

On the importance of configurational sampling in theoretical calculation of electronic properties of complex molecular systems: Acetone in water

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Abstract

In this work, we address the problem of the role and relevance of the aqueous environment configurational sampling on acetone electronic properties: the (vertical) absorption spectrum and corresponding excitation Helmholtz free energy. By comparing the results obtained by applying the perturbed matrix method (PMM) on molecular dynamics (MD) trajectories of different sampling efficiency, we specifically quantify the effects of the phase space sampling on acetone vertical electronic excitations. Results confirm that PMM provides an accurate and physically consistent description of the electronic excitation processes and show the crucial importance of an extended configurational sampling of the solvent environment in order to obtain a reliable (chromophore) absorption behaviour.

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1. Introduction

The theoretical modeling of electronic properties in complex systems still represents a challenge in theoretical/computational physical-chemistry. In fact, full quantum calculations are computationally limited by the number of electrons and, therefore, for condensed phase systems full electronic structure calculations are unfeasible. The main strategies developed are based on the approximation that the whole system can be divided into a quantum center (QC), where the electronic degrees of freedom are explicitly considered, and a semi-classical environment. In such methods the QC electronic structure can be usually obtained via high-level quantum chemical calculations and hence the modeling of the QC-environment interaction provides the main difference in these approaches. A rele-

vant part of the Letters dealing with the study of electronic properties of molecules (or part of) in liquids are based on the modelisation of the environment as a macroscopic (continuum) dielectric reacting to the QC electronic density via its polarization (see for example Tomasi and co-workers [1]). Alternatively the semi-classical environment, modeled at atomic level, is used to provide a perturbing electric field to be included into the Hamiltonian operator in order to obtain the QC (perturbed) electronic structure via standard quantum chemical calculations [2–4]. Both approaches have provided valuable information in the evaluation of spectroscopic data and reactivity. However, in the former the poor modelisation of the environment as a macroscopic continuum dielectric does not allow a fully reliable statistical-mechanical evaluation; the latter, requiring for each QC-environment atomic configuration heavy quantum chemical calculations, is still computationally too demanding to be used to obtain an extended phase-space sampling and therefore equilibrium and non-equilibrium statistical mechanical calculations are severely limited.

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In the perturbed matrix method [5–8] (PMM), we introduced in the last years, the use of a first principles quantum mechanical perturbation procedure allows the calculation of the (perturbed) QC electronic properties at a relatively low computational cost. In PMM, where the semi-classical environment is treated at full atomistic level, high level quantum chemical calculations of the QC electronic structure are required only in the reference condition (typically one or a few atomic configurations of the isolated, i.e., unperturbed, QC), thus allowing the evaluation of the QC perturbed electronic properties over an extended environment phase space sampling, as provided by classical molecular dynamics simulations. Previous Letters [5–8] clearly showed that when accurate molecular Hamiltonian and reference QC electronic structure are available and hence PMM provides a reliable description of the QC electronic behavior, the role of the statistical–dynamical coupling between QC electronic eigenfunctions and environment atomic motions is essential to model correctly the QC electronic processes.

In this work, we use the (vertical) absorption spectrum of an acetone molecule in water, as obtained by PMM, to point out the effect of phase space sampling in the calculations of the QC electronic properties. In particular, we show how an incomplete sampling does not allow a reliable evaluation of the shape and maximum of the (vertical) absorption spectrum and provides a completely wrong estimate of the excitation free energy determined by the tail of the excitation energy distribution.

2. Theory

In this section, we briefly describe the perturbed matrix method, remanding to literature [5,6] for a more extended description. In PMM, a part of the system (quantum center) is treated at full electronic quantum mechanical level and the rest of the system, i.e., the water in this case, is described as a semi-classical atomic environment and provides the perturbation. In practice, we calculate the unperturbed Hamiltonian matrix by quantum chemical calculations and, then, a molecular dynamics simulation is used to obtain a time-sequence of the perturbing electric potential and field acting at the QC geometrical center, to be used to construct the perturbed Hamiltonian matrix in time. Note that the perturbed Hamiltonian matrix is obtained via the multipolar expansion of the perturbation operator, typically truncated at the dipolar terms and approximating the effect of all the other terms as a short range potential independent of the electronic state [5–8]. Finally, diagonalisation of the perturbed Hamiltonian matrix, at each MD frame, provides a trajectory of QC perturbed eigenvalues (energies) and eigenvectors (\mathbf{c}_i) and, therefore, of whatever perturbed electronic property. In fact, a generic (electronic) property, defined by the operator \hat{a} , can be expressed by the corresponding matrix:

