EVB and polarizable MM study of energy relaxation in fluorine-acetonitrile reactions

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Abstract

The H-abstraction reaction between fluorine atom and deuterated acetonitrile (CD_3CN) is highly exothermic and the resulting deuterium fluoride (DF) molecule is formed with a significant amount of energy that requires several picoseconds to relax into the solvent environment. Previous empirical valence bond (EVB) modelling work (*J. Chem. Phys.* **2015**, *143*, 044120) showed that reproducing the experimental relaxation timescale is quite sensitive to the potential energy surface (PES) used, and the physical effects responsible for cooling were not fully clear. Here, we study the rate of cooling on two new carefully designed PESs, and by comparison to behaviour on other PESs, this provides additional insight into these effects. The first PES is a MMFF (Merck Molecular Force Field) based covalent-ionic two-state EVB model constructed utilizing the valence-bond resonance structures of DF, which is shown to give a good description of the PES for interaction of hydrogen fluoride through hydrogen bonding with one acetonitrile molecule, but performs relatively poorly in predicting the vibrational relaxation rate in bulk solvent. The second new PES uses the polarizable AMOEBA force field formalism, and describes both the DF-acetonitrile dimer PES and the rate of vibrational cooling very well, with good computational efficiency. Comparison of those PESs shows that as well as a good description of the non-bonded interactions in the DF-acetonitrile dimer, successful prediction of cooling dynamics requires a good description of

many-body effects involving the supramolecular complex formed by DF, the H-bonded CD₃CN and nearby solvent molecules.

Keywords :

H-abstraction Reaction; Empirical Valence Bond; Many-body Effect; Relaxation Dynamics; Force field.

Dedication:

This paper is dedicated with warm respect to Prof. Mike Ashfold, in recognition of his many contributions to physical chemistry, chemical physics, and the eponymous journal.

Introduction

Most chemical reactions of importance in synthesis, the environment, and biochemistry take place in solution. Accordingly, understanding reaction dynamics in the solution phase has been the focus of extensive experimental and theoretical research.^{1–13} The solvent can play a role either in affecting the reaction path followed, or in modifying the properties of the reactant, product or intermediate species, or in more subtle ways by changing the dynamical behaviour along the reaction pathway or in the energy transfer processes that occur prior to and post reaction. The precise effects will depend on the microscopic properties of the solvent molecules (e.g., their dipole moment or vibrational frequencies) and on the macroscopic properties of the bulk solvent (e.g., its viscosity or its dielectric constant). Significant advances have been achieved by using transient spectroscopic techniques and theoretical simulations in understanding the reaction and post-reaction dynamics behaviour in solvated reactions.^{1,4,8,14–21} Gaining detailed insight in this area is challenging due to the frequent collisions taking place in solution phase and the complex solvent-solute coupling effects, and this complexity impacts on both experimental and

computational attempts to distinguish between competing explanations for a given observed outcome.

Simulation methods have the advantage of tracking time-resolved structural and dynamical details of rapid events at the molecular level, thereby providing intrinsic access to the time- and length-scales relevant to elementary reaction steps. This is much more challenging for experimental scientists, even when using state of the art characterization techniques. Nevertheless, computation has its own challenges, including being able to produce an accurate representation of the modelled reactivity, in terms of the potential energy surfaces (PESs) and the dynamical treatment of the problem. Also, gaining insight into the basic physical effects at play in a given system can often be, just as in experiment, masked by the complexity of the simulation outcomes. Concerning the first problem, despite their simplicity, molecular mechanics force fields can provide surprisingly good descriptions of solute-solvent interaction potentials. However, they are not usually able to describe most types of chemical reaction. In recent years, we have found that the empirical valence bond (EVB) approach^{22,23} provides an efficient technique for describing *reactive* PESs through allowing mixing of multiple valence states, the energies of which are typically expressed by more or less standard empirical molecular mechanics force fields. This makes it possible to describe bond breaking and formation in an elegant and computationally efficient way. More detailed descriptions of the empirical valence bond (EVB) approaches can be found in reviews and book chapters elsewhere.^{24–27}

Hydrogen atom abstraction from polar solvents (e.g., acetonitrile or dichloromethane) by fluorine atom represents a class of exothermic reaction with a small energy barrier and strong solvent-solute coupling that has been extensively studied experimentally^{17,28} and provides valuable insight into vibrational energy

relaxation of transiently formed product species. Additionally, these reactions are good diagnostic systems to study how the solvent is coupled to the reaction coordinate and can damp the nuclear dynamics. In some cases, deuterated solvents have been used in such experiments, for reasons of convenience associated with the spectral regions covered by the H/D-F vibrations, and also because the D-F vibrational band is less broad than the H-F one.^{17,28}

