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On the performance of quantum chemical methods to predict solvatochromic effects: The case of acrolein in aqueous solution

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The performance of the Hartree–Fock method and the three density functionals B3LYP, PBE0, and CAM-B3LYP is compared to results based on the coupled cluster singles and doubles model in predictions of the solvatochromic effects on the vertical $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic excitation energies of acrolein. All electronic structure methods employed the same solvent model, which is based on the combined quantum mechanics/molecular mechanics approach together with a dynamical averaging scheme. In addition to the predicted solvatochromic effects, we have also performed spectroscopic UV measurements of acrolein in vapor phase and aqueous solution. The gas-to-aqueous solution shift of the $n \rightarrow \pi^*$ excitation energy is well reproduced by using all density functional methods considered. However, the B3LYP and PBE0 functionals completely fail to describe the $\pi \rightarrow \pi^*$ electronic transition in solution, whereas the recent CAM-B3LYP functional performs well also in this case. The $\pi \rightarrow \pi^*$ excitation energy of acrolein in water solution is found to be very dependent on intermolecular induction and nonelectrostatic interactions. The computed excitation energies of acrolein in vacuum and solution compare well to experimental data.

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I. INTRODUCTION

Theoretical considerations of solvatochromism have been a very active research area since the late 1950s.¹ Nevertheless, reliable protocols for calculating electronic transition energies and, in general, molecular properties of solvated molecules are still to be pursued.^{2–5} This is due to the fact that accurate calculations on large molecular systems as, for example, a solute plus an appropriate number of solvent molecules is, indeed, a very challenging task for electronic structure theory mainly due to its potentially high scaling. Therefore, models have been developed, in which the effect of the solvent on the solute is introduced by including effective operators in the molecular Hamiltonian. The effective models comprise the dielectric continuum models,^{6,7} which originate from the classical works of Onsager and Kirkwood,⁸ and the combined quantum mechanics/molecular mechanics (QM/MM) models, which were first applied to study enzymatic reactions⁹ and later extended to the calculation of excitation energies.^{10,11} Both the dielectric continuum and QM/MM methods have extensively been applied to investigate solvatochromic effects (see, for example, Refs. 2–5 and 12–32) with significant contributions to the development of general computational algorithms for modeling solvent effects.

Although the accuracy and flexibility of the solvent model is a very important aspect, the choice of the electronic structure method for calculation of electronic transition energies is also crucial. However, very little is, in fact, known concerning the performance and reliability of different *ab initio* methods to capture solvatochromic effects. For instance, the Hartree–Fock (HF) method is generally expected to give too high electronic absorption energies due to neglect of electron correlation. On the other hand, the application of accurate *ab initio* methods based on multiconfigurational and multireference approaches is limited due to their high computational cost, especially when introducing solvent molecules explicitly in the quantum chemical calculations.^{33–37} Here, time dependent density functional theory (TDDFT) is very attractive because it provides a good ratio between accuracy and computational efficiency. However, the results based on TDDFT will depend on the applied exchange–correlation (xc) functional. The purpose of this work is, therefore, to test the reliability of HF and mainly DFT methods in prediction of the solvatochromic effects in the electronic absorption energies.

Recently, we have developed a discrete QM/MM solvation model based on a coupled cluster (CC) description of the solute molecule and applied this model to study environmental effects on electronic excitation energies of solvated molecules.^{4,26–29,32} This model possesses the capability of explicitly including solvent polarization. In addition, the same

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solvent model may be applied in the situation where the solute is treated by using either HF or DFT.³⁰ Thereby, we are in a position where systematic benchmarks can be performed by using the CC based solvent model as the reference. In the present study we consider, in addition to the CC calculations, HF and DFT by using three xc functionals, namely, the B3LYP,³⁸ PBE0,^{39,40} and the recently developed Coulomb-attenuated B3LYP method (CAM-B3LYP),⁴¹ which has been previously shown to provide significantly improved excitation energies as compared to the conventional B3LYP method.⁴² We emphasize that our main focus is on comparison of different electronic structure methods while keeping other computational settings—basis set, molecular geometries, molecular mechanical potentials, etc.—unchanged. To introduce dynamical effects into the solvent model, we perform the electronic structure calculations on a number of solute-solvent configurations extracted from molecular dynamics (MD) simulations. The necessity of accounting for dynamical effects in the liquid by statistical averaging has, in recent years, proven to be mandatory for obtaining accurate predictions of solvent effects on molecular properties. The QM/MM approach allows a discrete description of the atomistic environment in the calculation and provides an accurate description of the electrostatic solute-solvent interactions. Recently, a comparison of the B3LYP, PBE0, and CAM-B3LYP xc functionals in predictions of the lowest singlet electronic excitation energy of coumarin derivatives in gas phase and solutions was reported.⁴³ However, this study used the dielectric continuum based solvent models and experimental data as a reference to gauge the performance of the methods.

In this work, we consider the lowest singlet $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ vertical electronic absorption energies of *s-trans* acrolein (propenal) and the corresponding gas-to-aqueous solution shifts. Acrolein represents the simplest compound within the class of unsaturated aldehydes. The presence of the C=O and C=C double bonds in acrolein introduces a degree of conjugation in the molecule and makes the photo-physics of acrolein particularly rich and interesting. Many experimental investigations have dealt with the UV absorption of acrolein. The $n \rightarrow \pi^*$ absorption of acrolein in the vapor phase exhibits a broad band between 3.20 and 5.00 eV,⁴⁴ with partially resolved vibronic structure,^{44–46} and the maximum in the absorption intensity at 3.69 eV.^{44–47} In aqueous solution, the maximum intensity of this transition was observed in the region of 3.78–3.98 eV in Ref. 48 and at 3.94 eV in Refs. 47 and 49. The $\pi \rightarrow \pi^*$ absorption of gaseous acrolein exhibits a broad structureless band,⁵⁰ and the peaks of the absorption intensity were observed at 6.41,⁵¹ 6.42,⁴⁷ and 6.49 eV.⁵⁰ The strongest $\pi \rightarrow \pi^*$ absorption of acrolein in aqueous solution was observed at 5.90 eV.⁴⁷ Based on the experimental data reported in Ref. 47, the $n \rightarrow \pi^*$ absorption is blueshifted by 0.25 eV going from gas phase to a water solution, whereas the $\pi \rightarrow \pi^*$ transition is strongly redshifted by -0.52 eV. We note that $n \rightarrow \pi^*$ electronic absorption band is seen to be slightly blueshifted even in apolar solvents, e.g., by 0.01, 0.02, and 0.05 eV in isooctane,⁴⁷ *n*-hexane,⁵² and 2-methyltetrahydrofuran⁵³ solutions, respectively, whereas the $\pi \rightarrow \pi^*$ transition suffers a

sizable gas-to-isooctane solution shift of -0.30 eV.⁴⁷ The latter observation indicates that the solvent shift in the electronic $\pi \rightarrow \pi^*$ transition of acrolein is to some extent governed by intermolecular interactions of nonelectrostatic origin, and both electrostatic and nonelectrostatic intermolecular interactions tend to redshift the absorption maximum for this specific transition.

To provide new insight into somewhat outdated experimental data, we have carried out new experimental studies of the singlet $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic absorptions of acrolein in the gas phase and in aqueous solution by using a modern UV spectroscopic apparatus.

The gas-to-aqueous solution shift in electronic $n \rightarrow \pi^*$ absorption energy has previously been theoretically considered by using different electronic structure methods in combination with a variety of solvent models including a supermolecular approach,^{54–56} the continuum solvation conductor-like screening model (COSMO),⁵⁷ reference interaction site model self-consistent field (RISM-SCF),⁵⁸ MD or Monte Carlo (MC) simulations followed by the QM/MM calculations^{56,59,60} and QM/MM in combination with the polarizable continuum model (PCM).⁶¹ In addition, the solvent effects on the $\pi \rightarrow \pi^*$ absorption were studied in Refs. 54, 55, and 57, whereas Ref. 60 considered also the effect of water on the singlet $n \leftarrow \pi^*$ emission of acrolein. The electronic absorption spectrum of acrolein in vacuum including both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions has recently been studied in Refs. 55 and 62 by using complete active space with second order perturbation theory (CASPT2) and symmetry-adapted cluster configuration interaction, respectively. To the best of our knowledge, the present work is the first attempt to elucidate solvatochromic effects in acrolein by using high-level CC theory.

