

# A benchmark study on computed photoabsorption intensities: A comparison of experimentally derived and TDDFT computed oscillator strengths

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Density-functional theory (DFT) is the most used electronic structure method in computational chemistry since it provides qualitatively accurate (and in some cases quantitatively accurate) results in a wide range of applications at a relatively low computational cost. Time-dependent DFT methods (TDDFT) can often accurately reproduce the energetics of electronic transitions resulting from single-photon absorptions.[1] However, the accuracy of TDDFT computed absorption intensities has not been extensively investigated. A difficulty such a study faces is that it is not straightforward to establish a quantitative equivalence between computed electronic transition probabilities (often reported as oscillator strengths or transition dipole moments) and the wavenumber-dependent attenuation coefficients reported in experimental spectra.

The present work employs a set of 164 transition oscillator strengths [2] derived from the UV-visible experimental spectra of one hundred small organic molecules to benchmark different TDDFT functionals.

Preliminary results for six hybrid and three pure functionals are presented (see **Index Terms**). The Tamm-Dancoff approximation (TDA) is found to consistently yield a two times larger mean absolute error compared to the random phase approximation (RPA). With RPA, most functionals yield a ~10% mean absolute error.

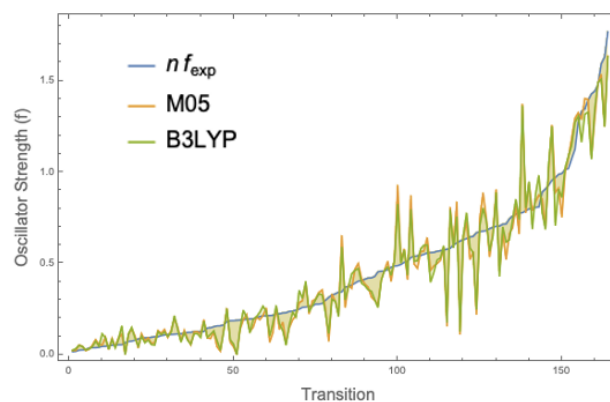


Figure 1: Compares computed (yellow and green) and experimental oscillator strengths (blue). The 164 transitions appear in order of increasing experimental oscillator strengths.

**Index Terms:** TDDFT, oscillator strength, B3P86, CAM-B3LYP, LC-wHPBE, M05, mPW1PW91, O3LYP, SVWN, wB97XD, B3LYP, TDA, RPA.

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