The reaction with CD₃CN has been studied the most, both experimentally and computationally. It leads to formation of vibrationally excited DF with roughly 55% in the $\nu = 2$ state and 44% in the $\nu = 1$ state.¹⁷ Strong interactions between the polar CD₃CN and DF molecules were suggested to play a role in damping the degree of excitation in the nascent product compared to what is observed in the gas phase.^{29,30} The nascent DF product undergoes a series of relaxation processes, with relatively rapid hydrogen bond formation with solvent (sub-picosecond) occurring in parallel with slightly slower vibrational relaxation by energy loss to solvent (~3-4 picoseconds).^{17,18} Both the transient spectral observations¹⁷ and theoretical simulations¹⁸ show complex competitive effects influencing the spectral behaviour of the DF product at short times, due to these two processes. Reaction with CH₃CN shows similar results.²⁸ However, experiment and theory also show that the timescale for vibrational cooling of nascent DF after D atom abstraction is very similar to that observed when pre-existing DF is vibrationally excited.^{17,18} Concerning this cooling, it takes what was described as “a surprisingly long time”,³¹ over multiple picoseconds, for the vibrationally excited DF to reach the ground vibration state, despite the in principle very strong interactions between this molecule and the solvent. Calculations show that this is part due to the fact that the timescale on which the solvent molecules rearrange themselves to accommodate the DF product is relatively long.

One noteworthy aspect of the computational studies of the reaction^{17,18} is that it proved surprisingly challenging to reproduce the observed timescale for vibrational coupling between the DF product and solvent. This was studied using classical trajectory simulations using an EVB approach to describe the reactive PES, and it was found that the rate of cooling depended strongly on the details of the PES, especially that part relating to the product DF region. In initial calculations,¹⁸ the interaction of DF with solvent was handled only through a simple electrostatic pairwise ansatz based largely on the Merck Mechanics Force field (MMFF).^{32–36} This initial PES, which could describe the initial D atom abstraction quite accurately, however led to very slow vibrational cooling. Artificial scaling of the D—F vibrational force constant, by leading to better spectral overlap with solvent, led to somewhat increased cooling rates, but still in very poor agreement with experiment. This deficiency in reproducing the time-evolution relaxation dynamics was attributed to the poor performance of the MMFF potential in describing structures within the CD₃CN---DF hydrogen bonded complex in which large vibrational stretching of the D—F bond leads to partial proton transfer character.¹⁸

Indeed, upon changing the PES so as to better describe the DF—acetonitrile interaction, much better cooling behaviour was obtained. This was done by expanding the EVB model significantly: the initial PES used just two EVB states, corresponding to F + CD₃CN and DF + CD₂CN connectivities, with the latter state also including the above-mentioned electrostatic interactions with solvent. The second-generation PES included a large number of proton-transfer CD₃CN⁺-D---F- states (and indeed one CD₂CN⁺-D---F- state) in the EVB description, with coupling parameters between these states and the standard neutral CD₃CN---DF state. The molecular mechanics terms used to describe the proton-transfer states, and the EVB coupling term, were chosen so as to reproduce the hydrogen-bond potential energy

surface in the bimolecular complex as determined from ab initio calculations. The resulting EVB model can be seen in Scheme 1. Although this model accounted well for experimental observations, it was computationally demanding, as it required a large number of valence states in the EVB modelling. Indeed, each additional solvent molecule in the simulation box required one additional state to construct the EVB matrix, thereby preventing the use of large solvent boxes and limiting its transferability to more complex systems.

Scheme 1. The multi-state EVB model adopted in the previous simulation work¹⁸ to study the reaction dynamics of $F + CD_3CN$. N corresponds to the number of solvent molecules in the periodic simulation box.

Also, this model, through its use of the proton-transfer states, leads to a quite complex modification of the underlying physical depiction of the interactions occurring between solvent and solute, making it harder to understand which physical effects are most important for accounting for the observed cooling behaviour. Accordingly, in this study we reexplore this system using a variety of different models, with the goal of gaining a better understanding of the precise solvation effects that are dominant, and thereby with the hope of assisting in models for

treating other solute-solvent coupling problems. Energy transfer between solutes and solvent is known to play a role in many chemical reactions.^{19,37–39}

One possible way to reduce the number of proton-transfer VB states would be, by analogy to the approach used when describing proton transport in protic solvents such as water, to dynamically adjust the number and nature of the EVB states included “on the fly” during the dynamics trajectory.^{15,40,41} We have chosen instead to test an EVB model providing an improved description of the DF electrostatics and intermolecular interactions, as well as a polarizable force-field approach. The first of these choices uses the two resonance forms of DF molecules – the covalent and ionic ones – familiar from traditional valence bond theory to provide an elementary description of this molecule and its interactions. The polarizable force field approach provides an alternative way to obtain an accurate treatment of the DF solute’s electrostatic potential in response to different solvent environments. In this work, we present detailed study of the parameterization of these two new models, and a detailed comparison of the description that they give of the relaxation dynamics, compared to the previous MMFF and EVB proton-transfer models. In line with most of the experimental work, we focus on relaxation dynamics of DF in the case of reaction in deuterated solvent, though of course the potential energy surfaces could equally well be used to treat the HF-containing system.

