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Vibrational echo spectral observables and frequency fluctuations of hydration shell water around a fluoride ion from first principles simulations[†]

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Abstract. Aqueous solution of a fluoride ion at 300 K is studied using the method of *ab initio* molecular dynamics simulation. Instantaneous fluctuations in vibrational frequencies of local OD stretch modes of deuterated water are calculated using a time-series analysis of the simulated trajectory. The vibrational spectral diffusion of OD modes in the first and second solvation shells and also in bulk of the aqueous fluoride ionic solution are studied through calculations of the frequency time correlation function (FTCF), joint probability distributions, slope of three pulse photon echo (S3PE) and two dimensional infrared spectrum (2D-IR). The vibrational spectral dynamics in the first solvation shell shows decay with three components which can be correlated with the dynamics of intact ion-water hydrogen bonds, ion-water hydrogen bond lifetime and the escape dynamics of water molecules from the solvation shell. The vibrational spectral diffusion of OD modes in the second solvation shell and in the bulk show very similar decay behavior. The timescales obtained from FTCF, S3PE and the slope of nodal line (SNL) of 2D-IR are found to be in reasonable agreement with each others.

Keywords. Vibrational echo; frequency fluctuations; hydration shell water; fluoride ion; *ab initio* molecular dynamics.

1. Introduction

Ions dissolved in liquid water play important roles in several chemical and biological processes.^{1,2} Similarly, water molecules in aqueous ionic solutions exhibit different dynamics in comparison to pure water.^{2–4} There are several aqueous phase chemical reactions like S_N2 nucleophilic substitution, unimolecular dissociation and acid dissociation reactions which involve solvated anions.⁵ In view of their huge importance in both energetics and dynamics of aqueous phase chemical reactions, aqueous ionic solutions have been studied extensively using both experimental and theoretical methods.^{2–15} The arrangement of water molecules around fluoride ions has been studied over a range of concentration in potassium fluoride solutions using the neutron diffraction technique.¹⁶ Recently, with the advent of time-dependent vibrational spectroscopy, there have been several spectroscopic studies which have intensively focused on solvation shell dynamics

and rate of vibrational spectral diffusion in aqueous solutions. In this regard, we note in particular the pump-probe experiments of aqueous ionic solutions which could differentiate the dynamics of water molecules in the solvation shell from those present in the bulk. Early experiments in this area found the decay of frequency correlations of water in the hydration shells of halide ions to be in the range of 10–25 ps.⁶ Subsequent experiments using improved techniques reported vibrational spectral diffusion timescale of 4.7 ps for 6m NaBr solution.¹⁷ The orientational dynamics of water molecules in ionic solutions has also been studied through femtosecond pump-probe spectroscopy. It was found that the rotational dynamics of water molecules beyond the first solvation shell was not influenced by the presence of ions.⁷ Similarly, there has also been a study of equilibrium dynamics of thiocyanate chemical exchange between free thiocyanate ion and calcium or magnesium thiocyanate complex using two dimensional infrared (2D-IR) spectroscopy.⁵

On the theoretical side, the structural order of water molecules around fluoride ions has been studied through classical molecular dynamics and combined quantum-classical (QM/MM) technique.^{18,19} Dynamic evolution

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[†]Dedicated to the memory of the late Professor Charusita Chakravarty.

of the solvation shells around ions was found to be slower in these studies. The effects of temperature and pressure on the hydration of ions in water and also the rotational motion of water molecules in the solvation shells have also been reported.²⁰ A recent study²¹ reported calculations of the pump-probe spectrum of aqueous solution of iodide ions using classical simulations. The long-time relaxation of frequency fluctuations was shown to be related to the escape dynamics of water from the solvation shells of iodide ions.²¹ The frequency fluctuations in solvation shells of halide ions have also been studied using *ab initio* molecular dynamics without involving any empirical models.²² These studies also calculated the average residence time of water in the hydration shells of halides using population time correlation approach and found an average residence time of 20–30 ps for these anions. Further, studies have also been reported for calculation of the transient hole burning spectroscopy and 2D-IR spectroscopy of water and aqueous ionic solutions from first principles simulations.^{22–24}

