


## Study of chemical bonding in the interhalogen complexes based on density functional theory

O. Kh. Poleshchuk<sup>1</sup>  · A. V. Fateev<sup>2</sup> · A. G. Yarkova<sup>2</sup> ·  
M. N. Ermakhanov<sup>3</sup> · P. A. Saidakhmetov<sup>3</sup>

Published online: 6 October 2016  
© Springer International Publishing Switzerland 2016

**Abstract** The density functional theory analysis was used for a number XYL complexes (XY is a dihalogen molecule and L is a Lewis base), formed between molecules I<sub>2</sub>, ICl, IBr and pyridine. The calculated geometrical parameters, IR spectra and nuclear quadrupole interaction constants of iodine are consistent with the data of microwave spectroscopy and nuclear quadrupole resonance. The good correlation between the experimental and calculated binding energies of the inner electrons of iodine, chlorine and nitrogen atoms were found with the calculation using both Gaussian and Slater functions. The comparison of experimental and calculated changes in the electron density on the atoms upon complex formation suggested the choice of scheme for calculating the effective charge on the atoms, which allow us to interpret the experimental spectra. It is shown that the use of both calculated schemes allows us to predict the enthalpy of complex formation in close agreement with the experimental values. The energy analysis shows that in the complexes the electrostatic binding energy dominates that of covalent binding.

**Keywords** Density functional theory · Quadrupole coupling constant · Photoelectron spectroscopy · Effective atomic charge

---

This article is part of the Topical Collection on *Proceedings of the International Conference on Hyperfine Interactions and their Applications (HYPERFINE 2016), Leuven, Belgium, 3–8 July 2016*

---

✉ O. Kh. Poleshchuk  
poleshch@tspu.edu.ru

<sup>1</sup> National Research Tomsk Polytechnic University, Tomsk, Russia

<sup>2</sup> Tomsk State Pedagogical University, Tomsk, Russia

<sup>3</sup> M. Auezov South Kazakhstan State University, Shymkent, Republic of Kazakhstan

## 1 Introduction

Structure and bonding in Lewis acid-base complexes is the subject of the chemical of interest [1]. Most of the complexes of halogens and interhalogens have dative chemical bonds that are intermediate between van der Waals interaction and fully formed chemical bonds [2]. On the one hand these complexes have an interesting structure, on the other -they provide an interesting perspective in understanding the nature of the donor-acceptor chemical bond.

The advantage of the study LXY complexes, where L is a Lewis base and X and Y = F, Cl, Br, or I consists in the fact that N, Cl, Br and I are quadrupole nuclei, and therefore rotational spectra of these complexes reveal nuclear quadrupole hyperfine structure.

Experimentally obtained spectroscopic properties relate to the isolated molecule and are therefore most relevant for comparison with the results of *ab initio* calculations at a high level of theory. Changes of nuclear quadrupole coupling constants (NQCC) of halogens observed when an organic ligand L is brought to its equilibrium position in LXY are of specific interest because they are simply related to the electric field gradients at the nuclei in question.

Comparison of the calculated and experimental values of NQCC in complexes of halogens with amines was made in our previous studies [3–5], and in a number of Karpfen's works [6–9]. It was shown that the use of diffuse and polarization functions leads to good agreement between experimental and calculated properties such as bond length, NQCC and the binding energy.

It is well known that the complexation of ICl, IBr, or I<sub>2</sub> with ligands containing nitrogen atoms leads to significant frequency shifts of <sup>35</sup>Cl, <sup>79</sup>Br, <sup>127</sup>I and <sup>14</sup>N [1–3] signals in nuclear quadrupole resonance spectra. If NQR frequencies of terminal iodine atoms, bromine, chlorine, and nitrogen are significantly shifted to lower frequencies in the spectrum, then NQCC of iodine atoms increase upon complexation. Some authors [10–12] have considered such changes in ICl complexes in terms of the approximate Dailey-Townes theory and the results showed the transfer of electron density to the chlorine atom and an increase positive charge on the iodine atom.

To evaluate the electronic structure of such systems is very important because halogen atoms are directly linked to donor atoms with bond directions roughly coinciding with the axes of the orbitals of the lone pairs in the non-complexes donor molecule [13]. The complex of iodine chloride and pyridine has been investigated in the gas phase by X-ray photoelectron spectroscopy [14]. The experiment showed that upon complexation there is a decrease of the binding energy of I (3d) by 0.8 eV, and vice versa, the binding energy of N (1s) pyridine increases by 0.9 eV.

We evaluated the change in the charge on the nitrogen atom in the complex as 0.1 e. Experimental Cl (2p) lines in the spectrum of this complex have revealed only one component having no broadening. On this basis, we concluded that the chemical shift of Cl (2p) on the formation of the complex should not exceed 0.3 eV, which, according to the authors of ref.14, confirmed the idea of transfer of charge only to the vacant orbital, localized on the atom of iodine. However, data on the NQR spectra of chlorine nuclei and X-ray fluorescence spectra [15] also indicate a significant change in the electron density of the chlorine atom.

