



Electronic structure and optical properties of boron difluoride dibenzoylmethane F₂Bdbm



V.I. Vovna^a, S.A. Tikhonov^a, M.V. Kazachek^a, I.B. Lvov^{a,*}, V.V. Korochentsev^a,
E.V. Fedorenko^b, A.G. Mirochnik^b

^a Far-Eastern Federal University, Russian Federation

^b Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences, Russian Federation

ARTICLE INFO

Article history:

Received 13 May 2013

Received in revised form 22 August 2013

Accepted 22 August 2013

Available online xxx

Keywords:

Electronic structure

Boron difluoride β -diketonates

Photoelectron spectra

ABSTRACT

The correlation between electronic structure and spectral features of boron dibenzoylmethane difluoride has been investigated by DFT (B3LYP5 functional, Ahlrichs def2-TZVPP basis set including polarization functions), UV and X-ray photoelectron spectroscopy. The results of quantum chemical simulation have been used for interpretation of spectral bands of photoelectron and absorption spectra.

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1. Introduction

β -Diketonates of difluoroboron are chelates that consist of enol form of diketone as a ligand and boron difluoride as a complexing agent. Unlike related 1,3-dicarbonyl compounds, difluoroboron β -diketonates show intensive luminescent properties both in solutions and in solid state [1–6].

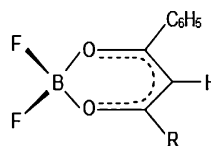
In going from boron difluoride acetylacetonate to benzoylacetonate the luminescence intensity significantly increases. The introduction of second phenyl ring (benzoylacetonate to dibenzoylmethane transition) leads to bathochromic shift in absorption and luminescence spectra and also to increasing of photostability and quantum yield of luminescence [7].

Boron difluoride dibenzoylmethane (F₂Bdbm) (I) is the basic boron difluoride complex with two benzene rings conjugated with chelate ring. F₂Bdbm has unique optical and photochemical properties: the formation of excimers [8,9], exciplexes with aromatic compounds [10], catalytic properties in photochemical reactions [11], photomechanical properties [12], photoconductivity [13,14] and photochromism of polymer compositions [15].

Supramolecular architecture of F₂Bdbm crystals [8] determines their nonlinear optical [16], size-dependent [17,18] and thermochromic luminescence [18,19] properties.

In the context of multifold possibilities of the complex (I) application, a study of interrelation between electronic structure

and spectral features of this interesting type of difluoroboron β -diketonate class is of the urgent concern.



R = C₆H₅ (I); CH₃ (II)

Previously we have reported electronic structure of boron difluoride acetylacetonate F₂Baa and its single benzene ring derivative results obtained by UPS and quantum chemistry methods [20] as well as electronic absorption spectra of a number of F₂Baa derivatives with one- or two-benzene ring aromatic substituents [21]. In this paper we are publishing results of our investigation of the electronic structure F₂Bdbm performed by quantum chemical DFT as well as by UPS (for vapor) and XPS (for polycrystal) methods. Found for occupied electronic levels regularities have been used in quantum-chemical simulation of the gas phase absorption spectrum. Our results concerning structure and optical properties of F₂Bdbm are related to the similar data on boron difluoride benzoylacetonate (F₂Bba) (II) that have been reported earlier in [20–22].

The samples of F₂Bdbm, F₂Baa and F₂Bba have been synthesized according the general procedure described in [7].

2. Experiment and calculation methods

All calculations have been performed using Firefly 7.1.G program package [23]. In DFT method a hybrid exchange-correlation

* Corresponding author. Tel.: +7 9243389961.

E-mail addresses: rv1098@list.ru, lvov.ib@dvfu.ru (I.B. Lvov).

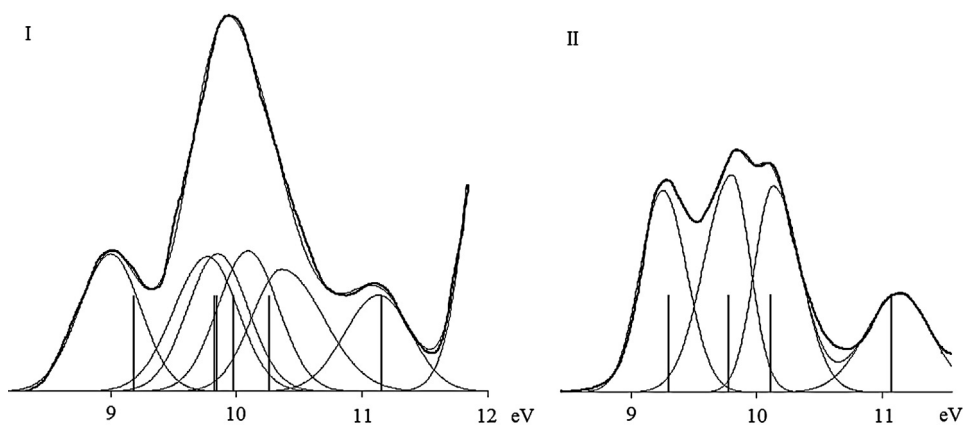


Fig. 1. UPS spectra (bold lines), fitted Gaussian components (thin lines) and calculated spectra (sticks) of compounds I and II.

