The 30 observations were formed into 8 normal places that together with the 27 normal places from the two previous apparitions yielded 70 equations of condition for a least squares' solution, from which resulted the following set of elements:

Osculation 1926 Nov. 30.0 U.T.

$$
\text{(III)}\quad
\begin{aligned}
T &= 1927 \text{ March } 22.19299 \pm 0.000721 \text{ U.T.} \\
\left.\begin{aligned}
\omega' &= 82^\circ 30' \; 9''.93 \pm 1''.032 \\
\Omega' &= 24^\circ 33' 13''.38 \pm 0''.426 \\
i' &= 31^\circ 30' 59''.83 \pm 0''.302
\end{aligned}\right\} &\text{ Equator 1950.0} \\
e &= 0.57496013 \quad \pm 0.000\,000370 \\
a &= 4.1701778 \quad \pm 0.000\,00019 \\
\left.\begin{aligned}
\omega &= 38^\circ 28' 43''.74 \\
\Omega &= 65^\circ 55' 50''.94 \\
i &= 13^\circ 45' 47''.67
\end{aligned}\right\} &\text{ Ecliptic 1950.0}
\end{aligned}
$$

$$
\begin{aligned}
x &= -0.9697348 \;(\cos E - e) - 3.2346013 \;\sin E \\
y &= +3.4320184 \;(\cos E - e) - 1.0605087 \;\sin E \\
z &= +2.1613068 \;(\cos E - e) + 0.2327200 \;\sin E
\end{aligned}
$$

The data for the 35 normal places are shown in Table c, where in columns 9 and 10 are listed the final residuals (O—C), derived from a direct comparison between the right ascensions and declinations of the normal places (columns 3 and 4) and the corresponding quantities computed from the above elements III for the time t—Ab.t. It should be mentioned that in all computations of right ascensions and declinations the rectangular solar co-ordinates have been corrected for $\Delta L\odot = +1''.00$, that is, the values provided by E. C. Bower (Lick Observatory Bulletin 445, p. 36) have been divided by 1.47.

University Observatory, Copenhagen,
1950 June.

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LOCALIZATION OF THE ELECTRONIC LINES IN CONTINUOUS ABSORPTION SPECTRA BY THE TEMPERATURE-EFFECT

BY

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København
I kommission hos Ejnar Munksgaard
1951

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I. INTRODUCTION

It is of the greatest importance for further development of the theory concerning the electronic structure of polyatomic molecules to find some experimental means for locating the various excited terms. In principle this can be done by an investigation of band spectra appearing in the visible and ultra-violet region. However, it is well known that these spectra—whether they are observed in the vapour, in solutions or in the crystal—most frequently are diffuse and only seldom show traces of vibrational structure. For these more or less diffuse spectra it is out of the question to locate the electronic line[1] of the band system by analysing the vibrational structure. Therefore the frequency of the maximum of absorption—or if the extinction curve shows more than one maximum, the one of lowest frequency—is generally chosen to represent the "frequency" of the absorption system. It is evident that this can only be considered as a rough approximation to the electronic line, and it may even destroy the possibilities for a corroboration of quantum mechanical calculations.

In two short communications[2] we have called attention to the possibility of using the temperature effect on the absorption curve as the basis for a method for localizing the electronic line. According to the Boltzmann distribution law the number of thermically excited molecules is enhanced at rising temperatures. It is therefore to be expected that the absorption will increase for all frequencies lower than that of the electronic line because this part of the spectrum is exclusively due to transitions from excited

[1] Throughout this paper we use the term "electronic line" for the $0 \rightarrow 0$ line, i. e. the line corresponding to a transition between the vibrationless groundlevels of two different electronic states of the molecule.

[2] A. Langseth and Svend Brodersen, Acta Chem. Scand. **3**, 778 (1949); *iidem*, Nature **165**, 931 (1950).

vibrational states[1]. A simple calculation shows that a quantitative measurement of the temperature effect should allow a localization of the electronic line.

The purpose of this paper is to consider this problem in some detail, as well theoretically as experimentally, and to discuss the possibilities for using the temperature effect as a general method for localizing the electronic lines of polyatomic molecules.

II. THEORY

In the ideal state the number of molecules populating the n'th energy level is given by

$$N_n = N_0 \frac{g_n e^{-E_n/kT}}{\sum_p g_p e^{-E_p/kT}} \tag{1}$$

where E_n is the energy and g_n the statistical weight of the level. The summation is to be extended over all levels.

The contribution given to the extinction coefficient, ε, by a transition from the n'th to the m'th level is proportional to N_n/N_0:

$$\varepsilon_{n \to m} = K_{n,m} \frac{N_n}{N_0}. \tag{2}$$

The probability factor, $K_{n,m}$, depends only on the two levels n and m, but is independent of the temperature.

To get the extinction coefficient for a certain frequency, ν, we have to take the summation of (2) over all transitions $n \to m$ satisfying the condition

$$E_m - E_n = h\nu.$$

[1] In principle this is the same argument as was used by KISTIAKOWSKY and SOLOMON (J. Chem. Phys. **5**, 609 (1937); cp. RADLE and BECK, ibid. **8**, 507 (1940)) for the investigation of the origin of certain vibrational bands in the absorption spectrum of the benzene vapour. As is well known it was these measurements which gave the clue to the correct analysis of this band system.

In a recent paper GRUBB and KISTIAKOWSKY (J. Amer. Chem. Soc. **72**, 419 (1950)) have furthermore shown that certain cases of thermochromism can also be explained in this way.

This gives

$$\varepsilon = \sum_{n,m}{}' K_{n,m} \frac{g_n e^{-E_n/kT}}{\sum_p g_p e^{-E_p/kT}}. \tag{3}$$

If we now from the ideal state (vapour at low pressure) pass on to solutions (in which we will be particularly interested because in praxis most absorption spectra can only be obtained in this way) we find, as is well known, certain alterations in the appearance of the spectra. There will be a certain shift, generally towards longer wave-lengths, and at the same time the structure becomes more fuzzy and may even completely disappear. The magnitude of these effects is to some extent dependent on the nature of the solvent. Both of them must be explained as perturbations due to the surrounding molecules of the solvent. Because of the disorder in the solution the degree of perturbation must be expected to vary statistically about some mean value, thus giving rise to the observed fuzziness of the absorption spectra. The shift of the band system as a whole in the spectral region indicates that the ground state and the excited state show different sensibility to the perturbation. On the other hand, the positions of the vibrational levels relative to the electronic level, to which they belong, seem to be surprisingly insensitive to these perturbations. Otherwise it would be difficult to understand why we get so sharp Raman lines and infrared absorption bands of liquids as we actually do.

At a certain height in the statistical "energy level diagram" describing the spectroscopical properties of the dissolved molecules we will therefore not find one (or none) definite level, but rather a collection of different levels belonging to differently pertubed, single molecules. As a first approximation to a theoretical treatment of the temperature effect we have therefore found it sufficiently justified to make the following fundamental assumptions:

1) The thermal distribution is assumed to be classical, i. e. all levels are smoothed out, and all statistical factors are considered to be equal.
2) The transition probability factor $K_{n,m}$ is assumed to be constant and independent of both levels involved. The effect of this approximation will be discussed later in this paper.

Finally we have found it convenient to start our considerations by making the further assumption (as a zero'th approximation) that all the electronic levels have a sharp lower limit. This is of course illogical, considering what was discussed just above. However, it makes the theoretical treatment easier to follow and below we are dropping this approximation.

1. Constant Transition Probability and Sharp Electronic Levels.

Under these conditions the number, dN, of molecules having a thermic energy within the interval E to $(E + dE)$ is given by

$$dN = N_0 \frac{e^{-E/kT}}{\int_0^\infty e^{-E/kT}\, dE}\, dE = \frac{N_0}{kT}\, e^{-E/kT}\, dE. \qquad (4)$$

Further, the contribution, $d\varepsilon$, to the extinction coefficient at the frequency ν caused by transitions between the two energy intervals

$$(E \,|\, E + dE) \rightarrow (E + h\nu \,|\, E + h\nu + dE)$$

will then be

$$d\varepsilon = K \frac{dN}{N_0} = \frac{K}{kT}\, e^{-E/kT}\, dE. \qquad (5)$$

In order to get the extinction coefficient at the frequency ν, we must integrate (5) over all transitions having the frequency ν.

One Substance.

Let us consider a pure substance whose absorption spectrum is due to transitions from the electronic ground state (with its attached vibrational-rotational levels) up to one single excited electronic state (similarly, with attached vibrational-rotational levels), and let ν_0 denote the "electronic line" ($0 \rightarrow 0$ frequency). We have now to distinguish between two cases (cp. Fig. 1):

a) for $\nu \geqq \nu_0$ we get

$$\varepsilon = \int_0^\infty \frac{K}{kT}\, e^{-E/kT}\, dE = K, \qquad (6)$$

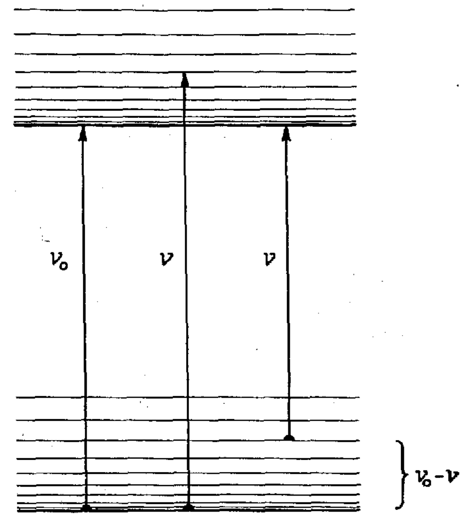

Fig. 1. Energy level diagram.

b) and for $\nu \leqq \nu_0$

$$\varepsilon = \int_{\nu_0 - \nu}^\infty \frac{K}{kT}\, e^{-E/kT}\, dE = K e^{-(\nu_0 - \nu)/kT}. \qquad (7)$$

To get a clearer idea of the meaning of these equations it is convenient to take the logarithm and to express the temperature effect as

$$\Delta \log \varepsilon = \log \varepsilon_{T_2} - \log \varepsilon_{T_1}.$$

This gives us

a) for $\nu \geqq \nu_0$: $\log \varepsilon = \log K$ (8)

and $\Delta \log \varepsilon = 0$, (9)

b) for $\varepsilon \leqq \nu_0$: $\log \varepsilon = \log K - \frac{0.4343}{kT}(\nu_0 - \nu)$ (10)

and $\Delta \log \varepsilon = \frac{0.4343}{k} \frac{T_2 - T_1}{T_1 T_2} (\nu_0 - \nu)$. (11)

Graphs of these simple expressions, which are linear in ν, are given in Fig. 2 and 3. The slope for $\log \varepsilon$ calculated for $T = 298°K$ is 2.10×10^{-3} cm, for $\Delta \log \varepsilon$ it is -0.275×10^{-3} cm for $T_1 = 298°K$ and $T_2 = 343°K$.