Computational Details

High level quantum chemical calculations using the complete active space self-consistent field (CASSCF) and the explicitly correlated multireference configuration interaction (MRCI-F12)^{42–44} method, combined with the aug-cc-pVTZ basis set, were conducted to calculate the energy and dipole moment of DF as a function of interatomic distance. Both the detailed results and detailed technical settings for these calculations are provided in the *Supporting Information*. Also, the

energies of previously studied¹⁸ different structures of the hydrogen-bonded CD₃CN---DF complex were refined using calculations at the CCSD(T)-F12_{45,46} level of theory using a larger cc-pVTZ-F12 basis set. The resulting potential energy surface is very close to that obtained previously, and again, more details are provided in SI. All these MRCI and CCSD(T) calculations were performed with the Molpro program.⁴⁷ Additional ab initio calculations were performed using various valence bond methods, especially the VBSCF/6-311+G** and VBCISD/6-311+G** (see ref. ⁴⁸ for a description of this method) approaches, using strictly localized VB occupied and virtual orbitals. These calculations were performed with the XMVB software.⁴⁹

EVB-related energy calculations and simulations were performed using our in-house⁵⁰ MPI-parallelized version of Tinker software.⁴⁹ Additional force-field terms such as standard and generalized Morse functions were also implemented for this purpose. In the covalent-ionic EVB model, the energy of the two diabatic states is modelled by a modified form of the MMFF force field. The van der Waals (vdW) parameter of atoms in CD₃CN and F⁻ in the ionic state used the original value, while the van der Waals terms were omitted for D⁺. For the covalent state, the vdW parameters for the D and F atoms were obtained by fitting to the CD₃CN---DF interaction energy surface. In the simulations utilizing the single-state (Non-EVB) MMFF and the covalent-ionic EVB model, the system was constructed by soaking one DF molecule in the centre of a pre-equilibrated CD₃CN solvent box of size 35.2 × 35.2 × 35.2 Å³ (density 0.84 g/ml), and the resulting system consisted of 1 CD₂CN, 1 DF and 499 CD₃CN molecules. Further equilibration was performed in the form of an NVT run of 100 ps with a time step of 1 fs at 300 K, followed by a further NVT run of 60 ps, from which six sets of coordinates and velocities were sampled every 10 ps. For these calculations, the Berendsen thermostat and the Velocity Verlet algorithm were used.

Additional EVB calculations were performed using the proton-transfer EVB model previously described,¹⁸ but which has been newly ported to be implemented using the in-house EVB Tinker code. For this system, a 2 ps simulation was performed using a cubic periodic box with length of 17.8 Å, containing 1 CD₂CN, 1 DF and 61 CD₃CN molecules, as in the previous work.

Polarizable MM simulations were performed using a single-state AMOEBA force field-type approach using Tinker version 8.5.⁵¹ In AMOEBA, the electrostatic interactions are described by permanent atom-centred multipoles up to quadrupoles, while the many-body polarization effect is explicitly considered by a mutual induced dipole scheme. The non-bonded parameters for CD₃CN adopted the original value in the force field,⁵² while the bonded parameters were slightly modified for the force constant of the C≡N and C—D bond stretches in order to reproduce the experimental frequencies (for details see **Table S3**). For the DF molecule, a polarizable and flexible AMOEBA model was constructed for this study. The D-F bond was treated by a standard Morse function with the form: $E_{DF} = D_e * (1 - e^{-\alpha(r-r_0)})^2 - D_e$, where D_e is the bond dissociation energy (BDE) of DF molecule, and $\alpha = \sqrt{\frac{D_e}{K}}$, K is the force constant (9.657 mdyn Å⁻¹) and r_0 is the DF equilibrium distance (0.917 Å). The vdW parameters of D and F were obtained by fitting to the ab initio post-product potential energy surface of the CD₃CN---DF complex. The atomic multipole parameter of DF was obtained by strictly following the seven-step protocol as addressed in the original AMOEBA paper.^{52,53} The resulting bonded and non-bonded parameters for the DF molecule in AMOEBA force field can be found in the *Supporting Information*. In the simulations, a solvent box with size of 25 × 25 × 25 Å³ was used, including 1 DF and 180 solvent molecules (the same density as above). Again as above, the system was initially equilibrated with a 1 ns NVT run at 300 K, and thirty sets of coordinates and velocities were then sampled every 10 ps from an

additional NVT run of 300 ps. Note that all parameter fitting carried out in this study was performed using python libraries and the nonlinear least-squares (NLLS) Marquardt-Levenberg algorithm.

