

# Wide-range IR spectra of diarylethene derivatives and their simulation using the Density Functional Theory

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## Research Article

**Keywords:** Diarylethenes (DAEs), density functional theory (DFT), B3LYP, ultraviolet (UV), TD-DFT

**Posted Date:** November 2nd, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-994401/v1>

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# Abstract

Diarylethenes (DAEs), promising photochromic molecular switches, undergo pericyclic reactions upon ultraviolet or visible light illumination. For this reason, most studies on DAEs employ UV-vis spectroscopies. However, also their infrared (IR) spectra are valuable in particular, for understanding the vibrational dynamics which accompanies the relevant photoreactions. An accurate assignment of IR bands to molecular modes can be achieved through a comparison between experimental and computed theoretical spectra. Even though more sophisticated computational methods are available, the density functional theory (DFT) is usually employed for this task, because of its modest cost and versatility. Here, we have tested the ability of several DFT functionals to reproduce the wide-range, 400-3200  $\text{cm}^{-1}$ , IR spectra of open and closed isomers of four representative DAE molecules. We find that global and range-separated, corrected for anharmonicity by scaling factors, hybrid DFT functionals are able to reproduce the IR spectra of DAEs accurately, especially in the low-frequency and fingerprint ranges. Instead of the most commonly used B3LYP functional, we recommend the use of dispersion-corrected PBE0 functional, which at the same cost as B3LYP, offers a more accurate and reliable performance, with a mean absolute error of just under 10  $\text{cm}^{-1}$  and a mean signed error of 0.2  $\text{cm}^{-1}$ .

## Introduction

Photochromic switches are compounds that undergo reversible structure rearrangements upon light illumination. The relevant achievable chemical forms feature distinct absorption spectra and other physicochemical parameters.<sup>1</sup> Thanks to these characteristics they have various potential applications in optical devices and spectroscopy.<sup>2-5</sup> One of the most promising groups of photoswitches are fluorinated diarylethenes (DAEs) which are thermally stable and have a relatively high fatigue resistance.<sup>6</sup> These compounds undergo a reversible pericyclic reaction. The open-ring forms of DAEs absorb only the ultraviolet (UV) light while the closed-ring isomers have optical absorption bands in both UV and visible spectral regions. One possible application of photoswitches are the alternative rewritable optical information storage devices.<sup>7,8</sup> In such devices, writing of information is performed by inducing a photochromic reaction of photochromic dye. For a non-destructive readout, the infrared (IR) light can be used since it does not initiate photoswitching.<sup>9,10</sup> For optimal employment of IR radiation, the spectrum of the light source should match the intense vibrational modes in the absorption spectra of open or closed isomers.

The dynamics of pertinent pericyclic reactions decides the potential applications of this class of photoswitches, hence its understanding becomes essential in materials design and applications. Modelling of dynamics of a photoreaction must involve an accurate computation of UV-vis spectra, but also of the molecular structure and of the IR frequencies. Since the electronic excitations are such essential features of diarylethenes, there is no shortage of theoretical and experimental studies on the UV-vis spectra of those systems. Even though to model the entire photochemical reaction of diarylethenes, multireference computational methods are needed,<sup>11,12</sup> the most popular approach for the spectrum

simulations remains the time-dependent density functional theory (TD-DFT), due to its relative inexpensiveness and accuracy. Several exchange-correlation functionals, including CAM-B3LYP<sup>13</sup>,  $\omega$ B97X-D<sup>14</sup>, PBE0<sup>15,16</sup>, M05-2X<sup>17</sup>, M06-2X<sup>18</sup> were successfully applied to model the geometries, absorption spectra and 0-0 transition energies. While TD-DFT cannot correctly describe the potential energy surfaces near the conical intersections, where the photoreactions usually take place, it can still be applied to model the dynamics of the excited-state relaxation.<sup>19-22</sup> In fact, for larger diarylethene molecules, the dynamics simulation based on TD-DFT, in a moderately sized basis set, is often the most advanced, but still viable computational technique. For a correct simulation of the dynamics of a photoreaction, an accurate description of both the electronic and the vibrational spectrum is necessary. Since the accuracy of the electronic spectrum simulation by DFT has been well studied, we seek to show the performance of DFT for the IR spectra.

