PHYSICAL REVIEW A VOLUME 51, NUMBER 2 FEBRUARY 1995

Electric quadrupole transitions in x-ray spectra: 3*d* transition-metal oxides

N. V. Dobrodey* and Yu. V. Luniakov

Institute of Automation and Control Processes, Far Eastern Division of Russian Academy of Sciences,
Radio 5, 690041, Vladivostok 41, Russia

(Received 26 April 1994; revised manuscript received 6 September 1994)

The intensities of the electric quadrupole transitions in the x-ray spectra of the 3*d*-transition-metal monoxide diatomic molecules were calculated using the discrete variational method of the local-density approximation. The quadrupole transition intensities have been found to be negligible for the left-hand-side 3*d* metal oxides. It was shown that the electric quadrupole transitions can appreciably contribute to the $MK\beta_5$ emission spectra of the right-hand-side 3*d* metal oxides, along with the dipole transitions.

PACS number(s): 33.20.Rm, 33.70.Ca, 33.70.Fd

I. INTRODUCTION

The subject of the present study is closely related to the interpretation of the x-ray emission $MK\beta_5$ spectra of 3*d*-transition-metal compounds. The mere fact that the high-energy satellites in the region of the x-ray $MK\beta_5$ transitions are symbolized by the $MK\beta_5$ ($1s \leftarrow 3d$ transition in terms of the atomic spectroscopy) shows that the satellites were originally interpreted [1] as the quadrupole x-ray transitions from valence states to the 1*s* level of a metal. The reason why the quadrupole transitions have been invoked for an explanation of the origin of the $K\beta_5$ spectra was that the 3*p* states of the 3*d* metal lie sufficiently deep and seemingly have not appreciably contributed to the valence region, and the 4*p* states of the free 3*d* metal atom are unoccupied. There are several points of view at the origin of the $K\beta_5$ spectra: (a) the spectrum is formed due to the dipole transitions from the valence states; therewith the 4*p* states of the metal admixed to the valence states mainly contribute to the intensities of the spectral lines [2–4]; (b) the spectrum is formed due to the dipole transitions as well; however, the 3*p* states of the metal (but not the 4*p* ones) appreciably contribute to the valence states and make the main contribution to the intensities of the spectral lines [5–7]; and (c) the spectrum is formed due to the quadrupole transitions from valence states which have an admixture of the *M*3*d* atomic states [8]. Kawai [7] noted, on the basis of the estimations of the electric dipole and quadrupole transition probabilities for the hydrogenlike ions [9], that it is reasonable to interpret the $K\beta_5$ of elements with $Z \geq 30$ as due to the quadrupole transitions, but for lower-*Z* elements the quadrupole transition probability is negligible. However, as far as is known by the authors of the present study, there have been no calculations of the electric quadrupole transition intensities for molecular or solid-state systems.

The main aim of the present work was to estimate a possible contribution of the electric quadrupole transitions to the x-ray spectra of the 3*d*-transition-metal monoxides. The monoxide diatomic molecules have been chosen for the investigation instead of the solid-state monoxides, in order that an influence of the cluster modeling of the solid-state monoxides, for example the extra negative charge, be excluded. Evidently, the mechanisms of formation of x-ray spectra of molecular systems do not differ in principle from that of solid-state systems.

II. INTENSITIES OF ELECTRIC DIPOLE AND QUADRUPOLE TRANSITIONS IN A SPECTRUM

The probability for emitting a photon with the momentum *L*, the momentum projection *M*, and the parity $(-1)^L$ in a unit time is expressed by the well-known formula [10] (from here on we shall use the atomic units)

$$W_{LM}=\frac{2(L+1)(2L+1)\omega^{2L+1}}{L[(2L+1)!!]^2c^{2L-2}}|Q_{LM}|^2 , \qquad (1)$$

where ω is the energy of the photon, *c* is the velocity of light, and Q_{LM} is the electric multipole momentum of the $x \leftarrow i$ transition:

$$Q_{LM}=\frac{1}{\sqrt{2L+1}}\langle x|r^L Y^*_{LM}|i\rangle , \qquad (2)$$

where *r* is the module of the radius vector, and Y_{LM} is the conventional spherical function.

