

Studies of Absorption Spectra

III. Absorption Bands as Gaussian Error Curves

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The bands of transition group spectra are shown to be approximated by Gaussian error curves with the wavenumber as the independent variable, and the characteristic parameters (height and wavenumber of the maximum and the halfwidths) are used for the description of several bands with good results (see Figs. 1-5). The resolution of more bands in complicated spectra is discussed, and related to the perturbation theory of crystal fields acting on transition group ions.

An absorption spectrum, *i. e.* the molar extinction coefficient ε as function of the wavenumber $\nu = \frac{1}{\lambda}$ in cm^{-1} (or the wavelength λ), consists very often of one or more bands, symmetrical around their maxima. Various expressions of the exact form of the bands have been proposed. Henri and Bielecki¹ described with success some bands of acetone in the ultraviolet by the formula

$$\varepsilon = a \nu e^{-b(\nu-\nu_0)^2} \quad (1)$$

where ν_0 is the wavenumber of the maximum and a and b are two constants, determining the height and width of the band. Kuhn and Braun² later discussed the far simpler Gaussian error curve as the best approximation of bands:

$$\varepsilon = \varepsilon_0 e^{-(\nu-\nu_0)^2/\delta^2} \quad (2)$$

Introducing $\delta = \vartheta\sqrt{\ln 2}$, this can be rewritten

$$\varepsilon = \varepsilon_0 2^{-\left(\frac{\nu-\nu_0}{\delta}\right)^2} \quad (3)$$

where ε_0 is the extinction coefficient in the maximum, and δ is the halfwidth (since $\varepsilon = \frac{\varepsilon_0}{2}$ for $\nu-\nu_0 = \pm\delta$). If (3) is valid, the half-widths are useful for

characterizing bands, as done by Linhard and Weigel^{3,4}. The area of a band will be proportional to the product of δ and ε_0 , since

$$\int_0^{\infty} e^{-kx^2} dx = \frac{\sqrt{\pi}}{2\sqrt{k}} \quad (4)$$

If $\nu_0 \gg \delta$, we therefore get from eq. 3

$$\int_0^{\infty} \varepsilon d\nu = 2\varepsilon_0 \int_0^{\infty} e^{-(\nu-\nu_0)^2/\delta^2} \ln 2 d(\nu-\nu_0) = \frac{\sqrt{\pi}}{\sqrt{\ln 2}} \varepsilon_0 \delta = 2.1289 \varepsilon_0 \delta \quad (5)$$

This area is proportional to the probability of the transition, causing the band, since the number of classical oscillators per absorbing molecule is

$$P = \frac{1000}{N} \cdot \frac{mc^2}{\pi e^2} \cdot 2.30 \int \varepsilon d\nu = 4.32 \cdot 10^{-9} \int \varepsilon d\nu \quad (6)$$

(N is Avogadro's number, e and m the charge and mass of the electron, and c the velocity of light *in vacuo*, cf. Broer, Gorter and Hoogschagen⁵).

Lowry and Hudson⁶ proposed the use of a Gaussian formula with λ as independent variable:

$$\varepsilon = \varepsilon_0 e^{-\left(\frac{\lambda-\lambda_0}{\beta}\right)^2} \quad (7)$$

and Mead maintained⁷ that bands in the absorption spectra of chromium(III) and cobalt(III) complexes could best be represented by (7).

While the question of the exact congruence of absorption bands with Gaussian ν - or λ -curves will be discussed in the following, it is at least certain at this point that the usual resonance formula:

$$\varepsilon = \frac{\varepsilon_0 \cdot \alpha}{\alpha + (\lambda - \lambda_0)^2} \quad (8)$$

is rarely or never applicable to spectra of solutions, although the formula is useful for the study of absorption lines of gases, *e. g.* Fraunhofer lines. It is seen that (8) implies a much slower decrease of ε for large values of $(\lambda - \lambda_0)^2$ than the Gaussian curves (3) and (7).

This fact is of theoretical interest, since the broadening of bands therefore is not alone due to Heisenberg's uncertainty principle

$$h \simeq \Delta E \cdot \Delta t$$

where h is Planck's constant and ΔE and Δt the corresponding uncertainties of energy and time. The observed ΔE would correspond to $\Delta t \sim 10^{-14}$ sec., which seems improbably small, even in these condensed systems.