In the present study, we present calculations of the non-linear vibrational spectroscopy of water molecules in the solvation shell of a fluoride ion and of bulk water from first principles simulations. We have performed the spectral calculations within the framework of second order cumulant approximation. We note that although the second order cumulant approximation for liquids with complex hydrogen bond network like water is not completely valid due to non-Gaussian features,^{25–30} the spectral diffusion timescales calculated within the approximation are found to be in reasonable agreement with the timescale of frequency correlation for water and ionic solutions.²³ In the present study, we have calculated the 2D-IR spectrum, slope of 3-pulse photon echo (S3PE) (an analogue of the peak shift) and frequency time correlation function (FTCF) of water in the first solvation shell, second solvation shell and also in the bulk. We have obtained the timescales of spectral diffusion from FTCF, normalized S3PE and slope of nodal line (SNL) of the calculated 2D-IR spectrum. We have calculated the fluctuations in vibrational frequencies of OD modes using the wavelet method of time-series analysis. In order to determine the fluctuations in the excited state, we have modeled the OD modes as Morse oscillators. The method has been described in details in our previous work.²³ We note that most of the experimental and simulation studies have looked at the spectral features of HOD in ionic solution of H₂O or D₂O.^{31–39} In the present study, we have considered an ionic solution of fluoride ion in D₂O. The spectral dynamics of an isolated OD/OH mode of HOD in ionic solution from *ab initio* perspective remains

a challenging task within the existing computational framework.

2. Theoretical formulation

In the current section, we present the theoretical formulation for the calculation of the response functions of the third order polarization as given by Mukamel.^{40–42} When a system is targeted with three electric field pulses with the propagation vectors k_1 , k_2 and k_3 , a macroscopic polarization is produced in the rephasing direction which is often termed as an echo and also a free induction decay (FID) in the non-rephasing direction. While the detailed derivation is available in the literature,^{40,41} we present here only the equations for response functions within the second order cumulant approximation. In the present study, we ignore the excited state lifetime effects and rotational effects. We refer to the time delay between the first and second pulses as t_1 , the time delay between the second and third pulses as t_2 and the time after the third pulse onward as t_3 . Within the above mentioned framework, the response functions are given as,⁴⁰

$$\begin{aligned} R_1(t_3, t_2, t_1) &= R_2(t_3, t_2, t_1) \\ &= \mu_{10}^4 \exp(-i\langle\omega_{10}\rangle t_3 + i\langle\omega_{10}\rangle t_1) \\ &\quad \times \exp(-g_1(t_1) + g_1(t_2) - g_1(t_3) \\ &\quad - g_1(t_2 + t_1) - g_1(t_2 + t_3) \\ &\quad + g_1(t_1 + t_2 + t_3)), \end{aligned} \quad (1)$$

$$\begin{aligned} R_3(t_3, t_2, t_1) &= -\mu_{10}^4 \kappa^2 \exp(i\Delta t_3) \\ &\quad \times \exp(-i\langle\omega_{21}\rangle t_3 + i\langle\omega_{10}\rangle t_1) \\ &\quad \times \exp(-g_1(t_1) + g_2(t_2) - g_3(t_3) \\ &\quad - g_2(t_2 + t_1) - g_2(t_2 + t_3) \\ &\quad + g_2(t_1 + t_2 + t_3)), \end{aligned} \quad (2)$$

$$\begin{aligned} R_4(t_3, t_2, t_1) &= R_5(t_3, t_2, t_1) \\ &= \mu_{10}^4 \exp(-i\langle\omega_{10}\rangle t_3 - i\langle\omega_{10}\rangle t_1) \\ &\quad \times \exp(-g_1(t_1) - g_1(t_2) - g_1(t_3) \\ &\quad + g_1(t_2 + t_1) + g_1(t_2 + t_3) \\ &\quad - g_1(t_1 + t_2 + t_3)), \end{aligned} \quad (3)$$

$$\begin{aligned} R_6(t_3, t_2, t_1) &= -\mu_{10}^4 \kappa^2 \exp(i\Delta t_3) \\ &\quad \times \exp(-i\langle\omega_{21}\rangle t_3 - i\langle\omega_{10}\rangle t_1) \\ &\quad \times \exp(-g_1(t_1) - g_2(t_2) - g_3(t_3) \\ &\quad + g_2(t_2 + t_1) + g_2(t_2 + t_3) \\ &\quad - g_2(t_1 + t_2 + t_3)), \end{aligned} \quad (4)$$

where $g_n(t)$ ($n = 1-3$) is related to the time correlations of fluctuating transition frequencies and the expressions for $g_1(t)$, $g_2(t)$ and $g_3(t)$ are given by

$$g_1(t) = \int_0^t d\tau' \int_0^{\tau'} d\tau'' \langle \delta\omega_{10}(0) \delta\omega_{10}(\tau'') \rangle, \quad (5)$$

$$g_2(t) = \int_0^t d\tau' \int_0^{\tau'} d\tau'' \langle \delta\omega_{21}(0) \delta\omega_{10}(\tau'') \rangle, \quad (6)$$

and

$$g_3(t) = \int_0^t d\tau' \int_0^{\tau'} d\tau'' \langle \delta\omega_{21}(0) \delta\omega_{21}(\tau'') \rangle. \quad (7)$$