functional B3LYP5 and Ahlrichs basis set def2-TZVPP including polarization functions have been used. Our choice of the basis set has been justified earlier on the example of zinc bis-acetylacetonate [24]. The choice of B3LYP5 functional is conditioned by test calculations of metal acetylacetonates [20,24]. In order to check correspondence between optimized structures and local minimum points on a surface of potential energy, calculations of Hessian matrix performed for all compounds. Calculations of the absorption spectra have been carried out within non-stationary TDDFT approximation.

As far as the F_2Bdbm complex has a planar structure in crystal phase [8], our calculations were conducted in terms of both structure with three coplanar rings and structure with 17° dihedral angle between chelate ring and phenyl groups (the latter has been predicted by procedure of geometry optimization).

Validity of the spectrum modeling procedure has been given earlier during the discussion of electronic structure of the complexes with a single aromatic substituent [21]. In order to find the origin of 30 calculated excited states we carried out an analysis of spin-adapted anti-symmetrised products (SAPS) [25]. The orbital assignment of excited states was made reasoning from either the highest contribution of Mulliken populations (for occupied MO) or relative sum of squared LCAO-MO coefficients (for unoccupied MO). Calculated spectra were evolved from (E_i, f_i) values by means of Gaussian curves $\sum_i G_i(E)$, where $G_i(E) = (f_i/d) \exp(-(1/2)(E - E_i)^2/d^2)$; E , energy; f , oscillator strength; i , serial number of a transition; d , half-width parameter, chosen to be 0.2 eV for all bands.

UV photoelectron spectra of F_2Bdbm and F_2Bba vapors were registered by ES-3201 spectrometer with He-I radiation source. Determination accuracy of band maxima is under 0.02 eV [26]. The temperature in ionization cell was 200°C . X-ray photoelectron spectra of I in condensed state were measured using high vacuum double-chamber system MXPS XP (manufacturer – Omicron, Germany) with hemispherical electrostatic analyzer. Radiation energy was 1253.6 eV (Mg K α). A spread function of the spectrometer in a mode of characteristic atomic level registration, which had been determined from Ag3d $_{5/2}$ band shape, has a half-width of 1.2 eV. Electron binding energy calibration (E_b) was performed basing on intrinsic standard method with C1s carbon level as a mark. While estimating atomic concentration of elements in a sample, we were taking into account relative ionization cross-sections and depth of electron efficiency.

Vapor-phase absorption spectra were registered by spectrometer KSVU-23 (Russia) in metal vapor-phase cell with quartz windows. Its length is 40 cm, diameter is 3 cm. The cell containing a testing sample had been pre-evacuated till 0.1 mm Hg, filled

with Helium to get a pressure of 0.1–0.5 atmosphere and after that it was heated at about 200°C (close to the point of sublimation) while measuring spectrum in range of 200–500 nm.

3. Results and discussion

Comparing the results of our calculations of F_2Bba in extended basis set def2-TZVPP with results obtained earlier in basis set 6-311G [20] we have got to conclusion that coplanarity of the complex structure is breaking under slight changes in energy values and MO composition. Dihedral angle between chelate and phenyl rings is 15° and the angle between chelate ring and OBO plane is 5° . Also, the extension of basis set has brought to a noticeable change in electron density distribution calculated in natural binding orbital (NBO) approximation. Thus, for F_2Bba in the basis set 6-311G a total charge for C_6H_5 was +0.11e and in the basis def2-TZVPP it was +0.07e.

As it results from our calculations, both phenyl rings in F_2Bdbm are twisted to the angle of 17° in the same direction with respect to the chelate ring (a C_s point group) while an angle between the chelate ring and OBO plane is found to be 16° . Calculations of coplanar structure in def2-TZVPP basis set have shown insignificant changes of both energy values (<0.1 eV) and MO localization; total energy shift is 0.0125 eV ($\sim 100\text{ cm}^{-1}$). At temperatures of about 200°C such a low rotational barrier for C_6H_5 -groups in the complex allows free torsion vibrations out of relatively planar conformation.

