



Theoretical-computational modelling of the vibrational relaxation of small inorganic species in condensed phase

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ABSTRACT

In this paper we apply a recently developed theoretical-computational procedure for modelling the Vibrational Energy Relaxation (VER) of solvated chromophores represented by small inorganic species. In particular we focus our attention on four different systems, all experimentally well characterized: aqueous cyanide ion and aqueous azide ion, nitrogen dioxide and water both in chloroform. Our method essentially reconstructs the whole vibrational relaxation kinetics (with the chromophore in the ground electronic state) by: (i) determining, through semiclassical Molecular Dynamics (MD) simulation, the electric field (perturbation) produced onto the chromophore by the solvent atom motions; (ii) using the electrostatic perturbation for directly determining the chromophore quantum vibrational dynamics; (iii) calculating the rate constant for the vibrational relaxation as occurring *without* quantum-classical energy exchange; (iv) introducing the latter effect, *a posteriori*, hence obtaining the actual relaxation kinetics. Our results, in satisfactory agreement with the available experimental data, show that the VER mechanism is almost entirely determined by the fluctuating perturbation field as produced by the time-dependent motions of the environment atoms (in these cases the solvent) similarly to the well-known effects of the electromagnetic wave causing absorption/emission processes.

Introduction

In a recent paper [1] we have described a new theoretical-computational method aimed at modelling the dynamics and the kinetics of the Vibrational Energy Relaxation (VER) [2–8] of a chromophore embedded in a complex atomic-molecular environment. The basic features of the proposed approach are essentially based on the effects of the perturbation of the electric field exerted by the atomic-molecular environment (e.g. the solvent) onto a chromophore, hereafter termed as Quantum Centre (QC), as obtained by classical Molecular Dynamics (MD) simulations of the whole system (i.e. QC and environment semiclassical degrees of freedom are treated as purely classical mechanical degrees of freedom and thus usual atomistic MD simulations can be employed). Such a time-dependent environment-induced perturbation, beyond providing the inhomogeneous broadening of the spectral line-shape [9] determines the quantum-state transitions as described in our recent paper [1], similarly to the well-known effects of the electromagnetic wave causing absorption/emission processes.

The evaluation 'a posteriori' of the density matrix of the perturbed QC quantum (vibrational) states along a series of independent MD trajectories, allows to reconstruct the VER kinetics to be compared to the experimental, essentially time-resolved spectroscopic [10] data. In this respect, although the above features could ascribe such a method to the

set of the well-assessed mixed Quantum-Classical approaches developed in the last years at the same purpose, (see for example Refs. [11–13] its theoretical framework as well as the VER interpretation, also based on its first application on aqueous deuterated N-methyl-acetamide (D-NMA) [1] appear as substantially different. As a matter of fact such application for modelling the kinetics of amide-I mode relaxation of aqueous D-NMA (accurately reproducing the experimental data [14–16]) strongly suggested that the main determinant of the whole VER process is to be identified with the semi-classical time-dependent perturbation acting on the QC. It readily follows that any other effect, possibly present and in principle important for driving the VER in the gas-phase systems, (see for example Fujisaki and coworkers [17]) plays a less relevant role for these processes in solution.

In this paper we report further applications of our method for better assessing its peculiar features, the advantages as well as possible limitations and drawbacks. In particular, as test cases, we have modelled the VER kinetics of a series of small inorganic solutes in solution [10], namely:

- (i) the relaxation of the vibrational mode of aqueous cyanide ion, an extensively investigated species both experimentally [18,19] and theoretically; [20–30]

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- (ii) the relaxation of the anti-symmetric stretching mode of aqueous azide ion; [31]
- (iii) the relaxation of the anti-symmetric stretching mode of nitrogen dioxide in chloroform; [32].
- (iv) the relaxation of the bending mode of water in chloroform [33,34].

In the first part of this work we concisely review the theoretical framework and its implications. Subsequently, after a description of the adopted computational protocol, we illustrate the results, their com-

$$\tilde{\rho}(t) = \left\langle e^{-\frac{i\hbar}{\hbar} \int_0^t \tilde{H}(t') dt'} c(t) c^\dagger(t) e^{\frac{i\hbar}{\hbar} \int_0^t \tilde{H}(t') dt'} \right\rangle = \frac{1}{N} \sum_{n=1}^N e^{-\frac{i\hbar}{\hbar} \int_0^t \tilde{H}_n(t') dt'} c_n(t) c_n^\dagger(t) e^{\frac{i\hbar}{\hbar} \int_0^t \tilde{H}_n(t') dt'} \quad (2)$$

parison with the experimental data as well as the implications emerged from analysis of our numerical experiments.