If the spectrum is not a composite of adjacent, overlapping bands, the graphic representation of $\log \varepsilon$ as function of ν will show parabolic curves if eq. (3) is valid, and this is quite common according to the atlas of Landolt-Börnstein tables⁸. But the special case of transition group spectra deserve closer investigation, one of the reasons being the crystal field calculations of Ballhausen⁹ *et al.*¹⁰.

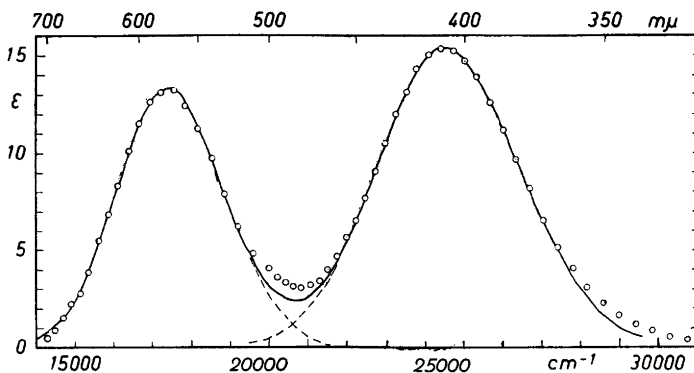


Fig. 1. Absorption spectrum of hexaquo chromium(III) ions. 0.06 M $\text{Cr}(\text{ClO}_4)_3$, 0.1 M HClO_4 . The calculated curve from eq. 3 with the parameters given in the text is drawn full. The partial bands are punctuated.

SELECTED EXPERIMENTAL DATA

Fig. 1 gives the absorption spectrum of $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ (in dilute HClO_4 to avoid hydroxo-complexes). The two bands resemble closely Gaussian error curves, but it is seen that they are slightly distorted towards high wavenumbers. If two slightly different halfwidths, $\delta(-)$ and $\delta(+)$ are used in the formula (3) for $\nu < \nu_0$ and $\nu > \nu_0$ respectively, it is seen that the spectrum can be described within the experimental accuracy of about one per cent. It is seen that the two bands of $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ can be described by the four parameters:

$\lambda_0 = \frac{1}{\nu_0}$	ν_0	ϵ_0	$\delta(-)$	$\delta(+)$
575 μm	17 400 cm^{-1}	13.3	1 550 cm^{-1}	1 700 cm^{-1}
408	24 500	15.3	2 050	2 250

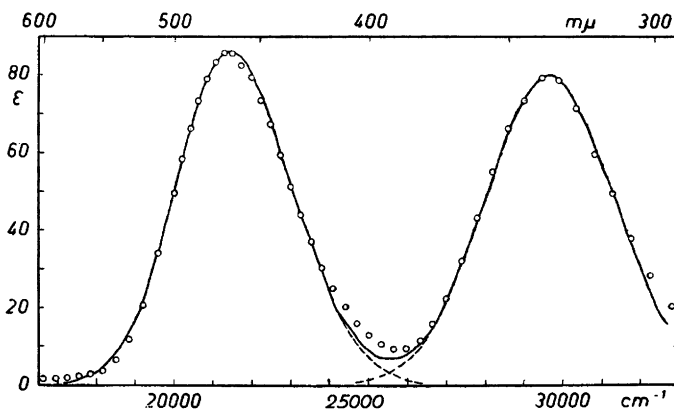


Fig. 2. Absorption spectrum of tris(ethylenediamine)cobalt(III) ions. 0.01 M $[\text{Co}(\text{en})_3]\text{Cl}_3$. The calculated curve from eq. 3 with the parameters given in the text is drawn full. The partial bands are punctuated.

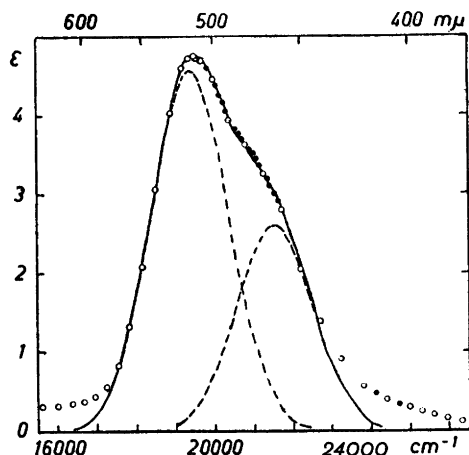


Fig. 3. Absorption spectrum of hexaquo cobalt(II) ions. 0.1–0.2 M $\text{Co}(\text{NO}_3)_2$. Open circles measurements by Lene Rasmussen, filled circles by the author. The calculated curve from eq. 3 with the parameters given in the text is drawn full. The partial bands, obtained by resolution, are punctuated.

