

## Intensities in Inorganic Complexes

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A method for calculating the intensity of  $d^n$  electronic transitions in inorganic complexes is developed and subsequently applied to the computation of the intensity of the visible absorption bands of Ti(III) and Cu(II) complexes. The observed and calculated oscillator strengths are in good agreement.

### INTRODUCTION

IT is now generally conceded that the visible absorption bands of inorganic complexes are vibronically allowed electric dipole transitions among the various  $d^n$  electronic configurations. However, to date, no quantitative confirmation of this assignment has been attempted.<sup>1</sup> In this paper we shall present a theory of vibronic (vibrational-electronic) interactions in inorganic complexes which, when applied to the determination of intensities, conclusively proves the hitherto assumed spectral assignments.

### THEORY

#### (a) Intensity Formulas

In the absence of symmetry-destroying vibronic perturbations, electric dipole transitions between the various  $d^n$  electronic states of "octahedrally" coordinated inorganic complexes are rigorously forbidden ( $g \rightarrow g$ ). Thus to compute the intensity of these  $d^n$  transitions, we must consider the scrambling of  $d^n$  configurations  $\Psi_g^0(d)$ , with  $d^{n-1}p$  configurations,  $\Psi_u^0(p)$ , under vibrational perturbations. To facilitate this computation we shall employ first-order perturbation theory.

According to the perturbation theory the required mixing coefficients,  $\gamma_d^{(k)}(p)$ , are given by

$$\gamma_d^{(k)}(p) = \frac{-(\Psi_u^0(p) | \mathcal{H}'(Q_k) | \Psi_g^0(d))}{E_p - E_d}, \quad (1)$$

and the corresponding first-order electronic wave functions by

$$\Psi(d) = \Psi_g^0(d) + \sum_k \sum_p Q_k \gamma_d^{(k)}(p) \Psi_u^0(p). \quad (2)$$

In Eq. (1),  $\mathcal{H}'(Q_k)$  represents the linear variation of the Hamiltonian,  $\mathcal{H}$ , as a function of the normal mode

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<sup>1</sup> The origin of the visible absorption spectra of rare earth and transition metal complexes has been qualitatively discussed by J. H. Van Vleck, *J. Phys. Chem.* **41**, 67 (1937), and by Broer, Gorter, and Hoogschagen, *Physica* **11**, 231 (1945).

$Q_k$ . Then, as the intensity, in terms of the oscillator strength,  $f$ , is given by<sup>2</sup>

$$f(d^n, v_k \rightarrow d^n, v_k \pm 1) = 1.085 \times 10^{11} (N_{v_k}/N) \times |(\Psi(d), v_k | \mathbf{r} | \Psi(d'), v_k \pm 1)|^2 \Delta E_{d^n} (\text{cm}^{-1}), \quad (3)$$

we have, to good approximation,

$$\begin{aligned} f(d^n \rightarrow d^n) &= \sum_k \sum_{v_k} f(d^n, v_k \rightarrow d^n, v_k \pm 1) \\ &= 1.085 \times 10^{11} \sum_k \coth(h\nu_k/2kT) \Delta E_{d^n} \\ &\quad \times |\sum_p (0 | Q_k | 1) [\gamma_d^{(k)}(p) (d' | \mathbf{r} | p) \\ &\quad + \gamma_{d'}^{(k)}(p) (d | \mathbf{r} | p)]|^2. \quad (4) \end{aligned}$$

In Eqs. (3) and (4),  $N_{v_k}$  is the molar population, in the ground electronic state,  $\Psi(d)$ , of the  $(v_k+1)$ th harmonic of the normal mode  $Q_k$  (frequency  $\nu_k$ ).

#### (b) Matrix Elements

Retaining only linear terms in the nuclear displacements  $\mathbf{s}_j$ , we have

$$\mathcal{H}'(\mathbf{s}) = \sum_j \mathbf{s}_j \cdot \nabla_{\mathbf{s}_j} \mathcal{H}(\mathbf{s}), \quad (5)$$

the sum being carried over all the atomic nuclei contained in the complex. Now, taking the ligands of the transition metal complex to be octahedrally situated point masses and charges (see Fig. 1), we have the

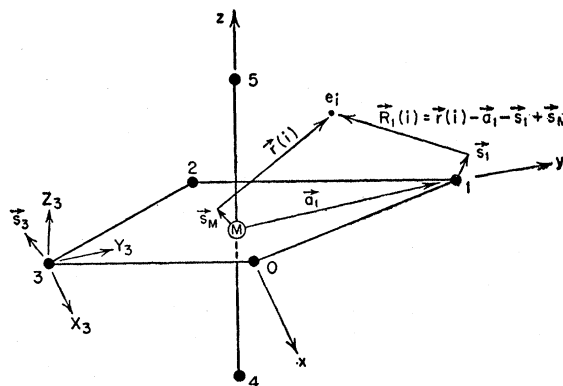


FIG. 1. Molecular geometry assumed for hexa-coordinated inorganic complexes.

