Assessment of PBE0 for Evaluating the Absorption Spectra of Carbonyl Molecules

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ABSTRACT: Using the parameter-free PBE0 hybrid functional, we compute the UV/Vis spectra of a series of solvated compounds presenting a carbonyl chromophoric unit linked to a carbon–carbon double bond. It turns out that PBE0 is extremely efficient for accurately reproducing experimental values, with a mean unsigned error of 7 nm for an extended set of compounds, although no fitting or statistical treatments are performed. PBE0 has a predictive efficiency comparable to the well-known Woodward–Fieser empirical formula, and can therefore be used to extend these rules without requiring additional experimental results. Consequently, the UV/Vis spectra of several compounds that have not yet been synthesized are predicted. © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 106: 1853–1859, 2006

Key words: absorption spectra; TD-DFT; carbonyls; PBE0; Woodward–Fieser rules

Introduction

The nineteenth century saw the blooming of tintorial industries, as synthetic dyes began to surge along with the elaboration of new chemical concepts. Hofmann-Witt’s attempts to rationalize the color of molecules in terms of aromatic cores and unsaturated substituents, as well as the availability of synthetic aniline, led to considerable diversification: fuchsin, alizarin, and Congo Red, for instance, were among the first of an endless series of coloring compounds to be synthesized [1]. With the emergence of new artificial fibers, today it is still a crucial industrial issue for optimizing factors such as color yield and fastness, the level of dyeing, or the penetration of the dye in the substrate. In other words, an understanding of dye/fiber interactions clearly needs an accurate description of both contributors.
Aside from the azo pigments, the carbonyl class of dyes is largely used under a variety of chemical forms, including anthraquinone, naphthaquinone, coumarins, indigoids, quinacridones, and perinones, having in common a C=O group, which may be considered an essential part of the chromophoric unit [2, 3]. The carbonyl dyes owe their success to their ability to provide a wide range of colors covering the entire visible spectrum, and to their capacity to show long wavelength absorption bands when combined with relatively short \( \pi \)-conjugated systems, i.e., to have small, yet colored molecules. The relationship between the structure and absorption spectrum of unsaturated ketones was first rationalized by Woodward [4, 5]. He proposed simple additive rules (similar to a first-order group contribution scheme) to estimate the shifts in \( \lambda_{\text{max}} \) induced by adding substituents in either the \( \alpha \) and \( \beta \) positions, or both (see Fig. 1). These rules helped identify the structure of various molecules of chemical interest, but also to predict the energy of the first dipole-allowed excited state of unknown molecules. Woodward original equations have been further refined by Fieser and Fieser [6, 7] and led to the well-known Woodward–Fieser (WF) rules, which have been used extensively to determine the position of double bonds and alkyl groups in conjugated biomolecules. These rules have been extended [8, 9] and are now described in most UV/Vis textbooks [10]; they have still been in use to help elucidate structure [11]. Nevertheless, the WF rules are not completely univocal because for some polysubstituted ketones, one can obtain different \( \lambda_{\text{max}} \), depending on how the molecule is broken into simple components.

Nowadays, molecular modelization techniques offer a competitive alternative for the interpretation of experimental data arising from industrial interest and applications. The accurate prediction of UV/Vis spectra of large molecules remains an area of concern [12], as semi-empirical methods, although specially tailored, are often found to be inaccurate when reproducing spectral patterns or trends. The improvements in cpu resources now allow the study, at correlated levels of approximation, of the absorption spectra of medium-size molecular species of practical interest. The most widely used approach is the time-dependent density functional theory (TD-DFT), which, with reasonable computational effort, commonly yields accurate results. Consequently, a huge number of TD-DFT applications can easily be found in literature [13–38]. In TD-DFT, the choice of a functional is often crucial, and one can find numerous discussions dealing with the determination of the pros and cons of each developed functional. In most studies, these assessments are performed by computing the properties (typically, thermochemistry and geometries) of small molecules (G3 set or alike) and comparing them with experimental data. Indeed, measurements on small molecules are generally more accurate than on large systems and, are essentially free of surrounding effects because such small compounds are in the gas phase at room temperature. However, the success of a theoretical approach for such restricted cases does not guarantee efficiency for large systems. It is now well established that hybrid functionals, which incorporate a fraction of exact exchange, are more accurate than pure functionals for evaluating the absorption spectra of conjugated organic molecules. Among the large number of hybrid functionals developed, two are quite popular: the original B3LYP [39], optimized to reproduce thermochemical data, and the parameter-free PBE0 [40], designed on the basis of purely theoretical considerations (see below). PBE0 has been shown to be efficient to estimate the absorption spectra of small gas-phase molecules [40], but also of some selected solvated compounds [15]. In the present work, we investigate the efficiency of the PBE0 functional for evaluating the excitation spectra of a series of unsaturated ketones, in order to confirm/refute the efficiency of PBE0 for a correct description of the C=O chromophoric group.