In Fig. 1 the photoelectron spectra of F_2Bdbm and F_2Bba are compared. The second band with a slight inflection in F_2Bdbm spectrum corresponds to ionization from four electron levels. It does not look feasible to get energy values and level types from deconvolution of this band prior to theoretical modeling of ionized states.

Fig. 2 presents the shapes of some MOs which are interesting for interpretation of both photoelectron and optical electronic spectra. Table 1 shows relative MO contributions from substituents and single or double phenyl ring chelate fragments. Correlation diagram for MO interaction of the F_2Baa chelate ring with the highest π -orbitals of the two benzene rings has been generated from our calculated data (Fig. 3).

π_3^B -orbital, as mixing with symmetrical combination b_1^+ of π -orbitals of phenyl groups, contributes comparable rates of respectively 56% and 48% to antibonding HOMO (# 70) and to the fifth occupied bonding orbital (# 66) (see Table 1). The ε_i values of two localized on phenyl groups – a_2^- MOs and b_1^- orbitals are 0.6 eV lower than ones for $C_6H_5-C_6H_5$ due to positive effective charge of 0.07e for each group C_6H_5 .

On deconvolution by Gaussians of the second strong band in the spectrum of the compound I we were taking into account data on

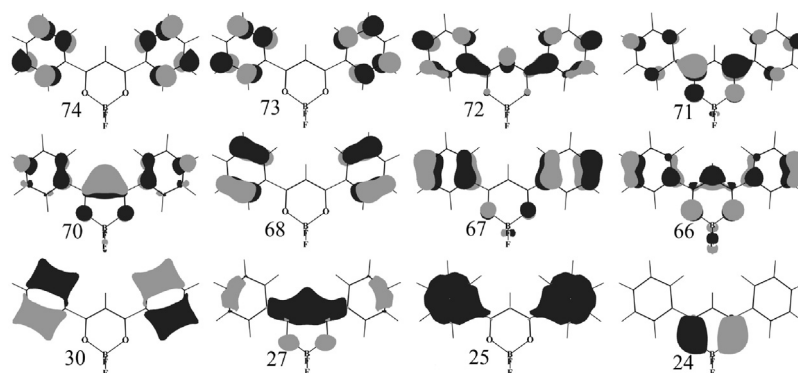


Fig. 2. Form and symmetry of four highest (70, 68, 67, 66), four occupied (24, 25, 27, 30) and four vacant (71–74) molecular orbitals of F₂Bdbm.

Table 1

MO localization (%); the energy of Kohn–Sham orbitals (ε_i , eV); experimental band maxima (IE_i , eV) and δ_i values (eV) of F₂Bdbm (I) and F₂Bba (II).

Compound	MO number	Contributions of cycles			ε_i	IE_i	δ_i	$\delta_i(\pi)$
		F ₂ B β^a	C ₆ H ₅	C ₆ H ₅				
F ₂ Bdbm (I)	70	56	22	22	6.98	9.00	2.02	2.20
	69	2	49	49	7.61	9.75	2.14	
	68	0	50	50	7.62	9.85	2.23	
	67	30	35	35	7.78	10.10	2.32	
	66	48	26	26	8.06	10.35	2.29	
	65 (n)	84	8	8	8.76	11.12	2.36	
F ₂ Bba (II)	54	68	32		7.22	9.25	2.03	2.08
	53	1	99		7.69	9.80	2.11	
	52	41	59		8.03	10.13	2.10	
	51 (n)	92	8		8.79	11.14	2.35	

^a $\beta = \text{O}-\text{C}-\text{CH}-\text{C}-\text{O}$ for I; $\beta = \text{O}-\text{C}(\text{CH}_3)-\text{CH}-\text{C}-\text{O}$ for II.

both a number of electron levels and interval (δ_i) values between them. Table 1 gives δ_i values as differences between ionization energies as follows from expansion procedure (IE_g) and ε_i . Earlier we have stated that for metal acetylacetonate complexes $M(\text{aa})_n$ δ value for an n -orbital is higher than that for $\delta(\pi)$ by 0.2 eV [20]. In marking calculated values of ε_i on spectra (see Fig. 1) we corrected