This method will perhaps be useful for the classification of the steadily increasing material of absorption spectra in the place of explicit tables or figures. The phenomenon that $\delta (+)$ is about ten per cent greater than $\delta (-)$ corresponds in this case to an approximate validity of formulae as (1) or (7), and it cannot be said with certainty which corresponds best with reality. The following examples will show that there is no reason to think that all absorption bands are of the same form when such small differences are discussed. It is theoretically inconvenient that the band has a discontinuous second differential quotient in the maximum when $\delta (-)$ and $\delta (+)$ are different. This fact has no influence on the representation of measurements, since their experimental uncertainty is large compared with the small changes of ϵ with ν near the maximum.

Fig. 2 shows the spectrum of $[\text{Co en}_3]^{+++}$, which can easily be prepared free of other coloured materials. It is evident from the measurements of Bjerum and Rasmussen¹¹ that many ethylenediamine cobalt(III) complexes have bands which resemble Gaussian error curves, and the two bands for $[\text{Co en}_3]^{+++}$ can be described by:

$\lambda_0 = \nu_0^{-1}$	ν_0	ϵ_0	$\delta(-)$	$\delta(+)$
467 m μ	21 400 cm^{-1}	86	1 600 cm^{-1}	1 900 cm^{-1}
338	29 600	80	1 900	2 000

The following paper in this series will show that many transition group ions have small bands with intensities (*i. e.* $\epsilon_0\delta$) only about one per cent of the intensity of ordinary bands, and which also seem to have Gaussian form. Among these are also $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ and $[\text{Co en}_3]^{+++}$, which each exhibit a small band in red which cannot be seen in Figs. 1 and 2.

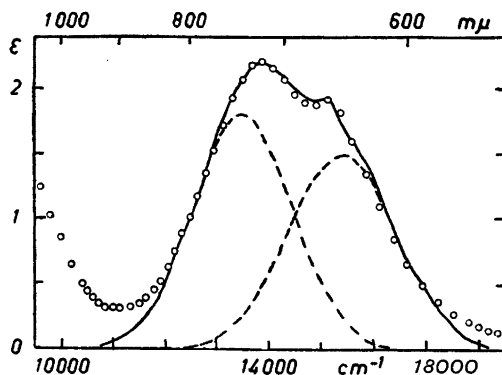


Fig. 4. Absorption spectrum of hexaquo nickel(II) ions (the red bands). 0.2 M $Ni(NO_3)_2$. The calculated curve from eq. 3 with the parameters given in the text is drawn full. The partial bands are punctuated.

In some cases the absorption spectrum seems to consist of two bands with a difference in wavenumber ν_0 of only the order of magnitude of δ . These bands are therefore overlapping and must be found by resolution of the experimental curve. Fig. 3 gives the spectrum of $[Co(H_2O)_6]^{++}$ (from the measurements of Lene Rasmussen¹²) showing the resolution into the two bands

$\lambda_0 = \nu_0^{-1}$	ν_0	ϵ_0	δ
514 m μ	19 400 cm $^{-1}$	4.55	1 150 cm $^{-1}$
454	21 550	2.6	1 150

(the tail in the red and probably also in the ultraviolet being due to the above mentioned small bands). Only one value of δ is given in order not to strain the experimental material too much. Similarly, Fig. 4 gives the red band of $[Ni(H_2O)_6]^{++}$ analyzed into:

$\lambda_0 = \nu_0^{-1}$	ν_0	ϵ_0	δ
740 m μ	13 500 cm $^{-1}$	1.8	1 100 cm $^{-1}$
650	15 400	1.5	1 200

the effect of the increasing infra-red band being notable at low wave numbers. The violet band of $[Ni(H_2O)_6]^{++}$ is single, as shown in Fig. 5 with the parameters

$\lambda_0 = \nu_0^{-1}$	ν_0	ϵ_0	$\delta(-)$	$\delta(+)$
395 m μ	25 300 cm $^{-1}$	5.2	1 500 cm $^{-1}$	1 500 cm $^{-1}$