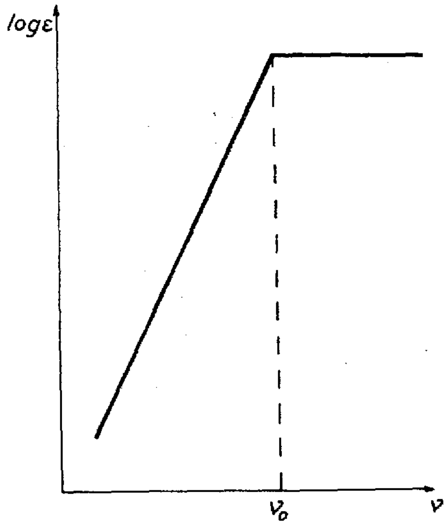

Fig. 2.

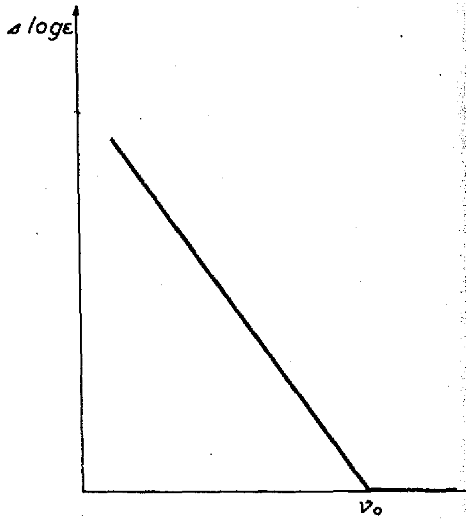

Fig. 3.

Two Substances.

We will now consider a mixture of two substances having the electronic frequences ν_a and ν_b (assuming $\nu_a > \nu_b$), the transition probabilities K_a and K_b and the molar concentrations c_a and c_b respectively. This consideration includes of course also one substance having two different electronic lines, in which case $c_a = c_b$.

As we in praxis mainly will be interested in the effect of a small contamination of the substance under investigation with some impurity having an absorption in this region, we will calculate the extinction coefficient relative to the concentration of the substance a.

We then get

$$\varepsilon = \varepsilon_a + \frac{c_b}{c_a}\varepsilon_b. \tag{12}$$

ε_a and ε_b being the extinction coefficient for the pure substance resp. the impurity. If we insert (6) and (7) in (12) we get

a) for $\nu_b < \nu_a \leq \nu$:

$$\varepsilon = K_a + \frac{c_b}{c_a}K_b \tag{13}$$

and hence

$$\Delta \log \varepsilon = 0, \tag{14}$$

b) for $\nu_b \leq \nu \leq \nu_a$:

$$\varepsilon = K_a e^{-(\nu_a - \nu)/kT} + \frac{c_b}{c_a}K_b \tag{15}$$

and

$$\Delta \log \varepsilon = \log \frac{1 + \dfrac{c_a K_a}{c_b K_b} e^{-(\nu_a - \nu)/kT_2}}{1 + \dfrac{c_a K_a}{c_b K_b} e^{-(\nu_a - \nu)/kT_1}}. \tag{16}$$

As we are often using this last function in the following we will introduce the expression $F(x, y)$ defined as:

$$F(x, y) = \log \frac{1 + x \times e^{-y/kT_2}}{1 + x \times e^{-y/kT_1}}. \tag{17}$$

Fig. 4 shows a graphical representation of this function. A corresponding table giving the numerical values will be found in an appendix.

Expression (16) is of special interest. When it is necessary to take the effect of an impurity into consideration we must use (16) rather than the simple expression (11). Because of the exponential decrease of ε, when we from ν_0 pass towards longer wavelengths, the effect of the impurity encreases rapidly and the more the bigger c_b and K_b are. It is seen from Fig. 4 that the temperature effect almost disappears if the value of $c_b K_b$ is approaching the value of $c_a K_a$. This can, at least theoretically, be counterbalanced by further purification of the substance a. But even impurities of considerably lower concentration than that always being present in "pure" substances are of importance here.

The situation is, however, quite different if we are dealing with two different electronic transitions of the same substance. In this case $c_a/c_b = 1$ and $c_a K_a/c_b K_c$ indicates the relative strength of the two absorption systems. We are here faced with the first serious shortcoming of the temperature effect as a method for locating electronic lines. If the intensity of the first absorption system has not decreased sufficiently before the next starts,

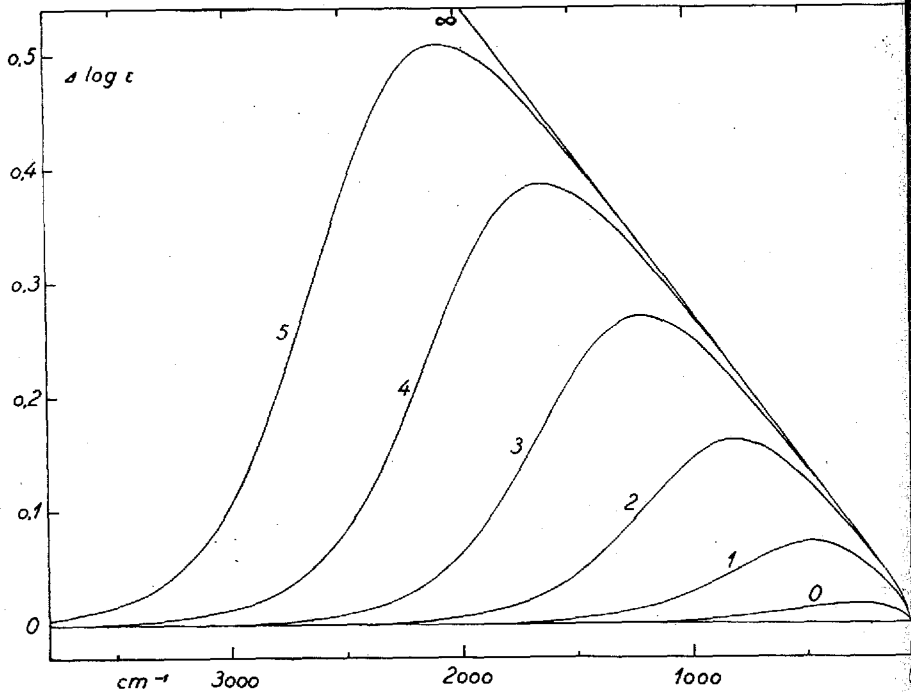

Fig. 4. $\Delta \log \varepsilon = F(x, y)$ calculated for $T_1 = 298° K$ and $T_2 = 343° K$. The numbers at the curves represent the parameter $\log x = \log (c_a K_a / c_b K_b)$.

which in praxis means at least to the intensity ratio 1:10 (cp. curve 1 of Fig. 4), it will be impossible with certainty to locate the second electronic line.

c) Finally, for the case: $\nu \leqq \nu_b < \nu_a$ we have

$$\varepsilon = K_a e^{-(\nu_a - \nu)/kT} + \frac{c_b}{c_a} K_b e^{-(\nu_b - \nu)/kT} \tag{18}$$

and

$$\Delta \log e = \frac{0.4343}{k} \frac{T_2 - T_1}{T_1 T_2} (\nu_b - \nu) + F\left(\frac{c_a K_a}{c_b K_b}, \nu_a - \nu_b\right). \tag{19}$$

Equation (19) is composed of the value for (16) for $\nu = \nu_b$ and the linear expression (11). This means that we get a straight line with the ordinary slope (as in Fig. 3), but instead of starting at $\Delta \log \varepsilon = 0$ it starts at a point whose ordinate may be found

from Fig. 4 by putting $y = \nu_a - \nu_b$. That the curve must start in this point may also be seen from (16), as this equation is valid for $\nu = \nu_b$.

Several Substances.

Expressions for three or more substances in a mixture (or a pure substance with three or more near-by electronic lines) may be derived in a way quite analogous to that used for (14), (16) and (19). As before the extinction coefficient is defined relatively to the substance a:

$$\varepsilon = \varepsilon_a + \frac{c_b}{c_a} \varepsilon_b + \frac{c_c}{c_a} \varepsilon_c + \cdots . \tag{20}$$

As an example may be given two of the formulas for the case where we have a mixture of three substances.

