

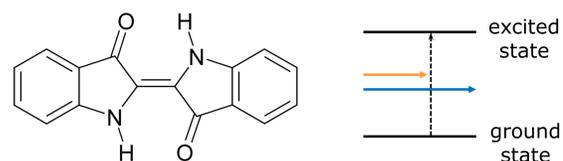
Color of Dyes and Indicators: Natural Resonance Theory of Excited States

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Introduction

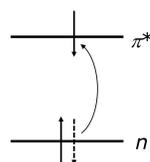
Some molecules are "colored" because specific wavelengths of visible light are absorbed as the molecules undergo electronic transitions from lower energy to higher energy states. For example, the dye indigo is a violet-blue color because it absorbs orange light as the indigo molecule is excited from its ground to first-excited state:



The color that a molecule appears is the complementary color, on the color wheel, of the color of light that is absorbed. So, for example, a molecule that absorbs violet light will appear to be colored yellow, the complementary color of violet.



In this work we use computational chemistry methods to calculate transition energies (and wavelengths) for excitation of several molecules from their ground to first-excited states. Time-dependent density functional theory (TDDFT) at the B3LYP level with the 6-311++G** basis sets were used to calculate ground and excited states. Each excited state is characterized by an $n \rightarrow \pi^*$ type transition of a single electron.



Calculations were performed using the Gaussian program, orbital images were created using Jmol, and analysis of the calculated states was performed using natural bond orbital (NBO) analysis.

Ground and excited states were analyzed using natural resonance theory (NRT). NRT represents the total electron density as a weighted average of electron densities for a set of candidate resonance structures. The weight of each structure is optimized to minimize the density error

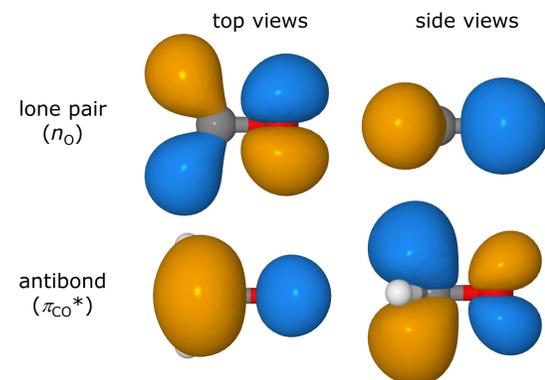
$$D(w) = \min || \Gamma_{\text{tot}} - \sum w_{\alpha} \Gamma_{\alpha} ||$$

where Γ_{tot} is the total electron density from Gaussian, Γ_{α} is the electron density of resonance structure α , and the weights w_{α} are non-negative and normalized ($\sum w_{\alpha} = 1$). The bond order between atoms A and B is defined as the weighted average of the integer number of bonds in each resonance structure

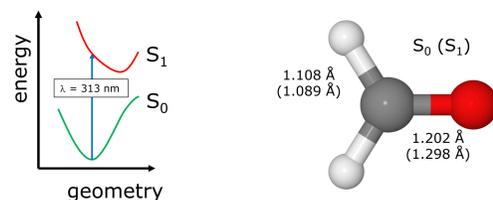
$$b_{AB} = \sum w_{\alpha} b_{AB}^{(\alpha)}$$

Formaldehyde

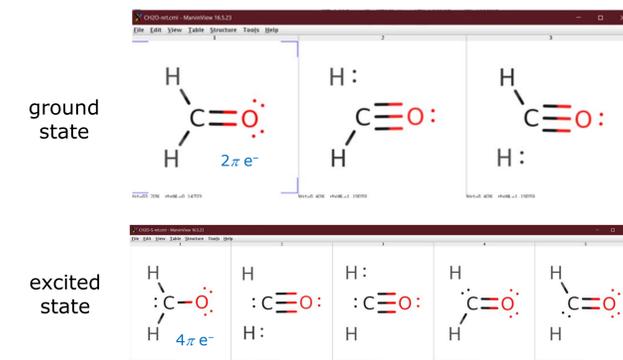
Pure formaldehyde (H_2CO) is a colorless gas at room temperature. Although not colored, this molecule served as a simple test case for our initial exploration of TD-B3LYP calculations and NRT analysis. The lowest energy transition is from the singlet ground state (S_0) to singlet excited state (S_1). The transition principally corresponds to a single electron excitation from an in-plane O p -type lone pair into the out-of-plane CO π^* antibond, i.e. $n_{\text{O}} \rightarrow \pi_{\text{CO}}^*$. The following images show the lone pair and antibond.



We calculated the vertical excitation energy of formaldehyde as the energy difference between the excited and ground states at the equilibrium geometry of the ground state (shown on the right). The excitation wavelength is **313 nm**.



NRT analysis of the ground and excited states reveals the following resonance hybrids:

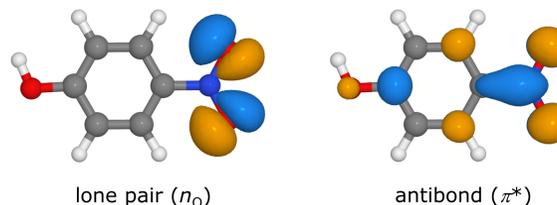


The CO bond order of 2.17 decreases considerably on excitation to 1.80 due to the loss of double-bond character. The CO bond is therefore observed to elongate from 1.202 Å to 1.298 Å in the excited state.

