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DFT calculation of core– and valence–shell electron excitation and ionization energies of 2,1,3-benzothiadiazole $C_6H_4SN_2$, 1,3,2,4-benzodithiadiazine $C_6H_4S_2N_2$, and 1,3,5,2,4-benzotrithiadiazepine $C_6H_4S_3N_2$

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ABSTRACT

The vertical core– and valence–shell electron excitation and ionization energies of the three title molecules, **1**–**3**, were calculated by density functional theory (DFT) using adequate functional for each type of processes and atoms under study. The inner shells treated were C1s, N1s, S1s, S2s, S2p. Molecular geometry was optimized by DFT B3LYP/6-311 + (d,p). The basis set of triple zeta plus polarization (TZP) Slater-type orbitals was employed for DFT calculations. The ΔSCF method was used to calculate ionization energies. The average absolute deviation (AAD) from experiment of 26 valence-electron ionization energies calculated by DFT for the three molecules **1**–**3** was 0.14 eV; while that of 24 calculated core-electron binding energies (CEBEs) from experiment was 0.4 eV. Selected core excitation energies were calculated by the multiplet approximation for the three molecules. The AAD of twelve calculated core excitation energies by the multiplet approximation that exclude S2s cases was 0.56 eV. Time-dependent DFT (TDDFT) was employed to calculate the excitation energies and corresponding oscillator strengths of core- and valence-electrons of the molecules. Some selected occupied core orbitals were used to calculate the core-excitation energies with the TDDFT (Sterner–Frozoni–Simone scheme). The core excitation energies thus calculated were in an average error of ca. 28 eV compared to observed values. They were shifted to the value calculated by the multiplet approximation. Convoluted spectra based upon the shifted energies and accompanying oscillator strengths reproduce low-energy region of observed spectra reasonably well, whereas they deviate from experiment in high-energy region. Reasonable agreement between theory and experiment was obtained for the valence electron excitations of the molecules.

1. Introduction

The title compounds are π-electron systems: 2,1,3-benzothiadiazole **1**, with 10 π-electrons; 1,3,2,4-benzodithiadiazine **2**, with 12 π-electrons [1]; and 1,3,5,2,4-benzotrithiadiazepine **3**, with 14 π-electron [2] (see Fig. 1). Hitchcock et al. [3] observed valence and inner-shell electronic and photoelectron spectra of **1**–**3** in order to probe fully their electronic structure. The observed spectra were analyzed and assigned based on the knowledge obtained from the molecular orbital calculation of neutral ground state molecules using the semi-empirical MNDO method.

The objectives of the present study are two folds: first, to calculate ionization energies of the title compounds **1**–**3** using techniques developed previously, and secondly to develop a computational technique to calculate excitation energies of the title compounds inner-core electrons [4] using the density functional theory. Spectra of the three molecules will be convoluted using the calculated excitation energies and oscillator strengths, and they will be used to analyze and assign the spectra from [3].

2. Method of calculation

The molecular geometry optimized by DFT with B3LYP/6-311 + (d,p) using the Gaussian03 program [5] was used for all types of calculations reported in the present work. In this study, the Amsterdam Density Functional (ADF) program was also employed [6]. The calculated ionization energies and excitation energies are all vertical type. The basis set of triple zeta plus polarization (TZP) was employed for ADF calculations.

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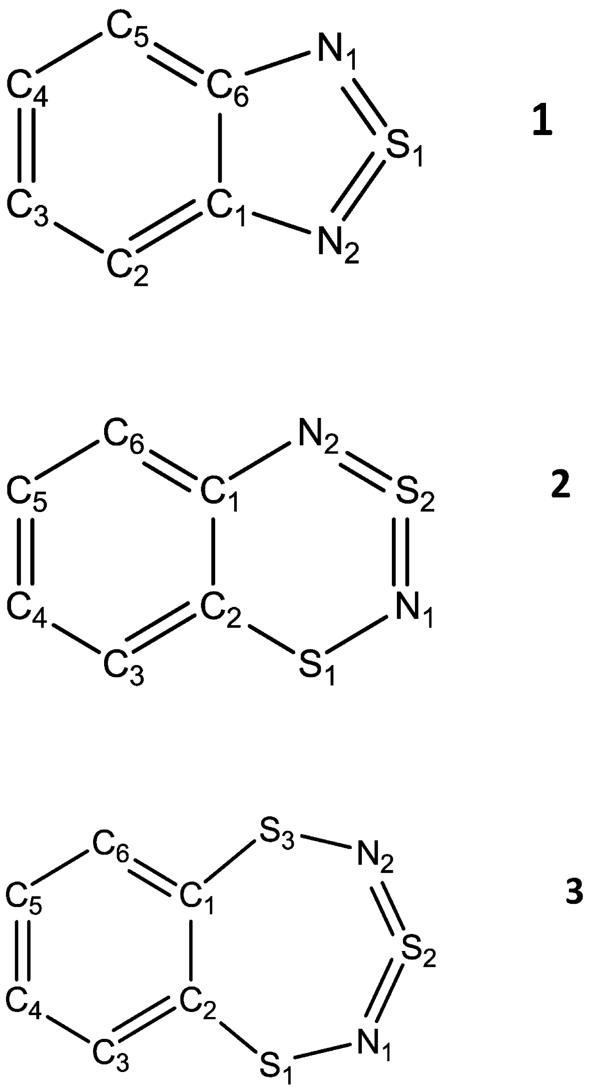

Fig. 1. The three molecules studied: 2,1,3-benzothiadiazole $C_6H_4SN_2$ (**1**), 1,3,2,4-benzodithiadiazine, $C_6H_4S_2N_2$ (**2**), 1,3,5,2,4-benzotrithiadiazepine $C_6H_4S_3N_2$ (**3**). Symmetry of **1** and **3** is C_{2v}, while that of **2** is C_s.