<sup>2</sup> R. S. Mulliken and C. A. Rieke, *Repts. Progr. in Phys.* **8**, 231 (1941).

TABLE I. Numerical results.

Ti <sup>+++</sup> ( $Z_{3d}=4.00$ ; $Z_{4p}=3.14$ ; $a=2$ Å)	Cu <sup>++</sup> ( $Z_{3d}=7.85$ ; $Z_{4p}=4.36$ ; $a=2$ Å)
$N = (d_{xy}, d_{xz}, d_{yz}); V = (d_x^2 - y^2, d_z^2)$	$N = (\Psi_x^0, \Psi_y^0, \Psi_z^0); V = (\Psi_x^0, \Psi_y^0, \Psi_z^0)$
$f_{N \rightarrow x^2 - y^2} = 2.43 \times 10^{-4} \times \lambda(\text{Ti})$	$f_{N \rightarrow xy} = 1.27 \times 10^{-5} \times \lambda(\text{Cu})$
$f_{N \rightarrow z^2} = 2.43 \times 10^{-4} \times \lambda(\text{Ti})$	$f_{N \rightarrow (x \text{ or } y)z} = 1.27 \times 10^{-5} \times \lambda(\text{Cu})$
$f_{N \rightarrow V} = 4.86 \times 10^{-4} \times \lambda(\text{Ti})$	$f_{N \rightarrow V} = 3.81 \times 10^{-5} \times \lambda(\text{Cu})$
$f_{N \rightarrow V} = 1.1 \times 10^{-4} (\text{Ti}(\text{H}_2\text{O})_6^{+++}, \text{experimental})^a$	$f_{N \rightarrow V} = 2.9 \times 10^{-4} (\text{Cu}(\text{H}_2\text{O})_6^{++}, \text{experimental})^b$
$\lambda(s) = (8/5)q^2(s) [R^2(E_V - E_N) / (E_p - E_d)^2] f_{d \rightarrow p}$ , ( $s = \text{Ti, Cu}$ ); $R = \text{Rydberg constant}$ .	

<sup>a</sup> Hartmann, Schläfer, and Hansen, *Z. anorg. u. allgem. Chem.* **284**, 153 (1956).  
<sup>b</sup> Bjerrum, Ballhausen, and Jørgensen, *Acta Chem. Scand.* **8**, 1281 (1954).

electronic potential energy,  $\mathcal{U}$ , as

$$\mathcal{U}(\mathbf{r}(i), \mathbf{a}_j) = - \sum_{i,j} \frac{q_j e^2}{|\mathbf{R}_j(i)|} = - \sum_{i,j} \frac{q_j e^2}{|\mathbf{r}(i) - \mathbf{a}_j|}, \quad (6)$$

where  $q_j$  is the effective charge associated with the  $j$ th ligand. In this approximation, the mixing coefficient  $\gamma_d^{(k)}(p)$  is defined by the following relation:

$$\sum_k Q_k \gamma_d^{(k)}(p) = (E_p - E_d)^{-1} \sum_{i=0}^5 \sum_{j=0}^5 (\mathbf{s}_j - \mathbf{s}_M) \cdot \nabla_{\mathbf{a}_j} \int \Psi_u^0(p) \frac{q_j e^2}{|\mathbf{r}(i) - \mathbf{a}_j|} \Psi_d^0(d) d\tau. \quad (7)$$

Since  $\mathcal{U}$  is thus the sum of one electron perturbations, we need only consider the interaction of individual  $d$  and  $p$  wave functions. Thus, after proper account has been taken of all the antisymmetrizing factors contained in  $\Psi_d^0(d)$  and  $\Psi_u^0(p)$ , the total vibrational perturbation in Eq. (7) is reduced to a sum of all permissible one electron  $d$  and  $p$  vibronic interactions.