In Eqs. 2 and 4, $\Delta = \langle \omega_{21} \rangle - \langle \omega_{10} \rangle$ and κ is equal to μ_{21}/μ_{10} . It may be noted that Δ is zero for a harmonic oscillator, hence its non-zero value measures the extent of anharmonicity of the system. In a conventional 2D-IR spectroscopic experiment, the third order polarization is obtained as the convolution of the third order response function and the externally applied electric field pulses. In the present study, we assume the external electric fields to be delta functions. Further, we obtain the spectrum in frequency domain by Fourier transformation along two of the frequency axes as a function of one of the time interval which is taken to be the interval between the second and third pulses. The equations for the 2D-IR spectrum in the frequency domain as Fourier transforms of the response functions is expressed as,⁴⁰⁻⁴³

$$S(\omega_3, t_2, \omega_1) = Re \left[\sum_{i=1}^6 S_i(\omega_3, t_2, \omega_1) \right], \quad (8)$$

where

$$S_i(\omega_1, t_2, \omega_3) = \int_0^\infty dt_1 \int_0^\infty dt_3 \exp(i\omega_3 t_3 - i\omega_1 t_1) R_i(t_1, t_2, t_3), \quad (9)$$

for $i = 1$ to 3 and

$$S_i(\omega_1, t_2, \omega_3) = \int_0^\infty dt_1 \int_0^\infty dt_3 \exp(i\omega_3 t_3 + i\omega_1 t_1) R_i(t_1, t_2, t_3), \quad (10)$$

for $i = 4$ to 6, respectively.

Similarly, in integrated three pulse photon echo peak shift (3PEPS) experiments, the integrated intensity along the rephasing direction is found out. The integrated echo intensity is expressed mathematically as,

$$I(t_1, t_2) = \int_0^\infty dt_3 \left| \sum_{i=1}^3 R_i(t_1, t_2, t_3) \right|^2. \quad (11)$$

The peak shift $t_1^*(t_2)$ for a given t_2 is defined as the value of t_1 for which the echo intensity exhibits a maximum.^{44,45} Theoretically, several alternatives to the peak shift (3PEPS) have been proposed.⁴⁶ The slope of 3-pulse photon echo (S3PE) is also known to capture the frequency correlation loss at both short and long timescales. The slope of three pulse photon echo (S3PE) is determined from the initial slope of the integrated three pulse photon echo intensity. The expression for the calculation of S3PE is given as,

$$S(t_2) = \frac{\partial I(t_1, t_2)}{\partial t_1} \Big|_{t_1=0}. \quad (12)$$

The normalized frequency time correlation function is then given by⁴⁵⁻⁴⁷

$$C(t_2) = \frac{S(t_2)}{S(0)}. \quad (13)$$

3. *Ab initio* simulations

The *ab initio* molecular dynamics simulation of the present study has been performed using the method of Car-Parrinello^{48,49} and the CPMD code.⁵⁰ The simulation system consists of a single fluoride ion and 107 D₂O molecules in a cubic box of edge length 15.0 Å. The edge length was determined from the known experimental density of the solution at 300 K.⁵¹ The electronic structure of the system was determined within the Kohn-Sham formulation⁵² of density functional theory.⁵³ The inner electrons were treated using the norm-conserving pseudopotentials of Troullier-Martins.⁵⁴ The plane wave expansion of the inner electrons was truncated at the kinetic energy cut-off of 80 Ry. A fictitious mass of 800 au was assigned to the electronic orbital degrees of freedom and the coupled equations of motion were integrated using a timestep of 5 au.

Several recent studies have shown that the equilibrium structure, dynamics and phase diagram of water improves on incorporation of dispersion corrections.⁵⁵⁻⁵⁹ In view of this, in the present study we have used the BYLP functional with dispersion corrections. The dispersion corrections were incorporated using the D2 scheme of Grimme.^{60,61} The initial configuration of system was obtained from classical molecular dynamics simulation followed by equilibration in the NVT ensemble using *ab initio* simulation for 15 ps. Finally, the production run was carried out for the duration of another 50 ps in the microcanonical ensemble for calculations of the vibrational frequency fluctuations, various observables of vibrational echo and 2D-IR spectroscopy and other dynamical quantities. As mentioned earlier, we have employed the second order cumulant approximation for spectral calculations. Thus, it is assumed that the dynamics is Gaussian and the transition dipole moment is independent of nuclear degrees of freedom. The ratio of the 0–1 and 1–2 transition dipole moments (κ) was determined using the eigenfunctions of Morse oscillators.

