Photoelectron spectra and electronic structure of acetylacetonate and bromoacetylacetonate of boron difluoride

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Abstract. The electronic structure and ionization processes of acetylacetonate and bromoacetylacetonate of boron difluoride were modeled using the method of outer valence Green's functions (OVGF). It was shown for boron difluoride acetylacetonate that for ionization energies exceeding 12 eV the OVGF method data (energies and a sequence of electronic levels, the electron density localization) differ significantly from the results of DFT calculations. Theoretical values of ionization energies from molecular orbitals with predominant contributions of atomic orbitals F 2p are higher by 1.6-2.2 eV than the corresponding Kohn-Sham energies shifted by the magnitude of the correction to the orbital energy. For all the considered electronic levels of both compounds, close theoretical values of the spectral intensities and good agreement between the results of calculations and the experimental data of the ultraviolet photoelectron spectroscopy method are observed.

1. Introduction

β-Diketonates of boron difluoride possess intense luminescence in solutions and crystals, the ability to form excimers and exciplexes, as well as liquid-crystalline properties. Compounds of this class are used as nanostructured optical materials: laser dyes, light-emitting diodes, optical chemosensors, active components of solar collectors, materials for nonlinear optics, and polymer optical materials.

A detailed study of the electronic structure of boron difluoride β-diketonates opens the possibility for directional synthesis of new compounds with specified spectral characteristics. A combined application of methods of ultraviolet photoelectron spectroscopy (UPS) and quantum chemistry makes it possible to obtain unambiguous data about the electronic structure of chemical compounds [1]. A use of calculation schemes based on the theory of Green's functions in the approximation of algebraic diagrammatic construction gives the possibility to determine the nature of wide bands of photoelectron spectra [2]. The OVGF method [3] is an approximation of the third order and it is a narrowly specialized approach for calculating the energies of transitions into cation states, which are described well in the terms of one-electron ionization for upper valence orbitals (the spectral range up to 17-18 eV).
Acetylacetonate (BF$_2$Acac) and bromoacetylacetonate (BF$_2$AcacBr) of boron difluoride are the simplest of boron difluoride β-diketonates (Figure 1). The research results of BF$_2$Acac by the UPS method were published earlier [4]. However, the use of the density functional theory approximation (DFT) did not allow to interpret unambiguously the UPS spectrum and to obtain reliable data about the nature and sequence of electronic levels. Using the OVGF ab initio method, new electronic parameters of BF$_2$Acac were obtained which are in better agreement with the experimental data, that made it possible to reconsider the UPS spectrum interpretation. In the present work the research results are presented of the electronic structure of BF$_2$Acac and BF$_2$AcacBr based on the UPS data and calculations using the OVGF method.

![Figure 1. Chemical structure of the studied complexes.](image)

2. Methods

The BF$_2$Acac UPS spectrum of vapor was obtained earlier in the Laboratory of Electronic Structure and Quantum-Chemical Modeling of the Far Eastern Federal University [4]. The UPS spectrum of BF$_2$AcacBr in the gas phase was obtained on a modified electronic spectrometer ES-3201 with a hemispherical electrostatic analyzer and a monochromatic radiation source He I (hν = 21.2 eV). In order to calibrate the spectrum, the inert gas Xe was introduced into the chamber simultaneously with the substance. The error in determining the band maxima did not exceed 0.04 eV. The temperature of the ionization cuvette was 220 °C.

At assigning the initial geometry of BF$_2$Acac and BF$_2$AcacBr, the X-ray diffraction data were used. All calculations were carried out using the program package GAUSSIAN 16 [5]. Geometry optimization of the complexes in the state S$_0$ was carried out in the DFT approximation using the basis set of atomic functions Def2-SVP and the hybrid functional B3LYP, which is successfully used to model the structure of boron difluoride β-diketonates [6]-[9]. In order to verify the correspondence of the optimized structures to the points of a local minimum on the potential energy surface, the Hessian matrix was calculated. At modeling the ionization processes using the OVGF method, the cc-PVTZ basis set was used.

