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X-Ray Emission Spectra and Quantum Chemical Calculations of Electronic Structure of Vanadium Oxides

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Electronic structure calculations for clusters in VO, V_2O_3, VO_2, and V_2O_5 have been carried out by the Mulliken–Wolfsberg–Helmholtz method with self-consistency on charges and configurations. The results of the calculations agree quite well with available experimental data and allow us to give a complete interpretation of X-ray emission and ESCA spectra. The effective charges and electron configurations for vanadium atoms in oxides have been obtained and chemical bonding effects are discussed.

The vanadium oxides VO, V_2O_3, VO_2, and V_2O_5, revealing a great variety of electrical and magnetic properties, are of considerable interest for inorganic chemistry. At room temperature the first two oxides are metals with rather high electrical conductivity. Vanadium dioxide possesses semiconducting properties; pure V_2O_5 is an insulator at all temperatures (*1*). Both V_2O_3 and VO_2 undergo sharp metal–nonmetal phase transitions at the appropriate Néel temperatures. Antiferromagnetic behavior at low temperatures was found for vanadium monoxide (*2*).

It is obvious that such anomalous properties of oxides, which have been studied in a great number of experimental works, are caused by the electron structure peculiarities and can be understood only if sufficiently detailed information about their electron structure is available. One of the direct methods for obtained such information is known to be X-ray emission and absorption spectroscopy, which is very intensively used in various studies of the electron structure of organic and inorganic compounds (*3*). However, the importance of experimental spectra was often considerably reduced due to the absence of sufficiently simple and reliable theoretical models for spectra interpretation. Progress reached in this field is connected with the application of the molecular orbital method (MO). When studying the compounds of 3*d*-metals in solids, the MO method is usually applied in the restricted version, i.e., only as the theoretical foundation for constructing empirical MO diagrams from a set of emission and absorption X-ray spectra. Such an approach (using some results of quantum-chemical calculation) is applied to high symmetry objects only, for instance, VO. For compounds of complicated low-symmetry structure, such as V_2O_3, VO_2, and V_2O_5, even if a sull set of well-resolved X-ray spectra is available, a construction of MO diagrams and determination of a clear-cut relation between the spectra peculiarities and the details of of electron distributions appear to be impossible when using experimental data only. This leads to the necessity for theoretical calculations of the real structural units in compounds by quantum chemistry methods. Such an approach allows one to give a reasonable explanation of experimental X-ray spectra and, together with them, provides valuable and detailed

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information about the electron structure characteristics and chemical bonding in the compounds of complicated structures.

In the present paper, using a full set of X-ray emission spectra and the results of quantum-chemical calculations of clusters by the semiempirical Mulliken–Wolfsberg–Helmholtz method with self-consistency on charges and configurations, we have carried out the study of the electronic structure, charge distributions, and effects of chemical bonding in the main vanadium oxides VO, V_2O_3, VO_2, and V_2O_5.

Experimental X-Ray Spectra

In spite of a number of experimental works on vanadium oxides, the sets of X-ray emission and absorption spectra available in the literature were not quite complete. Well-resolved L_α spectra of V_2O_3, VO_2, V_2O_5 have been obtained by Fisher (*4–6*). Oxygen K_α spectra for these compounds were also presented in (*4*), but the vanadium K_β spectra in a series of its oxides were unknown. We have obtained V $K_{\beta 5}$ emission spectra for all known binary oxides in the vanadium–oxygen system. The experimental procedure is given in (*7*). In this paper the results concerned with VO, V_2O_3, VO_2, and V_2O_5 are presented.

Using the spectra obtained and the data of papers (4, *7–9*) one may get a full set of X-ray emission spectra for the oxides under study. The arrangement of K and L spectra of vanadium in the common energy scale was carried out by the usual method of shifting the $K_{\beta 5}$ emission band according to the value of the energy of $K_{\alpha 1}$ line in these oxides (*7*). The spectra of different components can be correctly aligned when the energies of the V and O atom inner levels are known. For the oxides under study these data are available only for V_2O_5 (more detailed discussion is given below). Such an alignment appeared to be in complete accord with the results obtained by the ESCA method for V_2O_5 (*10*) (see Fig. 1). Therefore, the arrangement of different component spectra for other oxides where the data on inner level shifts are absent have been carried out by analogy with the V_2O_5 case, according to the results of experiments by valence band X-ray photoelectron spectroscopy (*10*) (Fig. 1).