$$[\tilde{a}]_{i,j} = \mathbf{c}_i^{*T} \tilde{a}^0 \mathbf{c}_j \quad (1)$$

$$[\tilde{a}^0]_{l,l'} = \langle \Phi_l^0 | \hat{a} | \Phi_{l'}^0 \rangle \quad (2)$$

where \tilde{a}^0 represents the observable \hat{a} in the unperturbed basis set (defined by the unperturbed Hamiltonian eigenfunctions Φ^0). In this work, we calculated the perturbed electronic excitation energies and corresponding perturbed transition dipoles ($\mu_{i,j}$), in order to obtain the electronic spectrum (considering a unitary radiation energy density per unit frequency and neglecting the vibrational contribution) via the molecular absorption coefficient (molecular extinction coefficient):

$$\epsilon_{i,j}(\nu) = \frac{B_{i,j}(\nu) \rho(\nu) h\nu}{c} \quad (3)$$

$$B_{i,j} = \frac{|\mu_{i,j}|^2}{6\epsilon_0 \hbar^2} \quad (4)$$

where $B_{i,j}$ is the Einstein coefficient (ϵ_0 is here the vacuum dielectric constant), $\rho(\nu)$ is the probability density in frequency (ν) space, i.e the probability to find the chromophore within a given excitation-energy interval divided by the corresponding ν interval, h is the Planck's constant ($\hbar = \frac{h}{2\pi}$) and c is the light speed. Note that the perturbed transition dipole squared lengths are obtained averaging over the distribution of the corresponding ν interval, provided by the sampling of the MD simulation.

3. Methods

Acetone geometry optimization and the calculation of the corresponding unperturbed properties were performed with the DALTON software package [9], at the Density functional theory level and using the aug-cc-pvdz basis set. After some tests with different functionals, we decided to use the PBE0 one. Such a procedure provided at low computational cost the unperturbed electronic properties, in the present case associated to the ground and first 20 excited states, utilized in PMM. Note that acetone is essentially a rigid molecule and therefore only the vacuo optimized structure unperturbed electronic properties were used in PMM calculations, as obtained by recent computational investigation [10]. The GROMACS software package [11] was used for the molecular dynamics simulations, with the isokinetic temperature coupling [12] algorithm to control the temperature (300 K) and acetone atoms were positionally constrained by the 'freeze' option. Hence, acetone was treated as a rigid molecule, i.e., its intramolecular degrees of freedom are considered as quantum vibrations, with rototranslational constraints to 'stop' the solute in the simulation box. After an equilibration of 500 ps, we used for PMM calculation a MD trajectory of 5.5 ns (time step of 2 fs) with the long range electrostatics calculated using the Particle Mesh Ewald (PME) method, with 34 wave vectors and a 4th order cubic interpolation. MD frames utilized in PMM calculations were saved each ps in order to remove any relevant time correlation in our

evaluations, see Fig. 1 where we show the excitation energy autocorrelation function indicating an average correlation time of about 0.2–0.3 ps. In addition another 100 ps MD trajectory, performed identically to the previous one although saving the MD frames every time step, was used to study the effect of the time correlation on QC electronic properties, providing the data used in Fig. 1. The force field for the acetone molecule, i.e., the charges, the Lennard-Jones parameters and the intramolecular energy terms, was taken from the works of Coutinho et al. [3], whereas for the water we used the SPC model [13]. Finally, the excitation distributions and (vertical) spectra were obtained using always the same set of frequency-energy intervals with a bin size of 0.1 and 0.05 eV, respectively. This was done in order to remove from our data to be compared any possible effect due to the arbitrary choice of these intervals. Note that for both properties the noise at each excitation energy interval was obtained by using five equivalent and independent subsamples, i.e., considering that the property obtained by the overall sample is the average of the subsamples values and hence its standard deviation is simply given by the standard deviation for the five property values divided by the square root of five.