II. METHODS

A. Experimental

UV spectra were recorded by using a Bruker IFS 66v/s Fourier Transform interferometer equipped with an UV extension package consisting of an external deuterium light source, a quartz beam splitter, and GaP-diode detector. Acrolein (stabilized with hydroquinone) from Merck was used without further purification. Two samples were prepared for use in obtaining the spectrum of acrolein in the liquid phase, one with 0.4% and another with 0.004% concentration of acrolein in water, respectively. This is related to the different (by a factor of 1000) intensities of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations. A 1 cm quartz cuvette was used for the measurements. The spectra of the liquid phases and of the cuvette containing only water were obtained by coadding 128 interferograms taken at a resolution of 12 cm^{-1} , and the Fourier transform was performed by using the Blackman-Harris three-term apodization function. Four spectra were taken on the same solution and these were averaged to give the final spectrum. For the gas-phase study, a small stainless steel cell, which is equipped with LiF windows and with a path length of 15 cm, was used. For additional information concerning the details of the cell, we refer to Ref. 63. The cell was filled

with acrolein vapor to a pressure of 60 mbar. The spectrum was obtained by coadding 128 interferograms at a resolution of 2 cm^{-1} .

B. Computational

1. Electronic structure calculations

A combined QM/MM scheme at the HF, DFT, or CC level of theory has been implemented^{30,64} in the DALTON quantum chemistry program (QCP).⁶⁵ The implementation allows the use of either nonpolarizable or polarizable MM potentials. On this basis, we are, thereby, able to compare the performance of both types of classical force fields in the calculation of solvatochromic effects in acrolein. For the nonpolarizable potential, the QM subsystem is polarized by the electric field generated by atomic partial point charges of fixed magnitudes assigned to the classical molecules in the MM subsystem. In contrast, the polarizable MM potential also includes, in addition to the point charges, electronic dipole polarizabilities, which give rise to induced dipole moments in the classical subsystem. The induced dipole moments are also affected by the electronic and nuclear charge distribution of the QM subsystem, which means that the QM and MM subsystems are allowed to mutually polarize each other. In the optimization of the wave function (electronic density), an additional iterative procedure for obtaining self-consistency between the electronic density and the induced dipole moments must, therefore, be used. Although the explicitly polarizable model is more realistic, it is at the same time more computationally demanding as compared to the case where only the nonpolarizable potential is used.

We use linear response theory^{66–68} to calculate the vertical electronic excitation energies, both in the vacuum and in the liquid phase. Response theory provides vertical electronic excitation energies as poles of the linear response function. The advantage of using response theory to calculate excitation energies is due to the fact that only the wave function of the electronic ground state needs to be explicitly considered. Particularly, response theory provides a way to obtain excitation energies from DFT even though DFT in its present standard form is a ground state theory. We also calculate the transition oscillator strengths that are obtained as residues of the electric dipole linear response function.

In this work, we compare the performance of the HF, B3LYP,³⁸ PBE0,^{39,40} and CAM-B3LYP (Ref. 41) approaches for the calculation of the solvatochromic effects and we consider the CC singles and doubles (CCSD) model as a reference. To obtain highly accurate excitation energies of acrolein in vacuum, the CC3 model⁶⁹ has also been employed. In the case of the CAM-B3LYP xc functional, the parameters α and β modifying the fraction of the exact HF exchange for short- and long-range interactions have been assigned values of 0.19 and 0.46, respectively, and the switching factor μ is equal to 0.33 as proposed in the original work.⁴¹ In the calculation of excitation energies at the CC level, we freeze the lowest orbitals (those of $1s$ character) for all heavy atoms in the molecular system. The molecular geometries are obtained from geometry optimization at B3LYP level of theory by using the GAUSSIAN 03 program⁷⁰ and at CCSD or CCSD

with perturbative treatment of triples [CCSD(T)] levels by using the DALTON QCP in combination with the aug-cc-pVTZ basis.⁷¹

The QM/MM scheme is applied for the molecular solute-solvent configurations extracted from the classical MD simulation (*vide infra*). The solute, or potentially the solute and a number of closest solvent molecules, is considered at the selected electronic structure method, whereas the rest of the solvent molecules are described by the MM potential. In the QM/MM calculations, we used the same force field for the water molecules as was employed in the MD simulation. The molecular properties in aqueous solution are obtained as a statistical average over a number of molecular configurations. The gas-to-aqueous solution shift in excitation energy is determined as a difference between excitation energies in aqueous solution and vacuum. The MIDASCPP program⁷² is used to create inputs for the combined QM/MM calculations and to perform the statistical analysis of the results.

2. MD simulations

We have conducted classical MD simulations of 1 rigid acrolein molecule and 511 rigid water molecules by using the MOLSIM program.⁷³ The liquid-phase geometry of acrolein was obtained from geometry optimization at the B3LYP/aug-cc-pVTZ level of theory, and the PCM model was applied to account for the bulk solvent effects (geometrical parameters will be given and discussed in the next section). Default settings of the PCM were always used for the water solvent as implemented in GAUSSIAN 03. The molecular geometry of a water molecule ($R_{\text{OH}}=0.9572\text{ \AA}$ and $\angle_{\text{HOH}}=104.49^\circ$) was taken from Ref. 74. The MD simulations were performed using either the nonpolarizable simple point charge (SPC) or the polarizable SPC plus polarization (SPCpol) force field. The force field parameters used in the simulations of both types are collected in Table I. The atom labeling used for acrolein is introduced in Fig. 1. For the nonpolarizable potential, the partial atomic point charges of acrolein were fitted to reproduce the QM electrostatic potential according to the CHELPG procedure⁷⁵ at the B3LYP/aug-cc-pVTZ/PCM level by using the GAUSSIAN 03 program. In addition, the electric dipole moment was constrained to its QM value. Herein, the PCM model is applied so that the point charges implicitly include the polarization due to the solvent. In the polarizable MD simulation, we use the CHELPG point charges calculated at the B3LYP/aug-cc-pVTZ level in vacuum employing the constraints for the dipole moment, and the solvent polarization is now modeled by assigning isotropic dipole polarizabilities to the atomic sites of the molecule. The atomic polarizabilities were calculated at the B3LYP/aug-cc-pVTZ level in vacuum by using the LOPROP approach⁷⁶ implemented in the MOLCAS program.⁷⁷ The polarizabilities derived from the LOPROP scheme implicitly include the many body polarization effects within the acrolein molecule, and the polarization interactions are only allowed among induced dipole moments located on different molecules. The nonelectrostatic intermolecular interactions are modeled by using a 6-12 type Lennard-Jones (LJ) potential and Lorentz–Berthelot mixing rules. For acrolein, we use LJ

TABLE I. The force field parameters for acrolein and water used in the MD simulation. The atom labeling for acrolein is introduced in Fig. 1. The same LJ parameters for acrolein are used in both the SPC and SPCpol MD simulations. The SPC potential for water is the TIP3P force field (Ref. 78). In the case of the SPCpol potential for acrolein, distributed isotropic polarizabilities are included.

Molecule	Atom	SPC			SPCpol			
		q (a.u.)	σ (Å)	ϵ (kcal/mol)	q (a.u.)	α (Å ³)	σ (Å)	ϵ (kcal/mol)
OC ₃ H ₄	O	-0.602 51	2.960	0.210	-0.4917	0.9474	2.960	0.210
	C1	0.570 19	3.750	0.105	0.5241	1.2614	3.750	0.105
	C2	-0.185 75	3.550	0.076	-0.1539	1.4391	3.550	0.076
	C3	-0.242 31	3.550	0.076	-0.2491	1.3235	3.550	0.076
	H1	0.001 31	2.420	0.015	-0.0293	0.4085	2.420	0.015
	H2	0.142 96	2.420	0.030	0.1234	0.3732	2.420	0.030
	H3	0.145 96	2.420	0.030	0.1263	0.3570	2.420	0.030
	H4	0.170 15	2.420	0.030	0.1502	0.3960	2.420	0.030
H ₂ O	O	-0.834 0	3.1507	0.1521	-0.6690	1.440	3.166	0.1555
	H	0.417 0	0.000	0.000	0.3345	0.000	0.000	0.000

parameters as reported in Ref. 56. For water, we employ the standard nonpolarizable TIP3P potential⁷⁸ or the polarizable force field by Ahlström *et al.*⁷⁹ In the latter case, the isotropic dipole polarizability is placed at the oxygen site of the water molecule.