4. Results and Discussions

4.1 Frequency fluctuation dynamics

The time dependent fluctuations in the vibrational frequencies of OD modes in their ground states were calculated using a time-series analysis of the trajectory obtained from simulations. Further, the fluctuations in the higher excited states are obtained by modeling the OD modes as Morse oscillators. The details of both the

methods are available in the literature.^{22,62,63} In order to identify the effects of the anion on vibrational dynamics of OD modes in different solvation shells, we have calculated the frequency distribution of OD modes present in the first and second solvation shells and also in the bulk which are shown in Figure 1. We have determined the solvation shells based on distance criteria. The OD modes found at a distance less than the first peak of the F-D radial distribution function from the fluoride ion, i.e., 2.5 Å, at a given time constitute the first solvation shell at that point of time. Similarly, OD modes which are found between 2.5 Å and 4.5 Å from the ion belong to the second solvation shell and remaining to the bulk. The average frequency of the OD modes present in bulk is found to be 2362 cm⁻¹. Similarly, the average frequency distribution of OD modes present in the second solvation shell is also found to be 2362 cm⁻¹ while that of OD modes present in first solvation shell is 2310 cm⁻¹. We note that while the time averaged frequency distribution of OD modes present in the second solvation shell is essentially indistinguishable from that of the bulk, a significant red shift is seen for distribution of OD modes present in the first solvation shell. This implies that the OD modes present in the first solvation shell of the fluoride ion have stronger hydrogen bonds due to which the average distribution gets red shifted. This also implies that the effects of fluoride ion solvation over vibrational fre-

quencies do not extend beyond the first solvation shell of the ion.

Further, we also calculated the frequency time correlation function (FTCF) of the OD modes in the first and second solvation shells and also in the bulk. The time dependent decay of FTFCF of OD modes in different solvation shells is shown in Figure 2. We note that the decay of frequency correlation of bulk and second solvation shells are rather similar to each other. The timescales of decay of the frequency correlations of OD modes in the bulk and second solvation shell were determined by using a biexponential fit of the type shown below,

$$f(t) = a_0 \exp\left(-\frac{t}{\tau_0}\right) + (1 - a_0) \exp\left(-\frac{t}{\tau_1}\right). \quad (14)$$

We note that the two timescale of decay of OD modes in the bulk are found to be 69 fs and 2.54 ps. For the second solvation shell, the shorter timescale of decay is 75 fs while the component corresponding to the longer time decay is found to be 2.7 ps. It can be seen that the vibrational frequency relaxation dynamics of the second solvation shell and bulk are very similar. The timescales of decay of the frequency correlation of OD modes in the first solvation shell are found out by using a triexponential fit as given below,

$$f(t) = a_0 \exp\left(-\frac{t}{\tau_0}\right) + a_1 \exp\left(-\frac{t}{\tau_1}\right) + (1 - a_0 - a_1) \exp\left(-\frac{t}{\tau_2}\right). \quad (15)$$

The short timescale of the decay is found to be around 50 fs while intermediate timescale is calculated to be 8.46 ps. The third longer timescale of the decay is found to be 27.5 ps. We note that the very fast timescale of the decay in the sub-femtosecond domain basically arises from the librational motion. Further, the intermediate time decay can be correlated with ion-water hydrogen bond lifetime and the very long third timescale of about 30 ps can be attributed to the average residence time of water molecules in the ion solvation shell. The oscillations in decay of frequency correlation for the first solvation shell is mainly due to fluctuations in the interactions between the ion and water molecules present in the solvation shell.

We have also calculated the time dependent joint probability distributions of vibrational frequencies of OD modes that are present in the solvation shells and bulk regions. In the calculation of joint probability distribution for first solvation shell, the water molecules within the distance cutoff of less than the first minima of *F* – *O* radial distribution function were considered. The results of these distributions are shown in

Figure 1. Frequency distributions of the OD oscillators in the first and second solvation shells and in the bulk regions of an aqueous solution containing a fluoride ion at 300 K.

