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Propagator Calculations of Electronic Spectra of Photochromic Spirooxazines

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Theoretical investigations were carried out on a series of spirooxazines which are known to exhibit photochromism. The calculational results obtained using polarization-propagator based *ab-initio* methods give fairly good qualitative predictions of the absorption maxima for this series of spirooxazines, however, the predicted shifts of the absorption maximum down the series is in the opposite direction of the experimental measurements. This is discussed.

Keywords: Spirooxazines; Polarization Propagator; RPA; SOPPA; CCLR; UV-spectra

INTRODUCTION

Among photochromic compounds, spirooxazines (SNOs) have received considerable attention because of their remarkably high fatigue resistance in comparison with well-known spiropyranes. Since it has been experimentally difficult to determine the structure of the open form, and since this structure plays a dominant role in SNOs' photochromism due to its unstable character, theoretical analysis based on molecular orbital calculations has been carried out in an attempt to elucidate the mechanism of SNOs' photochromism.

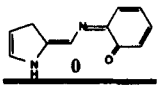
THEORETICAL BACKGROUND AND CALCULATION DETAILS

In this study, a series of propagator-based methods, namely, RPA (Random Phase Approximation), SOPPA (Second Order Polarization Propagator Approximation)[1] and CCLR (Coupled-Cluster Linear Response method)[2-4] have been employed to investigate the electronic spectra of the open form SNOs. These methods have a common advantage over the widely used conventional state-specific methods. First, the propagator approach only requires the ground state wave function to be determined and information about the electronic excitations are obtained from the polarization propagator (also called the linear response function), whereas in the conventional state-specific methods one needs to optimize both ground and excited state wave functions independently. Second, the propagator approach is essentially a 'black-box' approach that allows us to obtain the physical properties once the basis set has been determined, and thus circumvents the inherent difficulties of the state-specific approaches from individual optimization of the wave function for each state. Finally, the propagator approach is expected to offer a good compromise between computational cost and qualitative accuracy owing to recent development of numerical algorithms and systematic inclusion of electron correlation through first order (RPA), second order (SOPPA)[5], or higher order (CCLR)[6] in the fluctuation potential. However, the SOPPA, CC2, and CCSD models are only adequate if the excitation does not include more than 8-10% double excitations (the RPA model does not include double excitations at all). The most stable isomer of open form SNOs is believed to be the TTC-conformation (Table 1 and 2). This conclusion is based on results from NMR experiments and *ab-initio* studies, indicating that the single configuration Hartree-Fock approximation provides an adequate zeroth-order description of the SNOs since the dominant configuration is found to be of keto type and not of zwitterionic character[7]. The strategy of our study is as follows. Geometry optimizations of molecules **0-4** are carried out using Density Functional Theory (DFT) with the B3LYP functional and cc-pVDZ basis sets, and using Gaussian94 software[8]. Cs symmetry is imposed on the open form SNOs (being kept planar). The optimized geometries are available from the authors. Then RPA, SOPPA, and CCLR calculations are performed at the obtained equilibrium geometries using the DALTON program[7] to calculate the lowest valence π-π^* excitation energy, which is the excitation that determines the color of the open form SNOs. The carbon and nitrogen inner shells (1s) are frozen in order to reduce the computational costs of the SOPPA and CCLR calculations. Finally solvation effects are considered qualitatively at the

RPA level. The Dalton program includes a simple non-equilibrium self-consistent reaction field model for solvation effects on electronic excitation energies[10]. We have modelled methanol as solvent with static and optical dielectric constants of 32.63 and 1.731, and we have used a radius of 12.9 au for the spherical cavity.

RESULT AND DISCUSSION

The computational cost of SOPPA and CCLR calculations on molecules **1-3** grows quickly with basis set size and more than double zeta is too expensive with current computer power. In order to see if this study was meaningful, that is, if qualitatively correct results could be obtained with a double zeta basis set we first performed preliminary calculations for molecule **0** in order to examine the basis set convergence at the RPA, SOPPA, and three CCLR levels of approximation. Molecule **0** is a smaller model compound for molecules **1-3** (Table 1). The RPA excitation energy decreases from 3.26 eV to 2.97 eV when going from 3-21G up to aug-cc-pVDZ. The difference between RPA/cc-pVDZ and RPA/aug-cc-pVDZ excitation energy is 0.12 eV, indicating that basis set convergence has not been fully obtained. The RPA/4-31G and RPA/cc-pVDZ calculations which include a continuum description of solvation effects for methanol give a decrease in the excitation energy relative to the gas phase results of 0.16 eV and 0.11 eV, respectively, so the basis set effect on the solvent correction is smaller than on the gas phase results. The series of CCLR calculations in the hierarchy of coupled cluster models does not exhibit the same systematic behavior as the basis set study in RPA. The SOPPA model gives much lower results than the other methods. The difference of 0.20 eV between the SOPPA/3-21G and SOPPA/3-21++G calculations shows that diffuse orbitals are not essential for a qualitative description of this excitation. Based on these results we believe that within an absolute error of 0.25 eV the economic 4-31G basis is adequate, and we expect the basis set errors in the relative excitation energies to be smaller than the difference between these, that is, we do not expect basis set errors to cause prediction of the wrong trend in the series of molecules. Next, RPA and SOPPA calculations along with *ab-initio* CIS(CI-Singles) were performed on molecule **1-3** (Table 2). In experiment, the absorption maximum is bathochromically shifted as the π-conjugation is extended from molecules **1** to **3**. However, CIS, RPA and SOPPA yielded



