Russian Chemical Reviews

June 1987

Translated from *Uspekhi Khimii*, **56**, 889-910 (1987)

U.D.C. 541.49;539.194,196

The Electronic Structure of Superhalogens and Superalkalies

G.L.Gutsev and A.I.Boldyrev

Molecular systems with anomalous values of the first ionisation ptoentials or electron affinity have been examined. On the basis of the results of calculations by the DV-X_α method it has been possible to relate the values of the electron affinity and the first ionisation potential to the characteristic features of the electronic structure of these compounds. The analysis carried out has made it possible to distinguish two large classes of chemical compound: with an anomalously high electron affinity (superhalogens) and with anomalously low first ionisation potentials (superalkalies). Estimates of the maximum possible electron affinity of chemical compounds have been given, and ways of finding these systems have been outlined. Various possible manifestations of high electron affinity and low first ionisation potentials in the physicochemical properties of superhalogens and superalkalies have been examined.
The bibliography contains 133 references.

CONTENTS

I.	Introduction	519
II.	Electron affinity	520
III.	Electronic structure of superhalogens	521
IV.	Electronic structure of superalkalies	528

I. INTRODUCTION

Molecular systems exhibiting extremal characteristics are of particular interest from both theoretical and practical viewpoints. The theoretical study of these systems facilitates the appearance of new fundamental ideas on the physicochemical properties of matter, and the use of these systems in technology extends considerably the range of constructional materials.

The electron affinity (EA) and the first ionisation potential (IP) are the most important characteristics of molecules, so that molecules exhibiting the maximum values of the EA or the minimum values of the IP are of particular interest for chemistry. Systems with high EA play an important role in the synthesis of compounds of new classes. For example, the synthesis of the compound $Xe^+[PtF_6]^-$,[1,2] with which the chemistry of the noble gases began, was carried out using platinum hexafluoride PtF_6, which has a high EA. Subsequently, systems with high EA have been used to synthesise many new compounds, such as $XeF^+[RuF_6]^-$, $XeF_5^+[RuF_6]^-$,[3] $Xe_2F_3^+[AsF_6]^-$,[4] $KrF^+[SbF_6]^-$,[5] and many others,[6-12] and also compounds containing clusters of non-transition elements of the type Te_4^{2+}, Bi_5^{3+}, and S_8^{2+} as cations.[13]

Systems with high EA have recently been used as a basis for the synthesis of organic superconductors,[14-20] and also to modify the electronic structure of conjugated polymers (polymer doping) [21-25] and graphite (intercalation of graphite).[26] Systems with low first IP are also important for preparing new compounds, and the first salts of this type, $Li_3O^+[NO]^-$ and $Li_3O^+[NO_2]^-$ have already been synthesised.[27-29]

The anomalous EA and IP values are apparently related to the characteristic features of the electronic structure of the chemical compounds, so that it is of undoubted interest

to study the electronic structure of molecular systems exhibiting anomalously high EA values and anomalously low IP values. This problem is dealt with in the present review.

II. ELECTRON AFFINITY

The electron affinity of a molecule or radical is defined as the decrease in the energy of the system when one electron is added. For molecules it is possible to distinguish two types of EA: adiabatic and vertical. The adiabatic EA of a neutral molecule is the difference between the total energies of the neutral system for its equilibrium geometry (R_e) and the negatively charged system, again for the equilibrium geometry (R_e^-):

$$EA_{ad} = E(R_e) - E^-(R_e^-) \quad (1)$$

The vertical EA is the difference between the total energies of the neutral and charged systems for the equilibrium geometry of the neutral system (R_e):

$$EA_{vert} = E(R_e) - E^-(R_e) \quad (2)$$

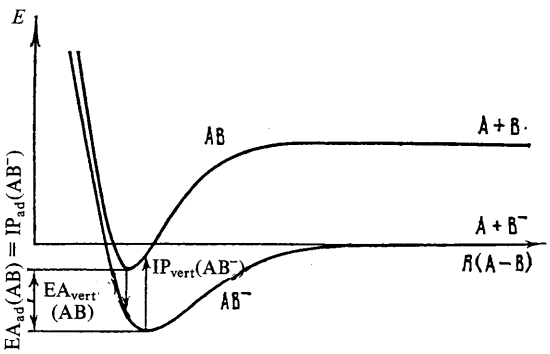


Figure 1. Diagram illustrating the definition of adiabatic and vertical EA and IP for the case of a diatomic molecule AB (R is the distance between the atoms A and B).

Moreover, for a negatively charged system it is possible to define the upper ionisation potential (IP), which also may be vertical and adiabatic. The adiabatic IP of a negative ion is equal to the difference between the total energies of the neutral system for its equilibrium geometry and the negatively charged ion for its equilibrium geometry:

$$IP_{ad} = -[E^-(R_e^-) - E(R_e)] \quad (3)$$

Eqn.(3) shows that the adiabatic IP of a negative ion coincides exactly with the adiabatic EA of the neutral molecule. The vertical IP is equal to the difference between the total energies of the charged system and the neutral system for the equilibrium geometry of the ion:

$$IP_{vert} = -[E^-(R_e^-) - E(R_e^-)] \quad (4)$$

The vertical IP of a negative ion differs from the vertical EA of the neutral system. The difference between the vertical and adiabatic values of the EA and IP is called the adiabatic correction.

$$EA_{ad} = EA_{vert} + \Delta EA_{ad}$$
$$IP_{ad} = IP_{vert} + \Delta IP_{ad} \quad (5)$$

These definitions of the EA and IP are illustrated graphically in Fig.1.

It should be emphasised that in practice, all three experimental values of EA_{ad}, EA_{vert}, and IP_{vert} are not known simultaneously for any system. The values are equal to within the adiabatic corrections, however, so that is is necessary to consider in more detail the estimation of the values of these corrections. An analysis of the experimental photoelectron spectra of the molecules SF_6, C_6H_6, MoF_6, WF_6, and UF_6 [30] showed that ΔIP_{ad} is generally small (usually 0.1–0.2 eV) and does not exceed 0.5 eV. The experimental photoelectron spectra of BrF_5 and IF_5 [31] also indicate that the difference between IP_{ad} and IP_{vert} is small (0.4–0.6 eV).

The low values of the adiabatic corrections for these molecules are related to the fact that the electron is removed from non-bonding molecular orbitals (MO). Approximately the same ΔEA_{ad} values should be expected in those cases where the additional electron occupies a non-bonding MO. In those cases where the electron enters an antibonding MO, however, the value of the adiabatic correction may reach 1.5–3 eV. According to non-empirical calculations of the electronic structure of the SF_6 molecule and the SF_6^- anion, allowance for geometric relaxation in the bond lengths of the SF_6 molecule leads to an increase in the EA by 2.5 eV.[32] Calculations of the EA of the molecules PF_5, AsF_5, and SbF_5 by the present authors show that for these molecules, $\Delta EA_{ad} \cong 2.8$ eV, and that the negative ion has a square pyramidal structure, whereas the neutral molecule has a trigonal bipyramidal structure.

Thus in the case where the additional electron occupies a non-bonding MO, the adiabatic correction is small (~0.5 eV). If the treatment is restricted to an error of 0.5 eV (this can be done in those cases where the EA value is small), then to determine the EA it is sufficient to know one of the quantities EA_{ad}, EA_{vert}, or IP_{vert}. In this approximation, the problem of calculating the EA is simplified considerably, since it is possible to replace the geometry of the radicals, which is often unknown, by the geometry of negative ions with closed shells, which is known from crystallographic data for corresponding salts.

Thus for systems of the type being discussed, it is possible to distinguish two levels of the study of EA. The first level corresponds to a crude estimate of the EA, when the difference between the values of EA_{ad}, EA_{vert}, and IP_{vert} is neglected. At this level, the errors in the estimation of the EA may reach 0.5–1.0 eV. At the second level, it is necessary to take account of ΔEA_{ad} and ΔIP_{ad}, and in the comparison with the experimentally determined values it is necessary to take account of the conditions under which the experiment was carried out. At the second level, the errors should not exceed 0.1–0.2 eV. At present, it is apparently possible to reach the second level of the determination of electron affinity for small radicals, but for most systems, existing theoretical methods make it necessary to restrict the treatment to the first level.

When the additional electron occupies an antibonding MO, all three quantities (EA_{ad}, EA_{vert}, and IP_{vert}) may differ considerably, and they must be examined separately.

A large number of methods are used for the experimental determination of the EA: photo-ionisation,[33,34] surface ionisation,[35,36] fragmentation by electron impact,[34] molecular photodissociation,[34] equilibrium sublimation,[37] radiative addition of an electron,[37] measurement of crystal lattice energies,[37] charge-transfer reactions,[38,39] photosensitive ionisation,[34] and others.[40,41] The greatest experimental success[34,40] has been achieved by the laser photo-ionisation of negatively charged systems, but it is applicable only to substances

which can be obtained in the gas phase in a sufficient concentration. In spite of the wide range of experimental methods, the results of the determination of the EA in early studies often do not agree with one another. For example, for the NO_2 radical the experimentally determined EA values lie in the range 1.6–4.0 eV; according to some authors, $EA(NO_2) > 3.613$ eV, and according to others, $EA(NO_2) < 3.063$ eV.[38,39]

An alternative method of estimating EA is provided by quantum-chemical calculations. One of the most important aims of both experimental and theoretical studies of EA is undoubtedly the search for simple models which would make it possible to predict qualitatively whether an EA has a high or a low value. The study of systems having anomalously high EA is of particular interest.

The direct calculation of EA is a difficult problem in quantum chemistry. The use of Koopmans' theorem[42] or the ΔSCF procedure[43] to estimate EA gives values which often differ from the experimental values by 2–3 eV.[44] The use of non-empirical methods with allowance for correlation[44–49] makes it possible to calculate EA with an accuracy of 0.1 to 0.2 eV, but their application at present is restricted to small molecules.

X_α methods, which make it possible to examine comparatively large systems, have recently begun to be used for EA calculations.[44]

Calculations of the electronic structure of a large number of molecules by X_α methods show that these methods are very effective for large systems and practically always ensure the correct order of magnitude of the calculated IP values with comparatively small deviations from the experimental IP values. The X_α calculation procedure has been described in sufficient detail,[44,50–55] and will not be described in the present work.

Among the elements of the periodic system, halogen atoms have the highest EA (3.0–3.6 eV). In molecules and polyatomic radicals, as a result of collective effects, the EA may be higher than the EA of the halogens. These systems are called superhalogens.

III. ELECTRONIC STRUCTURE OF SUPERHALOGENS

In the examination of systems with anomalously high EA values, two problems arise. Firstly, it is necessary to outline the range of molecules which can be regarded as superhalogens. Secondly, it is necessary to determine the highest EA values that molecular systems in general can have, and also the specific cases in which maximum EA values can be expected.

