

On some Intensity Problems in the Absorption Bands of Complex Ions

C. J. BALLHAUSEN

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

A qualitative estimate of the intensities in the absorption bands of complex ions may be obtained by a consideration of the symmetry properties of the complex. Special attention is directed (1) towards the vibrations of the ligands and (2) towards the selection rules for electric dipole transitions. These points of view are applied to the bands of some simple complexes of the first transition group.

A theory for the intensities of the absorption spectra of complex ions has been given by Van Vleck¹ and by Broer, Gorter and Hoogschagen². It is the intention here to study the application of the theory set forth by these authors to the absorption bands of some simple complexes of the first transition group.

Assuming³ that the absorption bands may be described as Gaussian curves, the probability of absorption P can be found as

$$P = 4.60 \cdot 10^{-9} \cdot \epsilon_0 \cdot \nu_{1/2} \quad (1)$$

ϵ_0 being the molar extinction coefficient of the maximum and $\nu_{1/2}$ being the halfwidth of the band measured in cm^{-1} .

The quantum mechanical expression for P is^{1, 2}

$$P = \frac{8\pi^2 mc}{3h} \nu M_{I, II}$$

$$M_{I, II} = \text{av} \sum_I \left| \int \psi_I \vec{r} \psi_{II}^* d^3r \right|^2 \quad (2)$$

ν is the position of the maxima of the absorption bands in wavenumbers and $M_{I, II}$ is the average over initial states I, and sum over the final states, II, of the squares of the matrix elements of the electric dipole vector \vec{r} . m and c are the mass of the electron and the speed of light, and h is Planck's constant.

It has been shown ⁴⁻⁶ that the absorption bands of complexes of the first transition group are due to transitions between the various levels in which the undisturbed terms of the metal ion split up under the influence of the ligand field. The resulting levels may be classified according to their Γ number ⁷. In a cubic complex (point group O) these numbers, which specify the symmetry properties of the level, go from Γ_1 to Γ_5 . If a complex of the first transition group has a center of symmetry all the lowest levels are "even" under reflections in space. It follows then from Laportes rule that $M_{I,II}$ is equal to zero. In a cubic complex MA_6 the dipole absorption is thus completely forbidden. However, as pointed out by Van Vleck ¹, dissymmetry caused by vibrations of the ligands demolishes the existence of such a center of symmetry. In a nonsymmetric complex the "even" wavefunctions coming from the d^n configurations can intermix with the "odd" wavefunctions of the $d^{n-1}p$ terms. This means that the perturbed wavefunctions are neither "even" nor "odd" and Laportes rule cannot be applied. That the existence of a symmetry center really is of significance for the intensities of the bands has been demonstrated experimentally by Basolo, Ballhausen and Bjerrum ⁶.

This is, however, only one side of the question. For pure symmetry reasons dipole transitions are only allowed between the following levels:

$$\Gamma_1 \rightarrow \Gamma_4; \Gamma_2 \rightarrow \Gamma_5; \Gamma_3 \rightarrow \Gamma_4 \text{ and } \Gamma_5; \Gamma_4 \rightarrow \Gamma_1, \Gamma_3, \Gamma_4 \text{ and } \Gamma_5; \Gamma_5 \rightarrow \Gamma_2, \Gamma_3, \Gamma_4 \text{ and } \Gamma_5.$$

These selection rules become more and more important the stronger the field. This is due to the general trend that the stronger the field, the better the quantum number Γ . These last selection rules are therefore rather important for Cr(III) and Co(III) complexes, but are of less importance for Ti(III), V(III), Co(II) and Ni(II) complexes. It must further be emphasized that the above discussion applies only to complexes with cubic symmetry.

