Molecular orbital modeling of solvent effects on excited states of organic molecules

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Abstract

The excited states of organic molecules are considerably affected in most cases by their environment. A simple example of this phenomenon is the blue-shift effect shown by $n\pi^*$ bands upon increasing the polarity of the solvent. The purpose of the current paper is to simulate the solvent effect on the excited states of two organic systems: furfural and 1-(N-methyl pyridyl) 2-(p-quinoyl) ethylene (also known as stilbazonium), by creating a set of clusters solute–(solvent)$_n$ compounded by distributing solvent molecules around the solute at random. These clusters were subsequently optimized using the semiempirical PM3 method to explore such multiple minima hypersurface of the supermolecular system. The minimal energy sets of each system were selected for the calculation of excited states by the CNDOL method combined with a procedure for singly excited configuration interaction. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Excited states; Solvent effects; Furfural; Stillbazonium

1. Introduction

The furfural molecule exists in two planar stable conformations (Fig. 1) [1]. The potential barrier between them is of about 10 kcal/mol and the energy difference is less than 1 kcal/mol [2–4], hence both coexist at room temperature, but their concentrations depend strongly on the polarity of the solvent [5]. The most polar rotamer, OO-*cis*, prevails in polar solvents, while the less polar, OO-*trans*, is abundant in non-polar solvents or in gas phase. This problem has been treated previously in our laboratory [6].

The influence of polar solvents, like water and ethanol, on $n\pi^*$ and $\pi\pi^*$ transitions of furfural is a classic example since both of them provoke blue shifts of the $n\pi^*$ band and red shifts of the $\pi\pi^*$. One of our

objectives is to reproduce these effects through successive additions of molecules of solvents to the furfural conformers.

The importance and nature of the solvatochromic effect is still studied nowadays [7]. It is associated with the dependence of absorption spectra upon the polarity of the solvent. In most cases of colored substances the intensive absorption bands, that normally correspond to $\pi\pi^*$ transitions, move to shorter wavelengths when changing to a more polar solvent and this is called a normal solvatochromic effect. However, there are molecules where the absorption maximum shifts to longer wavelengths when the solvent polarity increases. Thus solvatochromic effect is termed negative.

An interesting case of negative solvatochromic effect is that presented by the 1-(N-methyl pyridyl) 2-(p-quinoyl) ethylene, also known as stilbazonium

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Fig. 1. Conformational isomers of furfural.

(Fig. 2). The intense absorption band that presents in a polar solvent like water [8] displaces bathochromicaly in a medium like chloroform [9], considered as middling polar. We have succeeded in reproducing these experimental results by theoretical calculations, and we arrived at the conclusion that the effect presented in this system is due to a change in nature of the transition corresponding to the maximum when passing from one medium to another.

The calculation of electronic excitation properties of organic molecules has been an important goal of theoretical chemists since the very beginnings of the application of quantum mechanics to chemistry [10]. In this paper we have used an approach called CNDOL [11] for the calculation of excited states. This is another approach to SCF-MO-NDO calculations with a priori chosen parameters and configuration interaction of singly excited states, based on the PPP method. Thus, AVE NDO approximations have been modified in order to take into account independent monocentric terms in the Fock matrix elements for each type of azimuthal quantum number atomic orbital in the basis set, this explains its name: CNDO-l (or CNDOL).

Chemistry in solution has been, and still is, the main object of chemistry. There are different available approaches for studying liquids and solutions. They could be classified in four general methods based on: the elaboration of physical functions [12–14], computer simulations of liquids [15–17], continuous distribution of the solvent [18–24], and also methods
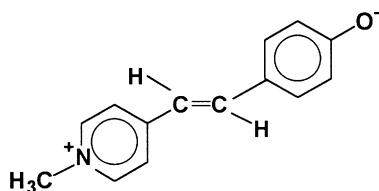
based on a supermolecular (or cluster) description of the system [25]. We shall consider this last approach in more detail in the present paper.

2. Theory and methods

In order to simulate the environment's collective effects on the excited states of the above mentioned molecules, the conformational isomers of furfural and the stilbazonium, we have proposed the creation of a collection of clusters solute–(solvent)$_n$, made at random by distributing solvent molecules around a central molecule, the solute, that subsequently were optimized at the PM3 [26, 27] level as implemented in MOPAC 6.0 [28]. All geometry optimizations were carried out with the keyword EF, leading to the eigenvector following method [29, 30] of energy minimization, and using the convergence criteria given by the keyword PRECISE as described in the program manual.