Theory

In this subsection we only provide a brief summary of the theoretical model described in details in our previous paper [1], and also in [Supporting Information](#) attached to this paper. The proposed model is entirely based on a number of basic assumptions/approximations which can be summarized as follows:

- We always focus our attention on a sub-part of the system to be described at quantum mechanical level, the quantum centre (QC), perturbed by a time-dependent field exerted by the atomic-molecular environment as obtained by, e.g., a semi-classical MD trajectory [35].

Of course the definition of the QC usually, though not necessarily [1,36] coincides with the solute under investigation.

- All the QC semi-classical coordinates (i.e. those degrees of freedom, either rototranslational or internal, well described by wave-packets)¹ are always decoupled from the QC quantum degrees of freedom (i.e. all the other degrees of freedom incompatible with any classical approximation) and, hence, always treated by means of classical MD simulations. Note that for all the degrees of freedom we disregard any possible quantum/classical change of character.

The main goal is, then, to evaluate the instantaneous QC dynamical quantum (vibrational) state along a MD trajectory. At this purpose we use the time-dependent eigenstates of the QC Hamiltonian operator (excluding the semi-classical kinetic energy) $\widehat{H}(\widehat{x}_q, \widehat{p}_q, x_{sc})$ as basis set, where \widehat{x}_q , \widehat{p}_q are the quantum coordinates and related conjugated momenta operators and x_{sc} are the semi-classical coordinates acting as time-dependent parameters. It readily follows that we can define the QC quantum state as

$$|\Psi(t)\rangle = \sum_j c_j(t) e^{-\frac{i\hbar}{\hbar} \int_0^t \mathcal{H}_j(x_{sc}(t')) dt'} |\phi(x_{sc}(t))\rangle \quad (1)$$

Where $\phi(x_{sc}(t))$ are the time-dependent Hamiltonian eigenstates (i.e. $|\phi_j\rangle = |\phi_e \phi_{v,j}\rangle$ with $|\phi_e\rangle$ the proper electronic eigenstate and $|\phi_{v,j}\rangle$ the corresponding j -th vibrational eigenstate) and $\mathcal{H}_j(x_{sc}(t))$ the corre-

¹ According to Quantum Mechanics the quantum state with a dynamics mostly resembling the classical one, is the wavepacket defined at each time by a wavefunction confined within a tiny phase-space volume. Once assuming the semi-classical coordinates well described by wavepackets in the whole process, then the dynamics of such degrees of freedom can be well approximated by the classical-mechanical equations of motions. (see for example P.A.M. Dirac 'Principles of Quantum Mechanics' - Oxford Science Publications)

sponding eigenvalues (note that we only consider Hamiltonian eigenstates involving the same electronic eigenstate as we deal with modelling typical vibrational relaxations).

The solution of the time-dependent Schroedinger equation, along a given trajectory by using the above defined ket, provides us with $c(t)$ of components $c_j(t)$ (i.e. the QC dynamical quantum state within the $e^{-\frac{i\hbar}{\hbar} \int_0^t \mathcal{H}_j(x_{sc}(t')) dt'} |\phi_j\rangle$ basis set) and, hence, with the density matrix (within the perturbed eigenstate $|\phi_j\rangle$ basis set)

Where \tilde{H}_n are the diagonal Hamiltonian matrices representing for each n -th trajectory the Hamiltonian operator within the corresponding eigenstate basis set, the angle brackets indicate an average over the proper statistical ensemble defined by N QC-environment independent trajectories and c^\dagger is the adjoint of c . Note that when dealing with QC-environment systems involving semi-classical degrees of freedom we should in principle have $N \rightarrow \infty$ in order to obtain a proper statistical ensemble within the system phase space. The diagonal elements of the density matrix

$$[\tilde{\rho}(t)]_{ll} = \rho_{ll} = \frac{1}{N} \sum_{n=1}^N c_{n,l}(t) c_{n,l}^*(t) = \langle c_l(t) c_l^*(t) \rangle = [\tilde{\omega}(t)]_{ll} = \omega_{ll} \quad (3)$$

provide the probability of each eigenstate with $c_{n,l}$ the l th component of the c_n vector and

