Proposed Exercise for the Physical Chemistry Section of the Teaching with Cache Workbook:

Solvent Stabilization of Charge Transfer Excited States

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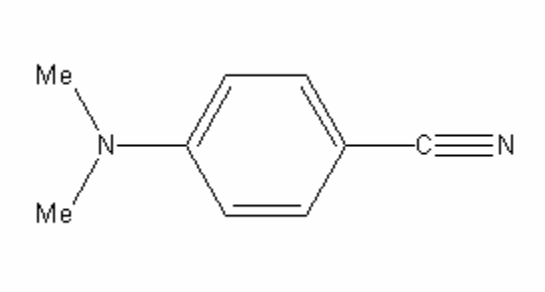
Overview

A series of molecules that have attracted interest to both experimental and theoretical chemists are those which exhibit dual-fluorescence (1-3). The simplest example of such a molecule is 4- (N,N-dimethylamino)benzonitrile (DMABN):



When placed in a polar solvent (such as acetonitrile) this molecule will absorb light at about 290 nm and will show fluorescence at both 350 nm and 475 nm. Only the first of these fluorescence peaks is seen in the gas-phase. Several explanations have been offered for this, but most involve the interaction of two singlet excited states of the molecule which are separated in the gas-phase but become close to one another in solution. The first state is called a local-excited (LE) state formed when electrons in the π orbital of the benzene ring are excited to a π^* orbital. The other state is called a charge-transfer (CT) state because it involves the excitation of electrons from the nitrogen (donor) to the CN group (acceptor). These qualitative descriptions of the excited states are only approximations, with the real electron density changes being more complicated, but they serve to organize our thinking about the molecule. Theoretical calculations have shown that the LE state is lower than the CT state in the gas phase, but that these two switch places in a polar solvent. In this experiment, you will calculate the excited states of DMABN in both gas-phase and solution and compare. Because the electronic subtleties of this molecule are important, we will need to use a rather sophisticated model: time-dependent density functional theory (TDDFT) as implemented in the Gaussian program. As a final check on whether the information about excited states is meaningful, students can repeat this computational study on the related molecule, 4-aminobenzonitrile (ABN). They will discover that this molecule (DMABN without the methyl groups) maintains the ordering of excited states in going from gas phase to solution and therefore does not present dual fluorescence.

Procedure

First you will simulate the gas-phase UV-Vis spectrum of the molecule using ZINDO as implemented in the CAChe program. This will allow examination of states and orbitals

involved in the transitions. Then we will use Gaussian to enhance our modeling of excited states by using a more accurate method to evaluate energies and also include the effects of solvation. During the investigation, you will need to find the output files for these calculations and open them using a text editor. These will be found in the location that you have saved your work, but in a folder with the ".io" extension. Finally you will remove the methyl groups from the molecule and repeat the experiment to see what effect these methyl groups have on the overall results.

Construction of DMABN in Workspace

1. Start by placing a benzene ring in the workspace.
2. Select one of the hydrogens on the ring and change it to a sp hybridized carbon.
3. Attach a nitrogen atom to this carbon and create a triple bond between the two atoms.
4. On the ring, move to the *para* position from the cyano group and select the hydrogen bonded to the *para* carbon.
5. Change the hydrogen atom to a sp^2 hybridized nitrogen atom.
6. Attach two methyl groups to this nitrogen.
7. Select **Beautify|Comprehensive**
8. Move the amino nitrogen up so that it is out of the plane formed by the atoms of the ring. Do this by selecting the nitrogen atom and holding down the Ctrl key and the left mouse button while moving with the mouse. It is important to move the nitrogen so that CAChe does not optimize to a transition state. The geometry at the nitrogen should be trigonal pyramidal.
9. Save this molecule and use a file name such as "DMABN"
10. Now optimize the geometry using AM1. Do this by running the following experiment:
    a. Property of: Chemical Sample
    b. Property: optimized geometry
    c. Using: AM1 geometry

Modeling the UV-Vis Spectrum using ZINDO

1. Run an experiment on DMABN with the following parameters:
    a. Property of: Chemical Samplin
    b. Property: UV-Visible Transitions
    c. Using: ZINDO CI at current geometry

   Make sure the optimized AM1 geometry (previously determined) is present in the workspace.
2. When the experiment finishes, select **View|UV-Visible Transitions** for this molecule. Choose **Window|Tile** so that there is one window with the spectrum and one window with the molecule side by side on the screen. Click on the small triangles of the spectrum to see the orbitals involved in the transition. What MOs are the main participants in the lowest two excited states for this molecule? (Remember the lowest energy states are the highest wavelengths) You may find it useful to locate the ZINDO output files for each molecule and to find the complete description of each state. These will be listed under the section with the

heading “Eigenvectors”. Do these results match with what CAChe was displaying for each molecule?

