

ON THE ABSORPTION SPECTRA OF OCTAHEDRAL CYANIDE COMPLEX IONS OF TRANSITION METALS

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The energy and the transitions of electrons will be investigated in the case of cyanide complex ions $[\text{Cr}(\text{CN})_6]^{3-}$, $[\text{Mn}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Ni}(\text{CN})_6]^{3-}$, $[\text{Mn}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{4-}$ by the LCAO-method. An analogous calculation was previously published by GILDE and BÀN [1] in the case of Cr(III)hexocyanide complex ion.

The complex ion $[\text{Me}(\text{CN})_6]^{2-}$ considered consists of a central metal ion (Me) and six cyanide ions so that the nucleus of the complex is surrounded by six cyanide groups with octahedral symmetry. According to well known experimental facts the central metallic ion, as well as the C and N atoms of the cyanide groups, respectively, are local on the axes of the octahedron so that the C atoms are nearer to the central ion.

It is assumed that between the central ion and the groups of the coordination zone covalent bonds exist. These bonds are the molecular orbitals composed by five 3d, one 4s and three 4p atomic orbitals of the central metallic ion and by the three 2p orbitals of the C atoms of the coordination zone as well. Let us suppose that the influence of the electrons of the closed shells of the metal ion and the C atoms, respectively, as well as the interactions between the cyanide groups can be neglected. So $24+n$ electrons must be placed on the molecular orbitals formed by the 27 atomic orbitals /n means the number of the 3d electrons of the central ions/.

Let the 27 atomic orbitals mentioned above be regarded as basic vectors of a 27-dimensional space of functions. Taking the symmetry O_h of the problems into account in this space of functions one can easily obtain the representation of the group. This reducible representation can be put in the form

$$\Gamma = \sqrt{\sigma} + \sqrt{\tau} + \sqrt{d^3} + \sqrt{d^2 sp^3} =$$

$$= 2A_{1g} + 2E_g + T_{1g} + 3T_{1v} + 2T_{2g} + T_{2v}$$

where Γ denotes the 27-dimensional reducible representation; $\sqrt{\sigma}$ means the 6-dimensional representation of the group corresponding to the orbitals in the directions of the axes of the octahedron; $\sqrt{\tau}$ denotes the 12-dimensional representation of the group corresponding to other atomic orbitals of the C-atoms; $\sqrt{d^3}$ and $\sqrt{d^2 sp^3}$ represent the orbitals of the central metallic ion. Finally, A, E and T, respectively, mean irreducible representations of the group O_h .

The basic vectors of the irreducible representation will be used as starting functions of the LCAO-method. The energy of the electrons can be calculated

in the usual way by the solution of the secular equation:

$$\left| H_{ij} - E S_{ij} \right| = 0 \quad (i, j = 1, 2, \dots, 27)$$

Owing to the reduction outlined above the determinant on the left number of this equation will be a product of three determinants of the first order belonging to the irreducible representation T_{1g} and T_{2g} resp.; three determinants of the second order belonging to T_{2g} , three determinants of the third order belonging to T_{1u} ; two determinants of the second order belonging to E_g , finally, one determinant of the second order belonging to the irreducible representation A_{1g} . The roots belonging to the A, E and T representations are one, two, and three fold degenerate, respectively.

H_{ij} mean the matrix elements of the Hamiltonian and S_{ij} denote the overlap integrals. It is assumed that the distances between the nucleus and the cyanide ions are 2.00 Å corresponding to the experimental value. Let us suppose that the matrix elements H_{ij} agree with the ionization energy of free neutral atoms and the matrix elements H_{ij} ($i \neq j$) are calculated by the formula of WOLFSBERG and HELMHOLZ. One can calculate the overlap integrals S_{ij} by the approximation methods suggested previously [2].