Figure 2. Time dependence of the correlation function of frequency fluctuations of OD stretch modes present in the first and second solvation shells and in the bulk of an aqueous solution containing a fluoride ion at 300 K.

Figure 3. The joint probability distributions of OD modes for smaller waiting times, say of 10 fs, are found to be elongated along the diagonals. However, as the waiting times are increased to 3 ps, the distributions have become completely spherical for OD modes in the second solvation shell and bulk regions which implies loss of frequency correlations in such timescales. We note that the timescales obtained from the FTCTF are also in the similar range. However, for OD modes present in the first solvation shell, the correlations persist even at longer waiting times of 5 ps as can be seen from Figure 3. Thus, the distribution plots also support the presence of a stronger temporal correlation of vibrational frequencies of OD modes in the ion solvation shell. The joint probability distribution for water molecules in first solvation shell shows two locally centered distributions. While the distribution centered along the lower frequency can be attributed to the water molecules with strong ion-water hydrogen bonds, the distribution centered at high frequency should refer to the remaining water molecules which are in solvation shell but are having water-water hydrogen bonds.

Finally, we have also calculated the ion-water hydrogen bond and residence time correlations^{64,65} of water in the solvation shell of the fluoride ion and the results are shown in Figure 4. The residence time of water molecules in the ion solvation shell is found to be 25.1 ps which is in reasonably good agreement with the third decay component of FTCTF for the first solvation shell. Further, the ion-water hydrogen bond lifetime obtained

by integrating the continuous hydrogen bond correlation function is found to be around 5.7 ps.

4.2 Echo intensity and S3PE

The echo signal measured in vibrational echo peak shift experiments corresponds to the absolute value of the third order polarization. In Figure 5 (a), we have shown the integrated echo intensity along the rephasing direction as function of different waiting times t_2 . The integrated echo intensity is shown for the bulk water. For the smaller values of t_2 , the intensity shows a peak which is often referred to as the vibrational echo. However as the waiting time increases, the echo intensity gradually decays due to inhomogeneous broadening and shows trends similar to the free induction decay (FID) as seen in the pump probe experiments.

The time dependent decay of the three-pulse photon echo peak shift (3PEPS) is known to capture the frequency correlation both at short and long timescales. However, the extraction of the slower timescales using 3PEPS involves several parameters and numerical fitting. As a result, several analogues have been introduced in the literature which can also extract the frequency correlation decay from the integrated echo intensity like the slope of 3-pulse photon echo (S3PE) as discussed in Section 2. Recent studies have shown that within impulsive limits, S3PE serves comparatively a better metric than the 3PEPS. In our present calculation, we have assumed the applied fields to be delta function pulses, thus the S3PE has been calculated to determine the frequency

Figure 3. Joint probability distributions of finding frequencies ω_1 and ω_3 at a time gap of t_2 for OD modes present in the first and second solvation shells and in the bulk of an aqueous solution containing a fluoride ion.

correlation loss of OD modes in the solvation shells and also in the bulk. The time dependent decay of S3PE for OD modes in the first and second solvation shells and also in the bulk are shown in Figure 5(b). We find that the decay of S3PE for the second solvation shell and the bulk are quite similar at short as well as long timescales. The timescales of spectral diffusion were calculated using a biexponential fit for the second solvation shell and bulk while a triexponential fit was used for the first solvation shell as per Eqs. 14 and 15. For bulk water, the shorter and the longer timescales of decay are found to be 64 fs and 2.48 ps, respectively. The longer timescale of decay for OD modes in the second solvation shell is found to be 2.94 ps which is not too different from that of bulk water. For water in the first solvation shell, a fast timescale of 52 fs, an intermediate timescale is 8.62 ps and then a longer timescale around 22.4 ps are found. We note that

the vibrational dynamics captured by S3PE in the solvation shells and the bulk are found to be in reasonably good agreement with that of FTCF.

4.3 2D-IR spectroscopy

The 2D-IR spectroscopy is known to capture the relaxation of the system in a very short time interval which is comparable to the time scale of vibrational dynamics. Unlike linear absorption spectroscopy which shows absorption averaged over time, 2D-IR spectroscopy captures time dependent absorption which can help to investigate the dynamics of different processes that lead to broadening of the linear spectrum. The 2D-IR spectrum of OD modes oscillating in the first and second solvation shells of the fluoride ion and also in the bulk for the waiting times of 10 fs, 3 ps and 20 ps are shown in

Figure 4. Time dependence of the residence correlation function and continuous ion-water hydrogen bond correlation function of OD modes.