The aim of our work is to analyze the nature of the chemical bond in the donor-acceptor interhalogen complexes using density functional theory within the Gaussian and Amsterdam Density Functional software packages. At the center of interest is the analysis of the electron density distribution in the atoms, as well as the gradient of the electric field near the nucleus.

An additional aim of our work is to describe the nature of the coordination bond in these complexes in terms of electrostatic and covalent interactions.

## 2 Computational details

The calculations were carried out using the Gaussian'09 [16] program package. The geometry optimizations for the complexes were carried out using—density functional theory (with the cam-B3LYP functional) [17], which is an improvement of the B3LYP functional. We used the advanced DGDZVP basis set for all atoms. The DGDZVP basis set is a fully-electronic valence-split basis with the addition of polarization functions. This basis set is optimized for use with—heavy atoms when applying density functional theory [18]. The geometrical parameters of molecules and clusters were fully optimized; no imaginary vibrational frequencies were detected, which confirmed the stationary character of the optimization. Dissociation energies have been adjusted to reflect the zero-point vibrational energy (ZPVE) and reduced to standard conditions (298.15 K, 1 atm) using thermal corrections to the free energy and enthalpy.

NQCC of  $^{127}\text{I}$  nuclei have been estimated from the calculated electric field gradient tensors. Experimental values for the electric quadrupole moments were taken from [19]. For analysis of the nature of the bonding in the complexes, we have chosen the approach of natural orbitals bond [20]. The geometry of some complexes has also been optimized using the software package ADF'2016 (Amsterdam density functional) [21]. We used the exchange functional OPTX [22], combined with the correlation functional PBE [23], using a full-electron triple- $\zeta$  based set of Slater orbitals with polarization functions. Relativistic effects of heavy atoms have been accounted for by using the zero-order regular approximation (ZORA) [24], which gives more realistic results than the widely used formalism of Pauli in the Gaussian package program. Effective atomic charges were estimated in the Mulliken, Hirschfeld, Voronoi and Multipole derived atomic charges approximations [21].

To assess the contributions of the donor-acceptor bond between XY and pyridine, we carried out an analysis of the energy decomposition [25] with the help of the software package ADF [21]. According to this scheme, the binding energy of the complex D-A, consisting of two fragments D and A can be divided into the following components:

$$D_e = -(\Delta E_{\text{prep}} + \Delta E_{\text{inter}}) \quad (1)$$

where  $\Delta E_{\text{prep}}$  is the preparation energy, describing the geometry distortion of each separate fragment from its equilibrium geometry to that it has in the complex;  $\Delta E_{\text{inter}}$  is the energy of interaction between the distorted fragments.

The last term can be further decomposed into three contributions:

$$\Delta E_{\text{inter}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{orb}} \quad (2)$$

where  $\Delta E_{\text{Pauli}}$  is the Pauli repulsion energy, which is the result of repulsion between the two fragments' filled shells;  $\Delta E_{\text{elstat}}$  is a term describing the energy of the electrostatic interaction between the two fragments at their original electron densities, that is, with the density that each component would have in the absence of another fragment;  $\Delta E_{\text{orb}}$  is orbital interaction components associated with the stabilization of the system. This last term includes both the charge transfer and polarization.

**Table 1** Experimental element-halogen bond lengths (Å) compared with those calculated at the cam-B3LYP/DGDZVP and BP86/TZ2P+ levels of theory and also calculated NQCC (MHz) in various iodine compounds

Compound	$R_{B-Y}^{exp.}$	$R_{B-Y}^{cal.}$ (GAUSS)	$R_{B-Y}^{cal.}$ (ADF)	$\chi_{I}^{exp.}$	$\chi_{Cl,Br,I,N}^{cal.}$ (GAUSS)	$\chi_{I}^{cal.}$ (ADF)
I <sub>2</sub>	2.667	2.714	2.650	-2151	-2502	-2064
ICl	2.321	2.373	2.402	-2928	-2993	-2543
IBr	2.470	2.510	2.460	-2731	-2823	-2303
Gal	2.575	2.635	2.610	-549	-471	-364
NaI	2.739	2.720	2.733	-327	-260	-310
LiI	2.392	2.468	2.388	-198	-317	-193
KI	3.050	3.157	3.019	-60	-115	-123
IO <sub>3</sub> <sup>-</sup>	1.820	1.844	1.815	1022	1073	602
ICl <sub>2</sub> <sup>-</sup>	2.340	2.392	2.360	3128	3020	2412
IF <sub>5</sub>	1.870	1.942	1.908	1073	989	609
	1.840	1.899	1.845			
I <sub>3</sub> <sup>-</sup>	2.920	2.997	2.928	2410	1072	1023
				1168	2701	2077
HI	1.609	1.635	1.612	-1823	-1882	-1474
CH <sub>3</sub> I	2.139	2.156	2.128	-1934	-2024	-1596
CH <sub>2</sub> I <sub>2</sub>	2.120	2.150	2.125	-1771	-1902	-1507
CH <sub>2</sub> CHI	2.092	2.106	2.077	-1847	-2043	-1514
CHICHI	2.030	2.106	2.080	-1848	-2131	-1576
CH <sub>3</sub> COI	2.210	2.209	2.202	-1570	-1704	-1235
I <sub>2</sub> Py	2.31	2.717	2.545	-2634	-2738	-2113
				-1370	-1979	-1515
IClPy	2.29	2.545	2.402	-3095	-3145	-2430
IBrPy	2.26	2.510	2.470	-2971	-3006	-2284