A set of configurations of minimal energy was obtained for each system after the exploration of such multiple minima hypersurfaces of supermolecules. Each optimized cell represents a local minimum and we assume they represent the lower energy distributions, i.e. the most probable distributions of the solvent around the solute, and they permit us, in statistical–thermodynamic terms, represent the numerous possible arrangements of the 'solvation box'. In other words, the appropriate collection of supermolecular arrangements obtained in this way as well as their respective energies and geometries must be a set of the most important states significant to the properties of the whole system.

Each configuration represents a microstate of the system. Their importance within the statistical set is given by the Boltzmann factor (q), in whose calculation the energy difference (ΔE) between the total PM3 energy of the configuration and the energy of

Fig. 2. 1-(N-methyl pyridyl)-2-(p-quinoyl) ethylene, stilbazonium.

Table 1
Spectral data of furfural in n-hexane solution [34]

$\nu_{max}(\mu m^{-1})$	$\lambda_{max}(nm)$	$\log \epsilon$
3.14	319	1.72
3.75	267	4.21
4.44	225	3.37

Calculated transitions of interest:

Conformer	$\nu_{max}(\mu m^{-1})$	$\lambda_{max}(nm)$	$\log \epsilon$	CI state	Composition
OO-*trans*	3.15	317	–	2	$n\pi^*$
	3.49	286	3.90	4	$\pi\pi^*$, $n\sigma^*$
	4.66	215	3.90	5	$\pi\pi^*$, $n\sigma^*$
OO-*cis*	3.21	311	–	2	$n\pi^*$
	3.49	286	3.93	4	$\pi\pi^*,n\sigma^*$
	4.72	212	4.03	5	$\pi\sigma^*,\pi\pi^*,n\sigma^*$

isolated molecules in the cluster, that is the reference state we have adopted, is very important,

$$q_i = Na \cdot \exp\left(\frac{-\Delta E_i}{kT}\right)$$

where Na is the Avogadro number, i is the number of system configurations that was taken into account, k is the Boltzmann constant and T is the temperature in Kelvin degrees (298 K).

The comparative populations of the different configurations were calculated as:

$$\frac{n_i}{N} = p_i = \frac{q_i}{\sum_i q_i}$$

Within the set of minima obtained we will always find a 'global minimum' that corresponds in a certain way to the most stable system configuration, although it is impossible to assure the obtaining of the true global minimum of the system.

We have chosen a semi-empirical SCF-MO Hamiltonian in order to avoid the computing time problems associated to the application of accurate ab initio SCF procedures. One of them is the massive effort required to calculate total energies of truly significant clusters with high level basis functions to reduce the basis set superposition error (BSSE), which usually arises to unexpectedly overestimate molecular interactions. Moreover, the great importance of correlation effect calculations when dealing with long range interaction energy among separate molecules in each cluster would require incompatible resources in this case. The PM3 Hamiltonian was selected because it reproduces very well internal hydrogen bonding patterns [26, 27].

Different starting random configurations were generated using a program for PCs written for this purpose [31]. For the furfural conformers, which were independently analyzed, clusters with water

Table 2
Spectral data of furfural in aqueous solution [35]

$\nu_{max}(\mu m^{-1})$	$\lambda_{max}(nm)$	$\log \epsilon$
3.61	277	4.18
5.20	192	4.18

Calculated transitions of interest:

System	$\nu_{max}(\mu m^{-1})$	$\lambda_{max}(nm)$	$\log \epsilon$	CI state	Composition
OO-*trans* + 10H$_2$O(n/N) = 0.731	3.77	265	2.97	6	$\pi\sigma^*,\pi\sigma^*$
	5.15	194	2.69	13	$\pi\sigma^*$
	5.28	189	2.10	14	$\pi\sigma^*,\pi\sigma^*$
OO-*cis* + 10H$_2$O(n/N) = 0.745	3.72	268	3.28	6	$\pi\sigma^*$
	5.19	193	3.29	14	$\pi\sigma^*,\pi\pi^*$

Table 3
Spectral data of furfural in ethanol [36]

