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# Solvent effect on electronic absorption, fluorescence, and phosphorescence of acetone in water: Revisited by quantum mechanics/molecular mechanics (QM/MM) simulations

Haibo Ma<sup>a)</sup> and Yingjin Ma

*Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering Nanjing University, Nanjing 210093, China*

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The accurate simulation of fluorescence and phosphorescence spectra in solution remains a huge challenge due to the difficulty of simulating excited state dynamics in condensed phase. In this work we revisit the solvent effect on the electronic absorption, fluorescence, and phosphorescence of acetone by virtue of quantum mechanics/molecular mechanics (QM/MM) equilibrium state dynamics simulations for both the ground state ( $S_0$ ) and the lowest excited singlet ( $S_1$ ) and triplet ( $T_1$ ) states of aqueous acetone, which use periodic boundary conditions and hundreds of explicit solvent molecules and are free of empirical electrostatic fittings for excited states. Our calculated solvent effects on acetone's  $n \rightarrow \pi^*$  ( $S_0 \rightarrow S_1$ ) absorption (0.25–0.31 eV) and  $n \leftarrow \pi^*$  ( $S_1 \rightarrow S_0$ ) emission (0.03–0.04 eV) as well as the Stokes shift (0.22–0.27 eV) are in good accordance with the experimental results (0.19 to 0.31, –0.02 to 0.05, and 0.14 to 0.33 eV, respectively). We also predict small water effects (–0.05 to 0.03 eV) for  $S_1 \rightarrow T_1$  and  $T_1 \rightarrow S_0$  phosphorescence emissions of acetone, which have no experimental data to date. For the recent dispute about the magnitude of the solvent effect for acetone's  $S_1 \rightarrow S_0$  fluorescence, we confirm that such effect is very small, agreeing well with the experimental determinations and most recent theoretical calculations. The large solvent effect for electronic absorption and small or negligible one for fluorescence and phosphorescence are shown to be related with much reduced dipole moments of acetone and accordingly much less hydrogen bonds for aqueous acetone in the electronic excited states  $S_1$  and  $T_1$  comparing to the ground state  $S_0$ . We also disclose that solvent polarization effects are relatively small for all the electronic transitions of aqueous acetone involved in this work through the investigation of the QM region size effect on QM/MM results. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4808442>]

## I. INTRODUCTION

Acetone is a widely used solvatochromic probe molecule where the change of the  $n \rightarrow \pi^*$  transition in water is well characterized by experiments.<sup>1–10</sup> Although many computational works<sup>11–25</sup> have been devoted to the study of electronic absorption in aqueous acetone, its fluorescence spectra received limited theoretical attentions<sup>26–30</sup> due to the difficulty of simulating excited state dynamics. Moreover, the magnitude of the solvent effect on the  $n \leftarrow \pi^*$  ( $S_1 \rightarrow S_0$ ) emission is still controversial to some extent despite of the fact that it has been well recognized that the water effect on the  $n \rightarrow \pi^*$  ( $S_0 \rightarrow S_1$ ) absorption is a blueshift of  $\sim 0.2$ – $0.3$  eV. In 2003, Canuto's group<sup>26</sup> presented a first theoretical study of the solvent effect on the Stokes shift of acetone in water using classical Monte Carlo simulations, while nearly at the same time Rörig *et al.*<sup>27</sup> investigated aqueous acetone's electronic absorption and fluorescence spectra through short time (8.2–12 ps) quantum mechanics/molecular mechanics (QM/MM) Car-Parrinello molecular dynamics (CPMD) simulations. Nevertheless, the solvent shifts for the  $n \leftarrow \pi^*$  ( $S_1 \rightarrow S_0$ ) fluorescence transition evaluated by these two groups

are quite distinct: 0.23 eV by the former group<sup>26</sup> vs. 0.01 eV by the latter group.<sup>27</sup> In 2007, Öhrn and Karlström<sup>28</sup> also predicted a rather small solvent effect (0.02–0.05 eV) for the fluorescence transition from hybrid QM/MM Monte Carlo simulations and a careful analysis of available experimental results was also presented by them with a conclusion that the solvent effect in this case should be very small, less than  $\sim 0.05$  eV. Later, Canuto's group<sup>29</sup> re-examined their previous classical Monte Carlo simulation work,<sup>26</sup> and they found including the solute's electronic polarizations of both the ground and the excited states through an iterative procedure will decrease the solvent effect of  $n \leftarrow \pi^*$  fluorescence from 0.23 eV to 0.01–0.08 eV. However, Adias *et al.*'s recent QM/MM calculations based on classical molecular dynamics (MD) trajectories predicted a solvent shift around 0.14 eV for fluorescence of acetone in water,<sup>30</sup> in contrast with the understanding concluded from the works by Rörig *et al.*, Öhrn and Karlström, and Canuto *et al.*<sup>27–29</sup> that the solvent effect for fluorescence of acetone in water should be negligible or small.

In the recent years, the triplet state and the phosphorescence of acetone in aqueous solution have also been explored by classical<sup>30</sup> and QM/MM<sup>31</sup> simulation techniques. These works estimated  $T_1 \rightarrow S_0$  emission energy of acetone in water to be 2.35–2.67 eV<sup>30,31</sup> and the solvent shift for it was

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: [haibo@nju.edu.cn](mailto:haibo@nju.edu.cn)

determined to be around 0.14 eV.<sup>30</sup> However, these results are still difficult to rationalize due to the absence of experimental data for the phosphorescence process of aqueous acetone.