For characterizing a line intensity in a spectrum, it is conventional to use the absolute oscillator strengths of the dipole transition defined as follows:

$$f^D_{xi}=-\frac{2\omega_{xi}}{3\gamma_x}\sum_{\kappa=1}^{3}\sum_{M_i,M_x}|\langle xM_x|\kappa|iM_i\rangle|^2 \qquad (\text{emission } x\leftarrow i) , \qquad (3)$$

$$f^D_{vx}=\frac{4\omega_{vx}}{3}\sum_{\kappa=1}^{3}\sum_{M_v,M_x}|\langle vM_v|\kappa|xM_x\rangle|^2 \qquad (\text{absorption } x\rightarrow v) , \qquad (4)$$

---

*Author to whom correspondence should be addressed; electronic address: srn@iapu.marine.su

©1995 The American Physical Society

TABLE I. The interatomic distances for molecular $3d$ metal monoxide diatomic molecules (in atomic units). References are in the brackets.

TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
3.061 [12]	3.003 [12]	3.052 [12]	3.343 [12]	3.073 [13]	3.118 [14]	3.194 [15]	3.258 [12]	3.401 [16]

where $\omega_{kl}=I_l-I_k$, I_i is the ionization potential of the ith one-electron state; κ is assumed to be x, y, and z; γ_x is the spatial degeneration of the initial x state; and the summation is carried out over all spatial projections of both the initial and final states.

The numerical calculation of the $\langle x|\mathbf{r}|i\rangle$ matrix element within the discrete variational method [11] is very simple:

$$\langle x|\mathbf{r}|i\rangle=\sum_{k=l}^{M}\Omega_k\Psi_x^*(\mathbf{r}_k)\mathbf{r}_k\Psi_i(\mathbf{r}_k)\;, \tag{5}$$

where Ω_k is a weight of the point with the $\mathbf{r}_k$ radius vector; $\Psi_x(\mathbf{r}_k)$ and $\Psi_i(\mathbf{r}_k)$ are the values of the one-electron wave functions of the initial $|x\rangle$ and final $|i\rangle$ states at the point with $\mathbf{r}_k$ radius vector; and the summation is carried out over all points of the selected grid. Quadrupole operator matrix elements are calculated in a similar manner.

Let us now introduce the quantities for the quadrupole momentum operator, which are similar to the dipole absolute oscillator strengths

$$f_{xi}^{Q}=-\frac{\omega_{xi}^{3}}{c^{2}40\gamma_x}\sum_{\kappa=1}^{5}\sum_{M_i,M_x}|\langle xM_x|q_\kappa|iM_i\rangle|^2 \qquad (\text{emission } x\leftarrow i)\;, \tag{6}$$

$$f_{vx}^{Q}=\frac{\omega_{vx}^{3}}{20c^{2}}\sum_{\kappa=1}^{5}\sum_{M_v,M_x}|\langle vM_v|q_\kappa|xM_x\rangle|^2 \qquad (\text{absorption } x\rightarrow v)\;, \tag{7}$$

where

$$\begin{aligned}q_1&=\frac{1}{\sqrt{3}}(r^2-3z^2)\;,\\ q_2&=2xz\;,\\ q_3&=2yz\;,\\ q_4&=x^2-y^2\;,\\ q_5&=2xy\;.\end{aligned} \tag{8}$$

III. DETAILS OF CALCULATIONS

The electronic structure and the absolute oscillator strengths were calculated by the discrete variational method of the local-density approximation with the use of a computer program DVMKLS [11]. The self-consistent-field procedure was used for all calculations. The Hartree-Fock-Slater form for the local exchange-correlation potential (X_α potential with $\alpha=1$) was used. The numerical basis set of neutral atom wave functions (O:$1s$-$2s$,$2p$;M:$1s$-$4s$,$2p$-$3p$,$3d$), extended by the polarization Slater-type $4p$ function of the $3d$ metal with an exponent of 1.5 has been chosen. The Hamiltonian and the dipole and quadrupole operator matrix elements were calculated by three-dimensional (3D) numerical integration using a grid of 4833 points. The interatomic distances for the monoxide molecules are listed in Table I.