$\nu_{max}(\mu m^{-1})$	$\lambda_{max}(nm)$	Log ϵ			
3.68	272	4.18			
4.42	226	3.60			
Calculated transitions of interest:					
System	$\nu_{max}(\mu m^{-1})$	$\lambda_{max}(nm)$	log ϵ	CI state	Composition
OO-*trans* + 5EtOH(n/N) = 0.949	3.67	273	2.41	4	$\sigma\pi^*,\sigma\sigma^*$
	4.32	231	2.89	9	$\pi\sigma^*,\pi\sigma^*,\pi\sigma^*$
	4.50	222	2.37	10	$\pi\sigma^*,\pi\sigma^*$
OO-*cis* + 5EtOH(n/N) = 0.980	3.82	262	2.36	6	$\underline{\pi\sigma^*},\pi\sigma^*$
	4.40	227	3.40	10	$\overline{\pi\sigma^*},\pi\pi^*,\pi\pi^*,\sigma\sigma^*$

from 1 to 10 molecules were created, and for each one 20 configurations were obtained. Clusters with ethanol from 1 to 5 molecules were also created, resulting in a total of 15 configurations. The clusters of stilbazonium, with water and chloroform, were created with 8 solvent molecules and 10 configurations were obtained in each case.

We have selected the most populated configuration of each system for the calculation of excited states, applying the CNDOL method [32] of the NDOL program [33]. In the single CI procedure 50 pure SCF electronic excitations were taken into account in the case of furfural and 75 for the stilbazonium molecule. The SCF convergence criterion was 0.0001 eV in the eigenvalues and for the other options we worked with the default values of the program.

Once the MO of the ground state of the molecule are calculated, less energy monoelectronic transitions are chosen to be linearly combined and coefficients are optimized. As result of this combination, singly excited configuration interaction states (CI states) are obtained. These CI states will be the recalculated electronic transitions of the system and each one

represents an electronic density change of the polyatomic system in relation to its ground state.

Detailing the composition of each CI state we will obtain information concerning the pure SCF electronic excitations that contribute more to them, which are those with higher squared coefficients in the linear combination that origin them. The nature of the CI states ($\sigma\sigma^*$, $n\sigma^*$, $\pi\pi^*$, $n\pi^*$, etc.) will be determined by the nature of the SCF excitation with higher squared coefficient (more than 0.5 in this work). However, there are cases where this assignment will not be possible because the great mixture of states (MOs) in nonplanar systems like solute–solvent supermolecules.

3. Results and discussion

3.1. Solvent effects on excited states of furfural

The experimental data of UV-visible spectra of furfural in n-hexane, water and ethanol appear in Tables 1, 2 and 3 [34–36]. The calculated transitions of each conformer to be compared in energy and

Table 4
Spectral shift of the $n\pi^*$ and $\pi\pi^*$ transitions of furfural in water System: OO-*cis* furfural + $n(H_2O)$

Transition →	$n\pi^*$		$\pi\pi^*$		
n	$\nu_{max}(\mu m^{-1})$	$\lambda_{max}(nm)$	$\nu_{max}(\mu m^{-1})$	$\lambda_{max}(nm)$	f
0	3.21	311	3.49	286	0.086
1	3.30	303	3.43	292	0.071
2	3.38	296	3.27	306	0.065
3	3.41	293	3.18	314	0.050
4	3.48	287	3.15	317	0.044
5	3.56	281	3.06	327	0.012

Table 5
Spectral shift of the $n\pi^*$ and $\pi\pi^*$ transitions of furfural in ethanol System: OO-*cis* furfural + n(EtOH)

Transition → n	$n\pi^*$ $\nu_{max}(\mu m^{-1})$	$_{max}$(nm)	$\pi\pi^*$ $\nu_{max}(\mu m^{-1})$	$\lambda\lambda_{max}$(nm)	f
0	3.21	311	3.49	286	0.086
1	3.36	298	3.47	288	0.061
2	3.46	289	3.26	307	0.048
3	3.48	287	3.12	320	0.037
4	3.57	280	3.03	330	0.025
5	3.80	263	2.84	352	0.001

intensity with the experimental values have also been shown and we have included a column detailing the composition of the CI states implied on each transition. The SCF excitations that determine their nature are underlined.

In a non-polar environment, simulating the vapor phase, the agreement between calculated and experimental values are acceptable, although not excellent, with differences of $\pm 0.2\ \mu m^{-1}$ depending the kind of calculation done. Taken this into consideration we should expect greater differences between experimental and calculated transitions in others media.