For $\nu_c < \nu_b \leqq \nu \leqq \nu_a$ we get:

$$\Delta \log \varepsilon = F\left(\frac{c_a K_a}{c_b K_b + c_c K_c}, \nu_a - \nu\right) \tag{21}$$

and for $\nu_c \leqq \nu \leqq \nu_b < \nu_a$:

$$\Delta \log \varepsilon = F\left(\frac{c_b K_b}{c_c K_c} \times 10^{\beta}, \alpha + \nu_b - \nu\right) \tag{22}$$

where

$$= \frac{T_2}{T_2 - T_1} \log\left[1 + \frac{c_a K_a}{c_b K_b} e^{-(\nu_a - \nu_b)/kT_2}\right] - \frac{T_1}{T_2 - T_1} \log\left[1 + \frac{c_a K_a}{c_b K_b} e^{-(\nu_a - \nu_b)/kT_1}\right]$$

and

$$\alpha = \frac{k}{0.4343} \frac{T_1 T_2}{T_2 - T_1} \times F\left(\frac{c_a K_a}{c_b K_b}, \nu_a - \nu_b\right).$$

2. Constant Transition Probability and Diffuse Electronic Levels.

As previously mentioned all of the equations (6)—(22) are derived by making the somewhat illogical assumption that the electronic lines are sharp, whereas the vibrational structure is smoothed out to a continuum. We will now drop the approx-

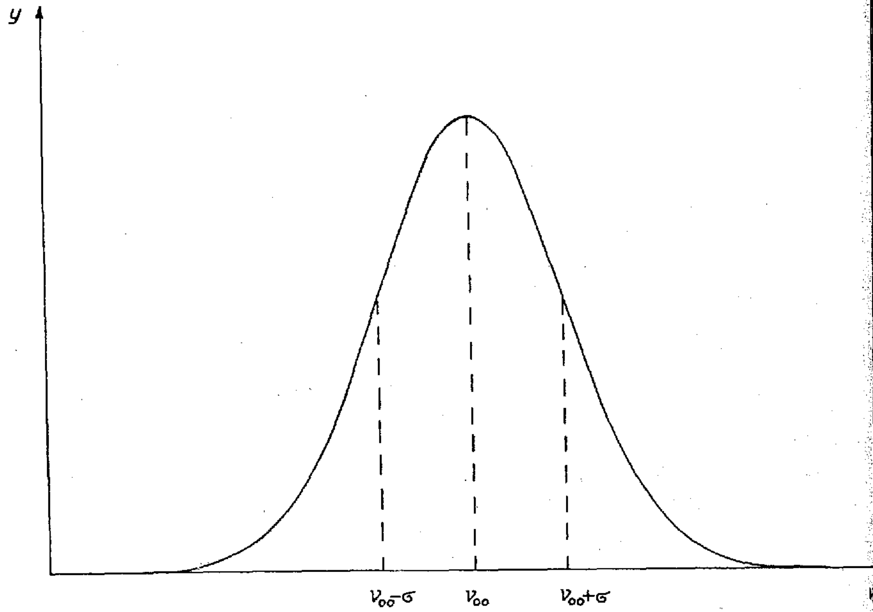

Fig. 5.

imation concerning the sharp electronic line. We assume that the frequency of the electronic transition, ν_0, is fuzzy corresponding to a statistical distribution about a mean value, ν_{00}, in accordance with the normal probability curve:

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(\nu_{00}-\nu_0)^2/2\sigma^2}. \tag{23}$$

The parameter σ is the standard deviation.

For each value of ν_0 we have to apply the expressions (6) and (7) and to integrate over the whole probability curve[1].

One (pure) Substance.

For a definite ν we get the contribution to the extinction coefficient arising from molecules having $\nu_0 < \nu$ by applying (6) and (23):

[1] This assumption seems to be a reasonable one if the broadening is caused by collisions with other molecules. If, however, it is due to intramolecular causes—and therefore already present in the spectrum of the vapour—the normal probability curve may not be the best approximation. This may give rise to discrepancies between the experimental results and the theoretical curves calculated from formulas (23)—(47).

$$\varepsilon_1 = \int_{-\infty}^{\nu} K \frac{1}{\sigma\sqrt{2\pi}} e^{-(\nu_{00}-\nu)^2/2\sigma^2} d\nu_0.$$

Further from (7) and (23) we get for all molecules having $\nu_0 > \nu$

$$\varepsilon_2 = \int_{\nu}^{\infty} K e^{-(\nu_0-\nu)/kT} \times \frac{1}{\sigma\sqrt{2\pi}} e^{-(\nu_{00}-\nu)^2/2\sigma^2} d\nu_0.$$

The sum of these two contributions gives the total extinction coefficient, ε, which may be written as:

$$\varepsilon = K \times G(\sigma, T, \nu_{00}-\nu) \tag{24}$$

where

$$G(\sigma, T, \nu_{00}-\nu) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{-\frac{\nu_{00}-\nu}{\sigma}} e^{-t^2/2} dt + e^{\frac{1}{2}(\sigma/kT)^2-(\nu_{00}-\nu)/kT} \times \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\frac{\nu_{00}-\nu}{\sigma}-\frac{\sigma}{kT}} e^{-t^2/2} dt. \tag{25}$$

Both of the two integrals in (25) are tabulated in statistical tables[1]. The numerical computation of the function is therefore comparatively easy. A graph of log G is given in Fig. 23.

It might be useful to state the following limiting values[2] for the function:

$$\lim_{\nu\to\infty} G = 1 \quad (T \text{ and } \sigma \text{ const.}) \tag{26}$$

$$\lim_{\nu\to-\infty} G = e^{\frac{1}{2}(\sigma/kT)^2-(\nu_{00}-\nu)/kt} \, (T \text{ and } \sigma \text{ const.}). \tag{27}$$

For the temperature effect we find:

$$\Delta \log \varepsilon = \log \frac{G(\sigma_2, T_2, \nu_{00}-\nu)}{G(\sigma_1, T_1, \nu_{00}-\nu)}. \tag{28}$$

Here, σ_1 and σ_2 mean the standard deviations for the two temperatures T_1 and T_2 respectively.

[1] We have used: W. F. SHEPPARD: The Probability Integral. British Association Mathm. Tables VII, 1939.

[2] The condition $\nu \to -\infty$, though physically meaningless, is stated here and in the following for mathematical convenience. It is easily seen that (27) is valid also for $\nu \to 0$ for all interesting values of the parameters.

For $\nu \to \infty$ we find from (24), (28) and (26)

$$\lim_{\nu \to \infty} \varepsilon = K \tag{29}$$

and

$$\lim_{\nu \to \infty} (\Delta \log \varepsilon) = 0. \tag{30}$$

The equations (6) and (9) are therefore still valid as limiting values.

For $\nu \to -\infty$ it follows from (24), (28) and (27) that:

$$\lim_{\nu \to -\infty} \varepsilon = e^{\frac{1}{2}(\sigma/kT)^2} \times K \times e^{-(\nu_{00}-\nu)/kT} \tag{31}$$

and

$$\lim_{\nu \to -\infty} (\Delta \log \varepsilon) = \frac{0.4343}{k} \frac{T_2 - T_1}{T_1 T_2} \left[(\nu_{00} - \nu) + \frac{1}{2k} \frac{T_1 T_2}{T_2 - T_1} \left\{ \left(\frac{\sigma_2}{T_2}\right)^2 - \left(\frac{\sigma_1}{T_1}\right)^2 \right\} \right]. \tag{32}$$

In these cases we do not get the equations (7) and (11) as limiting values. However, the corrections are simple: (32) represents a straight line with the usual slope, but shifted in the direction of the ν axis with the amount:

$$\alpha = \frac{1}{2k} \frac{T_1 T_2}{T_2 - T_1} \left\{ \left(\frac{\sigma_2}{T_2}\right)^2 - \left(\frac{\sigma_1}{T_1}\right)^2 \right\}. \tag{33}$$

In order to evaluate α the temperature dependence of the standard deviation, σ, must be known. (Compare the discussion pag. 29—31). For mathematical reasons we assume that σ is proportional to the temperature in a definite power, θ:

$$\frac{\sigma_2}{\sigma_1} = \left(\frac{T_2}{T_1}\right)^\theta. \tag{34}$$

If $\theta = 0$, i. e. σ is independent of the temperature, we get

$$\alpha = -\frac{1}{2k} \frac{T_1 + T_2}{T_1 T_2} \sigma^2. \tag{35}$$

If $\theta = 1$, i. e. σ proportional to T, it follows from (33) that $\alpha = 0$. This reduces (32) to the same form as (11).

If $\theta = 2$ we find

$$\alpha = \frac{1}{2k} \frac{T_2(T_1 + T_2)}{T_1^3} \sigma_1^2. \tag{36}$$

In the following Table I we give the numerical values of α calculated for different σ_1 and θ, for the two temperatures used in this investigation: $T_1 = 298° K$ and $T_2 = 343° K$.

Table I.

σ_1	α		
	$\theta = 0$	$\theta = 1$	$\theta = 2$
100 cm^{-1}	— 45 cm^{-1}	0 cm^{-1}	60 cm^{-1}
200 ,,	— 180 ,,	0 ,,	239 ,,
300 ,,	— 406 ,,	0 ,,	538 ,,
500 ,,	—1130 ,,	0 ,,	1490 ,,
1000 ,,	—4510 ,,	0 ,,	5980 ,,

This survey shows that the asymptote is shifted proportional to σ^2 towards lower frequencies if $\theta < 1$, but towards higher frequencies if $\theta > 1$. If $\theta = 1$ σ is proportional to T, i. e. there is no shift.

How the course of the curve will be between the two asymptotical parts can only be found by a numerical calculation. Only if $\nu = \nu_{00}$ and $\theta = 1$ it is seen from (25) and (28) that $\Delta \log \varepsilon = 0$, i. e. that in this special case the Δ log ε curve passes through ν_{00}.

One Substance plus Impurity.