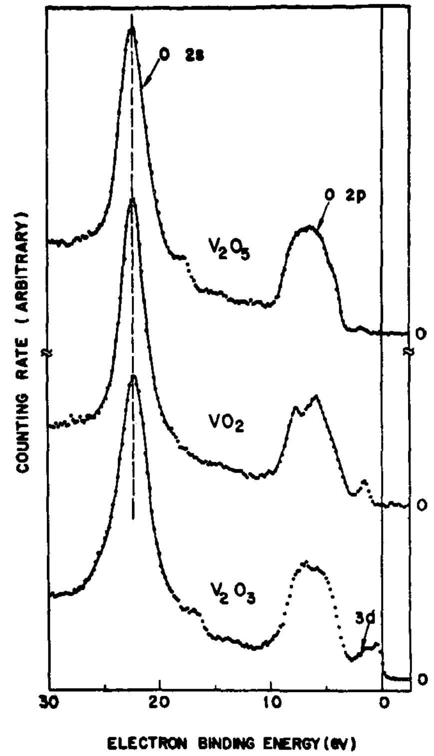

FIG. 1. Experimental X-ray photoelectron spectra of V_2O_3, VO_2, V_2O_5 (*10*).

The full sets of emission spectra for vanadium oxides aligned in this manner are given in Figs. 2 and 3.

The Structure of Clusters: The Method of Calculation

The excitations corresponding to X-ray transitions are essentially localized and can be described in terms of the electronic structure of clusters in the solid, which consist of the metal atom surrounded (for the oxides) by the nearest oxygens. The geometric structures of these clusters in vanadium oxides determined from the data of X-ray analysis are shown in Fig. 4. It can be seen that the cluster geometry in different oxides varies significantly. If the cluster in VO is the regular octahedron with the length of

V–O bond of 2.04 Å (*11*), in V_2O_3 such an octahedron is essentially distorted (*12*). The distortion further increases for VO_2 (*13*) and for the cluster in V_2O_5 the distortions of the octahedron appear to be so large that a question arises as to whether the sixth oxygen atom removed at 2.8 Å from vanadium actually enters into the first coordination sphere of vanadium atom and is connected with the latter by a chemical bond or the vanadium in V_2O_5 has a fivefold coordination.

Hence it follows that the interpretation of X-ray emission spectra on the basis of an MO scheme for an undistorted octahedron is possible for only VO (see *15*). The application of a similar diagram for the contruction of empirical MO systems for the other oxides (as was done, for example, in (*6*) for V_2O_3) is not quite correct, because the MO's of the low symmetry clusters in V_2O_3, VO_2, and V_2O_5 are strongly split and involve atomic contributions from the orbitals of other irreducible representations of the octahedron and, because of this, cannot be definitely related to any representations of O_h and to concrete bands in the X-ray spectra. Therefore the construction of an empirical MO scheme in these oxides is hardly possible and may result in erroneous conclusions. Hence, it is necessary to perform quantum-mechanical calculations of the particular clusters in the given compounds.

In the present paper such calculations have been carried out by the Mulliken–Wolfsberg–