$$\tilde{\omega}(t) = \langle c(t) c^\dagger(t) \rangle = \frac{1}{N} \sum_{n=1}^N c_n(t) c_n^\dagger(t) \quad (4)$$

the density matrix representing the density operator within the time and trajectory dependent $e^{-\frac{i\hbar}{\hbar} \int_0^t \mathcal{H}_j(t') dt'} |\phi_j\rangle$ basis set. In typical condensed phase conditions we can safely assume that the density matrix rapidly converges to the statistical regime [1] and thus the density matrix diagonal elements can be equivalent to the solution of usual kinetic equations. Therefore, we can reconstruct the whole kinetics by evaluating the 2×2 density matrices providing the two-state relaxations for each of the relevant vibrational eigenstate couple inter-conversions (i.e. each inter-conversion rate constants are independent of the other inter-conversions). Considering as the initial state, for the relaxation reaction, a given vibrational excited state of the electronic ground state (i.e. the vibronic reactant, R) we can thus describe the relaxation process by modelling independently all the relaxations from R to (in principle) each of the other vibrational eigenstates of the electronic ground state (i.e. the vibronic reactant, P).

By using Eq. (1) in the time-dependent Schroedinger equation and making use of proper derivations, we can obtain the equation for the coefficients of the reactant (c_R) and product (c_P) vibrational eigenstate [1]

$$\begin{bmatrix} \dot{c}_R \\ \dot{c}_P \end{bmatrix} = \begin{bmatrix} 0 & \Omega \\ -\Omega^* & 0 \end{bmatrix} \begin{bmatrix} c_R \\ c_P \end{bmatrix} \quad (5)$$

where by adopting the following approximations [1]:

- Invariant mode approximation [37]: we assume environment perturbation affecting the mode frequency without significantly

altering the vibrational mode definition (i.e. the mass-weighted Hessian eigenvector).

- Negligible anharmonic coupling among the quantum vibrational modes (we only consider intramode anharmonic effects);
- Negligible multiple mode excited eigenstates;
- Strong similarity between the QC perturbed and unperturbed electronic eigenstate;
- We only consider rigid or semi-rigid QC's: note that a flexible QC can be conceived as a collection of conformational basins, each basically equivalent to a rigid or semi-rigid QC, and thus even a flexible QC can be treated as a collection of rigid or semi-rigid QC's;
- Negligible shifts of the electronic energy minimum structure: in rigid/semi-rigid QC's significant shifts can only occur in the presence of extremely intense perturbing fields, far beyond the typical soft condensed matter perturbation [38]; the matrix element Ω is defined as

$$\Omega \cong \frac{-\dot{E} \cdot \sum_l \frac{\partial \mu^o}{\partial \beta_l^o} \langle \Phi_{v,R} | \Delta \beta_l | \Phi_{v,P} \rangle}{\mathcal{U}_R - \mathcal{U}_P} e^{-\frac{i\pi}{\hbar} \int_0^t (\mathcal{U}_P(t') - \mathcal{U}_R(t')) dt'} + \frac{-\dot{E} \cdot \frac{1}{2} \sum_l \sum_{l'} t \frac{\partial^2 \mu^o}{\partial \beta_l^o \partial \beta_{l'}^o} \langle \Phi_{v,R} | \Delta \beta_l \Delta \beta_{l'} | \Phi_{v,P} \rangle}{\mathcal{U}_R - \mathcal{U}_P} e^{-\frac{i\pi}{\hbar} \int_0^t (\mathcal{U}_P(t') - \mathcal{U}_R(t')) dt'} \quad (6)$$