It will be the most convenient to derive our expressions by assuming one of the substances to be present only in a low concentration as an impurity giving rise to a weak, but constant absorption. For the total extinction coefficient we then get from (12)

$$\varepsilon = K \times G(\sigma, T, \nu_{00} - \nu) + \frac{c_0}{c} K_0 \tag{37}$$

where c_0 and K_0 are the concentration rsp. transition probability of the impurity.

This gives for the temperature effect:

$$\Delta \log \varepsilon = \log \frac{1 + \frac{cK}{c_0 K_0} G(\sigma_2, T_2, \nu_{00} - \nu)}{1 + \frac{cK}{c_0 K_0} G(\sigma_1, T_1, \nu_{00} - \nu)}. \tag{38}$$

The form of (38) is analogous to (16); but it contains two extra parameters, σ_1 and σ_2, and is therefore rather complicated to calculate. We state the following limiting conditions:
For $\nu \to \infty$ we get from (26) that

$$\lim_{\nu \to \infty} (\Delta \log \varepsilon) = 0 \tag{39}$$

and for $\nu \to -\infty$ it follows from (27) that

$$\lim_{\nu \to -\infty} (\Delta \log \varepsilon) = F\left(\frac{cK}{c_0 K_0} \times 10^{\beta},\ \alpha + \nu_{00} - \nu\right) \tag{40}$$

where α has the same value as in (33) and

$$\beta = \frac{0.4343}{2\,k^2}\,\frac{1}{T_2 - T_1}\left(\frac{\sigma_2^2}{T_2} - \frac{\sigma_1^2}{T_1}\right). \tag{41}$$

In this case we therefore have the same abscissa correction as in (32), but moreover a correction in the "number" of the curve shown in Fig. 4. As well α as β is very sensitive to the value of θ. For α this has been discussed above. For β we find:

if $\theta = 0$

$$\beta = -\frac{0.4343}{2\,k^2}\,\frac{1}{T_1 T_2}\,\sigma^2\ . \tag{42}$$

i. e. a decrease in the temperature effect.
Similarly, if $\theta = 1$ we get

$$\beta = \frac{0.4343}{2\,k^2}\,\frac{1}{T_1^2}\,\sigma_1^2 \tag{43}$$

i. e. an increase in the temperature effect, and finally, for $\theta = 2$

$$\beta = \frac{0.4343}{2\,k^2}\,\frac{T_1^2 + T_1 T_2 + T_2^2}{T_1^4}\,\sigma_1^2 \tag{44}$$

i. e. a further increase in the effect.
The following Table II is calculated from (42), (43) and (44). As before $T_1 = 298°\,K$ and $T_2 = 343°\,K$.

Table II.

σ_1	β		
	$\theta = 0$	$\theta = 1$	$\theta = 2$
100 cm^{-1}	—0,04	0.05	0.176
200 ,,	—0.18	0.20	0.70
300 ,,	—0.40	0.46	1.58
500 ,,	—1.10	1.27	4.40
1000 ,,	—4.40	5.06	17.6

The figures 6, 7 and 8 (corresponding to Fig. 4) are graphical representations of the temperature effect. All the curves are calculated for $\sigma_1 = 300$ cm^{-1}, but θ has the values 0, 1 and 2 respectively. Compared to Fig. 4 it is seen how the curves in Fig. 6 ($\theta = 0$) are shifted to the left and at the same time downwards. In Fig. 8 ($\theta = 2$) the shift is in the opposite directions,

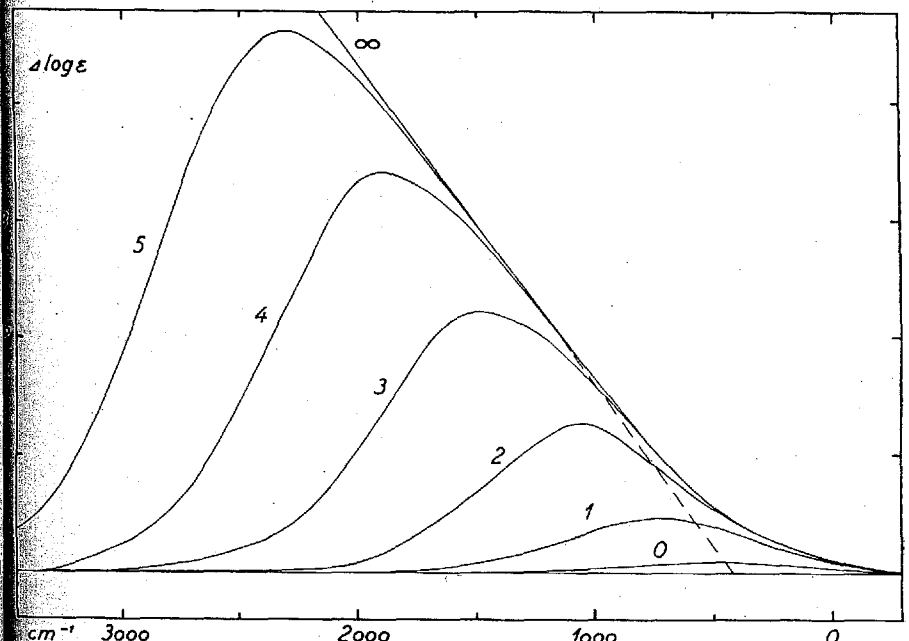

Fig. 6. $\Delta \log \varepsilon$ calculated from (38) for $\sigma_1 = 300$ cm^{-1}, $\theta = 0$, $T_1 = 298°\,K$ and $T_2 = 343°\,K$. The numbers at the curves represent the parameter $\log (cK/c_0K_0)$. The dotted line is the asymptote calculated from (32).

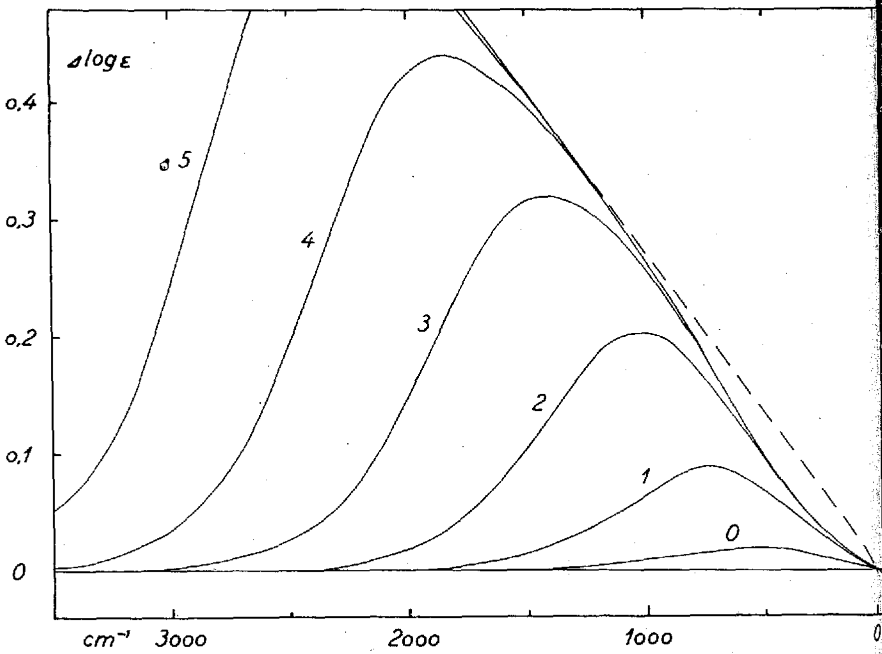

Fig. 7. $\Delta \log \varepsilon$ as in Fig. 6, but for $\theta = 1$.

to the right and upwards. The curves in Fig. 7 ($\theta = 1$) are ver[y] similar to those shown in Fig. 4. All the shifts are roughly pro[-]portional to σ^2. Therefore, if $\sigma <$ ca. 200 cm^{-1} the correction[s] are negligible so that the simple curves of Fig. 4 may be used[,] whereas for $\sigma >$ ca. 500 cm^{-1} the corrections are so large tha[t] the original form of the curves is almost completely obliterated[.]

Two Substances plus Impurity.

Using analogous denominations we derive the following ex[-]pression for a mixture of two substances, a and b, containin[g] some impurity with a constant absorption:

$$\Delta \log \varepsilon = \log \frac{1 + \frac{c_b K_b}{c_0 K_0} G(\sigma_{2b}, T_2, \nu_b - \nu) + \frac{c_a K_a}{c_0 K_0} G(\sigma_{2a}, T_2, \nu_a - \nu)}{1 + \frac{c_b K_b}{c_0 K_0} G(\sigma_{1b}, T_1, \nu_b - \nu) + \frac{c_a K_a}{c_0 K_0} G(\sigma_{1a}, T_1, \nu_a - \nu)} . \quad ($$

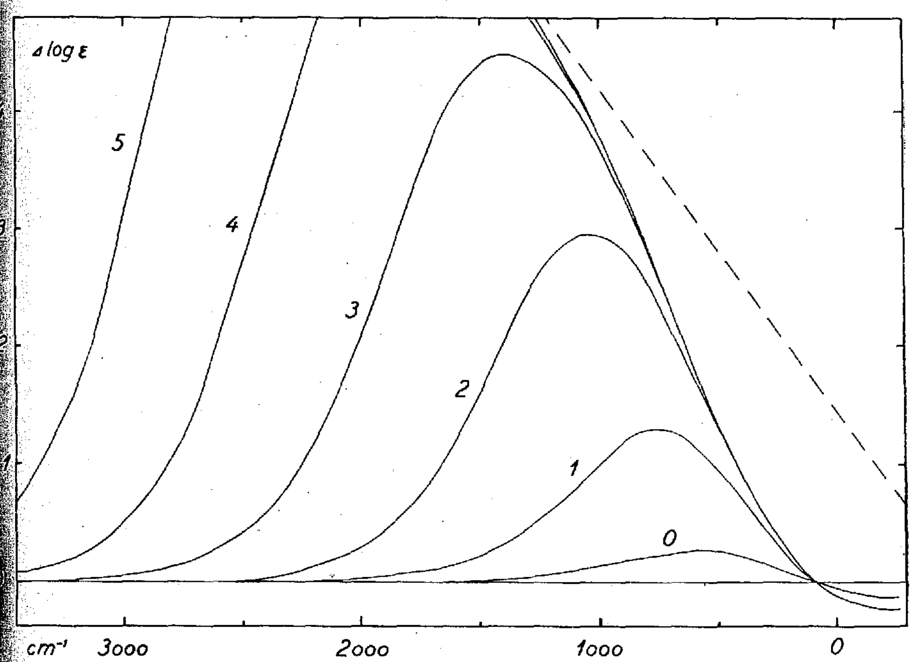

Fig. 8. $\Delta \log \varepsilon$ as in Fig. 6, but for $\theta = 2$.