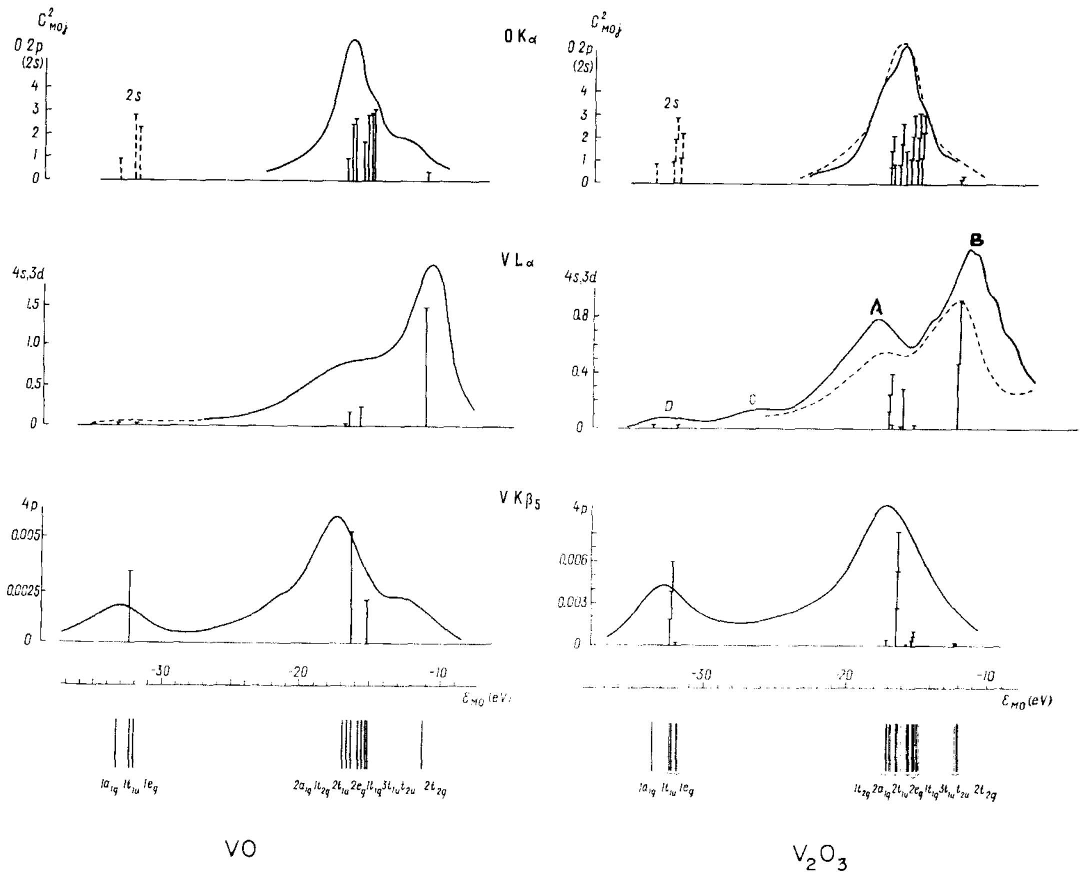

FIG. 2. Experimental X-ray emission spectra, calculated molecular orbitals, and their contributions to the spectra of different types for VO and V_2O_3. (The dotted line for V_2O_3 shows O $K\alpha$ and V $L\alpha$ spectra obtained by us.)

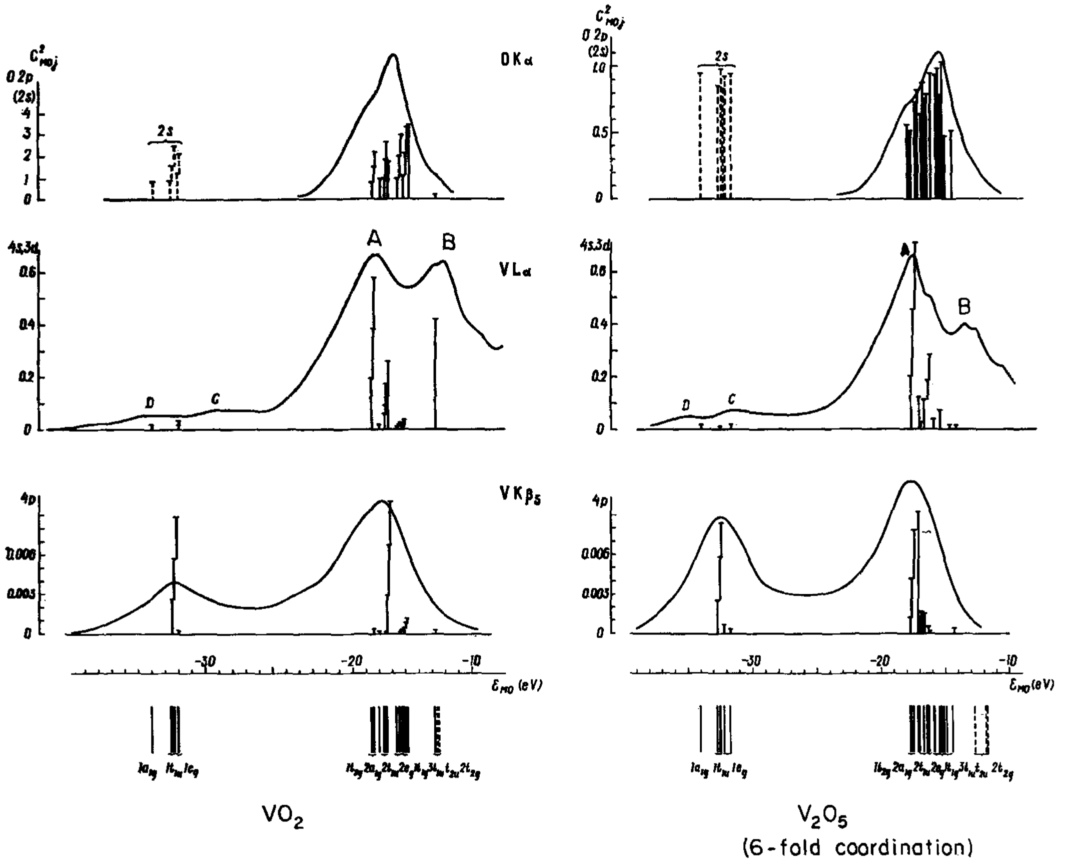

FIG. 3. Experimental X-ray spectra, calculated MO, and their contribution to the spectra of different types for VO_2 and V_2O_5 (sixfold coordination of vanadium atom).