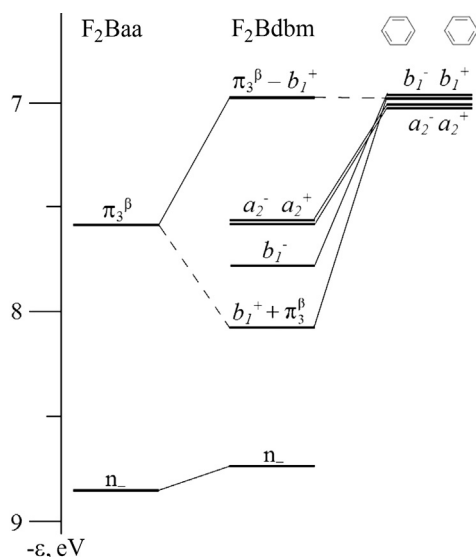


Fig. 3. Correlation of π -orbitals of F₂Bdbm with orbitals both F₂Baa and two benzene molecules (b_1 and a_2 are the π_3 and π_2 -MO of the phenyl groups accordingly; “+” and “−” signs define their symmetry in reflection operation to the plane which is orthogonal to the chelate ring; π_3^β means π_3 -orbital of the chelate ring. Terms “bonding” and “antibonding” mean the character of overlapping between molecular orbitals of phenyl groups and chelate ring).

theoretical scale for each compound by its respecting value of $\delta(\pi)$ imported from the Table 1. A value of δ for the n -orbital was increased by 0.2 eV. It engages one’s attention that for the first band its IE value estimated in frames of the outlined above method differs by 0.18 eV from its experimental value, whereas for the complex with one C₆H₅ group the most discrepancy of an experimental value from a calculated one does not exceed 0.05 eV (see Table 1). As revealed calculations of IE values based on total energy differences between ionized and ground states, the relaxation energy of the first complex is elevated by 0.25 eV due to electron withdrawal from HOMO followed by more profound rearrangement of electron density and this is what causes the increase of parameter δ .

X-ray photoelectron spectra of F₂Bdbm obtained with a radiation source Mg K α for valence and core electron levels have made it possible to find the following data: ionization energies for low valence levels with predominant contributions of 2s-AO of C, O and F atoms, bonding energy values of 1s-electrons as well as their correlation with calculated energy values and effective charge values of the atoms. Figs. 4 and 5 show spectra of C1s and valence band electrons. There are values of binding energies E_b for core electrons along with their band half-widths and relative concentrations of elements listed in the Table 2. As while estimating concentrations

Table 2

Binding energies (eV), band half-width (eV), and relative concentration of elements (%) in F₂Bdbm.

Level	E_b , eV	Half-width, eV	Relative concentration of elements	
			By formula	Experimental
C 1s	285.5	1.58	65.0	65.4
C β 1s	288.0	1.85	10.0	9.4
O 1s	533.7	1.94	10.0	10.8
B 1s	194.6	1.51	5.0	5.0
F 1s	686.8	1.84	10.0	9.4

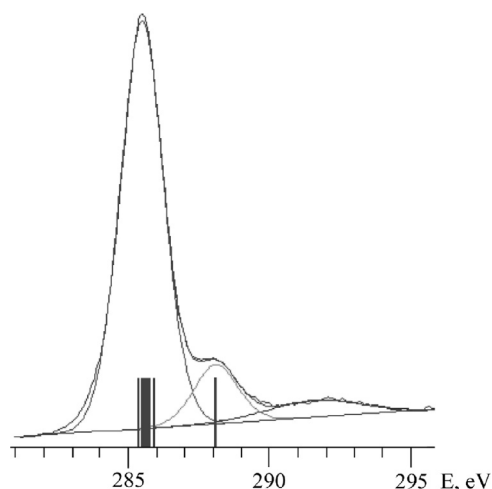


Fig. 4. XPS spectrum of carbon 1s-electrons and calculated 1s-AO energies of F₂Bdbm.

of elements in testing layer we had an error within our approximation under 10% [27], we could indicate just oxygen dash presence in the analyzed layer.

In stating energy scale with respect to C1s level of benzene rings we were taking into account electronic level stabilization of C₆H₅ within the complex. According to reference data a benzene molecule in condensed state shows E_b (C1s) value as much as 284.9 eV [27], yet in the compound under our study the energy stabilization value of totally localized on benzene rings π -levels # 68, 69 reaches 0.6 eV (see Table 1). Thus in the F₂Bdbm spectrum a value of 285.5 eV can be taken for C1s levels of two phenyl groups responsible for position of the carbon line peak.