Here, we present experimental IR spectra of a few DAE derivatives in open-ring form and their comparison with IR spectra calculated using density functional theory (DFT) using several different functionals. Selecting the DFT functional for which the computed spectra fit best the experimental ones will significantly facilitate a correct interpretation of vibrational bands. This, in turn, will allow for better understanding of time-resolved vibrational experiments performed to determine the structural rearrangements accompanying the cyclization and cycloreversion in DAEs.

## Methodology

All diarylethenes have been purchased from Yamada Chemical Co. Ltd. (Kyoto). We have studied four DAE derivatives including 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (1), 1,2-bis(3,5-dimethylthiophen-2-yl)hexafluorocyclopentene (2), 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (3), and 1,2-Bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene (4). Their chemical structures and photochemical reactions are shown in Fig. 1. The purities of compounds are the following as declared by the distributing company: (1) - 99.8%, (2) - 99.9 %, (3) - 99.8%, (4) - 98%.

DAEs were dissolved in hexane to prepare the solutions of open-ring isomers. These solutions were irradiated for approximately two hours to perform the ring closure reaction using the output from femtosecond laser set-up (300 nm,  $\sim 1 \mu\text{J}$ ,  $\sim 150 \text{ fs}$ ) which is described elsewhere.<sup>22</sup> After the irradiation, the solutions contained both open and closed ring isomers that were subsequently separated using thin layer chromatography (TLC). All separations were performed on the PTLC (preparative TLC) silica gel 60 glass plates with fluorescent indicator  $F_{254}$ , 1 mm, purchased from Sigma-Aldrich. Solvents used for separation and extraction of the products were purchased from Avantor Performance Materials Poland SA and used as received. The details of the separation procedure on TLC are included in supplementary information (SI). After the TLC, the solvent was let to evaporate, and the remaining powder was re-dissolved in  $\text{CCl}_4$ . The  $\text{CCl}_4$  has been selected because its IR spectrum contains only a small number of high-intensity bands that can overwhelm the bands of the solute. The infrared spectra of DAEs were recorded using a Fourier-Transform IR (FTIR) spectrometer (Avatar 330, ThermoFisher Scientific) and

demountable liquid cell (DLC, Harrick). The sample was placed between 2 mm thick KBr windows separated by 250  $\mu\text{m}$  spacer.

The density functional theory computations were performed using the Gaussian 09D software<sup>23</sup> and def2-SVP basis set<sup>24</sup>. The employed exchange-correlation functionals were chosen based on their popularity, cost (no double hybrids were included), stability of performance with respect to the grid and basis set, and previous proven performance for diarylethene UV-vis spectra and they include global hybrids B3LYP<sup>25</sup>, PBE0<sup>26</sup>, range-separated hybrids  $\omega$ B97X-D<sup>27</sup>, LC- $\omega$ PBE<sup>28</sup> and CAM-B3LYP<sup>29</sup> and the local meta-GGA, M06L<sup>30</sup>. To assess the influence of the London dispersion interaction, functionals with and without the Grimme's D3 dispersion correction<sup>31</sup> were considered, except for  $\omega$ B97X-D and M06L, which already account for dispersion without the correction. The open and closed structures of the studied molecules were optimized with the pertinent functionals and then the infrared spectra were calculated. To account for anharmonicity effects, the positions of IR peaks were adjusted by applying scaling factors.<sup>32</sup>

To compare the experimental (featuring broad vibrational bands) and the theoretical spectra (consisting of zero-width lines) with minimal bias, we have adopted one of the approaches introduced by Katari and coworkers who analyzed experimental and theoretical spectra of organometallic complexes.<sup>33</sup> In this strategy (recommended by the authors, and denoted by them as protocol P2), the highest peak in the spectral range of consideration in computed spectrum determines the predicted frequency value to be compared with the maximum of a band in the experimental spectrum. When several vibrational frequencies having similar intensities (equal to at least a half of the intensity of the most intense peak) are present, the mean of all these frequencies is taken for analysis. In our analysis, approximately 30 of the most intense bands in the experimental spectrum in the range of 400-3500  $\text{cm}^{-1}$  have been taken into account. After determination of maxima of these bands and corresponding predicted frequencies from theoretical spectrum using P2 protocol the mean absolute errors (MAE) have been calculated according to eq. (1) to estimate the accuracy of selected DFT functionals.  $MAE = \frac{|v_{predict}^v - v_{calc}^v|}{N}$  (1)

where  $N$  is a number of bands taken for analysis,  $v_{predict}^v$  is a frequency calculated from computed spectrum using P2 protocol and  $v_{calc}^v$  is a maximum of the experimental peak.