The calculated spectrum for the OO-*trans* conformer in the gas phase showed better agreement with the experimental one. This result should be expected because this is the most populated rotamer in this phase. According to that we can associate approximately the maximum reported in hexane at 3.14 and 3.75 μm^{-1} with the electronic transitions $n\pi^*$ (94%) and $\pi\pi^*$ (83%), respectively, and the other at 4.44 μm^{-1} with a mixture of $\pi\pi^*$ and $n\pi^*$ transitions where none is predominant.

It is difficult to assign the experimental bands in water and ethanol because there are not pure SCF electronic excitations with decisive influence in the calculated CI states. They are bands of mixed nature and a further analysis of electronic densities in the excited state is required for that purpose. The calculated transitions for the OO-*cis* conformer in the 'polar solutions' showed a better approximation to the experimental results and this fact corroborates the predominance of this rotamer in such media.

In order to model the effect of the polar solvents in study on the $n\pi^*$ and $\pi\pi^*$ transitions of furfural, we centered our attention only in the OO-*cis* conformer. Thus, we made sequential additions of solvent molecules, water and ethanol separately, from 1 to 5, and we followed the spectral displacement of its CI states 2 and 4, which correspond in gas phase to electronic transitions with predominant nature $n\pi^*$ and $\pi\pi^*$, respectively. It is worth noting that these bands do not appear in the spectrum of furfural in these media, nor in our calculations with a higher degree of solvation, as explained below.

The results obtained are shown in Tables 4 and 5, where f represents the oscillator strength. When increasing the number of polar solvent molecules blue shifts of the original $n\pi^*$ band and red shifts of

Table 6
Spectral data of stilbazonium in water [8] and chloroform [9]

Solvent	$\nu_{max}(\mu m^{-1})$	λ_{max}(nm)	$\log \epsilon$		
Water	2.25	444	4.45		
Chloroform	1.61	620	–		
Calculated transitions of interest:					
Solvent	$\nu_{max}(\mu m^{-1})$	λ_{max}(nm)	$\log \epsilon$	CI state	Composition
None	2.57	390	4.86	2	$\pi\underline{\pi^*}$
Water(n/N) = 0.569	2.30	435	4.15	3	$\overline{\pi\pi^*}$, $\sigma\sigma^*$
Chloroform (n/N) = 0.715	1.78	561	3.44	5	$\pi\pi^*$, $\underline{\sigma\sigma^*}$

Table 7
Nature of the stilbazonium's (S) MOs implied in the pure SCF excitations that originate the 10 CI states with less energy

MO	#	S	S + 8H$_2$O (n/N) = 0.569	S + 8CHCl$_3$(n/N) = 0.715
LUMO + 7	16	σ^*		
LUMO + 6	15	σ^*	π^*	
LUMO + 5	14	σ^*	σ^*	σ^*
LUMO + 4	13	π^*	σ^*	σ^*
LUMO + 3	12	σ^*	σ^*	σ^*
LUMO + 2	11	π^*	σ^*	π^*
LUMO + 1	10	σ^*	π^*	σ^*
LUMO	9	π^*	σ^*	σ^*
HOMO	8	π	π	π
HOMO − 1	7	n	σ	σ
HOMO − 2	6	σ	σ	σ
HOMO − 3	5	π	π	π
HOMO − 4	4	n	π	π
HOMO − 5	3	n	σ	σ
HOMO − 6	2	n	π	π
HOMO − 7	1	π		

the original $\pi\pi^*$ are produced, as expected. Additions of greater number of solvent molecules drove us to spectra with bands of indefinite nature, where is not possible to identify the originals CI $n\pi^*$ and $\pi\pi^*$ states.

3.2. Solvent effects on excited states of stilbazonium

The experimental data of UV-visible spectra of stilbazonium in water and chloroform and also the calculated spectra using the CNDOL procedure for the isolated and 'solvated' molecule appear in Table 6.

The correspondence between experimental and calculated transitions is excellent. Since experimental results in gas phase or in hydrocarbons were not found, it is impossible to judge the quality of the calculated spectrum for the isolated molecule, where an intense maximum (log ϵ = 4.86) is predicted around 2.57 μm^{-1} (390 nm). It displaces bathochromicaly in water, appearing at 2.30 μm^{-1} (435 nm), and even more in chloroform, 1.78 μm^{-1} (561 nm).