### 3 Results and discussion

Table 1 shows the experimental and calculated values of the main parameters describing the geometry of some simple iodides and LXY complexes. Comparison of bond lengths in complexes LXY calculated on the basis of cam-B3LYP/DGDZVP level of theory with experimental data [26, 27] is shown in Table 1. Analysis of the results led to the following correlation between the calculated and experimental L-I and I-Y bond lengths for the studied complexes (Fig. 1a):

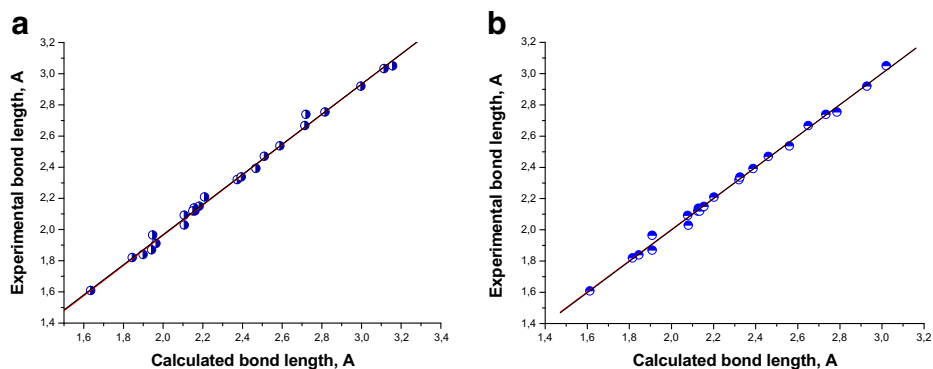
$$[R(cal.)/\text{Å}] = 0.04 + 0.97 [R(exp.)/\text{Å}] \quad (r = 0.998; s = 0.03; n = 24), \quad (3)$$

where  $r$  is the correlation coefficient,  $s$  is the standard deviation, and  $n$  is the number of compounds.

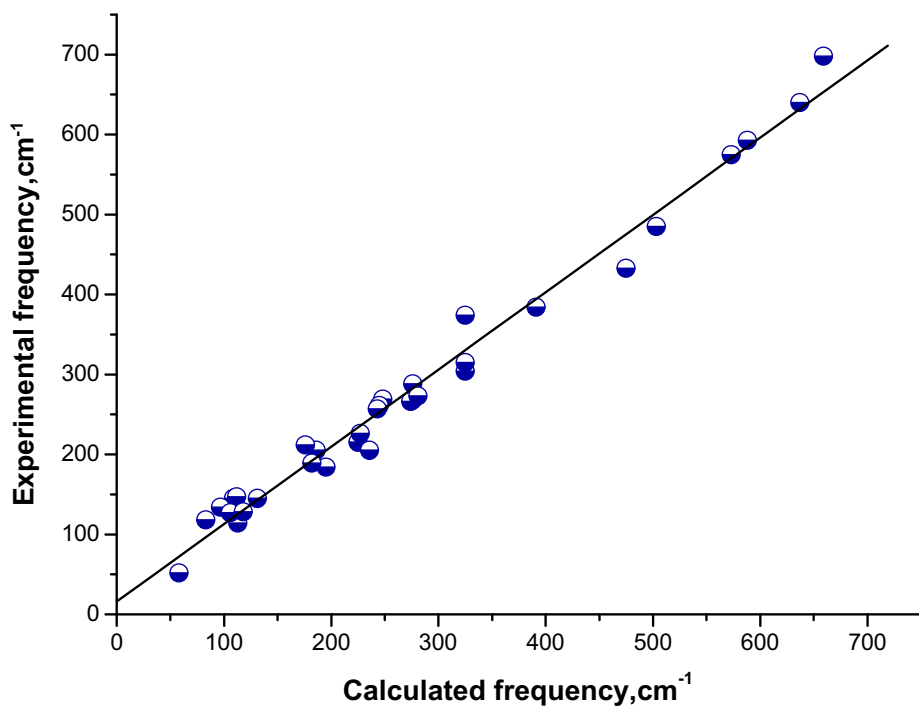
Similar correlation was obtained by comparing the experimental and BP86/TZ2P+ calculated bond lengths (Fig. 1b):

$$[R(cal.)/\text{Å}] = -0.01 + 1.003 [R(exp.)/\text{Å}] \quad (r = 0.998; s = 0.02; n = 22), \quad (4)$$