4. Results

In Table 1, we compare the vacuo and solution acetone excitation energy we obtained (for the latter the vertical absorption maximum provided by PMM and the 5.5 ns MD simulation) with the experimental values and other computational results. PMM provides excitation energy and shift matching the experimental values within the noise, confirming its accuracy. This result is a preliminary

Table 1

First, excitation energy in vacuum (first column), in water (second column) and corresponding shift (third column) as obtained by PMM in this work, using the polarizable continuum model (PCM) to treat the solvent, by quantum chemical calculations over a set of Monte Carlo configurations (MC), by quantum chemical calculations over a set of configurations provided by a quantum-classical Car-Parrinello simulation (CPMD) and by experimental data

	Unperturbed exc. energy (eV)	Perturbed exc. energy (eV)	Shift (eV)
This work	4.39	4.56 (0.02)	0.17 (0.02)
PCM [14]	4.44	4.60	0.16
MC [3]	n.a.	n.a.	0.16
CPMD [4]	3.85	4.10	0.25
Experimental data	4.49 [15]	4.68 [15]	0.19 (0.01) [15], 0.16–0.21[3,16]

When indicated the number within parenthesis is the total error.

condition to evaluate the role of the phase space sampling in such calculations.

The relevance of the sampling is directly investigated comparing (first) excitation energy probability distribution calculated in different ways (see Fig. 2): using the full sampling of 5500 configurations over the complete 5.5 ns trajectory, providing what we may consider as the converged distribution; using 400 configurations distributed over the 5.5 ns in order to evaluate the effect of pure sampling size reduction; using 400 frames taken from 10 ps of the 100 ps trajectory to include the time correlation effects, which are relevant in the subpicosecond range as shown by the excitation energy autocorrelation function (Fig. 1).

From Fig. 2 it is clear that in both the reduced sampling calculations the low energy tail is inaccurate (such a feature strongly affects the excitation free energy evaluation) and

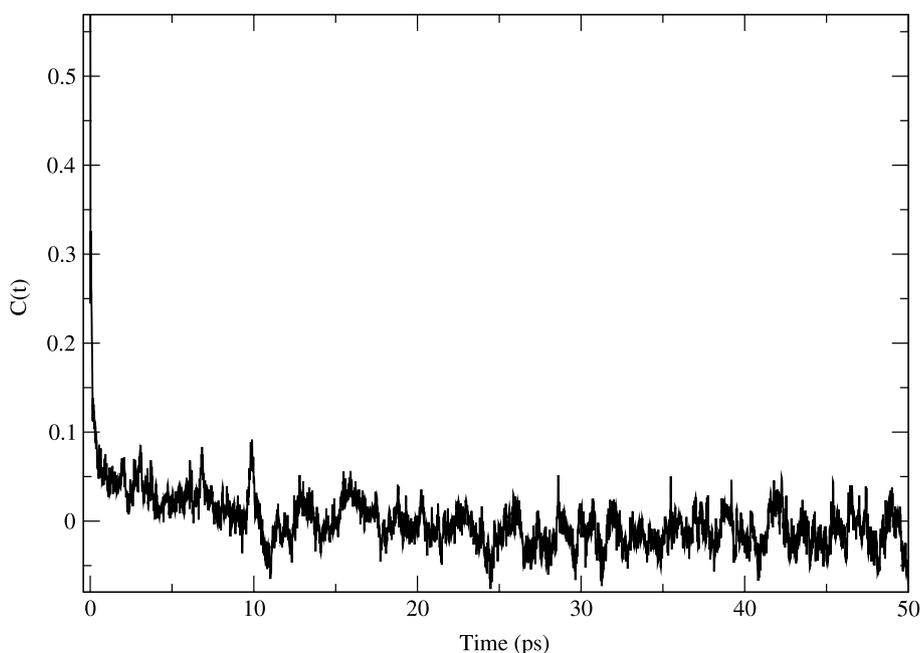


Fig. 1. Autocorrelation function of the excitation energies.