IV. RESULTS AND DISCUSSION

A. Diatomic molecules

As is seen from Fig. 1 and Table II, the intensities of the electric quadrupole transitions in the $MK\beta_5$-emission spectra (for convenience denoted further as $M1s^{-1}$) are negligible for the oxides from TiO to CrO. The intensities of the quadrupole transitions in the $M1s^{-1}$ spectra become significant beginning with CoO. The most intense quadrupole transition in the Co$1s^{-1}$-emission spectrum is the $1\sigma\leftarrow1\delta$ transition from the 1δ molecular orbital (MO), which is pure $3d$, to the 1σ MO (Co$1s$ level). The quadrupole transition from the 4π MO which contains a major contribution from the $3d$ atomic states [C_{3d} coefficient in the representation of MO as a linear combination of atomic orbitals (MOLCAO) is 0.84] is reasonably intense as well. Note that the dipole electric transi-

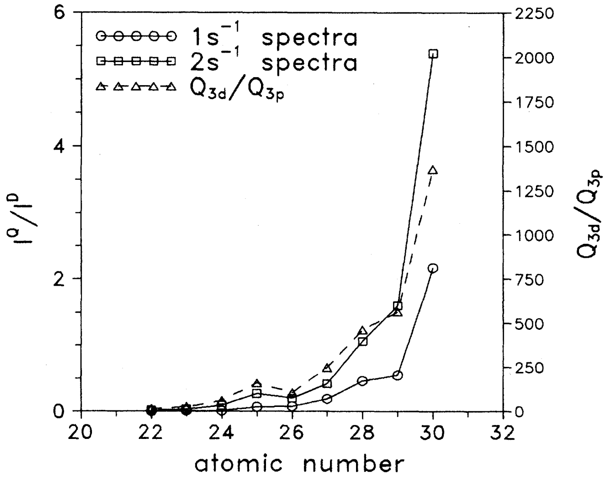

FIG. 1. The integral intensities of the electric quadrupole transitions from the valence MO's in the $M1s^{-1}$ and $M2s^{-1}$ emission spectra relative to the dipole intensities and the ratio of the total Q_{3d} to Q_{3p} Mulliken's populations for the valence MO's of the $3d$-transition-metal molecular oxides.

TABLE II. The integral intensities of the quadrupole electric transitions from the valence orbitals to the core levels of the metal (emission) and from the core levels to the vacant states (absorption) in percents of the respective dipole intensities for the transition 3d metal molecular monoxides.

Spectrum	TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
Emission									
$1s^{-1}$	0.2	0.7	1.1	7.0	8.0	19.0	46.4	54.8	217.0
$2s^{-1}$	1.6	3.2	9.2	27.0	20.0	42.0	106.0	160.7	539.0
$3s^{-1}$									31.0
Absorption									
$1s^{-1}$	0.7	1.5	3.0	5.6	16.0	10.0	3.0	4.1	
$2s^{-1}$	2.8	3.8	8.4	10.0	30.0	12.0	4.0		

tion $1\sigma \leftrightarrow 1\delta$ is forbidden for the $C_{\infty v}$ point symmetry group due to the selection rules. It is of interest that the quadrupole transition intensities in the $M2s^{-1}$-emission spectra become appreciable even for CrO (Table II). From Table II it will be obvious that the relative intensities of the quadrupole transitions in the $M2s^{-1}$ spectra of the oxides under investigation are larger than that of the $M1s^{-1}$ spectra. In the case of ZnO the intensities of the quadrupole transitions are significant in the $M3s^{-1}$ emission spectra as well (Table II).

