ФИЗИКАЛЫҚ ЖӘНЕ АНАЛИТИКАЛЫҚ ХИМИЯ
ФИЗИЧЕСКАЯ И АНАЛИТИЧЕСКАЯ ХИМИЯ
PHYSICAL AND ANALYTICAL CHEMISTRY

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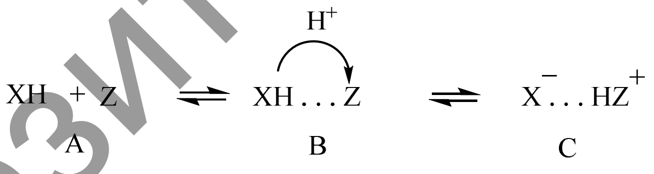
The investigations of acid-base properties of the several small molecules by quantum chemical methods

The values of ionization potentials calculated for several hydrides and fluorides were obtained by UHF 3–21, UHF 3–21+G and UHF 3–21++G *ab initio* methods. Quantum chemical calculations show that protonation reactions of the four-atomic hydrides of nitrogen subgroup elements give cations with tetrahedron geometry. Protonation reaction of molecules of the boron subgroup elements follow form with undefined structure.

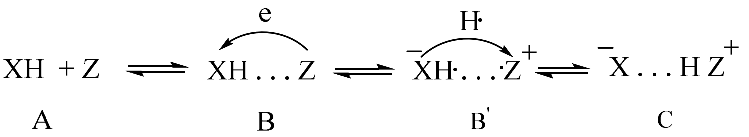
Key words: proton transfer, acid-base system, intermolecular hydrogen bond, electron transfer, ionization potentials, electron affinity.

There is generally known, the elementary proton transfer in acid-base system with intermolecular hydrogen bonds runs in accordance with scheme:



(1)

Here are: XH — H-acid; Z — base; B — molecular complex with hydrogen bond (MCHB) and C — reaction product; salt or ion pair — ionic complex with hydrogen bond (ICHB). But our EPR-investigations have showed that for formation salt C base Z has to the appropriate ionization potential. For example: the stable paramagnetic H-acid semiquinone radical 3,6-di-tert.buthyl-2-oxyphenoxyl (I) is formed with the very strong proton-acceptor as hexametapol only MCHB. The ionic pair C or ICHB is generated by addition donors of electron: alkaline metals, amines to I — hexametapol mixture. On the basis of available data and acid-base theory of M.I. Usanovitch may be suppose the next alternative scheme of the proton transfer reaction [1, 2]:



(2)

In according to this scheme (2) the quantum transfer of electron from base molecule to acid provokes the fast decoupling and transfer of hydrogen atom and formation ICHB C.

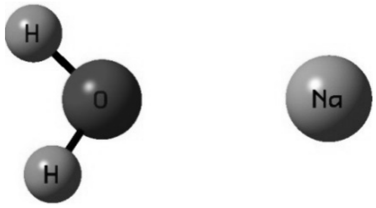


Figure 1. Calculating model for water-sodium system
corresponding to reactionary atom-molecular distance R_{ONa} = 2,4 Å

The MO-computing of the potential curve for simple acid-base model system as H_2O — Na, presented on Figure 1, shows the accurate division of charge in reaction. The separate MO-calculations of dissociation for different particles type of $^{-}XH^{\cdot}$and HZ^{+} demonstrated the energy profitability of homolytic decoupling of hydrogen atoms. This data were early obtained by us with using semi-empirical UHF PM3 method of quantum chemical program package MOPAC 7 presented on Figure 2 [3]. The artifact of this calculating method is the demonstration of one-electron giving of sodium atom to water molecule begins already at large distance between reactants more than R_{ONa} = 5Å. This quantum chemical data show that such properties of molecules as ionization potentials are the fundamental parameters ruling the direction of passing for red-ox or acid-base chemical reactions.