basis set	RPA	SOPPA	CCLR		
			CCS	CC2	CCSD
3-21G	3.26	2.17			
4-31G	3.18(3.02)	2.05	3.48	2.81	3.00
6-31G	3.17				
6-31G*	3.12				
6-31G**	3.12				
6-31++G**	3.04				
cc-pVDZ	3.09(2.98)		3.40	2.75	
aug-cc-pVDZ	2.97				

(solvent effect taken into consideration in parenthesis)

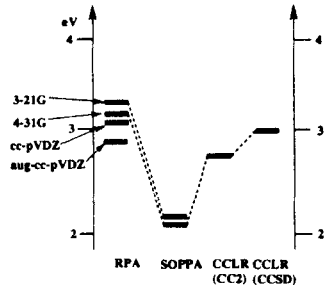
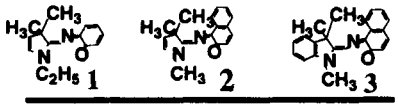


TABLE 1
Theoretical excitation energies for S_0 - S_1 transition on moecule 0

opposite trends to the experiment, showing the hypsochromic shift. As for SOPPA calculations, though the predicted excitation energies are also underestimated like those on molecule **0**, the absolute deviation from experimental value however is relatively small in comparison with other calculations. The quite large gap between the predicted excitation energies in RPA and that in SOPPA indicates that the higher order electron correlation (second order in the fluctuation potential) has the significant contribution to the lowest valence π-π^* excitation of SNOs. All models used in this study are only adequate if the excitation is dominated by single excitations, however, the excitation operators found in SOPPA and CCLR have about 11% double excitation character, which indicates that this excitation is a difficult case and that either multiconfigurational models or models including triple excitations are needed to get a good description of this specific excitation. Another aspect is that solvation effects can obviously have a big influence on the equilibrium geometry of the open form of the molecule and on the electronic excitations because of the interaction between the molecule and the solvent. We note that the predicted solvation effect on molecule **3** is so big, that the RPA predicted excitation energy now is below molecule **2**. A third aspect is that the DFT optimized geometries used in these calculations correspond to gas phase equilibrium geometries. Solvation also affects the equilibrium structures, and the excitation energy is also dependent on geometries. For molecules **1** and **2** we found an increase in the RPA predicted gas phase excitation energy of 0.18 eV and 0.14 eV respectively, when we used AM1 optimized geometries instead of the DFT/B3LYP optimized geometries. Geometry effects can thus not be excluded, if solvation leads to different types of geometry

changes in the three molecules it may give shifts of the same order of magnitude as the shifts between the molecules. Experiments were also performed in different solvents. It would be very desirable to get experimental results for all molecules in the same solvent, in order to really evaluate the theoretical calculations. Otherwise we cannot separate solvation effects from substitution effects when comparing the three molecules.



Mol.	CIS 4-31G	CIS cc-pVDZ	RPA 4-31G	RPA cc-pVDZ	SOPPA (4-31G)	experiment
1	3.30	3.22	3.02 (2.85)	2.97	1.81	2.30[11]
2	3.41	3.33	3.15 (2.97)	3.12	2.00	2.21[12]
3	3.44	3.69	3.22 (2.86)	3.18		2.03[13]

(solvent effect taken into consideration in parenthesis)

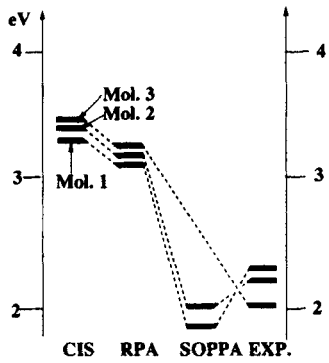


TABLE 2
Theoretical excitation energies for S_0 -S_1 transition on molecule 1,2,3

CONCLUSIONS

Our conclusion is that this π-π^* excitation in SNOs is a difficult case for a theoretical description. In future work it should be investigated if multiconfigurational descriptions or triple excitations are significant for molecule **0**, this should answer the question if SOPPA, CC2, or CCSD is adequate for molecules **1-3**. Furthermore, it is essential to work towards a better description of solvation effects in future work, if one wants to compare results for different solvents, or if one wants to make predictions of solvation effects before the experiments are performed. It would be desirable if experimental results for the three molecules were available in the same solvent.

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