It is hardly surprising that the quadrupole intensities are comparable with the dipole ones in the $M2s^{-1}$ and $M3s^{-1}$ emission spectra, insofar as the matrix elements squared for $2s \leftarrow 3p,4p$ and $3s \leftarrow 3p,4p$ dipole transitions and $2s \leftarrow 3d$ and $3s \leftarrow 3d$ quadrupole transitions are approximately same order of magnitude. For example, the calculation of the matrix elements of the dipole operator $\hat{\mathbf{d}}$ and quadrupole operator $\hat{\mathbf{q}}$ for the Zn free atom yields the results

$$|\langle 1s|\hat{\mathbf{d}}|3p\rangle|^2 = 1.413\times 10^{-4} ,$$

$$|\langle 1s|\hat{\mathbf{q}}|3d\rangle|^2 = 4.683\times 10^{-7} ,$$

$$|\langle 2s|\hat{\mathbf{d}}|3p\rangle|^2 = 6.333\times 10^{-4} ,$$

$$|\langle 2s|\hat{\mathbf{q}}|3d\rangle|^2 = 3.019\times 10^{-3} ,$$

$$|\langle 3s|\hat{\mathbf{d}}|3p\rangle|^2 = 4.901\times 10^{-1} ,$$

$$|\langle 3s|\hat{\mathbf{q}}|3d\rangle|^2 = 3.845\times 10^{-1} ,$$

$$|\langle 1s|\hat{\mathbf{d}}|4p\rangle|^2 = 3.905\times 10^{-6} ,$$

$$|\langle 2s|\hat{\mathbf{d}}|4p\rangle|^2 = 1.579\times 10^{-4} ,$$

$$|\langle 3s|\hat{\mathbf{d}}|4p\rangle|^2 = 4.031\times 10^{-3} ,$$

where Slater-type 4p functions were used [17].

Within the limits of the one-center approximation and MOLCAO approach, the intensity of the jth dipole line of a spectrum with the ns initial vacancy is expressed as follows:

$$I_j^D \sim C_{j3p}^2 |\langle ns|\hat{\mathbf{d}}|3p\rangle|^2 + C_{j4p}^2 |\langle ns|\hat{\mathbf{d}}|4p\rangle|^2 + 2C_{j3p}C_{j4p}\langle ns|\hat{\mathbf{d}}|3p\rangle\langle ns|\hat{\mathbf{d}}|4p\rangle , \tag{9}$$

where C_{ji} are the coefficients for the linear combination of atomic orbitals (LCAO) expansion of the jth MO (the contribution of the 2p states to the intensity is negligible because of negligible C_{2p} coefficients). The intensity of the jth quadrupole line in the spectrum is expressed as follows:

$$I_j^Q \sim C_{j3d}^2 |\langle ns|\hat{\mathbf{q}}|3d\rangle|^2 . \tag{10}$$

Furthermore, the C_{3p} and C_{4p} coefficients for the 8σ molecular orbital, which yields the most intense dipole lines in the Zn$1s^{-1}$, Zn$2s^{-1}$, and Zn$3s^{-1}$ spectra, are 0.037 and 0.025, respectively. The C_{3d} coefficients for the 3π and 1δ orbitals, which give the most intense quadrupole transitions, are equal to 1 for both the orbitals. With these data and with the calculated energies of the Zn1s, Zn2s, and Zn3s levels, which are equal to 9538, 1184 and 147 eV for ZnO, using formulas (3) and (9) and (6) and (10) it is easily seen that the small C_{3p} and C_{4p} coefficients with comparable dipole and quadruple matrix elements for the transitions to the Zn2s and Zn3s levels are the reason why the intensities of the quadrupole transitions are comparable to the dipole transition intensities for Zn$2s^{-1}$ and Zn$3s^{-1}$ emission spectra.

The analysis of the results of the calculations shows that the magnitude of the contribution of the 3p and 4p atomic states to the valence region is the quantity that predominantly defines the intensities of the quadrupole transitions relative to the dipole ones. This can be illustrated by the VO and ZnO example. The C_{3p} and C_{4p} coefficients for the 7σ MO of VO, which yields the most intense dipole transitions, are 0.2185 and 0.0257, respectively, and the squares of the C_{3p} coefficients for the 7σ MO of VO and for 8σ MO of ZnO differ by one order of magnitude, so the respective dipole intensities differ by one order as well ($f_{7\sigma 1s}^D = 3.21\times 10^{-4}$ for VO and $f_{8\sigma 1s}^D = 1.01\times 10^{-5}$ for ZnO).