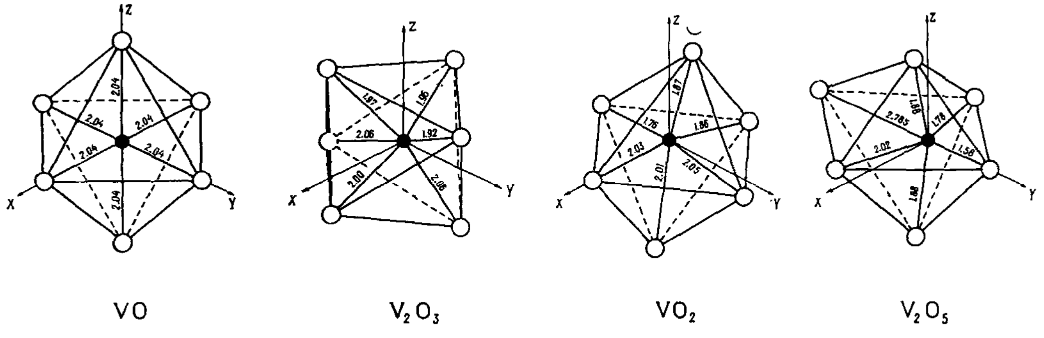

FIG. 4. The structure of the nearest environment of the vanadium atom in VO, V_2O_3, VO_2, V_2O_5.

Helmholtz (MWH) method with self-consistency on charges and configurations (*16*, *17*). The atomic orbital (AO) basis involved 4*s*, 4*p*, and 3*d* orbitals of the metal atom, and 2*s* and 2*p* orbitals of oxygens. The wavefunctions of V 4*s* and V 4*p* orbitals were taken from the papers of Richardson *et al.* (*18*, *19*), for 3*d* AO the five-exponential functions of (*20*) were adopted. The multi-exponential functions (*20*) were used also as 2*s* and 2*p* oxygen orbitals. The geometrical cluster parameters were taken from (*11–14*) (see Fig. 4). The MWH method was used in the ordinary version without any modification; the values of method parameters were taken from (*21*).

Results and Discussion

The cluster molecular orbitals obtained in calculations performed are given in Table I. For vanadium monoxide the MO are classified in accordance with the irreducible representations of the O_h group. Clusters in other oxides do not possess any symmetry

TABLE I

MO ENERGIES OF CLUSTERS IN VANADIUM OXIDES

Representation O_h	MO energies (eV)				
				V_2O_5	
				Six-fold	Five-fold
	VO	V_2O_3	VO_2	coordinations	
$1a_{1g}$	−33.354	−33.655	−33.898	−33.947	−33.877
$1t_{1u}$	−32.384	−32.513	−32.628	−32.646	−32.644
		−32.387	−32.471	−32.463	−32.461
		−32.346	−32.284	−32.457	−32.335
$1e_g$	−32.090	−32.052	−32.066	−32.165	—
		−31.951	−31.996	−31.653	−31.647
$1t_{2g}$	−16.679	−17.122	−17.518	−17.676	−17.653
		−17.067	−17.390	−17.584	−17.526
		−16.957	−17.386	−17.547	−17.491
$2a_{1g}$	−16.834	−16.915	−17.012	−17.081	−16.987
$2t_{1u}$	−16.407	−16.492	−16.643	−16.985	−16.641
		−16.471	−16.588	−16.656	−16.641
		−16.400	−16.524	−16.412	−16.382
$2e_g$	−15.862	−16.177	−16.396	−16.375	−16.359
		−16.176	−16.338	−16.234	−16.191
$1t_{1g}$	−15.585	−15.622	−15.684	−15.854	
		−15.562	−15.495	−15.819	
		−15.482	−15.412	−15.459	−15.482
$3t_{1u}$	−15.235	−15.258	−15.258	−15.332	−15.317
		−15.185	−15.063	−15.268	−15.245
		−15.150	−14.967	−15.094	−15.231
t_{2u}	−15.131	−14.999	−14.895	−15.038	
		−14.868	−14.849	−14.829	−14.819
		−14.792	−14.815	−14.393	−14.391
$2t_{2g}$	−11.306	−12.386	−12.739	−12.673	−12.627
		−12.275	−12.531	−11.745	−11.707
		−12.232	−12.418	−11.678	−11.644
$3e_g$	− 8.713	− 9.489	− 9.110	−10.162	−10.549
		− 8.917	− 8.726	− 9.105	− 9.113
$4t_{1u}$	14.632	13.993	15.167	14.833	11.656
		15.425	17.666	16.925	14.837
		15.759	20.787	17.163	16.601
$3a_{1g}$	16.011	21.319	20.891	20.287	18.726

and it is impossible to give a correct classification of MO's. However, one can pick out the groups of orbitals with close energies, for which the largest contribution is formed by the specific type of atomic orbitals, and in such a way give an approximate relation of these split orbitals with the types of MO's for O_h. Naturally, this procedure is very conventional, especially for V_2O_5, and is intended mainly for the convenience of notation and discussion.