A relative area of the main carbon band at 285.5 eV with regard to that of the carbonyl C-atom at 288.0 eV (see Table 2) has indicated that the concentration ratio of these two forms of carbon atoms is 7.0:1 at stoichiometric ratio given as 6.5:1. Calculated ε_i values for 1s-electrons of 15 carbon atoms of the complex are in a good agreement with the experimental spectrum provided 8.1 eV energy scale shift (see Fig. 4). Our value of 686.8 eV for E_b (F1s) in difluoroboron acetylacetonate upon correlated with that in both fluohydrocarbons (689–690 eV) and metal fluorides of high bond ionicity (684–686 eV) [27] affirms our assignment of the band with

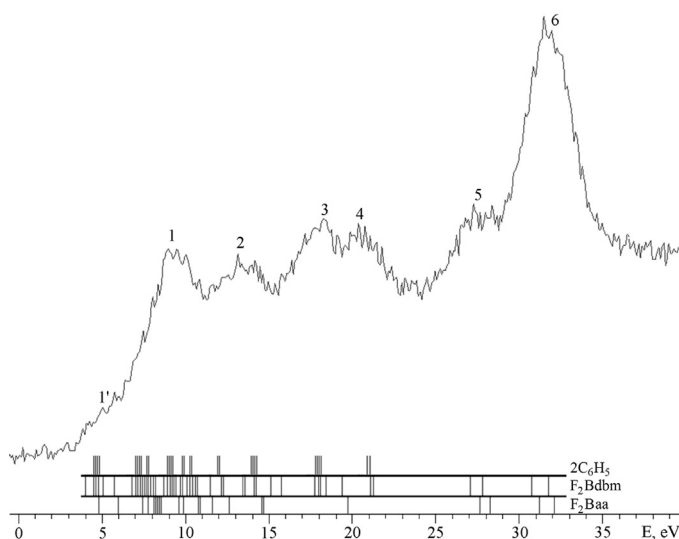


Fig. 5. XPS spectrum of F₂Bdbm (crystal phase) valence electrons and calculated energy levels for F₂Bdbm, initial F₂Baa and two phenyl groups.

Table 3

Experimental vertical ionization energies (IE_v , eV), the energy of Kohn–Sham orbitals (ε_i), H1s contributions (%) in benzene.

MO	IE_v	$-\varepsilon_i + 2.22$	δ	H1s
1a _{1g} (s)	25.90	25.49	0.41	4
1e _{1u} (s)	22.50	22.53	0.03	9
1e _{2g} (s)	19.20	18.63	0.57	16
2a _{1g}	16.85	16.51	0.34	33
1b _{1u} (s)	15.40	14.76	0.66	32
1b _{2u}	14.70	14.42	0.28	1
2e _{1u}	13.80	13.72	0.08	33
1a _{2u} (π)	12.10	12.29	0.19	–
2e _{2g}	11.49	11.62	0.13	29
1e _{1g} (π)	9.24	9.19	0.05	–

relatively low IE values within 12.8–13.3 eV to F2p-electrons [20]. A value 533.7 eV for E_b (O1s) exceeds all known suchlike values for β -diketonates of metals like Sc(aa)₃, Cr(aa)₃ and Mg(aa)₂ by 2.2–2.3 eV. This energy stabilization of O1s levels in β -diketonate difluoroboron complexes is in good agreement with that of valence n₂-electrons being 2.1–2.3 eV [28] upon substitution of the complexing metal by BF₂ group with its low electron donating ability [20]. According to reference data for boron atoms [27] a value of 194.6 eV is appropriate for those with high rates of oxidation.

In the valence band spectrum (see Fig. 5) between 2 and 36 eV may be discovered six overlapping spectral bands. Their intensities and half-widths are specified by the density of electronic states and ionization cross-sections of the levels. In order to find out an origin of states responsible for maxima in the spectrum of valence electrons we reproduced calculated energy levels for F₂Bdbm, initial F₂Baa and two phenyl groups beneath the spectrum in Fig. 5. Comparison analysis of energy values and electron density distribution have shown that in F₂Bdbm 35 valence MO of 50 orbitals are located at the chelate nucleus or benzene rings with the rate of 70% and higher that enables to specify a nature of the most part of electron levels in subzones of the molecular crystal under study. The results of calculations of relative ionization cross sections for 2s- and 2p-levels (σ_s , σ_p) of C, O and F atoms with Mg K α radiation source have shown a growth of ratios from 26 (C) to 74 (O) and 108 (F) provided σ_p values as 1:6:11 for the three atoms respectively [29,30].

In accordance with relative ionization cross sections, calculated energy values and composition of the wave functions, the bands 6 and 5 with maxima at 31.7 and 27.2 eV derive from ionization of levels F 2s and O 2s. Despite of oxygen dash presence in the sample (see Table 2), the area ratio of the bands 6 and 5 has been found to be 2.9. This value is much higher than expected value of 1.5 based on ionization cross sections. Discrepancy of our experimental data for ionization intensities of oxygen and fluorine 2s-levels is obviously caused not only by an error of calculation method in estimating of σ values for free atoms but also by delocalization of electron density within complexes. Specifically, both orbitals O 2s type are O–C-bonding with contribution of 26% into C 2s (see Fig. 2).