2.1. Ionization energies

Valence- and core-electron ionization energies (IE) were calculated by the ΔSCF method, Eq. (1):

$$\mathrm{IE} = [E_{\mathrm{KS}}(\mathrm{M}^+) - E_{\mathrm{KS}}(\mathrm{M})] + C_{\mathrm{rel}} \quad (1)$$

where $E_{\mathrm{KS}}(\mathrm{M}^+)$ is the Kohn–Sham total energy of the cation, M^+, and $E_{\mathrm{KS}}(\mathrm{M})$ is the Kohn–Sham total energy of the neutral ground state molecule M. Valence electron ionization potentials (VIP) were calculated by Eq. (1) without the relativistic correction, i.e. $C_{\mathrm{rel}} = 0$. The statistical average of orbital potentials SAOP [7,8] was employed for the SCF (=potential) part of the calculation and the energy counterpart was calculated using XC energy functional, PBE0 [9].

For the calculation of CEBEs for C1s and N1s, exchange-correlation (XC) functional pw86x-pw91c was used. A small relativistic correction C_{rel} was included in the CEBE calculations in Eq. (1). The relativistic corrections were approximated by an empirical equation [10]:

$$C_{\mathrm{rel}} = KI_{\mathrm{nr}}^{N} \quad (2)$$

where I_{nr} is the non relativistic CEBE and C_{rel} is the relativistic correction in eV. When I_{nr} is in eV, $K = 2.198 \times 10^{-7}$ and $N = 2.178$. For calculation of S1s CEBE, we adopted the method developed in a previous publication [11]. It uses Eq. (1) in which the statistical average of orbital potentials SAOP was employed for the SCF (=potential) part of the calculation and the energy counterpart was calculated using XC functional, BmTau1 [12]. The relativistic correction was calculated by Eq. (2), with $K = 6.250 \times 10^{-7}$ and $N = 2.0616$. For calculation of S2p CEBE, we followed a slightly different procedure reported in a previous publication [13]. The combination of OPTX exchange [14] and LYP [15] correlation functional was used. Relativistic effects have been estimated by the scalar zeroth-order regular approximation [16].

2.2. Excitation energies

For valence excitation spectra, we followed the usual procedure of TDDFT using XC potential SAOP. Such a method would be impossible for core-electron excitations because of the very large number of excited configurations. Fortunately, ADF has equipped an option to reduce the computational costs of core excitation energies by allowing only selected occupied orbitals and/or selected virtual orbitals in the TDDFT calculations. In this scheme, the complete one-electron excited state configuration space is reduced to the subspace where only the core electrons are excited. This scheme is based on the work of Sterner–Frozoni–Simone [17]. Let us call this scheme of calculating core excitation energies as, SFS scheme, in short. The principal advantage of the SFS scheme is its ability to calculate a large number of excitation energies and oscillator strengths in a single run in short time. Another advantage of the SFS scheme is to be able to neglect the coupling between core excitations and valence ionizations to the continuum, since the coupling between core excitations and valence ionization is expected to be very small [18]. Let us consider the case of the excitations from the molecular orbitals that are consisted of six carbon 1s (C1s) in molecule **1** as an example. The SFS scheme calculated the lowest excitation energy as 267.60 eV, whereas the corresponding observed value is 284.44 eV. The error is 16.84 eV. Average error of core excitation energies calculated by the SFS scheme for the five cases, C1s, N1s, S2p, S2s, and S1s of **1**, is 28.8 eV. The absolute core excitation energies are quite sensitive to the potential employed for calculation. The error could be reduced substantially by employing some other unknown optimum functionals. However, we do not invest our time and effort to search for such optimum functionals, in the present work, because the magnitude of the error does not matter for our technique that will be presented shortly (Eqs. (4) and (5)). In any case, we can expect that the SFS scheme may be able to calculate reasonable relative excitation energies and oscillator strengths. To calculate more accurate singlet core excitation energies ($\Delta E_{\mathrm{ex,S}}$) than the SFS scheme, we used the multiplet approximation (MA), Eq. (3);

$$\Delta E_{\mathrm{ex,S}} = (2E_{\mathrm{S/T}} - E_{\mathrm{T}}) - E_{\mathrm{gr,S}} \quad (3)$$

in which $E_{\mathrm{S/T}}$ is the average of the total energies for singlet and triplet excited states of a molecule, and E_{T} is the total energy of the triplet excited state of the molecule. $E_{\mathrm{gr,S}}$ is the total energy of the singlet ground state. For instance, there are six core molecular orbitals, φ_i^{C}, $i = 1, 2, \ldots, 6$, consisted of linear combinations of the six C1s atomic orbitals in **1**. Orbital energies corresponding to the six core orbitals are not identical but they are close to each other; $\varepsilon_1 < \varepsilon_2 < \cdots < \varepsilon_6$. The excitation energy from φ_1^{C} to the lowest unoccupied molecular orbital (LUMO), $\varphi_{\mathrm{LUMO}}^{\mathrm{V}}$, of the molecule **1** was calculated by the multiplet approximation to be 284.49 eV which is very close to the observed value of 284.44 eV. Disadvantage of the multiplet approximation is its inability to calculate oscillator strength of the corresponding transition. Oscillator strength of the corresponding transition can be calculated quite easily buy the SFS scheme. Combining the advantages of the SFS scheme and the