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ПОДОБИЕ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ ЩЕЛОЧНОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ С РЕДКОЗЕМЕЛЬНЫМИ. I. ВНУТРЕННИЙ ЭФФЕКТ ШТАРКА И ЕГО ПРИМЕНЕНИЕ К ЭНЕРГЕТИКЕ ИОНИЗАЦИИ СОЕДИНЕНИЙ ЭТИХ ЭЛЕМЕНТОВ. I$_А$ – МОНОГАЛОГЕНИДЫ И МОНОГИДРОКСИД СТРОНЦИЯ

В.Н. Беляев, В.В. Рыбкин

Валерий Николаевич Беляев (ORCID 0000-0001-7454-8472), Владимир Владимирович Рыбкин (ORCID 0000-0001-7295-7803)*

Кафедра технологии приборов и материалов электронной техники, Ивановский государственный химико-технологический университет, Шереметевский пр., 7, Иваново, Российская Федерация, 153000
E-mail: valerij.beliaew2016@yandex.ru, rybkin@isuct.ru*

Изложен в развитии внутренний эффект Штарка, примененный для определения потенциалов ионизации (эВ, ±0,017): 5,422 – SrOH, 5,257 – SrF, 5,523 – SrCl, 5,581 – SrBr, 5,661 – SrJ, 5,525 – CaF, 5,873 – CaCl, энергий диссоциации (кДж/моль) 582±6 (Sr^+-F), 430,8±2,1 (Sr^+-OH) и поляризуемостей катиона Sr^+ в этих ионных соединениях 1,117±0,014 ($X^2\Sigma^+$) и 1,986±0,017 $Å^3$ ($B^2\Sigma^+$). Итогом развития является разработка метода определения адиабатического потенциала ионизации I_o полярных молекул M^+X^- с высокой точностью (не хуже ±0,02 эВ) при малой трудоемкости обработки спектроскопических данных. В основу разработанного метода положено смещение внутренним полем аниона X^- молекулы ее электронных термов, образующих хорошо наблюдаемое в спектре начало (а не трудно измеряемый ионизационный предел) ридберговской серии, – в этом состоит принципиальная новизна подхода к решению данной сложной задачи. Расчет каждого значения занимает несколько минут на калькуляторе. Новый метод сопоставлен с наиболее часто используемыми в исследованиях существующими и описанными в литературе. Из сопоставления сделан вывод о высокой точности разработанного метода, превосходящего большинство тех, что представлены в литературе и используются в научной практике. В связи с этим предлагается сделать этот метод определения адиабатических потенциалов ионизации ионных молекул частью спектроскопических исследований вместе с определением из спектров остальных параметров молекул: межъядерных расстояний, частот колебаний ядер, энергий электронных состояний и т.д. Существенно уточнены данные об энергиях диссоциации ионов (кДж/моль) $D_o(Sr^+\text{-}F)=582\pm6$ и $D_o(Sr^+\text{-}OH)=430{,}8\pm2{,}1$. Получены новые более точные данные об эффективных поляризуемостях иона Sr^+ в составе моногалогенидов Sr^+X^-, включая его возбужденное состояние ($Å^3$): 1,117±0,014 в основном состоянии – $\sigma(5s)X^2\Sigma^+$, и 1,986±0,017 в первом возбужденном – $\sigma(5p)B^2\Sigma^+$ той же симметрии, что основное.

Ключевые слова: внутренний эффект Штарка, потенциалы ионизации моногалогенидов и моногидроксида стронция, поляризуемости их катиона

SIMILARITY OF PHYSICOCHEMICAL PROPERTIES OF ALKALINE EARTH ELEMENTS WITH RARE EARTH ELEMENTS. I. INTERNAL STARK EFFECT AND ITS APPLICATION TO THE ENERGY OF IONIZATION OF COMPOUNDS OF THESE ELEMENTS. I$_A$ – MONOHALIDES AND MONOHYDROXIDE OF STRONTIUM

V.N. Belyaev, V.V. Rybkin

Valeriy N. Belyaev (ORCID 0000-0001-7454-8472), Vladimir V. Rybkin (ORCID 0000-0001-7295-7803)*

Department of Electronic Devices and Materials, Ivanovo State University for Chemistry and Technology, Sheremetevskiy ave., 7, Ivanovo, 153000, Russia
E-mail: valerij.beliaew2016@yandex.ru, rybkin@isuct.ru*

The internal Stark effect is presented in development, applied to the study of ionization potentials (eV, ±0.017): 5.422 – SrOH, 5.257 – SrF, 5.523 – SrCl, 5.581 – SrBr, 5.661 – SrJ, 5.525 – CaF, 5.873 – CaCl, dissociation energies (kJ/mol) 582±6 (Sr^+-F), 430.8±2.1 (Sr^+-OH) and polarizabilities of the Sr^+ cation in these ionic compounds 1.117±0.014 ($X^2\Sigma^+$) and 1.986±0.017 Å^3 ($B^2\Sigma^+$). The result of the development is the creating of a method for determining the adiabatic ionization potential I_o of polar molecules M^+X^- with high accuracy (not worse than ±0.02 eV) and in short time based on spectroscopic data. The developed method is based on the shift of the electron terms of the molecule by the internal field of the anion X^-, which form the beginning (and not the difficult to measure ionization limit) of the Rydberg series in the spectrum. This is the fundamental novelty of the approach to solving this complex problem. The calculation of each takes several minutes on a calculator. The new method is compared with most frequent used in researches existed and outlined in literature. From comparison the conclusion is made about high accuracy of developed method excelling those that are presented in literature and used in research. In connection with this is proposed to make this method for determining the adiabatic ionization potentials of ionic molecules a part of spectroscopic studies along with the determination of other molecular parameters from the spectra: internuclear distances, nuclear vibration frequencies, energies of electron states, etc. The more precise data are presented about dissociation energies of ions (kJ/mol) $D_o(Sr^+\text{-}F)=582\pm6$ и $D_o(Sr^+\text{-}OH)=430.8\pm2.1$. The new and more accurate data are obtained about polarizabilities of Sr+ ion in molecules of monohalides including its excited states (Å^3): 1.117±0.014 in ground state, – σ(5s)$X^2\Sigma^+$, and 1.986±0.017 in first excited one – σ(5p)$B^2\Sigma^+$, same symmetry that ground one.

Keywords: internal Stark effect, ionization potentials of strontium monohalides and monohydroxide, polarizability of their cation

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INTRODUCTION

The adiabatic ionization potential I_o is the most important characteristic of the electron shell, the value of which establishes the starting point of its energy, which is of fundamental importance. At present, there are very few accurate data on I_o for molecules, especially low-volatile ones, due to the complexity of interpreting their experiments.

Remarkable examples of such experiments with electron impact with mass spectrometric registration (EI MS) of MX^+ ions are [1, 2]. In them, the potential of MX^+/MX appearance was measured with an accuracy of ±0.01-0.03 eV, and its difference from the adiabatic ionization potential of MX after appropriate justification did not exceed the vibrational quantum of MX – ±0.03-0.05 eV. These works played an important role in our research.

Another good example of such studies, initiated in 1985, is the work [3], which initiated the precision study of the ionization energetics of lanthanide monofluorides. Its result in eV $I_o(EuF) = 5.21\pm0.07 \approx 5.25\pm0.06 = I_o(SrF)$ coincided within the error with what was found in [2] for SrF. This coincidence, which remained unnoticed at the time, as it was then considered accidental, will become one of the starting points in the study of a new regularity, which consists in the fact that heavier lanthanides, due to the compression of their electron shells, become similar to lighter alkaline earth metals (AEMs).

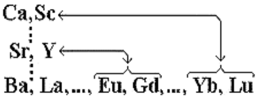
There are papers in which the equilibria involving SrOH and its ion $SrOH^+$ formed in natural gas flames with strontium additives were studied using the intensities of the emission spectra, and the energies of chemical bonds in kJ/mol were determined as $D_o(Sr–OH) = 401.8\pm3.0$ [4] and $D_o(Sr^+–OH) = 432.8\pm2.7$ [5].

