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Two-Dimensional Electronic-Vibrational Spectroscopic Study of Conical Intersection Dynamics: An Experimental and Electronic Structure Study

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Supplemental Information

Comparison of Computational Methods

Various electronic structure methods can be employed to explore the ground and excited state potential energy surfaces (PESs), while feasible choices are somewhat limited here due to the relatively large sizes of these molecules and the quest for vibrational frequencies. High-level wavefunction theories such as CASPT2 can be computationally demanding for systems of over 50 atoms, and its nuclear derivatives are not available in general electronic structure software packages. Time-dependent density functional theory (TDDFT) is the most widely used excited state method for medium to large molecular systems because of its reasonable balance between accuracy and computational cost. However, it has several deficiencies that may limit its use for the CV and MG systems. As a linear response method, the excited states are calculated without orbital relaxation, which often results in overestimation of excitation energies. On the other hand, TDDFT often fails to describe charge transfer states, yielding unphysically low excitation energies. These two effects can sometimes cancel each other, and thus the accuracy of TDDFT can largely depend on the functional employed. In the case of CV and MG, at the equilibrium structure of S_0, the excitation has less charge transfer character as indicated by the dipole moments (for CV, the dipole is zero for both ground and excited states; for MG, the dipole changes from 6.6 D to 9.1 D upon excitation), both BHHLYP and B3LYP overestimate the vertical excitation energy. At the optimized structures on the excited state surface, the excitation has a much more pronounced charge transfer character. For example, at $S_{1,min}$ upon excitation, the dipole of CV changes from 8.3 D to 5.6 D and flips direction upon excitation, and the dipole of MG changes from 0.65 to 11.8 D. For this reason, we see that TDDFT with the B3LYP functional gives very low excitation energy at S_{1min} or S_{1min}', while with BHHLYP, the excitation energy lowering is less significant because of its higher percentage of exact exchange.

The ΔSCF-DFT method describes both the ground and excited states using single-determinant wavefunctions, whose constituent molecular orbitals (MOs) are optimized (relaxed) self-consistently. Therefore, it computes the ground and excited states in a more equal-footed manner with similar costs. From Table S1 and S2, we can see that ΔSCF significantly improves the vertical excitation energies compared to TDDFT, and the results are also less functional-dependent.

However, both TDDFT and ΔSCF-DFT fail in the vicinity of the conical intersection (CI). TDDFT gives wrong topology for CIs that involve the reference state (in our case, the ground state), and ΔSCF-DFT becomes problematic when the wavefunction cannot be well represented by a single determinant. We note that for the $S_{1,min}$ structure of MG, which is quite close to the CI, ΔSCF-DFT and TDDFT both have convergence problems, leading to failure in locating $S_{1,min}$.

We thus turn to SF-TDDFT, which uses a high-spin state as the reference to target the lower-spin states. In our case, S_0 and S_1 are both constructed via spin-flip excitations from a triplet reference state so that they are treated in a more balanced way. This fixes the problem of TDDFT at CI, and gives better vertical excitation energies. The price to be paid is that SF-TDDFT calculations are carried out with unrestricted orbitals with the current implementation, so it is unable to produce a spin pure state (the same issue holds for ΔSCF-DFT).

The frequencies, on the other hand, seem to depend more on functionals rather than excited state methods. BHHLYP, which has a larger percentage of exact exchange, yields higher frequencies relative to B3LYP. The ordering of frequencies in different structures is in general consistent with the change of methods or functionals: for instance, frequencies of S_{1min} are always predicted to be red-shifted compared to those of $S_{0,eq}$. The amount of shift, however, shows a strong functional dependence, with BHHLYP predicting a larger shift than B3LYP.

Finally, we note that all the calculations we discussed above were performed in the gas-phase, while the experimental spectra were measured in methanol solution. To estimate the solvent effect, we combine TD-BHHLYP with the polarizable continuum model (PCM) for methanol to recalculate the energies and frequencies of CV and MG at $S_{0,eq}$ and $S_{1,min}$. The results (Table S3) show that for both complexes while the vertical excitation energies at $S_{0,eq}$ are slightly reduced (by 0.1-0.2 eV), the excited-state energy at $S_{1,min}$ (relative to $S_{0,eq}$) are raised by over 0.3 eV. As a result, the PESs for their S_1 states become much flatter in methanol solution. Meanwhile, compared to the gas-phase results, the harmonic frequencies are red-shifted in both ground and excited states (by roughly 15-25 cm^{-1}). As the nuclear gradient for SF-TDDFT/PCM is not available, we are currently unable to recalculate the stationary points on S_0 and S_1 as well as the MECP with that method. As indicated by the TDDFT/PCM results, the solvent has a non-negligible effect on the S_1 PES. For a better understanding of the experimental results from theoretical modeling, future work should seek for a more robust treatment of solvent by explicitly including solvent molecules via models such as polarizable QM/MM and performing molecular dynamics simulations to sample the possible solute-solvent configurations.