**Computational Details**

We have chosen the Gaussian 03 [41] program package to perform the geometry optimizations, vibrational analysis, as well as excited-state evaluations.

The ground-state geometry of each molecule has been fully optimized, using the Adamo and Barone PBE0 [40] hybrid functional and the split-valence
PBE0 in Evaluating Absorption Spectra of Carbonyl Molecules

Basis Set Study

For the molecules investigated, one could reasonably expect that any standard hybrid functional combined with a triple-ζ basis set, such as PBE0/6-311G(d,p), would yield accurate ground-state geometries. For the electronic excitation spectra, it is known that the basis set effects could be much larger [46]. Table 1 compares the \( \lambda_{\text{max}} \) computed with four basis sets [6-311+G(d,p), cc-pVTZ, aug-cc-pVTZ, and d-aug-cc-pVTZ] for selected conjugated carbonyls. It turns out that adding a set of diffuse functions tends to yield a slight increase (typically 4 nm) in the \( \lambda_{\text{max}} \) value, almost systematically improving the agreement with experiment. In contrast, the effect of a second set of diffuse orbitals has a completely negligible effect. In addition, one finds a striking agreement between the

<table>
<thead>
<tr>
<th>Structure</th>
<th>( \lambda_{\text{max}} )</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X Y Z</td>
<td>6-311+G(d,p)</td>
<td></td>
</tr>
<tr>
<td>H H H</td>
<td>202.6</td>
<td>207</td>
</tr>
<tr>
<td>H Me H</td>
<td>215.8</td>
<td>216</td>
</tr>
<tr>
<td>H OH H</td>
<td>255.0</td>
<td>254.6</td>
</tr>
<tr>
<td>H Cl H</td>
<td>235.5</td>
<td></td>
</tr>
<tr>
<td>Me H H</td>
<td>206.5</td>
<td>206.3</td>
</tr>
<tr>
<td>Me Me H</td>
<td>221.5</td>
<td>220</td>
</tr>
<tr>
<td>OH H Me</td>
<td>209.2</td>
<td>205</td>
</tr>
</tbody>
</table>

* The geometry was optimized at PCM(EOH)-PBE0/6-311G(d,p) level. Experimental values from Ref. [53].
6-311+ \text{+G(d,p)} \text{ and (d-)}\text{-aug-cc-pVTZ results (largest}
\text{deviation: 0.5 nm), strongly suggesting that the}
\text{former leads to } \lambda_{\text{max}} \text{ close from basis set conver-
\text{gence. Therefore, the former is used in this study.}

\textbf{COMPARISON WITH EXPERIMENT}

Tables II and III compare the available experi-
\text{mental results with the WF estimate and with PBE0}
\text{(see also Fig. 1 and Fig. 2). First, let us note that the}
\text{experimental values can differ quite significantly}
\text{from one textbook to another (by 1–4 nm). In that}
\text{case, we use the most recent data for the compari-
sions.}