## Results And Discussion

The experimental and computed IR spectra of DAEs are presented in Fig. 2 (in open form) and Fig. 3 (in closed form). The results of MAE calculations of theoretical and experimental frequencies for both open and closed isomers of DAEs in the range 900-1700  $\text{cm}^{-1}$  are gathered in Fig. 4c). This spectral range deserves the most attention since molecular vibrations involving carbon atoms reactive in photochromic reactions appear around 1500-1700  $\text{cm}^{-1}$ .<sup>34</sup> The low-frequency modes are also important because they are believed to facilitate the reaction by driving a DAE towards the photoproduct on the excited-state

potential energy surface.<sup>35</sup> The relevant comparisons between experimental and theoretical frequencies in other spectral ranges ( $400\text{-}900\text{ cm}^{-1}$  and  $2700\text{ cm}^{-1}$ ) are shown in Fig. 4b) and Fig. 4d).

From Fig. 4a), where the MAE of each functional, averaged across all molecules are plotted, it is clear that the global and range-separated hybrid functionals describe the IR spectra of diarylethenes accurately, even when a modest basis set is used. While the MAEs for the full range of IR spectrum for different functionals do not differ massively, the dispersion-corrected PBE0 functional is the best performer. Larger differences between functionals can be spotted when looking at the MAEs for the three ranges of the IR spectrum separately. Clearly, the largest errors come from the  $2700\text{-}3200\text{ cm}^{-1}$  range of the spectrum and the smallest from the low-wavenumber ( $400\text{-}900\text{ cm}^{-1}$ ) part of the spectrum. In the latter range, PBE0-D3's accuracy is not the highest [CAM-B3LYP-D3 is the most accurate in this case], but MAEs of all functionals are quite small in this range, with the highest one at  $8.7\text{ cm}^{-1}$ . In both the middle and the high-frequency parts of the spectra, the corrected and uncorrected flavors of the PBE0 functional are the most accurate.

To be a reliable method of predicting spectra, the functional should also not systematically under- or overestimate the position of the peak. This problem is partially solved with the use of scaling factors, which are, in principle, introduced to account for anharmonicity, but due to their empirical nature they also alleviate the bias of the functionals. A look at the mean signed error (MSE, Cf. Fig. 4) tells us that when it comes to a systematic error, PBE0 (corrected and uncorrected) is also the best performer. The MSE for the full range of the spectrum of PBE0-D3 is only  $0.2\text{ cm}^{-1}$ . The uncorrected B3LYP and M06L produce spectra most shifted towards lower frequencies, while LC- $\omega$ PBE overestimates the frequencies of peaks. In fact, the LC- $\omega$ PBE and LC- $\omega$ PBE-D3 approaches produce very large errors in the high-frequency limit of the spectrum.

Notice that for structure (2), the closed isomer (cf. Fig. 3), there is a small peak at  $1438\text{ cm}^{-1}$  which does not show up in the simulation. This is most likely due to the presence of the open form in the sample, which has an absorption band at this wavenumber.

## Conclusions

We have presented wide-range IR spectra of closed and open isomers of four different DAEs and we analyzed how accurately the most popular density functionals reproduce them. We find, that in fact, when the standard scaling factors are applied, the IR spectra are well reproduced with global hybrid and range-separated hybrid functionals, especially in the fingerprint region. The only local functional tested, M06L, performs worst when it comes to MAE. Interestingly, the most popular functional in organic chemistry, B3LYP, turns out to be one of the poorer performers in the tested set and significantly shifts the spectra towards lower frequencies. As an alternative to B3LYP, for computationally expensive tasks, we propose the dispersion-corrected PBE0 functional, which has the same computational cost as B3LYP but is much more reliable than the latter. Other possible choices include the range-separated hybrids, i.e.  $\omega$ B97X-D and the dispersion-corrected CAM-B3LYP functional. Each of those functionals is known to be capable of

describing the non-covalent interactions, and their good performance in predicting the molecular structures and UV-vis of DAEs has been shown previously.