Based on these data and taking into account $I_o(Sr)$ = = 5.694901(12) eV [6, 7], the adiabatic ionization potential was found as $I_o(SrOH)$ = 5.372±0.041 eV = = 43332± 329 cm^{-1} [4], which differs from the value of 5.1±0.2 eV [8] of the EI MS method.

In [9] the equilibrium with the participation of $EuOH^+$ was similarly studied and the value $D_o(Eu^+–OH)$ = 428±6 kJ/mol ≈ $D_o(Sr^+–OH)$ was found. When initiating the experiment on europium in 1996, attention was first drawn to the similarity of positions of spectral lines of europium with strontium, which was used in [10] to estimate the effective polarizabilities of the Eu^+ ion in Eu^+X^- in order to find $I_o(EuX)$, and formerly in 1989, to analogous similarity of the spectra of calcium with ytterbium and their compounds in flames [11]. All this together with the values in eV $I_o(Eu)$ = = 5.67045(3) ≈ 5.694901(12) = $I_o(Sr)$ and $I_o(Yb)$ = = 6.25394(3) ~ 6.113213(15) = $I_o(Ca)$ [6, 7, 12] also served as a starting point in the analysis of the similarity between AEMs and lanthanides [10, 11, 13].

SIMILARITIES BETWEEN ALKALINE EARTH ELEMENTS AND LANTHANIDES

The indicated coincidences are a manifestation of a new pattern – the similarity of alkaline earth elements with rare earth elements [11, 13], which consists in the proximity of spectra, structure, physical and chemical properties, in particular energy properties, of elements connected by a two-sided arrow:



Thus, calcium is similar to ytterbium, strontium is similar to europium with its most stable $4f^n$-core [14], and barium, located at the intersection of a column and a row, is the zero element ($4f^0$) of lanthanides, without which there are no multitudes in the mathematical sense of the word. But the most convincing argument for the reality of the similarity is the spectra (Fig. 1) [13]. Their coincidence clearly proves the similarity for very different elements located in different groups of the D. I. Mendeleyev table.

The Eu-Sr similarity occurs not only for free atoms and ions, but also in the condensed phase. Solid strontium and europium have the same type of crystal lattice with similar temperatures and heats of fusion: 1041 K and 9.20 kJ/mol – Sr, 1099 K and 9.21 kJ/mol – Eu [15]. Their densities are related as the atomic weights of these elements, which indicate similar cell parameters of their crystal lattices.

The reason for the Eu-Sr similarity lies in the proximity of the wave functions of their valence shells, since the energy characteristics of the atom and the chemical bond of its compounds are determined by the external asymptotes of the wave functions, i.e. the spatial distribution of its amplitude part at large distances from the nucleus. It is namely here that the main maxima of the valence electron density are located, which practically coincide: 0.1836 nm (Sr) and 0.1826 nm (Eu) [15]. Their external asymptotes are described by the exponentials A·exp[–γ·r] with close parameters: A = 0.86, γ = 0.647 for Sr and A = 0.89, γ = 0.646 for Eu [7] in au. This means that the root cause of the Eu-Sr similarity, as well as of the other elements connected by a double-sided arrow, lies in the coincidence of the characteristic sizes of the valence shells of these elements and the position of the main maxima of their densities.

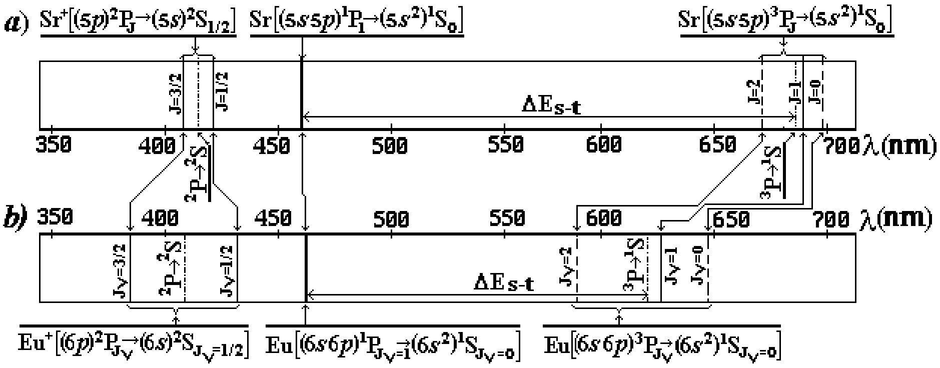


Fig. 1. Spectra of strontium and europium atoms and ions [13]. The dotted lines indicate the positions of optical transitions in spectrum forbidden in the dipole approximation, the dashed-dotted lines indicate lines in the absence of spin-orbit interaction, ΔE_{s-t} – singlet-triplet splitting: a) spectrum of Sr and Sr^+(n=5) [6]; b) spectrum of Eu and Eu^+(n=6) with the "disconnected" magnetic fields of $4f^7$ core [13]
Рис. 1. Спектры атомов и ионов стронция и европия [13]. Пунктиром дано положение линии, запрещенной в дипольном приближении, штрих-пунктиром – в отсутствии спин-орбитального взаимодействия, ΔE_{s-t} – синглет-триплетное расщепление: а) спектр Sr и Sr^+(n=5) [6]; b) спектр Eu и Eu^+(n=6) с «отключенными» магнитными полями $4f^7$-остова [13]

The same spatial distribution of valence electrons of $Sr(5s^2)$, $Sr^+(5s)$ and $Eu(6s^2)$, $Eu^+(6s)$ suggests the proximity of the parameters of molecules formed by these elements. Thus, for the most spectroscopically and mass-spectrometrically studied monofluorides of strontium [6] and europium [16, 17]: $r_o = 0.2078$ and 0.2083 nm, $\Delta G_{½} = 495.5$ and 493 cm^{-1}, $D_o = 540±6$ and 540±8 kJ/mol.

There is a coincidence in the equilibrium constant of the reactions $M^+ + H_2O \leftrightarrow MOH^+ + H$: $K^o(2696\ K, M=Sr) = 0.36 \approx 0.41 = K^o(2696\ K, M=Eu)$ [5, 9], also at different temperatures, which means the equality of the entropies of their participants and, therefore, the parameters of the ions. The proximity of the equilibrium constants means that the substitution of europium for strontium or vice versa in the substance does not change either the internuclear distances, or their vibration frequencies of nucleus, or the energy of the chemical bond and the electron shell as a whole, or its ionization potential in particular. But the substitution greatly changes the system of electron terms due to the unfilled $4f^7$ core of Eu, which, unlike the krypton-like $(4s^24p^6)^1S_0$ core of Sr, being a source of magnetic field, splits them in EuX into non-degenerate magnetic components. Thus, the ground term $SrF(X^2\Sigma_{0±½})$ is doubly degenerate without an internal magnetic field, and in Eu^+F^- it is split by it with an magnetic induction of $|\mathbf{B}| \approx 2000$ T into Zeeman components: the ground term $^{8+1}\Sigma_{7/2+½}$ and the low-lying $^{8-1}\Sigma_{7/2-½}$ with an energy of 1421 cm^{-1} [16], where 8 is the multiplicity of the $(4f^7)^8S_{7/2}$ core of Eu, as a source of the internal magnetic field.

INTERNAL STARK EFFECT

The intramolecular Stark effect (hereinafter referred to as the IMS effect) does not differ almost from the classical one [18]. In the latter, the energy levels of atomic particles (atoms, molecules, ions) change under the influence of an external homogeneous electric field. In the IMS effect, which has a basic and spectroscopic modifications, this occurs under the influence of an internal, non-uniform field of the ionic molecule $M^{|z|+}X^{|z|-}$, unattainable in the laboratory in its strength, consisting of its opposite electrically charged parts: a cation and anion, mutually polarized by it. Consequently, ionic molecules make it possible to expand the Stark effect to the region of super-strong fields with an intensity of $|\boldsymbol{\varepsilon}| = \varepsilon$ up to 500 MV/cm, whereas in the laboratory it is many thousands of times less.