Fig. 5 also gives the spectrum of $[Ni en_3]^{++}$, which shows three bands: the middle one is symmetrical and single, in contradistinction to the band in Fig. 4. The parameters are

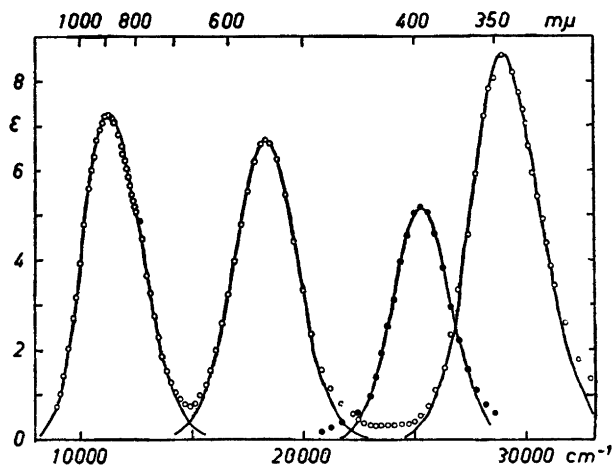


Fig. 5. Absorption spectrum of tris(ethylenediamine)nickel(II) ions (open circles) and violet band of hexaquo nickel(II) ions (filled circles). 0.1 M $Ni(NO_3)_2$ (0.5 M en added in the former case). Below 350 m μ , $Ni(ClO_4)_2$ and en was used. The calculated curves from eq. 3 with the parameters given in the text are drawn full.

$\lambda_0 = \nu_0^{-1}$	ν_0	ϵ_0	$\delta(-)$	$\delta(+)$
890 m μ	11 200 cm $^{-1}$	7.3	1 250 cm $^{-1}$	1 800 cm $^{-1}$
545	18 350	6.7	1 650	1 650
345	29 000	8.6	1 700	1 900

According to unpublished measurements by C. J. Ballhausen, the spectra of the mixed ethylenediamine-aquo-nickel(II) ions also have nearly Gaussian form.

The method of analysing spectra into a number of Gaussian curves can of course in some cases lead to results of no physical significance, since it is equally as general as, *e. g.* Taylor or Fourier analysis. It is only when a small number of high bands are obtained corresponding to the experimental curve that the method is reliable for finding the atomic transitions. It was used early by Brode¹³, and with success especially in the cases as $CoCl_4^{--}$ or MnO_4^- where there is clearly vibrational structure of the bands, in contrast to the normal bands studied here. Similar analyses were performed by Linhard and Weigel^{3,4}.

In the cases where the spectra cannot be measured directly, but are obtained from equilibrium mixtures of coloured complexes (analyzed using known mass action constants), it is necessary to take special precautions before Gaussian analysis. But for example the mixed complexes $[Ni(NH_3)_2(H_2O)_4]^{++}$ or $[Ni(NH_3)_3(H_2O)_3]^{++}$ show several bands¹⁴ which are similar in structure to the bands of $[Ni(H_2O)_6]^{++}$, in this case partially due to the two geometrical isomers.

In the copper(II) complexes¹⁰, several applications of the Gaussian analysis have been made. In some cases, as for $[Cu(NH_3)_4(H_2O)_2]^{++}$, the spectrum seems to correspond to only one band with $\delta(-)$ larger than $\delta(+)$. This is

also found in the spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{+++}$ and may be caused by perturbations from fields of lower symmetry^{10,15}, but more bands cannot be distinguished. The arguments¹⁰ connected with the ratio of the wave numbers of the two bands of, e. g., $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$, are not altered essentially by the possibility of slightly differing $\delta(-)$ and $\delta(+)$. If the partial bands are not assumed to be exactly symmetrical, the possible ratio of the wave numbers of the maxima is altered from 1.34 to 1.2—1.40. By examination of the observed spectrum¹⁰ of copper(II) aquo ions, it is seen that the lowest band in the infra-red cannot be placed at lower wave numbers than $9\,800\text{ cm}^{-1}$, and therefore the value 1.6, which would correspond to penta-configuration, is excluded.

The form of absorption bands can have considerable theoretical interest, since the oscillations of the ligands and the resulting fluctuation of their perturbation effects on the central ion¹⁰ might be investigated in this way especially if temperature effects are also considered.

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