Considering the relatively long lifetimes of the lowest singlet and triplet excited states ( $S_1$  and  $T_1$ ) which are reported to be around 2 ns<sup>32–34</sup> and 20  $\mu$ s,<sup>35–37</sup> respectively, the accurate theoretical studies of such excited state dynamics and related fluorescence and phosphorescence spectra which can clarify the above disputes are highly desired. In this work, we perform QM/MM equilibrium state dynamics simulations for both the ground state ( $S_0$ ), the lowest triplet state ( $T_1$ ) and the lowest excited singlet state ( $S_1$ ) of aqueous acetone. Our QM/MM framework is built with advanced quantum chemical methodologies, the time-dependent density functional theory (TDDFT)<sup>38</sup> and equation-of-motion coupled cluster method restricted to single and double excitations (EOM-CCSD),<sup>39</sup> as well as recently proposed flexible water model (simple point charge extended, SPC-Fw).<sup>40</sup> By virtue of such QM/MM treatments, the solute's electronic polarization which is vital for excited states under different environments can be reasonably accounted based on first-principles without empirical electrostatic fittings. For comparisons, results obtained by polarizable continuum model (PCM)<sup>41</sup> calculations are also presented in this work.

## II. SIMULATION AND COMPUTATION DETAILS

Our simulated solution system is composed of one acetone molecule and 383 water molecules located in a cubic cell with edge length 22.61 Å replicated in three dimensions by the periodic boundary conditions, which corresponds to a bulk density of 1.0 g/ml. The system is pre-equilibrated with a purely classical MD simulation under  $T = 298$  K for 2 ns. In this classical simulation, the OPLS (optimized potentials for liquid simulations)<sup>42</sup> potential energy parameters for acetone and the flexible SPC-Fw pair potential<sup>40</sup> for water molecules are used. Based on the last configuration of the pre-equilibration 2 ns classical MD simulation, we start three independent 160-ps QM/MM equilibrium state dynamics simulations for  $S_0$ ,  $T_1$ , and  $S_1$  states separately (80 ps of equilibration + 80 ps of production). In all classical and QM/MM MD simulations, a NVT ensemble (isochoric-isothermal conditions) and the weak-coupling algorithm for temperature regulation<sup>43</sup> are implemented. The long-range Coulomb interactions are treated using the Ewald summation algorithm,<sup>44</sup> and a cutoff distance of 1.2 nm is applied to the van der Waals (vdW) interactions for all cases. For QM-MM interactions, the long range electrostatics are neglected beyond the cutoff of 0.8 nm. The MD equations of motion are integrated using the leapfrog-type Verlet algorithm with a 1 fs time step.

Recent studies indicated the quantum effects are neglectable for solvent molecules in aqueous acetone solution because the solute-solvent interactions in this system are dominated by the classical Coulomb repulsions.<sup>23–25,27</sup> Therefore, we restrict our QM part to only the acetone molecule and treat all 383 water molecules with classical SPC-Fw model in our QM/MM simulations. During the QM/MM dynamics simulation, the QM part is treated by the density functional theory (DFT) for  $S_0$  and  $T_1$  states and TDDFT for  $S_1$  with

$\omega$ B97X-D functional<sup>45</sup> and Dunning's correlation-consistent basis set cc-pvdz. We use the electronic polarization embedding scheme<sup>46</sup> to describe the QM/MM coupling, by which the polarization of the QM subsystem induced by the charges residing on the MM atoms can be incorporated as follows:

$$E_{\text{QM/MM}}^{\text{electronic}} = \sum_{A \in \text{MM}} \int \rho(\mathbf{r}) \frac{Q_A}{|\mathbf{r} - \mathbf{R}_A|} d\mathbf{r} + \sum_{A \in \text{QM}} \sum_{B \in \text{MM}} \frac{Z_A Q_B}{R_{AB}} + \sum_{A \in \text{QM}} \sum_{B \in \text{MM}} \varepsilon_{AB} \left[ \left( \frac{\sigma_{AB}}{R_{AB}} \right)^{12} - \left( \frac{\sigma_{AB}}{R_{AB}} \right)^6 \right], \quad (1)$$

where the symbols have their usual meanings and the three terms denote the electrostatic interaction between the QM electron density and the MM point charges, the electrostatic interaction between the QM point charge nuclei and the MM point charges, and the van der Waals repulsion between the QM and MM atoms in order.

In the subsequential quantum chemical calculations for electronic transition energies of aqueous acetone, we select 100 uncorrelated geometrical configurations separated by 0.8 ps for the electronic structure QM calculations from each of the three proceeding QM/MM dynamics trajectories for  $S_0$ ,  $T_1$ , and  $S_1$  states, respectively. In our QM calculations, we take the solvent water molecules within a sphere with a cutoff radius  $r_{\text{cutoff}} = 20$  Å described as SPC-Fw simple point charges. In order to study the solvent polarization effect on the electronic excitation energies, calculations with larger QM regions (the solute +  $N_{\text{water}}^{\text{QM}}$  solvent molecules) embedded in the surrounding simple point charge sphere are also performed. The QM calculations of electronic excited states are performed using the TDDFT method with the  $\omega$ B97X-D functional and EOM-CCSD with Dunning's correlation-consistent basis set aug-cc-pvdz. The transition energy in solution is then evaluated as a statistical average of the vertical excitation energy results at 100 different configurations.

For comparisons, we also implement PCM calculations in this work, in which the geometries are optimized at the  $\omega$ B97X-D/cc-pvdz level and the excitation energies are evaluated at the  $\omega$ B97X-D/aug-cc-pvdz level.