Here ν_a and ν_b are the mean values of the electronic frequencies (corresponding to ν_{00}).

If we assume $\nu_b < \nu_a$, as we did above, we find that the func-tions $G(\sigma_{2b}, T_2, \nu_b - \nu)$ and $G(\sigma_{1b}, T_1, \nu_b - \nu)$ for $\nu > \nu_b$ are rapidly converging towards 1 if $\nu \to \infty$ and

$$\Delta \log \varepsilon \to \log \frac{1 + \frac{c_a K_a}{c_0 K_0 + c_b K_b} G(\sigma_{2a}, T_2, \nu_a - \nu)}{1 + \frac{c_a K_a}{c_0 K_0 + c_b K_b} G(\sigma_{1a}, T_1, \nu_a - \nu)} . \quad (46)$$

This means that for $\nu > \nu_b$ the influence of substance b is almost the same as that of an impurity. To this side the same conditions are prevailing as in the preceding section.

If, however, $\nu \to -\infty$ we get (cp. (22)):

$$\lim_{\nu \to -\infty} (\Delta \log \varepsilon) = F\left(\frac{c_b K_b}{c_0 K_0} \times 10^{\beta}, \alpha + \nu_b - \nu\right) \quad (47)$$

where

$$\beta = \frac{0.4343}{2\,k^2}\,\frac{1}{T_2 - T_1}\left[\frac{\sigma_{2b}^2}{T_2} - \frac{\sigma_{1b}^2}{T_1}\right]$$

$$+ \frac{T_2}{T_2 - T_1}\log\left[1 + \frac{c_a K_a}{c_b K_b}\, e^{(1/2k^2)\,[(\sigma_{2a}/T_2)^2 - (\sigma_{2b}/T_2)^2]}\, e^{-(\nu_a - \nu_b)/kT_2}\right]$$

$$- \frac{T_1}{T_2 - T_1}\log\left[1 + \frac{c_a K_a}{c_b K_b}\, e^{(1/2k^2)\,[(\sigma_{1a}/T_1)^2 - (\sigma_{1b}/T_1)^2]}\, e^{-(\nu_a - \nu_b)/kT_1}\right]$$

and

$$\alpha = \frac{k}{0.4343}\,\frac{T_1 T_2}{T_2 - T_1} \times F\left(\frac{c_a K_a}{c_b K_b} \times 10^{\beta'},\ \alpha' + \nu_a - \nu_b\right)$$

in which

$$\beta' = \frac{0.4343}{2\,k^2}\,\frac{1}{T_2 - T_1}\left[\frac{\sigma_{1b}^2 - \sigma_{1a}^2}{T_1} + \frac{\sigma_{2a}^2 - \sigma_{2b}^2}{T_2}\right]$$

and

$$\alpha' = \frac{1}{2\,k}\,\frac{T_1 T_2}{T_2 - T_1}\left[\left\{\left(\frac{\sigma_{2a}}{T_2}\right)^2 - \left(\frac{\sigma_{1a}}{T_1}\right)^2\right\} - \left\{\left(\frac{\sigma_{2b}}{T_2}\right)^2 - \left(\frac{\sigma_{1b}}{T_1}\right)^2\right\}\right].$$

Assuming a definite relation between σ and the temperature, the above equations may be considerably simplified.

3. Varying Transition Probability.

So far we have assumed a constant transition probability for the whole absorption system, which means that the extinction curve should be represented by a horizontal straight line for $\nu \geqq \nu_0$ (cp. Fig. 2). Considering the general appearance of the ultraviolet absorption spectra this is obviously a very crude approximation. Even if all traces of vibrational structure are completely obliterated, which is very often the case, the extinction curve shows a smooth form: increasing monotonously to a maximum and then slowly falling off again, as it should do according to the Franck-Condon principle. However, as long as the slope of the extinction curve is not very steep on the high-frequency side of the maximum this deviation from our assumption will not invalidate our derived expressions for the temperature effect seriously. The reason herefore is that we take the ratio of the extinctions for the two temperatures as a measure for the temperature effect. The only presumption for this procedure is that the transition probability is constant within a narrow region.

On the other hand, sometimes an absorption spectrum shows a pronounced vibrational structure, as e. g. the spectra of benzene, naphthalene, anthracene etc. It is well known that the vibrational structure is found to be broadened out at rising temperatures. This is a temperature effect of another nature than that in which we are mainly interested, but as it in some cases may obscure the general picture of the temperature effect in the idealized form, as has been described in the preceding pages, we will in the following consider this broadening-out effect.

We will consider a narrow band ("line") corresponding to a certain transition $E_1 \rightarrow E_2$ and being sufficiently pronounced as to allow us to neglect all other near-by bands. Further we assume this narrow band to have a shape which can be represented by the normal probability curve. In this case we can express the extinction coefficient as

$$\varepsilon = \frac{L'}{\sigma\sqrt{2\pi}}\, e^{-(\nu_1 - \nu)^2/2\sigma^2}\, \frac{g_1 e^{-E_1/kT}}{\sum\limits_n g_n e^{-E_n/kT}}. \tag{48}$$

Here L' is a transition probability factor (corresponding to K) and ν_1 is the mean frequency of the band. As before we will assume that the partition function $\sum\limits_n g_n e^{-E_n/kT}$ can be represented by the classical integral

$$\int_0^\infty e^{-E/kT}\, dE = kT. \tag{49}$$

If this is inserted and all constants collected into a single one we get

$$\varepsilon = \frac{L}{\sigma T}\, e^{-(\nu_1 - \nu)^2/2\sigma^2} \times e^{-E_1/kT} \tag{50}$$

and hence

$$\log \varepsilon = \log L - \log(\sigma T) - \frac{0.4343}{kT} E_1 - \frac{0.4343}{2\,\sigma^2}(\nu_1 - \nu)^2. \tag{51}$$

This expression gives a parabola, the form of which is determined exclusively by σ. Therefore, if there is an outstanding band present in the absorption spectrum we have in (51) a simple way to carry out an experimental determination of σ. However, such a determination can only be expected to give an upper limit, because the influence of near-by bands will tend to increase the apparant value.

For the temperature effect we find:

$$\left.\begin{aligned}\Delta \log \varepsilon = & -\log \frac{T_2}{T_1} - \log \frac{\sigma_2}{\sigma_1} + \frac{0.4343}{2}\left(\frac{1}{\sigma_1^2} - \frac{1}{\sigma_2^2}\right)(\nu_1 - \nu)^2 \\ & + \frac{0.4343}{k}\frac{T_2 - T_1}{T_1 T_2} E_1 .\end{aligned}\right\} \quad (52)$$

This is a parabola (if $\theta = 0$ expression (52) will represent a horizontal, straight line) with its vertex downwards at the ordinate:

$$(\Delta \log \varepsilon)_{\nu = \nu_1} = -(\theta + 1)\log \frac{T_2}{T_1} + \frac{0.4343}{k}\frac{T_2 - T_1}{T_1 T_2} E_1 \quad (53)$$

or for our usual temperatures:

$$(\Delta \log \varepsilon)_{\nu = \nu_1} = -(\theta + 1)\, 0.061 + 0.000275\, E_1 . \quad (54)$$

If the lower level, E_1, for a sufficiently prominent band in the spectrum is known it should theoretically be possible to determine θ from the measured temperature effect at the maximum of the band.

Neighbouring lines will of course restrict the validity of the expressions (50)—(52) to a narrow region around ν_1. In order to extend the theoretical considerations further it would therefore be necessary to treat all neighbouring lines and then approximate to the real effect by a summation of the extinctions. Quite apart from the fact that it would be an extremely tedious procedure it would require too many parameters to allow any calculation of practical value.

A Narrow Band plus Background.

Far greater interest is connected to a theoretical treatment of the temperature effect on single prominent bands protruding from a background, because this seems to be the easiest and most

natural way to approximate absorption spectra showing vibrational structure. This means that we have to combine our considerations concerning the single narrow band with the assumption of a constant transition probability for the neighbouring parts of the spectrum.