The sampled snapshots mentioned above were used as the starting points for the non-equilibrium vibrational relaxation dynamics (NEVRD) simulations, for the starting point of which the DF molecule was instantaneously vibrationally excited, by modifying the radial D and F velocities taken from the sampling, while preserving the centre of mass velocity of the DF molecule. NEVRD trajectories were then obtained by carrying out NVE (constant energy and volume) propagation with a duration of 50 ps for the single-state MMFF and covalent-ionic EVB potentials, and 10 ps for AMOEBA force field, in each case with a short time step of 0.1 fs in order to conserve total energy. In all MM calculations, the van der Waals interactions used a 12 Å cutoff switching from 9 Å, and the long-range electrostatic interaction was treated by the Particle Mesh Ewald method with a 12 Å real space cutoff. The method used to monitor the time-dependent bond energy of DF for each trajectory is to average the DF kinetic energy over a time window long enough (e.g., 250 fs) to span several vibration periods, and the total energy of DF is approximated to be twice the kinetic energy based on the virial theorem. Based on previous results, the error of this method for the anharmonic DF Morse oscillator is expected to be lower than 15 % in the energy regime studied here.¹⁸ The graphs of DF energy further involve averaging over multiple trajectories.

Results and Discussions

DF Covalent-Ionic EVB Model

In the valence bond view, bonding in the hydrogen fluoride molecule can be considered to involve the mixing of three resonance structures, namely the covalent form D-F, and the ionic D⁺F⁻ and D⁻F⁺ forms.⁴⁸ Given that the D-F⁺ form has been

found to have a negligible contribution ($\sim 1\%$),⁴⁸ we here only consider the covalent D-F and ionic D⁺F⁻ forms in our EVB parameterization. In standard molecular mechanics force fields with fixed charges, the contribution of these two forms is thereby also fixed, with the consequence that the subtle variation in charge-separation of the DF molecule along the vibration coordinate is not well captured (**Figure S1**). In the covalent-ionic EVB matrix, the diagonal H_{11} and H_{22} terms describe the energy of the covalent and ionic forms (or “states” in EVB), and the off-diagonal element $H_{12} = H_{21}$ describes the coupling term between the covalent and ionic states. The expressions used for the potential energy curves of the two diabatic states of isolated DF were initially chosen based on the calculated potential energy curves for these states obtained from *ab initio* valence bond calculations. The covalent curve was described using a VBSCF method which generates a purely neutral D-F bonding state without any charge-transfer character. The ionic state was described using a VBCISD approach which allows polarization of the fluoride through the SCF procedure and through CI excitations to virtual fluorine-based orbitals, but does not include any covalent-like resonance forms. The D-F covalent state is found to be well described using a generalized Morse function form:

$$H_{11} = D_{cov}(1 - e^{-\alpha_1 * P_1(r) * (r - c_1)})^2 + E_d$$

$$P_1(r) = 1 + p_1 * (r - c_1) + p_2 * (r - c_1)^2 + p_3 * (r - c_1)^3$$

where D_{cov} is the BDE in kcal/mol and c_1 is the equilibrium bond distance in Å of the covalent D-F state, r is the D-F interatomic distance (Å), and α_1 , p_1 , p_2 and p_3 are Morse potential parameters. E_d is the energy difference between the BDE of the covalent D-F state and the adiabatic BDE of the D-F molecule determined by the MRCI-F12 method; this parameter is included so as to ensure that the correct energy reference is used.

It proved relatively difficult to choose an adequate functional form for the ionic state curve, requiring careful account to be taken of the variation in dipole moment upon bond stretching. The procedure followed is shown in **Figure S2**. Briefly, the MRCI-F12 dipole moment first increases upon stretching from the equilibrium bond length, then decreases. This provides a guideline for the point at which ionic state admixture to the adiabatic wavefunction ceases to be important, and thereby also for the relative energy of the covalent and ionic states. Furthermore, we noted that the buffered coulombic expression³³ used in MMFF provides a reasonable zeroth-order description of the VBCI ionic state curve. The energy difference between VBCISD and the buffered coulombic term is well described by a generalized Morse form (**Figure S3**). The resulting final expression used to describe the ionic diabatic state of isolated DF is thereby as follows:

$$H_{22} = IP(D) + EA(F) + D_e + E_{Coulombic} + a_2 * (1 - e^{-b_2 * P_2(r) * (r - c_2)})^2 - a_2$$

$$E_{Coulombic} = \frac{332.0716 * q_D * q_F}{(r + 0.05)}$$

$$P_2(r) = 1 + p_4 * (r - c_2) + p_5 * (r - c_2)^2 + p_6 * (r - c_2)^3$$

in which $IP(D)$ is the ionization energy (kcal/mol) of the D atom, $EA(F)$ is the electron affinity of the F atom, the D_e is the BDE of ground state DF, $E_{Coulombic}$ is the electrostatic energy calculated by the buffered coulombic functional form, q_D and q_F are the charges (+1 and -1) on D and F, and a_2 , b_2 , c_2 , p_4 , p_5 and p_6 are the Morse parameters. By construction, this expression correctly reproduces the energy gap between the covalent and ionic states at the dissociation limit, *i.e.*, the value of $IP(D) + EA(F)$, since $E_{Coulombic}$ and the Morse part tend to zero in this limit (*Supporting Information for more details*).