All the QM calculations in this work are done with GAUSSIAN 09 program<sup>47</sup> and all the classical MM simulations are performed using AMBER 12.0 software package,<sup>48</sup> while the QM/MM simulations are implemented with an GAUSSIAN/AMBER interface.<sup>49</sup>

## III. RESULTS AND DISCUSSION

Before the study of the electronic state transitions, we first focus on the structural information of the different electronic states to investigate the microscopic solvation structure of the different electronic states of the aqueous acetone solution. In Table I we list the calculated bond length and bond angle values as well as the dipole moments for acetone in gas phase by QM optimization and aqueous solution by QM PCM optimization or QM/MM simulation. (The topology and atom labeling of acetone is shown in Fig. 1.) In general, we may find the solvation leads to the lengthening of both the CO and CC bond lengths for both the ground state



TABLE I. Calculated geometrical parameters and dipole moments  $\mu$  for acetone in gas phase (by QM optimization) and aqueous solution (by QM PCM optimization or QM/MM simulation).

	$r(\text{O1O1C1})$ (Å)	$r(\text{C1C2})$ (Å)	$\angle(\text{C2C1C6})$ (deg)	$\mu$ (D)
In gas phase (by QM optimization)				
$S_0$	1.210	1.515	116.3	2.80
$S_1$	1.303	1.510	119.4	1.91
$T_1$	1.322	1.514	118.3	1.66
In aqueous solution (by QM PCM optimization)				
$S_0$	1.216	1.510	116.4	3.56
$S_1$	1.303	1.515	119.0	2.38
$T_1$	1.323	1.516	118.0	2.08
In aqueous solution (by QM/MM simulation)				
$S_0$	1.223	1.518	116.9	4.33
$S_1$	1.310	1.519	120.3	2.93
$T_1$	1.326	1.525	118.9	2.59

$S_0$  and the excited states  $S_1$  and  $T_1$ , except the  $S_0$  case by PCM calculations. This discrepancy is due to the limitation of implicit solvation models such as PCM in which solvent-specific effects including hydrogen bonding cannot be well reproduced. However, solute-solvent interaction of O(acetone)–H(water) hydrogen bonding is obviously very important in the aqueous acetone solution. Therefore, hybrid QM/MM simulations should be preferable for such systems containing solute-solvent hydrogen bonds. Meanwhile, it is evident from both PCM and QM/MM results for aqueous solution that both the CO and CC bond lengths increase monotonically when the electronic state is changing from  $S_0$  to  $S_1$  and then  $T_1$ . Acetone in gas phase may also be found to have such monotonic behavior for CO bond length. One may notice that the electronic excited states  $S_1$  and  $T_1$  have smaller dipole moments than those of ground states for both gas phase and solution phase. All the dipole moments for different electronic states will be increased from the gas phase to solution phase and such polarization effects induced by the water environment are shown to be stronger in QM/MM simulations than PCM calculations. The dipole moments of acetone in  $S_0$ ,  $S_1$ , and  $T_1$  states change from 2.80 D, 1.91 D, and 1.66 D in gas phase to 4.33 D, 2.93 D, and 2.59 D in water solution, respectively, with increases of  $\sim 50\%$ . These dipole moment values are in good agreements with previous simulations.<sup>27,29,30</sup>

To study the collective behavior of acetone in water solution, we illustrate the radial distribution functions (RDFs)

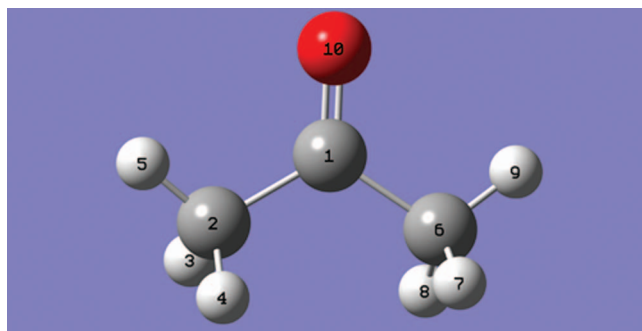


FIG. 1. Topology and atom labeling of acetone.

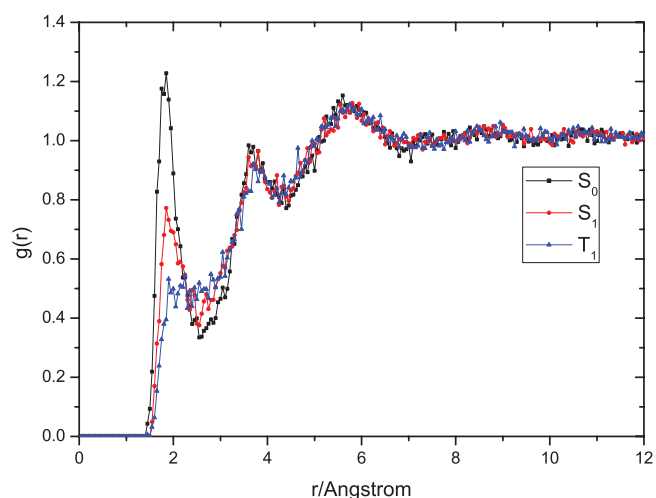


FIG. 2. Calculated radial distribution functions (RDFs) for O(acetone)–H(water) pair from the ground state ( $S_0$ ), the lowest triplet state ( $T_1$ ) and the lowest excited singlet state ( $S_1$ ) QM/MM simulations of aqueous acetone solution.