In the previous expression: (i) \dot{E} is the time-derivative of the perturbing electric field at the QC centre of mass (when using typical MD simulations E is approximated by the field due to the environment atomic charges); (ii) $\frac{\partial \mu^o}{\partial \beta_l^o}$ and $\frac{\partial^2 \mu^o}{\partial \beta_l^o \partial \beta_{l'}^o}$ are the first and second unperturbed electronic dipole derivatives evaluated at the minimum of the QC unperturbed electronic energy surface; (iii) β_l^o , $\Delta \beta_l$ are the unperturbed l -th mode coordinate and the (perturbed) l th mode coordinate shift from the actual energy minimum and (iiii) \mathcal{U}_R , \mathcal{U}_P are the reactant and product Hamiltonian eigenvalues (possibly involving intramode anharmonic effects), which when dealing with vibrational relaxations provide a corresponding energy shift ($\mathcal{U}_R - \mathcal{U}_P$ or $\mathcal{U}_P - \mathcal{U}_R$) that can be considered constant and given by its mean value, i.e. negligible effects of the vibrational excitation frequency time-dependent fluctuations [1]. Note that when dealing with typical vibrational relaxations, i.e. involving only vibrational eigenstates of the electronic ground state, the reactant state is an excited vibrational eigenstate and the product one corresponds either to the vibrational ground state or to another excited vibrational eigenstate (we only consider excited vibrational eigenstates involving a single mode excitation). As explained in details in our previous paper [1] (see also the [supporting information](#) of this paper) the numerical solutions of Eq. (5) evaluated *a posteriori* over a statistically meaningful set of QC-environment classical MD simulations (i.e. the classical dynamics is fully independent of any quantum transition), provide the reactant to product eigenstate relaxation kinetics within a peculiar statistical ensemble: the invariant free energy ensemble where the vibrational state transitions occur without energy exchange between quantum and semi-classical degrees of freedom, i.e. the only QC-environment energy exchange is purely classical with the quantum state transitions (involving only the QC modes) induced by the fluctuating perturbing electric field which is fully insensitive of the quantum state dynamics (similarly to quantum state transitions induced by stationary electro-magnetic waves). Therefore, the $R \rightleftharpoons P$ interconversions are statistically equivalent to invariant free energy transitions [1] (see also [supporting information](#)) and the rate constants for the two transitions (reactant to product and product to reactant) are the

same and termed as k_0 .

Defining with $P_R(t) = \rho_{R,R}(t) = \omega_{R,R}(t)$ the reactant eigenstate probability and with $P_P(t) = \rho_{P,P}(t) = \omega_{P,P}(t) = 1 - P_R(t)$ the product eigenstate one, we obtain (assuming $P_R(0) = 1$)

$$P_R(t) \cong \frac{1}{2} + \frac{e^{-2k_0 t}}{2} \quad (7)$$

$$P_P(t) \cong \frac{1}{2} - \frac{e^{-2k_0 t}}{2} \quad (8)$$

which provide, by means of fitting the reactant or product density matrix diagonal element as obtained by solving Eq. (5) over the set of classical MD trajectories, the rate constant k_0 for the vibrational eigenstate relaxation within the invariant free energy ensemble. It is worth to remark that k_0 is determined by the quantum state dynamical evolution due to the time-dependent perturbation (basically equivalent to a huge over-position of stationary electric field waves [1]), with no quan-

tum-classical energy flux. The $R \rightleftharpoons P$ process considered can be thus physically interpreted as provided by instantaneous energy exchanges between the fluctuating perturbation field (when close to the resonant frequency) and the QC quantum degrees of freedom, coupled to instantaneous kinetic energy immissions/removals into/from the semi-classical degrees of freedom in order to obtain a null quantum-classical energy flux within the QC-environment system (i.e. corresponding to an instantaneous inward/outward work-flux as provided by an external hidden energy source).

Finally, k_0 is corrected to obtain the proper $R \rightarrow P$ (k_R) and $P \rightarrow R$ (k_P) rate constants in the actual statistical ensemble in which the experiment takes place (i.e. taking into account the effects of the energy flux between quantum and semi-classical degrees of freedom and thus recovering the experimental canonical or isothermal-isobaric ensemble conditions) via the relations [1] (see the [supporting information](#))

$$k_R \cong k_0 e^{-\frac{\beta}{2}(E_{v,P} - E_{v,R})} \quad (9)$$

$$k_P \cong k_0 e^{-\frac{\beta}{2}(E_{v,R} - E_{v,P})} \quad (10)$$

Where $E_{v,R}$ and $E_{v,P}$ represent the equilibrium mean vibrational energies involved in the transition.

Computational details

Molecular dynamics simulations.