At ionization energies below 23 eV electron levels localized mainly on two C₆H₅-groups give the prevalent contribution into the spectrum. It is well known that in electron structure of benzene molecule, besides two π -MO, four levels with predominant contribution of 2s-AO and four σ -levels of p-type can be specified. Vertical IE of benzene [31] along with results of our calculations by DFT method with the B3LYP5 functional and def2-TZVPP basis set are listed in Table 3. The computational method correctly reproduces the order of IE but for three s-type MO Koopmans' defects exceed an average value by 0.4–0.6 eV. According to the results of calculations for the complexes and benzene rings, the bands 4 and 3 are formed by electrons similar to s-type ones on levels from 25

Table 4
The parameters of calculated F₂Bdbm absorption spectrum (S→S*-transitions).

N, state	Transition	Operator	E, eV	λ, nm	Oscillator strength, f	Transition type ^a
1, ¹ B ₂	70–71 (100%)	P _y (B2)	3.68	337	0.754	π(ab)–π(ab) ^a
2, ¹ A ₁	69–71 (94%)	P _z (A1)	4.08	304	0.009	π(b)–π(ab) ^a
3, ¹ B ₂	68–71 (96%)	P _y (B2)	4.09	303	0.033	π(b)–π(ab) ^a
4, ¹ A ₁	67–71 (91%)	P _z (A1)	4.46	278	0.072	π(b)–π(ab) ^a
5, ¹ B ₁	65–71 (97%)	P _x (B1)	4.63	268	0.003	n _– –π(ab) ^a
6, ¹ B ₂	66–71 (96%)	P _y (B2)	4.65	266	0.025	π(ba)–π(ab) ^a
7, ¹ A ₁	70–72 (89%)	P _z (A1)	5.06	245	0.026	π(ab)–π(b) ^a
8, ¹ B ₂	70–73 (55%)69–72 (36%)	P _y (B2)	5.31	234	0.000	π(ba)–π(b) ^a
9, ¹ A ₁	70–74 (48%)68–72 (41%)	P _z (A1)	5.32	233	0.000	π(b)–π(b) ^a
10, ¹ B ₂	69–72 (41%)70–73 (39%)	P _y (B2)	5.69	218	0.141	π(b)–π(b) ^a
21, ¹ B ₂	70–75 (50%)69–74 (37%)	P _y (B2)	6.35	195	0.210	π(b)–π(b) ^a

^a (a) – π-orbitals localized predominantly on chelate ring and (b) – π-orbitals localized predominantly on substituents.

to 33 of the monomer, six of which – 1a_{1g}(s), 1e_{1u}(s) – localized predominantly on aromatic nuclei (see Fig. 2).

Band 2 is caused by electron states corresponding levels from 34 to 40 of the free complex, with two pairs 1e_{2g}(s) among them (see Table 3). The first strong band with binding energy between 6 and 11 eV is due to energy-close p-type levels which include localized mostly on substituents from 1b_{1u}(s) to 2e_{2g}-MO, chelate ring π₁, π₂, F_{2p} orbitals and σ-MO as well.

Six described above the highest levels (see Table 1) that have been observed in gas-phase spectra (see Fig. 1) appear as a weak deflection on the first XPS-band 1' by the upper edge of the filled band.

The results of investigation of electronic structure of the complex I have been used in simulation of electronic absorption spectra. In spite of the slight disruption of coplanarity of the three rings, excited states to a first approximation can be conducted in terms of irreducible representations within the C_{2v} symmetry group for the planar complex. Table 4, besides energy parameters and oscillator strength values, shows (i) symmetry types of excited states, (ii) polarization of transitions and (iii) predominant localization of the excitation. Upon assigning types of transitions, we conventionally divided π-orbitals to ones localized predominantly on chelate ring (a) and others localized on substituents (b). If the sum of Mulliken atomic populations for MOs on the fragments differs less than twice then such unlocalized MOs are denoted as ab or ba depending on predominant localization.

Six the lowest excited states, according to computational results, appear as a result of electron transition from one of the six upper occupied MOs to the lower vacant orbital # 71 which is predominantly formed by πMO of the chelate ring (see Fig. 2, Table 1). The first transition with the largest oscillator strength 0.754 and operator P_y does not occur with appreciable electron density transfer because of proximity of contributions of the chelate ring π-orbitals (55–60%) and phenyl groups into HOMO (# 70) and LUMO (Table 5). The next two comparatively weak transitions with a charge transfer

Table 5
The effective charges Q, differences in effective charges ΔQ(a.u.) on chelate cycle and phenyl groups of F₂Bdbm in the first (1) and third (3) excited states in comparison with ground state (0).

