Experimental investigation of electron valence structure of xenon compounds

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A crystal-diffraction method is used to measure the chemical shifts of the $K_{\alpha 1}$ and $K_{\beta 1}$ x-ray emission lines of Xe in XeF_2, XeF_4, $NaHXeO_4$, and Na_4XeO_6 relative to X in hydroquinone clathrate. The obtained shifts and the published values of Mössbauer isomer shifts of these compounds are interpreted within the framework of the effective-free-ion concepts. The x-ray transition energies and the density of the electrons at the nucleus in such an ion are obtained by a unified self-consistent Dirac-Slater calculation. The effective Xe-ion valence-level populations obtained in the present study are calculated and compared with the results of other method and with molecular calculations. It is shown that $5d$-orbitals of xenon take part in the chemical bond of high-valence oxygen compounds of xenon.

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INTRODUCTION

Ever since the discovery of compounds of noble gases, their electronic structure has been the subject of intensive and theoretical investigations. These compounds were investigated, in particular, by methods such as Mössbauer spectroscopy,[1] NMR,[2-4] ESR,[5] and x-ray photoelectron spectroscopy.[6,7] The problem of the electron-valance structure of these compounds can, however, not yet be regarded as solved. In none of the methods used to study this problem is the number of experimentally obtained independent parameters sufficient. On the other hand, the simultaneous use of the results of different investigations is limited by the fact that the experimental quantities are interpreted in different studies by using different model representation. The same physical concepts, for example the effective charge, can have different meanings.[8] As to quantum-mechanical calculations of the molecular valence structure, their results depend on the details of the calculation procedure and on the choice of the dimension and composition of the atomic basis. The most debatable in the problem of the electron valance structure of Xe compound is that of the participation of excited $5d$-orbitals of Xe in the chamical bond,[9-11] and no means obtaining a purely theoretical answer to this question are known.[12,13] It is therefore reasonable to attempt to interpret the results of several methods within the framework of a single model.[1)] This has already been done before the x-ray chemical shift (XCS) of the K-series emission lines and for the isomer shift in the Mössbauer effect in the investigation of I compounds.[16]

In the present paper, just as in Ref. 16, the objects of the investigation are molecular crystals and complex ions. In these compounds, even in the crystalline state, the valence and higher free levels are not band-like,[17] the relative position of the levels of the central atom is determined only by its nearest neighbors. The XCS of the $K_{\alpha 1}$ and $K_{\beta 1}$ lines of Xe in XeF_2, XeF_4, $NaHXeO_4$, and Na_4XeO_6, measured in the present work, and the isomer shifts in ^{129}Xe known for these compounds from the literature are interpreted within the framework of concepts of the valent configuration of the effective free ion. The energy of the x-ray transitions and the density of the electrons at the nucleus in such an ion are calculated on the basis of a unified self-consistent atomic calculation after Dirac and Slater (DS) with account taken of the finite size of the nucleus, using the program described in Ref. 18.

EXPERIMENTAL PART

The XCS measurement procedure did not differ from the one used in Ref. 16. Since the shifts usually amounted to $\sim 10^{-3}$ of the line width, the XCS values were calculated by the least squares method (LSM).

The substances used to prepare the samples were synthesized by methods similar to those described in Refs. 11 and 19–21. The Xe fluorides were purified by gas chromatography and their purity was 99.0% for XeF_2 and 99.5% for XeF_4. To prepare the samples, fine powders of the investigated substances (with a content ~ 0.1 g of Xe per sample) were mixed with teflon powder and pressed into disks ~ 1 mm thick and 12 mm in diameter. In the preparation of the samples and in further work with them, measures were taken to prevent hydrolysis. Thus, the XeF_2 and XeF_4 samples prepared in a dry box were placed in hermetically sealed teflon containers. In the measurement of the XCS on $NaHXeO_4$, slight radiolysis took place accompanied by loss of Xe in the form of gas; this decreased somewhat the intensity of the fluorescence from the sample during the time of one experiment. This fact was taken into account in the calculation of the XCS by introducing suitable corrections. In the other investigated samples, no radiolysis was noted within the time of the experiment (approximately 1 day).

DISCUSSION OF RESULTS

Table I lists the measured values of the XCS as well as the employed isomeric shifts for the investigation of the compounds relative to Xe contained in hydroquinone clathrate. Mean-squared errors are cited. The isomeric shift of $NaHXeO_4$ is not known, and we therefore used a value obtained by averaging the shifts for chemically close compound, XeO_3, and the Xe compounds produced following β decay of I in $NaIO_3$.[1] This value should be regarded as an estimate. However, the smallness of the variations of the known experimental

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TABLE I. Experimental shifts.

