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UV-Vis absorption spectra and electronic structure of merocyanines in the gas phase

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Gas-phase absorption spectra of a merocyanine vinylogous series have been studied for the first time. In vapour, their long-wavelength absorption bands were found to be considerably shifted hypsochromically, broader, more symmetrical, less intense, and their vinylene shift much smaller than even in low-polarity *n*-hexane. This indicates that in the gas phase their electronic structure closely approaches the nonpolar polyene limiting structure. The TDDFT calculations of the long-wavelength electronic transitions in the studied merocyanines *in vacuo* demonstrated good-to-excellent correlation – depending on the functional used – with the obtained experimental data. For comparison, the solvent effects was accounted for using the polarizable continuum model (PCM) with *n*-hexane and ethanol as low-polarity and high-polarity media, and compared with the UV-Vis spectral data in these solvents. In this case, the discrepancy between theory and experiment was much greater, increasing at that with the polymethine chain length.

Keywords: merocyanine; electronic structure; TDDFT; solvatochromism.