Both the SPC and SPCpol MD simulations were performed in a cubic box within the *NVT* ensemble at the temperature of 298.15 K. The box side was fixed to 24.892 Å to reproduce the experimental density of liquid water. We employ periodic boundary conditions together with a spherical cutoff distance for the electrostatic interactions at half box length. To account for the long-range and polarization interactions, a reaction-field correction is considered. For the polarizable potential, the induced dipole moments were recalculated at every third time step with a relative tolerance of 10^{-7} . Also, we employ a linear damping scheme for the dipole-dipole interactions as described in Ref. 80. The initial equilibration was carried out for 400 ps with a time step of 2 fs followed by the production run of 1.2 ns. The configurations were dumped every 10 ps to assure that they are statistically uncorrelated. We, thus, obtained 120 molecular configurations to use in the subsequent QM/MM calculations. Furthermore, a spherical cutoff distance equal to 12 Å is applied for every configuration before submitting it to the QM/MM calculation. Such a cutoff distance includes 230–240 water molecules together with acrolein.

FIG. 1. (Color online) The structure and definitions of the atomic labels of acrolein.

III. RESULTS AND DISCUSSION

A. UV spectroscopic measurements

The recorded $n \rightarrow \pi^*$ electronic absorption spectra of acrolein in vapor phase and aqueous solution are shown in Fig. 2. The maximum in the absorption peak is observed at 29 800 (3.69 eV) and 31 800 cm⁻¹ (3.94 eV) in the gas- and liquid-phase spectra, respectively. The obtained results are in excellent agreement with the previously reported experimental data.^{44–47,49} Therefore, the gas-to-aqueous solution shift in the $n \rightarrow \pi^*$ absorption energy of acrolein is measured to be 0.25 eV.

The $\pi \rightarrow \pi^*$ absorption spectrum of acrolein in water solution is shown in Fig. 3. We note that in these measurements, we have used a liquid sample with a concentration of acrolein lower by a factor of 1000 than that in the measurements of the $n \rightarrow \pi^*$ transition. This is related to the much higher intensity of the $\pi \rightarrow \pi^*$ electronic transition of acrolein as compared to the intensity of the $n \rightarrow \pi^*$ transition. The maximum absorption in the $\pi \rightarrow \pi^*$ excitation is ob-

FIG. 2. The measured $n \rightarrow \pi^*$ absorption spectra of acrolein in vapor phase and aqueous solution.

FIG. 3. The measured $\pi \rightarrow \pi^*$ absorption spectrum of acrolein in aqueous solution.

served at $47\,500\text{ cm}^{-1}$ (5.89 eV) and is in good agreement with the previously reported value of 5.90 eV.⁴⁷ The spectrum shown in Fig. 3 was taken close to the upper limit of the spectrometer and, therefore, a degree of noise is present in the spectrum.

We were not able to record the $\pi \rightarrow \pi^*$ transition of acrolein in gas phase because of the technical limitations of the experimental setup. Therefore, we rely on the solvent shift in the vertical $\pi \rightarrow \pi^*$ excitation energy of acrolein equal to -0.52 eV as reported in Ref. 47. A detailed analysis of the recorded spectra is beyond the scope of present study.

B. The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations in vacuum

In Table II, we have collected all the geometrical parameters of acrolein (C_s symmetry) as used in this work. Experimental structural data of gaseous acrolein^{81,82} is also included in Table II. As a gas-phase reference, we use the acrolein geometry optimized at the B3LYP/aug-cc-pVTZ level of theory. As seen from Table II, the optimized B3LYP

TABLE III. Vertical $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic absorption energies (in eV) of acrolein in vacuum calculated at CAM-B3LYP and CCSD levels of theory and by using different basis sets. The geometry of acrolein was obtained from the B3LYP/aug-cc-pVTZ geometry optimization in vacuum. Also included are the corresponding CC3/aug-cc-pVDZ and experimental results. In the CC calculations, the four lowest orbitals on heavy atoms have been frozen. The third column, headed “nbf,” denotes the number of contracted basis functions on acrolein for each entry.

Method	Basis set	nbf	$E_{\text{ex}}^{n \rightarrow \pi^*}$	$E_{\text{ex}}^{\pi \rightarrow \pi^*}$
CAM-B3LYP	aug-cc-pVDZ	128	3.783	6.405
	aug-cc-pVTZ	276	3.800	6.399
	aug-cc-pVQZ	504	3.798	6.397
	d-aug-cc-pVDZ	180	3.781	6.399
	d-aug-cc-pVTZ	376	3.799	6.396
CCSD	aug-cc-pVDZ	128	3.934	6.887
	aug-cc-pVTZ	276	3.941	6.908
	d-aug-cc-pVDZ	180	3.929	6.870
	d-aug-cc-pVTZ	376	3.938	6.904
CC3	aug-cc-pVDZ	128	3.799	6.702
Expt.			3.69	6.42

geometry of acrolein compares reasonably well to the experimental gas-phase structure, although the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ double bond lengths are found to be somewhat underestimated. The liquid-phase geometry of acrolein is derived from B3LYP/aug-cc-pVTZ/PCM geometry optimization. The inclusion of solvent effects by the PCM model in the geometry optimization leads to a lengthening of the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ double bonds, whereas the $\text{C}-\text{C}$ single bond is shortened. This indicates an increased conjugation in the liquid-phase structure of acrolein as compared to that in vacuum.

In Table III, we show the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies of isolated acrolein calculated by using CAM-B3LYP or CCSD in combination with different Dunning-type correlation consistent basis sets.^{71,83} At the CAM-B3LYP level, both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation

TABLE II. Geometrical parameters (in Å and deg) of acrolein optimized at various levels of theory in vacuum and by using the PCM. The aug-cc-pVTZ basis set was used in all cases. The atom labeling for acrolein is introduced in Fig. 1. Also given are the experimental gas-phase structural data.

	Expt. ^a	Expt. ^b	B3LYP	CCSD	CCSD(T)	B3LYP/PCM
$R(\text{C1}=\text{O})$	1.219 ± 0.005	1.215 ± 0.002	1.209	1.209	1.217	1.220
$R(\text{C1}-\text{C2})$	1.470 ± 0.003	1.468 ± 0.003	1.471	1.477	1.477	1.462
$R(\text{C2}=\text{C3})$	1.345 ± 0.003	1.341 ± 0.004	1.331	1.335	1.342	1.334
$R(\text{C1}-\text{H1})$	1.108 ± 0.003	1.113 ± 0.003	1.109	1.105	1.108	1.108
$R(\text{C2}-\text{H2})$	1.084 ± 0.003	1.084 ± 0.004	1.083	1.082	1.084	1.087
$R(\text{C3}-\text{H3})$	1.086 ± 0.005	1.089 ± 0.007	1.084	1.084	1.086	1.085
$R(\text{C3}-\text{H4})$	1.086 ± 0.005	1.081 ± 0.003	1.081	1.081	1.083	1.083
$\angle \text{C2}-\text{C1}=\text{O}$	123.3 ± 0.3	123.9 ± 0.3	124.4	124.1	124.1	124.3
$\angle \text{C3}=\text{C2}-\text{C1}$	119.8 ± 0.2	120.3 ± 0.3	121.1	120.5	120.3	120.3
$\angle \text{C2}-\text{C1}-\text{H1}$	115.1 ± 0.2	114.7 ± 0.2	114.8	115.0	114.9	115.4
$\angle \text{C3}=\text{C2}-\text{H2}$	122.8 ± 0.2	122.4 ± 0.5	122.3	122.7	122.7	122.3
$\angle \text{C2}=\text{C3}-\text{H3}$	120.0 ± 0.2	119.8 ± 0.3	120.9	120.7	120.5	120.9
$\angle \text{C2}=\text{C3}-\text{H4}$	121.5 ± 0.2	122.2 ± 0.6	122.2	122.1	122.1	122.0

^aReference 81.

^bReference 82.

energies are found to be converged within a few hundredths of an eV using the aug-cc-pVDZ basis. The $n \rightarrow \pi^*$ excitation energy is also well converged using the aug-cc-pVDZ basis at the CCSD level. A somewhat larger change in the $\pi \rightarrow \pi^*$ excitation energy is observed by using CCSD when the basis is changed from double- ζ to triple- ζ quality. However, the effect of double augmentation acts here in the opposite direction but possesses almost the same magnitude as compared to the case where the cardinal number is changed from 2 to 3 (compare the CCSD aug-cc-pVDZ and d-aug-cc-pVTZ results in Table III). The aug-cc-pVDZ basis set, thus, provides fairly well converged CCSD $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ absorption energies of acrolein and will be exclusively used in the following calculations of excitation energies.

To evaluate the effect of triple excitations in the CC expansion, we have included in Table III the result for the excitation energies of acrolein obtained at the CC3/aug-cc-pVDZ level. As seen in Table III, the effect of triple excitations is to lower the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies by 0.135 and 0.185 eV, respectively, as compared to the corresponding CCSD results. The neglect of triple excitations in the CCSD calculation represents, therefore, one of the largest uncertainties in the absolute values of the excitation energies calculated both in the vacuum and in the liquid phase. However, this effect is expected to some extent to be cancelled in the calculation of the gas-to-aqueous solution shift in excitation energies.