The good correlation between the experimental and calculated bond lengths “iodine-halogen” and “ligand-iodine”, and the coefficient for  $R(exp.)$ , close to 1 reflect the high

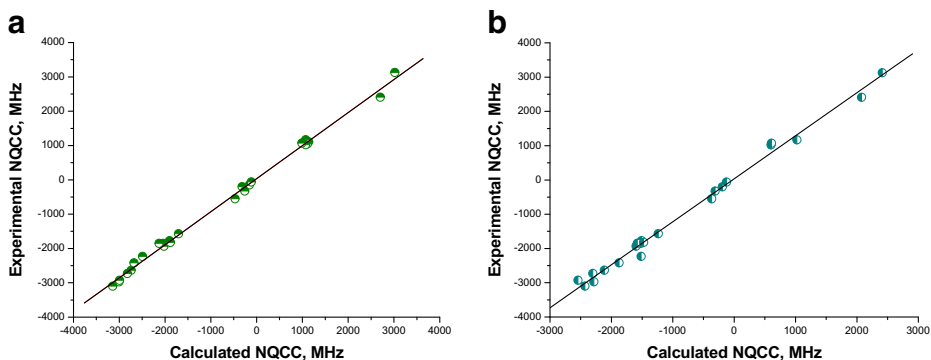


**Fig. 1** Correlation between experimental and calculated bond length using GAUSSIAN (a) and ADF (b) packages



**Fig. 2** Relationship between experimental IR-wavenumbers and those calculated at the cam-B3LYP/DGDZVP level of theory for various iodine compounds

reliability level used in the calculations. Table 1 shows that the intermolecular bond lengths are close to the experimental values obtained by microwave spectroscopy. However, for XY complexes with pyridine, the calculated values differ significantly from their experimental counterparts obtained by X-ray analysis, which is probably due to the inaccuracy of the experimental measurements, which were carried out in the 1960's.



**Fig. 3** Correlation between experimental and calculated NQCC obtained by using the GAUSSIAN (a) and ADF (b) packages

For some simple compounds of iodine and complexes LXY, the following correlation was obtained between the experimental [28, 29] and calculated vibrational frequencies of element-iodine bonds (Fig. 2):

$$[\omega(\text{exp.})/\text{cm}^{-1}] = 16 + 0.97 [\omega(\text{cal.})/\text{cm}^{-1}] \quad (r = 0.992; s = 21; n = 33) \quad (5)$$

These results have allowed us to carry out calculation of the NQCC of iodine atoms in a number of compounds in the present study. Using the cam-B3LYP/DGDZVP method, the correlation obtained between the experimental [5, 30] and calculated NQCC was (Fig. 3a):

$$[\chi_{\text{I}}^{\text{exp.}} (\text{MHz})] = 33 + 0.96 [\chi_{\text{I}}^{\text{cal.}} (\text{MHz})] \quad (r = 0.998; s = 104; n = 25) \quad (6)$$

A similar correlation between the NQCC calculated by the ADF method and the corresponding experimental NQCC of the various iodine nuclei is expressed as follows (Fig. 3b):

$$[\chi_{\text{I}}^{\text{exp.}} (\text{MHz})] = 33 + 1.25 [\chi_{\text{I}}^{\text{cal.}} (\text{MHz})] \quad (r = 0.996; s = 156; n = 22) \quad (7)$$

These dependences indicate that the use of the full-electron basis set DGDZVP and ZORA approximations in the ADF method gives acceptable values for the NQCC of iodine nuclei, both when compared with each other and with the experimental data.

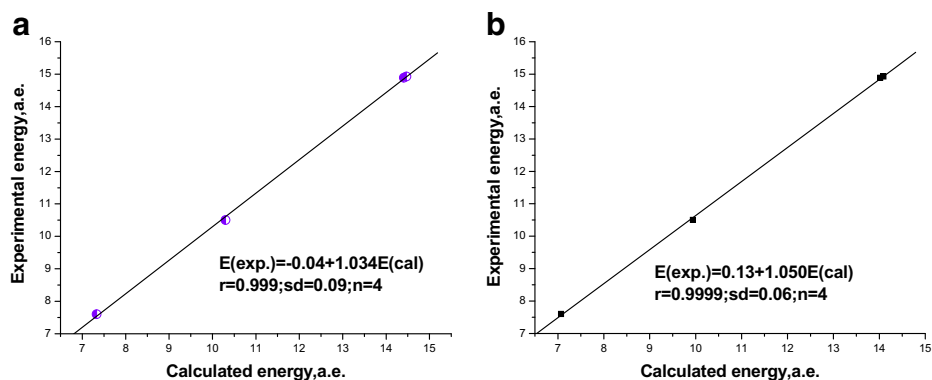
It is possible to compare estimates of the stabilization energy of XIL complexes, resulting from both methods of calculation with the experimental values of the enthalpy of complexation.