H_{12} is used to describe the coupling between the covalent and ionic state and is determined as the combination of three one-dimensional Gaussian functions of the

D-F distance (r), with the parameters chosen to get a satisfactory fit. The general expression used for H_{12} is shown as follows:

$$H_{12} = \sum_{i=1}^3 A_i * \exp \left\{ -\frac{1}{2} \left(\frac{(r - C_i)}{\sigma_i} \right)^2 \right\}$$

in which A_i , C_i and σ_i correspond to the amplitude, center and width of the i th Gaussian function. In the fitting, several parameters in the diagonal and off-diagonal matrix element expressions are varied in order to reproduce as accurately as possible both the MRCI-F12 energies and dipole moments. The final parameters are listed in Table S2.

The resulting covalent-ionic EVB model for the energy and dipole moment of the isolated DF molecule is displayed in **Figure 1**. The root mean square derivations (RMSD) of the energy with respect to MRCI-F12 is under 0.1 kcal/mol, and the RMSD in the dipole moment is 0.025 e*Å. As can be seen, the covalent H_{11} and ionic H_{22} curves have minima for interatomic distances near 0.86 Å and 0.98 Å, respectively, and the energy difference of these two states is at a minimum around the interatomic distance of 1.15 Å. The coupling H_{12} is large at shorter D-F distances, as expected since this off-diagonal coupling involves charge transfer.

Figure 1. Potential energy (kcal/mol) curve and dipole moment of DF molecule as a function of interatomic distance ($\text{\AA}$) obtained at the MRCI-F12/aug-cc-pVTZ (blue) level and the fitted covalent-ionic EVB model. H_{11} , H_{22} and H_{12} corresponds to the covalent state, ionic state and their coupling element.

We then applied this covalent-ionic model, that accurately describes the change in polarity of DF upon stretching, by carrying out simulations in a solvent box. In order to be able to treat the solvated system, van der Waals and Coulombic interactions between the solvent and the D and F atoms are included in the diagonal H_{11} and H_{22} terms, as well as all the other MM terms associated with the solvent. The H_{12} interaction parameterized for the isolated molecule is used without further modification. By including interaction with the solvent, the covalent-ionic EVB

model allows for polarization of the solute due to the environment. We first tested the accuracy of this new model by computing the potential energy surface of the $\text{CD}_3\text{CN} \cdots \text{DF}$ complex, yielding an RMSD of 2.9 kcal/mol with respect to the CCSD(T)-F12 energies (**Figure 2** for linear H-bonded complex and **Figure S4** for non-linear H-bonded complex). This compares very favourably to the results obtained with the previous EVB model including proton-transfer states (RMSD of 2.3 kcal/mol). As pointed out previously,¹⁸ the original MMFF underestimates the amount of coupling between CD_3CN and DF in regimes with elongated D-F distances and decreased N-D distance, and predicts a much larger energy for those structures, thus leading to a much larger RMSD of 16.0 kcal/mol. Hence the new covalent-ionic EVB model, as hoped, is able to provide a very good description of the solvent-solute interaction in the vicinity of the hydrogen-bonded complex, despite using a representation that is in many ways much simpler than the EVB model including proton-transfer states.

Figure 2. Contour plot of the covalent-ionic EVB energies (kcal/mol) in the potential energy surface of linear CD₃CN---DF complex as a function of the F-D and N-D distances. The colour of the points indicates the energy difference between the covalent-ionic EVB energy and CCSD(T)-F12 energy at the given geometry.

Accordingly, this new potential energy surface was used in NEVRD simulations in solution, in a similar way to those carried out previously.¹⁸ Vibrationally excited DF was generated with an initial energy of ~35 kcal/mol by instantaneous addition of the requisite kinetic energy into the radial D-F motion, otherwise taking the positions and velocities from standard molecular dynamics equilibration runs. Our calculations focus on the vibrational cooling, rather than the whole F atom reaction followed by cooling, even though this could be easily described by including one additional EVB state corresponding to reactants in the model. This choice was made because the full reactive dynamics was well-addressed in the previous EVB work, and that study additionally showed that NEVRD trajectories shows DF cooling at roughly the same rate as observed in the reactive dynamics.¹⁸ **Figure 3** shows the time-evolution of the vibrational energy of the DF molecule in NEVRD runs using the MMFF PES and the covalent-ionic EVB PES. The former approach is very similar to that reported previously, and indeed leads to very slow cooling. We note that the time constant obtained here (267.1 ps) differs from that reported earlier (764 ps) perhaps due to slight differences in the vibrational excitation protocol, the vibrational energy analysis routine, and the simulation code (Tinker vs. CHARMM). We note also that as the NEVRD runs were only 50 ps long and thereby much shorter than the cooling timescale, numerical error in fitting the time constant may also intervene.