Fragment	Q (0)	Q (1)	ΔQ (1)	Q (3)	ΔQ (3)
B	0.53	0.52	–0.01	0.53	0
2F	–0.62	–0.61	0.01	–0.62	0
2O	–0.44	–0.49	–0.05	–0.59	–0.15
2 C _β	0.65	0.34	–0.31	0.25	–0.40
C _γ	–0.32	–0.02	0.30	–0.34	–0.02
H _γ	0.15	0.15	0.15	0.15	0
2 C ₆ H ₅	0.05	0.11	0.06	0.62	0.57

C_β – carbon atoms connected with oxygen atoms of the chelate ring.

C_γ – carbon atom connected with C_β-atoms of the chelate ring.

H_γ – hydrogen atom connected with C_γ.

from phenyl nuclei to the chelate ring are responsible for a short-wave shoulder of the first band at 342 nm on the experimental spectrum (Fig. 6).

According to computational results, the second band on the experimental spectrum with a maximum at 264 nm is caused by two allowed transitions of π-electrons to the 4-th and 6-th states accompanied by both electron density transfer from phenyl groups to the chelate ring and intrachelate n_–→ π* transition. The luminescence excitation spectrum of F₂Bdbm in solution confirms the correspondence of the band near 264 nm to two nearby states (see Fig. 6).

The first transition from HOMO to the vacant π*-orbital # 72 of aromatic substituents corresponds to the seventh excited state with the energy value of 5.06 eV. In the gas-phase absorption spectrum a weak band at 236 nm can be assigned to the same transition (see Fig. 6). In the pre-vacuum range calculated spectrum contains a band at 218 nm corresponding to transitions to the 10-th state with f=0.141 localized on phenyl groups (see Table 4). In the vacuum range, as follows from our calculations, the strong band is assigned to transitions to the states from 20 to 32 with close energies and prevalent excitement localization on phenyl rings. Table 4 shows the most probable transition to the 21-st state.

On the computational spectrum the first band is short-wave shifted by 5 nm with respect to its experimental position, while the second band, assigned to two close transitions 4 and 6, is long-wave shifted by 8 nm. Insignificant errors of respectively 1.5% and 3% demonstrate a high prognostic power of the approach we have exploited. From calculations predicted energy interval between excited states 1 and 4 (0.78 eV) is less than experimental one between the two first bands (1.07 eV). This discrepancy between experimental and computed data results from the same method error as that in theoretical calculations of IE values in the approximation of the extended Koopmans' theorem (Table 4). Our calculation has given the energy interval value between MO 70 and

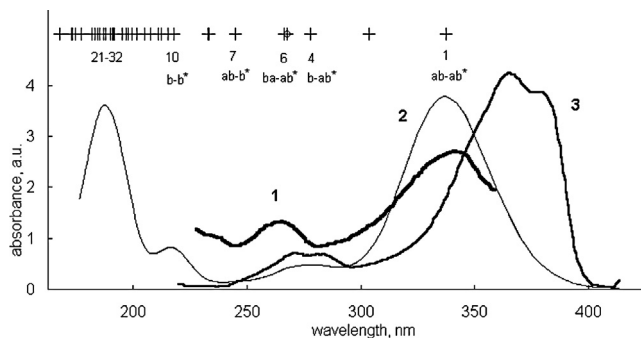


Fig. 6. Absorption gas-phase spectrum of F₂Bdbm (1); the spectrum calculated in TDDFT approximation (2) and luminescence excitation spectrum (3).

67 to be less by 0.30 eV with respect to that in UPS. The same error in method TDDFT brought to inaccuracy in $\Delta h\nu_{1-4}$.

4. Conclusions

The investigation of π -electrons of the chelate ring and phenyl groups in F₂Bdbm by UPS and quantum mechanical simulation in the DFT approximation revealed delocalization of the upper levels of conjugated rings as well as the same in the compound **II** with one phenyl group. As opposed to difluoroboron complex compounds with two phenyl rings as substituents (C₆H₅–C₆H₄ and so on), in which HOMO is localized predominantly on a substituent and one of the upper π -orbitals – on chelate ring [21], in compounds **I** and **II** HOMO is the antibonding combination of π_3^B and b_1^+ of the two phenyl groups.

Acknowledgements

The project was supported by the Scientific Fund of FEFU (Grant No. 12-03-13008-16/13) and Federal Targeted Program “Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009–2013” (Grant No. 14.A18.21.0792).