It is known in the literature that the enthalpy of complexation of the iodine with pyridine ( $-7.4 \div -8.6$  kcal/mol) only [31], which is consistent with that obtained in our calculation of value ( $-8.5$  in the program GAUSSIAN and  $-8.7$  kcal/mol in the program ADF). Energy stabilizations of complexes with iodine monochloride and iodine monobromide are somewhat larger ( $-13$  and  $-11.1$  chloride and  $-10$  and  $-9.6$  kcal/mol for the bromide, calculated by both methods). Thus, the force constant increases in the complexes in the order  $\text{I}_2 < \text{IBr} < \text{ICl}$ , corresponding to the order of the experimental enthalpy data [31]. The calculated enthalpy of formation of complexes of iodine monochloride and iodine monobromide with nitriles have values between  $-2$  and  $-9$  kcal/mol, which is fairly close to the experimental data [32]. The same applies to the iodine complexes with ethers and sulfides [32].

Also very interesting is the comparison of internal energy levels calculated under both methods with the experimental values of the binding energies from the X-ray photoelectron

**Table 2** Inner level energy of nitrogen, carbon, iodine and chlorine atoms (a.e.) calculated at cam-B3LYP/DGDZVP (a) and BP86/TZ2P+ (b)

Compound	N1s <sup>cal</sup>	C1s <sup>cal</sup>	Cl2p <sup>cal</sup>	I3d <sup>cal</sup>	N1s <sup>exp</sup>	C1s <sup>exp</sup>	Cl2p <sup>exp</sup>
ICl	–	–	7.33 <sup>a</sup> 7.07 <sup>b</sup>	23.08 <sup>a</sup> 22.42 <sup>b</sup>	–	–	7.6
Py	14.41 <sup>a</sup> 14.02 <sup>b</sup>	10.30 <sup>a</sup> 9.94 <sup>b</sup>	–	–	14.89	10.5	–
IClPy	14.47 <sup>a</sup> 14.09 <sup>b</sup>	10.34 <sup>a</sup> 9.97 <sup>b</sup>	7.27 <sup>a</sup> 7.00 <sup>b</sup>	23.05 <sup>a</sup> 22.38 <sup>b</sup>	14.93	–	<7.6

**Fig. 4** Correlation between experimental and calculated atom inner level of 1sN, 2pCl and 1sC at GAUSSIAN (a) and ADF (b)

spectra. Table 2 shows the calculated and the experimental energy of the inner levels [14] of the atoms that make up the complex ICl-Py.

The experimental energy difference of the 3d level of the iodine atom in the ICl complex is 0.03 a.u. The results indicate the good quality of the calculation. Changes in the calculated internal energy levels during the transition from individual molecules to complexes practically coincide with the experimental differences of the bond energy (Fig. 4).

Table 3 shows the values of changes in the electron density at the atoms in the complexes of halogens with pyridine, calculated in various approximations, using different schemes of calculation of the effective charges on the atoms: Mulliken (Mul), the atom in the molecule (AIM), Löwdin (Löw), multipole charges (Mult), due to natural orbitals bond (NBO), Hirschfeld (Hirsh), Voronoi (Voronoi).

Experimental data from the ESCA and NQR spectra indicate that complexation occurs with an increase in electron density on the terminal iodine atom and a halogen atom but with a reduction on the nitrogen atom of the pyridine molecule [33]. On the one hand, it indicates an increase of the binding energy of the nitrogen atom in the pyridine molecule and decreases the binding energy of the chlorine and iodine atoms [14]. A decrease of the NQCC on the nitrogen and chlorine atoms and an increase of that of the iodine atom [5] are also revealed. Table 3 shows that the experimental distribution of the electron density in the complex for all three systems corresponds only to the charges calculated by Hirschfeld, Voronoi and Multipole methods of describing the charge distributions.

**Table 3** Electron density change in IHalPy complexes, calculated at cam-B3LYP/DGDZVP (a), BP86/TZ2P+ (b) and AIM (c)

Complex	Atom	$\Delta q^{\text{Mul}}$ (a)	$\Delta^{\text{NBO}}$ (a)	$\Delta q^{\text{Mult}}$ (b)	$\Delta q^{\text{Hirsh}}$ (b)	$\Delta q^{\text{Voronoy}}$ (b)	$\Delta q^{\text{AIM}}$ (c)	$\Delta q^{\text{L6w}}$ (a)
IClPy	I	–	–	0.210	0.078	0.114	0.004	–0.030
	Cl	0.046	0.023	0.086	0.160	0.173	0.155	0.247
	N	0.189	0.155	–	–0.092	–0.022	0.023	0.027
IBrPy	I	–	–	0.283	0.060	0.095	–0.013	0.011
	Br	0.054	0.040	0.018	0.162	0.173	0.164	0.172
	N	0.183	0.152	–	–0.086	–0.014	0.019	–0.020
I <sub>2</sub> Py	I	–	–	0.250	0.040	0.076	–0.043	–0.007
	I	0.079	0.057	0.070	0.163	0.172	0.179	0.180
	N	0.181	0.151	–	–0.080	–0.006	0.014	–0.027
		0.080	0.033	0.196				