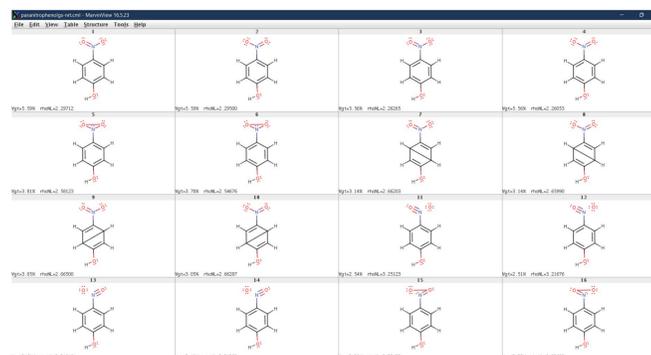
para-Nitrophenol

para-Nitrophenol is an indicator that is colorless in its acid form (the phenol) below pH 5.5 and yellow in its base form (the phenolate, or deprotonated phenol) above pH 7.5. At the TD-B3LYP/6-311++G** level we calculate an excitation wavelength of **328 nm** for the nitrophenol. This wavelength is in the ultraviolet region (< 400 nm) of the electromagnetic spectrum, so the molecule is, not surprisingly, colorless.

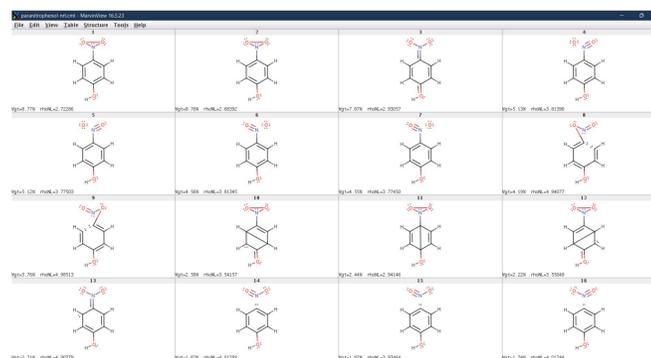
As with formaldehyde, the transition to the first excited state is principally characterized by the excitation of an in-plane O lone pair electron into an out-of-plane π^* antibond, $n_{\text{O}} \rightarrow \pi^*$. The following images show the O lone pair and π^* antibond of the excitation. Note that n_{O} is delocalized across the two O atoms of the nitro group and that the π^* is delocalized across the molecule.



For the ground state, the leading structures of the resonance hybrid reveal the expected delocalization of the nitrate group and the phenyl ring (pairs of Kekule structures). Each structure exhibits 12- π electrons.



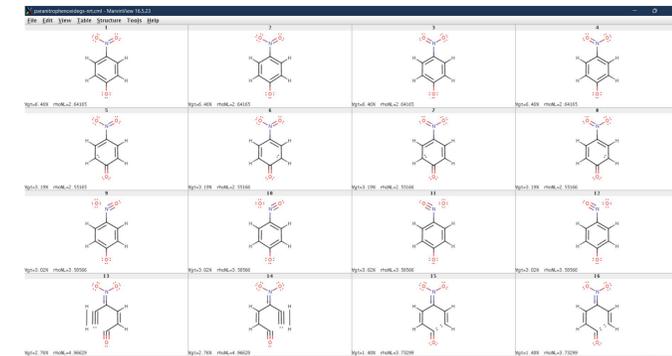
For the excited state, the resonance hybrid exhibits both 12- and 14- π electron structures.



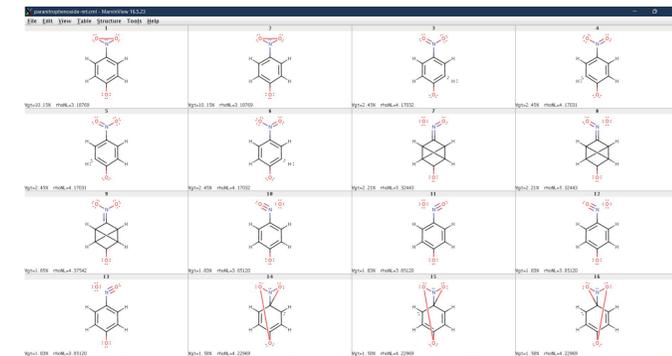
para-Nitrophenolate

The calculated excitation wavelength for para-nitrophenolate is **386 nm**, slightly lower than, but in rather good agreement with, the experimental λ_{max} value of 405 nm (violet). Because the phenolate absorbs violet light, it will appear yellow.

Ground state phenolate reveals a resonance hybrid with strong delocalizations in the nitrate and phenyl ring, similar to that of the ground state phenol.



The excited state of phenolate shows a combination of 12- and 14- π electron structures.



Future Work

NRT bond orders for para-nitrophenol and phenolate should be correlated with calculated bond lengths.

para-Nitrophenol is used as an aqueous indicator. The gas-phase calculations reported here should be extended to treat the influence of solvent effect in aqueous solution.

Acknowledgements

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