3. Record notes about the lowest two excited states. Which one would be considered a “local excited” (LE) state? Which one would be considered a “charge transfer” (CT) state? What are the relative strengths of these two transitions?

Modeling the Excited States Using TDDFT

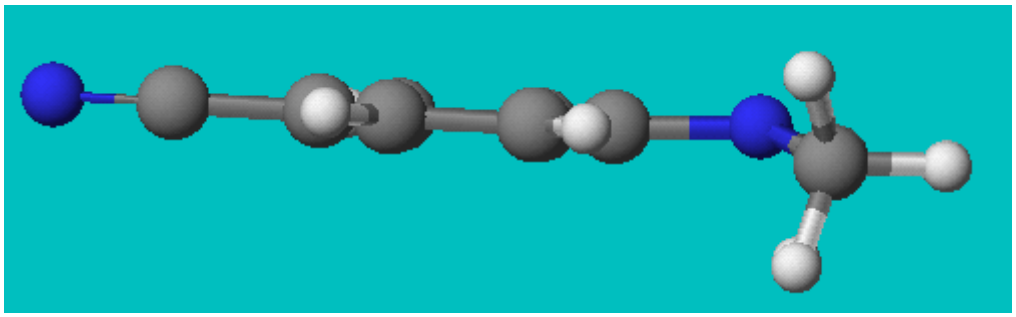
1. Now take the AM1 optimized geometry and perform a Gaussian calculation of the excited states. Here is the experimental setup:
    a. Property of: Chemical Sample
    b. Property: current energy
    c. Using: Gaussian User-Defined Model in Water
2. Before starting this experiment, you will need to edit the procedure. Click on the **Edit** button. Double-click where it says “Run Gaussian using Sample 1”.
3. Now make the following changes to the Gaussian Settings:
    a. Click the radio box under density functional and choose B3LYP as the functional.
    b. Under Solvent, pick acetonitrile
    c. Under basis set, choose 3-21G
    d. Go to the “IO file and extra keywords” tab and enter “TD” in the extra keywords box.
    e. Click **OK** and exit out of the windows associated with the procedure editor. Be sure to say yes when asked about saving changes.
    f. Click **Start** to begin the calculation.
4. You are now calculating the vertical excited states of this molecule in the presence of the solvent using TDDFT. Wait until the state of the calculation is done as reported in the status box in the experiment window.
5. Open the Gaussian output for DMABN, and find the section with information on the excited states. The output will have a section titled “Excitation energies and oscillator strengths.” The oscillator strength is labeled “f=” and the excitation energy is listed for each excited state. What changes have occurred upon calculating the spectrum in solution?

Additional Exercises

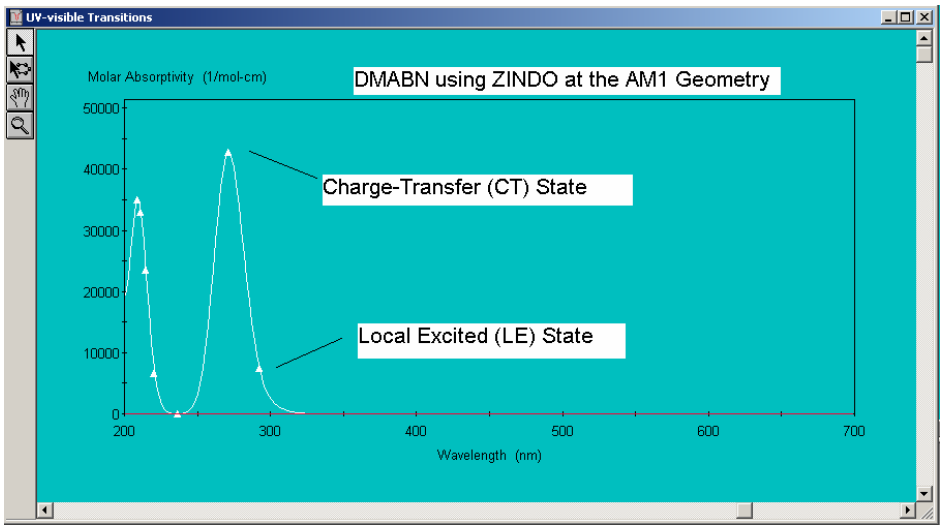
1. Repeat the DMABN calculation as before, but this time turning off the solvent. This would allow you to compare gas-phase TDDFT results to the solvated ones.
2. Repeat the entire exercise using 4-aminobenzonitrile (ABN) as the molecule. Simply remove the methyl groups from DMABN to construct this molecule. Compare both solvated and gas-phase excited states for ABN. What differences can be noted from the DMABN study. ABN does not demonstrate dual-fluorescence. Can you explain this based on your computational results?
3. Repeat some or all of the TDDFT calculations using the 6-31+G(d) basis set. This is a more complete basis set and would be considered the minimal basis set for any research-level TDDFT calculations. How do the 3-21G results compare to the 6-31+G(d) values?