We will, as before, first assume the electronic levels to be sharp. For bands at higher frequencies than ν_0 we then get the temperature effect by adding the equations (6) and (50).

$$\Delta \log \varepsilon = \log \frac{1 + \frac{L}{K}\frac{1}{\sigma_2 T_2} e^{-(\nu_1 - \nu)^2/2\sigma_2^2} e^{-E_1/kT_2}}{1 + \frac{L}{K}\frac{1}{\sigma_1 T_1} e^{-(\nu_1 - \nu)^2/2\sigma_1^2} e^{-E_1/kT_1}} . \quad (55)$$

Assuming the ground level as starting point for the transition this simplifies to

$$\Delta \log \varepsilon = \log \frac{1 + \frac{L}{K}\frac{1}{\sigma_2 T_2} e^{-(\nu_1 - \nu)^2/2\sigma_2^2}}{1 + \frac{L}{K}\frac{1}{\sigma_1 T_1} e^{-(\nu_1 - \nu)^2/2\sigma_1^2}} . \quad (56)$$

For bands at lower frequencies than ν_0 we find from (7) and (50):

$$\left.\begin{aligned}\Delta \log \varepsilon = & \frac{0.4343}{k}\frac{T_2 - T_1}{T_1 T_2}(\nu_0 - \nu) \\ & + \log \frac{1 + \frac{L}{K}\frac{1}{\sigma_2 T_2} e^{-(\nu_1 - \nu)^2/2\sigma_2^2} e^{-[E_1 - (\nu_0 - \nu)]/kT_2}}{1 + \frac{L}{K}\frac{1}{\sigma_1 T_1} e^{-(\nu_1 - \nu)^2/2\sigma_1^2} e^{-[E_1 - (\nu_0 - \nu)]/kT_1}} .\end{aligned}\right\} \quad (57)$$

And if we introduce the corresponding assumption: $E_1 = \nu_0 - \nu_1$, it follows that

$$\left.\begin{aligned}\Delta \log \varepsilon = & \frac{0.4343}{k}\frac{T_2 - T_1}{T_1 T_2}(\nu_0 - \nu) \\ & + \log \frac{1 + \frac{L}{K}\frac{1}{\sigma_2 T_2} e^{-(\nu_1 - \nu)^2/2\sigma_2^2} e^{-(\nu - \nu_1)/kT_2}}{1 + \frac{L}{K}\frac{1}{\sigma_1 T_1} e^{-(\nu_1 - \nu)^2/2\sigma_1^2} e^{-(\nu - \nu_1)/kT_1}} .\end{aligned}\right\} \quad (58)$$

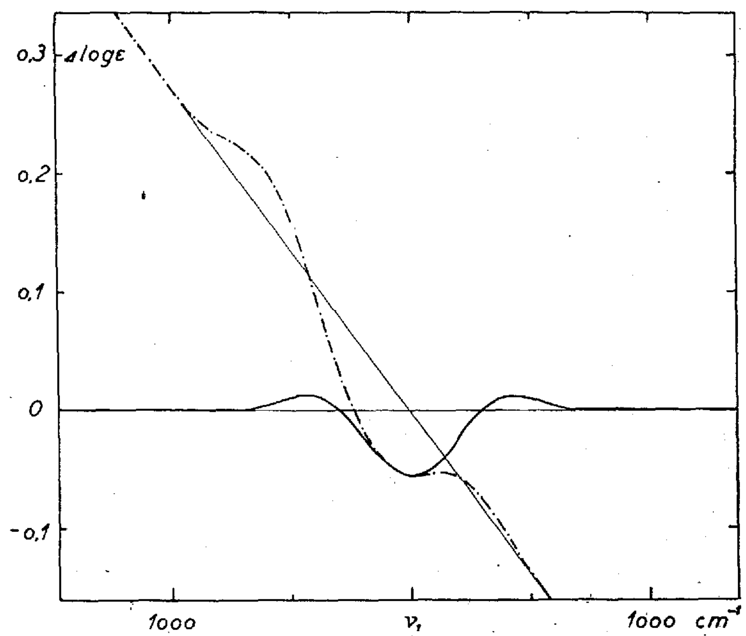

Fig. 9. The effect of a single, prominent band on $\Delta \log \varepsilon$: ——— calculated from (56), and —·—·— from (58) for the usual temperatures.

Of the two curves shown in Fig. 9 the one which has a horizontal asymptote is calculated from (56) and that with the oblique asymptote from (58). This figure is to be compared with the simple picture given in Fig. 3. The effect of a sudden jump in transition probability (corresponding to the appearance of a protruding band) causes a deviation from the simple curve, which is negative around the maximum, whereas it is positive to both sides. This corresponds to the qualitative picture of the temperature effect observed in band spectra[1]. It should further be noted that the electronic frequency, ν_0, does not appear in (58). Therefore the position of ν_0 is not indicated in Fig. 9.

If the presence of impurities is taken into account it is found that expression (58) changes into:

[1] Gibson and Bayliss, Phys. Rev. **44**, 188 (1933).
Gibson, Rice and Bayliss, Phys. Rev. **44**, 193 (1933).
Herczog und Wieland, Helv. Phys. Acta **21**, 436 (1948).
Weale, Helv. Phys. Acta **22**, 164 (1949).
Herczog und Wieland, Helv. Phys. Acta **22**, 552 (1949).
Sulzer u. Wieland, Helv. Phys. Acta **22**, 591 (1949).
Grubb and Kistiakowsky, Journ. Amer. Chem. Soc. **72**, 419 (1950).

$$\left.\begin{aligned} \Delta \log \varepsilon &= F\left(\frac{c_a K_a}{c_b K_b}, \nu_a - \nu\right) \\ &+ \log \frac{1 + \dfrac{c_a L}{c_b K_b} \dfrac{1}{\sigma_2 T_2} e^{-(\nu_1-\nu)^2/2\sigma_2^2} e^{-(\nu_a-\nu_1)/kT_2} \dfrac{1}{1+\dfrac{c_a K_a}{c_b K_b} e^{-(\nu_a-\nu)/kT_2}}}{1 + \dfrac{c_a L}{c_b K_b} \dfrac{1}{\sigma_1 T_1} e^{-(\nu_1-\nu)^2/2\sigma_1^2} e^{-(\nu_a-\nu_1)/kT_1} \dfrac{1}{1+\dfrac{c_a K_a}{c_b K_b} e^{-(\nu_a-\nu)/kT_1}}}. \end{aligned}\right\} \quad (59)$$

The difference is very little significant as long as the background curve is following the asymptote on the right-hand side of the maximum. If, however, (59) is calculated for a narrow band on the low-frequency side of the maximum, we get—as is seen from Fig. 10—an apparently quite new and strongly positive effect. This unexpected deviation is explained if one computes the extinction curve for the narrow band plus background, and then from this gets a corrected and ν-dependent value for the parameter x of the background curve, and finally from this the corresponding $\Delta \log \varepsilon$ curve. Compared with this last curve the deviation turns out to be exactly as that shown in Fig. 9 only with a slight displacement along the direction of the ν-axis. (Cp. the inserted diagram in Fig. 10).

If we now take into consideration that the electronic levels are diffuse, it is easily seen that this makes very little difference for the two outer regions where the G-function has attained to its asymptotic values. In between these two regions, however, we have to use new expressions. Here we are only giving those, which apply to the specially interesting case, where the prominent band is the electronic line itself. If impurities are taken into account we get

$$\left.\begin{aligned} \log \varepsilon &= \log \frac{c_0}{c_a} K_0 + \log\left[1 + \frac{c_a K_a}{c_0 K_0} G(\sigma, T, \nu_a - \nu)\right] \\ &+ \log\left[1 + \frac{c_a L}{c_0 K_0} \frac{1}{\sigma T} e^{-(\nu_a-\nu)^2/2\sigma^2} \frac{1}{1 + \dfrac{c_a K_a}{c_0 K_0} G(\sigma, T, \nu_a - \nu)}\right] \end{aligned}\right\} \quad (60)$$

and hence

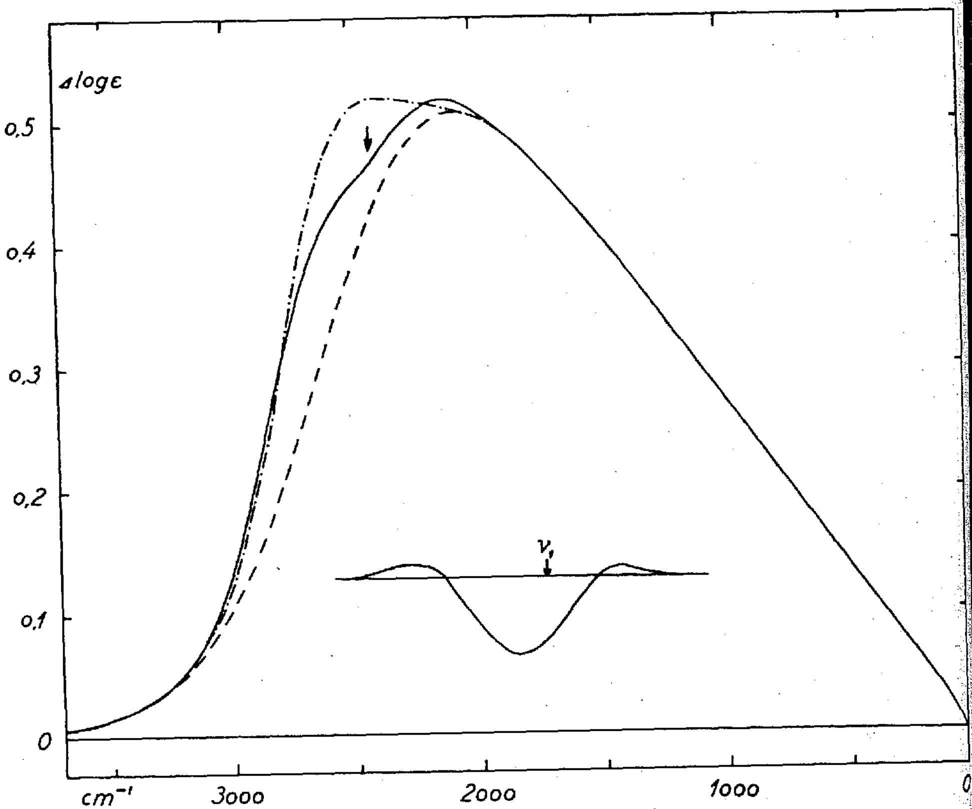

Fig. 10. The effect of a single, prominent band on $\Delta \log \varepsilon$: ---- calculated from (16), ——— from (59) for $\nu_a - \nu_1 = 2400\ \mathrm{cm}^{-1}$, and —·—·— from (16), but corrected for the presence of the narrow band. Inserted: the difference between —·—·— and ———.

$$\left.\begin{aligned}\Delta \log \varepsilon = {} & \log \frac{1 + \dfrac{c_a K_a}{c_0 K_0} G(\sigma_2,\ T_2,\ \nu_a - \nu)}{1 + \dfrac{c_a K_a}{c_0 K_0} G(\sigma_1,\ T_1,\ \nu_a - \nu)} \\ & + \log \left[1 + \frac{c_a L}{c_0 K_0} \frac{1}{\sigma_2 T_2} e^{-(\nu_a - \nu)^2/2\sigma_2^2} \frac{1}{1 + \dfrac{c_a K_a}{c_0 K_0} G(\sigma_2,\ T_2,\ \nu_a - \nu)} \right] \\ & - \log \left[1 + \frac{c_a L}{c_0 K_0} \frac{1}{\sigma_1 T_1} e^{-(\nu_a - \nu)^2/2\sigma_1^2} \frac{1}{1 + \dfrac{c_a K_a}{c_0 K_0} G(\sigma_1,\ T_1,\ \nu_a - \nu)} \right]. \end{aligned}\right\} \quad (61)$$

Curves calculated from (61) are given in Fig. 18.