The sign (–) corresponds to a decrease of the electron density

**Table 4** Energy decomposition and NBO analysis for iodine complexes (kcal/mol)

Complex	$\Delta E_{\text{Pauli}}$	$\Delta E_{\text{Elstat}}$	$\Delta E_{\text{Orb}}$	$D_e$	$E_{ij}^{(2)}$	$R_{\text{N-1}}^{\text{cal}}$
IClPy	61.3	–40.9	–31.5	11.1	56.8	2.402
I <sub>2</sub> Py	49.0	–32.1	–25.6	8.7	36.4	2.545
IBrPy	46.6	–31.3	–24.9	9.6	45.2	2.470

Using the method of energy decomposition, as defined in the ADF method, intermolecular bonds in IXPY complexes were analyzed. Three major components contributing to the energy of the chemical bond can be identified: Pauli repulsion, electrostatic attraction and covalent interactions. Frenking and colleagues [34] suggested that  $\Delta E_{\text{elstat}}$  should be used to assess the strength of the electrostatic binding, and  $\Delta E_{\text{orb}}$ —for covalent binding.

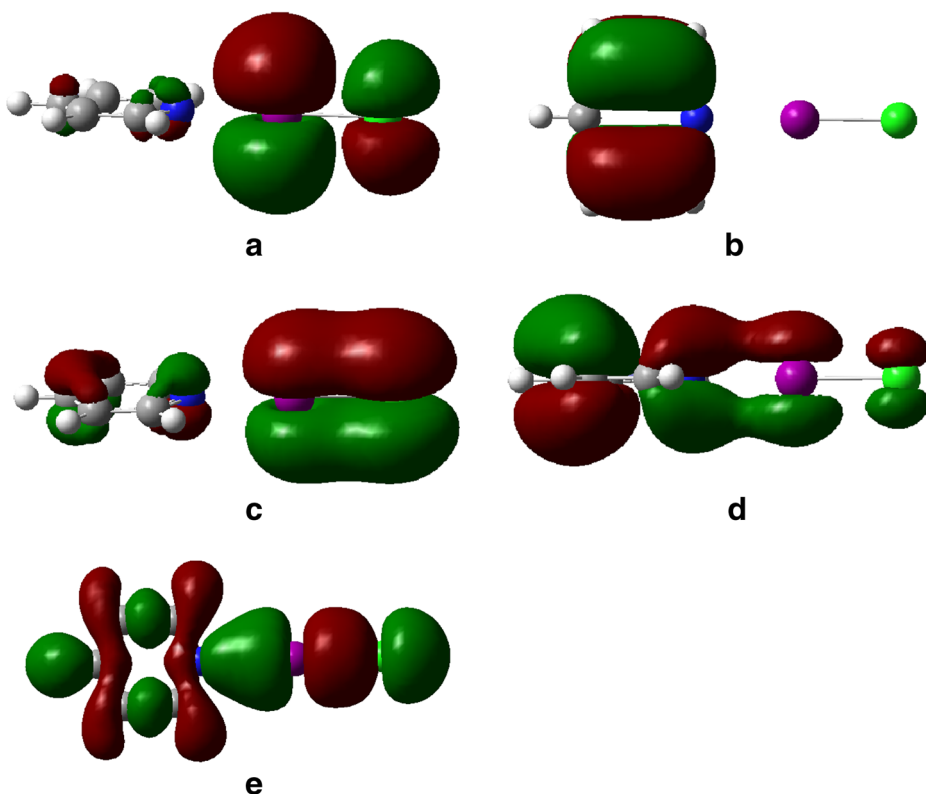
In LXY complexes, the term  $\Delta E_{\text{elstat}}$  dominates in comparison with  $\Delta E_{\text{orb}}$  term (Table 4). From this it follows that the binding of I-L in these complexes is more electrostatic than covalent. A larger contribution of electrostatic interactions in the case of complexes I<sub>2</sub>, IBr and ICl with all possible types of bases was assumed in [35].