of the solute-solvent pairs (O(acetone)–H(water))  $g_{\text{O-H}}$  under ambient conditions in Fig. 2. It can be found that,  $g_{\text{O-H}}$  has close first peak positions (1.85–1.90 Å) and also very close first minimum positions (2.3–2.55 Å) for all the three electronic states, indicating the hydrogen-bonds formed between the acetone oxygen and the water hydrogen. In computational studies, the average hydrogen-bonding number  $N_{\text{HB}}$  can be calculated by the integration of  $g_{\text{O-H}}$  in the first peak as

$$N_{\text{HB}} = 8\pi\rho \int_0^{r_{\text{O-H}}^{\text{min}}} g_{\text{O-H}}(r)r^2 dr, \quad (2)$$

where  $\rho$  is the number density of the solution and  $r_{\text{O-H}}^{\text{min}}$  is the distance when the O(acetone)–H(water) RDF minimum locates. From Fig. 2, the integrations up to the first minimum (2.55 Å for  $S_0$  and  $S_1$  while 2.3 Å for  $T_1$ ) give  $N_{\text{HB}}$  of 2.45, 1.92, and 1.02 for  $S_0$ ,  $S_1$ , and  $T_1$  states, respectively. This indicates that the hydrogen bonds in  $S_1$  and  $T_1$  states are much weakened comparing to those in  $S_0$  state as a result of reduced dipole moment of acetone shown earlier, in consistency with the variation trend of  $g_{\text{O-H}}$  peak magnitude. One may notice that our calculated  $N_{\text{HB}}$  number for  $S_1$  (1.92) is slightly larger than previous simulated results (1.6<sup>27</sup> and 1.54<sup>30</sup>) whereas our calculated  $N_{\text{HB}}$  number for  $T_1$  (1.02) lies between the earlier reported data (1.28<sup>30</sup> and 0.8<sup>31</sup>). It should be mentioned that these earlier reported results are based on classical simulations<sup>30</sup> with empirical electrostatic fittings for the excited states or QM/MM simulations<sup>31</sup> with non-periodic boundary conditions including only a small number (129) of explicit solvent molecules or QM/MM simulations<sup>27</sup> at restricted open-shell Kohn-Sham (ROKS)<sup>50</sup> level. Considering the fact that our QM/MM simulations use TDDFT method in stead of ROKS formalism with periodic boundary conditions and a larger number (383) of explicit solvent molecules and are also free of empirical electrostatic fittings for the excited states, it can be expected this work will give more reasonable and balanced descriptions for the solvation structures

TABLE II. Electronic absorption and emission energies of acetone in units of eV determined by experiments and QM/MM or PCM calculations.

Method	Absorption	Emission			Stokes shift
	$S_0 \rightarrow S_1$	$S_1 \rightarrow S_0$	$S_1 \rightarrow T_1$	$T_1 \rightarrow S_0$	$\Delta_{Stokes}(\text{fl})$
Experiments					
In gas phase	4.46 <sup>a</sup> , 4.48 <sup>b</sup> , 4.49 <sup>c</sup> , 4.38 <sup>d</sup>	3.01 <sup>e</sup>	...	...	1.37–1.48
In aqueous solution	4.68 <sup>c</sup> , 4.69 <sup>b</sup>	2.99 <sup>f</sup> , 3.06 <sup>g</sup>	...	...	1.62–1.70
$\Delta_{sol}$	0.19–0.31	−0.02 to 0.05	...	...	0.14–0.33
QM/MM( $\omega$ B97X-D/SPC-Fw)					
In gas phase	4.34	3.22	0.61	2.32	1.12
In aqueous solution <sup>h</sup>	4.59	3.25	0.58	2.33	1.34
In aqueous solution <sup>i</sup>	4.64	3.26	0.57	2.34	1.38
In aqueous solution <sup>j</sup>	4.65	3.26	0.56	2.35	1.39
$\Delta_{sol}$ <sup>h</sup>	0.25	0.03	−0.03	0.01	0.22
$\Delta_{sol}$ <sup>i</sup>	0.30	0.04	−0.04	0.02	0.26
$\Delta_{sol}$ <sup>j</sup>	0.31	0.04	−0.05	0.03	0.27
QM/MM(CCSD/SPC-Fw)					
In gas phase	4.39	3.20	0.38	2.54	1.19
In aqueous solution <sup>h</sup>	4.64	3.23	0.36	2.54	1.41
$\Delta_{sol}$ <sup>h</sup>	0.25	0.03	−0.02	0.00	0.22
PCM(acetone, $\omega$ B97X-D)					
In gas phase	4.48	3.17	0.62	2.25	1.31
In aqueous solution	4.60	3.35	0.58	2.48	1.25
$\Delta_{sol}$	0.12	0.18	−0.04	0.23	−0.06

<sup>a</sup>From Ref. 10.<sup>b</sup>From Ref. 6.<sup>c</sup>From Ref. 2.<sup>d</sup>From Ref. 8.<sup>e</sup>From Ref. 3.<sup>f</sup>From Ref. 5.<sup>g</sup>From Ref. 7.<sup>h</sup>Calculated with  $N_{water}^{QM} = 0$  and  $r_{cutoff} = 20 \text{ \AA}$ .<sup>i</sup>Calculated with  $N_{water}^{QM} = 6$  and  $r_{cutoff} = 20 \text{ \AA}$ .<sup>j</sup>Calculated with  $N_{water}^{QM} = 12$  and  $r_{cutoff} = 20 \text{ \AA}$ .

and hydrogen-bonding patterns of aqueous acetone in both the ground state and the excited states.