Compound	XCS, meV		Isomer shift,[1] mm/sec
	line	line	
Na_4XeO_6	515±5	773±15	0.19±0.02
Li_4XeO_6	520±5	782±15	—
$NaHXeO_4$	340±5	546±10	0.3±0.1 *
XeF_4	251±3	427±9	0.40±0.04
XeF_2	124±3	185±6	0.10±0.12

*See the text.

isomer shifts for oxygen compounds of the hexavalent Xe makes us certain that the true isomer shift of $NaHXeO_4$ lies within the one error assumed by us for this quantity and listed in Table I.

In each investigated compound, the Xe atom can be set in correspondence with an effective free ion such that its characteristics (change of the energies of the x-ray transitions or of the electron density at the nucleus relative to a reference ion with known configuration) agree with the experimental values. For Xe, the valent levels can be assumed to be $5s$, $5p$ and $5d$. By specifying various populations of the valent levels and carrying out each time the self-consistency procedure, we obtain a certain set of numerical values of the shifts, which can be represented by the system of equations

$$\delta_{\alpha 1}=f_{\alpha 1}(Q_{5s}, Q_{5p}, Q_{5d}), \quad \delta_{\beta 1}=f_{\beta 1}(Q_{5s}, Q_{5p}, Q_{5d}), \quad \delta_{\gamma}=f_{\gamma}(Q_{5s}, Q_{5p}, Q_{5d}). \quad (1)$$

Here $\delta_{\alpha 1}$, $\delta_{\beta 1}$, and δ_γ are the XCS of the $K_{\alpha 1}$ and $K_{\beta 1}$ lines respectively and the isomer shift relative to the $5s^2 5p^6$ configuration of the free Xe atom (this configuration was assumed for Xe in hydroquinone clatrate), Q_{5s}, Q_{5p}, and Q_{5d} are the populations of the valence levels. The assumption of the configuration $5s^2 5p^6$ for Xe in the clathrate is justified and was used earlier (see, e. g., Ref. 1), since the acceptor properties of the noble gases are weakly pronounced and the $5p \rightarrow 5d$ transition in Xe requires an appreciable energy that apparently cannot be compensated for by the weak bond in clathrate. Additional evidence against the assumption of a $5p \rightarrow 5d$ transition is provided by the practically zero isomer shift of the clathrate to solid Xe.

The energies of the x-ray lines are determined in the DS calculation as the differences between the corresponding single-electron orbital energies. The calculated changes of the electron density can be set in correspondence with the isomer shifts in the following manner (see, e. g., Ref. 22):

$$\delta_\gamma = {}^2/_5 \pi Z^2 e^2 R^2 \rho \Delta |\psi(0)|^2, \quad (2)$$

where Ze is the charge of the nucleus, R is the radius of the nucleus, $\rho = \Delta\langle R^2\rangle/\langle R^2\rangle$ is the relative change of the mean-squared charge radius of the nucleus on going to the isomer state, $\Delta|\psi(0)|^2$ is the change of the relativistic electron density at the nucleus for the two configurations. In our calculations we assumed $R = 1.2A^{1/3}$ (A is the mass number) and $\rho = 0.79 \times 10^{-4}$ for ^{129}Xe. The latter value was calculated from the ratio of the values of ρ for a number of nuclei in the sequence ^{119}Sn, ^{121}Sb, ^{125}Te, ^{129}I, and ^{129}Xe, obtained by Ruby and Shenoy,[23] and the value $\rho = 8.8 \times 10^{-4}$ obtained for ^{129}I from a calibration carried out in Ref. 16. The last quantity agrees well with the one recommended by de Waard.[24]

Since the level-population functions in the right-hand side of the system (1) are given numerically, there are two ways of solving the system: graphically, as in Ref. 16, and analytically, as in the present paper, after approximating the numerical values by a suitable function. It must be recognized that the results of a relativistic calculation for a given electron configuration depend on the specified distribution of the electrons of the outer unfilled shell over the sublevels of the fine-structure doublet, since the screening ability of electrons with total angular momenta $j = l \pm \frac{1}{2}$ (l is the orbital angular momentum) differs somewhat. In addition, in contrast to the $p_{3/2}$ electrons, the $p_{1/2}$ electron density in the region of the nucleus differs from zero. In the present paper we assume the model of a valence state with random direction of the valent-electron distribution,[25] according to which in our calculations the distribution of the electrons of over the levels of the fine-structure doublet is specified with a weight equal to the degree of degeneracy of the given sublevel relative to the projection of the total angular momentum. In this approach, the functions of the system (1) can be satisfactorily approximated, by least squares, by second-degree polynomials of the valent $5s$, $5p$, and $5d$ populations; the error in the coefficients of the polynomials is determined by the accuracy of the self-consistency and by the chosen parametrization of the approximating function. Substituting in the right-hand sides of the equations the polynomials obtained in this manner, and in the left-hand sides the experimental values of the shifts, we solve the system of equations for the populations by least squares. It should be noted that the result is stable against appreciable changes in the composition of the initial set of approximated shift values.