Table 4 shows that the interaction energy of the complexes correlates with the calculated intermolecular bond length; the more interaction, the shorter intermolecular distance:

$$D_e = 51.1 - 16.7 R_{\text{N-1}}^{\text{cal}} \quad (r = 0.985; s = 0.3; n = 3) \quad (8)$$

It is well known from the model of Mulliken and the interaction energy of the second order  $n\sigma$ -complexes from the method of natural bond orbitals [20] that the LP(N)  $\rightarrow$   $\sigma^*XY$  (LP = lone electron pair of the nitrogen atom of the pyridine) donor-acceptor interaction is the source of the intermolecular charge transfer [5]. The result, as established here, is a





**Fig. 5** Molecular orbitals of the ICIPy complex **a** HOMO, **b** HOMO-3, **c** HOMO-4, **d** HOMO-6, **e** HOMO-7

relationship between the energy of the interaction and the binding energy of complexes with pyridine according to (9):

$$D_e = 4.3 + 0.11\Delta E_{ij}^{(2)} (r = 0.998; s = 0.11; n = 3) \quad (9)$$

The existence of the equation (9) indicates that the term  $\Delta E_{ij}^{(2)}$  (describing the donor-acceptor energy) justifies use of the term ‘covalent’ to describe the intermolecular interactions in these complexes. A similar relationship was found by us for the complexes of sulfur trioxide [4, 5]. It should also be noted that in terms of molecular orbitals (Fig. 5), the highest occupied molecular orbital represents a lone pair of electrons of the halogen atoms (the HOMO-3) while the  $\pi$ -orbitals of the pyridine ring are the HOMO-4—bonding orbitals I-Cl. The donor-acceptor interaction is manifested only in the HOMO-6 and HOMO-7, which can be attributed to the orbital with a large contribution I-N bond.

## 4 Conclusions

The calculations clearly show that the calculated by Gaussian and ADF bond lengths correlate with the experimental values. The calculated IR-, rotational spectra and nuclear

quadrupole interaction constants of iodine are consistent with the data of microwave spectroscopy and nuclear quadrupole resonance. The calculated by both methods stabilization energies are close to the experimental values. The good correlation between experimental and calculated binding energies of the inner electrons of iodine, chlorine and nitrogen atoms were found with the calculation of Gaussian and Slater functions. The comparison of experimental and calculated changes in the electron density on the atoms upon complex formation allowed choosing the scheme of calculating the effective charge on the atoms, which allow interpreting the experimental spectra. From EPA scheme follows that for iodine complexes the electrostatic bonding is a little bit more than covalent bonding.

**Acknowledgments** We thank Prof. G. Frenking from Philipps-Universität Marburg for making calculations on Gaussian and ADF software packages. Special thanks to Prof. A. Legon from Bristol University for editing of this article.

## References

1. Hargittai, M., Hargittai, I.: *The Molecular Geometries of Coordination Compounds in the Vapour Phase*. Elsevier, Amsterdam (1977) 342p
2. Dvorak, M.A., Ford, R.S., Suenram, R.D., Lovas, F.J., Leopold, K.R.: van der Waals vs. covalent bonding: microwave characterization of a structurally intermediate case. *JACS* **114**, 108–115 (1992)
3. Poleshchuk, O.Kh., Legon, A.C.: Density functional theory studies of bonding in complexes H<sub>3</sub>N...XY of ammonia and dihalogen molecules: a comparison with experimental results from rotational spectroscopy. *Z. Naturforsch.* **57a**, 537–543 (2002)
4. Poleshchuk, O.Kh., Yureva, A.G., Fateev, A.V., Brabchadel, V.: Investigation of the electronic structure of SO<sub>3</sub> and I<sub>2</sub> complexes by density functional theory. *Butlerov. Commun.* **9**, 10–20 (2006)
5. Poleshchuk, O.Kh., Fateev, A.V., Legon, A.C., Frenking, G.: Hyperfine interactions and DFT study of the bonding in complexes of metal halides, interhalogen diatomics in SO<sub>3</sub> with Lewis bases. *Trends Phys. Chem.* **15**, 13–43 (2014)
6. Karpfen, A.: The intermolecular interaction in the charge-transfer complex between NH<sub>3</sub> and F<sub>2</sub>. *Chem. Phys. Lett.* **316**, 483–498 (2000)
7. Karpfen, A.: Charge-transfer complexes between NH<sub>3</sub> and the halogens F<sub>2</sub>, ClF, and Cl<sub>2</sub>: an ab initio study on the intermolecular interaction. *J. Phys. Chem.* **104A**, 6871–6879 (2000)
8. Karpfen, A.: Charge-transfer complexes between the amines (CH<sub>3</sub>)<sub>n</sub>NH<sub>3-n</sub> (n = 0–3) and the ClF molecule: an ab initio and density functional study on the intermolecular interaction. *J. Phys. Chem.* **105A**, 2064–2072 (2001)
9. Karpfen, A.: The intermolecular interaction in the charge-transfer complexes between amines and halogens: a theoretical characterization of the trends in halogen bonding. *Theor. Chem. Acc.* **110**, 1–9 (2003)
10. Fleming, C., Hanna, M.W.: Nuclear quadrupole resonance investigation of iodine monochloride complexed with pyridines. *JACS* **93**, 5030–5034 (1971)
11. Bowmaker, G.A., Hacobian, S.: Nuclear quadrupole resonance of charge-transfer complexes. II. The aminehalogen complexes. *Aust. J. Chem.* **22**, 2047–2059 (1969)
12. Bowmaker, G.A., Boyd, P.D.W., Sorrenson, R.J.: SCF-MS-X $\alpha$  study of the bonding and nuclear quadrupole coupling in trihalide ions XY<sub>2</sub><sup>-</sup> (X=I, Br or Cl; Y=I, Br, Cl or F) and xenon difluoride. *J. Chem. Soc. Faraday Trans.* **2**, 1125–1143 (1984)
13. Legon, A.C.: The interactions of dihalogens and hydrogen halides with Lewis bases in the gas phase: an experimental comparison of the halogen bond and the hydrogen bond. *Struct. Bond.* **126**, 17–64 (2008)
14. Mostad, A., Svensson, S., Nilsson, R., Basilier E., Gelius, U., Nordling, C., Siegbahn, K.: Pyridine-iodomono-chloride. A charge transfer complex studied by ESCA. *Chem. Phys. Lett.* **23**, 157–159 (1973)
15. Poleshchuk, O.Kh., Nogaj, B., Dolenko, G.N., Elin, V.P.: Electron density redistribution on complexation in non-transition element complexes. *J. Mol. Struct.* **297**, 295–312 (1993)
16. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J.A., Peralta,