As reported in the Introduction our method is primarily based on the evaluation electric field exerted by the solvent molecules onto the QC (corresponding, in all the investigated cases, to the solute). We have addressed four different systems in the present study. For all of them, the MD simulations have been carried out using the program Gromacs [39,40] version 5.1.2. The NVT ensemble has been used with a time step of 1.0 fs with the solute (i.e. the QC) positioned at the centre of a cubic box filled with solvent molecules. The density of the whole system, and hence the box size, was adjusted to reproduce the same average pressure obtained through MD simulations of the same number of the solvent molecules at their experimental density at the temperature and pressure of the experiment. The temperature was kept constant using the

Parrinello thermostat [41], the bond lengths were constrained using Lincs algorithm [42]. Long range electrostatic interactions were computed by the Particle Mesh Ewald method [43] with 34 wave vectors in each dimension and a 4th order cubic interpolation and a cut-off of 1.1 nm was used. For all the selected QC's we have adapted the Gromos force-field [44] (G53a6 version) with the geometry and the corresponding atomic charges recalculated through unperturbed Quantum-Chemical calculations (see next subsection). In all the cases, when necessary, a counter-ion has been added for ensuring the electro-neutrality of the box. Three different solvents were utilised:

- (i) water (920 molecules in the case of cyanide ion and 1564 molecules in the case of azide ion), using the spc model [45];
- (ii) deuterated water (920 molecules in the case of cyanide ion and 1564 molecules in the case of azide ion), using either the spc/hw model by Grigera [46] (D_2O)^a or a simple shift of the hydrogen masses in the SPC model (D_2O)^b (note that these two models are only slightly different);
- (iii) chloroform (1564 molecules in the case of nitrogen dioxide),
- (iv) using either the model by van Gunsteren [47] ($CHCl_3$)^a or a model identical to the previous one except for the atomic charges which were set identical to the ones provided by DFT calculations on gas phase chloroform ($CHCl_3$)^b.

This latter solvent model was utilized in the case of water in chloroform. The quality of the force field was estimated, whenever possible (i.e. for cyanide ion, nitrogen dioxide and water), by calculating the corresponding stationary IR-spectrum using a theoretical-computational procedure developed in our laboratory, [9] as shown in the [Supplementary Information](#).

The main computational strategy, adopted for all the investigated systems, is first based on the production of a 50.0 ns long simulation (hereafter termed as Equilibrium-MD, EqMD), carried out for equilibrating the system with an output frequency of one configuration per fs. Subsequently 100 uncorrelated portions of 3.0 ps length are extracted from EqMD.

In each of these 100 portions we calculated, at each frame, the electric field and potential exerted on the QC centre of mass. All this information (in conjunction with the unperturbed dipole derivatives, see next subsection) has been then utilised for integrating the time-dependent Schroedinger equation (i.e. the Eq. (5)) using a rather standard 4th order Runge-Kutta integrator with a time step of 0.001 atomic units of time, corresponding to $\approx 2 \cdot 10^{-5}$ fs. The obtained time-course of the density matrix diagonal elements were then fitted through Eqs. (7) and (8) and the rate constants in the actual ensembles were finally obtained through Eqs. (9) and (10) by using the experimental mean frequencies. Note that the effect of the perturbed frequency fluctuations, already demonstrated to provide negligible effects [1], was as usual disregarded. An estimation of the standard error was finally obtained by repeating the above procedures using three different sets of 100 trajectories.

Quantum chemical calculations

All the quantum-chemical calculations were performed in the framework of Density Functional Theory [48] using the hybrid Becke3LYP [49,50] functional in conjunction with the correlation consistent triple-zeta (cc-pVTZ) atomic basis set. Tests carried out on nitrogen dioxide and cyanide ion at the Coupled Cluster level of theory or using different functionals within the DFT framework, provided virtually identical results thus showing that for such kind of molecules DFT calculations are in general a good approximation, in line with data reported in literature [51].

The QC atomic charges were calculated using the RESP procedure [52]. All these calculations were performed with the package Gaussian09 [53]. The first and second derivatives of the QC dipoles were

calculated using finite differences along a grid of 0.05 atomic units constructed on the space of the normal modes evaluated from the diagonalization of the QC mass-weighted (unperturbed) Hessian.

Results and discussion

Vibrational relaxation data

The VER for aqueous cyanide ion has represented a sort of benchmark for all the theoretical-computational procedures developed in the last years. Experimentally [18] it is known that the aqueous cyanide VER mean lifetime (as obtained by a mono-exponential decay of the population in the first excited vibrational state) is shorter in water than in deuterated water and that the C-N frequency (modulated through isotopic labelling) affects the VER efficiency basically only in deuterated water. Therefore, it has been hypothesised the involvement of the vibrational energy exchange between chromophore and water quantum modes into the relaxation process.