\text{For the complete set of molecules, PBE0 provides}
\text{a mean signed error (MSE) of 4 nm (small overes-
timation of the experimental } \lambda_{\text{max}}, \text{ a mean un-
signed error (MUE) of 7 nm, and a root mean}
\text{square (RMS) deviation of 10 nm. The correspond-
ing values in eV are MSE = –0.05 eV, MUE = 0.13}
\text{eV, and RMS = 0.17 eV. These estimations can be}
\text{compared with recent TD-DFT investigations of the}
\lambda_{\text{max}} \text{ of dyes or conjugated molecules. The typical}
\text{TD-DFT error for the excitation energies of fluoro-
cent coumarins and uranic acid derivatives ranges}
\text{from 0.2 to 0.5 eV [47] and from 0.3 to 0.4 eV [48],}
\text{respectively. For 11 thiouracil derivatives treated in}
\text{Ref. [49], a MUE of 0.24 eV is obtained for the first}
\pi \rightarrow \pi^* \text{ singlet excitation. In the case of alkyl-
aminobenzonitrile compounds, Jamorska and Ca-
sida reported errors with respect to experiment}
\text{ranging between 0.10 and 0.30 eV. For a series of}
donor–acceptor organic chromophores, Masumov
\text{and Tretiak obtained MUE of 0.09, 0.11, and 0.20 eV}

\begin{table}[h]
\centering
\caption{Comparison between theoretical, Woodward–Fieser, and experimental } \lambda_{\text{max}} \text{ for conjugated carbonyls (Fig. 1).}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\text{Structure} & PBE0 & WF & Exp. [Ref.] \\
\hline
\text{H} & 202.6 & 208 & 207 [53], 208 [54] \\
\text{H} & 198.9 & 197 & 202 [55] \\
\text{H} & 215.8 & 218 & 216 [53] \\
\text{H} & 213.1 & 220 & 218 [53] \\
\text{H} & 225.4 & 230 & 228 [53] \\
\text{H} & 208.0 & 209 & 214 [55] \\
\text{H} & 234.7 & 231 & 239 [55] \\
\text{Me} & 206.5 & 215 & 210 [53] \\
\text{Me} & 221.5 & 225 & 220 [53] \\
\text{Me} & 217.6 & 227 & 224 [54], 220 [55] \\
\text{Me} & 231.5 & 239 & 235 [54], 236 [55] \\
\text{Me} & 245.8 & 249 & 249 [44] \\
\text{Me} & 222.3 & 225 & 221 [44] \\
\text{Et} & 222.6 & 225 & 220 [44] \\
\text{OH} & 209.2 & 205 & 205 [53] \\
\text{OH} & 208.9 & 205 & 204 [53] \\
\text{OH} & 246.8 & 230 & 228 [53] \\
\text{OH} & 239.7 & 230 & 238 [53] \\
\text{OH} & 233.0 & 235 & 226 [53] \\
\text{OH} & 233.8 & 235 & 221 [53] \\
\text{OH} & 227.2 & 217 & 228 [53] \\
\text{OH} & 220.6 & 215 & 213 [54] \\
\text{OH} & 216.8 & 215 & 216 [54] \\
\text{OH} & 216.1 & 217 & 216 [54] \\
\text{OH} & 226.8 & 227 & 221 [54] \\
\text{OMe} & 208.6 & 205 & 212 [53] \\
\text{NH}_2 & 191.4 & — & 198 [55] \\
\text{NH}_2 & 210.2 & — & 216 [53] \\
\hline
\end{tabular}
\end{table}

\text{\textsuperscript{a} The cis form is the most stable and has been used for theoretical calculations.}
(depending on the geometry chosen) [50]. Fabian [51] obtained an MUE of 0.24 eV for the \( \pi \rightarrow \pi^* \) transitions of 100 sulfur-containing compounds. Recently, Petit et al. [52] reported deviations of 0.30–0.40 eV for transition-metal complexes. These investigations use different functionals, various basis sets, incorporate or not solvation models, treat various classes of molecules and are not always focused on the first electronic transition. Consequently, a fair comparison is difficult. Nevertheless, it is clear that the PCM-PBE0/6-311++G(d,p) / PCM-PBE0/6-311G(d,p) model is more than adequate for investigating the absorption spectra of conjugated carbonyls, as the errors are clearly in the lowest portion of previously reported data.