The covalent-ionic EVB PES predicts a significantly faster relaxation dynamics, which is also well fitted using a single exponential decay function, with a time constant of 60.2 ps, i.e. much smaller than the one obtained with MMFF.

However, this timescale is still much longer than that observed in experiments¹⁷ and the multi-state EVB simulation with proton-transfer states,¹⁸ where cooling occurred in several ps. This shows that polarization of the DF solute by solvent, and accurate description of the hydrogen bond potential energy surface are not sufficient to ensure a good description of energy relaxation.

Figure 3. Energy relaxation profile of vibrationally excited DF molecule in equilibrated solvent predicted by the covalent-ionic EVB model and the original MMFF model.

Considering the failure of the original MMFF and covalent-ionic EVB PESs, and the success of the EVB PES including proton-transfer states,⁵⁴ we therefore conclude that some interactions present in the latter PES must play an important role in the energy relaxation. The original MMFF represents the simplest PES used so far to probe the relaxation dynamics; it omits changes in the charge distribution of the DF molecule as it vibrates and also misrepresents the section of the potential energy surface involving strong vibration of the hydrogen-bonded $\text{CD}_3\text{CN}\cdots\text{DF}$ complex so its failure is not surprising. On the other hand, the covalent-ionic EVB PES captures both of these effects, so the slow (albeit faster than MMFF) cooling is

more surprising. The proton-transfer EVB PES also accounts for these effects, but crucially it also leads to changes in the charge distribution within the hydrogen-bonded CD₃CN moiety, and indeed allows for some charge transfer to it. In turn, this leads to differences in the interactions between this ‘first solvation sphere’ CD₃CN molecule and the second sphere of solvent, and we suspected that these ‘many-body’ effects might be playing a role in the fast cooling. To test this hypothesis, we turned to a completely different approach, using a polarizable force-field, that also allows for such effects.

AMOEBA Polarizable Force Field

To provide an accurate description of the polarization effect, several approaches have been developed in recent years, such as assigning Drude oscillators^{55,56} around the atom, treating partial charges as dynamical variable (fluctuating charge model),⁵⁷ or incorporating both atomic higher order moments and atomic induced dipoles.^{52,53} The AMOEBA force field belongs to this last family of polarizable models was chosen for this study due to its flexibility and its availability in the Tinker software. As described in the computational details section, we have used existing AMOEBA parameters for CD₃CN (with slight modification of some bonding terms), and have developed our own parameters for the DF molecule. The post-product PES of linear CD₃CN---DF H-bonded complex predicted by our new AMOEBA force field is shown in **Figure 4**, and energies of the CD₃CN---DF complex for non-linear structures are shown in **Figure S5**. As seen, AMOEBA shows a satisfactory performance in reproducing the high-level CCSD(T)-F12 PES without requiring extensive parameter fitting (RMSD error of 2.2 kcal/mol). We note however that **Figure S5** shows that the AMOEBA potential does not describe the energies of highly bent structures all that accurately; since

during the dynamics the system mostly samples roughly collinear structures. The energy difference between AMOEBA and CCSD(T)-F12 at most linear geometries is less than 3 kcal/mol, and this highlights the capability of the intrinsic many-body polarization interaction scheme implemented in AMOEBA to capture the nature of the interaction between DF and CD₃CN.

Figure 4. Contour plot of the AMOEBA energies (kcal/mol) in the potential energy surface of linear CD₃CN...DF complex as a function of the F-D and N-D distances. The colour of the points indicates the difference between the AMOEBA energy and CCSD(T)-F12 energy at the given geometry.

Figure 5. NEVRD average relaxation profile of vibrationally excited DF obtained by using the AMOEBA force field. The profile is fitted by the sum of two exponential decay functions (black), with the indicated amplitudes and time constants.