The occupied molecular orbitals can be directly compared with the sets of X-ray emission spectra. Such comparisons are carried out in Figs. 2 and 3, where together with the experimental spectra the energies of occupied MO's and the contributions of atomic orbitals (C_{MO_j}) to the emission spectra of corresponding types are presented.

For the VO case we have shown in (*15*) that dividing the experimental spectra into separate gaussian components results in an MO diagram which is completely identical to the one obtained in calculations. A good agreement of the results of calculations with the experimental spectra obviously can be seen from Fig. 2: The data of the calculations allow one to describe quite correctly all the most characteristic peculiarities as $K_{\beta 5}$, V L_α, and O K_α spectra. The detailed interpretation of the X-ray emission spectra for vanadium monoxide has been given in (*15*) and in this paper only the final results are presented in Fig. 2.

The emission spectra of V_2O_3 differ noticeably from those of vanadium monoxide (Fig. 2). The cluster calculation results for V_2O_3 reveal the nature of these discrepancies. The $K_{\beta 5}$ spectrum of V_2O_3, in contrast to that for monoxide, does not contain the third emission subband at the high energy edge. From the data of calculations given in Fig. 2 it is obvious that this fact is connected with the sharp decrease of vanadium 4*p* AO contribution to the split $3t_{1u}$ orbitals. It can be seen that the distortions of the cluster lead to the appearance of a number of additional contributions to the $K_{\beta 5}$ spectrum from the other (not t_{1u}) molecular orbitals which are missing for the VO spectrum.

The peculiarities of the V L_α spectrum are also explained by the calculation results. The subband B (as was pointed out in (*5*)) is related to the $2t_{2g}$ orbital, significantly split and occupied by two unpaired electrons. The peak A has to be attributed to the t_{2g} MO, but not to the $2e_g$ MO (as was done in (*5*), from results of a model calculation for octahedral complex (*16*)), which has much smaller contributions of 3*d* AO as compared with the t_{2g} MO. As in the $K_{\beta 5}$ spectrum, in the V L_α one the orbital contributions missing for the regular octahedron can be seen.

The bands C and D are apparently related with the $1a_{1g}$ and $1e_g$ orbitals, but their calculated separation is much less than the experimental one. It is also possible that the C peak is caused by the transition $1e_g - 2p_{1/2}$ and not $1e_g - 2p_{3/2}$. Then the bands corresponding to $1a_{1g}$ and $1e_g$ orbitals are located in the region of the peak D, according to our MO calculations, The interpretation of the O K_α spectrum of V_2O_3 is essentially the same as in (*15*) for VO: All the orbitals with energies -14 to -16 eV possess almost the same contributions of oxygen 2*p* AO's, and the bands observed cannot be attributed only to $1a_{1g}$ and t_{2u} MO. The system of occupied molecular orbitals for V_2O_3 is given in the lower part of Fig. 2. The comparison with the MO levels scheme offered in (*6*) for V_2O_3 on the basis of calculations (*16*) for a model octahedron complex (far from the real structure of V_2O_3) and then correlated with X-ray spectra, show that the results of (*6*) do not seem to be very correct.

The interpretation of the V $K_{\beta 5}$ spectrum of VO_2 (Fig. 3) is completely similar to that for V_2O_3. Again the most intense bands are due to the large contributions of vanadium 4*p* AO to the $1t_{1u}$ and $2t_{1u}$ orbitals, even more split than in the V_2O_3 case. The $3t_{1u}$ orbital has a low intensity and does not appear in the $K_{\beta 5}$ spectrum. Being larger than for V_2O_3, the octahedron distortions in VO_2 result in the increase of contributions of other MO's to the V $K_{\beta 5}$ spectrum (see Fig. 3). In the V L_α spectrum the decrease of intensity of the *A* band is explained by decrease of the orbital contribution of the $2t_{2g}$ MO's, the lowest of which contains one electron. The *B* peak, as in the case of V_2O_3, is related to the contribution of the split $1t_{2g}$ orbitals, the intensity of the $2e_g$ orbital being twice lower. The noticeable contribution to the V L_α spectrum, comparable to the $2e_g$ MO contribution, is produced by the $2t_{1u}$ orbitals for the distorted VO_2 cluster containing a substantial admixture of V 3*d* orbitals. The bands C and D represent contributions of the $1a_{1g}$ and $1e_g$ orbitals. All molecular orbitals within the energy range of −12 to −18 eV give comparable contributions to the O K_α spectrum. The hump at the high energy side of the spectrum is probably related to the $2t_{2g}$ MO admixture of 2*p* ligand AO's in the $2t_{2g}$ orbitals.