Simple qualitative ideas relating the EA value to the characteristics of the electronic structures of chemical compounds have been formulated.[56–58] These ideas make it possible to distinguish a class of compound with high EA; the arguments on which they are based will be discussed in detail below.

For the development of models it is natural to use the orbital approach, which is widely employed to interpret electronic, photoelectron, and X-ray electron spectra, and which also forms the basis of the Woodward–Hoffman rules, according to which the energies of the MO formed by AO of the same type should lie in the following order: ε(bonding) > ε(non-bonding) > ε(antibonding). Thus the value of the EA can be related to the structure of the lowest unoccupied MO (LUMO) of the neutral system, which generally accepts the additional electron on formation of an anion, and the value of the first IP of the anion can be related to the structure of its highest occupied MO (HOMO). This gives the corresponding order: IP(bonding) > IP(non-bonding) > IP(antibonding), that is the EA value depends on the type of HOMO of the anion.

A second important factor influencing the magnitude of the EA of a molecule is the value of the EA of the atoms making up the molecule. The higher the EA of the atoms, the higher may be the EA of the compound as a whole. It is therefore possible to have cases where, in spite of the antibonding character of the HOMO of the anion, and as a result of the high EA of the atoms making up the molecule, the EA of the whole molecule will be greater than that of a molecule for which the HOMO of the anion is non-bonding or even antibonding, but in which the values of the EA of the individual atoms are low.

A third important factor influencing the value of the EA of a molecule is the degree of delocalisation of the "additional" electron. According to traditional ideas,[59] the smaller the fraction of an electron $\delta\bar{e}$, added to an atom, the easier it is for the atom to retain it. In the limiting case, when $\delta\bar{e} \to 0$, the IP of the anion approaches the IP of the neutral molecule, which is fairly high. Thus the EA should increase with increase in the extent of the delocalisation of the electron over an increasing number of electronegative atoms making up the molecule.

Calculations by the present authors for the model system $F + \delta\bar{e}$, where $\delta\bar{e} = 0.1, 0.2, \ldots 1.0$ show that the ratio $[E(F + \delta\bar{e}) - E(F^-)]/\delta\bar{e}$, where E is the total energy, increases with decrease in $\delta\bar{e}$. The greatest contribution to the difference in the energies is made by the energies of attraction to the nucleus and interelectron repulsion, and the contributions from the kinetic and exchange energies are small. The electron affinity of the F atom is determined by the energy of the HOMO of the anion, which in turn is determined by the overall potential. Increase in $\delta\bar{e}$ is accompanied by an increase in the shielding of the nucleus, that is the effective charge of the nucleus decreases, leading to a decrease in the energy of the level determining the EA.

In addition to these basic factors, the value of the EA is also influenced by various other specific factors, which will be discussed below. The above three factors are sufficient, however, to formulate the conditions which must be satisfied by systems with anomalous EA or IP values. These limiting cases and the possible consequences of anomalous IP and EA values for chemistry will be discussed in detail below.

The ideas presented above can be applied first to molecules and radicals of the type MX_k. For the EA of these systems to be high, it is necessary that the ligands X be electronegative atoms with high EA, for example halogen or oxygen atoms. Moreover, it is desirable that the HOMO of the corresponding anion be bonding. If however the ligands are halogen or oxygen atoms (and in general if the ligand atoms have many electrons), the HOMO of the compounds are either non-bonding or antibonding. When the HOMO is non-bonding, the EA of the compound MX_k will be greater than the EA of the ligand atoms X as a consequence of the high EA of the atoms and the effect of charge delocalisation.

It should be noted that in those cases where the HOMO, from its symmetry, is antibonding, but the actual contribution of the central M to this orbital is very small (that is, it is essentially non-bonding), high EA can be expected for MX_k. An additional reason for the appearance of high EA values is observed in compounds MX_k where the ligands X are halogen or oxygen atoms and the central atom M has a positive charge which ensures additional stabilisation of the electron delocalised over the ligands. Calculations carried out[56] for a system consisting of an F^- ion with a point positive charge, separated from the F^- nucleus by 3.0 a.u., showed that increase in the point charge by +0.1 e increases the EA of the F atom by ~1 eV. Thus the greater the charge on the M atom, the greater may be the EA.

The above ideas on the relationship between the magnitude of the EA and the electronic structure of a compound can be presented in the language of localised MO. If in an ion MX_k^- with electronegative ligands the central atom does not have lone pairs of electrons (LPE), while the radical MX_k does not contain unpaired electrons localised on the M atom, and all the valence electrons are distributed among the localised MO of the bonds and the LPE of the ligands X, the additional electron will be delocalised over the electronegative ligands, and the first IP of the ion MX_k^- should be high. On the other hand, if the central atom of the anion has LPE (or unpaired electrons) and these electrons are involved in the ionisation, then as a consequence of the low EA of the M atom, the first IP of the MX_k^- ion will be comparatively low.

The influence of the additional electron on the electronic and geometric structure of a molecule MX_k depends on whether the M atom is a transition or non-transition element. In compounds MX_k, where k is the maximum valence of the M atom, the additional electron is generally accepted by an antibonding MO. If M is a non-transition atom, the ion MX_k^- is deformed in such a way that this electron becomes part of an LPE of the M atom (or in the case of radicals becomes the unpaired electron of the M atom). For example, if an electron is added to the linear BeF_2 molecule, the electron occupies an antibonding MO, and the BeF_2^- ion undergoes an angular deformation,[60] which decreases the antibonding action of this MO. In this case the additional electron becomes an unpaired electron of the Be atom.

In contrast to this, the geometry of the molecules and radicals of transition metals generally does not change when antibonding HOMO are filled with electrons. For example, in the series of hexafluorides from ReF_6^- to AuF_6^-, the antibonding HOMO $4t_{2g}$ is filled successively, but the geometry of the molecules remains octahedral.[61–63]

It is therefore appropriate to examine the systems MX_k separately for the cases where M is a non-transition element and where M is a transition metal.

1. Superhalogens Containing *sp*-Elements

According to the above ideas, in systems MX_k where k is smaller than or equal to the maximum valence of the atom M, an additional electron is accepted either by an antibonding MO or by a non-bonding MO of the central atom (that is forms part of an LPE of the M atom). In both cases the EA of the entire molecule or radical is low, because of the low EA of the M atom. The results of *ab initio* calculations with allowance for correlation[44,64,65] and experimental data[66,67] confirm this conclusion. On the other hand, in radicals of the type MX_{k+1}, where k is the maximum valence of the M atom, an additional electron enters a non-bonding MO of the ligands, to which the AO of the central atom does not contribute for symmetry reasons, and the delocalisation of this electron over ligands with high EA leads to a high EA for the radical.

According to calculations of the electronic structure of the radicals BeF_3, BF_4, MgF_3, AlF_4, SiF_5, PF_6 [56–58] and $BeCl_3$, BCl_4, $MgCl_3$, $AlCl_4$, $SiCl_5$, PCl_6 [68,69] by the discrete variation (DV) X_α method, the EA of these radicals is greater than 3.5 eV, and they can all be described as superhalogens. The same is true of systems $MX_{(k+1)/2}$, where X is a divalent oxygen atom, and k the maximum valence of the atom M. Estimates based on calculations of the electronic structure of the radicals BO_2, NO_3, AlO_2, PO_3, and ClO_4 [56–58] indicate that the EA of these systems are greater than 3.5 eV. Thus radicals of this type can also be described as superhalogens.

To emphasise the importance of high ligand EA values for the production of high EA in compounds MX_{k+1}, radicals whose HOMO are bonding can be considered. It might seem that in this case the ionisation potential from the HOMO of the anions MH_{k+1}^- should be fairly high; however, the estimated values of the first IP according to Koopmans (which, judging overall, are 1.0–1.5 eV too high) for BeH_3^-, BH_4^-, MgH_3^-, and AlH_4^- [70,71] are lower than those for the corresponding ions MF_{k+1}^-,[71,72] whose HOMO are non-bonding. The reason for this is evidently the low EA of the H atom.

It is thus possible to outline the range of molecules containing *sp*-elements which must undoubtedly be classified as superhalogens. These are radicals of the type MX_{k+1} where X is a halogen atom, and of the type $MX_{(k+1)/2}$, where X is an oxygen atom. Various other individual molecules can of course have fairly high EA. Examples are provided by the compounds $SeHal_6$ and $TeHal_6$,[73–75] which are of the type MX_k, where k is the maximum valence of the M atom. The additional electron in the ions MX_k^- occupies an antibonding HOMO, and the EA of the MX_k molecules should be low. This is the case, for example, for SF_6, whose EA is only 0.5–0.7 eV.[41,66] For SeF_6 and TeF_6, however, the EA is nevertheless fairly high (3.0 ± 0.2 eV and 3.34 ± 0.2 eV respectively).[76] This is related to the high polarity of the Se–F and Te–F bonds, as a consequence of which, although the HOMO have antibonding character with respect to the central atom–ligand interaction, the actual contribution to these MO from the AO of the central M atom is very small. In fact, the LUMO of SeF_6 and TeF_6 are non-bonding ligand MO, and this leads to high EA values for these molecules. It may be noted that the ions SeF_6^- and TeF_6^-, like the "metallic" octahedra MoF_6^- and WF_6^-, in which the additional electron again occupies antibonding HOMO, preserve the octahedral configurations.[77,78]

The difference in the EA values in the series of valence-isoelectronic molecules SF_6–SeF_6–TeF_6 has a marked influence on their chemical properties. Thus SF_6, which has a low EA, is stable in the gas phase, whereas SeF_6 and TeF_6, which have high EA, are not detected in the gas phase. On the other hand, the $SeCl_6^{2-}$ and $TeCl_6^{2-}$ anions form stable crystalline salts, whereas the corresponding salts with the SCl_6^{2-} anion have not been obtained.

In addition to SeF_6 and TeF_6, other molecules of the type MX_k, where M represents atoms of IV, V, and subsequent periods, may have fairly high EA. For example, the adiabatic EA, calculated by the DV-X_α method by the present authors, are 0.7 eV and 2.5 eV for the molecules PF_5 and SbF_5 respectively, and for AsF_5 the values lie in the range 1.9–2.9 eV. These are much lower than the values obtained from thermochemical data:[26] ~3.5 eV for PF_5, ≥5.3 eV for AsF_5, and ≥6.4 eV for SbF_5. The values given in Ref. 26 are apparently far too high. Further experimental studies of the EA of pentafluorides by up-to-date physical methods are required.