NEVRD simulations using AMOEBA force field were conducted for 30 individual trajectories, and the average time-dependent vibrational energy of the DF molecule is shown in **Figure 5**. Within a few vibrations, an initial amount of ~5 kcal/mol amount of energy is rapidly relaxed to the solvent, with the remaining energy dissipating more slowly. In line with previous experience,^{17,18} this relaxation energy curve cannot be well fitted using a single exponential (see **Figure S6** in the SI), while a bi-exponential fit (as also shown in **Figure 5**) is very accurate. The first relaxation period, with an amplitude of 20.41 kcal/mol, occurs with a short time constant $\tau_1 = 1.89$ ps, followed by a slower process with $\tau_2 = 15.18$ ps and amplitude of 11.04 kcal/mol. Although the time constants and amplitudes do not match the previous results exactly (the proton-transfer EVB PES gave 0.49 ps, 5.0 ps for the timescales upon vibrational excitation of equilibrated DF as also done here), the qualitative agreement with the previous proton-transfer EVB work¹⁸ is excellent,

both in terms of the dual timescale and speed of relaxation. The origin of the multiple time-scales in the relaxation was previously suggested to be linked to the fact that at high vibrational energy, DF has extensive spectral overlap with the solvent, with this overlap decreasing at longer times. However it was also noted that multiple timescales for relaxation are commonly found in solution, due to differences in timescale for solvent translational, vibrational, and long-range relaxation to a perturbation. Similar reasons are no doubt operative here.

Returning to the main topic of this article, it can be seen that indeed many-body effects do seem to play an important role in relaxation (Table 1), since these effects are present in our new AMOEBA-based PES, and again fast relaxation is observed, as with the large EVB PES including proton-transfer states. Clearly, it is not sufficient to include a good description of DF anharmonicity and the two-body solute-solvent hydrogen bonding interaction in order to describe the phenomenon accurately. In order to understand this point more clearly, we decided to analyse the micro-environment of the DF molecule during the relaxation dynamics, as modelled by the original MMFF PES, the covalent-ionic EVB PES, the EVB PES with proton-transfer states, and the AMOEBA PES. For this purpose, two sets of simulations were analysed, based on additional simulation for a duration of 1 ps, initiated with either “hot” DF and the “cold” DF in the equilibrated solvent bath, in which “hot” means that the solute was initially placed in a vibrationally excited form in the same way as described above, whereas “cold” means that no such excitation was performed. The 1 ps timescale of these simulations is short enough that only mild cooling is expected to occur in the “hot” case.

Table 1. A summary of the properties of the four PESs used to model the dynamics of energy relaxation of DF in CD₃CN.

	MMFF	Covalent-Ionic EVB	Proton- Transfer EVB	AMOEBA
Polarizability of DF	no	yes	yes	yes
D-F anharmonicity treatment	good	good	good	good
Treatment of N---D hydrogen bond through	electrostatics	electrostatics ^a	Partly covalent	electrostatics ^b
PES for H-bond dimer	poor	good	good	good
Polarization of the H-bonded solvent	absent	absent	present	present
Vibrational relaxation rate	very slow	slow	fast	fast
Computational Expense	very low	low	medium	low

^a Also involving resonance between D-F and D⁺---F⁻ forms.

^b Polarized electrostatics.

Visual inspection and detailed analysis of these trajectories allowed us to identify one key coordinate which differs significantly between the ‘slow cooling’ MMFF and covalent-ionic EVB PESs and the ‘fast-cooling’ EVB with proton-transfer states and AMOEBA PESs. This is the distance between the nitrile sp carbon atom C_a of the hydrogen-bonded solvent molecule and the nitrogen atoms N_b of the next-nearest solvent molecules within the second coordination sphere. **Figure 6** shows calculated radial distribution functions $g(r)$ obtained for the C_a -- N_b distance for the fully equilibrated DF molecule, based on dynamics using the different PESs. As can be seen, the ‘fast cooling’ AMOEBA and EVB with proton-transfer states PESs show an onset for the main short-range peak at somewhat shorter distances. A similar difference is also observed when the DF molecule is vibrationally excited, see supporting information (**Figure S7**). The small but significant change in distribution for this distance can be attributed to the hydrogen-bonded molecule’s C_a

becoming more electron deficient upon interacting with DF, leading in turn to a more attractive interaction with the negatively-charged nitrile N_b.

The present results show that many-body effects obtained within solvent cages can impact severely on rates of energy transfer, especially when strong anisotropic interactions such as hydrogen bonds are present. One way of describing these effects emphasizes the quasi-molecular aspect of the formed assemblies: the DF, H-bonded solvent molecule and the nearby multiple solvent molecules are viewed to form a supramolecular interaction complex (**Figure 7**), in which energy relaxation adopts some of the character of intramolecular vibrational energy redistribution (IVR), thereby becoming faster than the intermolecular transfer needed when interactions are weaker. Patterns for IVR are well known to be complex,⁵⁸ but by and large intramolecular transfer does tend to be faster than intermolecular. Here, the covalent-ionic EVB PES and the original MMFF PES, which do not include any description of the necessary many-body character, lead to slow energy relaxation. In previous work for reaction with weak solute-solvent coupling, namely, for the $\text{CN} + \text{C}_6\text{H}_{12} \rightarrow \text{HCN} + \text{C}_6\text{H}_{11}$ reaction in dichloromethane solvent, a first phase of rapid efficient energy relaxation of the nascent HCN is observed, followed by slower cooling. This was attributed to initial cooling within a solvent-cage-coupled two-body dimer of HCN and the C₆H₁₁-coproduct, with slower cooling resulting after these coproducts diffuse away from each other.^{16,59,60} The situation becomes different for reactions with strong solute-solvent coupling, where multiple solvent molecules can participate to form a many-body complex including the solute, facilitating energy relaxation.