Among ionic molecules, the compounds of halides MX with X = F, Cl, Br and J are notable for the fact that their single-charged anion X^- ($|z| = 1$) has a filled electron shell of its neighbors in the Periodic Table – the inert gases Ne, Ar, Kr and Xe, respectively, stabilized by the field of the cation M^+. Therefore, it has all the properties inherent in them: the absence of low-lying electron states and high energy stability to excitation and ionization. It differs to halides from other ionic compounds of other classes: oxides, sulfides, etc., and places them and their similar analogs, hydroxides for example, first in the list of objects of our study, as the most suitable. In addition, many of the monohalides have been intensively studied by experimental methods. In this regard, it is possible to compare the experimental results with those obtained using the new approach based on the IMS effect.

The basic modification [19] is based on the linearity of the ionization potentials in the coordinates $I_o(MX) = f\{[r_0^{-4}\ (M\text{-}X)]\}$, which was initially shown for barium monohalides $BaX \equiv Ba^+X^- \equiv eBa^{2+}X^- \equiv$ $\equiv e_1Ba^{2+}e_2X$ in 1983, considered in the IMS model by the Ba^+ ion in Ba^+X^- – this conception was introduced by author [20] and used by author [21] in which the nonbonding electron is written from the left, and the bonding one – to the right of symbol of chemical element Ba. The indicated dependence intersects the ordinate axis at the internuclear distances $r(M\text{-}X) \to \infty$, at the point $I_o(Ba)$, corresponding to the ionization potential of the product of adiabatic dissociation $Ba^+X^- \to$ $\to Ba + X$, treated by the Ba^+ ion in the atom $Ba \equiv eBa^+$ $\equiv e_1Ba^{2+}e_2$. In other words, atom as $Ba \equiv Ba^+e$, and molecules as $Ba^+X^- \equiv Ba^+eX$, form a united multitude in which the atom Ba is its zero element with zero internal field and zero dipole moment, as the initial point of reference of its intensity is $\varepsilon = 0$, when removing the X^- anion to infinity, where $\varepsilon = 0$ and $|\mathbf{p}| = p = 0$ also. This modification of the IMS model is generalized to similar compounds of aluminum, thallium and the alkaline earth metals – calcium and strontium, chlorides and iodides of alkali metals [19, 22÷24]. Later [24, 25] it was successfully applied to lanthanide monohalides.

The linearity of the ionization potentials of a wide range of ionic compounds in the specified coordinates, in particular barium monohalides, is interpreted in terms of the quadratic Stark effect. This means that the field of the anion X^- with an intensity of ε polarizes the friable nonbonding orbital $\sigma(6s)$ with the ionized electron e of the cation $Ba^+ \equiv eBa^{2+}$, pushing it beyond the internuclear region, thereby inducing a dipole moment $\mathbf{p} = \hat{\alpha}\varepsilon = \varepsilon\tilde{\alpha} = \alpha\boldsymbol{\varepsilon}$ in it and increasing its energy by the value of the Stark (polarization) shift

$$\Delta E_n = \int_0^{\varepsilon}(\mathbf{p}\cdot d\boldsymbol{\varepsilon}) = \int_0^{\varepsilon}(\boldsymbol{\varepsilon}\tilde{\alpha}d\boldsymbol{\varepsilon}) = \alpha\int_0^{\varepsilon}(\boldsymbol{\varepsilon}\cdot d\boldsymbol{\varepsilon}) = ½\alpha(\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon}) = ½\alpha\varepsilon^2,$$

as if the free ion Ba^+ were placed in an external electric field. In other words, the field X^- in Ba^+X^- is external to Ba^+. The ionization potential – $I_o(Ba)$, during the formation of Ba^+X^- – $I_o(BaX)$, according to the Koopmans theorem, decreases as well: $I_o(BaX) = I_o(Ba) - \Delta E_n = I_o(Ba) - ½\alpha\varepsilon^2$ in accordance with the quadratic Stark effect – lower part of Fig. 2a.

$\Delta E_n = ½\alpha\varepsilon^2$ is obtained in the second order of perturbation theory and it is result of an interaction with dipole moment **p** induced by an external field by strength **ε** which is more weak as compared with inner atomic one. The quadratic Stark effect works also in powerful inner molecular field but polarizability α because of screening by M^{2+}core of the X^- anion field became effective magnitude. Therefore, the values $\Delta E_n = I_o(M) - I_o(MX)$ describe polarizative course of ionization potentials MX. The course as compared with $I_o(M) > 5$ eV is small – ≤ 0.6 eV. Therefore, it is considered as a perturbation of the energy of the ion M^+ in the atom $M \equiv eM^+$ with the formation of the molecule $e_1M^{2+}e_2X \equiv M^+X^- \equiv MX$ by its anion field X^-. In this case, the ionization potential changes from $I_o(M)$ in the process $M+X \equiv M+e+X \equiv M^++eX \equiv M^++X^- \rightarrow MX$ to $I_o(MX)$.

For a spherical $X^{|z|-}$ with a charge $|z|\cdot e$, the Stark shift in CGSE units is $\Delta E_n = ½\alpha(ze/r_o^2)^2 = ½\alpha(ze)^2/r_o^4$, where r_o is an internuclear distance of a $M^{|z|+}$-$X^{|z|-}$ molecule at the zero vibrational level, if we define its adiabatic ionization potential $I_o(MX)$, which is its parameter. At the same distances from the field source – X^-, $M^+ \equiv eM^{2+}$ has a part of the non-bonding orbital with electron e, “unshaded” by the core of M^{2+}, polarized by the field X^- beyond the internuclear region, i.e. beyond the core of M^{2+}.

As a result, we have the desired linear dependence $I_o(MX) = f\{[r_o^{-4}\,(M\text{-}X)]\}$ with its intersection of the ordinate axis at the point $I_o(M)$, which is confirmed by the experiment [19, 22÷26] using the example of monohalides ($|z| = 1$) of many metals:

$$I_o(MX) = I_o(M) - ½\alpha e^2/r_o^4 \tag{1}$$

The effective polarizability $\alpha \equiv \alpha_{zz}$ of the M^+ ion in $eM^{2+}X^-$, which is a diagonal element of the second-rank tensor matrix, is less than its full value α_o for M^+ in $M \equiv eM^+$, since the M^{2+} core screens most of the nonbonding orbital with the electron e removed during ionization. Their ratio α/α_o is the volume fraction of the “unshadowed” part of the nonbonding orbital. Thus, for barium, considered as an ion in its atom, the full polarizability $\alpha_o = 40\pm4$ Å^3 [7], and for its ion in Ba^+X^- the effective polarizability $\alpha = 1.93\pm0.4(2.8\sigma)$ Å^3 [19]. Hence $\alpha/\alpha_o \approx 0.05$, which means almost complete shading.

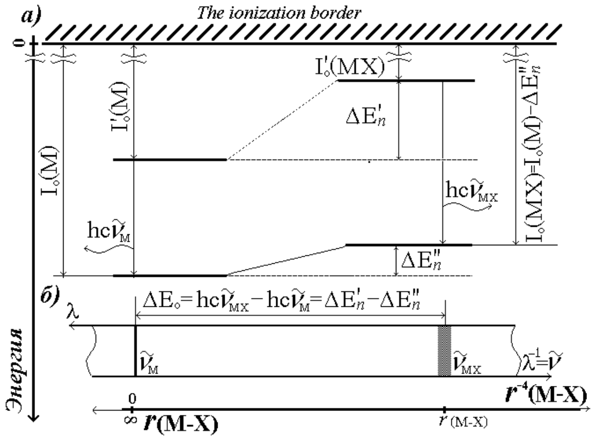


Fig. 2. a) Polarization shift of the levels of the M^+ ion in molecule M^+X^- by the axial field of its anion X^- relative to position its line in the $M \equiv M^+e$ atom. b) The magnitude ΔE_o determined below as optical shift of band MX of the M^+ ion in molecule M^+X^- by the axial field its anion X– relative to position of its line M in the $M \equiv M^+e$ atom

Рис. 2. а) Поляризационное смещение уровней иона M^+ в молекуле M^+X^- осевым полем аниона X^- относительно их положений в атоме $M \equiv M^+e$. b) Величина ΔE_o, определенная ниже как оптическое смещение полосы MX иона M^+ в молекуле M^+X^- осевым полем ее аниона X^- относительно положения его линии M в атоме $M \equiv M^+e$

Dependence (1) is consistent with the $I_o(M) - I_o(MX) = D_o(M^+\text{-}X) - D_o(MX) = \Delta E_n''$ cycle according to which the bond energy of the M-X molecule during its ionization: $MX \equiv e_1M^{2+}X^- \rightarrow M^{2+}X^-+e_1$, and the ionization potential $M \equiv e_1M^+ \rightarrow M^++e_1$ during localization of the cation-polarizing electron e_2 on the anion $e_2X \equiv X^-$, when $M^+e_2+X \rightarrow M^+e_2X \equiv MX$ is formed, change equally by the value $\Delta E_n''$. The cycle is linked with (1), where $I_o(M)$ is also the starting point for the value of $I_o(MX)$, due to its course in terms **of the IMS effect, proving its as a physical regularity, equal in importance to the classical Stark effect**, and not as a successful empiricism.

