Excited-State Vibrations of Solvated Molecules: Going Beyond the Linear-Response Polarizable Continuum Model

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ABSTRACT: In this work we compare the excited-state vibrational patterns computed in gas and condensed phases, the latter being modeled with the Polarizable Continuum Model. For the first time we compare the results of two alternative theoretical approaches that is a standard linear-response approximation and a state-specific description, within the corrected linear-response formulation. Using five test molecules, we show that the point group symmetry of the excited-state geometry might differ with the linear and corrected linear-response models. The vibrational frequencies obtained with the latter model are often rather close to their gas counterparts, whereas the linear-response model tends to overestimate solvation effects. The differences in zero-point vibrational energies between the excited and ground states have also been evaluated, and the impact of the selected solvent model is generally limited for this average parameter.

Gas 119 cm⁻¹
LR   90 cm⁻¹
cLR 117 cm⁻¹
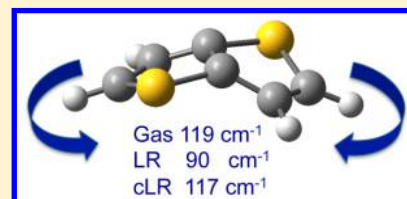
To account for the molecular environment surrounding a compound of interest, different computational approaches have been developed. Among these methods, continuum schemes, e.g., the Polarizable Continuum Model (PCM),[1] that treat the environment as a structureless material surrounding a cavity containing the studied molecule, are particularly efficient. Indeed, for ground-state (GS) properties, one can generally include PCM corrections without significantly increasing the computational effort. As the environmental effects tend to be larger for electronically excited states (ES) than for GS,[2] the coupling of continuum models with several ES theories has been achieved, e.g., Symmetry Adapted Cluster Configuration Interaction Model (SACCI),[3−5] Equation Of Motion Coupled-Cluster (EOM-CC),[6−8] Quantum Monte Carlo (QMC),[9] and second-order Algebraic-Diagrammatic Construction [ADC(2)],[10] as well as Time-Dependent Density Functional Theory (TD-DFT).[11−16] For TD-DFT, four methods, differing by the way in which the change of polarization of the cavity between the GS and the ES is modeled, are now available: (i) in the standard linear response (LR) approach, the transition density is used to calculate the variation of the PCM response with respect to the ground state;[11,12] (ii) in the perturbative corrected-LR (cLR) model,[14,17] the actual change in the one-particle density between GS and ES is used instead of the transition density thus recovering a state-specific variation of the PCM response upon excitation; (iii) in the self-consistent state-specific approach proposed by Improta and co-workers,[15] an iterative scheme using the full ES density (not only the change with respect to the GS) is introduced to obtain the PCM response in the ES; and (iv) in the self-consistent state-specific approach known as vertical excitation model (VEM),[16] a procedure

similar to the SS approach is used, but in this case the iterations are only on the density change while the GS reference is kept unchanged. Several studies demonstrate that the simplest LR model could fail to accurately capture solvent effects for ES,[14−18] that is, significant changes of the LR absorption and emission transition energies are found when applying cLR or the other state-specific models. Unfortunately, the ES analytical gradient is rather difficult to evaluate in the case of state-specific models, because often the ES energy is not stationary with respect to changes in the excitation amplitudes or even in the molecular orbital coefficients. Therefore, lacking an efficient implementation of the ES analytical gradients, the vast majority of these works have been performed using a fixed gas or LR geometry, corrections with more refined solvent models being applied only on the total and transition energies. In 2014, we presented the first investigation of the ES geometries at the cLR level, using carefully evaluated numerical gradients.[17] This initial work, as well as subsequent studies,[18−20] revealed that (i) the LR-PCM ES structures are often, but not always, in reasonable agreement with their cLR-PCM counterparts; (ii) LR-PCM (slightly) overestimates the solvent-induced variations of bond lengths; (iii) full cLR calculations generally allow a more accurate reproduction of the experimental solvatochromic shifts measured for emission than cLR calculations on LR geometries. However, in these works, the ES vibrations were not computed at the cLR level. In fact, the LR approach was used to ascertain the nature (minima) of the ES. In the present communication, we extend our approach to cLR ES vibrations that are, to the very best of our knowledge, computed for the

first time using carefully evaluated numerical second derivatives of the ES energy. Using the compounds shown in Scheme 1, we