In Table II we summarize the electronic absorption and emission energies as well as Stokes shift value determined by various experiments and QM/MM or PCM calculations. The Stokes shift for fluorescence is defined as the difference between the singlet absorption energy and the singlet emission energy. First, let us see the experimental data. Evidently, there are significant solvent effects on the  $S_0 \rightarrow S_1$  absorption energies ( $\sim 0.2$ – $0.3$  eV) whereas such effects for  $S_1 \rightarrow S_0$  emission energies are small or negligible. It can be also seen that the water environment will accordingly induce a positive solvent shift for the Stokes shift. Second, let us compare the TDDFT results with the EOM-CCSD results for the same system (for example, in the gas phase or within the same QM/MM scheme  $N_{water}^{QM}=0$  and  $r_{cutoff} = 20 \text{ \AA}$ ). It is shown that the  $\omega$ B97X-D based singlet absorption and emission energies ( $S_0 \leftrightarrow S_1$ ) are smaller than CCSD results by less than 0.05 eV and such differences increase to around 0.2 eV for describing phosphorescence emission energies ( $S_1 \rightarrow T_1$  and  $T_1 \rightarrow S_0$ ). However, the calculated solvent shifts by TDDFT and EOM-CCSD are very close to each other because the errors in the calculation of electronic transition energies in gas phase and in aqueous solution tend to be canceled. Encouragingly, such calculated solvent shifts by QM/MM scheme for  $S_0 \rightarrow S_1$  absorption (0.25–0.31 eV) and  $S_1 \rightarrow S_0$  emission

(0.03–0.04 eV) are in reasonable agreements with the experimental determinations (0.19 to 0.31 eV and  $-0.02$  to 0.05 eV, respectively). Importantly, we also correctly reproduce that the solvent effect for  $S_1 \rightarrow S_0$  emission is much smaller than that for  $S_0 \rightarrow S_1$  absorption, consistent with the experimental findings and recent theoretical results.<sup>27–29</sup> This provides significant improvements over recent QM/MM calculations<sup>30</sup> which predicted the water solvent shift of the fluorescence transition of acetone to be around 0.14 eV and conflicted with experiments. On the contrary, the QM PCM calculations predict much smaller solvent effects for  $S_0 \rightarrow S_1$  absorptions and much larger solvent effects for  $S_0 \leftarrow S_1$  emissions when comparing the experimental data or our QM/MM simulated results, due to the well-known limitation of implicit solvation model that cannot properly describe the solvent-specific interactions such as hydrogen-bonding. At the same time, it seems that our calculated Stokes shifts in both the gas phase and aqueous solution are still small (1.1–1.4 eV) when compared with experimental values (1.4–1.7 eV). In fact, to our knowledge all the other theoretical works<sup>27,30</sup> also predicted small Stokes shifts around 1.3–1.5 eV. Therefore, it is still questionable if the discrepancy between the calculated Stokes shifts of acetone in gas phase and aqueous solution and the experimentally determined ones is due to the deficiencies of the theoretical simulations or caused by the problems of measuring and interpreting the experimental spectra. Probably, theoretical

calculations based on the simple Franck-Condon approximation which neglects the rotational and vibrational couplings with electronic transitions prohibit the well-established comparisons between them with the experiments.<sup>30</sup> Anyway, our QM/MM calculations correctly predict positive and reasonably non-negligible water solvent shifts for the Stokes shift (0.27 and 0.22 eV by TDDFT and EOM-CCSD, respectively), in very good accordance with the experimental determinations (0.14–0.33 eV).

Table II also summarizes the phosphorescence emission energies of  $S_1 \rightarrow T_1$  and  $T_1 \rightarrow S_0$  transitions. To our knowledge, no experimental data are available for such emissions in gas phase and in aqueous solution. However, one may also notice that experimental reports for  $T_1 \rightarrow S_0$  emission energy of neat liquid acetone (2.82 eV)<sup>51</sup> and acetone in ether-isopropanol mixture (2.72 eV)<sup>5</sup> are close to our determined values (2.33–2.54 eV) for aqueous acetone. Interestingly, both the QM/MM and PCM calculations present a small solvent effect (−0.05 to −0.02 eV) for  $S_1 \rightarrow T_1$  emission while QM/MM calculations predict a small solvent effect (0.00–0.03 eV) on the contrary to the large shift (0.23 eV) by PCM calculations for  $T_1 \rightarrow S_0$  emission. Adias *et al.*'s recent QM/MM work also notices such a disagreement for  $T_1 \rightarrow S_0$  emission and they ascribed it to the missing solvent polarization effect in the solute-only QM/MM calculations (i.e.,  $N_{water}^{QM} = 0$ ).<sup>30</sup> For the purpose of investigating the solvent polarization effect on the electronic excitation energies, calculations with larger QM regions (the solute +  $N_{water}^{QM}$  solvent molecules) embedded in the surrounding simple point charge sphere are also performed and illustrated in Table II. Alternatively, solvent polarization effect on the spectral shift can be taken into account by virtue of using polarizable solvent models<sup>52–55</sup> which perform self-consistent solvent dipole calculations for both the ground state and the excited state. It can also be expected that majority of such solvent polarization effect is included with a sufficiently large  $N_{water}^{QM}$  value in our QM/MM scheme. From Table II we may clearly see that such solvent polarization effect is rather small (less than 0.06 eV) for all the electronic transitions of aqueous acetone. This is in good agreements with recent studies of solvent polarization effect on the singlet absorption energy of acetone in water by Lin and Gao<sup>23</sup> and us.<sup>25</sup> Even with the majority of the solvent polarization effect included ( $N_{water}^{QM} = 12$ ), the nearly converged solvent shift for  $T_1 \rightarrow S_0$  emission is still only 0.03 eV, much deviated from the PCM calculated 0.23 eV. Therefore, we consider the small solvent effect for  $T_1 \rightarrow S_0$  emission should be attributed by its inherent electronic transition nature, not caused by the missing of solvent polarization in the solute-only QM/MM calculations. Therefore, our general conclusion for the water effects on acetone's phosphorescence emission energies of  $S_1 \rightarrow T_1$  and  $T_1 \rightarrow S_0$  transitions is that they are small or negligible.