The spectroscopic modification [26] of the IMS model is based on the same quadratic Stark effect, but applied not to one electronic state – the ground state, as in the basic version with $r_o'' \equiv r_o$ and $\alpha'' \equiv \alpha$, but to a set of them, including, in addition to the ground state, also excited states with r_o' and α', the optical transitions from which form the beginning of the Rydberg series, which is reliably observed in the spectrum and, moreover, is, as a rule, well structured. The spectroscopic modification of the IMS model, initially discovered on strontium monohalides in 1981, was demonstrated on similar calcium compounds [26]. Later [11] this version was successfully applied to the study of the ionization energetic of monohalides and monohydroxide of AEMs and ytterbium, as one of the representatives of the lanthanides.

Table

Parameters of strontium monohalides SrX($X^2\Sigma^+$ and $B^2\Sigma^+$)

***Таблица*. Параметры моногалогенидов стронция SrX($X^2\Sigma^+$ и $B^2\Sigma^+$)**

Parameter/Molecule			$^{88}Sr^{19}F$ [31÷34]	$^{86,88}Sr^{35,37}Cl$ [34, 35]	$^{88}Sr^{79,81}Br$ [36, 37]	$^{88}Sr^{127}J$ [37, 38]
r_o'' (Å)			2.07858308(165)	2.57872214(184)	2.73751853(541)	2.975789285(426)
r_o' (Å)			2.08335249(964)	2.5593398(106)	2.7098090(138)	2.9299177(109)
$T_o(B^2\Sigma^+)$ (см$^{-1}$)			17264.14176(237)	15725.11121(179)	15355.77946(344)	14820.1619(7)
I_o(SrX)	«S»	eV cm^{-1}	5.2571177(524) 42401.52(42)	5.5234359(224) 44549.52(18)	5.5810737(177) 45014.40(14)	5.6606228(127) 45656.00(10)
	«**R**»	eV cm^{-1}	**5.2571±0.0166** **42402±134**	**5.5234±0.0166** **44550±134**	**5.5811±0.0166** **45014±134**	**5.6606±0.0166** **45656±134**
	[24]	eV	5.21±0.06	5.51±0.06	5.56±0.06	5.62±0.06

Note: 1 eV = 8065.54445±0.00151 cm^{-1} = 1/ce : hc/e^2·10^8 = 1/14.3996445 : 8.61022578·10^{-6} = e·10^8/hc^2 = 96.4853377(233) kJ/mol = eN$_A$/100c, hN$_A$/8π^{2}c = 16.85762909(396) (g/mol·Å^2)×cm^{-1} [27]. Experiment: 5.25±0.06 eV [24] is the EI MS result, and 5.18±0.10 eV was obtained by recalculating the experiment data on studying the ionic-molecular equilibrium by method of spectrum photometry of flames – IME SPhF data [39] (as for SrOH [4, 5]). For SrCl, 5.51±0.08 eV is the IME SPhF result [41], 5.59±0.10 eV is the EI MS result [40], and 5.41±0.12 eV [23, 42] is the threshold energy of the reaction $Sr+Cl_2 \rightarrow SrCl^+ + Cl^-$ – TER. The bottom line contains the results [23]. The IMS model application improves the accuracy in I_o(SrX) [23] by almost 4 times

Примечание: 1 эВ = 8065,54445±0,00151 см$^{-1}$ = 1/ce : hc/e^2·108 = 1/14,3996445 : 8,61022578·10^{-6} = e·10^8/hc^2 = 96,4853377(233) кДж/моль = eN$_A$/100c, hN$_A$/8π^{2}c = 16,85762909(396) (г/моль·Å^2)×см$^{-1}$ [27]. Эксперимент: 5,25±0,06 эВ [24] результат ЭУ МС, а 5,18±0,10 эВ получен пересчетом данных эксперимента по изучению ионно-молекулярного равновесия методом спектро-фото-метрии пламен – ИМР СФП [39] (как для SrOH в [4, 5]). Для SrCl – 5,51±0,08 эВ результат ИМР СФП [41], 5,59±0,10 эВ результат ЭУ МС [40], а 5,41±0,12 эВ [23, 42] есть пороговая энергия реакции $Sr+Cl_2 \rightarrow SrCl^+ + Cl^-$ – ПЭР. В нижней строке – результаты [23]. Внутримолекулярная Штарк (ВМШ) модель, ее применение точность в I_o(SrX) [23] улучшает почти в 4 раза

The beginning of the Rydberg series T_o(MX) in the spectrum, counted from the line E(M) of the excited product M* of adiabatic dissociation into a neutral pair (Fig. 2*b*) of the excited molecule MX* → → M*+X: $T_o(MX)–E(M) = \Delta E_n'–\Delta E_n''$, determines the difference in the Stark (polarization) shifts (Fig. 2a) – $\Delta E_n'$ and $\Delta E_n''$, called the optical shift:

$$\Delta E_o = \Delta E_n' - \Delta E_n'' = T_o(MX) - E(M) =$$

$$= ½[\alpha'(\varepsilon')^2 - \alpha''(\varepsilon'')^2] = ½e^2[\alpha'/(r_o')^4 - \alpha''/(r_o'')^4] =$$

$$= \frac{e^2}{2}\left(\frac{\alpha'-\alpha''}{r_c^4} + 4\frac{\alpha'+\alpha''}{r_c^5}\Delta r_o + \ldots\right),$$

where $r_c = (r_o''+r_o')/2$, $\Delta r_o = (r_o''-r_o')/2$ (2)

as a measure of the shift in the spectrum of band of M^+ ion in molecule $M^+X^- \equiv e_1M^{2+}e_2X \equiv eM^{2+}X^-$, polarized by the axial field of the electron e_2 localized in electronic shell of X^- anion – T_o(MX), from line of this M^+ ion in atom $M \equiv eM^+ \equiv e_1M^{2+}e_2$, polarized by the central field of this electron e_2 delocalized in electronic shell of atom M – E(M) [11], Fig. 2b.

The ionization potential $I_o(MX^*) \equiv I_o'(MX) = I_o(MX) - T_o(MX)$ of excited molecule $(M^+X^-)^*$ with spherical X^- anion at a distance r_o' from $(M^+)^*$ looks similar to (1):

$$I_o'(MX) = I_o'(M) - \Delta E_n' =$$

$$= I_o(M^*) - ½\alpha'(\varepsilon')^2 = I_o(M) - E(M) - ½\alpha' e^2/(r_o')^4, \quad (3)$$

where the quantities included in (1) and (3) are related by the optical shift $\Delta E_o = hc\tilde{\nu}_{MX} - hc\tilde{\nu}_M = T_o(MX) - E(M)$ – Fig. 2, determined by equation (2).

Equation (2) can be verified since T_o(MX), E(M), r_c and Δr_o are found from the spectrum (Table) and applied to the graph $T_o(SrX) = f(r_c^{-4})$ – Fig. 3a. It is linear, like $I_o(MX) = f[(r_o'')^{-4}]$ in [19, 22÷25].