Computational studies carried out in the last two decades for reproducing the observed mean lifetimes have provided a wide range of results based on both purely classical MD approximations (58 ps [21], 19 ps [27,54] and 34 ps (in deuterated water) [27]) and mixed quantum-classical strategies (138 ps [29], 200 ps [30] (with rigid water model), 30 ps (with flexible water model) [24]. Moreover, other studies, making use of the Ehrenfest method (based on a classical approximation) with quantum corrections [25,26] have reported different values pointing out their strong sensitivity to the model adopted for the cyanide ion and, most importantly, have suggested a bi-exponential nature of the VER dominated by a fast channel of 20 ps interpreted as an energy exchange with the water bending vibration, and by a slow channel of 180 ps interpreted as an energy exchange with the water (semiclassical) roto-translational degrees of freedom.

More recently [28], a study based on classical MD simulations (using a polarizable force-field with either rigid or flexible solvent models) in conjunction with the Schofield quantum correction factor [55] and the Landau-Teller approximation [56], well reproducing the experimental data, has further shown that both the solvent vibrational and roto-translational degrees of freedom (both treated classically) may play an important role in cyanide ion VER.

Well aware of the relevance of the solute-solvent force field as well as of the electronic structure calculations in the final outcome of the computed vibrational relaxation, we preliminarily tested the quality of the utilized force field (constructed using the QC unperturbed electronic ground state atomic charges) and quantum chemical properties by calculating the cyanide infrared (IR) equilibrium spectrum using the Perturbed Matrix Method (PMM) as widely described in the literature [1,9]. We obtained an IR spectrum (see [Supplementary Information](#)) centered at 2073 cm^{-1} with a full width at half maximum of 20 cm^{-1} in very good agreement with experimental data reporting a maximum at 2080 cm^{-1} with a full width at half maximum of 16 cm^{-1} [57].

Such results clearly show that the force field adopted in the MD simulation, and hence the consequent intensity and fluctuation of the H_2O electric field exerted on the cyanide ion, as well as the unperturbed properties evaluated through quantum chemical calculations are reasonably accurate. Considering this latter aspect, it is also important to underline that the use of different DFT functionals or even of Coupled Cluster calculations virtually provide the same results (see the [Supporting Information](#)). We then performed four sets of EqMD simulations: (i) cyanide ion in water, (ii) cyanide ion in deuterated water, (iii) isotopic-labelled cyanide ion in water and (iv) isotopic-labelled cyanide ion in deuterated water. Such simulations were then used to obtain the QC quantum trajectories and related density matrix for the relaxation of the solute first excited vibrational eigenstate. Note that we used only the cyanide ion to define the QC and hence the quantum relaxation process modelled in this study cannot involve any quantum mode-mode (i.e. solute-mode-to-solvent-mode) energy exchange, and hence corresponds

to the first excited to ground eigenstate relaxation channel (necessarily characterized by a mono-exponential kinetics) with the energy exchanges occurring only with the semiclassical degrees of freedom (essentially the solvent roto-translational degrees of freedom).

In the case of aqueous azide ion (in water and deuterated water) and nitrogen dioxide in chloroform, never addressed to the best of our knowledge in previous theoretical-computational studies and experimentally investigated for the relaxation of the first excited eigenstate of the anti-symmetric stretching mode, a similar procedure has been utilised.

However, the relaxation modelling of these polyatomic species should take into account all the possible intramolecular relaxation channels beyond the direct excited to ground state one, each involving a solute-mode to solute-mode energy exchange (again we disregard the chromophore-water quantum mode–mode energy exchange). Interestingly, our calculations indicate that the only kinetically relevant process in both systems is the anti-symmetric stretching mode excited to ground eigenstate relaxation (i.e. the mode–mode relaxation channels provide negligible contributions to the overall relaxation rate), thus necessarily implying also in these cases mono-exponential decay of the excited eigenstate population in line with the experimentally observed first order kinetics. Finally, in the case of the relaxation of the water bending mode in chloroform we can safely expect a scenario somewhat similar to the cyanide ion one. In fact, considering as physically unrealistic the energy exchange from a lower energy mode to a higher energy one, the direct decay to the ground vibrational state can be considered as the only viable relaxation path.

Also for nitrogen dioxide and water in chloroform we performed a force field appraisal by modelling the corresponding asymmetric stretching and bending stationary IR-spectrum. The results are reported in the [Supplementary Information](#).

