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Erratum

Valence one-electron and shake-up ionization bands of fluorene, carbazole and dibenzofuran

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ABSTRACT

A comprehensive study of the He (I) ultra-violet photoelectron spectra of fluorene, carbazole and dibenzofuran is presented with the aid of one-particle Green's Function calculations employing the outer-valence Green's Function (OVGF) approach and the third-order algebraic diagrammatic construction [ADC(3)] scheme, along with Dunning's correlation consistent basis sets of double and triple zeta quality (cc-pVDZ, cc-pVTZ). Extrapolations of the ADC(3) results for the outermost one-electron π-ionization energies to the cc-pVTZ basis set enable theoretical insights into He (I) measurements within ~0.15 eV accuracy, up to the σ-ionization onset. The lower ionization energy of carbazole is the combined result of mesomeric and electronic relaxation effects. OVGF/cc-pVDZ or OVGF/cc-pVTZ pole strengths smaller than 0.85 systematically corroborate a breakdown of the orbital picture of ionization at the ADC(3) level. Comparison is made with calculations of the lowest doublet–doublet excitation energies of the radical cation of fluorene, by means of time-dependent density functional theory (TDDFT).

1. Introduction

Fluorene is an angular polycyclic aromatic hydrocarbon, possessing a 5-membered ring in between two benzenoid rings. The cation of this compound has been identified as one of the possible carriers of some diffuse interstellar absorption bands associated to reddened stars [1]. Carbazole and dibenzofuran are isoelectronic heterocyclic analogs obtained by replacing the $-CH_2-$ group of fluorene by a –NH– group or O atom. The advantageous electronic properties of these compounds, characterized primarily by extensive π conjugation, make them promising candidates for use in such diverse technologies as organic light-emitting diodes, thin-film transistors, chemical sensors, photovoltaics, photorefractives, holography, electronic data storage, and electroluminescent devices [2–13]. As electron-donating functional units in copolymers, dendrimers, and ambipolar systems, fluorene heterocyclic analogs are typically combined with electron acceptor units to create compounds with finely tuned optoelectronic properties. Dibenzofuran is also important from the environmental viewpoint in being a parent representative of a hazardous class of anthropogenic and naturally occurring pollutants, namely, polychlorinated dibenzofurans (PCDFs) [14]. These compounds display a highly acute toxicity to humans and animals and are characterized by a substantially prolonged period of excretion, as well as tumor-promoting and teratogenic potential similar to that of polychlorinated dioxins [15,16]. Finally, carbazole is considered very toxic to aquatic organisms and is also suspected to be carcinogenic.

The outer valence shell electronic structure of fluorene, carbazole and dibenzofuran has been comparatively investigated long ago using He (I) photoelectron spectroscopy [17], along with theoretical calculations employing the empirical Hückel approach, using parameterized matrix elements in order to account for inductive effects. More recently, the He (I) valence photoelectron spectrum of carbazole has also been presented in Ref. [18], where it has been interpreted at the RHF/3-21G level, under the assumption that Koopmans' theorem is valid. At such theoretical levels, misorderings of ionization energies most frequently occur, due to the neglect of electron correlation and relaxation effects. Furthermore, shake-up states corresponding to excited configurations of the cation remained clearly outside the scope of these studies. We note that for large conjugated compounds such as polycyclic aromatic hydrocarbons [19–22], these states may borrow a most important fraction of the total ionization intensity, even at relatively low electron binding energies.

The outermost valence bands in the photoelectron spectrum of fluorene have been more reliably assigned [23] through comparison with the electronic absorption spectrum of the radical cation, and calculations of the corresponding vertical electronic excitation energies and oscillator strengths using Time-Dependent Density Functional Theory (TDDFT) [24,25], in conjunction with the standard 6-31G** basis set and various exchange–correlation functionals, such as the SVWN (Slater – Vosko – Wilk – Nusair [26,27]), BLYP

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(Becke – Lee – Yang – Parr [28,29]) and B3LYP (hybrid Becke – three parameters – Lee Yang Parr [30,31]) functionals. If this approach enables the identification of ionized shake-up states among the electronically excited states of the radical cation, it may fail in correctly locating the σ-ionization onset [21,22], due to well-known shortcomings of standard exchange–correlation functionals [32,33], such as an overestimated localization of the exchange–correlation hole, an incomplete cancelation of the self-interaction, and a too-rapid decay of the corresponding potentials in the asymptotic region. As a consequence, TDDFT yields substantial underestimations of charge-transfer excitation energies [34–37].

The purpose of the present work is to assign the available photoelectron spectra of fluorene, carbazole and dibenzofuran, taking in particular into account the dispersion of the ionization intensity from the main one-electron ionization lines to shake-up bands, due to configuration interactions in the cation. To date, the most efficient approach for reliably describing such complex situations where the orbital picture of ionization breaks down [38] is (still) the so-called third-order algebraic diagrammatic construction [ADC(3)] scheme [39–42], which has been derived within the framework of one-particle Green's Function theory [38,43] (or equivalently, one-electron propagator theory [44–48]). For the sake of more accurate insights into one-electron binding energies, ADC(3) computations are supplemented with OVGF (Outer Valence Green's Function [40,43]) calculations, using a larger basis set.