It is of interest to study how quantities which mainly determine the value of the quadrupole transition intensity relative to the dipole one depend on the 3d metal atomic number. As seen from Figs. 2 and 3, the values of the

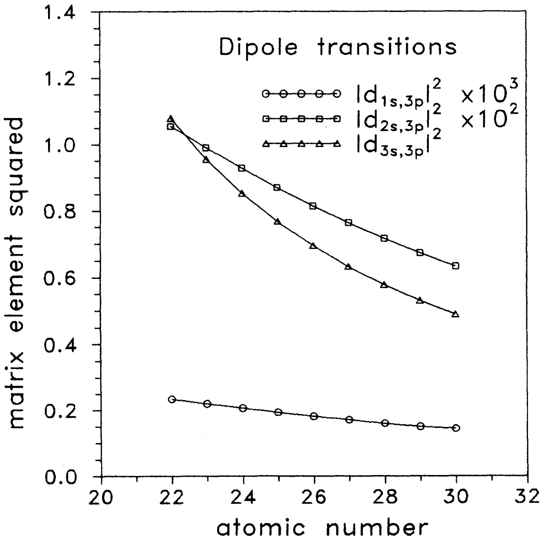

FIG. 2. The matrix elements squared for the electric dipole transitions $Ms^{-1} \leftarrow M3p$ in the neutral 3d-transition-metal atoms.

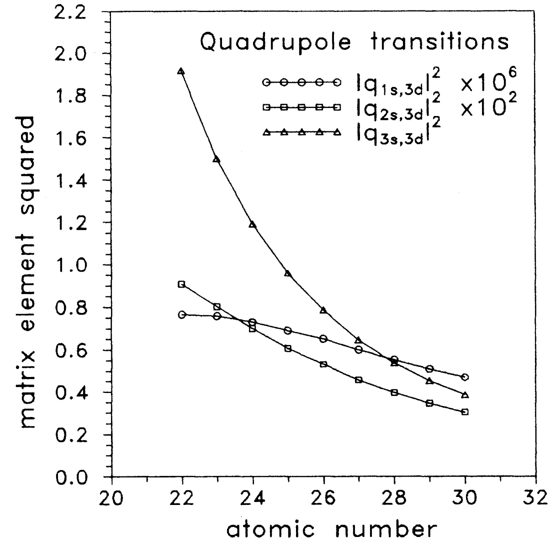

FIG. 3. The matrix elements squared for the electric quadrupole transitions $Ms^{-1} \leftarrow M3d$ in the neutral 3*d*-transition-metal atoms.

matrix elements squared for both the dipole and quadrupole transitions decrease when the atomic number increases. On the other hand, for the monoxides the ratio of the total Mulliken population of the metal 3*d* atomic states for the valence MO's (Q_{3d}) to the population of the 3*p* states increases when the atomic number increases (Fig. 2). The character of the change of the Q_{3d}/Q_{3p} ratio with changing metal atomic number is in complete agreement with the change of the relative intensity of the quadrupole transitions (Fig. 1).

It should be noted that a variation of the interatomic distance also can influence the intensity of the quadrupole transitions relative to the dipole ones. The overlap integrals between the *O*2*s* and *O*2*p* and *M*3*p* and *M*4*p* atomic orbitals decrease as the *M*-*O* distance increases, it follows that the contributions of the *M*3*p* and *M*4*p* states to the valence MO's decrease and the intensities of the dipole transitions in the Ms^{-1} spectra decrease as well. The C_{3d} MOLCAO coefficients for the valence MOs which have the highest quadrupole intensities, on the other hand, practically have not undergone a change when the interatomic distance increases, so the absolute intensities of the quadrupole transitions in the Ms^{-1} spectra do not change. To illustrate an influence of the interatomic distance variation on the dipole and quadrupole transition intensities the calculation of the spectra for ZnO have been performed for Zn-O distance of 3.2 a.u. References to Tables III and IV show that the quadrupole transition intensities actually are not altered when the Zn-O distance increases, whereas in so doing the dipole transition intensities decrease.