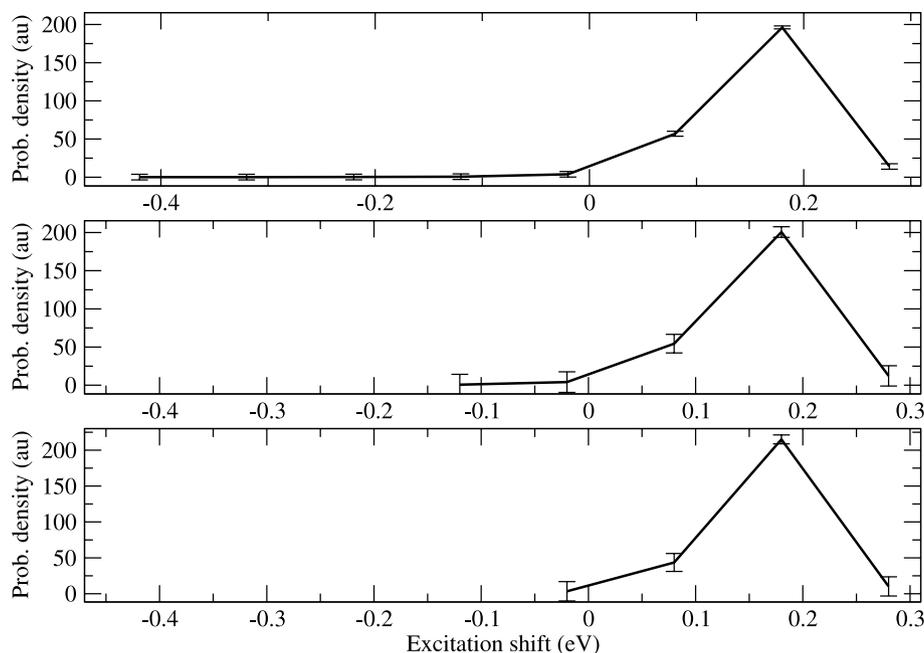


Fig. 2. First, excitation energy distribution obtained with different samplings. Full sampling (5500 configurations over the 5.5 ns trajectory), upper panel; reduced sampling (400 configurations over the 5.5 ns trajectory), middle panel; reduced sampling and time correlation (400 configurations over 10 ps of the 100 ps trajectory), lower panel. The error bars correspond to a standard deviation of the property.

the noise is significantly increased. Interestingly, the distribution obtained by the time correlated 400 MD frames deviates more from the full sampling curve and, as expected, provides the worst estimate of the low energy tail. In Fig. 3, we show the excitation free energy [7,8] as obtained for an increasing simulation time used. This figure demonstrates that even for a small rigid molecule like acetone a reasonable convergence is achieved only after 1 ns, thus showing that no proper information on the low energy

tail of the excitation energy distribution can be obtained using a subnanosecond simulation sampling. When the excitation spectrum is considered, the sampling effects are also evident. In Fig. 4, we show, similarly to Fig. 2, the first excitation (vertical) spectrum calculated in different ways: using the full sampling of 5500 configurations over the complete 5.5 ns trajectory, providing what we may consider as the converged spectrum; using 400 configurations distributed over the 5.5 ns in order to evaluate the effect of

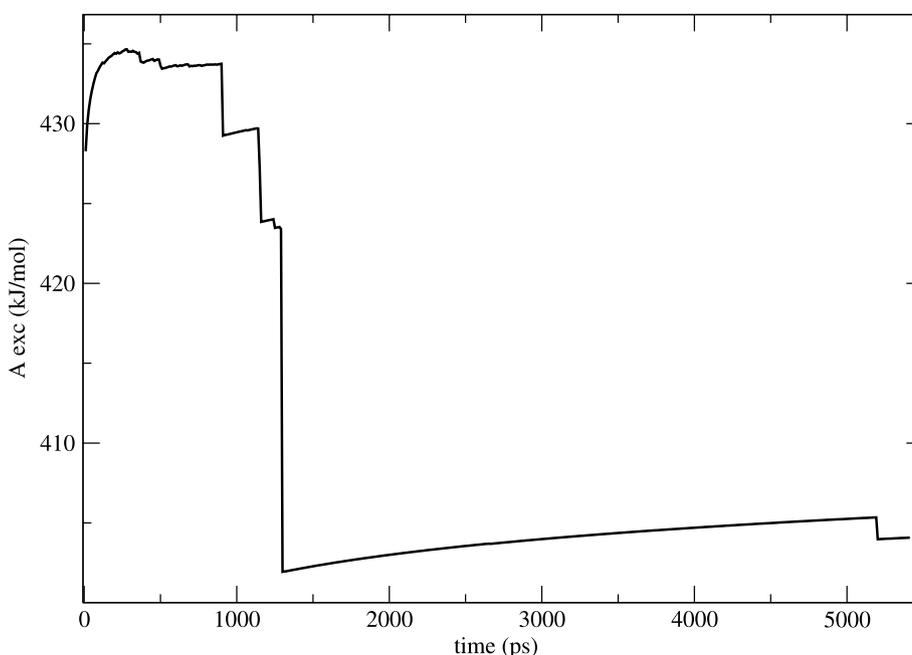


Fig. 3. Excitation Helmholtz free energy estimated using an increasing simulation time.