The inner electric field of X^- anion also as outer one besides of induced dipole removes three-multiple degeneration of 5p-orbital splitting its on non degenerative axial $5p_z$ component and twice multiple degenerative $5p_{x,y}$ components lying in plane perpendicular to z axe so far so this field shifts these Zeeman components by variable manner: more strong p_z oriented to field source than $p_{x,y}$. This shifting in absence of degeneration on l-numbers is described in second order of perturbation theory out of dependence from degeneration on m-numbers which fix in space 5p orbital orientation. In our work the $5p_z$ component shifting is studied only in approximation of quadratic Stark effect neglecting by 5p-orbital splitting and its $5p_{x,y}$ components together with its polarizabilities α_{xx} and α_{yy}.

The zero vibrational level of the term $\sigma(5p)B^2\Sigma^+$ with the symmetry of the ground one – $\sigma(5s)X^2\Sigma^+$, is taken as T_o(SrX), since the transitions from it form the beginning of the Rydberg series in the spectrum. It adiabatically dissociates into Sr[$(5s5p)^3P$] with the energy E(Sr) = (14317.520+14504.351+14898.563)/3 = = 14573.478(17) cm^{-1} [6] of the first metastable state. Unlike $\pi(5p)A^2\Pi$, $\sigma(5s)X^2\Sigma^+$ and $\sigma(5p)B^2\Sigma^+$ have not spin-orbit and vibronic (Renner-Teller, as in SrOH) interactions, which, superimposed on the Stark interaction, would distort it. There is also the perturbations between the near lying $A^2\Pi$ and $B^2\Sigma^+$ states, the largest in the monoiodide – 12.7 cm^{-1} = 14820.1619–14807.5 [28, 29], much smaller than the spin-orbital (> 200 cm^{-1} [6]). Interaction between identical terms formed by different electron configurations is also possible, for example, between $(np^2)^1D$ and $(nsnd)^1D$ in Mg, Al^+, etc., when their energies coincide. In Mg it is so strong that it inverts the sign of the singlet-triplet $(3s3d)^3D$-$(3s3d)^1D$ splitting [30], but this phenomenon is rare. Because of $\Delta r_o << r_o'' \approx r_o'$ the second term on the right-hand side of (1) is small, especially for SrF and SrCl, which is why the least squares method (LSM) straight line with the slope $\Delta\alpha = \alpha'$–α'' passes 1.9 cm^{-1} below the point of the monofluoride and 4.5 cm^{-1} above the monochloride, cutting off the value 14570.9 ± 20.9(4.3σ) cm^{-1} on the ordinate axis, that is very close to the energy E(Sr) = 14573.478(17) cm^{-1} of the $(5s5p)^3P$ term with the "disconnected" spin-orbit interaction – fragment **A** in Fig. 3a. The deviations of points SrJ and SrBr from the LMS straight line are noticeably greater – fragments **B** and **C** in Fig. 3a, respectively. The deviation reasons are presented below.

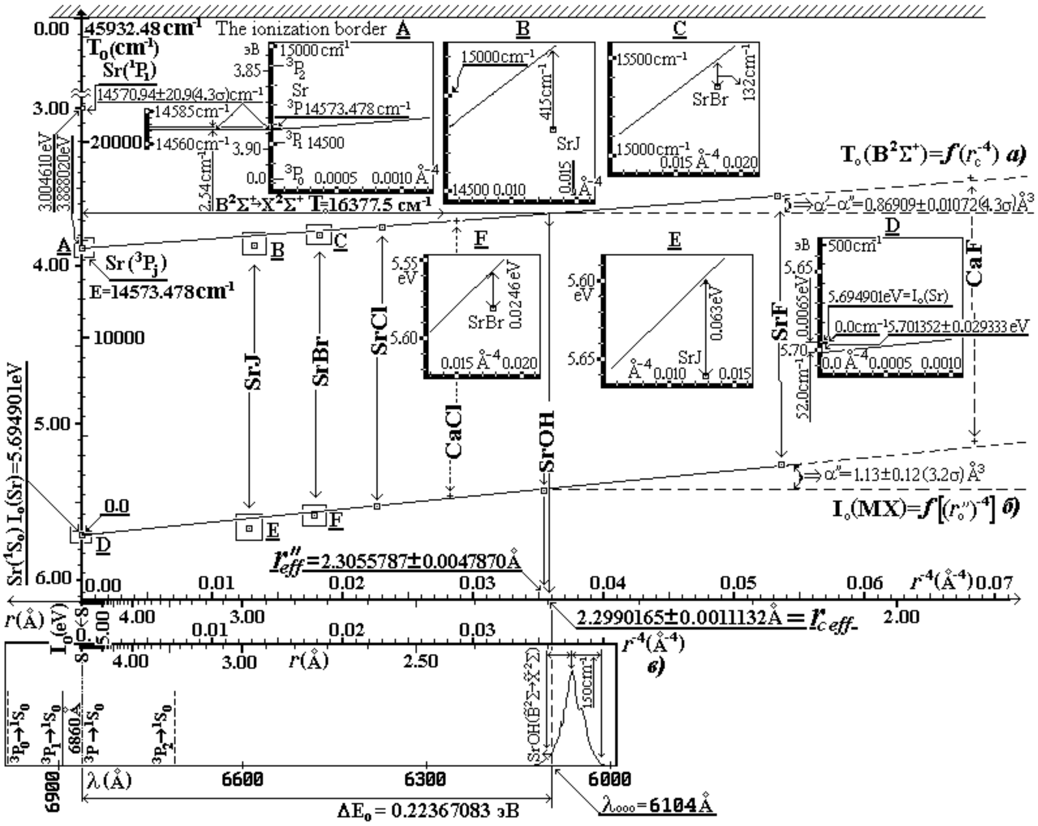


Fig. 3. a) The energy of the excited term $T_o[MX,\sigma(5p)B^2\Sigma^+] = f(r_c^{-4})$ – symbol ▣ – M=Sr, scale in cm^{-1}, which is to the right of the ordinate axis, is linear with high accuracy from the inverse to the fourth power of the average distances rc from cation M^+ to the source of the internal field – anion X^-. The linear part of this dependence – SrF, SrCl and product of their adiabatic dissociation – Sr, is developed by the least square method. The dotted line shows the expansion of the dependence by including CaCl and CaF [6] – symbol +. With the growth of $r_c \rightarrow \infty$ the terms $T_o(SrX) \rightarrow E(Sr)$, therefore they – $T_o(SrX)$, form the beginning of the Rydberg series. b) The graph of $I_o[MX,\sigma(5s)X^2\Sigma^+] = f[(r_o'')^{-4}]$ is constructed using the table data – symbol "S", the scale in eV, which is to the left of the ordinate axis with its counting from the ionization limit; symbol ▣ – M=Sr, symbol + – CaCl and CaF, their ionization potentials were calculated according to the spectroscopic data of [6, 7] similarly to SrX. LSM development includes the linear part of dependence: SrF, SrCl, SrOH and product of their adiabatic dissociation – Sr. c) Spectrum of the Sr^+ ion in atom the $Sr^+ \equiv Sr^+e$ atom and in the monohydroxide $Sr^+(O–H) \equiv Sr^+(eOH)$

Рис. 3.a) Энергия возбужденного терма $T_o[MX,\sigma(5p)B^2\Sigma^+]=f(r_c^{-4})$ – значок ▣ – M=Sr, шкала в $см^{-1}$, что справа от оси ординат, – с высокой точностью линейна от обратных в четвертой степени средних расстояний r_c от катиона M^+ до источника внутреннего поля – аниона X^-. Линейная часть этой зависимости –SrF, SrCl и продукт их адиабатической диссоциации – Sr, обработана методом наименьших квадратов. Пунктиром показано расширение зависимости включением в нее CaCl и CaF [6] – значок +. С ростом $r_c \rightarrow \infty$ термы $T_o(SrX) \rightarrow E(Sr)$, поэтому они – $T_o(SrX)$, образуют начало ридберговских серий. b) График $I_o[MX,\sigma(5s)X^2\Sigma^+] = f[(r_o'')^{-4}]$ построен по данным табл. – литера «S», шкала в эВ, что слева от оси ординат с ее отсчетом от ионизационного предела; значок ▣ – M=Sr, значок + – CaCl и CaF, их потенциалы ионизации рассчитаны по спектроскопическим данным [6, 7] аналогично SrX. МНК обработка включает линейную часть зависимости: SrF, SrOH, SrCl и продукт их адиабатической диссоциации Sr. c) Спектр иона Sr^+ в атоме $Sr \equiv Sr^+e$ и в моногидроксиде $Sr^+(O–H) \equiv Sr^+(eOH)$

