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Electronic excitation of sulfur-organic compounds – performance of time-dependent density functional theory

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Abstract. To define the scope and limitations of the time-dependent density functional theory (TDDFT) method, spectral absorption data of a series of about 100 neutral or charged sulfur-organic compounds with up to 24 non-hydrogen atoms and up to four sulfur atoms were calculated in the near-UV, visible and IR regions. Although the theoretical vertical transition energies correspond only approximately to experimental absorption band maxima, the mean absolute deviation was calculated to be 0.21 eV (1600 cm⁻¹). The main absorption features of various compounds with mono-coordinated or dichloroordinated sulfur atoms are well reproduced. As far as possible TDDFT results were compared with those of semiempirical Zerner’s intermediate neglect of differential overlap (ZINDO/S) and of Pariser–Parr–Pople (PPP) calculations. TDDFT also works well in cases where the semiempirical methods fail. Limitations of TDDFT were encountered with calculations of spectral absorptions of dye molecules. The “vinylene shift” of polymethine dyes is not reproduced by TDDFT. Whereas electronic excitation energies delocalized polar and betainic chromophores are reasonably well reproduced, excitation energies of charge-transfer-type and charge-resonance-type transitions of weakly interacting composite chromophores are significantly underestimated.

Key words: Sulfur-organic compounds – Dyes – Time-dependent density functional theory – Zerner’s intermediate neglect of differential overlap – Pariser–Parr–Pople

1 Introduction

If light absorption occurs in the experimentally easily accessible spectral region longer than 200 nm the characteristics of the electronic spectra may play a considerable role in structural analysis. Compounds absorbing light between about 400 and 800 nm are colored. Conjugated organic compounds generally exhibit spectral absorptions in the near UV (NUV), visible and sometimes in the near-IR region (NIR). The absorption wavelengths depend on the molecular and electronic structure. Because of the delocalized nature of the electronic excitation, empirical spectroscopic increments are of little value in UV/vis/NIR spectroscopy. Quantum chemical methods have rather to be used to predict and rationalize spectral absorption data. For planar conjugated compounds the semiempirical Pariser–Parr–Pople (PPP) method [1] developed in the mid-1950s is very useful. This method enables spectral absorptions caused by π→π* transitions to be calculated. The PPP calculation makes use of a limited configuration interaction (CI) of singly excited configurations. The extension of the PPP approximation to the all-valence electron system [2] was based on the complete neglect of differential overlap (CNDO) or intermediate neglect of differential overlap (INDO) methodologies developed by Pople and coworkers. Application to spectroscopy required a modification of the methods. The resulting methods were CNDO/S, INDO/S, LINDO/S (local neglect of differential overlap), CNDO (azimuthal quantum number 1 dependency) and other related methods. These methods were parameterized for sulfur-containing compounds [2, 3]. To better match the maximum absorption wavelengths Ridley and Zerner [4] introduced a weighting of both the π-type and σ-type overlap. This method, known as Zerner’s intermediate neglect of differential overlap (ZINDO/S), is readily available from commercial program packages. Like PPP this method was primarily parameterized with spectral data of planar cyclic conjugated compounds. It is also a single configuration CI method. The method was mainly tested and applied for calculations of π→π* and n→π* transitions of compounds with first-row elements of the periodic chart [4]. ZINDO/S also allows the calculation of sulfur-organic compounds [5]. Neglect of diatomic differential overlap CI methods such as MNDO-CI (modified neglect of differential overlap), AM1-CI (Austin model 1) and PM3-CI (parametrized model 3) are used without scaling [6], whereas MNDO/C takes
into account the correlation effect with modified MNDO parameter sets [7].

The simplest ab initio approach to calculate transition energies is the Hartree–Fock-based singles-only CI method (CIS) and the random-phase approximation (RPA) [8]. Excitation energies calculated by these methods are much too low. The equation-of-motion method with coupled-cluster reference states (EOM–CCSDT) [9], the multireference configuration interaction method (MRCI) [10] and the multiconfigurational self-consistent-field method including second-order perturbation theory (CASSCF/CASPT2) [11] are high-level ab initio methods with a good performance in calculating transition energies. EOM–CCSD(T) is a response theory approach directed at the calculation of energy differences. The ground-state calculation is followed by the solution of a resonance eigenvalue equation that gives the vertical excitation energy directly. The spectrum is predicted in a single essentially black box calculation. On the other hand, multiconfigurational methods calculate the two states involved in the electron transition explicitly and independently. Since the active space in a CASSCF calculation has to be chosen for each state, the calculation becomes exceedingly difficult for larger compounds. In spite of the difficult choice of the active space and other user-determined computational choices in CASSCF/CASPT2 calculations, Roos and coworkers calculated a representative series of organic compounds [11] including three sulfur-containing compounds, thiophene, bithiophene and terthiophene [12]. Multiconfigurational methods require extended basis sets. The calculations are computationally demanding for larger compounds and are expensive with atoms of second- or higher-row elements. Because of the high expenditure these methods are less attractive in deriving relationships between spectral absorption (color) and structure.