The EA of superhalogens of the type MX_{k+1} should increase with increase in k as a consequence of the delocalisation of the additional electron over a larger number of ligands. Thus in the series MgF_3 (~3.8 eV) < AlF_4 (~6.1 eV) < SiF_5 (~6.3 eV) < PF_6 (~6.6 eV) and AlO_2 (~3.4 eV) < PO_3 (~4.4 eV) < ClO_4 (~6.3 eV), the EA increases from 3.8 eV to 6.6 eV in the first case and from 3.4 eV to 6.3 eV in the second.[44] Extremal EA values should also be expected for MX_k with $k > 6$, but increase in k may also lead to a decrease in the EA. In particular, in the series $MgCl_3$ (~4.5 eV)–$AlCl_4$ (~5.2 eV)–$SiCl_5$ (~4.4 eV)–PCl_6 (~4.0 eV), beginning from $AlCl_4$ the EA decrease as a consequence of the strong repulsion of the ligands.[68,69] This last feature is related to the fact that the HOMO in the ions MX_{k+1}^- is non-bonding

with respect to the central atom–ligand interaction, whereas with respect to the ligand–ligand interaction it has antibonding character. When k is sufficiently large, the mutual repulsion of the ligands predominates over the effect of electron delocalisation, leading to a decrease in the EA. For the optimum values of k, the effect of ligand–ligand antibonding is slight, and does not predominate over the delocalisation of the additional electron, and this leads to an increase in the EA. Of the superhalogens containing sp-elements which have been studied up to the present, the optimum ratio of antibonding and stabilisation is achieved for AsF_6 and SbF_6, which have high EA (~7 eV).[44]

The adiabatic EA is usually understood to be the difference between the total energies of the stable configurations of the anion and the neutral system. Available experimental data[40, 78–81] and the results of non-empirical calculations[82,83] indicate that the isolated anions MF_{k+1}^-, where k is the maximum formal valence of the central atom M, are energetically stable with respect to monomolecular dissociation to MF_k and F^-. Published estimates[78–83] of the energy of this dissociation are fairly high, 80–120 kcal mole^{-1}. At the same time, experimental data[84] indicate that MF_{k+1} radicals either have a very low energy of dissociation to MF_k + F or are generally unstable. It should be noted that the adiabatic EA of a radical can be determined even when it is unstable, since the necessary condition for the existence of EA is the existence of a stable negative ion. In this case the first IP_{vert} of the anion gives the upper limit of the EA_{ad} values of the neutral system.

The low energetic stability of MF_{k+1} radicals compared with the corresponding anions MF_{k+1}^- does not agree with the traditional ideas of the method of molecular orbitals, according to which the stability of a molecular system with respect to monomolecular dissociation should increase if the electron is removed from an antibonding MO, decrease if the electron is removed from a bonding MO, and remain unchanged if the electron is removed from a non-bonding MO. In all anions of the type MF_{k+1}^-, the highest occupied MO is non-bonding with respect to the central atom–ligand interaction, and consists only of ligand AO,[85] so that the removal of an electron from the HOMO of the anion should not lead to significant destabilisation of the resulting radical.

To investigate the reason for this discrepancy between the prediction based on the qualitative concepts of MO theory and available experimental data, the electronic structures of the anions BF_4^- and AlF_4^- and of the corresponding radicals BF_4 and AlF_4 were calculated by the discrete variation X_α method in the present work.

Data on the geometric structure are available only for the anions, and the calculated non-empirical equilibrium bond lengths in the isolated anions,[82] R(B–F) = 1.43 Å and R(Al–F) = 1.72 Å, are close to the corresponding values for the anions in inorganic salts:[86–88] R(B–F) = 1.37–1.39 Å and R(Al–F) = 1.69–1.70 Å. The equilibrium bond lengths in the anions, calculated by the DV-X_α method by the present authors, are R(B–F) = 1.44 Å and R(Al–F) = 1.69 Å, in good agreement with the above values. There are no published data on the geometric structure of the radicals BF_4 and AlF_4, so that their equilibrium bond lengths were optimised by the DV-X_α method assuming that they have a tetrahedral structure. The potential curves have minima in both cases, corresponding to the bond lengths R(B–F) = 1.44 Å and R(Al–F) = 1.69 Å. Thus the calculated bond lengths for the tetrahedral configurations of the radicals and anions practically coincide. The existence of minima on the potential curves of the radicals naturally does not mean that they are energetically stable with respect to monomolecular decomposition. To resolve the question of the stability of the radicals, it is necessary to carry out additional calculations of the total potential surfaces by non-empirical methods with allowance for correlation energy. These calculations cannot be carried out at present, because of the extremely large expenditure of machine time required. Although the present calculations do not make it possible to reach any conclusion about the stability of the radicals MF_{k+1}, they can be used to investigate the reasons for the destabilisation of these radicals.

The removal of an electron from a non-bonding MO of an anion should not in principle lead to destabilisation of the resulting radical if the composition of all the other MO remains unchanged. Since in the case being considered there is appreciable destabilisation of the radicals, it is natural to expect that this is the result of changes in the composition of the bonding MO as a result of electronic relaxation. The nature of the changes in the valence MO can be investigated using the data in Table 1, which gives the composition of these MO for both radicals and anions, for the equilibrium values of the bond lengths.

Table 1. Characteristics of the molecular orbitals of BF_4, BF_4^-, AlF_4, and AlF_4^-; the Mulliken populations of the bonding MO (q), the charges on the atoms (Q), and the overlap populations [Q(M–F)] for BF_4, BF_4^-, AlF_4, and AlF_4^- (in fractions of e).

Parameter	BF_4		BF_4^-		Parameter	AlF_4		AlF_4^-	
	B	ΣF	B	ΣF		Al	ΣF	Al	ΣF
$q(4t_2)$	0.22	5.78	0.26	5.74	$q(5t_2)$	0.37	5.63	0.48	5.52
$q(3t_2)$	1.03	4.97	1.11	4.89	$q(4t_2)$	0.63	5.37	0.72	5.28
$q(4a_1)$	0.39	1.61	0.40	1.60	$q(5a_1)$	0.36	1.64	0.36	1.64
Q_F	−0.23		−0.40		Q_F	−0.28		−0.45	
Q_B	+0.91		+0.61		Q_{Al}	+1.13		+0.78	
Q(B–F)	+0.47		+0.59		Q(Al–F)	+0.51		+0.62	
Q(F–F)	−0.05		−0.07		Q(F–F)	−0.01		−0.01	

It can be seen that the removal of an electron from the HOMO of the anion leads to a decrease in the contribution of the AO of the central atom to the bonding MO by ~0.3 e, and this explains the low stability of the radicals, compared with the corresponding anions. The reasons why ionisation from a non-bonding purely ligand HOMO of the anion leads to this rearrangement of electron density in the resulting radical can be understood on the basis of model representations of superhalogens in which the framework of fluorine atoms in the superhalogens has a high collective electronegativity. Thus if the process of ionisation of the anion is arbitrarily divided into two stages corresponding to the removal of an electron from the HOMO without change in the composition of any of the MO and the subsequent relaxation of the MO, then the loss of an electron by the framework of fluorine atoms in the first stage of the ionisation is partly compensated by the transfer of ~0.3 electron from the central atom.

A similar decrease in the energetic stability of the radicals compared with the corresponding anions should also be observed in all other systems of the type MF_{k+1} and MF_{k+1}^-.

2. Superhalogens Containing Transition Metals

In transition metal compounds of the type MX_k, the filling of antibonding HOMO generally does not lead to distortion of the geometry of highly symmetrical configurations, so that

the behaviour of the EA of these systems may show a number of characteristic features.[89-94] The dependence of the EA on the electronic structure of transition metal hexafluorides can be considered in more detail. It is appropriate to begin the examination with the hexafluorides of the 5*d*-metals, since the characteristic features of the electronic structure are revealed most clearly in this case. Table 2 gives the IP from the valence MO. It can be seen that on going from Hf to Hg there is a change from the filling of a non-bonding purely ligand HOMO of the $1t_{1g}$ type (Hf, Ta) to the filling of an antibonding MO of the $4t_{2g}$ type, antibonding with respect to the central atom–ligand interaction (W–Au) and then to the filling of the next antibonding MO of the $6e_g$ type (Hg).

Table 2. Valence ionisation potentials (eV) of the negative ions of the hexafluorides of metals of the third transition series.[90]

MO	Spin*	HfF_6^-	TaF_6^-	WF_6^-	ReF_6^-	OsF_6^-	IrF_6^-	PtF_6^-	AuF_6^-	HgF_6^-
$6e_g$	—	—	—	—	—	—	—	—	—	4.5
$4t_{2g}$	l	—	—	2.2	3.5	4.7	5.9	6.1	6.8	7.6
	h	—	—	—	—	—	4.5	5.6		7.2
$1t_{1g}$	l	7.5	7.1	7.3	7.1	7.6	7.4	7.2	6.9	7.3
	h	6.8		6.9	6.7	6.6	6.6	6.7		7.0
$9t_{1u}$	l	7.3	7.3	7.7	7.6	7.7	7.9	7.5	7.3	8.0
	h	6.8		7.3	7.2	7.1	7.1	7.1		7.3
$2t_{2u}$	l	8.0	7.5	7.5	7.8	8.0	7.9	7.7	7.4	7.8
	h	7.2		7.3	7.3	7.2	7.1	7.2		7.5
$8t_{1u}$	l	8.3	8.0	8.1	8.4	8.7	8.6	8.5	8.2	9.0
	h	7.5		7.9	7.9	7.9	8.0	8.1		8.5
$8a_{1g}$	l	8.3	8.0	8.1	8.4	8.7	8.6	8.5	8.2	9.0
	h	8.2		8.7	8.7	8.8	8.9	9.0		9.5
$3t_{2g}$	l	9.9	10.1	10.5	11.3	12.1	12.2	12.4	13.4	16.3
	h	9.3		10.0	10.2	10.2	10.9	12.0		15.7
$5e_g$	l	10.3	10.6	11.0	11.5	12.5	12.2	12.5	13.6	17.2
	h	9.9		10.6	10.7	10.9	11.4	12.1		17.0

*The letters l and h denote transitions into the low-spin and high-spin final states of MF_6 respectively.

The data in Table 2 reveal the following characteristic features of the change in the IP from the valence MO in the series being considered. Firstly, it is irregular : the IP decreases sharply on going from TaF_6^- to WF_6^-, after which it increases regularly from WF_6^- to AuF_6^-, and decreases again on going to HgF_6^-. Secondly, the IP of the "ligand" $1t_{1g}$–$8a_{1g}$ MO remain practically unchanged. Thirdly, the IP from the bonding $3t_{2g}$ and $5e_g$ MO increase almost regularly, although the change in their energies on going along the series is smaller than the change in the energies of the 5*d* AO [90,92] of the corresponding central atoms.