The results of our population analysis for the investigated compounds are given in Table II. The population errors listed in Table II are determined only by the statistical errors of the experimental results and by the errors of the coefficients of the polynomials, with account taken of the correlations between the latter, and do not include the possible systematic error due to the calibration of the isomer shift. The value $\rho = 0.79 \times 10^{-4}$ used by us for ^{129}Xe is known with accuracy 15%.[23,24] A decrease in the assumed value of ρ leads in the case of $NaHXeO_4$, XeF_2 and XeF_4 to a certain increase of the $5s$ population and a practically equal decrease of the $5p$ population, while for Na_4XeO_6 the order of the change in the population is reversed. The population of the $5d$ level remains unchanged within the limits of errors. For XeF_4 these changes are maximal and amount to 0.5 electron when ρ is decreased 20%. In the DS calculation, taking into account the diffuseness of the $5d$ orbitals,[13] we used Latter's correction[26] for the variation of the potential at large distances from the nucleus. If the cor-

TABLE II. Matched configurations.

Compound	Level population			Effective charges	
	Q_{5s}	Q_{5p}	Q_{5d}	Xe	ligands
Na_4XeO_6	1.52±0.02	2.60±0.03	0.83±0.12	3.05±0.15	−1.18±0.03
$NaHXeO_4$	1.89±0.07	3.03±0.07	0.40±0.13	2.68±0.15	−1.17±0.04
XeF_4	2.00±0.03	3.39±0.03	0.12±0.11	2.49±0.14	−0.62±0.04
XeF_2	1.94±0.09	4.61±0.09	0.54±0.27	0.91±0.30	−0.47±0.15

TABLE III. Valence configurations according to Ref. 1.

Compound	Level population			Effective charges	
	Q_{5s}	Q_{5p}	Q_{5d}	Xe	ligands
Na$_4$XeO$_6$ *	1.60	4.80	0	1.6	−0.93
Na$_4$XeO$_6$ **	1.60	4.80	3.20	−1.6	−0.4
XeF$_4$	−	3.00	−	3.00 ***	−0.75
XeF$_2$	−	4.57	−	1.43 ***	−0.72

*Assuming sp^3 hybridization.
**Assuming sp^3d^2 hybridization.
***Assuming $Q_{5s} = 2$ and $Q_{5d} = 0$.

TABLE IV. Valence configurations from molecular-calculation data.

Compound	Q_{5s}	Q_{5p}	Q_{5d}	Effective charge of Xe	Reference
XeF$_4$	2.03	3.63	−*	2.45	[6]
	2.00	3.66	−*	2.34	[28]
XeF$_2$	2.02	4.79	−*	1.30	[6]
	2.00	4.80	−*	1.20	[28]
	1.96	4.74	0.26 **	1.00	[29]

*Calculation without $5d$ orbitals in the basis.
**$Q_{4f} = 0.04$.

rection is not used, the values of Q_{5d} are lower than those in Table II by less than one experimental error. Table II gives also the effective charges of the Xe atoms, calculated from the obtained populations, and the effective charges of the ligands, obtained from the condition that the molecule be electrically neutral (the effective charges on the Na and H atoms were assumed to be +1). The errors of the effective charges were determined with allowance for the correlations between the population errors. The large error for Q_{5d} in XeF$_2$ is due to the fact that at low effective charges of the ion the XCS depends little on Q_{5d}. The same follows also from earlier self-consistent calculations for I.[16]

A comparison of populations obtained for the compounds of I (Ref. 16) and Xe (present work) show that the populations in the isoelectronic Na$_4$XeO$_6$ and Na$_2$H$_2$IO$_6$ are close. The relatively high population of the $5d$ level in these compounds allows us to state that in this case the $5d$ electrons of Xe take part in the chemical bond. The compound NaHXeO$_4$ turns out to be similar to KIO$_3$. In the isoelectronic compounds of Xe, the relative participation of the $5s$ electrons in the bond (relative to the $5p$ electrons) is lower than I compounds, this being natural because $\varepsilon_{5p} - \varepsilon_{5s}$ is larger, where ε_{nl} are the single-electron orbital energies (cf. Ref. 27). The charges on the central atom are higher in Xe compounds. The charges on the oxygen atoms are practically equal. It is concluded in Ref. 16 that the experimental shifts in KICl$_2$ and KICl$_4$ can be satisfactorily explained without assuming that the $5d$ electrons take part in the bond. The same can be said of XeF$_2$ and XeF$_4$ which are electron-isovalent to KICl$_2$ and KICl$_4$, respectively, although in the case of XeF$_2$ the error in Q_{5d} is too high.