In Table 7 we have shown the nature of the stilbazonium's MOs implied in the pure SCF excitations with higher weight in the linear combinations that originate the 10 CI states with less energy of these systems, and in Table 8 the composition of these states is detailed. We have pointed out the SCF excitations that determine their nature, in the cases where this situation was presented {(coef. IC)^2. > 0.50}.

For each system a high intensity transition was obtained. They present the same origin, but different

Table 8
Pure SCF electronic excitations that more contribute to the 10 CI states with less energy in stilbazonium (S)

CI state	S	S + 8H$_2$O(n/N) = 0.569	S + 8CHCl$_3$(n/N) = 0.715
1	$\underline{\pi_8\sigma_{10}^*}$	$\underline{\pi_8\sigma_9^*}$	$\underline{\pi_8\sigma_9^*}$
2	$\underline{\pi_8\sigma_9^*}$	$\underline{\pi_8\sigma_{11}^*}$	$\underline{\pi_8\sigma_{10}^*}$
3	$\underline{n_7\pi_9^*},\sigma_6\pi_9^*$	$\underline{\pi_8\pi_{10}^*},\sigma_7\sigma_9^*$	$\pi_5\sigma_{10}^*,\pi_5\sigma_9^*$
4	$\underline{\sigma_6\pi_9^*},n_7\pi_9^*$	$\pi_5\sigma_{11}^*,\pi_5\sigma_9^*$	$\pi_8\sigma_{13}^*,\pi_6\sigma_9^*,\pi_6\sigma_{10}^*$
5	$\underline{\pi_8\sigma_{12}^*}$	$\pi_8\sigma_{12}^*,\pi_8\sigma_{13}^*,\pi_2\sigma_9^*$	$\pi_8\pi_{11}^*,\underline{\sigma_7\sigma_9^*}$
6	$\pi_8\sigma_{15}^*,\pi_8\sigma_{14}^*,\pi_1\sigma_{10}^*$	$\pi_8\sigma_{12}^*,\pi_8\sigma_{14}^*$	$\pi_8\sigma_{13}^*,\underline{\pi_8\sigma_{14}^*},\pi_8\sigma_{12}^*$
7	$\pi_8\sigma_{15}^*,\pi_8\sigma_{14}^*,\pi_8\sigma_{16}^*$	$\underline{\sigma_7\pi_{10}^*}$	$\sigma_7\sigma_{10}^*,\sigma_6\sigma_9^*,\sigma_6\sigma_{10}^*$
8	$\underline{\pi_8\pi_{11}^*},\sigma_6\sigma_{10}^*$	$\sigma_7\sigma_{11}^*,\sigma_6\sigma_{11}^*,\pi_8\pi_{15}^*$	$\pi_8\pi_{11}^*,\sigma_7\sigma_{10}^*$
9	$\underline{n_3\pi_9^*},\sigma_6\sigma_{11}^*$	$\sigma_6\sigma_9^*,\sigma_6\sigma_{11}^*$	$\pi_8\sigma_{13}^*,\pi_6\sigma_9^*,\pi_4\sigma_9^*$
10	$\underline{\pi_8\pi_{13}^*}$	$\pi_8\pi_{1o}^*,\sigma_7\sigma_9^*$	$\pi_4\sigma_9^*,\pi_8\sigma_{13}^*$

Table 9
Stilbazonium's atomic centers with higher participation (in descendent order) in the MOs implied in the pure SCF electronic transitions with higher weight in the CI state of highest intensity

Transition (l → m) Solvent ↓	$\pi\pi^*$ MO_l (atoms)	MO_m(atoms)	$\Delta E_{lm}(eV)_a$	$(coef.IC)_b^2$	$\sigma\sigma^*$ MO_l(atoms)	MO_m(atoms)	$\Delta E_{lm}(eV)_a$	$(coef.IC)_b^2$
None	HOMO (9,7,11,13,4)	LUMO (8,4,6,2,12)	5.586	0.911	< HOMO − 7	> LUMO + 7	> 13.642	0.000
Water (n/N) = 0.569	HOMO (9,7,11,13,12)	LUMO + 1 (4,8,6,2,12)	5.676	0.662	HOMO − 1 (8,7,10,9,24)	LUMO (5,7,4,6,3)	7.544	0.231
Chloroform (n/N) = 0.715	HOMO (7,9,11,13,12)	LUMO + 2 (8,4,6,2,12)	5.825	0.283	HOMO − 1 (8,7,10,20,9)	LUMO (3,7,4,5,18)	5.680	0.663