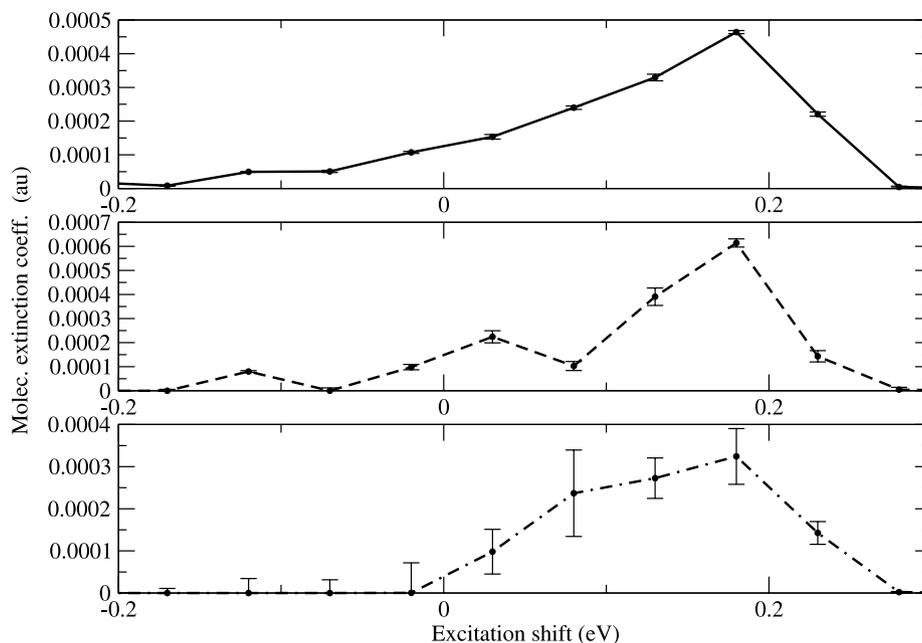


Fig. 4. First, excitation spectra obtained with different samplings. Full sampling (5500 configurations over the 5.5 ns trajectory), upper panel; reduced sampling (400 configurations over the 5.5 ns trajectory), middle panel; reduced sampling and time correlation (400 configurations over 10 ps of the 100 ps trajectory), lower panel. The error bars correspond to a standard deviation of the property.

pure sampling size reduction; using 400 frames taken from 10 ps of the 100 ps trajectory to include the time correlation effects. Note that the noise shown, as for Fig. 2, was obtained rescaling the errors of the ‘converged’ curve (obtained using 5500 frames over the complete trajectory) according to the number of statistically independent frames utilized (estimated by the excitation energy average correlation time). This last figure clearly shows that a reduced sampling, as obtained by picoseconds range simulations, results in a relevant noise possibly providing an unreliable spectrum evaluation.

5. Conclusions

In this Letter, we showed that an extended phase space sampling is essential to obtain a reliable and accurate evaluation of the electronic excitation behaviour of a chromophore embedded in a complex molecular system. Comparison of absorption spectra obtained via PMM using different sampling conditions, clearly indicates that a limited number of configurations and/or simulation time length provide an estimated absorption behavior which may be affected by a significant error. In fact, the far tail of the excitation energy distribution, essential for free energy evaluation, can be obtained only via an extended phase space sampling and the absorption maximum although reasonably reproduced by limited sampling simulations (i.e., hundreds of configurations/tens of picoseconds) is affected by a large noise which may result in an unreliable excitation shift. Such a crucial importance of the phase space sampling should be even more carefully considered when addressing electronic properties in sys-

tems characterized by a very complex anisotropic dynamical-mechanical behaviour, e.g., biomacromolecules.

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