Instructor's Notes

When optimizing the geometry of DMABN be sure that the structure is pyramidal at the Nitrogen. Planar geometries at the amino Nitrogen correspond to transition structures on the PES. Here is a side view of DMABN:



Using ZINDO to simulate the UV-visible spectrum is a quick way for students to observe the nature of the two lowest excited states of the molecule. The spectrum will show a large peak at 275 nm and then a shoulder on this peak at higher wavelength. The actual experimental spectrum in acetonitrile would have the shoulder on the left not on the right. The strong peak is due to the Charge-Transfer (CT) excited state. It has a large oscillator strength. The other peak is a local excited (LE) state corresponding to electrons going into an anti-bonding orbital associated with the benzene ring. Viewing the orbitals in CAChe through the UV-Vis transitions allows some insight as to the nature of the transitions taking place. However, CAChe often misrepresents the main contributing orbitals of an excited state transition, and it is necessary to find the results in the ZINDO output file. Below is an example of what to look for in the ZINDO output file to find information on the excited states.



Portion of ZINDO Output

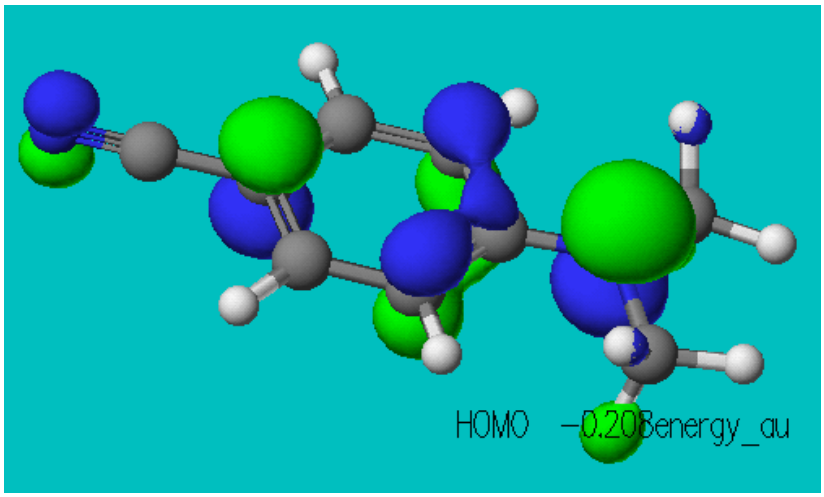
EIGENVECTORS

	STATE:	1	2	3	4	5
EIGENVALUES (CM-1):		.0	34019.0	36466.6	42610.6	45567.5
CONFIGURATIONS:						
1 (0-> 0)	0	1.000000	.000000	.000000	.000000	.000000
2 (21-> 29)	0	.000000	-.000001	-.000001	.015655	-.014757
3 (21-> 30)	0	.000000	-.000001	.000011	-.000111	.000135
4 (21-> 31)	0	.000000	-.000059	-.000718	.000007	.000008
5 (21-> 32)	0	.000000	-.000003	-.000001	.015139	-.013317
6 (21-> 33)	0	.000000	-.002475	.000648	.000004	-.000005
7 (21-> 34)	0	.000000	-.000298	.000142	.000012	-.000017
8 (21-> 35)	0	.000000	.000008	.000001	-.007421	.006049
9 (21-> 36)	0	.000000	.005987	-.000427	-.000002	-.000001
10 (22-> 29)	0	.000000	-.000003	.000001	.078253	-.059666
11 (22-> 30)	0	.000000	0.000000	0.000000	.000054	-.000097
12 (22-> 31)	0	.000000	.000138	-.028182	-.000006	-.000002
13 (22-> 32)	0	.000000	-.000005	.000001	.107552	-.094709
14 (22-> 33)	0	.000000	.021111	.000088	-.000042	.000014
15 (22-> 34)	0	.000000	-.003182	.000025	.000012	-.000016
16 (22-> 35)	0	.000000	.000002	-.000001	-.077672	.067465
17 (22-> 36)	0	.000000	-.012105	-.000079	.000012	-.000003
18 (23-> 29)	0	.000000	0.000000	.000161	.001684	-.001865
19 (23-> 30)	0	.000000	-.000161	0.000000	-.010975	.009621
20 (23-> 31)	0	.000000	.010574	-.000420	-.001345	-.001547
21 (23-> 32)	0	.000000	0.000000	.000194	.001788	-.001844
22 (23-> 33)	0	.000000	-.000178	.030976	.000003	.000006
23 (23-> 34)	0	.000000	-.000142	.016933	.000002	.000004
24 (23-> 35)	0	.000000	0.000000	-.000159	-.001271	.001267
25 (23-> 36)	0	.000000	-.000011	-.001128	.000001	-.000002
26 (24-> 29)	0	.000000	-.000005	-.030143	-.000004	-.000008
27 (24-> 30)	0	.000000	.070589	.000120	-.000013	.000006