[a] Energy difference between the MOs implied in the transition ($MO_l \to MO_m$).
[b] Squared of the coefficient of participation of a pure SCF excitation in a CI state.
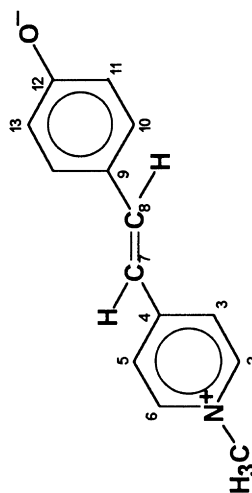
nature, since they are the result of different perturbations. Our attention will be focused on them.

In Table 9 we show the stilbazonium's atomic centers with higher participation (in descending order) in the MOs implied in the pure SCF electronic transitions with higher weight in the CI states (see Table 6). The first row refers the isolated system, the second the cluster with water and the third one the cluster with chloroform. This will help us to have a better idea in relation to the zones of higher electronic density of those MOs and the electronic displacements produced in the molecule by transitions between them $(MO_l \rightarrow MO_m)$.

The squared of the coefficient of participation, (coef. IC)^2, of each pure SCF excitation in the linear combination of a CI state is a measure of its influence in the nature of the last one. Thus for the isolated molecule the intense band calculated corresponds to a 91% $\pi\pi^*$ transition, (coef. IC)^2 = 0.911, produced between HOMO and LUMO. This is an internal charge transfer band because the atomic centers with higher participation in these orbitals are in different sides of the molecule.

This $\pi\pi^*$ transition is the same presented in the CI state analyzed of the other systems because the MOs involved have practically the same distribution in the molecule. The environment determines its degree of participation in the CI state.

In water, this CI state of $\pi\pi^*$ nature in the isolated system is presented with a 23% of $\sigma\sigma^*$ 'contamination' that does not affect drastically its nature, the transition correspondent to the maximum is mainly $\pi\pi^*$ (66%), but reduces its energy difference with the ground state provoking a bathochromic displacement.

The perturbation produced by the MOs of the water molecules has the same influence on the stilbazonium's MOs involved in the $\pi\pi^*$ transition because the energy difference between them does not change significantly. Both are stabilized in the same way since the polarity of the system in these states is similar.

The effect of this perturbation is important on the σ orbitals implied in the (HOMO − 1) → (LUMO) transition because their energy difference diminishes drastically in relation to the isolated system. It suggests an excited state with higher polarity that is more stable. When the energy of the $\sigma\sigma^*$ transition decreases, its contribution to this CI state is increased and provokes the red shift of the maximum in water.

In chloroform the solvent effects are such that they transform almost completely the nature of the CI state of the maximum that appear now with a 66% of $\sigma\sigma^*$ character and only a 28% of $\pi\pi^*$. Its nature is basically $\sigma\sigma^*$. The collective action of the environment makes bigger the energy difference between the π orbitals and smaller the existent between the σ if we compare it to the changes produced in water in relation to the isolated system (see ΔE_{lm} values in Table 9). The smaller the energy difference between the σ orbitals the greater the contribution of the $\sigma\sigma^*$ transition to this CI state and the red shift of the maximum.

When passing from a polar to a less polar system changes the nature of the electronic transition correspondent to the maximum in stilbazonium because changes the selective influence of the environment on the MOs of our molecule.

4. Conclusions

Applying the proposed method, after searching multiple minima hypersurfaces of appropriate solute–solvent supermolecules, we can model the solvent effects on the excited states of furfural and stilbazonium. When increasing the number of polar solvent molecules around furfural, blue shifts of the $n\pi^*$ band and red shifts of the $\pi\pi^*$ are produced, as expected. The correspondence between experimental and calculated spectra in polar media is fair.

We could discuss the nature of the negative solvatochromic effect of stilbazonium taken into account the composition of the CI state of its calculated spectrum. The maximum in water and chloroform corresponds to different electronic transitions: in water it is basically $\pi\pi^*$, but in chloroform it is $\sigma\sigma^*$. When passing from water to chloroform the $\sigma\sigma^*$ contribution in the CI state of the maximum increases because the energy difference between these orbitals becomes smaller, and as result of this, the energy difference of this CI state decreases with respect to the ground state. That is the interpretation of the bathochromic displacement made by our computational model.

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