In [Fig. 1](#) we report, for each of the investigated systems, the diagonal element of the density matrix corresponding to the reactant eigenstate probability ($w_{R,R}(t)$, see Eq. (4)), as obtained within the invariant free energy ensemble, and – in red – the corresponding fitting of the two state model of Eq. (7) (i.e. the reactant relaxation kinetics in the invariant free energy ensemble). Note that in [Fig. 1](#), for the sake of clarity and brevity, we only show data as obtained using the $(D_2O)^b$ and $(CHCl_3)^b$ solvents. The mean lifetimes as obtained by the fitting procedure hence need to be

Table 1

Comparison of the theoretical-computational relaxation mean lifetimes and associated standard errors we obtained with the corresponding experimental ones. $(D_2O)^a$ is the solvent model by Grigera. $(D_2O)^b$ is the spc model with modified hydrogen masses. $(CHCl_3)^a$ is the model by van Gunsteren. $(CHCl_3)^b$ is the model by van Gunsteren with DFT atomic charges replacing the semi-empirical ones.

System	Calculated τ (ps)	Experimental τ (ps)
Cyanide ion (H_2O)	22 ± 3	28 ± 7 (Ref. [18])
Cyanide ion $(D_2O)^a$	80 ± 6	71 ± 3 (Ref. [18])
Cyanide ion $(D_2O)^b$	73 ± 10	
Labelled Cyanide ion (H_2O)	27 ± 3	31 ± 7 (Ref. [18])
Labelled Cyanide ion $(D_2O)^a$	73 ± 6	120 ± 3 (Ref. [18])
Labelled Cyanide ion $(D_2O)^b$	86 ± 10	
Azide ion (H_2O)	0.69 ± 0.02	0.81 ± 0.06 (Ref. [31]) 1.2 (Ref. [10])
Azide ion $(D_2O)^a$	1.23 ± 0.04	2.4 (Ref. [10])
Azide ion $(D_2O)^b$	1.32 ± 0.07	
Nitrogen dioxide $(CHCl_3)^a$	89 ± 5	23 ± 2 (Ref. [32])
Nitrogen dioxide $(CHCl_3)^b$	49 ± 8	
Water $(CHCl_3)^a$	27 ± 3	8.5 ± 0.4 (Ref. [33])
Water $(CHCl_3)^b$	10 ± 1	

corrected taking into account the quantum–classical energy exchange effects (see Eq. (9)). These corrected values are reported in [Table 1](#). It is worth noting that the relaxation mean lifetimes reported in [Table 1](#) are much smaller than the ones provided by the invariant free energy ensemble (i.e., obtained by the fitted two state model as in [Fig. 1](#)), as the correction accounting for the quantum–classical energy exchange is large.

From the table it is evident that the employed theoretical-computational model rather accurately reproduces the experimental relaxation mean lifetimes, with only two systems/conditions (labelled cyanide ion in D_2O and nitrogen dioxide in chloroform) where our estimate deviates significantly from the experimental one. However, even for these latter cases the theoretical-computational model provides the correct mean lifetime order of magnitude, thus suggesting that the discrepancy could be mainly due to the inaccuracies of the QC unperturbed (i.e. gas-phase) quantum properties and empirical force field