Figure 6. Radial distribution function $g(r)$ of the C_a-N_b distance during the 1 picosecond dynamics trajectories of vibrationally ground state DF in equilibrated solution as modelled by different PESs. C_a denotes the nitrile sp-hybridized C of the H-bonded solvent molecule and N_b is the N atom of other solvent molecules.

Figure 7. A typical snapshot (with distances in Å) of the supramolecular complex in its microsolvation environment. Colour scheme for the solvation environment near the solute: H: white, F: pink, C: cyan, N: blue.

Conclusions

In this work, the nature of the interactions leading to vibrational energy relaxation of a ‘hot’ DF solute in acetonitrile solvent has been explored using classical molecular dynamics and a variety of different interaction potentials. This includes a modified form of MMFF, a covalent-ionic two-state EVB PES describing D-F in terms of resonance between a covalent D-F form and an ionic $D^{+...}F^{-}$ form, the previously reported multi-state EVB PES including multiple proton-transfer $CD_3CN-D^{+...}F^{-}$ states, and a newly parameterized AMOEBA polarizable force field for DF in acetonitrile. MMFF leads, as reported previously, to extremely slow vibrational cooling, in very poor agreement with experiment. The new covalent-ionic EVB PES shows a much better performance than MMFF for describing the vibrational anharmonicity of the DF bond and its H-bond interaction with a single solvent molecule. This also leads to improved relaxation behaviour, faster than that with MMFF by a factor of four, but still much slower than experiment. The new AMOEBA PES, on the other hand, emulates the previously described proton-transfer EVB model in reproducing the rapid cooling.

One important note concerns the efficiency of the different PESs: the MMFF PES is simplest and also allows for the fastest calculations. The new covalent-ionic PES is also very efficient. The EVB model with many proton-transfer states is relatively efficient, but limits simulations to relatively small solvent boxes as it requires one additional EVB state for each additional solvent molecule, at least with the approach used here. The newly parameterized AMOEBA model is thereby much more efficient computationally, and indeed we have been able to perform much

larger simulations with this model than with the previous proton-transfer EVB PES. However, at present this model is not able to describe the chemical reaction, only the post-reaction dynamics of DF in solvent.

The different outcomes of the relaxation dynamics using the different PESs confirm that the DF-acetonitrile system is extremely sensitive to the detailed description of the interaction between DF and solvent. Even the simplest PES used here – based on the MMFF forcefield – provides a reasonable description of the key interactions involved, in that both the structure and the dissociation energy of the $\text{CD}_3\text{CN}\cdots\text{DF}$ hydrogen-bonded complex are fairly well reproduced.¹⁸ This MMFF potential is similar in quality to that used in many molecular dynamics studies of vibrational energy relaxation. Our work suggests that caution is needed when interpreting the results of such MD studies whenever complex interactions of the type present here are suspected. We previously suggested¹⁸ that a key factor in reproducing the rate of vibrational cooling was to include a satisfactory description of the PES in this complex at distorted structures around its equilibrium structure, especially upon partial D^+ transfer to solvent. However, the two PES models used in our previous study differed in multiple ways, not just in terms of this aspect, so it was difficult to be certain about which factor exactly was dominant.

Analysis of the microsolvation structure around the DF molecule during these dynamics simulations with these different PESs suggests that the difference in cooling behaviour between the different models relates to the way in which additional solvent molecules interact with the $\text{CD}_3\text{CN}\cdots\text{DF}$ hydrogen-bonded pair. As both the AMOEBA model and the proton-transfer state EVB model lead to polarization of the hydrogen-bonded acetonitrile, it interacts more attractively with additional solvent molecules. Our work thereby shows that a good description of the solute-solvent interaction may not always be a sufficient factor for modelling energy

relaxation from solute to solvent bath, as second solvent-sphere interactions may also play a role. We note that agreement with experiment concerning the rate of vibrational cooling provides only an ambiguous criterion for judging the accuracy of a PES, since it is conceivable to have good agreement for the rate of cooling with an otherwise very imperfect potential energy surface, and pinpointing which particular feature of a PES leads to poor agreement concerning the rate of cooling is also very difficult. The present comparative study of four different PESs for a very sensitive case however provides new insights into the factors that are important in solvent-solute coupling, by analysing the different PESs and the properties of the ensembles of structures that they generate during dynamics, and correlating these with the observed rate of cooling.

Conflicts of Interest

There are no conflicts to declare.

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