- J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Salvador, P., Dannenberg, J.J., Dapprich, S., Daniels, A.D., Farkas, O., Foresman, J.B., Ortiz, J.V., Cioslowski, J., Fox, D.J.: Gaussian Inc., Wallingford CT (2009)
17. Yanai, T., Tew, T., David, P.N., Handy, N.C., Tew, D.P.: A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **393**, 51–57 (2004)
  18. Yurieva, A.G., Poleshchuk, O.Kh., Filimonov, V.D.: Comparative analysis of a full-electron basis set and pseudopotential for the iodine atom in DFT quantum-chemical calculations of iodine-containing compounds. *Russ. J. Struct. Chem.* **49**, 548–552 (2008)
  19. Pyykko, P.: Spectroscopic nuclear quadrupole moments. *Mol. Phys.* **99**, 1617–1629 (2001)
  20. Glendening, E.D., Reed, A.E., Carpenter, J.E., Weinhold, F.: NBO Version 3.1
  21. ADF2016, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, <http://www.scm.com/>
  22. Handy, N.C., Cohen, A.J.: Left-right correlation energy. *Mol. Phys.* **99**, 403–412 (2001)
  23. Perdew, J.P., Burke, K., Wang, Y.: Generalized gradient approximation for the exchange–correlation hole of a many-electron system. *Phys. Rev. B* **54**, 16533–16539 (1996)
  24. te Velde, G., Bickelhaupt, F.M., van Gisbergen, S.J.A., et al.: Chemistry with ADF. *J. Comput. Chem.* **22**, 931–967 (2001)
  25. Ziegler, T., Rauk, A.: On the calculation of bonding energies by the Hartree Fock Slater method. *Theor. Chim. Acta* **46**, 1–10 (1977)
  26. Bazanov, S.S.: *Strukturная Khimija. Fakti i zavisimosti*. Dialog MGU, Moscow (2000) 292p
  27. Hargittai, M.: Molecular structure of metal halides. *Chem. Rev.* **100**, 2233–2302 (2000)
  28. Forster, R.: *Organic Charge-Transfer Complexes*. Academic, New York (1969) 369p
  29. Friedrich, H.B., Person, W.B.: Infrared Spectra of Charge-Transfer Complexes. VI. *Theory. J. Chem. Phys.* **44**, 2161–2187 (1966)
  30. Karpfen, A.: Theoretical characterization of the trends in halogen bonding. *Struct. Bond.* **126**, 1–22 (2008)
  31. Guryanova, E.N., Goldshein, I.P., Romm, I.P.: *Donorno-akceptornaya sviaz*. Khimia, Moscow (1973) 400p
  32. Legon, A.C.: Prereactive complexes of dihalogens XY with lewis bases B in the Gas phase: a systematic case for the halogen analogue  $B \cdots XY$  of the Hydrogen Bond  $B \cdots HX$ . *Angew. Chem. Int. Ed.* **38**, 2686–2714 (1999)
  33. Ouvrard, C., Le Questel, J.-Y., Berthelot, M., Laurence, C.: Halogen-bond geometry: a crystallographic database investigation of dihalogen complexes. *Acta Cryst.* **B59**, 512–526 (2003)
  34. Poleshchuk, O.Kh., Latosinska, J.N., Koput, J., Nogaj, B.: Ab initio study of the bonding and nuclear quadrupole coupling in the  $PyICl$  complex. *J. Mol. Struct.* **513**, 29–34 (1999)
  35. Frenking, G., Frohlich, N.: The nature of the bonding in transition-metal compounds. *Chem. Rev.* **100**, 717–774 (2000)