Before the end of the paper, we would like to discuss about the reliability of our QM/MM strategy. Obviously, such reliability is governed by many technical factors, such as the size of QM region, the choice of the density functional, and the choice of the basis set as well as the sampling time length. Rörig *et al.*'s QM/MM CPMD study on the ground state and the first excited singlet state of acetone in water<sup>27</sup> has shown

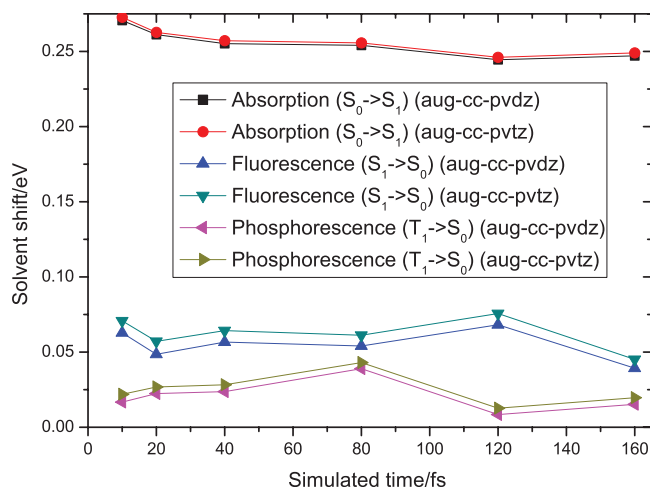


FIG. 3. Time evolution of solvent effects on the electronic transition energies of aqueous acetone by solute-only QM/MM calculations ( $N_{water}^{QM}=0$ ) with  $\omega$ B97X-D functional and different basis sets.

that purely classical description of the solvent is sufficient for this system, since inclusion of the first solvent shell of 12 water molecules into the quantum system does not show a significant effect on the electronic transition. Also considering the fact that many other works<sup>23–25</sup> have also found classical Coulomb repulsions dominating the intermolecular interactions between acetone and water, one may consider QM/MM simulation with the solute-only ( $N_{water}^{QM} = 0$ ) QM region should be a reasonable choice with a good compromise between accuracy and efficiency. In our recent paper,<sup>25</sup> we made a detailed comparison for the dependence of calculated electronic excitation energy on the different chosen density functionals and demonstrated that density functionals with long-range corrections such as  $\omega$ B97X-D can give reasonable descriptions for aqueous acetone system. Therefore, our discussion about the reliability of our QM/MM strategy here will only focus on the result's dependencies on the basis set and the sampling time length.

In Fig. 3, we illustrate calculated solvent effects on the electronic transition energies of aqueous acetone over different simulated time lengths. Obviously, although slight fluctuations of the simulated solvatochromic shifts with the increasing  $t$  can be observed, such shifts are generally stable for various kinds of electronic transitions provided that the simulation time is sufficiently long (around or more than tens of femtoseconds). We also analyze the statistical errors ( $\sqrt{\frac{1}{N} \times \frac{\sum_{i=1}^N (\Delta_i - \langle \Delta \rangle)^2}{N}}$ ) of our statistical average process. It is found that such statistical errors with  $N = 100$  are also stably around 0.01 eV for all three types of electronic transitions with simulation time around or more than tens of femtoseconds, which will not influence our qualitative conclusion about solvent effects on acetone's electronic spectra. In view of the facts that the averaged solvatochromic shifts are stable and the statistical errors are relatively small, we consider our simulated time (160 ps) is sufficiently long for achieving reliable statistical average results for aqueous acetone system. From Fig. 3, one may also notice that basis set has a neglectable effect for QM/MM calculations of the

TABLE III. Calculated geometrical parameters for acetone by QM optimization with different basis sets.

	$r(\text{O1O1C1})$ (Å)	$r(\text{C1C2})$ (Å)	$\angle(\text{C2C1C6})$ (deg)
$\omega\text{B97X-D/cc-pvdz}$			
$S_0$	1.210	1.515	116.3
$S_1$	1.303	1.510	119.4
$T_1$	1.322	1.514	118.3
$\omega\text{B97X-D/aug-cc-pvdz}$			
$S_0$	1.213	1.513	116.6
$S_1$	1.300	1.512	119.1
$T_1$	1.321	1.515	118.4

solvatochromic shifts here since the differences between the results by our adopted aug-cc-pvdz basis and those by more polarized aug-cc-pvtz basis are less than 0.01 eV for all calculated cases. In our QM/MM dynamics simulations, we adopt cc-pvdz basis set instead of aug-cc-pvdz due to the limits of computational costs. In Table III, we also compare the optimized acetone geometrical differences for these two basis sets. It is clearly shown that, such differences are very small (less than 0.002 Å for bond lengths and less than 0.3° for bond angles). Therefore, one may expect that QM/MM dynamics simulations with cc-pvdz basis could also give reasonable potential energy gradients and accordingly reliable geometrical structures for the later subsequent higher level electronic structure calculations. In a word, our current QM/MM scheme (160 ps  $\omega\text{B97X-D/cc-pvdz}$  solute-only QM/MM dynamics simulation + TDDFT or EOM-CCSD/aug-cc-pvtz QM/MM electronic structure calculations at 100 uncorrelated snapshots) is shown to be able to produce reliable estimations of solvent effect on various electronic spectra of aqueous acetone with the consideration of a good balance between the high accuracy and feasible computational costs.