2. Computational details

All calculations described in the present work are based on geometries which have been optimized under the constraints of the C_{2v} symmetry point group, using density functional theory (DFT) along with the B3LYP exchange–correlation functional, in conjunction with Dunning's correlation consistent polarized valence basis set of triple zeta quality (cc-pVTZ [49,50]). ADC(3) calculations have been carried out using Dunning's correlation consistent polarized valence basis set of double zeta quality (cc-pVDZ [49,50]), by means of the original 1p-GF/ADC(3) package of programs, [51] in a version that was interfaced to GAMESS [52]. The efficiency of this approach stems in particular from a separate block-Lanczos diagonalization [53,54] and reduction in pseudo-eigenspectrum form of the 2p-1h/2p-1h block matrix pertaining to electron attachment. A threshold on pole strengths of 0.005 has been retained in the final diagonalization step, which has been performed using the iterative block-Davidson diagonalisation procedure [55,56]. The assumption of frozen core electrons has been used throughout these calculations and the full molecular symmetry point group (C_{2v}) has been exploited. The symmetry labels presented in the sequel are consistent with the standard molecular orientation, according to the conventions described in the book by Jaffe [57]: for all target compounds, the carbon skeleton lies in the *yz* plane, with the C_2 rotation axis coinciding with the *z*-axis. Static self-energies have been obtained using charge-consistent one-electron densities [58] ensuring their correct size-intensive scaling [59]. OVGF calculations have been carried out using the cc-pVDZ and cc-pVTZ basis sets, by means of the semi-direct and integral-driven algorithms implemented within the GAUSSIAN-98 package of programs [60].

In the sequel, ultra-violet photoelectron spectra are compared with convolutions drawn from the ADC(3) ionization spectra, using as spread function a combination of a Lorentzian and Gaussian with equal weight and width (FWHM = 0.6 eV). In these simulations, photoionization cross sections are neglected, i.e., line intensities are simply scaled according to the pole strengths (Γ_i) computed by summing the 1h (one-hole) and 1p (one-particle) components of the ADC(3) eigenvectors. These pole strengths define the norm of Dyson orbitals [61–63], which represent partial overlaps between the initial neutral and final ionized states, and provide therefore a means to estimate intensity ratios for ionization lines originating from the same orbital [64].

3. Results and discussion

3.1. General observations

The theoretical ADC(3) ionization spectra of fluorene, carbazole and dibenzofuran are compared to the experimental [He(I)] spectra by Ruščić et al. [17] in Figs. 1–3, respectively. The reader is correspondingly referred to Tables 1–3 for a detailed assignment of spectral bands and comparison with the results of HF (Hartree–Fock) and OVGF calculations using the cc-pVDZ and cc-pVTZ basis sets. In these tables, ADC(3) results for one-electron ionization energies are also extrapolated to the cc-pVTZ basis set, by adding to the ADC(3)/cc-pVDZ values the differences in between the correspondingly obtained OVGF/cc-pVDZ and OVGF/cc-pVTZ results.

Although cross section effects are neglected and vibrational effects are only accounted for in an average way, it is immediately apparent from Figs. 1–3 that the main spectral features that are seen experimentally are correctly reproduced by our simulations. For all three compounds, Tables 1–3 confirm the rule [20–22] that OVGF pole strengths smaller than 0.85 reliably and very systematically foretell a breakdown of the orbital picture of ionization [38]: in such situations, one systematically observes at the ADC(3) level a dispersion of the ionization intensity into sets of shake-up lines with comparable and limited intensity.

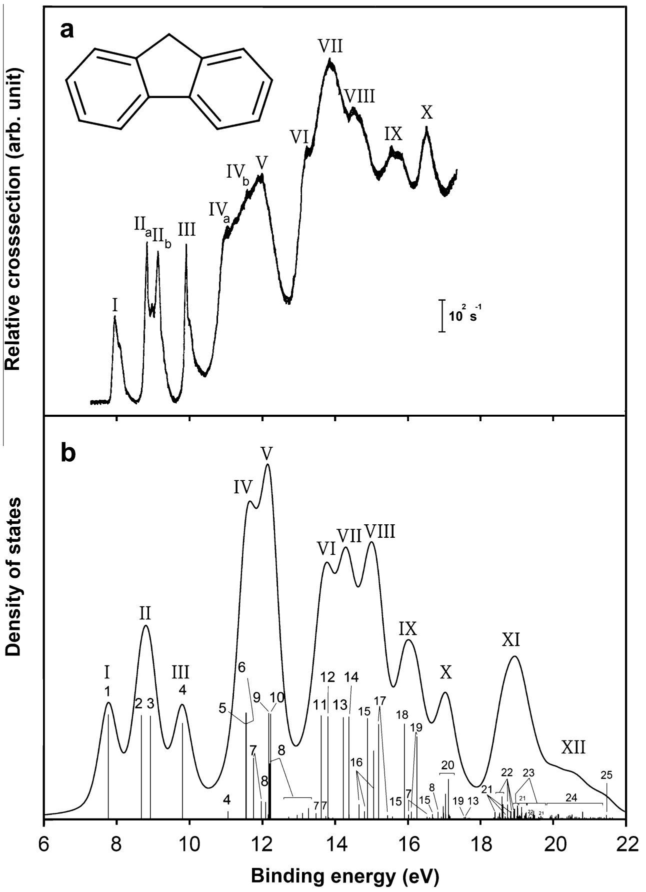

Fig. 1. Comparison of (a) the [He (I)] ultra-violet photoelectron spectrum with (b) the ADC(3)/cc-pVDZ ionization spectrum (FWHM = 0.6 eV) of fluorene. See Table 1 for detailed orbital assignment.