Thus, both modifications of the IMS model are confirmed by experiment. The linearity of the graph $T_o[SrX,\sigma(5p)B^2\Sigma+] = f(r_c^{-4})$ in Fig. 3a, constructed using precision spectroscopic data, indicates that the behavior of the excited terms of SrX also corresponds to the quadratic Stark effect, as the ground ones in the example of $I_o(MX)$ [11, 19, 22÷26], in particular $I_o(BaX)$. This allows us to find with high accuracy the adiabatic ionization potential of the M^+X^- molecule by position (not intensity, which is very important) in the spectrum of its $T_o(MX)$ band relative to the E(M) line – the product of adiabatic dissociation of excited MX*, i.e. by the optical shift ΔE_o – Fig. 2. Let us extract $\Delta E_n''$ from ΔE_o, equation (2), by multiplying ΔE_o by the fraction $\Delta E_n''/\Delta E_o$ of the value $\Delta E_n''$ in it:

$$\Delta E_n'' = \Delta E_o \times \Delta E_n''/\Delta E_o =$$

$$= [T_o(MX) – E(M)]\cdot\alpha''(r_o')^4/[\alpha'(r_o'')^4 – \alpha''(r_o')^4] \qquad (4)$$

And then, to obtain the desired $I_o(MX)$, we subtract $\Delta E_n''$ from $I_o(M)$:

$$I_o(MX) = I_o(M) - \Delta E_n'' = I_o(M) - \frac{\Delta E_n' - \Delta E_n''}{\frac{\alpha'}{\alpha''}\left(\frac{r_o''}{r_o'}\right)^4 - 1} =$$

$$= I_o(M) - \frac{T_o(MX) - E(M)}{\frac{\alpha'}{\alpha''}\left(\frac{r_o''}{r_o'}\right)^4 - 1} \qquad (5a)$$

Equation (5*a*) does not include $\alpha'' = 0.8\text{-}1.9$ Å^3 [11, 23], r_o'' and α', r_o' as in (1) and (3), but their ratios $\alpha'/\alpha'' = 1.7÷1.9$ [11] and $r_o''/r_o' \sim 1$ – Table, which change little for different M^+ in M^+X^-. Therefore, equation (5*a*), which represents the spectroscopic modification "S" of the IMS model can be used without internuclear distances, without significantly losing accuracy. Hence, (5*a*) is more preferable to (1) and (3), i.e. its basic version.

The spectroscopic version of the IMS model has a greater development potential compared to the basic one. Thus, to use the latter, calibration experiments are required to determine the effective polarizability, and knowledge of internuclear distances. In (5*a*), the latter do not play a large role. In addition, it is easier to estimate the ratio of effective polarizabilities than the quantities themselves. Nevertheless, calibration of equation (5*a*) is necessary. The "S" IMS model admits an improvement **that allows its application without a calibration experiment** if the effective polarizabilities of the cation and atom M in (5a) are replaced by the quantities from the spectrum: $\alpha'/\alpha'' = 2–\Delta E/\Delta I_o = 2–[E(M^+) - E(M)]/[I_o(M^+) - I_o(M)]$. In the formula for α'/α'' the quantity $E(M^+) = (23715.19 + 24516.65)/2 = 24115.92(14)$ cm^{-1} [6], if $M^+[(np)^2P] = Sr^+[(5p)^2P]$, determines the energy of the excited term of the free ion M^+ – the product of diabatic dissociation of the excited $MX[\sigma(np)B^2\Sigma^+] \rightarrow M^+[(np)^2P]+X^-$ into an ion pair, and $I_o(M^+) = 11.0302(20)$ eV [6, 7], if $M^+=Sr^+$, is its ionization potential. Substituting these values into the formula for α'/α'' together with the above values of $I_o(Sr)$ and E(Sr), we obtain $\alpha'/\alpha'' = 1.7782482(832)$. Substituting the formula for α'/α'' itself into (5*a*), we obtain the working equation:

$$I_o(MX) = I_o(M) - \Delta E_n'' = I_o(M) - \frac{T_o(MX) - E(M)}{\left[2 - \frac{E(M^+) - E(M)}{I_o(M^+) - I_o(M)}\right]\left(\frac{r_o''}{r_o'}\right)^4 - 1} =$$

$$= I_o(M) - \frac{T_o(MX) - E(M)}{\left[2 - \frac{E(M^+) - E(M)}{I_o(M^+) - I_o(M)}\right]\left[1 + 8\frac{\Delta r_o}{r_c} + 32\left(\frac{\Delta r_o}{r_c}\right)^2 + 88\left(\frac{\Delta r_o}{r_c}\right)^3 + 144\left(\frac{\Delta r_o}{r_c}\right)^4 + ..\right] - 1} \qquad (5b)$$

Neglecting the internuclear distances – $r_o''/r_o' \approx 1$, or the value $8\Delta r_o/r_c$ together with the remaining degrees of decomposition r_o''/r_o', the formula is extremely simplified:

$$I_o(MX) = I_o(M) - {}^1/_2\,\alpha''\, e^2\Big/r_o^4 \approx I_o(M) -$$

$$- \frac{[I_o(M^+) - I_o(M)]\cdot[T_o(MX) - E(M)]}{[I_o(M^+) - I_o(M)] - [E(M^+) - E(M)]} \qquad (5c)$$

This is a rare case when the energy of a multielectron shell of a molecule is represented by the simplest formula and with high accuracy. It is noteworthy that equations (5*b*) and (5*c*), unlike (1), (3) and (5*a*), include only spectroscopic quantities.

It is noteworthy that the formula for α'/α'' does not include the parameters of the M^+X^- molecule, but introduces them for the M^+ and M particles included in it. The simplicity of the formula for α'/α'' is determined by the constancy of other interactions, except for the polarization one, which changes the energy of the electron shell of the ion in the atom $M \equiv eM^+ \rightarrow \rightarrow M^+ + e$ when the valence electron *e* in M is replaced by the X^- anion in the course of $M+X \equiv M^+e+X \rightarrow$

$\rightarrow M^{+}+eX \equiv M^{+}+X^{-} \rightarrow M^{+}X^{-}$. The M^{+} (or M) particle, polarized by the X^{-} field, is the product of the diabatic dissociation of the excited molecule into an ion pair (or adiabatic dissociation into neutral particles):

$$\mathbf{M^{+}X^{-}[B^{2}\Sigma^{+}]} \longrightarrow \begin{cases} \mathbf{M^{+}[^{2}P]+X^{-}} \\ \mathbf{M^{+}e[^{3}P]+X} \end{cases} .$$

Note that equations (5) include the only parameter $T_o(MX)$ of the molecule, which constitutes its optical shift, determines the polarization and the beginning of the Rydberg series relative to the line of the product of its adiabatic dissociation, and the ratio of the internuclear distances is only a correction to the polarization.