References

- [1] H.-D. Ilge, D. Fabler, H. Hartmann, Z. Chem. 24 (1984) 218–219.
- [2] H.-D. Ilge, H. Hartmann, Z. Chem. 26 (1986) 399–400.
- [3] G. Gorlitz, H. Hartmann, J. Kossanyi, P. Valat, V. Wintgens, Phys. Chem. 102 (1998) 1449–1458.
- [4] A.G. Mirochnik, E.V. Gukhman, V.E. Karasev, P.A. Zhikhareva, Russ. Chem. Bull. 49 (2000) 1024–1027.
- [5] T. Liu, A.D. Chien, J. Lu, G. Zhang, C.L. Fraser, J. Mater. Chem. 21 (2011) 8401–8408.
- [6] S. Xu, R.E. Evans, T. Liu, G. Zhang, J.N. Demas, C.O. Trindle, C.L. Fraser, Inorg. Chem. 52 (2013) 3597–3610.
- [7] V.E. Karasev, O.A. Korotkikh, Russ. J. Inorg. Chem. 31 (1986) 869–872.
- [8] A.G. Mirochnik, B.V. Bukvetskii, E.V. Gukhman, P.A. Zhikhareva, V.E. Karasev, Russ. Chem. Bull. 50 (2001) 1612–1615.
- [9] A. Sakai, M. Tanaka, E. Ohta, Y. Yoshimoto, K. Mizuno, H. Ikeda, Tetrahedron Lett. 53 (2012) 4138–4141.
- [10] Y.L. Chow, C.I. Johansson, J. Phys. Chem. 99 (1995) 17558–17565.
- [11] Z.-L. Liu, M.-X. Zhang, L. Yang, Y.-C. Liu, Y.L. Chow, C.I. Johansson, J. Chem. Soc. Perkin Trans. 2 (1994) 585–590.
- [12] A.A. Karpenko, E.V. Fedorenko, A.G. Mirochnik, Lumines 26 (2011) 223–228.
- [13] T.E. Goliber, J.H. Perlstein, Photogr. Sci. Eng. 26 (1982) 236–238.
- [14] G. Tamulaitis, V. Gulbinas, A. Undzenas, L. Valkunas, J. Lumin. 82 (1999) 327–332.
- [15] A.G. Mirochnik, E.V. Fedorenko, D.Kh. Gizzatulina, V.E. Karasev, Russ. J. Inorg. Chem. A 81 (2007) 1880–1883.
- [16] A.G. Mirochnik, E.V. Fedorenko, I.G. Nagorny, A.N. Pavlov, Optics Spectroscopy (English translation of Optika i Spektroskopiya) 114 (2012) 568–569.
- [17] A.G. Mirochnik, E.V. Fedorenko, A.A. Karpenko, D.A. Gizzatulina, V.E. Karasev, Lumines 22 (2007) 195–198.
- [18] A.G. Mirochnik, E.V. Fedorenko, V.G. Kuryavyy, B.V. Bukvetskii, V.E. Karasev, J. Fluoresc. 16 (2006) 279–286.
- [19] A.G. Mirochnik, E.V. Fedorenko, B.V. Bukvetskii, V.E. Karasev, Russ. Chem. Bull. 54 (2005) 1060–1062.
- [20] V.I. Vovna, S.A. Tikhonov, I.B. L'vov, Russ. J. Phys. Chem. A 85 (2011) 1942–1948.
- [21] V.I. Vovna, M.V. Kazachek, I.B. L'vov, Optics Spectroscopy (English translation of Optika i Spektroskopiya) 112 (2012) 497–505.
- [22] V.I. Vovna, S.A. Tikhonov, I.B. L'vov, Russ. J. Phys. Chem. A 87 (2013) 688–693.
- [23] A.A. Granovsky, Firefly version 7.1.G, <http://classic.chem.msu.su/gran/firefly/index.html>
- [24] V.I. Vovna, V.V. Korochentsev, A.A. Docenko, Russ. J. Coord. Chem. 38 (2012) 36–43.
- [25] A. Dreuw, M. Head-Gordon, Chem. Rev. 105 (2005) 4009–4037.
- [26] A.V. Borisenko, V.I. Vovna, V.V. Gorachakov, O.A. Korotkikh, Russ. J. Struct. Chem. 28 (1987) 127–130.
- [27] V.I. Nefedov, X-ray Photoelectron Spectroscopy of Chemical Compounds, Khimiya, Moscow, 1984 (in Russian).
- [28] V.I. Vovna, Koordinatsionnaya Khimia 21 (1985) 435–450 (in Russian).
- [29] V.I. Nefedov, V.I. Vovna, Electronic Structure of Chemical Compounds, Nauka, Moscow, 1987 (in Russian).
- [30] Casa XPS Version 2.3.12., Casa Software Ltd., 1999–2006.
- [31] V.I. Vovna, Electronic Structure of Organic Compounds: Photoelectron Data, Nauka, Moscow, 1991 (in Russian).