The discrepancies between theoretical and experimental results in Table III could, to some extent, be attributed to the inaccuracies in the B3LYP based geometry of acrolein. As mentioned above, the B3LYP method underestimates the lengths of the C=O and C=C double bonds as compared to experimental data (see Table II). In fact, the $n \rightarrow \pi^*$ excitation energy of acrolein was found in Ref. 61 to be rather dependent on the length of the C=O bond. The high sensitivity of the $n \rightarrow \pi^*$ transition energy on the distance of the C=O double bond length is likely to be a general feature of molecules containing this specific chemical group. For instance, this has previously been observed in the case of acetone.^{4,18,84} In Fig. 4, we show the dependences of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic excitation energies of acrolein on the C=O or C=C bond lengths. The C=O and C=C bond distances were varied between their values found in vacuum and PCM, and all other geometrical parameters were fixed to have their B3LYP optimized values in vacuum. As seen from Fig. 4, the lengthening of both the C=O or C=C bonds leads to the reduction in the excitation energies. By enlarging the C=O bond length by 0.01 Å, the $n \rightarrow \pi^*$ excitation energy is lowered by 0.046 eV, whereas the corresponding lengthening of the C=C double bond results in the reduction in the $\pi \rightarrow \pi^*$ absorption energy by 0.055 eV. We, therefore, conclude that slight changes in the molecular geometry have a non-negligible impact on the calculated vertical excitation energies of acrolein.

To explore the geometrical effects on excitation energies of acrolein in more detail, we have optimized the geometry of acrolein by using high-level CCSD and CCSD(T) electronic structure methods and the aug-cc-pVTZ basis set. The

FIG. 4. Vertical $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic absorption energies (in eV) of acrolein as functions of the C=O (a) and C=C (b) bond lengths. Results refer to CAM-B3LYP/aug-cc-pVDZ.

CC optimized geometrical parameters of acrolein are given in Table II. In particular, the acrolein geometry optimized at the CCSD(T) level of theory compares very well to the experimentally determined structure of acrolein, and only the C–C single bond length is found to be somewhat overestimated.

In Table IV, we present the results for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies calculated by using different electronic structure methods on acrolein geometries derived from the B3LYP, CCSD, and CCSD(T) geometry optimizations. Experimental results are also included in Table IV. In all cases, the $n \rightarrow \pi^*$ excitation energy is found to be slightly larger and the $\pi \rightarrow \pi^*$ slightly smaller in the case of CCSD optimized geometry of acrolein compared to the B3LYP based geometry. The smallest magnitudes of the excitation energies are found for the CCSD(T) geometry of acrolein, as could be expected from geometrical considerations. The HF method is seen to overestimate the $n \rightarrow \pi^*$ excitation energy by ~ 0.8 – 0.9 eV as compared to experiment, although it unexpectedly provides a reasonably accurate value for the $\pi \rightarrow \pi^*$ transition energy, especially in the case of the accurate CCSD(T) based geometry of acrolein. The B3LYP and PBE0 xc functionals, on the other hand, underestimate the excitation energies in all cases, with somewhat better performance

TABLE IV. Vertical $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic absorption energies (in eV) of acrolein calculated by using HF, B3LYP, PBE0, CAM-B3LYP, CCSD, and CC3 electronic structure methods in combination with the aug-cc-pVDZ basis set. The geometries of acrolein as indicated in the second column were obtained from B3LYP, CCSD, or CCSD(T) geometry optimizations in vacuum. The basis set used in the geometry optimization was aug-cc-pVTZ. Also included are the corresponding experimental gas-phase results.

Method	Geometry	$E_{\text{ex}}^{n \rightarrow \pi^*}$	$E_{\text{ex}}^{\pi \rightarrow \pi^*}$
HF	B3LYP	4.555	6.736
	CCSD	4.561	6.729
	CCSD(T)	4.520	6.646
B3LYP	B3LYP	3.574	6.168
	CCSD	3.584	6.160
	CCSD(T)	3.538	6.111
PBE0	B3LYP	3.618	6.311
	CCSD	3.629	6.302
	CCSD(T)	3.584	6.243
CAM-B3LYP	B3LYP	3.783	6.405
	CCSD	3.792	6.397
	CCSD(T)	3.749	6.331
CCSD	B3LYP	3.934	6.887
	CCSD	3.943	6.885
	CCSD(T)	3.894	6.843
CC3	B3LYP	3.799	6.702
	CCSD	3.808	6.698
	CCSD(T)	3.755	6.646
Expt.		3.69	6.42

of the latter functional. The CAM-B3LYP method provides a very accurate estimate of the $n \rightarrow \pi^*$ excitation energy for the CCSD(T) based acrolein geometry as compared to both experimental data and corresponding CC3 predictions (see Table IV). The computed CAM-B3LYP $\pi \rightarrow \pi^*$ absorption energy for the CCSD(T) geometry possesses now a smaller magnitude as obtained for the B3LYP optimized geometry. The very good agreement between the experimental and the CAM-B3LYP results obtained for the B3LYP optimized geometry of acrolein is, therefore, to some extent incidental.

The CCSD model provides overestimated excitation energies (see Table IV), and the changes in the excitation energy due to different geometries of acrolein are much smaller than discrepancies with respect to experimental data. The CC3 model provides improved excitation energies of acrolein upon the corresponding CCSD results. In particular, the calculated CC3 $n \rightarrow \pi^*$ absorption energy agrees well with experimental data. The CC3 method still overestimates the $\pi \rightarrow \pi^*$ excitation energy by 0.226 eV, but the comparison with experiment is also subject to some limitations. There are two aspects which make the comparison between experimentally determined and theoretically computed vertical excitation energies difficult. First, the electronic absorption bands in the experimental UV spectrum are usually very broad. The vertical excitation energies are then assumed to be at the point where the maximum absorption occurs, and

this is of course an approximation. Second, measured electronic transitions occur between vibronic (or rovibronic) energy levels in the molecule. However, response theory provides excitation energies as vertical transitions between two points on the potential energy surfaces of the ground and excited states, and vibrational effects are, therefore, not accounted for in the calculation, including the difference in zero-point energy and the deviation from a simple Frank-Condon picture. A well-founded comparison of experimental and theoretical vertical excitation energies is, therefore, difficult to achieve. Very accurate and reliable estimates for the 0-0 electronic transitions compared to experimental data are, however, possible, but it is usually important to utilize highly correlated electronic structure methods along with diffuse and flexible basis sets.⁸⁵ In this particular case, the energy interval having more than two-third of the maximum absorbance extends over ~ 0.5 eV for both states (see Figs. 2 and 3), which clearly indicates the limitation of a one-to-one comparison between the peak of maximum absorption and the theoretical vertical excitation energy.

C. Benchmark of HF and DFT against CCSD predicted solvatochromism

In this section, we proceed to discuss the large-scale QM/MM calculations by using different electronic structure methods. First, we have to address the issues related to the convergence of the results with respect to (a) the number of solvent molecules included in the molecular configurations, (b) the number of configurations to average over, and (c) the number of solvent molecules explicitly included into the QM region around the solute. The latter point is particularly informative because it enables us to draw important conclusions about the nature of intermolecular interactions causing certain solvent effects. It should, however, be noted that upon inclusion of specific water molecules into the QM region, we improve the description of the electrostatics as well as account for interactions of nonelectrostatic origin.

As mentioned in the previous section, we use in this work a spherical cutoff radius of 12 Å and, therefore, include ~ 230 –240 water molecules together with acrolein in the molecular configuration. According to our test calculations and findings in previous studies,^{27,32} this number of water molecules is, indeed, sufficient to obtain converged results. In Fig. 5, we show the convergence of the statistically averaged $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ vertical absorption energies of acrolein with respect to the number of molecular configurations included into the averaging. The excitation energies begin to converge with 70 configurations, and including around 120 molecular configurations into the averaging procedure provides apparently sufficiently converged results. In this work, we, thus, always use 120 molecular solute-solvent configurations in the averaging of the QM/MM results.