## Declarations

## Acknowledgments

This research was supported by the National Science Centre of Poland under grants no. 2015/19/D/ST4/01813 and 2017/26/D/ST4/00780.

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## Figures

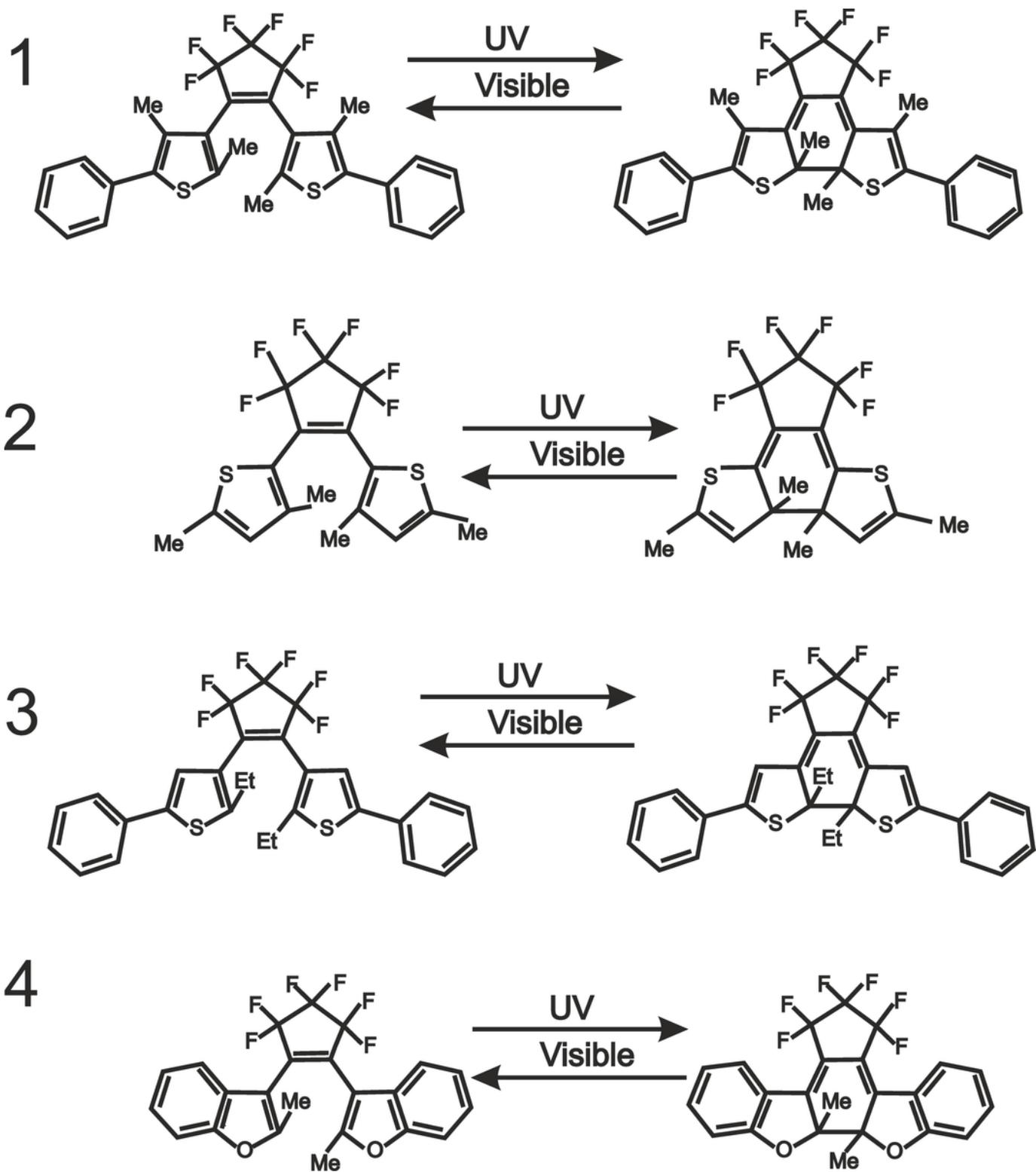
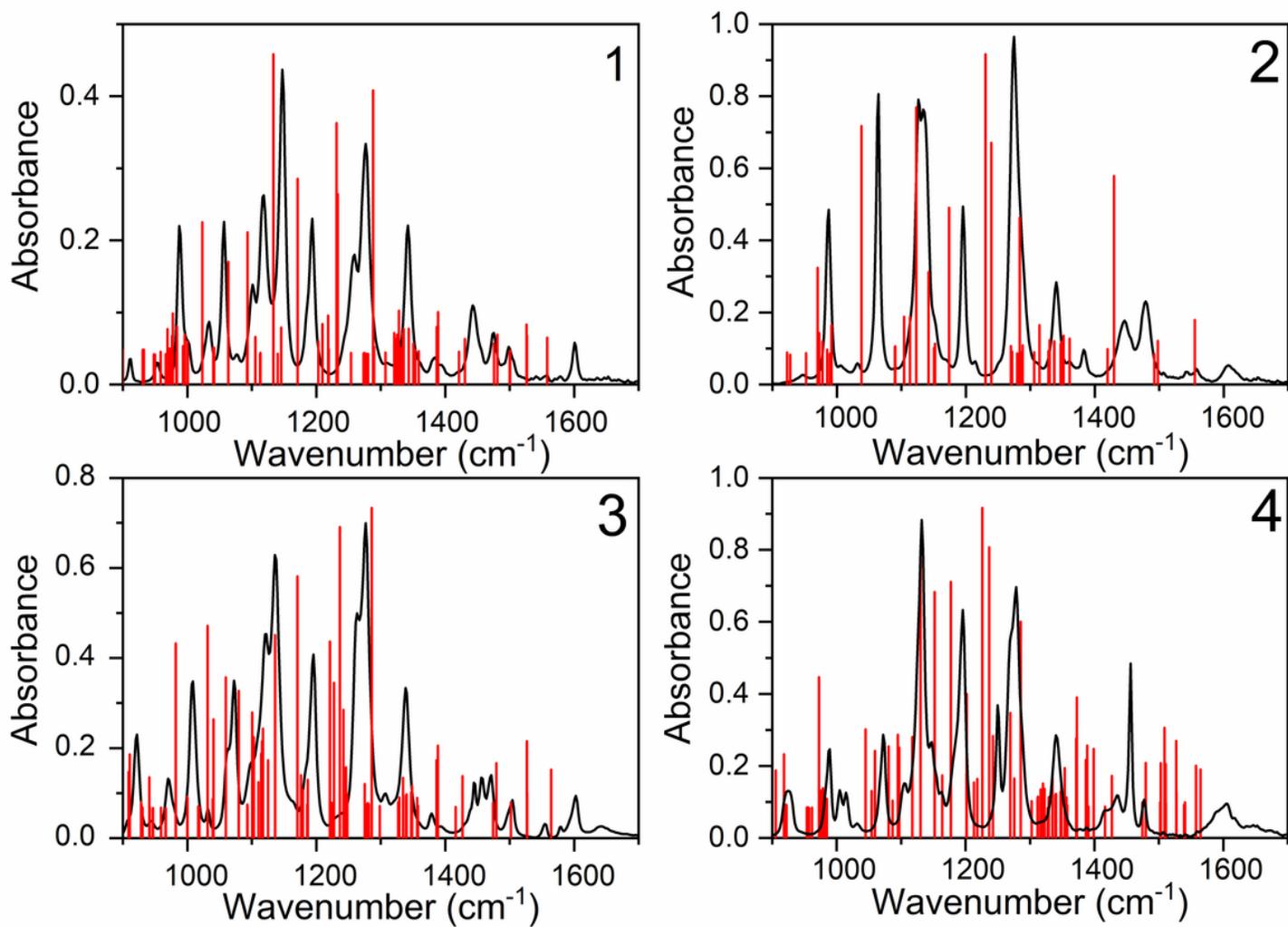