Van Vleck was mainly interested in the intensity problems for the absorption bands of the rare earths. However, the results of Van Vleck ¹ may also be used in this connection. The ligands are then supposed to be placed in a potential hole of the shape $V = \frac{\beta}{r^6} - \frac{Z\mu}{r^2}$, where β is a constant, μ the value of the

electric dipole moment of the ligand, Z is the charge of the metal ion and r the distance. The intensity due to vibrations of the ligands is then ¹:

$$P = \nu \left(\frac{\pi_{\text{hol}}}{\nu^+} \right)^2 \cdot e \cdot \frac{r_0^2}{\sqrt{\mu Z M}} 10^{-7} \quad (3)$$

ν^+ is the distance to the nearest "odd" level, π_{hol} is the holoedric crystal field, e the degeneracy of the upper level, M the molecular weight of the ligand and r_0 the equilibrium distance of the ligands. It is difficult to estimate a value of π_{hol} . For the purpose here it is set equal to $2(E_1 - E_2)$. r_0 is equal to 2 \AA and $\sqrt{\mu Z M} \sim 16$, μ being measured in Debye units.

Then:

$$P_\nu = \nu \cdot \left(\frac{E_1 - E_2}{\nu^+} \right)^2 \cdot e \cdot 10^{-7} \quad (4)$$

Further if there are several bands in a complex, the ratio between the absorption probabilities of different bands may be taken, thereby obtaining a formula which does not contain the more uncertain factors of (3):

$$\frac{P_{\nu n}}{P_{\nu m}} = \frac{\nu_n \cdot e_n}{\nu_m \cdot e_m} \quad (5)$$

Ti ⁺⁺⁺	3d ¹	$\nu^+ = 13 \cdot 10^4 \text{ cm}^{-1}$		
	$(E_1 - E_2)_{\text{aq}} = 20\,000 \text{ cm}^{-1}$	$\nu_1 = 20\,000 \text{ cm}^{-1}$		
	$P_{\nu 1}$ found ⁹ : $1.6 \cdot 10^{-4}$	$P_{\nu 1}$ calc.: $1.0 \cdot 10^{-4}$		
V ⁺⁺⁺	3d ²	$\nu^+ = 15 \cdot 10^4 \text{ cm}^{-1}$		
	$(E_1 - E_2)_{\text{aq}} = 20\,500 \text{ cm}^{-1}$	$\nu_1 = 17\,200 \text{ cm}^{-1}$	$\nu_2 = 25\,000 \text{ cm}^{-1}$	
		$\nu_3 = 37\,000 \text{ cm}^{-1}$ (calc.)		
	$P_{\nu 1}$ found ¹⁰ : $9.3 \cdot 10^{-5}$	$P_{\nu 1}$ calc.: $10 \cdot 10^{-5}$		
	$P_{\nu 2}$ — — — $18 \cdot 10^{-5}$	$P_{\nu 2}$ — — — $14 \cdot 10^{-5}$		
	$P_{\nu 3}$ — — — ?	$P_{\nu 3}$ — — — $6 \cdot 10^{-5}$		
Co ⁺⁺	3d ⁷	$\nu^+ = 10 \cdot 10^4 \text{ cm}^{-1}$		
	$(E_1 - E_2)_{\text{aq}} = 9\,000 \text{ cm}^{-1}$	$\nu_1 = 8\,000 \text{ cm}^{-1}$	$\nu_2 = 16\,000 \text{ cm}^{-1}$	
		$\nu_3 = 20\,200 \text{ cm}^{-1}$		
	$P_{\nu 1}$ found ¹¹ : ?	$P_{\nu 1}$ calc.: $2.0 \cdot 10^{-5}$		
	$P_{\nu 2}$ — — — $\sim 0.1 \cdot 10^{-5}$	$P_{\nu 2}$ — — — $1.2 \cdot 10^{-5}$		
	$P_{\nu 3}$ — — — $9 \cdot 10^{-5}$	$P_{\nu 3}$ — — — $5.0 \cdot 10^{-5}$		
Ni ⁺⁺	3d ⁸	$\nu^+ = 11 \cdot 10^4 \text{ cm}^{-1}$		
	$(E_1 - E_2)_{\text{aq}} = 7\,600 \text{ cm}^{-1}$	$\nu_1 = 8\,000 \text{ cm}^{-1}$	$\nu_2 = 14\,000 \text{ cm}^{-1}$	
		$\nu_3 = 25\,300 \text{ cm}^{-1}$		
	$P_{\nu 1}$ found ¹² : $2 \cdot 10^{-5}$	$P_{\nu 1}$ calc.: $1.2 \cdot 10^{-5}$		
	$P_{\nu 2}$ — — — $3.5 \cdot 10^{-5}$	$P_{\nu 2}$ — — — $2.0 \cdot 10^{-5}$		
	$P_{\nu 3}$ — — — $7.2 \cdot 10^{-5}$	$P_{\nu 3}$ — — — $3.6 \cdot 10^{-5}$		
		$\frac{P_{\nu 1}}{P_{\nu 2}}$ found: 0.57	calc.: 0.60	
		$\frac{P_{\nu 2}}{P_{\nu 3}}$ found: 0.49	calc.: 0.55	
	$(E_1 - E_2)_{\text{en}} = 10\,500 \text{ cm}^{-1}$	$\nu_1 = 11\,200 \text{ cm}^{-1}$	$\nu_2 = 18\,350 \text{ cm}^{-1}$	
		$\nu_3 = 29\,000 \text{ cm}^{-1}$		
	$P_{\nu 1}$ found ¹² : $9.0 \cdot 10^{-5}$	$P_{\nu 1}$ calc.: $3.0 \cdot 10^{-5}$		
	$P_{\nu 2}$ — — — $10.2 \cdot 10^{-5}$	$P_{\nu 2}$ — — — $5.0 \cdot 10^{-5}$		
	$P_{\nu 3}$ — — — $14.2 \cdot 10^{-5}$	$P_{\nu 3}$ — — — $8.0 \cdot 10^{-5}$		
		$\frac{P_{\nu 1}}{P_{\nu 2}}$ found: 0.88	calc.: 0.60	
		$\frac{P_{\nu 2}}{P_{\nu 3}}$ found: 0.70	calc.: 0.62	
	$\frac{P_{\nu 3(\text{aq})}}{P_{\nu 3(\text{en})}}$ found: 0.50	calc.: 0.45		