The intensities of the quadrupole transitions in the $M1s^{-1}$ absorption spectra are significant only for the FeO and CoO (Table II). The quadrupole transitions

TABLE III. The orbital energies ε_i and the absolute oscillator strengths for the emission (absorption) dipole f_{ix}^{D} and quadrupole f_{ix}^{Q} electric transitions from the valence orbitals to the core levels (from the core levels to the vacant states) in the spectra of the ZnO molecule (ground-state configuration $9\sigma^2 4\pi^4 1\delta^4$). The vacant orbital are starred.

Spectrum	MO	$-\varepsilon_i$ (eV)	f_{ix}^{D}	f_{ix}^{Q}
$\mathrm{Zn}1s^{-1}$	7σ	29.02	0.0	8.34×10^{-6}
	8σ	24.48	1.01×10^{-5}	6.00×10^{-8}
	9σ	10.70	1.50×10^{-6}	6.00×10^{-8}
$\mathrm{Zn}1s^{-1}$	$10\sigma^*$	7.63	1.07×10^{-4}	3.60×10^{-7}
	3π	28.67	9.00×10^{-7}	1.50×10^{-5}
	4π	9.76	6.80×10^{-6}	4.29×10^{-6}
	1δ	28.67		1.42×10^{-5}
$\mathrm{Zn}2s^{-1}$	7σ	29.02	2.00×10^{-6}	7.01×10^{-5}
	8σ	24.48	4.40×10^{-5}	6.10×10^{-6}
	9σ	10.70	6.00×10^{-6}	2.00×10^{-7}
	$10\sigma^*$	7.63	4.57×10^{-4}	4.00×10^{-7}
	3π	28.67	2.00×10^{-6}	1.53×10^{-4}
	4π	9.76	1.70×10^{-5}	0.0
	1δ	28.67		1.53×10^{-4}
$\mathrm{Zn}3s^{-1}$	7σ	29.02	1.00×10^{-6}	9.73×10^{-6}
	8σ	24.48	1.24×10^{-4}	3.60×10^{-7}
	9σ	10.70	1.40×10^{-5}	0.0
	$10\sigma^*$	7.63	8.85×10^{-4}	0.0
	3π	28.67	2.50×10^{-5}	2.01×10^{-5}
	4π	9.76	0.0	1.70×10^{-7}
	1δ	28.67		1.99×10^{-5}

TABLE IV. The orbital energies ε_i and the absolute oscillator strengths for the emission (absorption) dipole f_{ix}^{D} and quadrupole f_{ix}^{Q} electric transitions from the valence orbitals to the core levels (from the core levels to the vacant states) in the spectra of ZnO molecule (ground-state configuration $9\sigma^2 4\pi^4 1\delta^4$). The vacant orbitals are starred. The results were obtained at Zn—O interatomic distance of 3.2 a.u.

Spectrum	MO	$-\varepsilon_i$ (eV)	f_{ix}^{D}	f_{ix}^{Q}
$\mathrm{Zn}1s^{-1}$	7σ	31.62	5.00×10^{-6}	6.11×10^{-6}
	8σ	28.50	1.41×10^{-5}	1.86×10^{-6}
	9σ	14.94	5.40×10^{-6}	0.0
	$10\sigma^*$	11.28	1.36×10^{-4}	1.08×10^{-6}
	3π	30.54	4.00×10^{-7}	1.46×10^{-5}
	4π	14.42	1.34×10^{-5}	3.86×10^{-6}
	1δ	30.52		1.41×10^{-5}
$\mathrm{Zn}2s^{-1}$	7σ	31.62	2.80×10^{-5}	4.82×10^{-5}
	8σ	28.50	6.20×10^{-5}	2.85×10^{-5}
	9σ	14.94	2.20×10^{-5}	2.00×10^{-7}
	$10\sigma^*$	11.28	5.78×10^{-4}	6.00×10^{-7}
	3π	30.54	1.00×10^{-6}	1.54×10^{-4}
	4π	14.42	4.10×10^{-5}	0.0
	1δ	30.52		1.54×10^{-4}
$\mathrm{Zn}3s^{-1}$	7σ	31.62	2.70×10^{-5}	7.14×10^{-6}
	8σ	28.50	1.87×10^{-4}	2.70×10^{-6}
	9σ	14.94	4.30×10^{-5}	0.0
	$10\sigma^*$	11.28	1.17×10^{-3}	4.00×10^{-8}
	3π	30.54	1.10×10^{-5}	1.95×10^{-5}
	4π	14.42	1.70×10^{-5}	1.90×10^{-7}
	1δ	30.52		1.95×10^{-5}