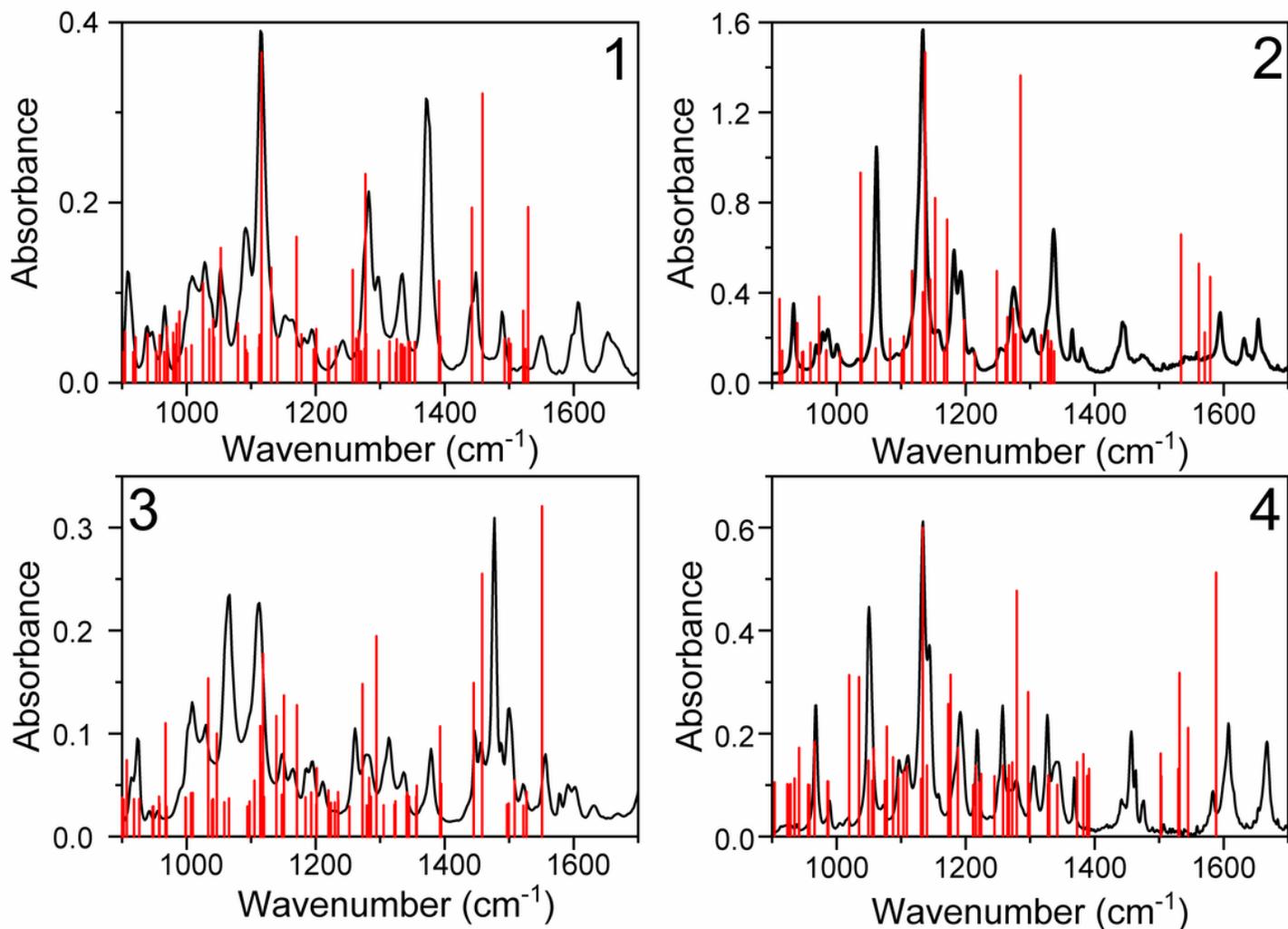
Figure 1

DAE derivatives and their photochemical reactions studied in this manuscript.



**Figure 2**

The experimental (black lines) and simulated using PBE0-D3 functional (red lines) IR spectra of open ring isomers of DAEs.



**Figure 3**

The experimental (black lines) and simulated using PBE0-D3 functional (red lines) IR spectra of closed ring isomers of DAEs.