In Table V, we show the convergence of the excitation energies with respect to the number of water molecules quantum-mechanically treated together with acrolein. In this study, we used the CAM-B3LYP xc functional, the aug-cc-pVDZ basis set, and the TIP3P potential for the classical water molecules. The molecular configurations are taken from the SPC MD simulation. Spherical integration of the

FIG. 5. The dependence of the statistically averaged vertical $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic excitation energies on the number of molecular configurations included into averaging procedure. The results are obtained from the CAM-B3LYP/aug-cc-pVDZ calculations on acrolein, and the TIP3P potential was used for all water molecules. The statistical errors are calculated as $\sigma/\sqrt{N}$ (σ is the standard deviation).

first peak in the O(acrolein)–H(water) SPC or SPCpol radial distribution functions (RDFs) shown in Fig. 6 gives coordination numbers equal to 2.17 and 1.90, respectively. Our results are, thus, in agreement with the coordination number of 2.1 found from a previous SPC-type MD simulation⁵⁹ of acrolein in water. The coordination number derived here represents an upper bound to the averaged number of hydrogen bonds formed between acrolein and water. We have also analyzed the acrolein-water hydrogen bonding by using geometrical criteria for the hydrogen bond.^{86,87} We define the hydrogen bond between acrolein and a water molecule for $R[\text{O}(\text{acrolein})\text{--O}(\text{water})] \leq 3.18 \text{ \AA}$ and $\angle[\text{O}(\text{acrolein})\text{--O}(\text{water})\text{--H}(\text{water})] \leq 45^\circ$. This definition of the hydrogen bond is based on the analysis of the O(acrolein)–O(water) radial and O(acrolein)–O(water)–

TABLE V. Vertical $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic absorption energies (in eV) of acrolein in aqueous solution for different number of water molecules quantum-mechanically treated. Results refer to CAM-B3LYP/aug-cc-pVDZ and the TIP3P potential for water. Water molecules closest to oxygen atom and the midpoint in the C=C double bond have been included into the QM region, and the first column gives the total number of water molecules.

No. of (H ₂ O) _{QM}			$E_{\text{ex}}^{n \rightarrow \pi^*}$	$E_{\text{ex}}^{\pi \rightarrow \pi^*}$
Tot	O	C=C		
0	0	0	4.043 ± 0.010	6.207 ± 0.005
2	2	0	4.056 ± 0.010	6.136 ± 0.006
2	0	2	4.039 ± 0.010	6.138 ± 0.008
3	1	2	4.050 ± 0.010	6.095 ± 0.008
3	2	1	4.054 ± 0.010	6.090 ± 0.008
4	2	2	4.053 ± 0.010	6.066 ± 0.009
6	2	4	4.050 ± 0.010	6.039 ± 0.009
7	3	4	4.052 ± 0.010	6.023 ± 0.009
8	3	5	4.051 ± 0.010	6.005 ± 0.010
10	4	6	4.052 ± 0.011	5.992 ± 0.011
12	5	7	4.052 ± 0.010	5.982 ± 0.010
14	6	8	4.051 ± 0.010	5.973 ± 0.010

FIG. 6. The O(acrolein)–H(water) radial distribution functions from SPCpol (solid line) and SPC (dashed line) MD simulations.

H(water) angular distribution functions. According to this geometrical analysis of the SPC and SPCpol based molecular configurations, acrolein forms on average 1.99 and 1.69 hydrogen bonds with water, respectively.

Based on the discussion above, we thereby begin the convergence analysis by including the two water molecules closest to the oxygen atom site of acrolein in the QM region. As seen from Table V, the $n \rightarrow \pi^*$ transition energy is now found to be somewhat increased in magnitude by 0.013 eV as compared to the case where all water molecules are classically treated, whereas the $\pi \rightarrow \pi^*$ absorption energy is decreased by 0.071 eV. Due to the presence of the highly polarizable delocalized π -electron system in acrolein, it might be important, especially for the $\pi \rightarrow \pi^*$ transition, to quantum-mechanically describe not only the hydrogen bonding but also the water molecules surrounding the π -electron shell of acrolein. We, thus, have included into the QM region two water molecules now closest to the middle point of the C=C double bond and not the ones closest to the oxygen atom site. As shown in Table V, the $n \rightarrow \pi^*$ excitation energy is now slightly decreased and the $\pi \rightarrow \pi^*$ transition is downshifted almost by the same magnitude as previously seen in the case where acrolein-water hydrogen bonding was treated at the QM level. By including four water molecules in the QM part—two closest to the oxygen site and two to the midpoint of the C=C bond—the $n \rightarrow \pi^*$ excitation is increased by 0.010 eV with respect to the purely classical treatment of the solvent and the $\pi \rightarrow \pi^*$ transition energy is decreased by 0.141 eV. Further inclusion of water molecules into the QM region leads only to small changes in the $n \rightarrow \pi^*$ excitation energy within statistical errors, and overall, the solvent shift in the $n \rightarrow \pi^*$ excitation energy is, thereby, mainly due to electrostatic solute-solvent interactions. This has also been indicated in Ref. 61.

A more complex situation is found for the $\pi \rightarrow \pi^*$ electronic transition. In this case, the inclusion of explicit water molecules in the QM region leads to a considerable decrease in the magnitude of the $\pi \rightarrow \pi^*$ transition energy of acrolein in water solution. The convergence here is very slow. As shown in Table V and illustrated in Fig. 7, the $\pi \rightarrow \pi^*$ exci-

FIG. 7. The convergence of the vertical $\pi \rightarrow \pi^*$ electronic absorption energy with respect to the number of water molecules quantum-mechanically treated. Results refer to CAM-B3LYP/aug-cc-pVDZ, and the TIP3P potential was used for classical water molecules.

tation energy is seen to be hardly converged even for as many as 12 water molecules included around acrolein in the QM part. The spherical integration of the first peak in the acrolein-water center-of-mass RDF gives the number of water molecules in the first solvation shell as 24 for both SPC and SPCpol MD simulations. Thus, more than half of the first solvation shell has to be quantum-mechanically described to obtain fully converged results. We note that the convergence pattern obtained by using the polarizable potential is qualitatively the same, as shown in Fig. 7. As will be discussed later, a very good agreement between the experimental and QM/MM results based on a classical description of all water molecules, by either the nonpolarizable or polarizable potentials, for the $n \rightarrow \pi^*$ transition was found. This indicates that the charge distribution of each water molecule is accurately described by using the current force fields. Thereby, we conclude that a significant part of the solvent shift in the $\pi \rightarrow \pi^*$ transition energy is caused by nonelectrostatic intermolecular interactions.

Due to the particularly high scaling of the CC methods, only a limited number of water molecules can be included in the QM part of the CC/MM calculation. At best, our present computational resources allow us to treat three water molecules together with acrolein at the CCSD level of theory. To compare the HF, DFT, and CCSD methods for predicting solvatochromism, we report statistically averaged results where none or three water molecules—one water molecule closest to oxygen atom and two closest to the midpoint of the C=C bond in acrolein—are included in the QM region. Even though three quantum-mechanically described water molecules do not represent fully converged results for the $\pi \rightarrow \pi^*$ transition energy, the induced changes in the $\pi \rightarrow \pi^*$ excitation energy are prominent, as seen in Table V. Therefore, we are in the position to fully compare the ability of different electronic structure methods to describe solvatochromic effects, which is the main purpose of this study, since all computational settings apart from the different electronic structure methods are kept to be the same. Later, based on the results of the comparison, we give our best estimates

TABLE VI. Gas-to-aqueous solution shifts in vertical $n \rightarrow \pi^*$ electronic excitation energy (in eV) of acrolein calculated by using various electronic structure methods and classical force fields. None or three water molecules—one closest to O atom site and two closest to midpoint of the C=C bond—are included into the QM region in the QM/MM model. Results are statistical averages over 120 molecular configurations, and the statistical errors are calculated as $\sigma/\sqrt{N}$ (σ is the standard deviation). Gas-phase references for each electronic structure method are given in Table IV for the B3LYP based gas-phase geometry of acrolein.

Method	TIP3P		SPCpol	
	0 (H ₂ O) _{QM}	3 (H ₂ O) _{QM}	0 (H ₂ O) _{QM}	3 (H ₂ O) _{QM}
HF	0.380 ± 0.011	0.406 ± 0.011	0.364 ± 0.012	0.385 ± 0.012
B3LYP	0.276 ± 0.011	0.278 ± 0.010	0.266 ± 0.011	0.268 ± 0.011
PBE0	0.274 ± 0.010	0.277 ± 0.010	0.263 ± 0.011	0.269 ± 0.011
CAM-B3LYP	0.260 ± 0.010	0.267 ± 0.010	0.253 ± 0.010	0.259 ± 0.010
CCSD	0.230 ± 0.011	0.235 ± 0.010	0.225 ± 0.010	0.231 ± 0.011

for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies of acrolein in water solution and the corresponding gas-to-aqueous solution shifts achieved by including a larger number of water molecules in the QM region of the model.