Figure 5. (a) Integrated echo intensity for the bulk water as a function of t_1 , (b) S3PE of the OD stretch modes in the first and second solvation shells of the fluoride ion and in bulk.

Figure 6. Two dimensional infrared spectra of OD stretch modes in first and second solvation shells of the fluoride ion and in the bulk of an aqueous fluoride solution for different waiting times.

Figure 6. We note that while the nodal line separating the $0 \rightarrow 1$ and $1 \rightarrow 2$ resonances of the spectra for the bulk and second solvation shells get completely aligned with the horizontal frequency (ω_1) axis by 3 ps, the 2D-IR spectrum of the first solvation shell is still asymmetrical and the nodal line is aligned along the antidiagonal even at the waiting time of 20 ps. Several metrics have been proposed to obtain the timescales of vibrational spectral diffusion from the 2D-IR spectrum. In the present work, we have used the slope of the nodal line (SNL) to get the

timescale of frequency correlation from the 2D-IR spectrum. The time dependent decays of SNL for the 2D-IR spectra of bulk and solvation shells are shown in Figure 7. The timescales are obtained by using similar fits as already discussed in subsection 4.1. Three timescales are obtained for the first solvation shell which are: A very fast timescale of 30 fs in the sub-picosecond domain, an intermediate timescale of 8.59 ps and a longer timescale of 33 ps. Further, for the second solvation shell, two time scales are found which are 71 fs and 2.94 ps. The cor-

Figure 7. Time dependence of the slope of nodal line (SNL) of 2D-IR spectra of OD stretch modes in the first and second solvation shells of the fluoride ion and in the bulk of an aqueous fluoride solution.

Figure 8. Time dependence of the FTCF (fit), S3PE and SNL of water molecules in the first solvation shell of the fluoride ion in an aqueous fluoride solution.

responding timescales for the bulk solution are found to be 64 fs and 2.48 ps respectively. We note that the timescales for the second solvation shell and the bulk are quite comparable while that of the first solvation

shell is slower and has multiple timescales. Further, the timescales obtained for each of the cases are also in good agreement with those found for the decay of S3PE and FTCF. Finally, we have compared the FTCF, S3PE and

Table 1. Time scales of correlation decay of FTCF and vibrational echo spectral observables for water molecules in the first solvation shell, second solvation shell and the bulk region.

Metric	1 st Solv. Shell	2 nd Solv. Shell	Bulk
FTCF	50 fs, 8.46 ps, 27.5 ps	75 fs, 2.7 ps	69 fs, 2.54 ps
S3PE	52 fs, 8.62 ps, 22.4 ps	79 fs, 2.94 ps	64 fs, 2.48 ps
SNL	30 fs, 8.59 ps, 33.0 ps	71 fs, 2.94 ps	64 fs, 2.5 ps

SNL as a measure of spectral diffusion timescales in Figure 8. We note that the S3PE and FTCF are in very good agreement both at the short and long timescales. However, the agreement between the SNL and FTCF tends to get even better at longer timescales. In Table 1, we have included all the time scales of decay of FTCF and different metrics of 2D-IR spectrum that are calculated in the current study.

5. Conclusions

In the present work, we have performed *ab initio* molecular dynamics simulation of an aqueous solution containing a fluoride ion. We have investigated the dynamics of water molecules in the solvation shells of the ion by calculating the frequency time correlation function, joint probability distribution and also through calculations of various observables of vibrational echo and 2D-IR spectroscopy like S3PE and SNL. The decay of all the metrics for the second solvation shell and the bulk are found to be very similar at both the short and long timescales. This implies that the effects of the fluoride ion do not extend beyond the first solvation shell. The water molecules in the second solvation shell feel similar local environment as in the bulk. In contrast, the dynamics of water molecules in the first solvation shell is much slower and show multiple timescales with an overall temporal behavior that is different from that of the second solvation shell and bulk regions.

The calculations of residence time, ion-water and water-water hydrogen bond lifetimes show that for water in the bulk and second solvation shell, the longer timescales of decay of the frequency correlations are determined by the water-water hydrogen bond lifetime. For the first solvation shell, two slower timescales are found in the decay of FTCF, S3PE and SNL which are attributed to the ion-water hydrogen bond lifetime and residence time of water in the ion's first solvation shell. Further, we also note that the decay of FTCF is in good agreement with that of S3PE and SNL which

is a reaffirmation of the assertion that vibrational echo spectroscopic observables identify the loss of frequency correlation with time.

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