#### IV. SUMMARY AND CONCLUSION

In this work, we re-examine the solvent effect on the electronic absorption, fluorescence and phosphorescence of acetone through QM/MM equilibrium state dynamics simulations for aqueous acetone's three electronic states, including  $S_0$ ,  $S_1$ , and  $T_1$  states. Our general finding is that the solvent effect on acetone's  $S_0 \rightarrow S_1$  absorption is large (0.25–0.31 eV) and those for  $S_1 \rightarrow S_0$  fluorescence and  $S_1 \rightarrow T_1$  and  $T_1 \rightarrow S_0$  phosphorescence are small (0.03 to 0.04 eV and –0.05 to 0.03 eV, respectively). These values as well as the Stokes shift (0.22–0.27 eV) agree well with available experimental results. Such results support the experimental determinations and most recent theoretical calculations for the recent dispute about the magnitude of the solvent effect for acetone's  $S_1 \rightarrow S_0$  fluorescence.

We further disclose that the dipole moments of acetone in the electronic excited states  $S_1$  and  $T_1$  are significantly smaller than that in the ground state  $S_0$  for both the gas phase and condensed phase and the solvent effect will result in increases of ~50% for acetone's dipole moments under all these three electronic states. The smaller dipole moments of acetone in  $S_1$  and  $T_1$  comparing to  $S_0$  then lead to the evidently reduced

numbers of hydrogen bonds formed between the carbonyl oxygen atom of acetone and the hydrogen atom of water in  $S_1$  and  $T_1$  (We determine  $N_{\text{HB}}$  to be 2.45, 1.92, and 1.02 for  $S_0$ ,  $S_1$ , and  $T_1$  states, respectively.), and accordingly fluorescence and phosphorescence emissions have much smaller solvent effect than electronic absorption for acetone as we have shown.

Through the investigation of the QM region size effect on QM/MM results, we also reveal that solvent polarization effects are rather small (less than 0.1 eV) for all the electronic transitions of aqueous acetone in this work. We confirm small solvent effects for  $S_1 \rightarrow T_1$  and  $T_1 \rightarrow S_0$  phosphorescence are due to their inherent electronic transition nature, not caused by the missing of solvent polarization in the solute-only QM/MM calculations.

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- <sup>1</sup>G. W. Luckey and W. Albert Noyes, Jr., *J. Chem. Phys.* **19**, 227 (1951).
- <sup>2</sup>N. S. Bayliss and E. G. McRae, *J. Phys. Chem.* **58**, 1006 (1954).
- <sup>3</sup>J. Hecklen and W. A. Noyes, Jr., *J. Am. Chem. Soc.* **81**, 3858 (1959).
- <sup>4</sup>W. P. Hayes and C. J. Timmons, *Spectrochim. Acta* **21**, 529 (1965).
- <sup>5</sup>R. F. Borkman and D. R. Kearns, *J. Chem. Phys.* **44**, 945 (1966).
- <sup>6</sup>N. S. Bayliss and G. Wills-Johnson, *Spectrochim. Acta, Part A* **24**, 551 (1968).
- <sup>7</sup>G. D. Renkes and F. S. Wettack, *J. Am. Chem. Soc.* **91**, 7514 (1969).
- <sup>8</sup>K. N. Walzl, C. F. Koerting, and A. Kuppermann, *J. Chem. Phys.* **87**, 3796 (1987).
- <sup>9</sup>G. E. Bennett and K. P. Johnston, *J. Phys. Chem.* **98**, 441 (1994).
- <sup>10</sup>I. Renge, *J. Phys. Chem. A* **113**, 10678 (2009).
- <sup>11</sup>J. Gao, *J. Am. Chem. Soc.* **116**, 9324 (1994).
- <sup>12</sup>M. A. Thompson, *J. Phys. Chem.* **100**, 14492 (1996).
- <sup>13</sup>F. C. Grozema and P. T. van Duijnen, *J. Phys. Chem. A* **102**, 7984 (1998).
- <sup>14</sup>J. Li, C. J. Cramer, and D. G. Truhlar, *Int. J. Quantum Chem.* **77**, 264 (2000).
- <sup>15</sup>M. Cossi and V. Barone, *J. Chem. Phys.* **112**, 2427 (2000).
- <sup>16</sup>M. E. Martin, M. L. Sanchez, F. J. Olivares del Valle, and M. A. Aguilera, *J. Chem. Phys.* **113**, 6308 (2000).
- <sup>17</sup>F. Aquilante, M. Cossi, O. Crescenzi, G. Scalmani, and V. Barone, *Mol. Phys.* **101**, 1945 (2003).
- <sup>18</sup>K. Aidas, J. Kongsted, A. Osted, K. V. Mikkelsen, and O. Christiansen, *J. Phys. Chem. A* **109**, 8001 (2005).
- <sup>19</sup>J. Neugebauer, M. J. Louwerse, E. J. Baerends, and T. A. Wesolowski, *J. Chem. Phys.* **122**, 094115 (2005).
- <sup>20</sup>T. L. Fonseca, K. Coutinho, and S. Canuto, *J. Chem. Phys.* **126**, 034508 (2007).
- <sup>21</sup>Y.-K. Li, Q. Zhu, X.-Y. Li, K.-X. Fu, X.-J. Wang, and X.-M. Cheng, *J. Phys. Chem. A* **115**, 232 (2011).
- <sup>22</sup>D. M. Chipman, *J. Chem. Phys.* **131**, 014104 (2009).
- <sup>23</sup>Y.-L. Lin and J. Gao, *J. Chem. Theory Comput.* **3**, 1484 (2007).
- <sup>24</sup>A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Chem. Theory Comput.* **6**, 2829 (2010).
- <sup>25</sup>H. Ma and Y. Ma, *J. Chem. Phys.* **137**, 214504 (2012).
- <sup>26</sup>K. Coutinho and S. Canuto, *J. Mol. Struct.: THEOCHEM* **632**, 235 (2003).
- <sup>27</sup>U. F. Rörig, I. Frank, J. Hutter, A. Laio, J. VandeVondele, and U. Rothlisberger, *ChemPhysChem* **4**, 1177 (2003).
- <sup>28</sup>A. Öhrn and G. Karlström, *Theor. Chem. Acc.* **117**, 441 (2007).
- <sup>29</sup>Y. Orozco-Gonzalez, K. Coutinho, and S. Canuto, *Chem. Phys. Lett.* **499**, 108 (2010).
- <sup>30</sup>K. Aidas, K. V. Mikkelsen, B. Mennucci, and J. Kongsted, *Int. J. Quantum Chem.* **111**, 1511 (2011).
- <sup>31</sup>G. Brancato, N. Rega, and V. Barone, *Chem. Phys. Lett.* **453**, 202 (2008).