Scheme 1. Sketch of the Investigated Molecules
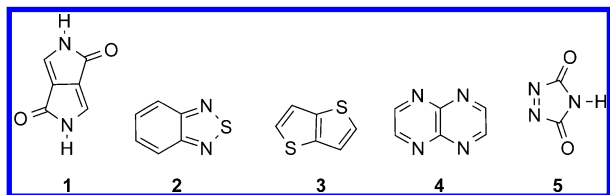
wish to tackle three goals: (i) to assess the differences between gas, LR, and cLR vibrational ES frequencies; (ii) to ascertain the nature of the minima with cLR and determine if the point-group symmetry of the ES might change when going from LR to cLR; and (iii) to compute the difference of zero-point vibrational energies between the ES and the GS, $\Delta E^{ZPVE} = E^{ZPVE}(ES) - E^{ZPVE}(GS)$, and assess if this term is significantly tuned by the selected solvation model. This latter objective is justified by the fact that ΔE^{ZPVE} enters in the calculation of 0−0 energies, that become increasingly popular.[21−25]

All calculations have been performed with the latest version of the Gaussian09 program[26] that was modified to allow numerical cLR geometry optimizations and vibrational calculations, as detailed in ref 17. We have selected the M06-2X/6-31G(d) approach[27] and systematically used dichloromethane as solvent. It is clearly not our purpose here to discuss the dependencies between the selected exchange-correlation functional (or atomic basis set) and the accuracy of the obtained ES vibrations nor to analyze the general validity of TD-DFT for the investigated molecules.[28] Default parameters have been used for the PCM cavity, and the equilibrium limit, suited for slow phenomena, was applied at all steps. During the calculations, we have improved the energy convergence threshold (10^{-10} a.u.), the geometry optimization threshold (10^{-5} a.u. on the residual root-mean-square force), and the integral accuracy parameter (10^{-12} a.u.), and we have used the so-called *ultrafine* DFT integration grid, so to guarantee the numerical stability of the data.

Table 1 lists the ES point group for the compounds of Scheme 1. For each molecule, we considered the lowest excited-state that presents a $\pi \rightarrow \pi^*$ character for molecules **1**−**3**, accompanied by a significant charge-transfer effect in **2**, and a $n \rightarrow \pi^*$ character for **4** and **5**. In four out of five cases, the

Table 1. Point Group of the ES Geometry with the Three Environmental Models[a]

| | ES point group | | | | ΔE^{ZPVE} | | |
compd	gas	LR-PCM	cLR-PCM	ν^{imag} cLR-PCM	gas	LR-PCM	cLR-PCM
1	C_s	C_{2h}	C_s	72i	−0.106	−0.097	−0.084
2	C_{2v}	C_{2v}	C_{2v}		−0.114	−0.112	−0.096
3	C_2	C_2	C_2		−0.119	−0.115	−0.120
4	D_{2h}	D_{2h}	D_{2h}		−0.118	−0.123	−0.122
5	C_{2v}	C_{2v}	C_{2v}		−0.038	−0.038	−0.041

[a]When the LR and cLR symmetries are different, the amplitude of the imaginary mode(s) obtained at the cLR level when enforcing the LR symmetry is given (ν^{imag} in cm^{-1}). On the right hand side, the difference between the zero-point energies of the ES and GS are listed (in eV) for the three models.

selected environmental model does not affect the ES symmetry. For these four molecules, we note that the point group is also identical to its GS counterpart, with the exception of **3** that undergoes puckering at the ES, an effect discussed in more detail in ref 17. For the remaining case, namely **1**, LR-PCM foresees that the GS symmetry is conserved at the ES, a prediction in disagreement with both gas and cLR-PCM calculations that indicate a lower symmetry in the ES than in the GS. Interestingly, the gas and cLR point groups are identical. Moreover, the cLR imaginary frequency obtained when constraining the molecules to the C_{2h} symmetry presents a large amplitude, indicating that this finding is not related to a numerical instability.

Table 1 also provides the ΔE^{ZPVE}. Unsurprisingly the amplitudes of ΔE^{ZPVE} are in the −0.04/−0.12 eV range which is typical for organic molecules.[21−23,29] For compounds **3**, **4**, and **5**, the ΔE^{ZPVE} are essentially identical with all environmental models, the variations when going from gas to LR or cLR being smaller than ±0.005 eV. For **1** we note a +0.009 eV (+0.013 eV) variation of the ΔE^{ZPVE} when going from gas to LR (from LR to cLR). For **2**, ΔE^{ZPVE} is almost identical with gas and LR but is significantly smaller for cLR (+0.016 eV compared to LR). The fact that the cLR ΔE^{ZPVE} is not systematically bracketed by its gas and LR counterparts is discussed in the next paragraph. For **1**, the range of variations between the different models remains ±0.020 eV, a change that can be considered as small in the framework of the calculations of 0−0 energies.