1. The $n \rightarrow \pi^*$ transition

In Table VI, we have collected the statistically averaged gas-to-aqueous solution shifts for the $n \rightarrow \pi^*$ excitation of acrolein based on the QM/MM calculations by using HF, DFT, and CCSD electronic structure methods. The classical water molecules are treated by using either the TIP3P or SPCpol potentials, and in addition, we report results where three water molecules together with acrolein are described by using electronic structure theory as described in previous section. As seen from Table VI, the results obtained for different water force fields are rather similar, and the polarizable force field leads to somewhat smaller solvent shifts. We also observe that for both types of potentials, the inclusion of explicit water molecules into the QM region has a slight upshifting effect, but the differences here are within the statistical errors. Therefore, the use of a polarizable potential for the water molecules does not change the conclusion on the electrostatic origin of the solvent shift in the $n \rightarrow \pi^*$ electronic transition of acrolein. The dominance of the electrostatic contribution to the solvent shift in the $n \rightarrow \pi^*$ electronic excitation has also been observed in the case of acetone.^{88,89}

Compared to the CCSD predictions, HF is found to give considerably overestimated values for the solvent shift in the $n \rightarrow \pi^*$ electronic transition. Also overestimated are the absolute magnitudes for the excitation energies in gas phase and solution (see Tables IV and VI). We, therefore, find that the HF approach is insufficient for providing an accurate description of the $n \rightarrow \pi^*$ excitation of acrolein in vacuum and water solution. The three DFT xc functionals considered provide very similar results for the solvent induced shifts. These shifts are slightly larger as compared to the corresponding CCSD based shifts. It is seen from Table VI that the CAM-B3LYP solvent shifts are by ~ 0.01 eV smaller compared to B3LYP and PBE0, which give essentially the same results for the shifts, and they are consequently closer

TABLE VII. Oscillator strengths in length gauge of the vertical $n \rightarrow \pi^*$ electronic excitation energy (dimensionless) of acrolein in vacuum and solution calculated by using HF, DFT, and CCSD methods in combination with the SPCpol force field for classical water molecules. None or three water molecules—one closest to O atom site and two closest to midpoint of the C=C bond—are included into the QM region in the QM/MM model. Results in aqueous solution are statistical averages over 120 molecular configurations, and the relative statistical errors are not higher than 5%.

Method	f_{vac}	${}^{\text{0w}}f_{\text{liq}}$	${}^{\text{3w}}f_{\text{liq}}$
HF	0.0005	0.0006	0.0006
B3LYP	0.0002	0.0003	0.0003
PBE0	0.0002	0.0003	0.0003
CAM-B3LYP	0.0003	0.0003	0.0004
CCSD	0.0003	0.0003	...

to the CCSD results. Overall, the agreement between the three xc functionals and CCSD solvent shifts is considered as fairly good and, therefore, DFT is seen to provide reliable results for the solvent shifts in vertical $n \rightarrow \pi^*$ excitation energies of acrolein. By inspecting the results for vacuum excitation energies in Table IV, we expect the absolute $n \rightarrow \pi^*$ excitation energies based on B3LYP and PBE0 to be underestimated as compared to the CC results. However, the CAM-B3LYP xc functional is promising in predicting the $n \rightarrow \pi^*$ excitation energies in vacuum and solution as indicated by the close agreement with vacuum CC3 absolute excitation energies and the reasonable agreement with the CCSD solvent shifts.

In this work, we concentrate on the solvent effects on excitation energies and, therefore, we only briefly discuss the oscillator strengths. The oscillator strengths of the $n \rightarrow \pi^*$ electronic transition of acrolein calculated at the HF, DFT, and CCSD levels in vacuum and solution are given in Table VII. However, we did not calculate the oscillator strength by using the CCSD method when explicit water molecules are quantum-mechanically treated because of the computational demands. The liquid-phase results for oscillator strengths obtained by using either TIP3P or SPCpol potentials for water molecules are identical. As seen from Table VII, the three xc functionals and CCSD give very similar results, whereas HF oscillator strengths are around two times larger as compared to DFT and CCSD. There is a tendency for the oscillator strengths to be slightly increased

when going from gas phase to aqueous solution. The magnitude of the $n \rightarrow \pi^*$ oscillator strength in the condensed phase is found to be mainly governed by the electrostatic intermolecular interactions.

2. The $\pi \rightarrow \pi^*$ transition

In Table VIII, we have collected the gas-to-aqueous solution shifts in vertical $\pi \rightarrow \pi^*$ excitation energy of acrolein calculated by using different electronic structure methods in exactly the same manner as the $n \rightarrow \pi^*$ solvent shifts given in Table VI. As expected, the magnitude of the solvent shift in the $\pi \rightarrow \pi^*$ excitation energy is increased at all levels of theory when three water molecules together with acrolein are quantum-mechanically considered. However, we note that the effect of nonelectrostatic interactions is more pronounced in the case of the nonpolarizable water potential. In general, the solvent shifts calculated by using polarizable force field are roughly by a factor of 1.5 larger as compared to the shifts obtained from the nonpolarizable QM/MM calculation. Keeping in mind the experimental $\pi \rightarrow \pi^*$ gas-to-aqueous solution shift of -0.52 eV, we expect the intermolecular induction interactions, which in the QM/MM scheme are effectively handled via the polarizable potential, to be important for accurate predictions of the $\pi \rightarrow \pi^*$ -type excitation energies of molecules in liquid phase.

It is evident from Table VIII that the HF method, in contrast to the case of the $n \rightarrow \pi^*$ transition, underestimates the solvent shift in the $\pi \rightarrow \pi^*$ excitation energy and also, the effect of nonelectrostatic interactions is found to be smaller as compared to CCSD. The B3LYP xc functional provides even smaller $\pi \rightarrow \pi^*$ solvent shifts than the HF method. The PBE0 functional performs slightly better than B3LYP, but the results are still of HF quality. Moreover, when explicit water molecules are included in the QM region, a mixing in the order of excitations takes place at B3LYP and PBE0 levels of theory, and each molecular configuration has to be inspected to find the position of the $\pi \rightarrow \pi^*$ transition. This indicates the incapability of the B3LYP and PBE0 methods to correctly predict the magnitudes and order of the high-lying excitation energies of molecules in solution. Additional support for this conclusion can be found in a recent study of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations of the uracil molecule in aqueous solution.⁹⁰ In that work, the gas-to-aqueous solution

TABLE VIII. Gas-to-aqueous solution shifts in vertical $\pi \rightarrow \pi^*$ electronic excitation energy (in eV) of acrolein calculated by using various electronic structure methods and classical force fields. None or three water molecules—one closest to O atom site and two closest to midpoint of the C=C bond—are included into the QM region in the QM/MM model. Results are statistical averages over 120 molecular configurations, and the statistical errors are calculated as $\sigma/\sqrt{N}$ (σ is the standard deviation). Gas-phase references for each electronic structure method are given in Table IV for the B3LYP based gas-phase geometry of acrolein.

Method	TIP3P		SPCpol	
	0 (H ₂ O) _{QM}	3 (H ₂ O) _{QM}	0 (H ₂ O) _{QM}	3 (H ₂ O) _{QM}
HF	-0.144 ± 0.004	-0.199 ± 0.005	-0.280 ± 0.005	-0.303 ± 0.006
B3LYP	-0.116 ± 0.005	-0.165 ± 0.012	-0.216 ± 0.006	-0.250 ± 0.013
PBE0	-0.162 ± 0.005	-0.242 ± 0.013	-0.262 ± 0.006	-0.304 ± 0.015
CAM-B3LYP	-0.198 ± 0.005	-0.310 ± 0.008	-0.303 ± 0.006	-0.398 ± 0.010
CCSD	-0.233 ± 0.008	-0.328 ± 0.009	-0.346 ± 0.009	-0.412 ± 0.012

shift in the $\pi \rightarrow \pi^*$ electronic absorption energy was found to be -0.02 eV by treating all the solvent molecules by the SPC-type potential and by employing the B3LYP description for the uracil, whereas the experimental value is ~ -0.30 eV. Based on our findings, the large discrepancy between theoretical and experimental results might be attributed to (a) the use of the inappropriate B3LYP xc functional and (b) neglect of induction and nonelectrostatic solute-solvent interactions. A much improved result of -0.20 eV was obtained by treating nine water molecules together with uracil at the B3LYP level.