Since the octahedral cluster in V_2O_5 is distorted very strongly, the calculated molecular orbitals include significant contributions of different atomic orbitals. Due to this, the procedure of assignment of the MO orbitals with maximum contributions of the AO's of given type and determination of their connection with the MO's of an octahedron is even more conventional in V_2O_5 than for V_2O_3 and VO_2. The results of the calculations given in Fig. 3 show that all MO's give contributions to almost all types of emission spectra. The most intensive bands in the vanadium $K_{\beta 5}$ spectrum correspond to the highly split $1t_{1u}$ and $2t_{1u}$ orbitals, the $3t_{1u}$ orbital practically does not contain the contribution of V 4*p* AO. The orbitals marked as $1t_{2g}$ and $2a_{1g}$ also give large contributions to the V $K_{\beta 5}$ spectrum, even exceeding the contribution of the $2t_{1u}$ orbital. The V L_α spectrum of V_2O_5 reveals only the intense A band. The fine structure at the high energy side of the spectrum, as shown in (*4*), is probably connected with satellite emission from a multiple ionization. The A band represents the contribution of split $1t_{2g}$ orbitals, but other MO's of the cluster, as is obvious from Fig. 3, also give significant contributions to the V L_α spectrum. The characteristic absence of a low intensity shoulder at the high energy edge of the O K_α spectrum of V_2O_5, as can be concluded from the results of calculations, is explained by the lack of electrons in the $2t_{2g}$ MO.

We have also carried out a calculation of the cluster in V_2O_5 with fivefold coordination of the vanadium atom. The results are given in Table I and Fig. 5. From Table I it follows that the rejection of the sixth oxygen atom, corresponding to the V–O bond with length 2.8 Å, does not essentially change the system of molecular orbitals except for the disappearance of one of the orbitals marked $1e_g$ (being formed by the oxygen 2*s* atomic orbitals) and that of three orbitals which enter into the groups of nonbonding $1t_{1g}$ and t_{2u} orbitals at the energies close to −15.2 eV (the ionization energy of O_{2p} orbitals). The contribution of MO's for the cluster with fivefold vanadium coordination to the different X-ray spectra are shown in Fig. 5. The comparison with corresponding results for the sixfold coordination of V (Fig. 3) obviously demonstrates that the removed oxygen atom has negligible influence on the nature of the chemical bonding of the vanadium with its five nearest neighbors and, thus, should be attributed to the next coordination sphere of the vanadium atom, which is apparently fivefold coordinated. From the results obtained it follows that taking into account that atoms are out of the nearest metal environment does not lead to any significant changes in the electronic structure of clusters.

The MO systems obtained for oxides in the calculation of the corresponding clusters are presented in Fig. 6. Despite large splitting of the degenerate MO's, the ordering of levels in a series of oxides remains almost invariable. The only exception is the change of the order of $2a_{1g}$ and $1t_{2g}$ orbitals when going from VO to V_2O_3, which is inherent to other oxides. The same order of levels is also found in (*15*) for vanadium carbides and nitrides. The decrease of cluster symmetry in the series of oxides results in significant increasing of orbital splittings, which often exceeds the energy differences between orbitals of different types and for V_2O_5 reaches the value of electronvolts. But, on the whole, the distance between molecular orbitals with large admixtures of 2*s* and 2*p* AO's remains the same and is approximately equal to 16 eV. This fact agrees completely with the ESCA data presented in Fig. 1. The noticeable increase of splittings between the $2t_{2g}$ and $3e_g$ orbitals is also very characteristic of the oxides under study (see Fig. 6). The data of Fig. 6 can be directly compared with other available experimental estimations of energy level splittings in oxides. From ESCA experiments (*22*) the authors have found that for V_2O_5 the width of a valence band, including mainly O 2*p* states, equals 4.5 eV; the gap between O 2*p* and valence 3*d*, 4*s* bands equals 2.4 eV. The corresponding values of 3.3 and 1.8 eV obtained in our calculations agree reasonably with these estimations. Analogous comparisons of theoretical and experimental data for V_2O_3 and VO_2 which can be easily performed using the data of Figs. 1 and 6 also show good agreement.