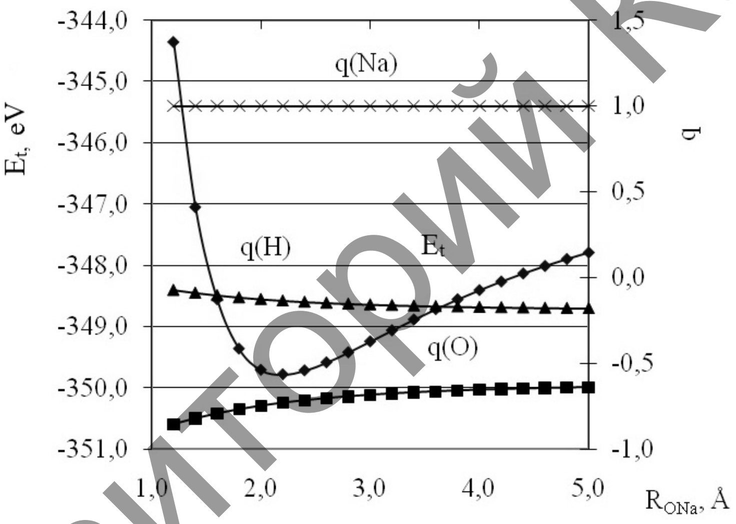


Figure 2. Dependencies of total energy and charges on reference atoms for acid-base reaction
between sodium atom and water molecule, obtained by UHF AM1 quantum chemical method

In this work we investigated the values of ionization potentials for a certain simple molecules with known Brönsted — Lewis acid and base properties by using ab initio calculating methods of quantum chemical program package «Gaussian-2009» [4]. The counting parameters of adiabatic (IP_a) and vertical (IP_v) ionization potentials presented in Table 1. You see here the values of molecular electron affinities obtained also by UHF 3–21G non-empirical methods. It was interested to analyse the changes of these physical parameters and protonation specificities under transition from molecules of simple Brönsted bases to Lewis acids.

For counting of adiabatic ionization potential values of the molecules (M) the known formula was used:

$$IP_a = E_t(M) - E_t(M^+), \tag{3}$$

where $E_t(M)$ is the full optimized value of total energy for molecule M, obtained by mentioned *ab initio* quantum chemical method and $E_t(M^+)$ is the analogous parameters for this ionized molecule. Calculation of vertical ionization potentials is carried out without optimization of total energy of cation M^+.

The expression for determination of electron affinity values has the next form:

$$EA = E_t(M) - E_t(M^-). \tag{4}$$

Here $E_t(M^-)$ is the quantum-chemical optimized value of total energy for corresponding anion.

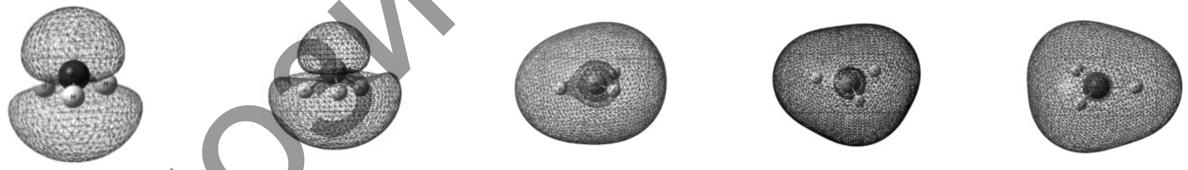
Table 1

The values of ionization potentials for several hydrides and fluorides obtained by UHF 3–21 *ab initio* method

Molecule	IP-a, eV	IP-v, eV	EA, eV
Subgroup of nitrogen			
NH_3	–8,053123362	–8,735889041	–6,541158517
PH_3	–8,713114230	–8,350384801	–3,596868282
AsH_3	–6,990082772	–6,967110130	–1,924056298
SbH_3	–6,556301450	–6,548478273	–0,930385627
NF_3	–12,42701180	–11,60640836	–0,375076602
PF_3	–8,426575135	–8,167906843	2,463388614
AsF_3	–8,497538045	–8,754888187	1,950047568
SbF_3	–8,288269057	–8,431184304	1,918899080
Subgroup of boron			
BH_3	–11,58105657	–12,69066778	–1,408854495
AlH_3	–9,262907927	–10,78132855	–0,520527191
GaH_3	–9,635543068	–10,61045814	–0,551374986
InH_3	–	–9,801563752	–0,331320794
BF_3	–16,54787898	–16,40642148	–3,763387490
AlF_3	–12,37690471	–14,66207541	–1,901988455
GaF_3	–12,01797489	–12,45765061	–1,437478526
InF_3	–	–	–0,575937626

It is known that derivatives of nitrogen subgroup elements have Brönsted basicity connected with proton-accepted properties of the lone-electron pairs of corresponding atoms. Compounds of boron subgroup elements own the Lewis acids nature and are the strong oxidizers. It was interested to see the influence of existence or absence of lone-electron pairs in investigated model acid-base molecules on character their redox properties and protonations.

