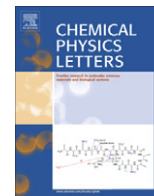




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On the absorption properties of the excited states of DMABN

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ABSTRACT

There is some recent controversy on whether the excited state absorption spectrum features of DMABN can be explained only with the two excited states responsible for the dual fluorescence in this compound. We have performed CASPT2 calculations on the optimized $\pi\pi^*$ excited state in gas phase and in water. The results reproduce the main experimental features of the spectra, leading to the conclusion that the participation of another excited state of different nature is not needed to explain the observed absorption bands.

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The photophysical properties of 4-(*N,N*-dimethylamino) benzonitrile (DMABN) and related molecules have been the subject of a great number of theoretical and experimental studies [1–15] since the discovery of the dual fluorescence of DMABN [16]. When the fluorescence spectrum of DMABN is recorded in non-polar solvents, it displays the typical single fluorescence band; but as the polarity of the solvent is increased, another red-shifted band appears, first as a shoulder and progressively more intense, while the 'normal' band becomes weaker and almost disappears in very polar solvents. This phenomenon was attributed from the beginning to the existence of two excited states of different electronic structure. The first state, originating the 'normal' fluorescence band, is commonly named the locally excited (LE) state, because it results from an excitation of the electrons in the π ring; the polarity of the LE state would be very similar to that of the ground state, so that its stability and the corresponding band maximum would shift only slightly when the solvent polarity is increased. The second state, originating the red-shifted band appearing in polar solvents, is supposed to be an internal charge transfer (ICT) state, where part of the electron density shifts from the amine nitrogen to the nitrile group; the dipole moment of this state would be greatly enhanced, which would favor its stability in polar solvents, accounting for the observed red shift and increased intensity of the corresponding fluorescence band.

The main controversy regarding this system concerns the exact nature and geometry of the ICT state, and the mechanism which leads from the initial excitation of the ground state to the two different fluorescent excited states. The two more accepted models nowadays propose either a twisted (90° with respect to the phenyl ring) dimethylamino group or a planar structure for the ICT state,

and thus are named twisted or planar ICT (TICT and PICT). Experimental support for one or the other model is usually derived from the study of similar molecules with different substituents or structural variations, which does not, in our opinion, rule out the possibility of a different model being applicable for each case. In relation to the mechanism of population of the two states, Zachariasse et al. have repeatedly provided experimental evidence supporting a mechanism where the initial excited molecules (to the S_2 state) undergo ultrafast internal conversion reaching the LE state, and then an equilibrium is established between LE and ICT populations [8,11]. But Lim et al. have recently argued that, in addition to the above states, there is an intermediate dark state of $\pi\sigma^*$ character (arising from the promotion of an electron from a phenyl π orbital to the σ^* orbital in the nitrile group), which is the precursor of an ICT state, and that the fluorescent LE and ICT states are populated through separate paths from the initial excitation [12], or that there are two differing ICT states, only one of them fluorescent [13].

One of the reasons in favor of the $\pi\sigma^*$ intermediate is the fact that the excited state absorption (ESA) spectrum of DMABN in non-polar solvents shows a band at around 750 nm (1.65 eV) [8], and the TDDFT calculations performed by Lim et al. did not find any transition in the LE state for this energy, while they found a suitable transition in the $\pi\sigma^*$ state [12]. In this communication we report that our multiconfigurational *ab initio* calculations do, in fact, predict absorption bands for the LE state in good agreement with the observed ESA spectrum.

We have studied the DMABN molecule in gas phase and in solution, using ASEP/MD (average solvent electrostatic potential from molecular dynamics) [17], a QM/MM method that combines high-level quantum calculations for the solute, an explicit representation of the solvent, and the mean field approximation to reduce the number of calculations needed. Briefly, the method involves performing molecular dynamics on the solute–solvent system, creating a set of point charges that reproduce the average solvent

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electrostatic potential on the solute, and doing a quantum calculation of the solute in the presence of these charges; the electron distribution obtained from the quantum calculation serves to define a set of point charges for the solute that will be used in a new molecular dynamics, and the process is repeated until convergence. Further details on the method and its adaption to geometry optimization and electron transitions can be found elsewhere [18–20], we note here only that vertical transition energies are computed with ‘frozen solvent’, where the solvent structure is in equilibrium with the initial state of the transitions: in this case, the LE excited state.