In contrast to B3LYP and PBE0 functionals, the CAM-B3LYP functional is seen to provide solvent shifts in the $\pi \rightarrow \pi^*$ excitation of acrolein in very good agreement with the corresponding CCSD results, especially when a number of water molecules is quantum-mechanically described together with acrolein. In addition, the $\pi \rightarrow \pi^*$ transition is now the second lowest excited state in all molecular configurations, showing the great capacity of the CAM-B3LYP method to predict the high-lying excitation energies of solvated molecules in an efficient and reliable manner. The success of the CAM-B3LYP xc functional is attributed to the improved long-range behavior of the exchange potential compared to the conventional DFT functionals. However, the CAM-B3LYP and CCSD methods recover only around 80% of the experimental solvent shift equal to -0.52 eV. To improve the agreement, a larger number of solvent molecules around the solute have to be considered at the QM level (recall Fig. 7). While this is hardly possible at the CC level of theory, the CAM-B3LYP xc functional in combination with the polarizable water potential, thus, represents a reliable and cost-effective alternative.

Accurate theoretical predictions of the excitation energies of solvated molecules require a high level of theory as well as a reliable solvent model and may possibly involve dynamical averaging. Therefore, such calculations are usually very time consuming. To speed up the procedure, one could calculate the absolute magnitude of the excitation energy of the molecule in vacuum by using an expensive and accurate method, whereas the solvent shift could be obtained from the computations at a lower level of theory. The excitation energy in solution is then obtained as a sum of the calculated gas-phase absorption energy and solvent shift, assuming that the latter is independent of the electronic structure method employed. This is, for example, the essence in the ONIOM model.⁹¹ However, the findings of the present study imply that such an approach might lead to erroneous results because different electronic structure methods can describe solvent effects on excitation energies with varying quality, as exemplified in Table VIII. This might also apply to other properties than the excitation energies. For instance, very recently, we have demonstrated that different electronic structure methods and even different xc functionals can lead to very different results for the shifts in the NMR isotropic shielding constants due to hydrogen bonding, implying similar conclusions to be valid for the solvent shifts.⁹²

We do not discuss here the oscillator strengths of the $\pi \rightarrow \pi^*$ transition of acrolein in vacuum and solution because we find these not to be converged by using the

TABLE IX. The comparison between calculated and experimental vertical $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies (in eV) of acrolein in vacuum and water solution. The statistical error of statistically averaged excitation energies in aqueous solution and solvent shifts is 0.01 eV.

Method	Solvent model	$E_{\text{ex}}^{\text{vac}}$	$E_{\text{ex}}^{\text{liq}}$	ΔE_{ex}
$n \rightarrow \pi^*$				
HF	3 (H ₂ O) _{QM} SPCpol	4.56	4.94	0.38
B3LYP	3 (H ₂ O) _{QM} SPCpol	3.57	3.84	0.27
PBE0	3 (H ₂ O) _{QM} SPCpol	3.62	3.89	0.27
CAM-B3LYP	3 (H ₂ O) _{QM} SPCpol	3.78	4.04	0.26
CAM-BELYP	12 (H ₂ O) _{QM} SPCpol	3.78	4.04	0.26
CCSD	3 (H ₂ O) _{QM} SPCpol	3.93	4.16	0.23
CC3 ^a	...	3.75	...	...
Expt.		3.69 ^b	3.94 ^c	0.25 ^d
$\pi \rightarrow \pi^*$				
CAM-B3LYP	12 (H ₂ O) _{QM} TIP3P	6.41	5.98	-0.43
CAM-B3LYP	12 (H ₂ O) _{QM} SPCpol	6.41	5.95	-0.46
CAM-B3LYP ^e	12 (H ₂ O) _{QM} SPCpol	6.41	5.94	-0.47
CC3 ^a	...	6.65	...	...
Expt.		6.41 ^f	5.90 ^g	-0.52 ^g
		6.42 ^g	5.89 ^h	
		6.49 ⁱ		

^aBased on the CCSD(T) optimized geometry of acrolein.

^bReferences 44–47 and present work.

^cReferences 47 and 49 and present work.

^dReference 47 and present work.

^eBased on molecular configurations extracted from the nonpolarizable MD simulation.

^fReference 51.

^gReference 47.

^hPresent work.

ⁱReference 50.

aug-cc-pVDZ basis set at the CCSD level, and at least, the basis of triple- ζ quality is required for converged results. Further complications are related to the rather difficult convergence of the oscillator strengths with respect to the number and position of the water molecules included into the QM region.

D. Comparison to experimental data

In Table IX, we compare a selection of our results for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations of acrolein in vacuum and aqueous solution to the experimental data. In the case of the $n \rightarrow \pi^*$ transition, we give only the statistically averaged liquid-phase results obtained by using the polarizable SPCpol potential for water, since, as seen in Table VI, the SPC and SPCpol potentials lead to much similar $n \rightarrow \pi^*$ excitation energies in solution. Compared to experimental data, all DFT xc functionals considered lead to very accurate predictions of the solvent shift in the $n \rightarrow \pi^*$ absorption of acrolein. The CCSD model is also seen to perform very well, and only the HF method gives severely overestimated solvent shift. The absolute magnitudes of the $n \rightarrow \pi^*$ excitation energy calculated by using DFT are in very satisfactory agreement with experimental data, the PBE0 functional exhibiting perhaps the best performance. However, the results here may intrinsically contain inaccuracies due to the B3LYP optimized gas- and liquid-phase geometries of acrolein. As seen in Table IV, the absolute excitation energies are lowered

TABLE X. Summary of previously reported and present theoretical results for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies (in eV) of acrolein in vacuum and water solution and corresponding solvent shifts. Also included are experimental results.

Reference	Method	$E_{\text{ex}}^{n \rightarrow \pi^*}$ (vac)	$E_{\text{ex}}^{n \rightarrow \pi^*}$ (liq)	$\Delta E_{\text{ex}}^{n \rightarrow \pi^*}$	$E_{\text{ex}}^{\pi \rightarrow \pi^*}$ (vac)	$E_{\text{ex}}^{\pi \rightarrow \pi^*}$ (liq)	$\Delta E_{\text{ex}}^{\pi \rightarrow \pi^*}$
Iwata and Morokuma (Ref. 54)	SCF/EHP supermolecule	4.44	5.02	0.58	7.86	7.61	-0.25
Ten-no <i>et al.</i> (Ref. 58)	RISM-SCF	...	...	0.19	...	...	...
do Monte <i>et al.</i> (Ref. 57)	MR-CISD+ Q COSMO	3.85	4.09	0.24	7.15	6.75	-0.40
Aquilante <i>et al.</i> (Ref. 55)	MS-CASPT2 PCM	3.63	3.96	0.33	6.10	6.00	-0.10
	MS-CASPT2 supermolecule/PCM	3.63	4.06	0.43	6.10	...	...
	PBE0 PCM	3.66	3.86	0.20	6.35	6.13	-0.22
	PBE0 supermolecule/PCM	3.66	4.05	0.39	6.35	...	...
Martín <i>et al.</i> (Ref. 59)	CASSCF ASEP/MD	3.97	4.16	0.19 ± 0.01	...	...	...
	CASPT2 ASEP/MD	3.69	3.90	0.21 ± 0.02	...	...	...
Georg <i>et al.</i> (Ref. 56)	B3LYP MC QM/MM(SPC)	3.60	3.80	0.20 ± 0.10	...	...	...
Brancato <i>et al.</i> (Ref. 61)	B3LYP supermolecule/PCM	3.58	3.98	0.40	...	...	...
	B3LYP ADMP QM/MM(SPC) 2 (H ₂ O) _{QM} PCM	3.58	3.84	0.26 ± 0.01	...	...	...
Losa <i>et al.</i> (Ref. 60)	CASSCF ASEP/MD(SPC)	3.97	4.17	0.20 ± 0.01	...	...	...
	CASSCF ASEP/MD(SPCpol)	3.97	4.16	0.19 ± 0.01	...	...	...
	CASPT2 ASEP/MD(SPCpol)	3.77	3.96	0.19 ± 0.01	...	...	...
Present work	CAM-B3LYP MD QM/MM(SPCpol) 12 (H ₂ O) _{QM}	3.78	4.04	0.26 ± 0.01	6.41	5.95	-0.46 ± 0.01
	CCSD MD QM/MM(SPCpol) 3 (H ₂ O) _{QM}	3.93	4.16	0.23 ± 0.01	6.89	...	...
	CC3 ^a	3.75	...	...	6.65	...	...
Expt. ^b		3.69	3.94	0.25	6.41	5.90	-0.52
					6.42	5.89	
					6.49		

^aBased on the CCSD(T) optimized geometry of acrolein.^bSee Table IX for references to experimental data.

for the highly accurate CCSD(T) optimized vacuum geometry of acrolein compared to that based on B3LYP and, therefore, we expect the CAM-B3LYP to be superior among the considered xc functionals in the calculation of the $n \rightarrow \pi^*$ excitation energy in acrolein.