III. EXPERIMENTAL PROCEDURE

For all the absorption measurements we have used a Beckman spectrophotometer, model DU, which was modified so as to suit the special purpose of this investigation. The two quartz cells (1 or 5 cm long) were placed in a brass block fitted with resistance wire for electrical heating and with a thermoelement. It was found possible to adjust the temperature to the desired value, simply by regulating the heating current by hand. In this way the temperature could be kept constant within $\pm 0.5°$ C. The brass block was mounted on the displaceable table in the original cell compartment of the spectrophotometer.

Because of the thermal expansion of the liquid the cells, which were closed by a grounded stopper, could not be completely filled. Care was taken to keep the air bulb out of the light path.

For the first measurements the original photo-electrical outfit of the spectrophotometer was used. However, gradually it became clear that we could not get the accuracy which was desirable for these special measurements. Therefore the photocell was replaced by a photomultiplier cell (*R.C.A., IP28*). Instead of the Beckman amplifier we used a single electrometer tube in a selfcompensating circuit. This made it possible to diminish the working resistance to 0.5 meg ohm and thereby to remove the extremely high demands on the insulation. A pile of anode batteries was used as the power supply for the photomultiplier cell, and the compensating voltage was taken from the potentiometers in the Beckman apparatus.

Because of its glass envelope the photomultiplier could not directly be used further out in the ultraviolet than to about 36000 cm^{-1} (ca. 2800 Å). Therefore, a thin layer of highly purified anthracene—molten and then by cooling crystallized in between a plane quartz plate and a plano-convex glass lens—was placed close to the window of the photomultiplier. In this manner the ultraviolet light by way of absorption and subsequent fluorescence was transformed into light of a wavelength almost exactly corresponding to the sensitivity maximum of the cell. The inevitable high loss in light energy (about 90 %) by this arrangement was to a great extend counterballanced by the higher sensitivity of the photomultiplier cell to the fluorescence light from the anthracene. Moreover, by this arrangement we achieved an almost constant sensitivity throughout the whole ultraviolet region. The short-wave limit for our measurements were now determined by the Beckman hydrogen lamp, whose intensity drops rapidly off beyond 2500 Å owing to its glass envelope. Nevertheless we were able to extend the range for the spectrophotometer with about 2000 cm^{-1} further out in the ultraviolet region, and at the same time to increase the accuracy of the intensity measurements considerably.

It is our experience from the present work that the measuring accuracy must be further improved in order to allow an investigation of the finer details of the temperature effect. For our continued work we are therefore building a new spectrophotometer constructed especially for this purpose.

As solvent we have almost exclusively used ethanol because of its well known broadening-out effect on the vibrational structure. The 96 % ethanol was distilled in an all-glass apparatus, chiefly in order to remove suspended dust particles. The spectroscopic purity was sufficient.

The substances investigated were carefully purified by repeated recristallization, fractionated distillation or sublimation. The anthracene was purified according to the method given by DERMER and KING[1].

For each substance the most concentrated solution measured was almost saturated or, if solvent and substance were miscible, about 10 %. The solution was then diluted 10 times and this procedure repeated as often as was necessary to cover the whole extinction range.

The extinctions were measured at 25° and 70°; the higher temperature was chosen in order to avoid any boiling of the ethanol. For each concentration measurements were made first at 25° for a number of frequencies at suitable intervals and then at 70° for the same frequencies. The results obtained were corrected for differencies in the absorption of the quartz cells and then converted into molar extinction coefficients. For the higher temperature a correction for thermal expansion was performed.

Diagrams of the results obtained are given in the following.

[1] DERMER and KING, J. Amer. Chem. Soc. **63**, 3232 (1941).

In all the graphs $\log \varepsilon$ (at 25° C) and $\Delta \log \varepsilon$ (for 25° and 70° C) are plotted versus frequency (in cm^{-1}).

The following substances have been investigated: benzene, naphthalene, anthracene, fluorobenzene, chlorobenzene, diphenyl, 1,4-diphenylbutadien, cycloöctatetraene and acetone. These were chosen in order to represent the most different kinds of spectra.

IV. DISCUSSION

For the 9 substances investigated we have found in all 13 electronic lines. These 13 absorption systems will be treated separately and denoted as naphthalene I, anthracene II etc. as indicated in the Figures.

As an introduction to the discussion it might be helpfull to give the following survey of the classification of these band systems. This is a result of the investigation, and we are thus anticipating the following discussion.

Group A, characterized by a small σ (ca. 100—200 cm^{-1}) and a strong (allowed) electronic line:
naphthalene I, anthracene I, fluorobenzene I and chlorobenzene I.

Group B, characterized by a small σ (ca. 100—200 cm^{-1}) and a weak (forbidden) electronic line:
benzene I.

Group C, characterized by a great σ (> 300 cm^{-1}) and a strong (allowed) electronic line:
naphthalene II and III, anthracene II and diphenylbutadiene I.

Group D, characterized by a great σ (> 300 cm^{-1}) and a weak (forbidden) electronic line:
diphenyl I, acetone I and cycloöctatetraene I.

It will be seen that the groups *A* and *B* comprise substances whose corresponding spectra in the gaseous state show fine structure[1]. This means that the broadening of the lines in these

[1] Anthracene I seems to be an exception. It might be mentioned that PRINGSHEIM (Ann. Acad. sci. tech., Varsovie V, 29 (1938)) has reported fine structure in the corresponding fluorescence spectrum.

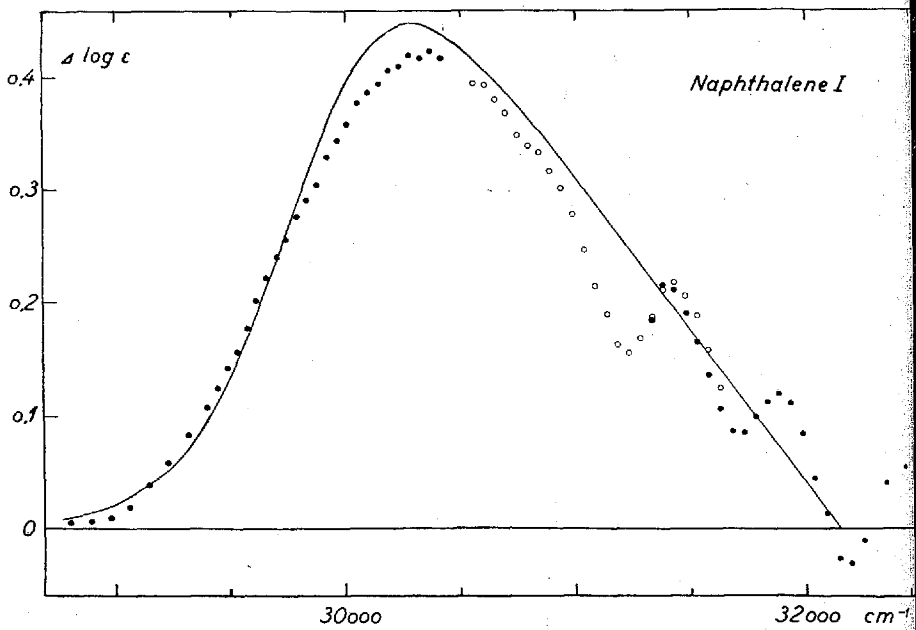

Fig. 11. Δ log ε for naphthalene I. The different signatures for the observed points indicate three different series of measurements. The theoretical curve is calculated from (16) for $\log(c_aK_a/c_bK_b) = 4.5$.

cases must be due to perturbations caused by the molecules of the solvent. We should therefore expect a pronounced dependence for σ on the nature of the solvent as well as a considerable increase at rising temperatures. For these substances one can, in praxis, content oneself with a comparison of the observed Δ log ε curve with the simple theoretical curves shown in Fig. 4.

The distinction between the two groups arises from the fact that in group *A* the electronic line is prominent, thus giving rise to a corresponding negative effect in the Δ log ε curve. In fact, the maximum of this negative effect seems to give the best determination of the location of the electronic line. In group *B* (where the electronic line is weak) neighbouring bands will generally cause a positive temperature effect at the position of the electronic line, and thus confuse the picture.

