center. See the inset of Fig. 5(a) for the angle definition.

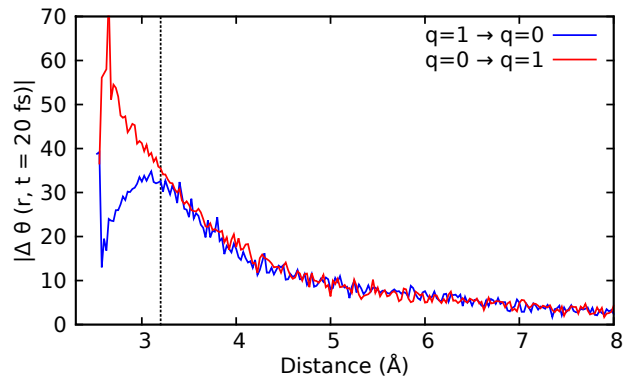


FIG. 7: The magnitude  $|\Delta\theta(r, t = 20 \text{ fs})| = |\theta(r, t = 20 \text{ fs}) - \theta(r, t = 0)|$  of the nonequilibrium averaged-angle difference Eq. 2 evaluated at the end, 20 fs, of the key time period distinguishing the librational response behavior of the two different solute charge change cases.

in this case ( $0 \rightarrow 1$ , see Fig. 7), it is difficult to transfer energy since there are very few molecules, compared with the case  $1 \rightarrow 0$ , for which Fig. 8(b) indicates that these short distances are instead highly populated. The lack of an efficient power transfer for the  $0 \rightarrow 1$  case explains why the faster rotational dynamics is only barely visible

in Fig. 2.

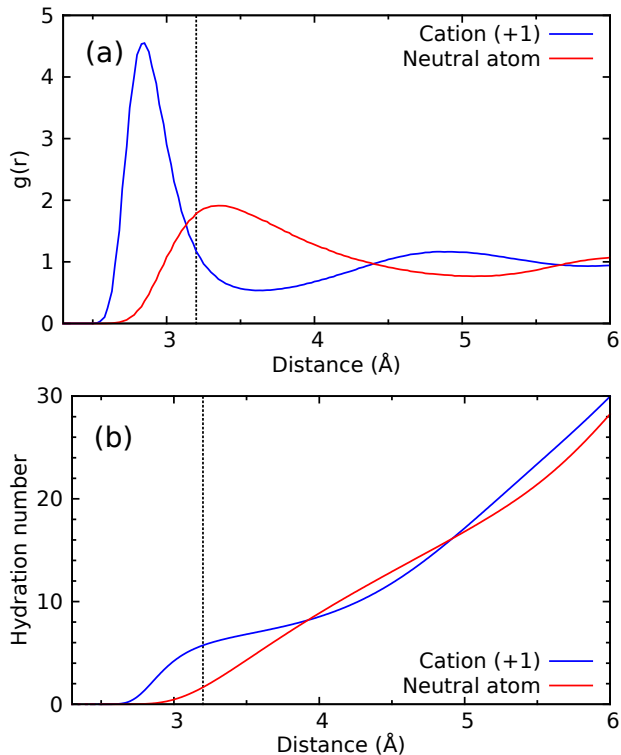


FIG. 8: Water solvent structural measures for the different solute charge cases, versus water oxygen distance from the solute center. (a) Equilibrium radial distribution function; (b) hydration number.

## V. CONCLUDING REMARKS

In this work we have analyzed—via energy flows and the evolution of water spatial and angular configurations—the origin of the asymmetry of the dynamic water solvent response for charge extinction and creation in a dissolved solute, which was discovered by Maroncelli and Fleming in their original simulation of solvation dynamics<sup>20</sup>. We have found that this asymmetry effect, which is a hallmark of the water solvent’s nonlinear response, is dominated by the translational motion of the water molecules near the charge-changed solute, and not by the water rotational/librational motion, even though the latter motions are more rapid and are dominant for the energy transfer.

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