3. Result and Discussion

As in [4], the optimization of the geometric parameters of the complex BF$_2$Acac led to the minimum energy configuration corresponding to the obscured position of the three hydrogen atoms – two hydrogen atoms of the methyl groups and H atom at C$_y$. Owing to the absence of a hydrogen atom in the γ-position for BF$_2$AcacBr, the displacement of H atoms of the methyl groups by 60 degrees is observed relative to BF$_2$Acac. Dihedral angles between the planes O-B-O and O$_y$C$_y$O for BF$_2$Acac and BF$_2$AcacBr are of 3 and 10 degrees, respectively.

According to the calculated data, in BF$_2$Acac the effective charge (Mulliken) of the boron atom is +0.49e, and the boron gives most of the electron density to two fluorine atoms -0.65e, but not to two oxygen atoms -0.52e, whose donors are carbon atoms in the β positions +0.74e. At transition from
BF₂Acac to BF₂AcacBr, the carbon atom charge in the γ-position changes from -0.42e to -0.17e, that is determined mainly by the difference between the atom charges of hydrogen (0.18e) and bromine (-0.11e).

In order to interpret the photoelectron spectra, an analysis of the results of modeling the upper valence levels was performed using data of the Hartree-Fock (HF) method. Figure 2 shows the shapes of molecular orbitals (MO) of interest at interpretation of the photoelectron spectra of BF₂Acac and BF₂AcacBr. Table 1 presents the results of calculations of the electronic structure for the studied compounds. The type and energies of the upper occupied MOs were determined from the contributions of the Mulliken atomic populations of the HF orbitals. Orbitals of the molecular fragments are mixed if the sum of atomic populations for each of them exceeds 20%. For convenience of comparing the MOs, the irreducible representations of the symmetry group $C_{2v}$ are used.

The electronic structure calculation of BF₂Acac by the HF method showed that the two upper MOs $\pi_3$ and $n_-$ are virtually localized on the chelate ring atoms like in the enol form of acetylacetone (Figure 2). The next orbitals are $\pi_2$–Me and $n_++$Me with contributions of atomic orbitals (AO) F 2p 17% and 20%, respectively (Table 1). The further MO Me–$\pi_1$ has a contribution of 2p-fluorine AO of 24%. Among the six MOs with HF energies from 15.58 to 16.50 eV, three orbitals are localized predominantly on two F atoms, and the rest three MOs have F 2p contributions from 14% to 23%. The group of four levels with HF energies from 17.35 to 17.54 eV corresponds to the delocalized MOs with contributions of AO F 2p from 10% to 46%.

Figure 2. Shapes of the four upper occupied molecular orbitals of BF₂Acac and BF₂AcacBr.

For BF₂AcacBr the noticeable mixing of orbitals $\pi_3$ and AO Br 4p is observed (Figure 2, Table 1) that determines the HOMO level destabilization by 0.45 eV relative to BF₂Acac. Due to the influence of Br 4p orbitals, the level of MO $n_-$ is stabilized by 0.57 eV. For the five upper occupied MOs BF₂AcacBr, the contributions of AOs F 2p do not exceed 6%.

The first two bands of the BF₂Acac UPS spectrum correspond to MOs $\pi_3$ and $n_-$ (Table 1). The UPS spectrum of BF₂Acac [4] differs significantly from the spectra of acetylacetonates of non-transition elements M(Acac)ₙ (n = 1, 2, 3) [10], [11]. The IE values for MOs of the chelate cycle BF₂Acac are meaningfully overestimated, and also the overlap of several bands in an energy range of 12.5-13.5 eV is observed, that masks the position of the band of $n_-$ electrons. Using the DFT analogue of the Koopman’s theorem, it was shown [4] that the band at 12.8 eV is caused...
by ionization processes from three electronic levels with predominant contributions (48-92%) of AO F 2p, and each of the bands at 14.3 eV and 15.7 eV corresponds to six orbitals.