From the results given above it follows that

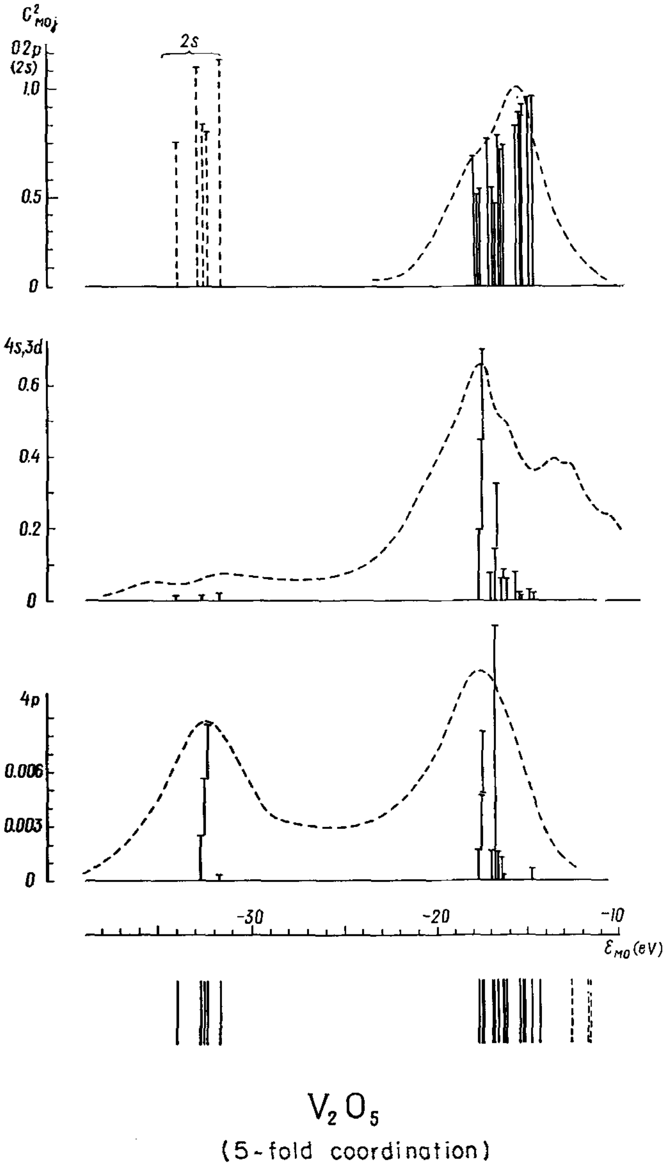

FIG. 5. Calculated emission spectra of V_2O_5 for fivefold coordination of vanadium.

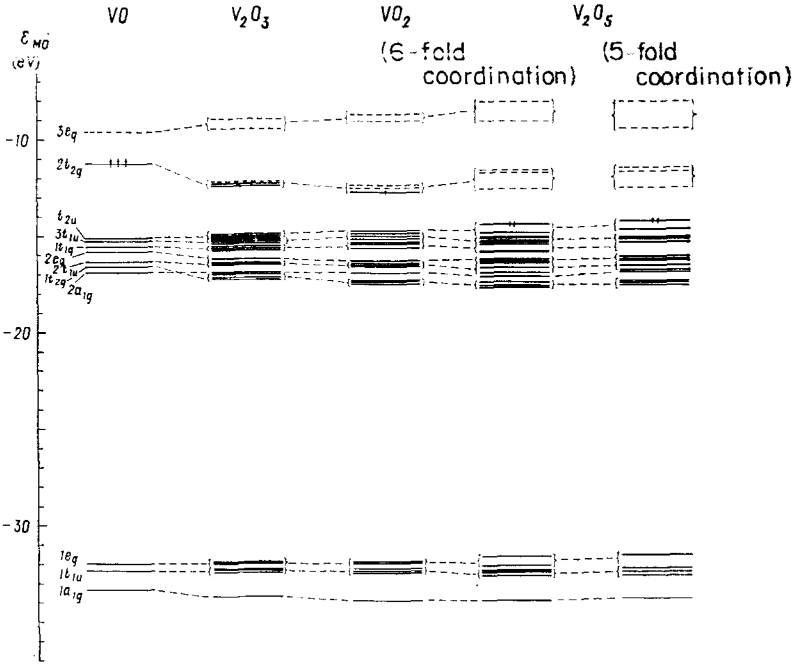

FIG. 6. The calculated systems of MO for clusters in vanadium oxides.