The reason for this behaviour of the IP can be understood by analysing the composition and symmetry of the MO. For Hf and Ta hexafluorides, the HOMO is a non-bonding ligand orbital, and the EA of these compounds is high as a consequence of the delocalisation of the additional electron over the six strongly electronegative F atoms, in accordance with the above ideas on the superhalogens containing *sp*-elements. The EA of these two hexafluorides are close to the EA of the most electronegative superhalogens among compounds of the *sp*-elements: AsF_6 and SbF_6. On going to WF_6, the EA decreases, due to the filling by electrons of a HOMO of antibonding type; the energy gap between the nearest $4t_{2g}$ and $1t_{1g}$ MO is ~4 eV. Since the $4t_{2g}$ MO is antibonding, it might have been expected that its subsequent filling would lead to a decrease in the EA in the series being considered. Instead of this, however, there is a regular increase in the EA,[90] which reaches ~7 eV for AuF_6, and the gap between the $4t_{2g}$ and $1t_{1g}$ MO practically disappears.

The composition of the $4t_{2g}$ MO can be analysed in more detail. The nature of this orbital changes in the hexafluoride series[90] from appreciably antibonding (WF_6^-) to non-bonding (AuF_6^-). With decrease in the antibonding, its energy decreases, approaching the energy of the non-bonding MO of the ligands ($1t_{1g}$, $9t_{1u}$, $2t_{2u}$), and the EA for AuF_6 is close to the EA for TaF_6, in which the additional electron occupies a $1t_{1g}$ MO which is purely ligand from symmetry. On going from AuF_6^- to HgF_6^-, the next $6e_g$ MO is filled, accompanied by a decrease in EA, due chiefly to the extensive splitting of the $6e_g$–$4t_{2g}$ orbitals under the influence of the ligand field, since the $6e_g$ MO is essentially a ligand orbital. Thus the contribution of the 5*d* AO to the $6e_g$ MO is ~25%, and practically coincides with the contribution of the 5*d* AO to the $4t_{2g}$ MO of the AuF_6^- anion.[90] At the same time, an increase in the Hg–F overlap population is observed for HgF_6^-, compared with AuF_6^-.

It is of interest to relate the change in the EA in the series of hexafluorides Hf–Hg to the energy of the atomic 5*d* levels. On going along this series, the energy of the 5*d* AO decreases,[90,92] leading to stabilisation of the $3t_{2g}$ and $5e_g$ MO, and these MO are transformed to an increasing extent into non-bonding 5*d* AO. In other words, the 5*d* electrons tend to be localised close to the central atom M, leading to a decrease in the population of the 5*d* AO in the higher orbitals $4t_{2g}$ and $6e_g$ and to the approach of the $4t_{2g}$ MO to the ligand MO. This conclusion is confirmed by the decrease in the overlap population from WF_6^- to AuF_6^- and by its increase on going to HgF_6^-, since in this case the 5*d* electrons, for symmetry reasons, are forced to partly occupy the antibonding $6e_g$ MO.

The principal features of the electronic structure are the same for the hexafluorides of the 4*d* metals and the hexafluorides of the 5*d* metals, but some differences are also observed. Firstly, the block of valence MO of the ligand type for the hexafluorides of the 4*d* metals on the whole lie slightly higher (by 0.3–0.5 eV) than those for the 5*d* metals. This agrees with available experimental data on the IP of the compounds MoF_6 and WF_6,[30] which differ by ~0.3 eV. Moreover, the HOMO of the t_{2g} type for MoF_6^- lies 1.3 eV closer to the block of valence MO than in the case of WF_6^-, as a result of which the EA for MoF_6 is ~1 eV higher. The calculated differences between the IP of the $4t_{2g}$ and $1t_{1g}$ levels for WF_6^- and the IP of the $3t_{2g}$ and $1t_{1g}$ levels for MoF_6^- agree with the difference between the energies of the first optical transitions for the compounds MoF_6 and WF_6 [$\Delta\nu_1(WF_6) - \Delta\nu_1(MoF_6) = 1.33$ eV [95]]. The lower energy of the upper t_{2g} MO in MoF_6^- compared with WF_6^- is related to the lower degree of antibonding character of this MO, and this in turn is due to the higher energy of the 4*d* AO of the Mo atom.[90,92]

With further filling of the HOMO of the t_{2g} type, the degree of antibonding character of this MO in the 4*d* hexafluorides is again lower than in the 5*d* hexafluorides, leading to its more rapid approach to the block of ligand MO. Moreover, for AgF_6^-, where the $3t_{2g}$ HOMO is fully occupied, the energy of this MO is lower than the energies of the purely ligand $1t_{1g}$ and $1t_{2u}$ MO. For AuF_6^-,[90] this inversion of the levels is not observed. The sequence order of the MO in AgF_6^- does not agree with the traditional picture of the energy

sequence for MO of different character (see above): ε(bonding) > ε(non-bonding) > ε(antibonding). This contradiction is eliminated, however, in a more detailed analysis of the nodal structure of the valence MO, represented schematically in Fig. 2. It can be seen that the $3t_{2g}$ MO is an antibonding MO of the π-type with respect to the central atom–ligand interaction, and a bonding MO of the σ-type with respect to the ligand–ligand interaction; the $1t_{1g}$ MO is σ-antibonding and purely ligand from symmetry; and $7t_{1u}$ and $1t_{2u}$ MO are orbitals of the π-type, and the first contains a small contribution from the central atom, whereas the second is a purely ligand antibonding MO.

On going from MoF_6^- to AgF_6^-, the contribution of the M atom to the $3t_{2g}$ MO decreases sharply, and in AgF_6^- the entire block of $3t_{2g}$–$1t_{2u}$ MO can be regarded as purely ligand, and the central atom–ligand interaction can be neglected.[92] In this case, from the ligand–ligand interactions and in accordance with classical ideas, the following sequence of MO energies can be expected: $3t_{2g}$ (bonding MO of the σ-type) > $7t_{1u}$ (antibonding, π-type) > $1t_{2u}$ (antibonding, π-type) > $1t_{1g}$ (antibonding, σ-type). This MO sequence is in fact observed for AgF_6^- and CdF_6^-, that is the electronic structure of the hexafluorides at the end of the 4d metal series is determined by purely ligand interactions.

The principal characteristic features of the change in the EA and IP in the series of 3d metal hexafluorides are on the whole the same as in the series of 4d and 5d metal hexafluorides,[90,92] although they are less clearly defined. In particular, the antibonding HOMO of the $2t_{2g}$ type in CrF_6^- lies only 1.5 eV above the block of purely ligand MO, whereas the corresponding values for the $3t_{2g}$ and $4t_{2g}$ MO in MoF_6^- and WF_6^- are 3.8 eV and 5.1 eV respectively. On further filling of the $2t_{2g}$ MO in the anions of the 3d element hexafluorides, its energy rapidly approaches the energies of the ligand MO, and inversion with respect to the $1t_{1g}$ MO takes place at FeF_6^-, whereas the corresponding inversion of the $3t_{2g}$ and $1t_{1g}$ MO is observed only at the end of the 4d series, for AgF_6^-. This behaviour of the $2t_{2g}$ MO is related to its lower antibonding character, compared with the $3t_{2g}$ MO for the 4d element hexafluorides, resulting from the higher energies of the 3d AO of the atoms in the first transition series. A decrease in the antibonding character of the HOMO of the t_{2g} type with increase in the energy of the atomic d-orbitals was also observed on going from the hexafluorides of the 5d elements to the hexafluorides of the 4d elements, although to a smaller extent than on going from the hexafluorides of the 4d elements to the hexafluorides of the 3d elements. In this connection it should be noted that small changes in the energies of the atomic d-orbitals lead to fairly large changes in the energies of HOMO of the t_{2g} type. The small contribution of the central atom to the HOMO of the hexafluorides of the 3d elements leads to high values (6–7 eV) of the EA for the entire series (with the exception of CrF_6, whose EA is also fairly high, 5.0–5.5 eV).

The above detailed analysis of the relationship between EA and electronic structure shows that the hexafluorides of the d-elements differ significantly from the fluorides of the sp-elements; practically all transition metal hexafluorides (with the possible exception of WF_6) can be regarded as superhalogens. At the same time, the dependence of the value of the EA on the electronic structure in each specific case is fairly complex. Nevertheless, it can be stated that among the hexafluorides of the 4d and 5d metals, the highest EA will be shown by those in which the HOMO is almost completely filled (that is NbF_6, TaF_6, AgF_6, and AuF_6). The hexafluorides of the 3d metals almost all have high EA.[44]

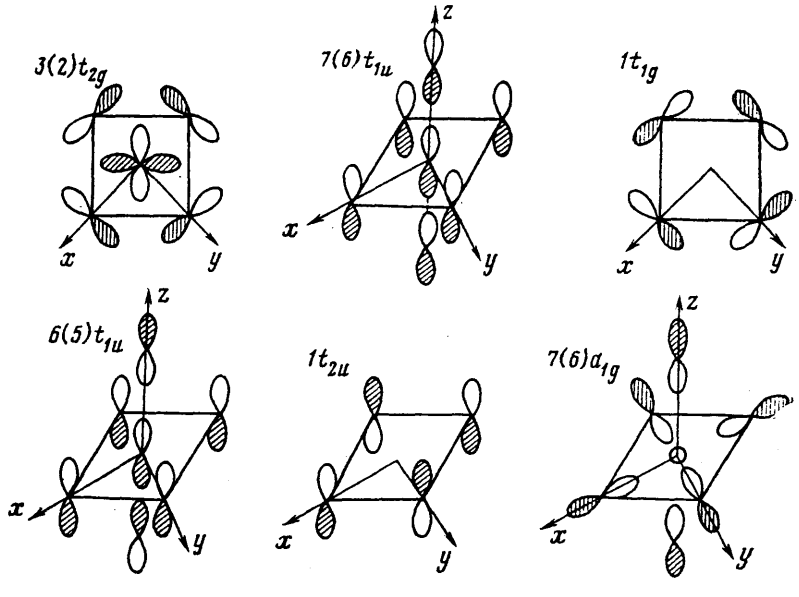


Figure 2. Schematic representation of the highest valence MO of transition metal hexafluorides.[92]

As noted above, in the estimation of EA_{ad} for systems in which the additional electron enters an antibonding MO it is necessary to investigate the dependence of the first IP_{vert} of the anion on the M–F bond length. To investigate this relationship, the electronic structure of the anions CrF_6^- and AgF_6^- has been calculated.[92] The distances R(Cr–F) = 1.75 Å and 1.85 Å and R(Ag–F) = 1.85 Å and 1.98 Å were used in the calculations. The calculations showed that the change in the IP from the HOMO of CrF_6^- does not exceed 0.5 eV, and that from the HOMO of the anion AgF_6^- does not exceed 0.15 eV. It may therefore be expected that for other transition metal hexafluorides, small changes in the interatomic distances will not lead to changes in the EA value exceeding 0.5 eV. The influence of R(M–F) on the EA value is a maximum for the atoms of group VI, since the HOMO of their hexafluorides has the most antibonding character with respect to the central atom–ligand interaction, and decreases in the same sense as the decrease in the antibonding towards the end of the period.