Table III lists the atomic populations for XeF$_2$, XeF$_4$, and Na$_4$XeO$_6$ obtained from nuclear gamma resonance (NGR) experiments,[1] under the assumption of a pure p character of the bond in XeF$_2$ and XeF$_4$, and sp^3 or sp^3d^2 hybridization in Na$_4$XeO$_6$. The results of Table III for XeF$_2$ and XeF$_4$ do not contradict those obtained in the present paper, but are in marked disagreement for Na$_4$XeO$_6$, mainly because of the assumptions made concerning the type of hybridization, with an a priori connection between the change of the population in the formation of the chemical bond, namely $\Delta Q_{5p} = 3\Delta Q_{5s}$. This assumption was necessary because of the insufficient number of experimental quantities in the Mössbauer effect to be able to separate the contributions of the ss, p, and d electrons to the isomer shift.

We present below the effective charges of the F atoms, obtained from the data of Ref. 1 from the condition of electroneutrality of the molecule and directly from measurements of the NMR on ^{19}F,[2–4] and also from data of x-ray electron spectroscopy[7]:

XeF$_4$:	−0.55 [2]	−0.48 [3]	−0.50 [4]	−0.75 [1]	−0.24 [7]
XeF$_2$:	−0.70 [2]	−0.69 [3]	−0.58 [4]	−0.72 [1]	−0.24 [7]

The agreement with the results of the present paper is good, except for the last reference. A possible cause of the discrepancy is the point-charge model assumed in that reference.

Table IV shows the results of an analysis of the populations after Mulliken in non-empirical molecular calculations for XeF$_2$ and XeF$_4$. The studies in Refs. 6 and 28 were made with a limited basis (without inclusion of the $5d$ orbitals), while in Ref. 29 an extended basis was used, with partial allowance for the correlation effects. The results of the present paper are in sufficiently good agreement with those obtained in the most accurate quantum-mechanical calculations.

The XCS for Na$_4$XeO$_6$ and Li$_4$XeO$_6$ were measured before,[20] and the opinion was advanced that it is necessary to take into account the participation of the $5d$ orbitals of Xe in the bond in order to explain the large experimental XCS values which, assuming $Q_{5d} = 0$, led to an unjustifiably large charge on the Xe atom (>4.3e). The reverse transfer of the charge from the ligands to the free $5d$ orbitals of Xe (e. g., in accord with the $p_\pi - d_\pi$ binding scheme) makes it possible to explain the given XCS at a smaller charge on the central atom: lowering Q_{5s} and Q_{5p} and raising of Q_{5d} leads to the same effect, namely an increase of the energy of the $K_{\alpha1}$ line.[14] However, quantitative results could not be obtained without resorting to self-consistent calculations.

The method used in the present paper yields electronic valent configurations without any a priori assumptions on the character of the hybridization of the valence electrons.

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[1] In principle, the problem of determining the valence configuration of a given atom in its compound can be solved by measuring the x-ray chemical shifts of all the intense emission lines of the K series,[14] but for lines corresponding to transitions from upper atomic levels the XCS cannot be satis-

factorily described within the framework of the simple model of the effective free ion. In this case effects not accounted for in the one-center self-consistent calculation influence strongly the XCS.[14,15]

[2)]The less rigorous procedure used in Ref. 19 to reduce the experimental results led to a noticeable systematic underestimate of the XCS.

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Coulomb excitation of atoms by fast protons

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A Green's function technique is developed for calculating the dependence of the energy loss of heavy charged particles on the impact parameter in the quasiclassical approximation. Formulas are derived for the probabilities of bound-bound transitions in hydrogenlike atoms, and for their asymptotic values in the dipole approximation and in the strong coupling approximation. Simpler expressions than those previously derived are obtained for bound-free transitions. An analysis of the contributions of various Coulomb excitation channels is carried out on the basis of the results. An exact calculation of the energy losses shows that the mean-frequency approximation is not valid for the inner shell electrons.

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1. INTRODUCTION

Originally, interest in processes of Coulomb excitation of atoms arose in the study of energy losses of fast electrons, protons and alpha particles in the medium. The corresponding quantum theory was constructed by Bethe.[1] It is applicable in the case in which the ratio of the velocity of the electron in the atom v_0 to the velocity of the incoming particle

$$\xi = v_0/v = \hbar \lambda / mv = Z_a e^2 / \hbar v \tag{1}$$

is much less than unity (m is the mass of the electron, Z_a is the charge of the nucleus of the target atom).

In collisions with the participation of heavy particles ($M \gg m$), the deBroglie wavelength $\hbar / Mv$ is, as a rule much less than the characteristic atomic dimensions $1/\lambda$. This allows us to assume the trajectory of the incoming particle to be classical, and to consider the ex-