APPLICATION OF THE INTERNAL STARK EFFECT TO THE STUDY OF IONIZATION ENERGY OF STRONTIUM MONOHALIDES AND MONOHYDROXIDE

Let us write for $SrX[\sigma(5p)B^{2}\Sigma^{+}]$ – Fig. 3*a* and 3*c*, the optical shift $\Delta E_o = T_o[SrX,\sigma(5p)B^{2}\Sigma^{+}]–E[Sr,(5s5p)^{3}P]$. For $SrOH[\sigma(5p)\tilde{B}^{2}\Sigma^{+} \rightarrow \sigma(5s)\tilde{X}^{2}\Sigma^{+}]$ it is equal to ΔE_o = [16377.505(1)–14573.478(17)] = = 1804.027(17) cm^{-1} = 0.22367083(211) eV [6, 7, 43]. The intersystem crossing transition $Sr[(5s5p)^{3}P \rightarrow \rightarrow (5s^{2})^{1}S_o]$ is shifted by the OH^{-} field from the red region (686 nm) to the orange (606 nm), becoming molecular – Fig. 3*c*. ΔE_o in equations (5) is related to $\Delta E''_n = \Delta E_o \Big/ \left[\frac{\alpha'}{\alpha''}\left(\frac{r''_o}{r'_o}\right)^{4} - 1 \right]$. The ionization potential of strontium decreases by $\Delta E_n''$ when it combines with hydroxyl (if X=OH) to form SrOH – Fig. 2. The factor $\left(r''_o/r'_o\right)^{4} \approx 1+8\Delta r_o/r_c+\ldots$ in the denominator of (5*b*) takes into account the change in internuclear distances during the transition $\sigma(5p)\tilde{B}^{2}\Sigma^{+} \rightarrow \sigma(5s)\tilde{X}^{2}\Sigma^{+}$, on which $\Delta E_n'$ and $\Delta E_n''$ depend, which are a measure of the optical shift of the SrX bands relative to the line of the Sr atom included in SrX, and the difference between $I_o(SrX)$ and $I_o(Sr)$. For Sr-OH, r_c = 0.210472(7) nm and Δr_o = 0.000656218(514) nm [43]. Due to the non-sphericity of OH, we take instead of r_c its effective value $r_{c\,eff}$ = 0.22990165(479) nm > r_c – Fig. 3*a*, since the source of the internal field – OH^{-}, the excess electron on oxygen O^{-}, is shifted towards hydrogen atom H: $\{[r_{ceff}\pm\delta r_{ceff}+\Delta r_o\pm\delta(\Delta r_o)]/[r_{ceff}\pm\delta r_{ceff}-\Delta r_o\mp\delta(\Delta r_o)]\}^{4}$ = = 1.0230975±0.0001893 ≈ ≈ $1+8\Delta r_o/r_{c\,eff}$ = 1.02283 ≈ 1 + + $8\Delta r_o/r_{c\,eff}+32(\Delta r_o/r_{c\,eff})^{2}$ = 1.023095.

Let us calculate the effective polarizabilities $Sr^{+} \equiv eSr^{2+}$ in $eSr^{2+}X^{-}$, which have independent scientific interest. They are a solution of the system of linear equations:

$$\begin{cases} \alpha' - (2 - \Delta E/\Delta I_o)\alpha'' = 0 \\ \alpha' - \alpha'' = \Delta\alpha \end{cases} \tag{6}$$

with the determinant $\varDelta = 1–\Delta E/\Delta I_o = 1 - \frac{24115.92(14)-14573.478(17)}{[11.0302(20)-5.694901]8065.54445}$ = 0.778248(83) = = $\Delta\alpha'/\alpha''$ normalized to 0.27, where ΔI_o = 11.0302(20)–5.694901 = 5.3353(20) eV [6, 7] and ΔE = = [24115.92(14)–14573.478(17)]/8065.54445 = = 1.1831119(174) eV [6]. According to Cramer α'' = = $\Delta\alpha/\varDelta$ = (0.86909±0.01072)/(0.7782482±0.0000832) = = $1.1167\pm[(0.01072/0.7782482)^{2}+(0.86909\cdot8.32\cdot10^{-5} / 0.7782482^{2})^{2}]^{1/2}$ = **1.117±0.014** Å^{3}, $\alpha' = \alpha''+\Delta\alpha$ = (1.1167 ± 0.0138)+(0.86909 ± 0.0107) = 1.9858 ± $(0.0138^{2} + 0.0107^{2})^{1/2}$ = **1.986±0.017** Å^{3}.

Let us demonstrate, using (5*b*), the calculation on the monohydroxide: $I_o(SrOH)$ = 5.694901(12)–0.22367083(211)/[1.7782482(832)·1.0230975(1893)–1] = $\underline{5.421906\pm0.000116}$ eV with error $\pm1.16\cdot10^{-4}$eV = = $\pm[(1.2\cdot10^{-5})^{2}+(2.6\cdot10^{-6})^{2}+(2.8\cdot10^{-5})^{2}+(1.1\cdot10^{-4})^{2}]^{1/2}$ = = ±0.94 cm^{-1}, where $2.6\cdot10^{-6} = 2.1\cdot10^{-6}/(1.7782\cdot1.0231 -1)$, $2.84\cdot10^{-5} = 0.2236708\cdot1.02310\cdot8.32\cdot10^{-5} / (1.778248\cdot1.02310-1)^{2}$ and dominant $1.122\cdot10^{-4} = 0.2236708\cdot1.778248\cdot1.89\cdot10^{-4} / (1.778248 \cdot 1.023098-1)^{2}$. Calculation using (5*c*) $I_o(SrOH)$ = = 5.694901–0.22367083·5.3353/(5.3353–1.1831119) = = 5.40750 eV differs from that obtained using (5*b*) by only 0.0144 eV. The ionization potentials of strontium monohalides were calculated in the same way using equation (5*b*). They are given in the table, in its lines with the letter "S".

The graph of $I_o(SrX) = f[(r''_o)^{-4}]$ in Fig. 3*b* is linear, like $T_o[SrX,\sigma(5p)B^{2}\Sigma^{+}]=f(r_c^{-4})$ in Fig. 3*a* and $I_o(BaX) = f[(r''_o)^{-4}]$ in [19, 22, 23]. From the slope α'' = = 1.13±0.12(3.2σ) Å^{3}, which is close to the spectroscopic value. The LSM straight line passes below the SrF point by 67 cm^{-1}, above SrOH by Δ_{max} =69 cm^{-1} and SrCl by 49 cm^{-1}, intersects the ordinate axis at 52 cm^{-1} = 0.0064 eV (!) below $I_o(Sr)$ in Fig. 3*b*.

The points SrBr – fragment **F**, and SrJ – **E**, on the graph in Fig. 3*b* are not included in the LSM processing due to deviations from the LSM straight line greater than the spread of the points SrF, SrOH, SrCl and Sr, which make up its linear part. The deviation is especially pronounced for the monoiodide. The same points on Fig. 3*a* – **B** and **C**, were not processed for the same reason. It is not in the second term in (1) with $\alpha'+\alpha''$, which gives positive curvature (concavity) to the graph $T_o[SrX,\sigma(5p)B^{2}\Sigma^{+}] = f(r_c^{-4})$ – Fig. 3*a*, since $\alpha' > \alpha'' > 0$, and the point SrJ makes it convex, whence $\alpha'+\alpha'' < 0$. It is connected with the fact that the IMS does not take into account a number of effects, the main one of which is the deviation from the ionicity of the bond in SrX, especially at X = J. This also applies to the function $I_o(SrX) = f[(r_o^{''})^{-4}]$, since the ionization potentials are the energies of the term $\sigma(5s)X^2\Sigma^+$, measured from the ionization limit – Fig. 2 and 3*b*. Therefore, it is impossible to determine the sum of effective polarizabilities from the curvature of the Stark dependence, at least for small $\Delta r_o << r_c$. In SrBr, covalence is barely evident, while in SrJ it is obvious.

Formal calculation of the error in $I_o(SrX)$ by adding the dispersions in the values $r_o^{''}$ of and r_o', E(Sr) and E(Sr$^+$), I_o(Sr) and I_o(Sr$^+$), T_o(SrX) in formula (5*b*) gives its value less than ±1 cm^{-1} ($\pm 1.16\cdot 10^{-4}$ eV ≈ ≈ ±0.9 cm^{-1}, if X=OH), as from the boundary of convergence of the discrete spectrum with the continuous one. The accuracy of the "S" IMS method requires analysis. Here (table) the upper uncertainty limit is estimated: $\pm\delta I_o(MX) \approx \pm\delta(\alpha'/\alpha'')\times(\Delta E_o)_{max} = \pm\frac{1}{2}(1.7852349–1.7678118)\times 1.9 \approx \pm 0.01655$ эВ ≈ ≈ ±134 cm^{-1}, due to the spread of α'/α'' applied to the maximum optical shift $(\Delta E_o)_{max}$ = 1.9 eV present in MgF – see below. Then the "S" IMS result is $I_o(SrOH)=5.4219\pm 0.0166$ eV$=43731\pm 134$ cm^{-1}, consistent with the IME SPhF method – 5.3724±0.0408 eV = 43332±329 cm^{-1} [4]. The uncertainty in $(r_{eff}^{''}/r_{eff}^{'})^4 = \{[(r_{c\ eff}\pm\delta r_{c\ eff})+(\Delta r_o\pm\delta(\Delta r_o))]/[(r_{c\ eff}\pm\delta r_{c\ eff}) - (\Delta r_o\pm\delta(\Delta r_o))]\}^4 = 1.0231\pm 0.0002$ does not affect the overall error $\delta[I_o(SrOH)]$ in the value of the SrOH ionization potential of due to the smallness of its contribution – only 0.000112 eV.