On the other hand, the more recently developed electron-density-based methods find increasing interest in calculations of electron transition energies [13–22]. According to the first results time-dependent density functional theory (TDDFT) is a good compromise between accuracy and computational efficiency. Like EOM–CCSD(T), TDDFT is a response method. The whole spectrum is calculated in a single run. The computational costs are much lower than those of the high-level ab initio calculations. Extended basis sets are not required. When the one-electron basis set and the functional are chosen the complete set of excitation energies is available. A disadvantage of the method is the fact that performance can hardly be improved without introduction of better functionals, which are, however, not available in any straightforward way. In addition, two-electron excitations are not calculated and the Rydberg-type transition energy may be seriously in error. Fortunately these transitions generally occur only at higher energies. Modified TDDFT methods were put forward, such as TDDFT in the Tamm–Dancoff approximation [23] and DFT/CIS [24, 25] and DFT/MRCI methods [26], including, in part, few empirical parameters. The more approximate and, therefore, more efficient density functional–tight binding (DFTB)–time-dependent local density approximation (TDLDA) method recently developed [27] makes use of the local density approximation. The deviations between TDDFT-calculated and experimental excitation energies were reported to be between 0.0 and 1.0 eV [14, 18, 19, 22]. The average accuracy for polycyclic hydrocarbons is about 0.3 eV [19]. A first systematic comparison of results of TDDFT calculations and CASPT2 calculations has been made recently [22]. In the last mentioned study attention was mainly placed on compounds that absorb in the short wavelengths region of the UV, where both valence-type and Rydberg-type transitions are important. The comparison revealed that the two methods give similar results, in general, but TDDFT may exhibit erratic behavior in the high-energy region. Although encouraging results were reported with the study of the pigments porphin [14, 16, 21] and chlorophyll [20], the performance of TDDFT is less well known for compounds with absorptions at longer wavelengths. Except for the thiophene parent compound [22] sulfur-organic chromophores were apparently not calculated by TDDFT. We recently reported calculations of spectral data of thioacetamides that were found to be about 0.2 eV in error with respect to the few experimental data available [28]. In addition, the enigma of the color of 1,2-dithia[29] was solved: while semiempirical all-valence electron calculations and ab initio CIS calculations failed in predicting the long-wavelength absorption, TDFFT calculations resulted in the experimentally found color band. The nature of the color band was discussed in terms of the Kohn–Sham orbitals involved in the electronic transition.

The aim of this work is to evaluate the performance of the TDDFT method by examining a series of about 100 sulfur-organic compounds of quite different structure. Compounds with monocordinated (C=S) and dicordinated sulfur (S=) are mainly considered, with various planar or nonplanar structures. Owing to the presence of sulfur atoms these compounds absorb, in general, at relatively long wavelengths. The spectra cover the UV and possibly the visible and NIR region.

2 Computational details

The TDDFT program used is part of the GAUSSIAN98 suite of programs [30]. Becke’s three-parameter Lee-Yang-Parr functional (B3-LYP) [31] has been widely used in the calculation of molecular geometries and parameters of organic compounds. The functional has also been tested in TDDFT calculations [14, 16, 17, 21].

Since the results of the calculations are hardly dependent on the basis set the early recommended [16] 6-31 + G* basis set was used throughout this work. The B3-LYP/6-31 + G* approximation was also employed in optimizing the molecular geometries in this study except for some larger molecules where the lower level B3-LYP/3-21G geometries were taken [24, 55, 59 and 60]. Along these lines, geometry optimization and TDDFT calculations were done in a single run through a checkpoint file. The effect of diffuse functions is less marked on the geometrical parameters than on the spectral data. The comparison between the calculated DFT B3-LYP bond lengths and the experimental gas-phase structural data of thioacrolein (3), dimethyl sulfide (13), methylvinylsulfide (17), dimethyl disulfide (21), 1,2-dithiin (23), thiophene (26) and 4H-thiopyran-thione (25) r_2 or r_3- geometries [32] showed an absolute mean deviation of 0.010 Å for CC (nine values), 0.019 Å for CS (nine values) and 0.06 Å for SS (two values). As is well known, bond