Tetra-anions MX_4^-, where X = F, O, and Cl, are also encountered in salts. It is therefore of interest to study the dependence of the EA of these anions on the characteristic features of their electronic structure. The tetraoxyanions can be considered as an example. The orbital energies of the tetraoxyanions of the 4*d* metals are given in Table 3. The following characteristic features of the change in the IP from the valence MO can be observed on going along the series. Firstly, the change is irregular: the IP value decreases on going from TcO_4^- to RuO_4^-, then increases from RuO_4^- to AgO_4^-, and decreases again on going to CdO_4^-. Secondly, the IP of the block of "ligand" $1t_1$, $8t_2$, and $7a_1$ MO remain practically unchanged on going along the series, like the IP of the $6t_2$ and $6a_1$ orbitals, formed predominantly by the 2*s* orbitals of the O atom. Thirdly, the IP of the bonding $7t_2$ and 2*e* MO increase regularly along the series.

Table 3. One-electron energies (eV) of the valence MO of 4*d*-metal tetraoxyanions.[94]

Anion (configuration)	MoO_4^- ($1t_1^6$)		TcO_4^- (closed)	RuO_4^- ($3e^4$)		RhO_4^{2-} ($3e^4$)		PdO_4^{2-} ($3e^4$)		AgO_4^{3-} (closed)	CdO_4^{4-} ($9t_2^6$)	
Spin	α	β	α=β	α	β	α	β	α	β	α=β	α	β
$9t_2$	—	—	—	—	—	—	—	—	—	—	3.4	—
$3e$	—	—	—	3.1	—	3.8	—	4.1	3.5	4.4	4.4	4.3
$1t_1$	5.6	4.8	4.9	4.8	4.5	5.1	4.2	4.8	4.2	4.7	4.5	4.3
$8t_2$	5.8	5.4	5.5	5.5	5.2	5.7	5.0	5.5	5.1	5.4	5.5	5.0
$7a_1$	6.2	5.8	6.2	6.0	5.8	6.0	5.6	5.8	5.5	5.8	6.3	5.5
$7t_2$	8.3	8.0	8.7	9.0	8.8	9.3	9.2	10.2	10.1	12.4	15.6	15.3
$2e$	8.3	7.9	8.5	9.0	8.7	10.0	9.3	10.7	10.5	13.6	17.8	17.8
$6t_2$	20.9	20.3	20.5	20.4	20.1	20.7	19.9	20.4	20.1	20.4	20.6	20.1
$6a_1$	21.1	20.5	20.6	20.6	20.2	20.7	20.0	20.5	20.1	20.5	21.0	20.6

Overall, the characteristic features of the change in the valence IP in the series of oxyanions are approximately the same as in the hexafluoride series. A difference is that in the tetraoxyanions, a HOMO of the *e* type is filled first, and the filling of the antibonding MO of symmetry t_2 begins from CdO_4^-. Moreover, the actual EA values for the tetra-oxides and their abrupt changes on going to the filling of antibonding MO of the *e* and t_2 types are appreciably smaller than for the hexafluorides. The changes in the upper valence IP on going along the series of 3*d* metal tetraoxyanions are similar to the changes in the upper valence IP in the series of 4*d* metals. As in the case of the hexafluorides of the 3*d* and 4*d* metals, however, the actual EA values for the tetra-oxides of the 3*d* metals are greater, and the abrupt changes on going to the filling of the antibonding MO are smaller, than in the case of the tetra-oxides of the 4*d* metals. On the whole, the EA values for the tetra-oxides are greater (3.5–5.0 eV), and practically all transition metal oxyanions, with the possible exception of RuO_4, can be classified as superhalogens.

A similar analysis of the dependence of the EA on electronic structure can be carried out for pentafluorides MF_5, tetrafluorides MF_4, trifluorides and trioxides MX_3, difluorides and dioxides MX_2, etc. High EA are shown not only by superhalogens of the type MX_{k+1}, where k is the maximum formal valence of the metal and X is a monovalent ligand, but also by systems of the type MX_k if the antibonding HOMO of the corresponding anion is completely or almost completely filled.

3. The Search for Systems with the Maximum Possible Electron Affinity

Theoretical studies of superhalogens and various experimental estimates show that chemical compounds may have very high EA, exceeding the EA of halogen atoms. Two questions naturally arise: what is the maximum EA that superhalogens can have, and among which systems should they be sought? According to the above ideas, these systems should contain as ligands the maximum possible number of fluorine atoms, since the energy of the HOMO of the anions of these systems would approach the energy of the HOMO of neutral fluorides, as a consequence of the delocalisation of the additional electron over a large number of ligands. Thus the value of the first IP of neutral fluorides can be regarded as the upper limit of the maximum possible EA values. According to available experimental data, the first IP in the fluoride series SF_6, WF_6, SiF_6, CF_4,[90] etc. are 15–17 eV, so that the value 17 eV can be taken as the upper limit of EA values for chemical compounds.

Various ways of searching for systems with maximum EA may be noted. One way is to increase the number of ligands in mononuclear systems of the type MF_{k+1}. However, with increase in the number of ligands, beginning from a certain value of k, the effects of destabilisation of the HOMO of the ion MF_{k+1}^- as a result of inter-ligand repulsion may predominate over the stabilising effects of delocalisation, so that further increase in the EA will not take place, as for example in the chlorides of the *sp*-elements examined above. Another possible way to increase the number of ligands is by changing to polynuclear superhalogens, of the type Al_2F_7, Sb_2F_{11}, or in general M_nX_{nk+1}. In these systems, inter-ligand repulsion does not increase with increase in the number of ligands, and as a result of the maximum delocalisation of the electron, the EA of these systems may approach the maximum possible value. These ideas are of course qualitative, and indicate only the trends in the change in the EA, and to obtain quantitative estimates it is necessary to carry out calculations for each specific case.

To follow the trend in the change in the EA with increase in the number of ligands, it is possible to use the results of calculations by the DV-X_α method of the electronic structure of the anions MnF_8^- and TcF_8^- (mononuclear anions of the type MF_{k+1}^-) and $Al_2F_7^-$, $P_2F_{11}^-$, $As_2F_{11}^-$, and $V_2F_{11}^-$ (dinuclear anions of the type $M_2F_{2k+1}^-$).[96,97] The geometric structure of the dinuclear anions is shown in Fig. 3.

In the series of mononuclear anions ScF_4–VF_6–MnF_8, the EA increases sharply on going from ScF_4 (4.8 eV) to VF_6 (6.7 eV), and then remains unchanged on going from MnF_8

(6.7 eV). On going from NbF_6 (6.8 eV) to TcF_8 (5.8 eV), it even decreases. This indicates that the optimum combination of stabilising and destabilising factors to achieve the highest EA values in mononuclear complexes is obtained in the six-coordinate fluorides. Further increase in the number of ligands does not lead to an increase in the EA, because of the increase in the strength of the inter-ligand repulsion. Calculations by the DV-X_α method indicate that the maximum EA in mononuclear complexes (TaF_6 and AuF_6) is 7–8 eV.[90]

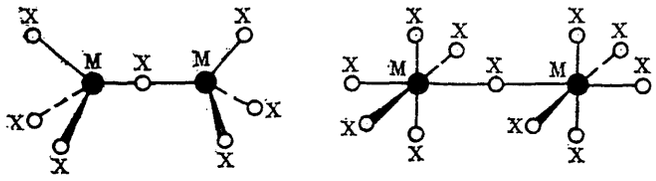


Figure 3. Geometric structure of dinuclear superhalogens.

On going from the mononuclear to the corresponding dinuclear complexes, the EA increases systematically by 1–2 eV. Thus for example the EA values for AlF_4 and Al_2F_7 are 6.1 eV and 7.5 eV, for PF_6 and P_2F_{11} 6.7 eV and 8.6 eV, for AsF_6 and As_2F_{11} 7.2 eV and 8.6 eV, and for VF_6 and V_2F_{11} 6.7 eV and 8.0 eV respectively.[90] Thus the maximum EA for dinuclear systems is apparently 9–10 eV. In particular, these EA values may be shown by the systems Ta_2F_{11} and Au_2F_{11}. Thus the change from mononuclear to polynuclear superhalogens is a promising way of searching for systems with the maximum possible EA values. Polynuclear superhalogens whose EA are more than twice the EA of halogen atoms should rather be called hyperhalogens. They may be used to obtain new classes of salt with non-traditional cations. Stable salts with Ar^+ cations may possibly be obtained using complex polynuclear hyperhalogens.

Table 4. Theoretical estimates of the EA of various superhalogens, obtained by the DV-X_α method*.[44]

Radical	EA, eV	Radical	EA, eV	Radical	EA, eV
BeF_3	4.1 (4.5)	PdF_6	6.1	TcF_8	5.8
MgF_3	3.2 (3.8)	AgF_6	6.4	Al_2F_7	7.5
BF_4	6.2 (6.2)	CdF_6	4.8	P_2F_{11}	8.6
AlF_4	6.1 (6.2)	AsF_6	7.2	As_2F_{11}	8.6
SiF_6	6.4 (6.3)	SbF_6	7.0	V_2F_{11}	8.0
PF_6	6.8 (6.6)	HfF_6	8.8	MoO_4	6.2
TiF_6	7.5	TaF_6	8.4	TcO_4	4.9
VF_6	6.7	$BeCl_3$	4.5 (4.2)	RuO_4	3.1
CrF_6	5.0	BCl_4	4.9 (4.5)	PhO_4	3.8
MnF_6	5.9	$MgCl_3$	4.5 (4.5)	PdO_4	4.7
FeF_6	7.0	$AlCl_4$	5.8 (5.0)	AgO_4	4.4
CoF_6	6.8	$SiCl_6$	4.9 (4.2)	CdO_4	3.4
NiF_6	6.9	PCl_6	4.3 (3.7)	CrO_4	6.1
CuF_6	6.1	SCl_6	3.4	MnO_4	5.0
ZnF_6	5.8	$SeCl_6$	4.3	FeO_4	3.7
ZrF_8	7.1	$TeCl_6$	3.5	CoO_4	5.2
NbF_6	6.8	$SbCl_6$	5.6	NiO_4	4.7
TcF_6	4.3	$AsCl_6$	5.4	CuO_4	4.4
RuF_6	5.2	VF_4	4.8	ZnO_4	3.9
RhF_6	6.1	MnF_6	6.7	HgF_6	5.8

*The values in brackets were calculated in a two-exponent Clementi basis set with the addition of polarisation functions of the central atom.

Finally, Tables 4–6 summarise available theoretical and experimental estimates of the EA of superhalogens.

Table 5. Theoretical and experimental estimates of the EA (eV) of various superhalogens.