However, in formula (5) the selection rules of the Γ 's are not considered.

Some examples taken from the literature will now be compared with the theory. Due to the points previously discussed only cubic MA_6 complexes which can be treated from the standpoint of the weak crystal field will be considered. This leaves out Cr(III) and Co(III) where the selection rules of the Γ 's are important, and Cu(II) complexes which have a distinctly tetragonal structure^{4, 13}.

The values of ν^+ have been taken from "Atomic Energy Levels" (National Bureau of Standards 467 (1949)).

It is seen, that while the absolute values of P calculated by means of (4) are of the right order of magnitude, the intensity ratios determined by means of (5) are, at least for the Ni(II) complexes, in much better agreement. However, the part played by the selection rules can be clearly seen in Ref.³, Fig. 5. The second band in the spectrum of Ni_3^{++} due to a $\Gamma_2 \rightarrow \Gamma_4$ transition has a smaller intensity than the first band which is due to a $\Gamma_2 \rightarrow \Gamma_5$ transition. The same explanation may account for the discrepancy found for P_{ν_2} in Co(II) complexes.

P is seen to be proportional to $\epsilon_0 \cdot \nu_1$. As pointed out by Bjerrum, Ballhausen and Klíxbüll Jørgensen¹³, and as shown by Orgel¹⁴ ν_1 is proportional to the slopes of the energy levels for the transition in question. This means, all other things being equal, that if the differences in the slopes are great and consequently ν_1 large, then the molar extinction coefficient are likely to be small.

The picture of the complex molecule as a metal ion surrounded by point dipoles is of course very crude, and one must expect that exchange phenomena *etc.* will play an important role for a detailed description. It seems however that the main features of the intensities may be described within the simple picture offered by the crystal field theory.

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