the data of quantum-mechanical calculations are in good agreement with the X-ray and photoelectron spectra of compounds and give reasonable ideas about the chemical bonding in oxides. A number of other electron structure characteristics for vanadium oxides is presented in Table II. The orbital populations calculated show that not only 3*d* and 4*s*, but also 4*p* atomic orbitals of the metal, which are often neglected in energy band calculations, play a prominent role in the chemical bonding. The population of 4*s* orbitals in a series of oxides increases noticeably from VO to V_2O_5, as well as the 4*p* populations, which considerably exceed the populations of 4*s* AO. Vanadium 3*d* orbitals are populated in a rather nonuniform manner (see Table II). Such irregularity of the t_{2g} orbital populations probably finds its reflection in the anisotropy of conductivity of oxides discovered experimentally. The total electron configurations of the vanadium atom in the oxides (Table II) differ sharply from those in the crystal field model. The population of *d* orbitals in all the investigated compounds is large and slightly decreases in the VI–V_2O_5 series. From the calculated bond populations it is clear that the chemical bonds in the clusters of the vanadium oxides are significantly inequivalent (except for VO). For V_2O_5 the population of the bond with the most distant oxygen is extremely small (0.02) and once more confirms the negligible effect of this atom on the electron structure of the fivefold coordinated cluster in V_2O_5.

The calculated values of the charges on the metal atoms (Table II) show that this parameter increases in a series of oxides, but in a far less degree than adopted in crystal field theory. It is well known that the charge value can be experimentally measured from the inner level shifts of the atom under consideration. One can find a number of experimental papers devoted to the measuring of the $2p_{3/2}$ level shift in vanadium oxides (*22*, *25–27*), but the results of different investigations are in a poor agreement. The increasing of the V 2*p* level energy by 1.1 eV was found in (*27*) for V_2O_3, VO_2. and V_2O_5

TABLE II

THE POPULATIONS OF ORBITALS, ATOMS, BONDS, AND VANADIUM CHARGES IN VO, V_2O_3, VO_2, AND V_2O_5

	AO population of metal				
				V_2O_5	
Atomic orbital of vanadium	VO	V_2O_3	VO_2	Six-fold coordinations	Five-fold
$4s$	0.155	0.177	0.185	0.185	0.178
$4p_x$	0.074	0.094	0.106	0.114	0.114
$4p_y$	0.073	0.100	0.111	0.124	0.124
$4p_z$	0.073	0.093	0.106	0.142	0.161
$3d_{x^2-y^2}$	0.348	0.673	0.635	0.701	0.719
$3d_{xz}$	1.091	0.901	1.222	0.682	0.675
$3d_{z^2}$	0.348	0.584	0.667	0.719	0.720
$3d_{yz}$	1.091	0.718	0.598	0.764	0.755
$3d_{xy}$	1.091	0.917	0.569	0.766	0.757
Vanadium configuration	$4s$ 0.154	$4s$ 0.177	$4s$ 0.185	$4s$ 0.185	$4s$ 0.178
	$3p$ 0.218	$4p$ 0.286	$4p$ 0.324	$4p$ 0.381	$4p$ 0.403
	$3d$ 3.968	$3d$ 3.788	$3d$ 3.691	$3d$ 3.632	$3d$ 3.626
Bond populations	0.208	0.230	0.283	0.852	0.858
		0.248	0.280	0.067	
		0.284	0.274	0.275	0.282
		0.367	0.387	0.439	0.453
		0.336	0.401	0.439	0.453
		0.290	0.599	0.570	0.600
Vanadium charges	0.66	0.75	0.80	0.80	0.79

when the valence of the vanadium increases by 1. The following values of the V $2p$ level energy were obtained in (*6*): V_2O_3, 517.6 eV; VO_2, 516.5 eV; V_2O_5, 515.6 eV; but the authors did not give the energy of the $2p_{3/2}$ level in the metal. For V_2O_5 the value of the V $2p$ level energy of 516.6 eV was given in (*25*), and the energy of this level in the metal was estimated as being equal to 512.4 eV. Different results were given in (*22*): $EV2p$ for V_2O_5 equalled 521 eV. The energy of this level in the metal was 517 eV. Hence, all the experimental results on level shifts in oxides give a clear idea about the increase of charge on the metal atoms in the VO–V_2O_5 series. However, due to the lack of agreement between experimental data, rather correct estimations of the charge value can be obtained only for V_2O_5 (1.01 (*25*)). The calculation by the MWH method gives a somewhat underestimated value for V_2O_5 (see Table II). The results of calculations carried out by the CNDO method, which will be described in a subsequent paper, resulted in $q_V = 1.0$ and agree with the experiments better.

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