We now analyze the vibrational frequencies. Selected vibrations of the five derivatives are shown in Table 2. A general and expected trend is that the ES vibrational frequencies tend to be smaller than their GS counterparts (the central CC stretching in **3** is an exception), which is consistent with the negative sign of the ΔE^{ZPVE}. For **1**, the cLR ES vibrational frequencies are generally bracketed by the gas and LR data but for one of the two N−H stretching modes. This ordering is consistent with the ranking of the corresponding bond lengths.[17] The picture is somewhat different when investigating the impact of the change of electronic state. Indeed, for the lowest out-of-plane deformation, the GS to ES differences are −5 cm^{-1}, −4 cm^{-1}, and −8 cm^{-1} for gas, LR, and cLR, respectively. The corresponding values for the first C=O stretching are −73 cm^{-1} (gas), −78 cm^{-1} (LR), and −59 cm^{-1} (cLR), illustrating that while the ES cLR frequencies are intermediate between the gas and LR values, this is not necessarily the case for the GS to ES difference. In turn, this explains the order of the cLR ΔE^{ZPVE} of **1** (see above). In **2**, the ES frequencies are rather similar with all environmental models, and significantly smaller than in the GS, a result that we attribute to the strong elongation of the NS bond after photon absorption (+0.065 Å in the gas phase). In **3**, the first vibration corresponds to a "flapping" mode of the two rings. In the planar GS, this vibration is more energetic than in the puckered ES, and LR that overestimates the puckering angle[17] logically yields the lowest frequency (90 cm^{-1} compared to 117 cm^{-1} for cLR). Likewise, for the stretching of the CC bond shared by the two thiophenes, the cLR and gas phase values are in good agreement, whereas the LR figure is significantly larger. For the two $n \rightarrow \pi^*$ systems, **4** and **5**, the LR and cLR ES frequencies are essentially equivalent, as are the ES geometries.[17] Taking into account all frequencies listed in Table 2, we determined a mean absolute difference between the gas and LR (cLR) ES frequencies of 17 cm^{-1} (12 cm^{-1}),

Table 2. GS and ES Harmonic Vibrational Frequencies for Selected Modes (cm^{-1})

compd	mode	ES			GS	
		gas	LR-PCM	cLR-PCM	gas	PCM
1	lowest twisting	121	125	121	126	129
	CO stretching	1804; 1841	1745; 1796	1764; 1816	1877; 1897	1823; 1860
	NH stretching	3632; 3686	3641; 3647	3605; 3673	3687; 3688	3670; 3671
2	lowest twisting[a]	136	149	151	191	190
	five-m. cyc. breathing	629	631	628	843	841
	sym. NS stretching	772	767	767	895	894
3	lowest twisting	119	90	117	201	201
	central CC stretching	1525	1556	1518	1506	1504
	sym. CH stretching	3290	3295	3294	3302	3303
4	lowest twisting	137	138	137	154	151
	sym. CC stretching	1605	1605	1604	1655	1663
5	lowest twisting	182	186	186	136	145
	NN stretching	1674	1671	1670	1720	1727
	CO stretching	1891; 1937	1859; 1925	1852; 1923	1954; 2018	1920; 2007
	NH stretching	3664	3647	3646	3693	3667

[a]Note that the lowest twisting modes in **2** have a different nature in the GS and ES.

confirming that LR overestimates the solvent effects on the ES vibrations but that the average variations are quite small.

In summary, we have for the first time determined excited-state vibrational patterns using a solvent model going beyond the linear-response approach. Our calculations, performed at the M06-2X/6-31G(d) level for five compact organic molecules, indicated that (i) the ES symmetry may differ with the LR and cLR models. If the gas and LR ES point groups are different, cLR apparently provides a point group identical to the gas phase case; (ii) all PCM models give rather similar ΔE^{ZPVE}. The cLR ΔE^{ZPVE} is not necessarily in between its gas and cLR counterparts and it can be smaller or larger than the gas phase ΔE^{ZPVE}; and (iii) on average the vibrational frequencies computed with cLR resemble more their gas than their LR counterparts, though no systematic sign of variation (increase or decrease) could be found when comparing LR and cLR frequencies.

Of course, a panel of five molecules constitutes a rather small set and obtaining general conclusions would require a significantly extended investigation (a task that would necessitate analytical cLR derivatives), but this communication already highlights that large gas-LR vibrational differences should be viewed as a warning sign: the cLR-LR differences might be significant as well.

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