Table 1. Type and symmetry of MO, Mulliken populations according to the HF method. Vertical ionization energies IEi (eV) calculated by the methods HF (Koopman's theorem) and OVGF.

| MO          | Contribution (%) | HF IEi | OVGF IEi | Exptl IEi data* |
|-------------|-----------------|--------|----------|-----------------|
| BF2Acac     |                 |        |          |                 |
| H, b_(π1)   | 1               | 21     | 74       | 3               | 10.4 | 9.69 | 9.85 |
| H-2, a_(π2-Me) | 1         | 48     | 8        | 27              | 0  | 14.6 | 13.08 |
| H-3, a_(n1+Me) | 2         | 37     | 17       | 21              | 5  | 15.0 | 13.33 |
| H-4, b_(Me-π1) | 2         | 29     | 11       | 34              | 2  | 15.1 | 13.52 |
| H-5, b_(Me)   | 1               | 7      | 8        | 71              | 0  | 15.5 | 14.28 |
| H-6, b_(F 2p) | 7               | 2      | 3        | 18              | 0  | 15.8 | 14.19 |
| H-7, a_(Me-π) | 1               | 17     | 16       | 45              | 7  | 16.0 | 14.64 |
| H-8, a_(F 2p-Me) | 6         | 1      | 1        | 32              | 0  | 16.3 | 14.74 |
| H-9, a_(Me-F 2p) | 2         | 4      | 13       | 55              | 5  | 16.3 | 14.95 |
| H-10, b_(F 2p) | 6               | 18     | 6        | 16              | 0  | 16.5 | 14.71 |
| H-11, a_(π0+Me) | 2         | 31     | 13       | 36              | 0  | 17.3 | 15.75 |
| H-12, a_(F 2p-Me) | 4         | 4      | 19       | 29              | 2  | 17.4 | 15.68 |
| H-13, b_(π1+Me) | 3               | 15     | 21       | 34              | 0  | 17.5 | 15.97 |
| H-14, b_(Me+n0) | 1               | 26     | 23       | 41              | 0  | 17.5 | 15.71 |
| H-15, b_(F 2p) | 6               | 19     | 10       | 2               | 1  | 19.3 | 17.49 |

| BF2AcacBr    |                 |        |          |                 |
| H, b_(π3-Br 4p) | 1               | 14     | 50       | 2               | 33  | 9.95 | 9.22 | 9.46 |
| H-1, b_(Br 4p) | 0               | 5      | 5        | 4               | 86  | 12.0 | 11.17 | 11.0 |
| H-2, b_(Br 4p+π0) | 1          | 9     | 22       | 3               | 65  | 13.2 | 12.19 | 11.9 |
| H-3, b_(n1)   | 6               | 47     | 21       | 16              | 10  | 13.7 | 11.94 | 12.2 |
| H-4, a_(n1+Br 4p) | 4         | 26     | 29       | 2               | 39  | 14.8 | 13.49 |

* The position is indicated for the ionization spectrum maximum in which this transition makes contribution.

The modeling results of the ionization processes by the methods HF and OVGF, as well as the experimental maxima of the UPS spectra of the studied complexes are presented in Table 1. The theoretical values of the relative spectral intensities for twenty-one IEs of BF2Acac and BF2AcacBr are in a range from 0.89 to 0.91. As one can see from Table 1, the HF ionization energies for both complexes differ significantly from those calculated using the OVGF method. Depending on the transition, the differences are from 0.71 eV to 1.83 eV. Such large changes at transition from the HF method to the OVGF method indicate the important role of the effects of electron correlation and orbital relaxation for describing the ionization processes of the studied complexes.

The calculation data of the first two IEs of BF2Acac by the OVGF method correlates well with the experimental data, the deviations are of 0.16 eV and 0.09 eV (Table 1). According to the OVGF data, the band at 12.8 eV in the BF2Acac UPS spectrum corresponds to three electron levels with insignificant contributions of AO F 2p. The bands at 14.3 eV and 15.7 eV are determined by the ionization processes from six and four MOs, respectively. The calculated ionization energy from HOMO–15 is 17.49 eV, that does not allow to assign this orbital to the band at 15.7 eV. For BF2Acac the theoretical values of ionization energies from molecular orbitals with predominant contributions of atomic orbitals F 2p (Table 1) are higher by 1.6-2.2 eV than the corresponding Kohn-Sham energies shifted by the value of the correction to the orbital energy [4]. The calculated values IEs of BF2AcacBr agree qualitatively with the UPS spectrum, and the ionization energy from HOMO–4 is 13.49 eV, that determines unambiguously its assignment to the unresolved spectral region.
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