

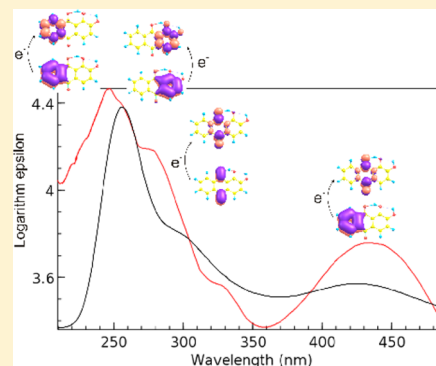
Application of Time-Dependent Density Functional and Natural Bond Orbital Theories to the UV–vis Absorption Spectra of Some Phenolic Compounds

Svetlana Marković* and Jelena Tošović

Faculty of Science, University of Kragujevac, 12 Radoja Domanovića, 34000 Kragujevac, Serbia

S Supporting Information

ABSTRACT: The UV–vis properties of 22 natural phenolic compounds, comprising anthraquinones, neoflavonoids, and flavonoids were systematically examined. The time-dependent density functional theory (TDDFT) approach in combination with the B3LYP, B3LYP-D2, B3P86, and M06-2X functionals was used to simulate the UV–vis spectra of the investigated compounds. It was shown that all methods exhibit very good (B3LYP slightly better) performance in reproducing the examined UV–vis spectra. However, the shapes of the Kohn–Sham molecular orbitals (MOs) involved in electronic transitions were misleading in constructing the MO correlation diagrams. To provide better understanding of redistribution of electron density upon excitation, the natural bond orbital (NBO) analysis was applied. Bearing in mind the spatial and energetic separations, as well as the character of the π bonding, lone pair, and π^* antibonding natural localized molecular orbitals (NLMOs), the “NLMO clusters” were constructed. NLMO cluster should be understood as a part of a molecule characterized with distinguished electron density. It was shown that all absorption bands including all electronic transitions need to be inspected to fully understand the UV–vis spectrum of a certain compound, and, thus, to learn more about its UV–vis light absorption. Our investigation showed that the TDDFT and NBO theories are complementary, as the results from the two approaches can be combined to interpret the UV–vis spectra. Agreement between the predictions of the TDDFT approach and those based on the NLMO clusters is excellent in the case of major electronic transitions and long wavelengths. It should be emphasized that the approach for investigation of UV–vis light absorption based on the NLMO clusters is applied for the first time.



1. INTRODUCTION

Polyphenols form a class of chemical compounds characterized with large number of phenolic functional groups. In recent years, these compounds have been attracting attention of researchers in the fields of chemistry, food, pharmacy, and medicine, due to their antioxidative, anti-inflammatory, antimutagenic, anticancer, antibacterial, vasodilatory, antiproliferative, and antiviral properties. This work is focused on several groups of naturally occurring polyphenols: anthraquinones, neoflavonoids, and flavonoids (Figure 1).

The majority of 9,10-anthraquinone derivatives present in higher plants and fungi are of phenolic nature.^{1,2} Hydroxyanthraquinones have been applied as dyes, catalysts in industrial processes, materials for data storage and processing devices, indicators, analytical reagents, etc. In addition, they are biologically active compounds and medical agents.^{3–8} Flavonoids belong to one of the largest groups of natural products and are universally distributed in higher plants.⁹ Many members of flavonoids are physiologically active substances.^{10–13} Several representatives proved to be helpful anticancer promoters and cancer chemopreventive agents.^{14–17} As typical phenolic compounds, they behave as powerful antioxidants and metal chelators.^{18–23} Neoflavonoids are natural products derived from 4-phenylcoumarin. A class of neoflavonoids, neoflavones,

exhibits various pharmacological properties, which makes these compounds highly valuable and interesting.^{24–27}

Simulation of UV–vis spectra of conjugated phenolic compounds has become a crucial support for experimental results. Among various semiempirical, *ab initio*, and density functional theory (DFT)-based quantum mechanical methods^{28–35} designed to examine excited states and predict their properties, time-dependent density functional theory (TDDFT) turned out to be an approach of choice for this purpose (see the review of Casida³⁵ and references therein). Within this theory a time-dependent oscillating electric field is applied on a molecular system in its ground state, and linear response of the system is used to determine its excitation energies and transition vectors, and, consequently, UV–vis absorption energies and corresponding oscillator strengths. Usually, there is a set of particle-hole pairs that contribute to a certain transition. Natural transition orbital (NTO) analysis simplifies qualitative description of electronic transitions by creating the unique particle-hole pairs via diagonalization of the transition density matrix.³⁶ TDDFT calculations identify

Received: May 29, 2015

Revised: July 27, 2015

Published: August 14, 2015