- <sup>32</sup>M. O'sullivan and A. C. Testa, *J. Am. Chem. Soc.* **92**, 5842 (1970).
- <sup>33</sup>G. M. Breuer and E. K. C. Lee, *J. Phys. Chem.* **75**, 989 (1971).
- <sup>34</sup>A. M. Halpern and W. R. Ware, *J. Chem. Phys.* **54**, 1271 (1971).
- <sup>35</sup>G. Porter, R. W. Yip, J. M. Dunston, A. J. Cessna, and S. E. Sugamori, *Trans. Faraday Soc.* **67**, 3149 (1971).
- <sup>36</sup>G. Porter, S. K. Dogra, R. O. Loufty, S. E. Sugamori, and R. W. Yip, *J. Chem. Soc., Faraday Trans.* **69**, 1462 (1973).
- <sup>37</sup>N. J. Turro, H.-C. Steinmetzer, and A. Yekta, *J. Am. Chem. Soc.* **95**, 6468 (1973).
- <sup>38</sup>C. A. Ullrich, *Time-Dependent Density-Functional Theory – Concepts and Applications* (Oxford University Press, New York, 2012).
- <sup>39</sup>M. Kállay and J. Gauss, *J. Chem. Phys.* **121**, 9257 (2004).
- <sup>40</sup>Y. Wu, H. L. Tepper, and G. A. Voth, *J. Chem. Phys.* **124**, 024503 (2006).
- <sup>41</sup>S. Miertus, E. Scrocco, and J. Tomasi, *Chem. Phys.* **55**, 117 (1981).
- <sup>42</sup>W. L. Jorgensen, D. S. Maxwell, and J. TiradoRives, *J. Am. Chem. Soc.* **118**, 11225 (1996).
- <sup>43</sup>H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak, *J. Chem. Phys.* **81**, 3684 (1984).
- <sup>44</sup>P. P. Ewald, *Ann. Phys.* **369**, 253 (1921).
- <sup>45</sup>J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.* **10**, 6615 (2008).
- <sup>46</sup>D. Bakowies and W. Thiel, *J. Phys. Chem.* **100**, 10580 (1996).
- <sup>47</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.
- <sup>48</sup>D. A. Case, T. A. Darden, T. E. Cheatham III, C. L. Simmerling, J. Wang, R. E. Duke, R. Luo, R. C. Walker, W. Zhang, K. M. Merz, B. Roberts, S. Hayik, A. Roitberg, G. Seabra, J. Swails, A. W. Götz, I. Kolossvary, K. F. Wong, F. Paesani, J. Vanicek, R. M. Wolf, J. Liu, X. Wu, S. R. Brozell, T. Steinbrecher, H. Gohlke, Q. Cai, X. Ye, J. Wang, M.-J. Hsieh, G. Cui, D. R. Roe, D. H. Mathews, M. G. Seetin, R. Salomon-Ferrer, C. Sagui, V. Babin, T. Luchko, S. Gusarov, A. Kovalenko, and P. A. Kollman, AMBER 12, University of California, San Francisco, 2012.
- <sup>49</sup>A. W. Götz, M. Clark, and R. C. Walker, "An extensible interface for QM/MM molecular dynamics simulations with Amber," *J. Comput. Chem.* (submitted).
- <sup>50</sup>I. Frank, J. Hutter, D. Marx, and M. Parrinello, *J. Chem. Phys.* **108**, 4060 (1998).
- <sup>51</sup>U. Pischel and W. M. Nau, *J. Am. Chem. Soc.* **123**, 9727 (2001).
- <sup>52</sup>M. A. Thompson and G. K. Schenter, *J. Phys. Chem.* **99**, 6374 (1995).
- <sup>53</sup>J. Gao and K. Byun, *Theor. Chem. Acc.* **96**, 151 (1997).
- <sup>54</sup>L. V. Slipchenko, *J. Phys. Chem. A* **114**, 8824 (2010).
- <sup>55</sup>K. Sneskov, T. Schwabe, O. Christiansen, and J. Kongsted, *Phys. Chem. Chem. Phys.* **13**, 18551 (2011).