The calculated values of ionization potentials and electron affinities presented in Table 1 show that they for all molecules vary depending on central atomic radius and decrease with growth of the molecular mass values of concerned compounds. This data demonstrate also that presented in Table 1 four-atomic Lewis acid molecules have more large values of ionization potentials then analogous Brönsted bases — four-atomic compounds of nitrogen subgroup elements.

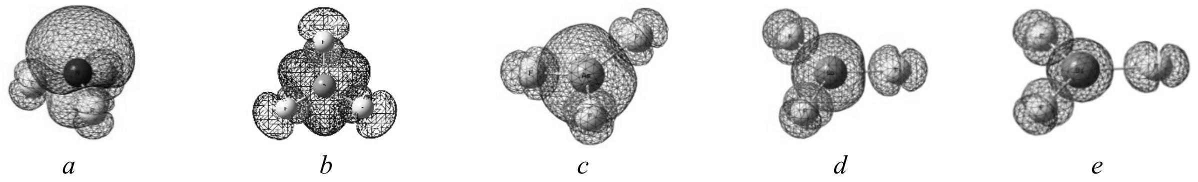


a *b* *c* *d* *e*

a — NH_3; *b* — PH_3; *c* — AsH_3; *d* — SbH_3; *e* — BiH_3

Figure 3. The electronic structure of HOMO of the molecules, obtained by UHF 3–21G *ab initio* method

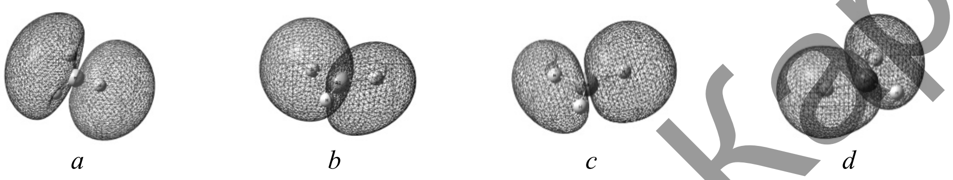
The Figure 3 illustrates the spatial structure and wave function of higher occupied molecular orbital (HOMO) with lone-electron pairs for hydrides of nitrogen subgroup elements. We can see that if molecules of ammonia and phosphine have pyramidal structure while the molecules of arsinestibine and bismuthine are plane triangle. The disappearance of lone-electron pairs in these molecules is determined by property of As-, Sb- and Bi-atoms which valence s-electron promote to higher-level p- and d-orbitals and make their hydrides structural like to analogous molecules of boron subgroup elements [5]. It is interesting to note that all fluorides of these compounds have planar structure except the nitrogen derivative (see Fig. 4).



a — NF_3; *b* — PF_3; *c* — AsF_3; *d* — SbF_3; *e* — BiF_3

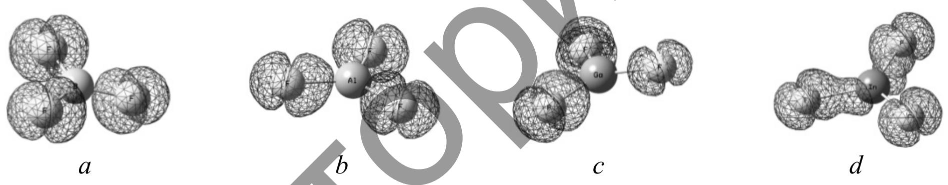
Figure 4. The electronic structure of HOMO of the fluorides of nitrogen subgroup element, obtained by UHF 3–21G *ab initio* method

The data of Table 1 show that the values of ionization potentials for boron subgroup element hydrides and fluorides larger then for analogous compounds of nitrogen subgroup elements. The Figures 5 and 6 show that all of these molecules have planar geometric structure since their central atoms have not lone-electron pairs as correspondent compounds of nitrogen subgroup elements.



a — BH_3; *b* — AlH_3; *c* — GaH_3; *d* — InH_3

Figure 5. The electronic structure of HOMO of the hydrides of boron subgroup elements, obtained by UHF 3–21G *ab initio* method



a — BF_3; *b* — AlF_3; *c* — GaF_3; *d* — InF_3

Figure 6. The electronic structure of HOMO of the fluorides of boron subgroup elements, obtained by UHF 3–21G *ab initio* method

It is known the free proton is most strong H-acid and our quantum chemical calculations show that protonation reactions of all represented in Table 1 the four-atomic hydrides of the nitrogen subgroup elements give cations with tetrahedron geometry. Protonation reaction of analogous molecules of boron subgroup elements follow form with undefined structure. The such effect obtained in the investigated molecules of the fluorides.