The HF approach, as expected, gives significantly overestimated $n \rightarrow \pi^*$ excitation energies of acrolein (Table IX). CCSD also severely overestimates this transition. A good agreement between theoretical CC and experimental $n \rightarrow \pi^*$ excitation energies is possible provided that the triples excitations in the CC expansion are taken into account. However, we emphasize that the inaccuracies in the calculation of the excitation energy in vacuum and liquid phase due to, for instance, inaccurate molecular geometries or neglect of triples excitations tend to cancel in the calculation of the solvent shift.

As demonstrated and previously discussed, the $\pi \rightarrow \pi^*$ excitation energy of acrolein in aqueous solution shows a high sensitivity to the nonelectrostatic intermolecular solute-solvent interactions (see Fig. 7). We have, therefore, carried out the extensive calculation of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies of acrolein in liquid phase where we include 12 water molecules in the QM region by using the CAM-B3LYP xc functional, which was previously shown (see Table VIII) to give reliable results of CCSD quality for the $\pi \rightarrow \pi^*$ excitation energy of acrolein in aqueous solution. The results are shown in Table IX. A very prominent finding in Table IX is that the CAM-B3LYP xc functional gives very accurate absolute $\pi \rightarrow \pi^*$ excitation energies of acrolein in vacuum and solution. By using the SPCpol potential, the computed solvent shift of -0.46 ± 0.01 eV is still somewhat underestimated with respect to the experimental data. The

solvent shift equal to -0.43 ± 0.01 eV is obtained when the nonpolarizable SPC potential (and molecular configurations from the SPC MD simulation) was employed. We have also performed the QM/MM calculation by using the SPCpol water potential on the molecular configurations taken from the SPC MD simulation. The solvent shift is now equal to -0.47 ± 0.01 eV and slightly higher compared to the case where the SPCpol water potential was used in consistent way, that is, the same potential in the MD simulation and in the QM/MM calculation. This is due to the larger intensity of hydrogen bonding between acrolein and water in the case of the SPC MD simulation, as seen in Fig. 6. We, therefore, again are left with the conclusion that the polarizable potential is important to use for the accurate prediction of the $\pi \rightarrow \pi^*$ excitation energy of solvated molecules.

The remaining discrepancies between the experimentally observed and theoretically calculated solvent shifts in the $\pi \rightarrow \pi^*$ excitation are likely partly due to imperfections in the MM potential of acrolein used in the MD simulation and partly due to imperfections in the comparison of theory and experiment as to what is the meaning of the energy of maximum absorption. In addition, even though we use the CAM-B3LYP xc potential in the QM/MM calculations with a substantial number of water molecules quantum-mechanically treated, problems related to the long-range solute-solvent dispersion interactions might persist.

E. Comparison to other computational approaches

In Table X, we present some previously published theoretical results for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies of acrolein in vacuum and aqueous solution along with the

results of the present study and experimental data. Interestingly, the continuum based solvent models lead to relatively good results for solvent shift in the $n \rightarrow \pi^*$ excitation.^{55,57} However, when a more realistic situation, that is, a molecular aggregate consisting of acrolein and two hydrogen-bonded water molecules, is considered, the solvent shift is severely overestimated,^{55,61} showing the failure of the supermolecular approach in this case. All studies which involve the dynamical averaging of the results over a number of molecular configurations show fairly accurate and stable results for the $n \rightarrow \pi^*$ solvent shift, although the shifts in Refs. 56, 59, and 60 are somewhat underestimated with respect to the experimental value. We want to emphasize that the solvent shifts in the $n \rightarrow \pi^*$ excitation energy calculated by using a variety of electronic structure methods are very similar in magnitude—in line with the findings of the present study. The results in Ref. 60 confirm that the polarizable and non-polarizable solvent models lead to very similar magnitudes of the solvent shift in the $n \rightarrow \pi^*$ absorption energy. The absolute $n \rightarrow \pi^*$ excitation energy of acrolein in gas phase is reproduced at the DFT level with satisfactory agreement with the experimental value.^{55,56,61}

The theoretical studies of the $\pi \rightarrow \pi^*$ electronic excitation of acrolein in aqueous solution are much more scarce. Up until now, this transition was studied by using only supermolecular or continuum type solvent models. In agreement with our findings, the SCF and PBE0 based solvent shifts in the $\pi \rightarrow \pi^*$ excitation energy are severely underestimated as compared to experimental data, as seen in Table X. A rather good performance of the MR-CISD + Q /COSMO approach in the calculation of the solvent shift is found, although the absolute excitation energies are severely overestimated. As demonstrated in Refs. 54, 55, and 57 and the present study, the vertical $\pi \rightarrow \pi^*$ electronic excitation energy of acrolein both in vacuum and aqueous solution is a challenging case for electronic structure theory and theoretical solvent models. However, this system serves as an ideal probe for testing the accuracy and reliability of computational approaches.

IV. SUMMARY

The main objective of this study is to investigate the performance of different electronic structure methods, primarily the DFT xc functionals, to predict solvatochromic effects. We have considered the HF method and three xc functionals B3LYP, PBE0, and CAM-B3LYP and we use the high-level CCSD model as a theoretical reference. For all electronic structure methods considered, we use a sophisticated solvent model based on the combined QM/MM methodology together with dynamical averaging over the molecular configurations dumped in the classical MD simulation. In the QM/MM calculation, we use either polarizable or non-polarizable force fields. As a test system, we have chosen the challenging case of acrolein in aqueous solution and we consider the solvatochromic effects on the vertical $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic absorption energies in this molecule. We also compare theoretical predictions to the experimental data. In addition to the previously published experimental

results, we have carried out new experimental UV measurements of acrolein in vapor phase and water solution.

The main conclusions of this work can be summarized as follows:

- The vertical $n \rightarrow \pi^*$ electronic absorption energies of acrolein in the vapor and liquid phases were measured to be 3.69 and 3.94 eV, respectively, in excellent agreement with previously published experimental data. This implies a gas-to-aqueous solution shift in the $n \rightarrow \pi^*$ transition of 0.25 eV. The maximum intensity in the $\pi \rightarrow \pi^*$ absorption of acrolein in aqueous solution was observed at 5.89 eV and compares well with the previously reported value of 5.90 eV. Due to technical issues, we were not able to record the $\pi \rightarrow \pi^*$ absorption spectrum of gaseous acrolein.
- The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies of acrolein were found to be well converged by using the aug-cc-pVDZ basis set at the HF, DFT, and CCSD levels of theory. The effect of the triples excitations in the CC expansion was found to be substantial in the calculation of the excitation energies. For very accurate results, the necessity of highly accurate, e.g., CCSD(T) based, molecular geometries is stressed.
- All three xc functionals considered provide very similar results for the solvent shifts in the $n \rightarrow \pi^*$ excitation energy and compare well to the corresponding CCSD predictions and experimental data. The HF approach, however, gives severely overestimated $n \rightarrow \pi^*$ solvent shifts as compared to CCSD and experiment.
- The HF, B3LYP, and PBE0 methods severely underestimate the solvent shift in the $\pi \rightarrow \pi^*$ absorption energy as compared to CCSD results. When explicit water molecules together with acrolein were quantum-mechanically considered at the B3LYP or PBE0 level, a severe mixing in the order of the states was observed within the molecular configurations. The B3LYP and PBE0 functionals are not capable of describing the $\pi \rightarrow \pi^*$ and other high-lying excitation energies of acrolein in aqueous solution. The CAM-B3LYP functional is found to provide the solvent shift in the $\pi \rightarrow \pi^*$ transition in very good agreement with CCSD.
- The solvent shift in the $n \rightarrow \pi^*$ absorption energy is essentially of electrostatic origin. In contrast, the magnitude of the $\pi \rightarrow \pi^*$ excitation energy in solution was found to be strongly dependent on the nonelectrostatic intermolecular interactions. The $\pi \rightarrow \pi^*$ excitation energy exhibits very slow convergence with respect to the number of water molecules together with acrolein quantum-mechanically treated.
- The solvent shifts in the $n \rightarrow \pi^*$ transition obtained by using polarizable or nonpolarizable water potentials are very similar in magnitude and are slightly larger in the case of the latter. In contrast, considerably larger solvent shifts in the $\pi \rightarrow \pi^*$ excitation energy are found by using the polarizable water potential, indicating the

importance of explicit consideration of intermolecular induction in this case.

- Our best estimate for the solvent shift in the $\pi \rightarrow \pi^*$ excitation is obtained by treating acrolein and the 12 closest water molecules at the CAM-B3LYP level and applying the SPCpol potential for the classical water molecules. This shift is equal to -0.46 ± 0.01 eV, compared to the experimental result of -0.52 eV.

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