TABLE V. The integral intensities of the quadrupole electric transitions from the valence orbitals to the core levels of the metal (emission) in percents of the respective dipole intensities for the $MO_6{}^{10-}$ clusters.

Spectrum	$VO_6{}^{10-}$	$MnO_6{}^{10-}$	$FeO_6{}^{10-}$	$CoO_6{}^{10-}$	$NiO_6{}^{10-}$	$CuO_6{}^{10-}$
$1s^{-1}$	2	8	15	17	23	22
$2s^{-1}$	2	9	14	20	28	32

make a noticeable contribution to the $M2s^{-1}$ absorption spectra for the oxides from CrO to CoO (Table II).

B. Solid oxides

Since the relative intensities of the quadrupole transitions are very sensitive to the admixture of $3p$ and $4p$ orbitals of the metal to the valence states, it is instructive to consider systems with coordination bonds. For solid-state monoxides we used the traditional cluster approach within the framework of the usual ionic limit model. In this case the minimal cluster is MO_6^{10-}. The results are presented in Table V. As in the case of the diatomic molecules, the quadrupole transitions make appreciable contributions to the $1s^{-1}$ and $2s^{-1}$ emission spectra of the clusters beginning with MnO_6^{10-}. It is hard to tell whether the quadrupole contribution can appreciably affect the *shape* of the $K\beta_5$ of the right-hand-side $3d$ metal solids monoxides because these compounds are referred to as Mott insulators, and the intensities of spectral lines for such objects cannot be calculated within a one-electron approach [18–20].

V. CONCLUDING REMARKS

As can be seen from Table II, the intensities of the quadrupole electric transitions in the $M1s^{-1}$ emission spectra become appreciable beginning with MnO. Unfortunately, a comparison of the $M1s^{-1}$ emission spectra, calculated within the framework of the one-electron approach, with the experimental data is meaningless because of strong many-electron effects accompanying the ionization of both the core and valence levels of the right-hand-side $3d$ metal monoxides [18–20]. Let us briefly discuss this problem. Many-electron interactions result in appearance of bands of additional transitions (shake-up, shake-down, shake-off, and Coster-Kronig satellites) in the region of an emission spectrum where only the diagrammatic lines are situated within framework of the one-electron approximation. For every band there is a specific one-electron orbital, in this case a distribution of intensity within the band coincides with the intensity distribution within the respective band of photoelectron spectra (the so-called correspondence theorem [21]). As a consequence of such correspondence the sum rules for emission spectra are formulated [22]. The integral intensity of the $k \rightarrow x$ band in the emission spectrum coincides with the intensity of the $k \rightarrow x$ line calculated within the frozen-orbital approximation. Because of this, the relative integral intensities of the quadrupole transitions calculated for the $3d$ metal monoxides cannot be significantly wrong.

VI. CONCLUSION

The calculations of the absolute oscillator strengths for the dipole and quadrupole electric transitions in the x-ray spectra of the $3d$-transition-metal molecular monoxides show that the quadrupole transitions can make an appreciable contribution to the $M1s^{-1}$ and $M2s^{-1}$ emission spectra of the right-hand-side $3d$-transition-metal monoxides, whereas their contribution to the spectra of the left-hand-side metal oxides is negligible.

The following may be concluded about the origin of the $MK\beta_5$-emission spectra.

(1) The emission $MK\beta_5$ spectra of the left-hand-side $3d$-transition-metal monoxides are formed mainly due to the electric dipole transitions from the valence MOs.