In the Tables 2 and 3 similar parameters for above shown molecules are presented but obtained by UHF *ab initio* method with accounting of diffuse functions in basis sets 3–21+G and 3–21++G of quantum chemical calculations [4].

Table 2

The values of ionization potentials for several hydrides and fluorides obtained by UHF 3–21+G *ab initio* method

Molecule	IP-a, eV	IP-v, eV	EA, eV
1	2	3	4
Subgroup of nitrogen			
NH_3	–8,500638036	–9,129992274	–2,971613532
PH_3	–8,581889802	–8,276219311	–1,665882720
AsH_3	–7,192469029	–7,164029223	–1,328474329

1	2	3	4
SbH_3	–	–	–
NF_3	–12,58624445	–12,02901834	–
PF_3	–12,63763350	–11,56198259	0,437208129
AsF_3	–10,37844455	–10,28899761	4,093003997
SbF_3	–	–	–
Subgroup of boron			
BH_3	–11,29320096	–12,57223680	–0,739783799
AlH_3	–	–10,82773099	–0,246205740
GaH_3	–9,203207520	–10,77361912	–0,212760287
InH_3	–	–	–
BF_3	–17,07865230	–17,08566565	–1,719291713
AlF_3	–16,07819768	–15,79191629	0,065521054
GaF_3	–12,46018976	–13,61590734	0,665290405
InF_3	–	–	–

Table 3

The values of ionization potentials for several hydrides and fluorides obtained by UHF 3–21++G *ab initio* method

Molecule	IP-a, eV	IP-v, eV	EA, eV
Subgroup of nitrogen			
NH_3	–8,495280265	–9,128818348	–1,19460462
PH_3	–8,578321493	–8,271293395	–1,07699436
AsH_3	–7,178162592	–7,147352349	–1,26907407
SbH_3	–	–	–
NF_3	–12,58624445	–12,02901834	–
PF_3	–12,63763350	–11,56198259	0,437208129
AsF_3	–10,37844455	–10,28899761	4,093003997
SbF_3	–	–	–
Subgroup of boron			
BH_3	–11,28893222	–12,56792125	–0,73660979
AlH_3	–	–10,81909935	–0,23378237
GaH_3	–9,806925877	–10,76245294	–0,19892543
InH_3	–	–	–
BF_3	–17,07865230	–17,08566565	–1,719291710
AlF_3	–16,07819768	–15,79191629	0,065521054
GaF_3	–12,46018976	–13,61590734	0,665290405
InF_3	–	–	–

The mark «–» in the Tables 1–3 means impossibility of calculations connected with quantum chemical instability of corresponding ionic structures indicated in formulas 3 and 4.

In summary we can say that the presented in this work quantum chemical data, that described such physical molecules property as ionization potential are the most principal parameters which determine their basic or acid behavior in correspondent bimolecular reactions. As a rule the molecules of bases have more less values of ionization potentials then acids molecules and they can lose our one electron, for example, in the first elementary step of protolytic reaction with acids molecule, which will play here the role of oxidizing agent.

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Квантты-химиялық әдістермен кішігірім молекулалардың қышқыл-негіздік қасиеттерін зерттеу

Мақалада *ab-initio* әдісімен UHF жуықтауының 3–21, UHF 3–21^{+} және UHF 3–21^{++} базистерінде кейбір гидридтер мен фторидтердің иондану потенциалы есептелді. Квантты-химиялық есептеулер азот топшасының элементтері протондау кезінде тетраэдрлік геометриялы гидрид-катиондар беретіндігін көрсетті. Бор топшасының элементтері протондау кезінде нақты құрылысы жоқ молекулалар түзетіндігі анықталды.

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Исследование кислотно-основных свойств некоторых небольших молекул квантово-химическими методами

Ab-initio методом в приближении UHF с базисами 3–21, UHF 3–21^{+} и UHF 3–21^{++} рассчитаны значения потенциалов ионизации для некоторых гидридов и фторидов. Квантово-химические расчеты показывают, что реакции протонирования элементов подгруппы азота дают гидрид-катионы с тетраэдрической геометрией. Реакция протонирования элементов подгруппы бора приводит к образованию молекул с неопределенной структурой.

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