Compound	Experimental estimate	Calculation by the DV-X_α method	Calculation by the DV-X_α method; HF (DE) basis set
BO_2	3.6±0.2 [40]	—	4.6 (3.6) [56]
AlO_2	4.1±0.2 [40]	—	3.7 (3.4) [56]
NO_3	3.68±0.20 [66]; 3.77±0.25 [41]	—	4.0 (3.6) [56]
PO_2	4.9 [99]	—	5.3 (4.4) [56]
ClO_4	5.8 [67]; 6.2 [100]	6.9 [98]	6.9 (6.3) [56]
SF_6	0.30 [41]; 0.75 [66]	0.5 [101]; 0.7 [102]	0.3 (0.6) [73]
SeF_6	3.0±0.2 [76]	2.9 [102]	2.1 (3.0) [73]
TeF_6	3.34±0.2 [76]	2.6 [102]	1.2 (2.2) [73]
MoF_6	5.14 [76]; 3.6±0.2 [103]; 5.36±0.06 [104]; 4.5 [105]; 5.77 [106]	4.5—4.8 [101]	3.2 [92]
WF_6	3.51±0.10 [40]; 4.9 [105], 3.7 [107]; 5.1±0.5 [76]; 3.36 [108]; 3.5 [26]	4.5—5.1 [101]	3.5 [90]
ReF_6	4.6 [26]	5.3—6.3 [101]	4.8 [90]
OsF_6	5.9 [26]	6.2—7.3 [101]	6.0 [90]
IrF_6	4.34 [67]; 5.1±0.5 [76]; 7.0 [26]	7.0—8.3 [101]	7.2 [90]
PtF_6	5.1—7.9 [109]; 8.2 [26]	7.9—9.1 [101]	7.4 [90]
AuF_6	—	8.4—10.1 [101]	8.1 [90]
UF_6	4.9±0.5 [110]; 5.0 [111]; 3.6 [79]; 4.3 [112]; 5.1; 4.85±0.25; 5.60±0.25 [113]	5.0 [101]	—

Note. Numbers in square brackets denote references (Ed. of Translation).

Table 6. Experimental estimates of the EA of various superhalogens.

Radical	EA, eV	Refs.	Radical	EA, eV	Refs.
MnF_3	5.27±0.20	[111]	CrO_3	3.7	[114]
FeF_3	4.25±0.20	[111]	$MoOF_4$	4.0±0.4	[103]
PtF_3	2.1	[109]	UF_5	3.5	[113]
MnF_4	5.22	[109]	U_2F_9	4.2±0.5	[115]
FeF_4	5.40±0.20	[111]	U_2F_{10}	4.5±0.4	[115]
PtF_4	5.11±0.36	[109]	U_2F_{11}	6.1±0.7	[115]
PtF_5	6.5	[109]	U_2F_{12}	7.9±0.8	[115]

4. Characteristic Physicochemical Properties of Superhalogens

Molecules with high EA show a whole series of fundamentally important distinguishing properties. Thus the high EA of $SeCl_6$ and $TeCl_6$ makes possible the existence of the anions $SeCl_6^{2-}$ and $TeCl_6^{2-}$, which are unusual from the traditional chemical viewpoint.

A high EA makes it possible to obtain fundamentally new salts with unusual cations, such as $O_2^+[PtF_6]^-$, $XeF_5^+[PtF_6]^-$, $Xe_2F_{11}^+[AuF_6]^-$, etc.[1–12] The molecules O_2, XeF_5, and Xe_2F_{11} have high IP, so that to obtain salts with their cations it is necessary to use superhalogens with anomalously high EA, such as, for example, PtF_6, AuF_6, etc. Thus superhalogens open up extensive possibilities for the synthesis of new non-traditional salts with both organic and inorganic cations.

Another unusual property of systems containing superhalogen groups is related to the high IP of the anions of superhalogens. Compounds in the gas phase in most cases dissociate homolytically, to give a pair of neutral fragments. This rule may not extend to molecules containing superhalogens, however. Thus the values of the IP of the alkali metals are 3.9–5.4 eV, and the EA of superhalogens may exceed these values. In these cases, heterolytic dissociation may be more favourable. For example, the salt Cs–AlF_4

dissociates to Cs^+ and AlF_4^-, and not to Cs and AlF_4. This heterolytic dissociation makes it possible to obtain a low-temperature molecular plasma by simple heating, and this in turn ensures increased conductivity of the vapours of these salts. The gas-phase mixtures of $NaAlCl_4$ and $KAlCl_4$ with $AlCl_3$–Al_2Cl_6 [116] have electrical conductivity values which are fairly high for gases, amounting to 10^{-11}–10^{-6} Ω^{-1} cm^{-1} in the temperature range 500–900 K. The partial pressure of ions in the gas reaches 10^{-8} atm at a partial pressure of $NaAlCl_4$ of 0.1 atm.

Superhalogens are widely used to modify the electronic characteristics of one-dimensional and two-dimensional organic compounds to obtain materials with metallic conductivity, and also organic superconductors.[14–26] All organic superconductors obtained up to the present contain superhalogens anions as counter-ions. It is suggested that the geometric structure of the anion is important for the conversion of quasi-one-dimensional organic systems to the superconducting state.[18] Thus for the synthesis of new organic superconductors with a higher critical temperature T_c it is necessary to have a wide range of superhalogens with different geometric structures.†

On the other hand, the class of counter-ions suitable for obtaining organic superconductors can be extended considerably using the cations of superalkalies, since the quasi-one-dimensional stacks of organic conjugated molecules forming the starting material have not only donor but also acceptor properties. The synthesis of organic systems using superalkali cations as counter-ions would extend considerably the range of organic semiconductors, metals, and superconductors, and would also be extremely interesting for theoretical chemistry.

IV. ELECTRONIC STRUCTURE OF SUPERALKALIES

After the detection of the large class of molecular systems having high EA (superhalogens) there arose the question, which is important for extending the concept of electronegativity and electropositivity, of the lowest possible IP values of neutral molecules and radicals, that is the EA of the corresponding singly charged cations. Among the elements of the periodic system, the lowest first IP are shown by alkali metal atoms, so that systems whose first IP are lower than those for alkali metal atoms are naturally called superalkalies.

From the ideas presented in section II, it follows that to achieve a low first IP of a neutral system of the type ML_{k+1}, it is necessary that the HOMO be antibonding with respect to the central atom–ligand interaction, and, in addition, that the ligands have low upper IP. In this case, on formation of the compound ML_{k+1}, the electrons of the L atoms will enter an antibonding MO, and the energy of their bond in the ML_{k+1} molecule will be lower than in the isolated L atom. It should therefore be promising to look for "superalkalies" in the class of systems ML_{k+1}, where L are alkali metal atoms.

To verify this suggestion, the DV-X_α method was used[117,118] to calculate the electronic structure of a number of radicals of this type. Table 7 gives the results of the calculation of the first IP of radicals ML_{k+1}, and also available experimental estimates. The IP of the radicals were calculated for the equilibrium geometry of the corresponding cations, that is the values of the first IP of the radicals ML_{k+1} given in Table 7 are equal to EA_{vert} for the cations ML^+_{k+1}. Clementi's double-exponent (DE) basis set was used in the calculations.[117,118] It was shown for the typical superalkalies $ClNa_2$ and PNa_4 that expansion of the DE basis set by including polarisation (3*d*) and diffuse (3*s*, 3*p*) functions of the central atom, and also polarisation (3*p*) functions of the ligand atoms, leads to only slight changes (~0.1 eV) in the first IP and the composition of the HOMO.

Table 7. First ionisation potentials (eV) of superalkali radicals.

Radical	Experiment	Calculation (Refs.117,118)
FLi_2	—	3.6
$ClNa_2$	4.15±0.20 [119]	3.7
FNa_2	—	3.7
FCs_2	—	2.6
$ClCs_2$	—	2.3
OLi_2	4.54±0.20 [120]	3.4*
ONa_2	3.90±0.15 [121]	3.5
OK_2	3.65±0.04 [121]	—
ONa_4	3.95±0.10 [121]	—
OK_4	3.62±0.04 [121]	—
SLi_3	—	3.2
SNa_2	—	3.3
NLi_4	—	3.6
NNa_4	—	3.7
PLi_4	—	3.0
PNa_4	—	3.2
NH_4^{**}	4.6 [125] 4.73±0.06 [126]	4.1

Non-empirical calculation with allowance for correlation energy (MP2/6-311) [122] gives the value 3.37 eV.
**See Ref. 123 and references therein up to 1984; non-empirical calculation with allowance for correlation energy[124] (SDFI) gives the values IP_{ad} = 4.41 eV and IP_{vert} = 4.43 eV.
Note. Numbers in square brackets denote references (Ed. of Translation).

The coefficients of the LCAO expansion of the valence MO in the DE basis set for the radicals FLi_2, OLi_2, and NLi_4 are given in Ref. 118. The MO have a similar structure for other radicals of corresponding types. According to Ref. 118, the doubly occupied MO consist chiefly of the AO of the central atom, whereas the highest half-filled MO consist chiefly of the AO of the ligands. For these radicals, the HOMO are antibonding with respect to the central atom–ligand interaction, and according to traditional views of the structure of MO its energy should be higher than the energies of the AO of both the central atom and the ligands. In fact, in all cases the IP of the radicals (see Table 7) are lower than the IP of the alkali metal atoms, which lie in the range 3.9–5.4 eV for Cs–Li. Thus the ML_{k+1} cations being considered must be regarded as superalkalies, since the first IP of the corresponding radicals are lower than the first IP of alkali metal atoms.

The above radicals were chosen so that it would be possible to follow the change in the IP with change in the ligand L and the central atom along a sub-group, and also with increase in the number of ligands. The replacement of Li by Na leads to small changes in the IP, and no regular trends could be established from the results of the calculations. The replacement of Na by Cs in the series FNa_2–FCs_2 and $ClNa_2$–$ClCs_2$, however, leads to a significant decrease in the IP. When a ligand is replaced by a heavier ligand from the same sub-group, a decrease in the EA of the corresponding cation should apparently be expected. The replacement of the

†In view of the importance of the tetrahedral structure of the counter-ion for increasing T_c (for example ClO_4^- [18]), the anions of transition metal tetra-oxides can be recommended as counter-ions for the production of new superconductors.

central atom by a heavier atom from the same sub-group will also lead to a decrease in the EA, although the relative changes are small. With increase in the number of ligands in series of the type FLi_2^+–OLi_3^+–NLi_4^+, the EA on the whole decreases, although the decrease is small. For the EA of the cation to be small, it is not necessary that the IP of the ligands be low. If the antibonding of the HOMO is strong, the energy of the binding of an electron in the neutral system ML_{k+1} may be low, in spite of a high EA for the cation L^+.