(2) The electric quadrupole transitions can contribute appreciably to the $MK\beta_5$ emission spectra of the right-hand-side $3d$-transition-metal monoxides along with the dipole transitions.

ACKNOWLEDGMENT

The authors are indebted to Dr. Jun Kawai for his interest to this work.

---

[1] W. W. Beeman and H. F. Freidman, Phys. Rev. **56**, 392 (1939).
[2] V. A. Gubanov, J. Electron Spectrosc. Relat. Phenom. **9**, 85 (1976).
[3] S. P. Freidman *et al.*, Z. Phys. B **46**, 31 (1982).
[4] V. I. Nefedov *et al.*, Zhurn. Strukt. Khim. **13**, 637 (1972).
[5] V. A. Nasluzov *et al.*, Chem. Phys. Lett. **146**, 253 (1988).
[6] N. V. Dobrodey, A. V. Kondratenko, and G. L. Gutsev, Zh. Fiz. Khim. **63**, 120 (1989).
[7] J. Kawai, E. Nakamura, and Y. Nihei, Spectrochim. Acta **45B**, 463 (1990).
[8] T. Okura and T. Kanazawa, Mater. Sci. Lett. **9**, 790 (1990).
[9] J. P. Briand, in *Fundamental Processes in Energetic Atomic Collisions,* Vol. 103 of *NATO Advanced Study Institute Series B: Physics,* edited by H. O. Lutz, J. S. Briggs, and H.

Kleinpoppen (Plenum, New York, 1983).

[10] V. B. Berestezky, E. M. Lifshits, and L. P. Pitaevsky, *Quantum Electrodynamics* (Moscow, Atomizdat, 1984).

[11] G. L. Gutsev and A. A. Levin, Chem. Phys. **51**, 459 (1980).

[12] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[13] L. P. Ephimov *et al.*, in *Properties of Inorganic Compounds*, edited by L. Rabinovitch (Khimia, Leningrad, 1983).

[14] R. A. Lidin, L. L. Andreeva, and V. A. Molochko, in *Handbook on Inorganic Chemistry. Constants of Inorganic Compounds*, edited by R. A. Lidin (Khimia, Moskow, 1987).

[15] C. W. Bauschlicher, Jr., C. J. Nelin, and P. S. Bagus, J. Chem. Phys. **82**, 3265 (1985).

[16] G. De Maria *et al.*, Trans. Faradey Soc. **61**, 2146 (1965).

[17] Notice that the dipole matrix elements squared $|\langle 1s|\hat{\mathbf{r}}|4p\rangle|^2$, $|\langle 2s|\hat{\mathbf{r}}|4p\rangle|^2$, and $|\langle 3s|\hat{\mathbf{r}}|4p\rangle|^2$ for the numerical $4p$ wave function obtained from the calculation of the free Zn atom are practically the same as that for the Slater $4p$ functions: $|\langle 1s|\hat{\mathbf{r}}|4p\rangle|^2=3.397\times 10^{-6}$, $|\langle 2s|\hat{\mathbf{r}}|4p\rangle|^2=1.310\times 10^{-4}$, and $|\langle 3s|\hat{\mathbf{r}}|4p\rangle|^2=2.813\times 10^{-3}$.

[18] G. A. Sawatzky, in *Proceedings of the Tenth Taniguchi International Symposium*, Kashikojima, Japan, 1987, edited by J. Kanamori and A. Kotani, Springer Series in Solid-State Sciences Vol. 81 (Springer-Verlag, Heidelberg, 1988), p. 99.

[19] J. Kawai, M. Takami, and C. Satoko, Phys. Rev. Lett. **65**, 2193 (1990).

[20] A. V. Kondratenko and L. S. Cederbaum, Phys. Rev. B **43**, 10 595 (1991).

[21] A. V. Kondratenko, L. N. Mazalov, and G. F. Khudorozhko, Theo. Chim. Acta **64**, 31 (1983).

[22] A. V. Kondratenko and K. M. Neyman, *Quantum Chemistry and Spectroscopy of Highly Excited States. Transition d-metal Coordination Compounds* (Nauka, Novosibirsk, 1990).