The results of the present investigations can be summarized as follows:

- 1./ The energies calculated on the basis of the secular equation are given in Table I. in eV units.
- 2./ The selection rules render possible the determination of the transition energies of the electrons represented in Table II. in cm^{-1} units. The values in the second column of this table correspond to the maxima of the experimental absorption curves measured by KISS, CSÁSZÁR and LEHOTAI [3]. The values in brackets denote the inflexion points of the absorption curves having nearly horizontal tangents.
- 3./ One can see that more transition energies have been found than were found experimentally. As a matter of fact, this can be explained as follows:
 - /i./ It can immediately be seen that one part of the calculated values cannot be found in the interval of the spectra measured.
 - /ii./ The other part of the transitions calculated form different groups containing nearly equal transitions; the mean values of the transitions in the different groups correspond very well to the experimental data.
 - /iii./ One can also find calculated transition lines in the interval $10,000 - 20,000 \text{ cm}^{-1}$ however, this interval of the absorption spectra cannot be measured by the experimental equipment of the cited author.
 - /iv./ As far as is known to us, in the case of the complex ions of Co^{2+} and Mn^{3+} , respectively, experimental data have not been published.
- 4./ Finally, one can put the following question: If the cyanide groups of the coordination zone are separated from the central metallic ion, then - since in the case of increasing distance the interactions between the groups and the metallic ion decrease - the energies and the transition energies of the electrons of the complex ion respectively, would be reduced into those of the free central ion and the free cyanide group as well. As a matter of fact there may exist three classes of transitions which correspond to the transitions of the free central ion, of the free cyanide ions, and the interaction between the central ion and the cyanide

Table I

	Cr ³⁺	Mn ³⁺	Fe ³⁺	Co ³⁺
1a _{1g}	-9.88	-10.29	-10.62	-10.72
2a _{1g}	-4.10	-4.12	-3.87	-3.52
1e _g	-10.99	-11.91	-12.28	-10.81
2e _g	-0.21	-3.66	-5.70	-6.45
t _{1g}	-7.80	-7.80	-7.80	-7.80
1t _{1u}	-8.70	-8.71	-8.74	-8.74
2t _{1u}	-7.81	-7.80	-7.80	-7.80
3t _{1u}	-3.88	-4.33	-4.88	-3.94
1t _{2g}	-7.54	-9.87	-11.20	-9.66
2t _{2g}	-7.80	-7.79	-7.79	-7.79
t _{2u}	-7.80	-7.80	-7.80	-7.80
	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ³⁺
1a _{1g}	-10.11	-10.27	-10.17	-10.66
2a _{1g}	-4.52	-4.96	-5.25	-3.22
1e _g	-12.24	-12.56	-10.97	-9.69
2e _g	-2.16	-4.80	-6.07	-6.95
t _{1g}	-7.80	-7.80	-7.80	-7.80
1t _{1u}	-8.70	-8.70	-8.70	-8.76
2t _{1u}	-7.81	-7.80	-7.80	-7.80
3t _{1u}	-4.35	-4.96	-4.08	-3.61
1t _{2g}	-9.87	-11.20	-9.66	-8.58
2t _{2g}	-7.79	-7.79	-7.79	-7.79
t _{2u}	-7.80	-7.80	-7.80	-7.80

Table II

Cr^{3+}		Mn^{3+}	
Calculated	Observed	Calculated	Observed
2098		7342	5600
7261	5000	16701	
9359		27997	27000
25738	26800	29691	30500
29853		33161	33000
31627	32000	33400	
37114	37800	37000	37000
48410		44698	41000
57366		46745	46000
		48085	
Fe^{3+}		Co^{3+}	
Calculated	Observed	Calculated	Observed
7504	5000	7584	6340
16943		10892	
23559	24000	15507	
24447		18476	
24432	25000	24286	25000
31708	31000	31143	32000
36146	33000	34532	
39212	39000	42117	38500
46312	45500	46151	
50992			

Table II. /Continued/

Mn ²⁺		Fe ²⁺	
Calculated	Observed	Calculated	Observed
7261		7261	
16701		22833	
26464		22914	
27830	27400	24205	
33725	31000	30175	30750
35823	36200	31466	
44537		34693	
45505		38405	
46473	47700	42762	
52767		57527	
Co ²⁺		Ni ³⁺	
Calculated	Observed	Calculated	Observed
7261		6293	
13958		6858	
15007		7745	
20574		14603	
21220		15249	
25577		33806	
27836		36953	
30014		40099	
42762		44698	
45021		49055	

groups, respectively. Nevertheless, these classification of the transition lines cannot be put into correlation with well known experimental classifications, namely, these transition lines corresponding to the different groups are not localized on different parts of the spectra.

References

- [1] Gilde, F.J.; M.J.Bán: Acta Phys. et Chem Szeged, 3, 44 /1957/.
- [2] Gilde, F.J.: Thesis /1958/.
- [3] Kiss, Á., J.Császár, L.Lehotai: Magyar Tud. Akad, Kémiai Tud. Oszt. Közl., 9, 281 /1957/.