

# Electronic Transition Strengths: Connecting Theory and Experiments

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## Abstract

Electronic (UV-visible) transition strengths are experimentally reported as frequency-dependent molar extinction/attenuation coefficients  $\epsilon(\nu)$ , absorption cross sections  $\sigma(\nu)$ , Einstein coefficients, etc. On the other hand, electronic structure calculations typically report excitation strengths as single-valued transition dipole moments ( $\mu$ ) or oscillator strengths ( $f$ ). These quantities are all related. However, the comparison of single-valued quantities (e.g.,  $\mu$  and  $f$ ) with frequency-dependent quantities (e.g.,  $\epsilon$  and  $\sigma$ ) becomes complicated due to broadening and solvation effects, especially when multiple close electronic transitions give rise to overlapping spectral bands. We attempt to address these challenges as we present a benchmark study of oscillator strengths computed from time-dependent density functional theory with different functionals and excited-state wave function methods, compared to experimental data derived from the UV-visible spectra of 100 organic molecules in solution. We find that the calculations consistently overestimate the absorption strengths compared to experiments. The origin of this systematic error is discussed.

## References

<sup>1</sup> Tarleton, A.S.; Garcia-Alvarez, J.C.; Wynn, A.; Awbrey, C.M.; Roberts, T.P.; Gozem, S. *J. Phys. Chem. A.* **2022**, *126*, 3, 435–443.