Table S1. Energies and frequencies of CV at the various optimized geometries computed with different methods. The energies are referenced to the ground state energy of S_0.

TDDFT	BHHLYP			
structure	$E(S_0)$ (eV)	$E(S_1)$ (eV)	Frequency(cm^{-1})	Intensity(km/mol)
$S_{0,eq}$	0.00	3.00	1715	3626
$S_{1,min}$	1.29	2.46	1670	5111
$S_{1,meta}$	0.68	2.53	1718	1341

ΔSCF-DFT	BHHLYP			
structure	$E(S_0)$ (eV)	$E(S_1)$ (eV)	Frequency(cm^{-1})	Intensity(km/mol)
$S_{0,eq}$	0.00	2.18	1715	3626
$S_{1,min}$	1.30	2.15	1673	6669
$S_{1,meta}$	0.62	2.19	1716	1037

TDDFT	B3LYP			
structure	$E(S_0)$ (eV)	$E(S_1)$ (eV)	Frequency(cm^{-1})	Intensity(km/mol)
$S_{0,eq}$	0.00	2.57	1654	3001
$S_{1,min}$	1.26	1.57	1648	2124
$S_{1,meta}$	0.59	1.63	1652	1059

ΔSCF-DFT	B3LYP			
structure	$E(S_0)$ (eV)	$E(S_1)$ (eV)	Frequency(cm^{-1})	Intensity(km/mol)
$S_{0,eq}$	0.00	1.94	1654	3001
$S_{1,min}$	Unable to locate			
$S_{1,meta}$	0.69	2.27	1644	1139

Table S2. Energies and frequencies of MG at the various optimized geometries computed with different methods. The energies are referenced to the ground state energy of S_0.

TDDFT	BHHLYP			
structure	$E(S_0)$ (eV)	$E(S_1)$ (eV)	Frequency(cm^{-1})	Intensity(km/mol)
$S_{0,eq}$	0.00	2.89	1714	1821
$S_{1,min}$	1.85	2.34	1678	4584
$S_{1,min}$’	1.00	2.36	1737	458
$S_{1,meta}$	0.78	2.29	1736	519

ΔSCF-DFT	BHHLYP			
structure	$E(S_0)$ (eV)	$E(S_1)$ (eV)	Frequency(cm^{-1})	Intensity(km/mol)
$S_{0,eq}$	0.00	1.91	1714	1821
$S_{1,min}$		Unable to locate		
$S_{1,min}$’	1.02	2.03	1694/1715	430/552
$S_{1,meta}$	0.64	1.94	1696	909

TDDFT	B3LYP			
structure	$E(S_0)$ (eV)	$E(S_1)$ (eV)	Frequency(cm^{-1})	Intensity(km/mol)
$S_{0,eq}$	0.00	2.57	1654	1628
$S_{1,min}$		Unable to locate		
$S_{1,min}$’	0.97	1.43	1641/1662	633/251
$S_{1,meta}$	0.75	1.38	1664	413

ΔSCF-DFT	B3LYP			
structure	$E(S_0)$ (eV)	$E(S_1)$ (eV)	Frequency(cm^{-1})	Intensity(km/mol)
$S_{0,eq}$	0.00	1.73	1654	1628
$S_{1,min}$	1.80	1.87	1639	906
$S_{1,min}$’	1.02	2.15	1644/1657	278/376
$S_{1,meta}$	0.04	1.70	1661	489

Table S3. Energies and frequencies of CV and MG computed with TD-BHHLYP/6-31G(d) and the PCM model for methanol. The energies are referenced to the ground state energy of S_0.

structure	**$E(S_0)$ (eV)**	**$E(S_1)$ (eV)**	**Frequency(cm^{-1})**	**Intensity(km/mol)**
CV $S_{0,eq}$	0.00	2.87	1698	5279
CV $S_{1,min}$	1.15	2.80	1657	3837
MG $S_{0,eq}$	0.00	2.71	1691	2224
MG $S_{1,min}$	1.71	2.64	1659	3494

(1) K. Andersson, P.A. Malmqvist, B. O. Roos, A. J. Sadlej and K. Wolinski. Second-order perturbation theory with a CASSCF reference function. *J. Chem. Phys.* **1990**, *94*(14), 5483-5488.

(2) K. Andersson, P.A. Malmqvist, B. O. Roos. Second-order perturbation theory with a complete active space self-consistent field reference function. *J. Chem. Phys.* **1992,** *96*(2), 1218-1226.