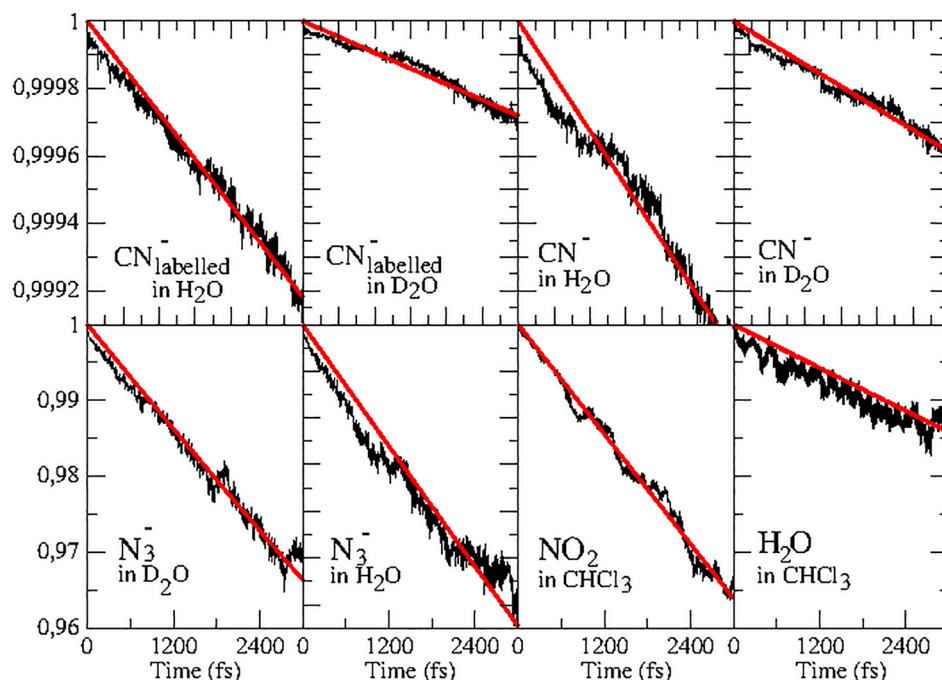


Fig. 1. Diagonal element of the density matrix corresponding to the reactant eigenstate probability $w_{R,R}(t)$ as obtained within the invariant free energy ensemble (black curves), and related fitted two-state kinetic model (in red, Eq. (7)). Upper panels: cyanide ion in all the investigated cases. Lower panels: azide ion, nitrogen dioxide and water. Note that in the upper panels the y-axis and x-axis are always the same. In the lower panels the y-axis is the same for the azide ion and water, whereas for nitrogen dioxide, for the sake of clarity, the lower value on the y-axis is equal to 0.999. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

utilized in the MD simulation, in line with the variations due to the slightly different solvent force field used (note that for the labelled cyanide as well as for nitrogen dioxide no optimized force field was available). Interestingly, for nitrogen dioxide the computed frequency for the gas-phase condition is at best 70–80 cm^{-1} above the experimental value and the solution IR spectra using the two CHCl_3 force fields are unable to properly reproduce both the experimental maximum and full width at half maximum, thus supporting the hypothesis of an inaccurate nitrogen dioxide unperturbed properties and force field. Such results, beyond showing that the model captures the essential features of the relaxation process in general, indicate that at least for cyanide and azide ions as well as the water in chloroform the intramolecular excited to ground eigenstate relaxation channel involving only the energy exchange with the semiclassical degrees of freedom (essentially the solvent roto-translational ones) could account for the observed experimental kinetics, without necessarily invoking the chromophore-solvent quantum mode–mode energy exchange. It is worth to note that the use of different DFT functionals or even of the Coupled Cluster calculations results in relaxation mean lifetimes which are indistinguishable within the noise (see [Supporting Information](#)).

Concluding remarks

In this study we have assessed the accuracy of the theoretical-computational model, we very recently introduced, by applying it to describe in details the Vibrational Energy Relaxation (VER) of four condensed-phase systems: aqueous cyanide and azide ions and nitrogen dioxide and water in chloroform. The results obtained for the systems investigated confirmed that this method can provide a reasonable quantitative description of VER on the basis of a physical consistent and robust theoretical framework, pointing out the relevance of both the QC unperturbed properties and MD force field used in the evaluation of the relaxation mean lifetime. Interestingly, our model furnishes a relatively simple description of the VER mechanism based on the effects of (i) the fluctuating perturbation field resonant with the excitation energy and (ii) the quantum–classical energy flux provided by the vibrational state transitions (essentially the QC vibrational to solvent roto-translational energy exchange). Moreover, the main approximations used (i.e. the perturbation approximated at the dipolar terms with the electric field provided by the environment atomic charges, use of typical atomistic classical MD simulations, QC defined only by the solute thus neglecting the solute–solvent quantum mode–mode energy exchange, etc) do not seem to provide relevant inaccuracies, hence indicating that higher levels of approximation involving either unfeasible or very expensive computational strategies are likely to be unnecessary to capture the essential mechanism of usual vibrational relaxation. It is also worth to remark that our theoretical-computational procedure makes use of the density matrix time behavior along the MD trajectories instead of first order approximations like in the Landau-Teller approach, thus in principle reconstructing the exact quantum state relaxation kinetics along the MD simulations. All the results obtained indicate that the use of a fully affordable level of the computational procedures, i.e. DFT calculations and typical atomistic MD simulations, can provide a reasonably accurate reproduction of the experimental data hence allowing the application of the method to investigate the VER in biomacromolecules. However, in these latter cases in order to include all the relevant mode–mode vibrational quanta exchanges a proper QC definition might include peptide groups H-bonded to the vibrational center [58].

Declaration of Competing Interest

There are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rechem.2022.100305>.

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