### (c) Calculation of the Intensities

The calculation of the intensities now proceeds as follows<sup>3</sup>:

(1) The electronic integrals of Eq. (7) are evaluated by use of antisymmetrized products of  $3d$  and  $4p$  hydrogenic wave functions.

(2) The nuclear displacements of Eq. (7) are then expressed in terms of symmetry coordinates. In the octahedral point group  $O_h$  only perturbing nuclear displacements of symmetry  $\tau_{1u}$  and  $\tau_{2u}$  yield nonzero mixing coefficients. Thus only the  $\tau_{1u}$  and  $\tau_{2u}$  symmetry coordinates appear in (7).

(3) The normal coordinates are determined.

(4) The symmetry coordinates of step (2) are then replaced by the appropriate linear combination of normal coordinates.

(5) The result of steps (1) through (4) is substituted into Eq. (4) and the intensities are computed.

<sup>3</sup> We have omitted the details of the calculation as the algebra involved, although long and tedious, is quite straightforward. The final intensity formulas, if published, would fill an entire page of the Journal. As these formulas are not very inspiring, we have not published them.

## RESULTS

In calculating the normal vibrations we have employed the vibrational potential of Wilson.<sup>4</sup> Taking  $\nu_1 = 300$  cm<sup>-1</sup>,  $\nu_2 = 275$  cm<sup>-1</sup>, and  $\nu_5 = 150$  cm<sup>-1</sup>, we obtain  $\nu_3 = 137$  cm<sup>-1</sup>,  $\nu_4 = 356$  cm<sup>-1</sup>, and  $\nu_6 = 106$  cm<sup>-1</sup>. The substitution of these latter vibrational frequencies in Eq. (4) yields the results given in Table I (for room temperatures). In Table I,  $q^2(s)$ , ( $s = \text{Ti, Cu}$ ), represents the square of the effective charge associated with the crystal field of the ligands,  $E_p - E_d$  is the mean energy separation of the  $d$  and  $p$  orbitals, and  $f_{d \rightarrow p}$  is the mean oscillator strength of an ordinary  $d \rightarrow p$  transition.

Now for the complexes under consideration, we have  $E_V - E_N \approx (2/11)R$ , ( $R$  is the Rydberg constant),  $E_p - E_d \approx \frac{1}{2}R$ , and  $f_{d \rightarrow p} \approx 0.2$ .<sup>5</sup> Thus  $\lambda(s)$  is approximately given by  $0.5q^2(s)$ , ( $s = \text{Ti, Cu}$ ). As a simple crystal field calculation yields  $q^2(\text{Ti}) = 0.56$  and  $q^2(\text{Cu}) = 15$  for the hexaquo complexes, we have  $f_{N \rightarrow V}(\text{Ti}) = 1.4 \times 10^{-4}$  and  $f_{N \rightarrow V}(\text{Cu}) = 2.9 \times 10^{-4}$ . These values are in good agreement with experiment (see Table I).<sup>6</sup> Moreover, we also have the result

$$\frac{f_{N \rightarrow V}(\text{Cu})}{f_{N \rightarrow V}(\text{Ti})} = \frac{q^2(\text{Cu}) \times 0.78 \times 10^{-1}}{q^2(\text{Ti})} = 2.1,$$

independent of our choice of  $\lambda(s)$ , ( $s = \text{Ti, Cu}$ ). This proportionality of the intensity to the square of the

<sup>4</sup> Quoted by Yost, Steffens, and Gross, *J. Chem. Phys.* **2**, 311 (1934). The formulas given in this paper contain several errors. They should read as follows [using the now standard notation of G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945)]:

$$\begin{aligned} m\lambda_1 &= K + 10K_1; & m\lambda_2 &= (K - 2K_1); \\ m^2\lambda_3\lambda_4 &= [(M + 6m)/M](2K_\alpha)(K - 2K_1); \\ m(\lambda_3 + \lambda_4) &= [(M + 4m)/M](2K_\alpha) + [(M + 2m)/M](K - 2K_1); \\ m\lambda_5 &= 4K_\alpha; & m\lambda_6 &= 2K_\alpha; \end{aligned}$$

$$V = K \sum_{i=1}^6 (\Delta r_i)^2 + 2K_1 \sum_{i,j=1; i \neq j}^6 (\Delta r_i)(\Delta r_j) + K_\alpha \sum_{i=1}^{12} (r \Delta \alpha_i)^2.$$

<sup>5</sup> For the free ions,  $E_p - E_d \approx R$ . However, the ligand crystal field lowers the free-ion value to about  $\frac{1}{2}R$  (assuming that the strong absorption of all complexes at  $\sim 2000$  Å is due in part to a  $d \rightarrow p$  transition).