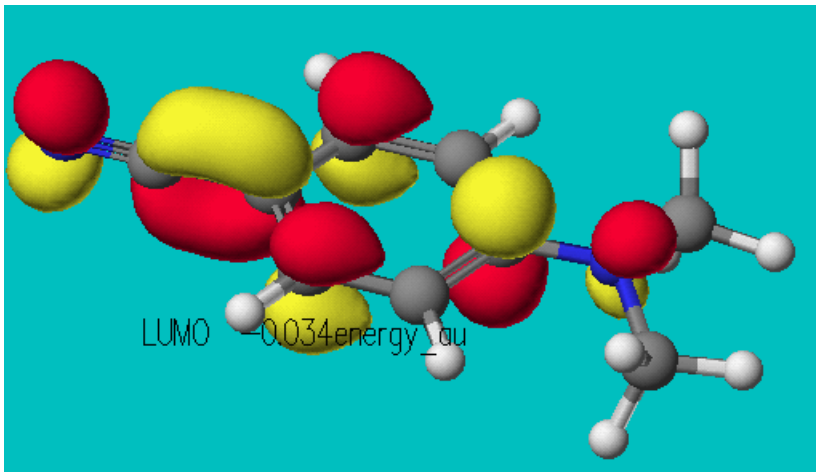
Note that ZINDO reports each possible transition as an eigenvector, and the resulting eigenvalue reported under each state is the contribution of that transition to the excited state. The larger eigenvalues show a larger contribution to the transition present in the excited state. State 1 is designated as the ground state and therefore the 0-0 transition is reported as the entire excited state.

The two lowest energy transitions investigated here are taking place mainly as transitions from HOMO to LUMO+1 and HOMO to LUMO, respectively. Viewing the UV-Vis transitions in CAChe will allow students to see that the lower energy transition has a much smaller transition dipole than the second excited state. Unfortunately there is some confusion in how CAChe selects the orbitals to be displayed, and selecting the state in the UV-Vis spectra does not always report the main contributing orbital transition to the excited state. Therefore, it may be necessary to go directly into the ZINDO output as described above to determine which orbitals play the largest role in the transition. Note that you can then go back into CAChe and manually select those orbitals by selecting **Analyze|Show Surfaces** and selecting the two surfaces responsible for the transition from the list. The transition to the LE state is from HOMO to LUMO+1 and the transition to the CT state is from HOMO to LUMO. These two states will switch in order in going to the solvated system.

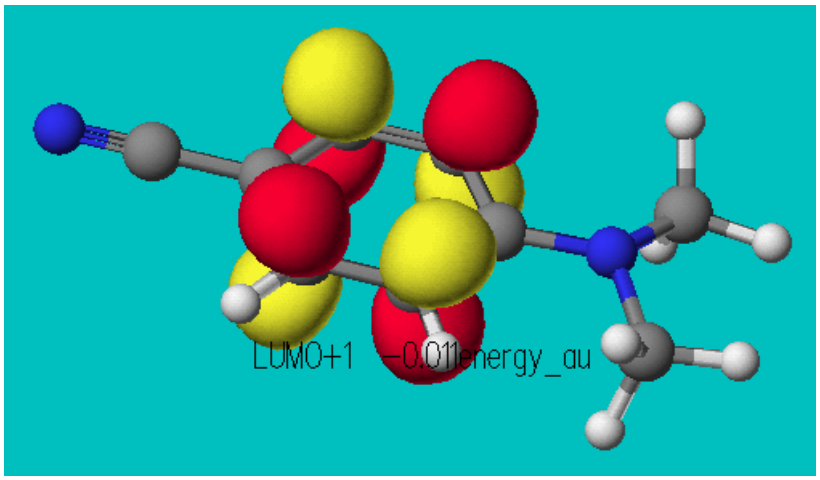
If you want students to view the orbitals as computed in Gaussian, you can change the procedure under **Modeling the Excited States Using TDDFT**, step 1b. Instead of current energy, you can have them choose to calculate the HOMO-5 to LUMO+4 orbitals. You will still need to edit the first step in this CAChe procedure as before. Here are screenshots of the Gaussian orbitals involved in the transitions:



HOMO of DMABN



LUMO of DMABN



LUMO+1 of DMABN

For the TDDFT calculations in Gaussian, it will be necessary for the students to locate the following section of the output file:

```
Excitation energies and oscillator strengths:

Excited State   1:   Singlet-A      4.5652 eV  271.58 nm  f=0.6123
38 -> 41        -0.10276
39 -> 40         0.63897
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI
density.

Excited State   2:   Singlet-A      4.6141 eV  268.71 nm  f=0.0256
38 -> 40         0.22695
39 -> 41         0.65533

Excited State   3:   Singlet-A      5.8012 eV  213.72 nm  f=0.0000
37 -> 42        -0.12442
39 -> 42         0.69177
```

Another variation of this experiment is to use a more realistic basis set for the Gaussian calculations. We have chosen 3-21G here because of computational speed. The 6-31+G(d) basis set would be the recommended basis set for a minimal TDDFT calculation.

Here is a summary of the results obtained from this laboratory:

DMABN Excited States using AM1 optimized geometry

	ZINDO wavelength (nm)	ZINDO Oscillator Strength	TD-B3LYP 3-21G Wavelength (nm)	TD-B3LYP 3-21G Oscillator Strength	TD-B3LYP 6-31+G(d) Wavelength (nm)	TD-B3LYP 6-31+G(d) Oscillator Strength
Gas-Phase						
State 1	292.684	0.0213	265.73	0.0232	278.08	0.0258
State 2	271.290	0.6281	257.21	0.5127	271.22	0.4801
Solvated						
State 1	n/a	n/a	271.59	0.6123	287.01	0.6357
State 2	n/a	n/a	268.65	0.0253	279.63	0.0271

ABN Excited States using AM1 optimized geometry

	ZINDO wavelength (nm)	ZINDO Oscillator Strength	TD-B3LYP 3-21G Wavelength (nm)	TD-B3LYP 3-21G Oscillator Strength	TD-B3LYP 6-31+G(d) Wavelength (nm)	TD-B3LYP 6-31+G(d) Oscillator Strength
Gas-Phase						
State 1	289.501	0.0200	256.14	0.0255	268.25	0.0205
State 2	261.013	0.5802	237.06	0.4345	253.18	0.3772
Solvated						
State 1	n/a	n/a	258.12	0.0308	267.90	0.0245
State 2	n/a	n/a	249.95	0.5612	266.84	0.5810

In the gas-phase DMABN results, the oscillator strength of the first state is much weaker compared to the second state. When the calculation is done in acetonitrile, the weaker state is now the second excited state. The transitions reported show that the states switch places in going from gas phase to solvent, and the transition from HOMO to LUMO becomes lower in energy than the transition from HOMO to LUMO+1 in the solvated system. This reversal of states in going from gas-phase to solvated could explain why there is dual fluorescence for DMABN in polar solvents, but not in gas-phase. It is fluorescence from this CT state that corresponds to the long-wavelength peak that is only seen in spectra obtained in solution.

This pattern does not repeat for ABN. In that molecule, both the gas-phase and solvated results are the same as far as the weaker state being the lowest in energy. The methyl groups must play an important role in mediating the solvent effect on the two excited states. It is known experimentally that ABN does not show dual fluorescence (not even in polar solvents), and the results of this study offer at least one explanation as to why.

References

(1) Rettig, W.; Zietz, B. *Chem. Phys. Lett.* **2000**, 317, 187.

(2) Mennucci, B.; Toniolo, A.; Tomasi, *J. Am. Chem. Soc.* **2000**, 122, 10621.

(3) Jamorski, C.; Foresman, J. B.; Thilgen, C; Luthi, H. *J. Chem. Phys.* **2002**, 116, 8761.