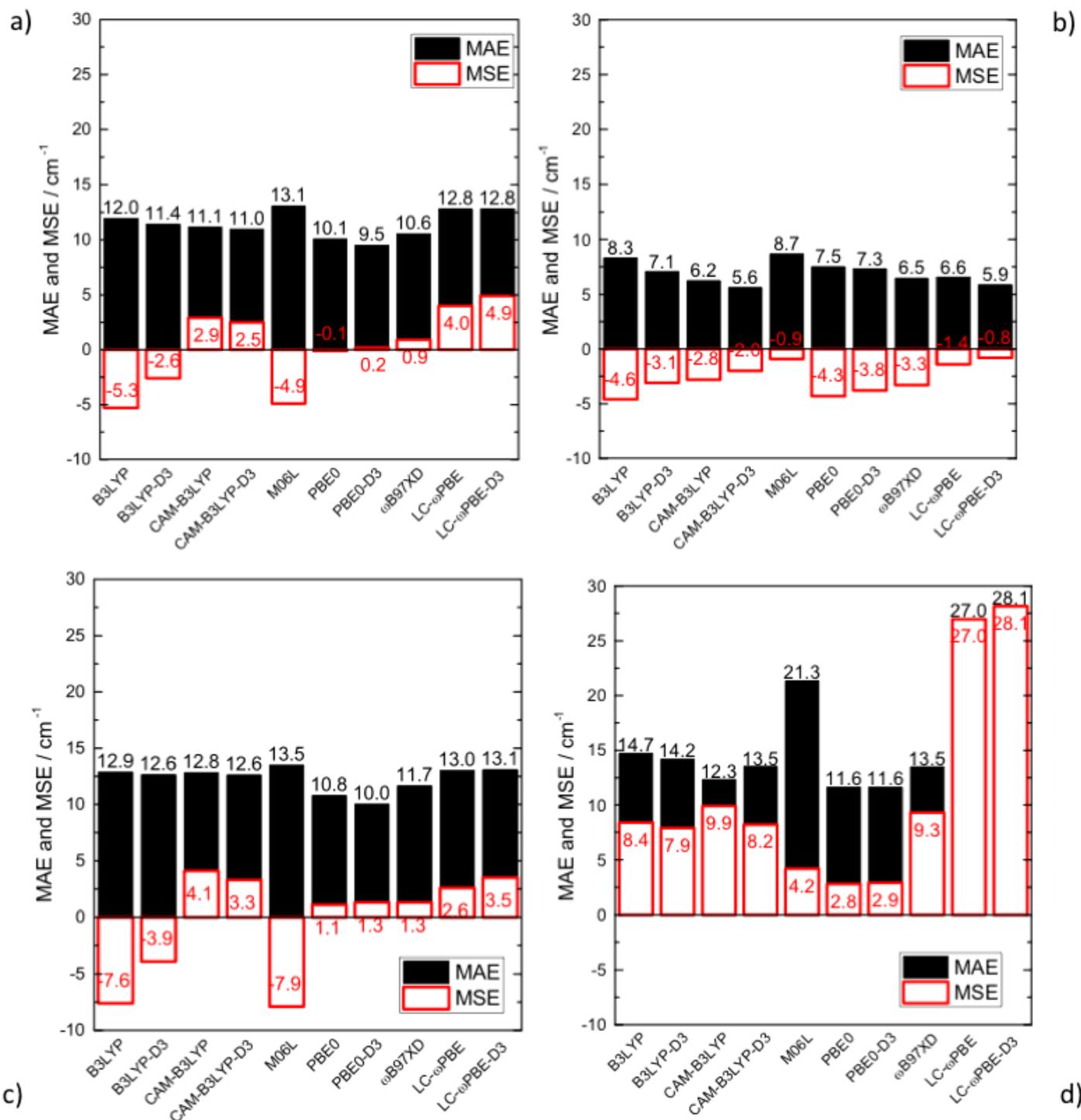


Figure 4

The results of MAE and MSE calculations between theoretical and experimental frequencies for various DFT functionals for a) full-range spectra (400-3200  $\text{cm}^{-1}$ ), b) low wavenumbers (400-900  $\text{cm}^{-1}$ ), c) middle wavenumbers (900-1700  $\text{cm}^{-1}$ ), d) high wavenumbers (2700-3200  $\text{cm}^{-1}$ ).

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