For the compounds for which WF rules for \( \lambda_{\text{max}} \) are applicable, Figure 3 provides a comparison of the experiment, WF, and TD-DFT approaches. For this set of compounds, the MSE are 1 nm (WF) and 2 nm (PBE0), both statistically overestimating the \( \lambda_{\text{max}} \); MUE are 4 nm (WF) and 5 nm (PBE0), whereas RMS amounts to 5 nm (WF) and 7 nm (PBE0). By performing simple linear regression, one obtains almost equal \( R \) (0.97 in both cases). One can therefore state that the ab initio approach, which can be used for any compounds, is as efficient as empirical rules, although the latter has been specially tailored for a peculiar class of molecules. In addition, this illustrates that the PCM-TD-PBE0 ap-

PREDICTIONS FOR UNKNOWN COMPOUNDS

As supplementary information, we provide the predicted \( \lambda_{\text{max}} \) for more than 100 compounds presenting the typical structure depicted in Figure 1. It is striking that the agreement between PBE0 and WF rules is often excellent, except for some “crowded” molecules, for which they differ. This is quite understandable, as the additive WF approach is based on experimental values for molecules with generally few (nonalkyl) substituents and is comparable to a first-order group contribution approach. If chlorine is added to the \( \alpha, \beta, \) and \( \beta' \) positions, the simple additive character is not con-

TABLE III

Comparison between theoretical, Woodward–Fieser, and experimental \( \lambda_{\text{max}} \) for the molecules of Fig. 2.*

<table>
<thead>
<tr>
<th>Structure</th>
<th>Solvent</th>
<th>PBE0</th>
<th>WF</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>EtOH</td>
<td>248.8</td>
<td>249</td>
<td>247</td>
</tr>
<tr>
<td>II</td>
<td>EtOH</td>
<td>253.4</td>
<td>254</td>
<td>252</td>
</tr>
<tr>
<td>III</td>
<td>EtOH</td>
<td>229.0</td>
<td>239</td>
<td>235</td>
</tr>
<tr>
<td>IV</td>
<td>Heptane</td>
<td>239.0</td>
<td>243</td>
<td>239</td>
</tr>
<tr>
<td>V</td>
<td>Hexane</td>
<td>265.2</td>
<td>252</td>
<td>261</td>
</tr>
<tr>
<td>VI</td>
<td>Heptane</td>
<td>298.2</td>
<td>288</td>
<td>283</td>
</tr>
<tr>
<td>VII</td>
<td>EtOH</td>
<td>319.0</td>
<td>293</td>
<td>297</td>
</tr>
<tr>
<td>VIII</td>
<td>Hexane</td>
<td>266.3a</td>
<td>—</td>
<td>260</td>
</tr>
<tr>
<td>IX</td>
<td>Water</td>
<td>274.0</td>
<td>—</td>
<td>263</td>
</tr>
<tr>
<td>X</td>
<td>Hexane</td>
<td>327.8</td>
<td>—</td>
<td>300</td>
</tr>
<tr>
<td>XI</td>
<td>MeOH</td>
<td>272.6</td>
<td>—</td>
<td>259</td>
</tr>
<tr>
<td>XII</td>
<td>MeOH</td>
<td>285.0</td>
<td>—</td>
<td>271</td>
</tr>
<tr>
<td>XIII</td>
<td>MeOH</td>
<td>341.5</td>
<td>—</td>
<td>314</td>
</tr>
</tbody>
</table>

* Experimental values have been taken from Ref. [55].

a The cis form is the most stable and has been used for theoretical calculations.

FIGURE 2. Sketch of compounds reported in Table III.
served. For such molecules, we are more confident in the PBE0 estimates than in the WF predictions.

Conclusions

We have computed the $\lambda_{\text{max}}$ of various compounds presenting a conjugated carbonyl chromophore. It turns out that the PCM-TD-PBE0/6-311+ +G(d,p)//PCM-PBE0/6-311G(d,p) provides accurate estimates of the experimental values with a mean unsigned error limited to 7 nm (0.13 eV), confirming the qualities of Adamo and Barone’s functional. Indeed, this error is smaller than expected from previous TD-DFT calculations that typically report errors within the 0.2–0.3 eV range, but most of this studies neglect medium effects. When comparison is possible, the accuracy of PBE0 is similar to that of experiment-based WF rules. Therefore, PBE0 is a scheme of choice, not only to predict the $\lambda_{\text{max}}$ of unknown compounds (of the same family), but also to extend the existing empirical rules by quantifying the contribution of extra substituents. We are currently performing a similar study for substituted aromatic compounds.

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FIGURE 3. Comparisons between the $\lambda_{\text{max}}$ obtained by experiment, WF, and PBE0. All values are in nanometers (nm).

References