<sup>6</sup> Since copper does not form truly octahedral complexes, we have compared our octahedral intensities with the sum of the intensities of the two observed electronic transitions ( $N \rightarrow \Psi_{xy}^0, \Psi^0(x \text{ or } y)z$ ) of the tetragonal ( $D_{4h}$ ) copper complexes. Note, however, that the octahedral model predicts an intensity ratio for these two bands of 2:1, in good agreement with the observed ratio of 3:1 (reference b).

crystal field parameter  $q$  explains the observed correlation between the intensity and position in the spectrochemical series.

### DISCUSSION

As the predicted and observed oscillator strengths are in good agreement for Cu(II) and Ti(III) complexes, we may say that in these molecules the intensities of the visible absorption bands are predominantly governed by vibronic perturbations. We expect that the interaction of vibrational and electronic motions

will quantitatively account for the intensities of other transition metal complexes also. It is also hoped that the calculations now in progress will confirm this expectation.

The theory outlined in this paper for the  $d^n$  electronic configurations of the transition metal complexes applies equally well to the  $f^n$  configurations of the rare earth complexes. A future calculation of the intensities of the  $f^n$  electronic transitions of the rare earth complexes is planned.

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## Auger Electrons in the Secondary Electron Spectrum in Magnesium\*

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By continuously depositing fresh magnesium onto a target surface in high vacuum, it was possible to obtain the spectrum of secondary electrons liberated from atomically clean metal. The results show excellent agreement with predicted Auger transitions, and the continuous background spectrum between Auger peaks vanishes.

A SECONDARY electron spectrum has been obtained from a freshly deposited surface of magnesium evaporated onto a metal surface in vacuum. The procedure was not originally planned for production of uncontaminated surfaces, but the results and the method used pointed strongly to the conclusion that clean surfaces were being obtained and to the interest of the results for publication. Extensive reconstruction of the equipment was called for to attain any further results, and this has added to the desirability of communicating the results in their present form without delay.

The spectrometer used was a conventional, ring-focus type described by DuMond.<sup>1</sup> The vacuum chamber was metal; the anode was stainless steel. Magnesium in an auxiliary anode was bombarded by electrons from an auxiliary filament (3000–5000 volts, 5–20 ma) causing the magnesium to evaporate in gram amounts and deposit on the stainless steel anode (and elsewhere). The mechanism of evaporation was not certain because of the use of a nontransparent tube, but it appeared to be a critical factor in the success of the experiment. A discharge between the auxiliary filament and anode seemed to occur although it would have had to be in metal vapor because the ionization gauge showed far too little gas, its reading being in the range of  $(2-4) \times 10^{-6}$  mm Hg. The source anode, however,

did not seem to have been melted as etched crystalline planes were visible after disassembly.

The experiment began with a preliminary bombardment of the stainless steel anode as a degassing operation. A temperature of 400°C was maintained until massive gas evolution had ceased. At this point, the evaporation of magnesium was begun and, simultaneously, automatic, repetitive taking of secondary spectra was initiated using a primary voltage of 235

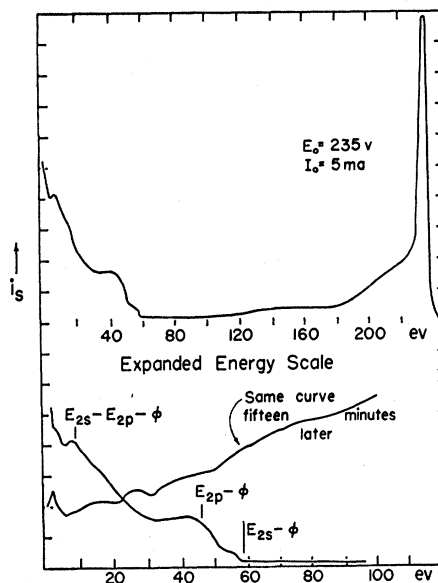


FIG. 1. Secondary electron spectrum of evaporated magnesium.

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<sup>1</sup> J. W. DuMond, Rev. Sci. Instr. 20, 160 and 616 (1949).