The full details of the calculations, along with the results concerning the solute geometry, solvent structure, absorption spectrum of the ground state, and emission from the LE and ICT states, are presented in another publication [14]. Here we will only mention our results for the ESA spectrum of the LE state, of $\pi\pi^*$ character.

For the quantum calculations we used the 6-311G** basis set, and the geometries were optimized at CASSCF level, with 12 electrons and 11 orbitals in the active space. The final transition energies were calculated at CASPT2 level using a state-average (10 states) CASSCF wavefunction as reference. We used water as solvent, and modelled the solute–solvent interactions with the OPLS-AA force field, except the atomic charges for the solute, which are obtained from the quantum calculations through the CHELPG method, as usual with ASEP/MD.

At the optimized LE geometry, the LE state is S_1 , and the ICT state is S_2 , very close in energy (less than 0.5 eV, in the infrared), the transitions we find in the (300–1000) nm region ((1.2–4.1) eV) are then $LE \rightarrow S_3$ and to higher excited states. In gas phase, we obtain absorptions with a non-negligible oscillator strength at 1.78, 2.76 and 3.89 eV, in excellent agreement with the main experimental bands found in *n*-hexane at around 1.66, 2.79 and 3.87 eV [8,21].

In water solution, we obtain 1.68, 2.88 and 3.52 eV for the transition energies, again close to the bands measured in acetonitrile at around 1.75, 2.82 and 3.49 eV [8,12].

The above results are summarized in Table 1. These, therefore, support the assignment of the main bands observed in the ESA spectrum of DMABN to the LE state, and the 750 nm band does not seem to require a $\pi\sigma^*$ state to explain it. Zachariasse et al. have also shown that a similar band is observed for DMABN analogues without the $C\equiv N$ group that cannot have the bent $\pi\sigma^*$ state [21].

According to our calculations, the 750 nm band corresponds to a charge transfer from the amine nitrogen to the nitrile, as can be observed in Figure 1. This charge transfer character of the transition could be part of the reason why it is not obtained at TDDFT level since, as pointed out by Lee et al. [12], this method tends to have problems with charge transfer states.

Another argument in favor of the $\pi\sigma^*$ state is the blue shift suffered by the 750 nm band from *n*-hexane to acetonitrile. This shift of about 0.1 eV is, indeed, not explained by our calculations, which actually predict a red shift instead between gas phase and water.

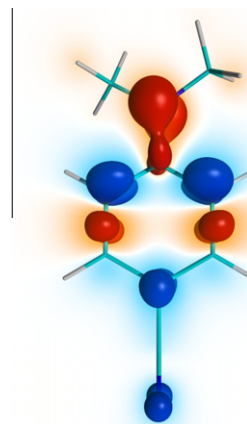


Figure 1. Electron density change in the $LE \rightarrow S_3$ transition (750 nm band) of DMABN. Isosurfaces for a change of $\pm 0.0032 e/a_0^3$, red for a decrease in density, blue for an increase. Densities calculated at SA-CASSCF/6-311G** level. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

For the 450 and 350 nm bands, the predicted shifts are in better agreement with the experimental observations.

Despite the conflict between the experimental and calculated shifts of the lower energy band, one should note that the magnitude of the shift in either direction is only around 0.1 eV, which, considering the different approximations and limitations of the method, might not be significant enough to allow an accurate prediction. Unfortunately, the current state of the art for electron transition calculations in solution does not reach this level of accuracy.

From the results here presented, we can draw two main conclusions:

1. The presence of the 750 nm band in the ESA spectra for DMABN is explained with CASPT2 calculations for the $\pi\pi^*$ LE state. It is not necessary to resort to a different $\pi\sigma^*$ excited state.
2. One should be very cautious when accepting TDDFT results, especially for high excited states, if, as reported by Lee et al. [12], this theory does not predict a 750 nm absorption for the LE state of DMABN.

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Table 1

Excitation energies for the LE state of DMABN, in eV. In parentheses, experimental band maxima of ESA spectra, according to Ref. [8]. The column headers are only the approximate location of the bands.

	750 nm	450 nm	350 nm
Gas	1.78	2.76	3.89
<i>n</i> -Hexane	(1.66)	(2.79)	(3.87)
Acetonitrile	(1.75)	(2.82)	(3.49)
Water	1.68	2.88	3.52

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