The recommended ionization potentials are the results of the "S" IMS method with the maximum estimated error, exceeding all previous ones in accuracy. They are highlighted with the letter "**R**" in the Table.

The ratio $\left(\alpha'/_{\alpha''}\right)_{Mg^+} = 2 - \frac{35715.095-21877.349}{(15.0354-7.6463)8065.54445} = 1.7678118$ [6, 7] for Mg$^+$ in Mg$^+$X$^-$ also coincides within a fraction of a percent with its values for Sr$^+$ and Ca$^+$ in their monohalides. The coincidence interval ~0.5% also includes $\left(\alpha'/_{\alpha''}\right)_{Ca^+} = 1.7830824$ – the difference with α'/α'' ~ ~ 0.3% and the maximum value $\left(\alpha'/_{\alpha''}\right)_{Ba^+} = 2 - \frac{21106.992-12805.792}{(10.004-5.2117053)8065.54445} = 1.7852349$ [6, 7] for Ba$^+$ in Ba$^+$X$^-$, which together with the minimum $\left(\alpha'/_{\alpha''}\right)_{Mg^+}$ form their boundaries used above for the upper estimate of the error the "S" IMS method for the largest value of $(\Delta E_o)_{max} \approx 1.9$ eV ≈ ≈(37168.3 – – 21877.3)/8065.54445 in MgF [6, 7].

We see that all AEMs and even excited helium (!) – He(1*s*2*s*-2*p*), for which $\left(\alpha'/_{\alpha''}\right)_{He^+} = 2 - \frac{[(329182.23 - 329179.768) - (169087.25 - 166277.54)]}{8065.54445[(54.418 - 40.813) - (24.5876 - 20.6160)]} = 2.0361$ [7], have close α'/α'' for the terms obtained from *nsnp* configurations with *n* = 2-6, i.e. He and from Be, with $\left(\alpha'/_{\alpha''}\right)_{Be^+}$ = 2–(31932.05–21979.49) / / [8065.54445(18.211–9.3228)] = 1.8611687 [6, 7] to Ba. This proves that polarization in an electric field is uniform, it does not depend on whether it is external or internal, **thereby indicating the integrity and identical significance of the classical and internal Stark effects** – polarization is determined by the structure of the electron shell, and not by the type of field source – internal, like an anion in an ionic molecule, or external, like the surface of electrodes under voltage in a laboratory setup.

CONCLUSION

Over a century and a half of research into the ionization energy of atoms and molecules, three approaches to determining ionization potentials have been developed:

- through observation of the ionization limit in the spectrum of the Rydberg series, with the help of which the ionization potentials of atoms have been found very accurately;
- through the study of the equilibrium of ion-molecular reactions;
- through the balance of energy in collisions of molecules with electrons or photons.

The approach presented by "S" IMS is closer to the first: «through observation of the ionization limit in the spectrum of the Rydberg series». In it, instead of the ionization limit, located at the end of the Rydberg series and poorly defined for molecules, especially those that are difficult to volatile due to the broadening of their bands and the convergence of electron states in the pre-ionization region, the optical shift of the beginning of the Rydberg series in spectrum of the studied molecule caused by intramolecular fields is measured, which is well observed and, as a rule, structured in the spectrum, especially for di- and triatomic compounds. High accuracy follows from this.

The authors propose to include the "S" IMS method in spectroscopic studies. This will greatly expand the capabilities of spectroscopy in terms of determining the adiabatic ionization potential of molecules. This magnitude will be determined along with vibrational, rotational and electronic parameters as naturally as the listed characteristics of the molecule. The researcher can perform them quite professionally, which makes it possible to use the natural starting point for counting energy – from the ionization boundary of the convergence of the discrete spectrum into a continuous one. An example is the works [31÷38] used in our article, the authors of which, if they knew how to do this, would have also determined the value of $I_o(SrX)$, where X=F, OH, Cl, Br and J, the importance of which is difficult to overestimate.

Firstly, it would solve to a large extent the problem of determining the adiabatic ionization potentials of molecules, at least ionic ones, reducing it to the simplest calculation using formula (5*b*, or 5*c*) in the presence of the necessary spectroscopic data – internuclear distances (desirable, but not obligatory) and the energy of the excited term (required), forming the beginning of the Rydberg series, converging to the sought ionization limit. The necessity of including the IMS model is increased by the fact that measuring the value of I_o for molecules is a difficult and labor-intensive task, even for the simplest diatomic compounds, if we are not talking about the appearance potential obtained by EI MS and close to the vertical ionization potential, a value interesting and necessary in science, but useless in calculating ion-molecular equilibria [23]. Moreover, the peculiarity of the current state of research in this area is that the overwhelming majority of our knowledge about the ionization energy of chemical compounds and, therefore, about the energy of their electron shells, namely, the natural counting of their energies is from the ionization limit; – most of this information was obtained by EI MS. To relate the appearance potential obtained by EI MS to the adiabatic one is a non-trivial task, even for compounds of two atoms [23], and in the case of polyatomic ones, it is often not solvable. Therefore, there are few accurate data on I_o for low-volatile compounds.

Secondly, the "S" IMS model studies the ionization energy of a family of molecules. Due to this, their values are internally consistent with the course of excited terms converging to the ionization limit with a common starting point for the energy of all molecules included in this family – Fig. 3.

Thirdly, the IMS model establishes relationships between other characteristics of the electronic shells of molecules and reveals new regularities in the structures of ionic substances.

In essence, the "S" IMS method is a new way of studying the adiabatic ionization potential of a molecule not from the intensities of the spectrum or ion currents of the mass spectrum, but from the precisely measured optical shift determined by the position of the bands relative to the metal line – the product of its adiabatic dissociation. In this, it compares favorably with methods with calibration experiments: electron impact, flame spectrophotometry, threshold reaction energy, etc. The scope of the "S" IMS model includes many substances with ionic bonds, including lanthanide compounds, including organometallic ones.

Thanks to the research of spectroscopists, the entropy part of the accuracy class of the thermodynamic properties of alkaline earth metal monohalides according to the classification [6] has reached the highest degree "I" – ≤0.03 J/(mol·K). Its energy component for the ions of these substances has come close to the accuracy class "C" – ~130 cm^{-1}, from formerly the lowest "F" and "G" in [6] – ~2500 cm^{-1}. This research has made a significant contribution to its increase.

In conclusion, we present (kJ/mol) the value $D_o(Sr^+\text{-}F)$ = **582±6**, calculated with $I_o(SrF)$ found here and the value of $D_o(SrF)$ taken in [6]. We also present the mean weighted value $D_o(Sr^+\text{-}OH) = (432.87/2.7 + {}$ $+ 428.1/3.4)/(2.7^{-1}+3.4^{-1})\pm(2.7^{-2}+3.4^{-2})^{-1/2} =$ **430.8±2.1 = = 36009±177** cm^{-1}, calculated with $D_o(Sr^+\text{-}OH) = {}$ $= 432.87\pm2.7$ [5] and 428.1 ± 3.4 **=** **[**$401.8+(5.694901-{}$ $-5.4219)\cdot96.48534]\pm[3.0^2+(0.0166\cdot96.48534)^2]^{1/2}$, where $D_o(Sr\text{-}OH) = 401.8\pm3.0$ [4] and the ionization potential $I_o(SrOH) = 5.4219\pm \pm0.0166$ eV has been obtained in this work.

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