Another type of molecular radical ML_{k+1} with low values of the first IP may be provided by Rydberg radicals, in which the additional (relative to the corresponding cation) electron enters a Rydberg AO of the central atom. In this case, since the Rydberg AO of the M atom are fairly high, the IP from these AO should be low. An example of these systems may be provided by ammonium radicals NR_4, where R is an organic group. For the simplest system NH_4, detailed *ab initio* calculations have been carried out with variation of the geometry of the cation NH_4^+ and the radical NH_4 separately, and with allowance for the correlation energy by the configuration interaction method with the addition of Rydberg orbitals to the basis set.[127] These calculations showed that the HOMO in NH_4 consist chiefly of the Rydberg AO of the N atom, and the value of IP_{ad} for the NH_4 radical (or EA_{ad} for the NH_4^+ cation) is 4.3 eV. This value shows good agreement with the experimental estimates 4.6 ± 0.2 eV [125] and 4.73 ± 0.06 eV.[126] Other radicals NR_4 for which R has electron-donor properties should have even lower IP, and all these radicals can apparently be classified as alkalies or superalkalies.

Both superalkalies and Rydberg radicals are stable with respect to monomolecular dissociation,[119–126] although the dissociation energy is relatively low. At the same time the corresponding cations are extremely stable with respect to monomolecular dissociation. Thus the dissociation energy of $ONa_3^+ \rightarrow ONa_2 + Na^+$ is 87 kcal $mole^{-1}$,[122] and that of $NH_4^+ \rightarrow NH_3 + H^+$ is 217 kcal $mole^{-1}$.[124]

The low EA of "superalkali" cations indicates the possibility of synthesising new classes of salt in which the anions are molecular systems with low EA. The first salts of this type, $LiO_3^+NO^-$ and $Li_3O^+NO_2^-$, have already been synthesised, and X-ray diffraction has confirmed that they contain Li_3O^+ cations.[27–29] Superalkali cations can form salts in cases where the formation of the corresponding salts with alkali metal atoms may be energetically unfavourable either because of the relatively high IP of the metal atom or because of steric hindrance. Salts consisting of superalkali cations and superhalogen anions can apparently have very low heterolytic dissociation energies, and this is of interest from the viewpoint of the physics of low-temperature molecular plasma.

In recent years, *ab initio* calculations have revealed a new class of so-called hyperlithium compounds OLi_4, OLi_5, CLi_5, CLi_6, etc.[128–132], in which the formal valence of the central atom is greater than the maximum classical valence. According to the calculations, the first IP of these compounds are relatively low, and these systems can also apparently be regarded as superalkalies. The question of the existence and energetics of hyperlithium compounds requires further theoretical and experimental studies, however.

---o0o---

The rapid extension of the possibilities provided by computing techniques suggest that in the near future it will be possible to calculate the electron affinity and ionisation potentials of chemical compounds of increasing complexity. Nevertheless, qualitative models which would make it possible to estimate these quantities without laborious calculations are of considerable interest. The analysis carried out in the present review has shown the existence of two important classes of chemical compound: with anomalously high EA (superhalogens) and with anomalously low first IP (superalkalies). Both classes of compound are of considerable interest for theoretical chemistry, since they extend the traditional concepts of the electronegativity and electropositivity of chemical groups. At the same time these compounds are important for practical purposes, for example for the synthesis of new chemical compounds and in the planned search for new dopants to increase the electrical conductivity of polymers, and also new counter-ions for the production of organic superconductors.

It is hoped that the above discussion of the electronic structure of superhalogens and superalkalies will attract the attention of experimental workers and find further theoretical development.

REFERENCES

1. N.Bartlett and D.H.Lohmann, Proc.Chem.Soc., 1962(1), 115.
2. N.Bartlett and D.H.Lohmann, J.Chem.Soc., 1962(12), 5253.
3. N.Bartlett, M.Gennis, D.D.Gibler, B.K.Morrell, and A.Zalkin, Inorg.Chem., 1973, **12**(8), 1717.
4. F.O.Sladky, P.A.Bulliner, N.Bartlett, B.G.DeBoer, and A.Zalkin, Chem.Communs., 1968(17), 1048.
5. K.O.Christe, W.W.Wilson, and R.D.Wilson, Inorg. Chem., 1984, **23**(14), 2058.
6. K.O.Christe, W.W.Wilson, R.D.Wilson, R.Bougon, and T.Bui Huy, J.Fluor.Chem., 1983, **23**(4), 399.
7. T.E.Mallouk, G.L.Rosenthal, G.Mueller, R.Brusasco, and N.Bartlett, Inorg.Chem., 1984, **23**(20), 3167.
8. D.E.McKee, C.J.Adams, and N.Bartlett, Inorg. Chem., 1973, **12**(8), 1722.
9. K.O.Christe and W.W.Wilson, Inorg.Chem., 1983, **22**(13), 1950.
10. K.Leary, A.Zalkin, and N.Bartlett, Inorg.Chem., 1974, **13**(4), 775.
11. K.O.Christe, W.W.Wilson, and E.C.Curtis, Inorg. Chem., 1983, **22**(21), 3056.
12. R.Bougon, W.W.Wilson, and K.O.Christe, Inorg. Chem., 1985, **24**(14), 2286.
13. R.C.Burns, R.J.Gillespie, J.A.Barnes, and M.J.McGlinchey, Inorg.Chem., 1982, **21**(2), 799.
14. D.Jerome, Ann.Chem., 1984, **9**(7/8), 921.
15. F.Wudl, Acc.Chem.Res., 1984, **17**(9), 227.
16. J.M.Williams, The Stream Chemiker, 1984, **10**(1), 3.
17. K.Bechgaard, Mol.Cryst.Liq.Cryst., 1981, **79**(1), 1.
18. J.M.Williams, M.A.Beno, H.H.Wang, P.C.W.Leung, T.J.Emge, U.Geiser, and K.D.Carlson, Acc.Chem. Res., 1985, **18**(11), 261.
19. E.B.Yagubskii, I.F.Shchegolev, V.K.Laukhin, L.A.Kononovich, M.V.Kartsovnik, A.V.Zvarykina, and L.I.Buravov, Pis'ma v Zhur.Eksp.Teor.Fiz., 1984, **39**(1), 12.
20. V.A.Merzhanov, E.E.Kostyuchenko, V.N.Laukhin, R.M.Lobkovskaya, M.K.Makova, R.P.Shibaeva, I.F.Shchegolev, and E.B.Yagubskii, Pis'ma v Zhur. Eksp.Teor.Fiz., 1985, **41**(4), 146.
21. J.C.W.Chien, "Polyacetylene: Chemistry, Physics and Materials Science", Acad.Press, New York, 1984.
22. S.Etemad, A.J.Heeger, and A.G.MacDiarmid, Ann. Rev.Phys.Chem., 1982, **33**, 443.
23. H.W.Streitwolf, Phys.Stat.Sol., 1985, **1276**(1), 11.

24. H.W.Gibon, in B.M.Culbertson and C.U.Pittman, "Polymer Science and Technology, Vol.25, New Monomers and Polymers", Plenum Publishing, New York, 1984, p.381.
25. L.W.Shacklette, J.E.Toth, N.S.Murthy, and R.H.Baughman, J.Electrochem.Soc., 1985, **132**(7), 1329.
26. N.Bartlett and B.W.McQuillan, "Intercalation Chemistry", Acad.Press, New York, 1982, p.19.
27. J.Jensen, Angew.Chem., 1976, **88**(11), 412.
28. J.Jensen, Angew.Chem., 1977, **89**(15), 5567.
29. J.Jensen, Z.anorg.Chem., 1977, **435**(2), 513.
30. L.Karlsson, L.Mattsson, R.Jadrny, T.Bergmark, and K.Siegbahn, Phys.Scripta, 1976, **14**(5), 230.
31. R.L.De Kock, F.R.Higginson, and D.R.Lloyd, Disc. Faraday Soc., 1972, **54**(1), 84.
32. P.J.Hay, J.Chem.Phys., 1982, **76**(2), 502.
33. L.M.Branscomb, "Atomic and Molecular Processes" (Edited by D.R.Bates), Acad.Press, New York, 1962.
34. R.S.Berry, Chem.Rev., 1969, **69**(4), 533.
35. P.P.Sutton and J.E.Mayer, J.Chem.Phys., 1935, **3**(1), 20.
36. A.L.Farragher, F.M.Page, and R.C.Wheeler, Disc.Faraday Soc., 1964, **37**(2), 203.
37. B.L.Moiseiwitsch, Adv.Mol.Phys., 1964, 1, 61.
38. W.A.Chupka, J.Berkowitz, and D.Gutman, J.Chem. Phys., 1971, **55**(6), 2724.
39. W.A.Chupka, J.Berkowitz, and D.Gutman, J.Chem. Phys., 1971, **55**(6), 2733.
40. L.N.Sidorov, Uspekhi Khim., 1982, 51(4), 625 [Russ. Chem.Rev., 1982(4)].
41. H.S.W.Massey, "Cambridge Monographs on Physics: Negative Ions" (Translated into Russian), Izd.Mir, Moscow, 1979.
42. T.Koopmans, Physica, 1933, 1, 104.
43. P.E.Cade, J.Chem.Phys., 1967, **47**(7), 2390.
44. G.L.Gutsev and A.I.Boldyrev, Adv.Chem.Phys., 1985, **61**, 169.
45. J.Simons, Ann.Rev.Phys.Chem., 1977, **28**, 15.
46. B.T.Pickup and O.Goscinski, Mol.Phys., 1973, **26**(4), 1013.
47. L.S.Cederbaum and W.Domcke, Adv.Chem.Phys., 1977, **36**, 205.
48. G.Hohlneicher, F.Ecker, and L.S.Cederbaum, in "Electron Spectroscopy" (Edited by D.H.Shirley), North-Holland, Amsterdam, 1972.
49. J.J.Novoa and F.Mota, Chem.Phys.Letters, 1985, **119**(2/3), 135.
50. J.C.Slater, "Self-Consistent Field Methods for Molecules and Solids" (Translated into Russian), Izd. Mir, Moscow, 1978.
51. K.H.Johnson, Adv.Quant.Chem., 1973, **7**, 143.
52. E.J.Baerends, D.E.Ellis, and P.Ros, Chem.Phys., 1973, **2**(1), 41.
53. D.E.Ellis and G.S.Painter, Phys.Rev., 1970, **B2**(8), 2887.
54. G.L.Gutsev and A.A.Levin, Zhur.Strukt.Khim., 1978, **19**(6), 976.
55. G.L.Gutsev and A.A.Levin, Zhur.Strukt.Khim., 1978, **19**(6), 982.
56. G.L.Gutsev and A.I.Boldyrev, Chem.Phys., 1981, **56**(3), 277.
57. G.L.Gutsev and A.I.Boldyrev, Zhur.Neorg.Khim., 1981, **26**(9), 2353 [Russ.J.Inorg.Chem., 1981(9)].
58. G.L.Gutsev and A.I.Boldyrev, Zhur.Neorg.Khim., 1981, **26**(9), 2557 [Russ.J.Inorg.Chem., 1981(9)].
59. J.P.Lowe, J.Amer.Chem.Soc., 1977, **99**(17), 5557.
60. S.Canuto, J.Phys.B., 1981, **14**(19), 3557.
61. K.S.Krasnov, N.V.Filippenko, V.A.Bobkova, N.L.Lebedeva, E.V.Morozov, T.I.Ustinova, and G.A.Romanova, "Molekulyarnye Postoyannye Neorganicheskikh Soedinenii" (The Molecular Constants of Inorganic Compounds), Izd.Khimiya, Leningrad, 1979.
62. K.Leary, A.Zalkin, and N.Bartlett, Chem.Communs., 1973(4), 131.
63. J.A.Ibers and W.C.Hamilton, J.Chem.Phys., 1966, **44**(5), 1748.
64. P.Rosmus and W.Meyer, J.Chem.Phys., 1978, **69**(6), 2745.
65. K.D.Jordan, K.M.Griffing, J.Kenney, E.L.Andersen, and J.Simons, J.Chem.Phys., 1976, **64**(11), 4730.
66. B.M.Smirnov, "Otritsatel'nye Iony" (Negative Ions), Atomizdat, Moscow, 1978.
67. L.V.Gurvich, G.V.Karachevtsev, V.N.Kondrat'ev, Ya.A.Lebedev, V.A.Medvedev, V.K.Potapov, and Ya.S.Khodeev, "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu" (The Energies of Rupture of Chemical Bonds. Ionisation Potentials and Electron Affinity), Izd.Nauka, Moscow, 1974.
68. G.L.Gutsev and A.I.Boldyrev, Zhur.Neorg.Khim., 1982, **27**(4), 868 [Russ.J.Inorg.Chem., 1982(4)].
69. G.L.Gutsev and A.I.Boldyrev, Chem.Phys.Letters, 1981, **84**(2), 352.
70. A.I.Boldyrev, L.P.Sukhanov, and O.P.Charkin, Koord.Khim., 1982, **8**(4), 430.
71. A.I.Boldyrev and O.P.Charkin, Koord.Khim., 1982, **8**(5), 618.
72. A.I.Boldyrev, V.G.Zakzhevskii, and O.P.Charkin, Koord.Khim., 1982, 8(4), 437.
73. G.L.Gutsev and A.P.Klyagina, Zhur.Strukt.Khim., 1982, **29**(9), 2173.
74. A.P.Klyagina and G.L.Gutsev, Zhur.Neorg.Khim., 1983, **28**(3), 570 [Russ.J.Inorg.Chem., 1983(3)].
75. G.L.Gutsev and A.P.Klyagina, Chem.Phys., 1983, **75**(2), 243.
76. R.N.Compton, P.W.Reinhardt, and C.D.Cooper, J.Chem.Phys., 1978, **68**(5), 2023.
77. G.A.Tsigdinos and F.W.Moore, "Ann.Rep.Inorg.and Gen.Synth.", Wiley, New York, 1974, p.157.
78. J.Burgess and R.D.Peacock, J.Fluor.Chem., 1977, **10**(6), 479.
79. T.Mallouk, B.Desbat, and N.Bartlett, J.Fluor. Chem., 1982, **21**(1), 88.
80. L.N.Sidorov, M.I.Nikitin, E.V.Skokan, and I.D.Sorokin, Int.J.Mass Spectr.and Ion Phys., 1980, **35**(3/4), 203.
81. L.N.Sidorov, Int.J.Mass Spectr.and Ion Phys., 1981, **39**(3), 311.
82. V.G.Zakzhevskii, A.I.Boldyrev, and O.P.Charkin, Chem.Phys.Letters, 1981, **81**(1), 93.
83. V.G.Solomonik, V.M.Ozerova, and K.S.Krasnov, Koord.Khim., 1984, **10**(12), 1613.
84. R.D.Srivastava, O.M.Uy, and M.Farber, J.Chem. Soc., Faraday Trans.I, 1974, **70**(6), 1033.
85. J.L.Bills and F.A.Cotton, J.Phys.Chem., 1960, **64**(10), 1477.
86. M.J.R.Clark and H.Lynton, Canad.J.Chem., 1969, **47**(14), 2579.
87. G.Brunton, Acta Cryst., 1968, **B24**(24), 1703.
88. Yu.Sh.Kalaichev, K.P.Petrov, and V.V.Ugarov, Zhur.Strukt.Khim., 1983, **24**(5), 176.
89. G.L.Gutsev and A.I.Boldyrev, J.Chem.Phys. Letters, 1983, **101**(4/5), 441.
90. G.L.Gutsev and A.I.Boldyrev, Koord.Khim., 1984, **10**(11), 1455.

91. G.L.Gutsev and A.I.Boldyrev, Mol.Phys., 1984, 11(1), 1.
92. G.L.Gutsev and A.I.Boldyrev, Koord.Khim., 1985, 11(4), 435.
93. G.L.Gutsev and A.I.Boldyrev, Chem.Phys.Letters, 1984, **108**(3), 225.
94. G.L.Gutsev and A.I.Boldyrev, Zhur.Strukt.Khim., 1985, **26**(1), 134.
95. R.McDiarmid, Chem.Phys.Letters, 1980, **76**(2), 300.
96. G.L.Gutsev and A.I.Boldyrev, Chem.Phys.Letters, 1984, **108**(3), 250.
97. G.L.Gutsev and A.I.Boldyrev, Zhur.Strukt.Khim., 1984, **25**(5), 16.
98. J.G.Norman, Jr., Mol.Phys., 1976, **31**(4), 1191.
99. M.Henchman, A.A.Viggiano, J.F.Paulson, A.Freedman, and J.Wormhoudt, J.Amer.Chem.Soc., 1985, **107**(5), 1453.
100. R.Prins, J.Chem.Phys., 1974, **61**(7), 2580.
101. J.E.Bloor and R.E.Sherrod, J.Amer.Chem.Soc., 1980, **102**(3), 4333.
102. M.Boring, Chem.Phys.Letters, 1977, **46**(2), 242.
103. L.N.Sidorov, A.Ya.Borshchevskii, E.B.Rudnyi, and V.D.Butskii, Chem.Phys., 1982, **71**(1), 145.
104. J.Burgess, I.Haigh, R.D.Peacock, and P.Taylor, J.Chem.Soc., Dalton Trans., 1974(10), 1064.
105. B.P.Mathur, E.W.Rothe, and G.P.Reck, J.Chem. Phys., 1977, **67**(2), 377.
106. J.D.Webb and E.R.Bernstein, J.Amer.Chem.Soc., 1978, **100**(2), 483.
107. H.Dispert and K.Lacmann, Chem.Phys.Letters, 1977, **45**(2), 311.
108. A.A.Viggiano, J.F.Paulson, F.Dale, M.Henchman, N.G.Adams, and D.Smith, J.Phys.Chem., 1985, **89**(11), 2264.
109. L.N.Sidorov, M.I.Nikitin, and V.M.Korobov, Dokl. Akad.Nauk SSSR, 1979, **248**(6), 1387.
110. J.L.Beauchamp, J.Chem.Phys., 1976, **64**(3), 929.
111. L.N.Sidorov, E.V.Skokan, M.I.Nikitin, and I.D.Sorokin, Int.J.Mass Spectr.and Ion Phys., 1980, **35**(3/4), 215.
112. A.T.Pyatenko, A.V.Gusarov, and L.N.Gorokhov, Zhur.Fiz.Khim., 1982, **56**(8), 1906 [Russ.J.Phys. Chem., 1982(8)].
113. A.T.Pyatenko, A.V.Gusarov, and L.N.Gorokhov, Zhur.Fiz.Khim., 1984, **58**(1), 1 [Russ.J.Phys. Chem., 1984(1)].
114. E.B.Rudnyi, L.N.Sidorov, L.A.Kuligina, and G.A.Semenov, Int.J.Mass Spectr.and Ion Phys., 1985, **64**(2), 95.
115. A.T.Pyatenko and L.N.Sidorov, Chem.Phys.Letters, 1984, **105**(2), 205.
116. E.W.Dewing, J.Phys.Chem., 1971, **75**(9), 1260.
117. G.L.Gutsev and A.I.Boldyrev, Zhur.Neorg.Khim., 1983, **28**(9), 2179 [Russ.J.Inorg.Chem., 1983(9)].
118. G.L.Gutsev and A.I.Boldyrev, Chem.Phys.Letters, 1982, **92**(3), 262.
119. K.I.Peterson, P.D.Dao, and A.W.Castleman, J.Chem. Phys., 1983, **79**(2), 777.
120. C.H.Wu, H.Kudo, and H.R.Ihle, J.Chem.Phys., 1979, **70**(4), 1815.
121. P.D.Dao, K.I.Peterson, and A.W.Castleman, J.Chem.Phys., 1983, **80**(1), 563.
122. E.U.Wuerthwein, P.v.R.Schleyer, and J.A.Pople, J.Amer.Chem.Soc., 1984, **106**(23), 6973.
123. G.L.Gutsev, Teor.i Eksper.Khim., 1985, **21**(1), 10.
124. J.Kaspar, V.H.Smith, and B.N.McMaster, Chem. Phys., 1985, **96**(1), 81.
125. B.W.Williams and R.F.Porter, J.Chem.Phys., 1980, **73**(11), 5598.
126. G.I.Gellene, D.A.Cleary, and R.F.Porter, J.Chem. Phys., 1982, **77**(7), 3471.
127. H.Cardy, D.Liotard, A.Dargelos, and E.Poquet, Chem.Phys., 1983, **77**(2), 287.
128. E.D.Jemmis, J.Chandrasekhar, E.U.Wuerthwein, P.v.R.Schleyer, J.W.Chinn, F.J.Landro, R.J.Lagow, B.Luke, and J.A.Pople, J.Amer.Chem.Soc., 1982, **104**(15), 4275.
129. P.v.R.Schleyer, E.U.Wuerthwein, and J.A.Pople, J.Amer.Chem.Soc., 1982, **104**(21), 5839.
130. P.v.R.Schleyer, E.U.Wuerthwein, E.Kaufmann, T.Clark, and J.A.Pople, J.Amer.Chem.Soc., 1983, **105**(18), 5930.
131. P.v.R.Schleyer, Pure Appl.Chem., 1984, **56**(1), 151.
132. P.v.R.Schleyer, "New Horizons in Quantum Chemistry" (Edited by P.O.Löwdin and B.Pullman), Reidel, Dodrecht, 1983, p.95.
133. N.M.Klimenko, V.G.Zakzhevskii, and O.P.Charkin, Koord.Khim., 1982, **8**(7), 903.

Section of the Institute of Chemical Physics,
Academy of Sciences of the USSR,
Chernogolovka