Group *C* and *D* comprise absorption systems showing no vibrational structure even in the gaseous state. In these cases σ must therefore be considered as composed of two parts, one of

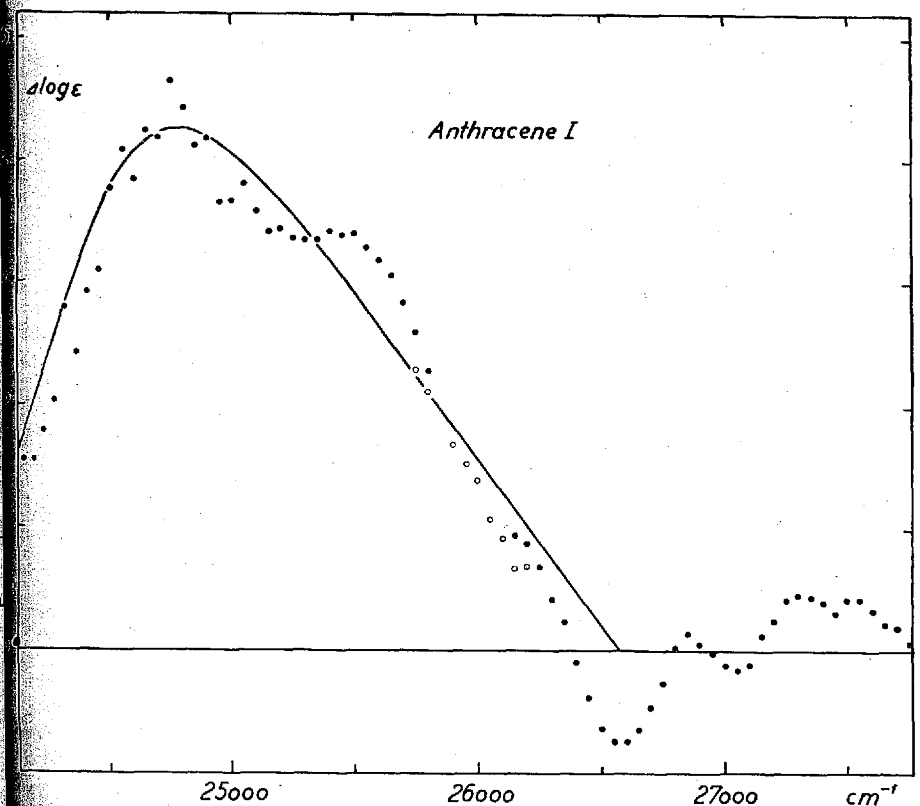

Fig. 12. Δ log ε for anthracene I. The different signatures for the observed points indicate three different series of measurements. The theoretical curve is calculated from (16) for $\log(c_aK_a/c_bK_b) = 4.3$.

which must correspond to σ in the groups *A* and *B*, whereas the other part will be independent of the nature of the solvent and of the temperature. For these substances we are compelled to use the theoretical expressions which make allowance for the diffuse electronic levels.

The distinction between group *C* and *D* is qualitatively the same as that between *A* and *B*.

Group A.

Figs. 11, 12, 13 and 14 show our experimental results for Δ log ε for naphthalene I, anthracene I, fluorobenzene I and chlorobenzene I. The theoretical curves are calculated from

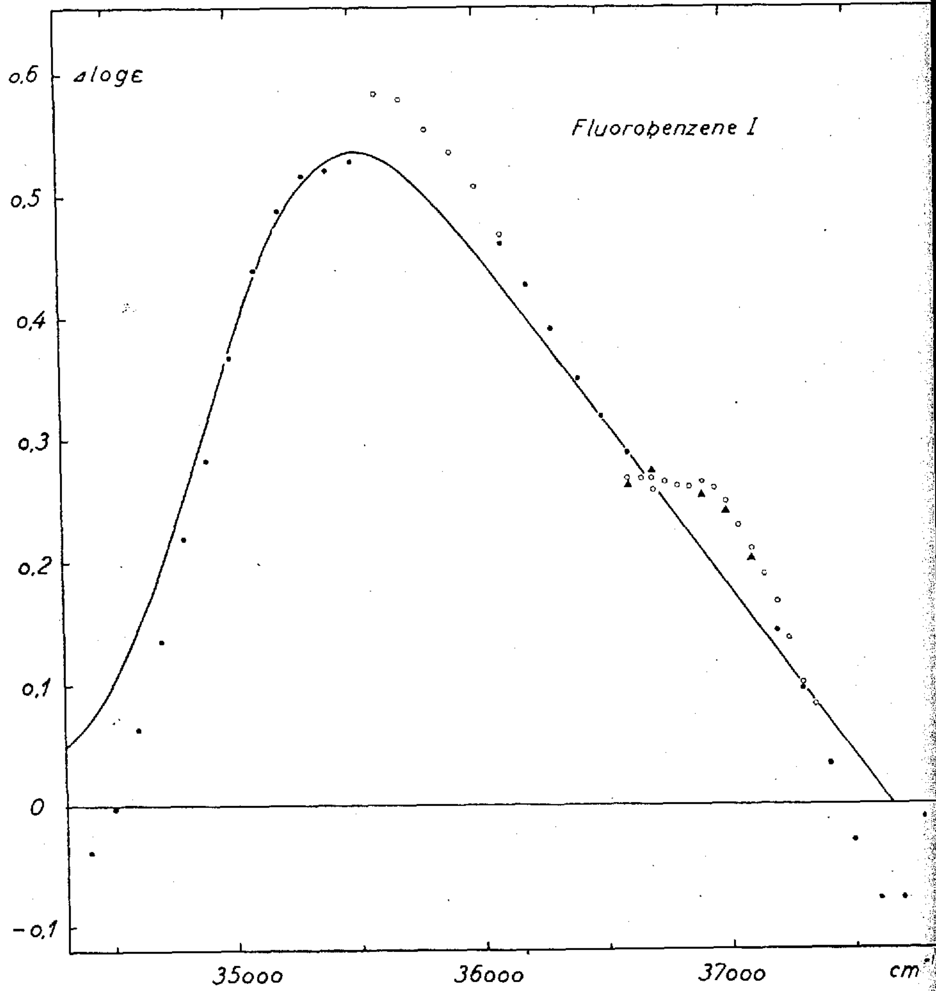

Fig. 13. $\Delta \log \varepsilon$ for fluorobenzene I. The different signatures for the observed points indicate six different series of measurements. The theoretical curve is calculated from (16) for $\log(c_a K_a/c_b K_b) = 5.2$.

the simple expression (16). The values of the parameters are stated under each figure.

The agreement between experimental and theoretical curves may all in all be regarded as satisfactory. Most of the deviations can be fully explained by the effect of the prominent bands of the vibrational structure (cp. pag. 24). From Fig. 15 (pag. 34) and 16 (pag. 35) as well as from Fig. 21 (pag. 42) and 22 (pag. 43)

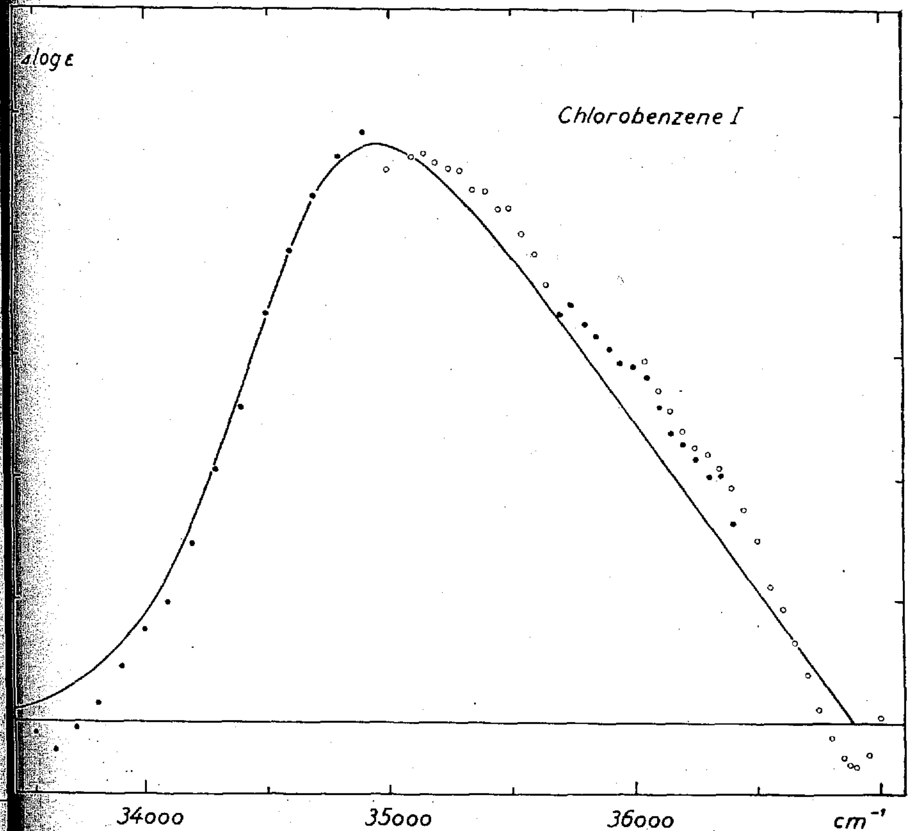

Fig. 14. $\Delta \log \varepsilon$ for chlorobenzene I. The different signatures for the observed points indicate four different series of measurements. The theoretical curve is calculated from (16) for $\log(c_a K_a/c_b K_b) = 4.7$.

it is seen that a maximum in the extinction curve always gives rise to an additional negative effect in $\Delta \log \varepsilon$, and a minimum in extinction to an additional positive effect in $\Delta \log \varepsilon$, as should be expected according to the theory.

As mentioned in the theoretical part (pag. 22) it is possible to estimate the values of σ_1 and σ_2 by comparing these prominent bands with the parabola calculated from equation (51). However, this method is inclined to give values which are too big. We find σ from ca. 120 to ca. 200 cm^{-1}, σ_2 always being a little greater than σ_1. Theoretically it should be possible from these values to calculate the α- and β-corrections (33) and (41). We

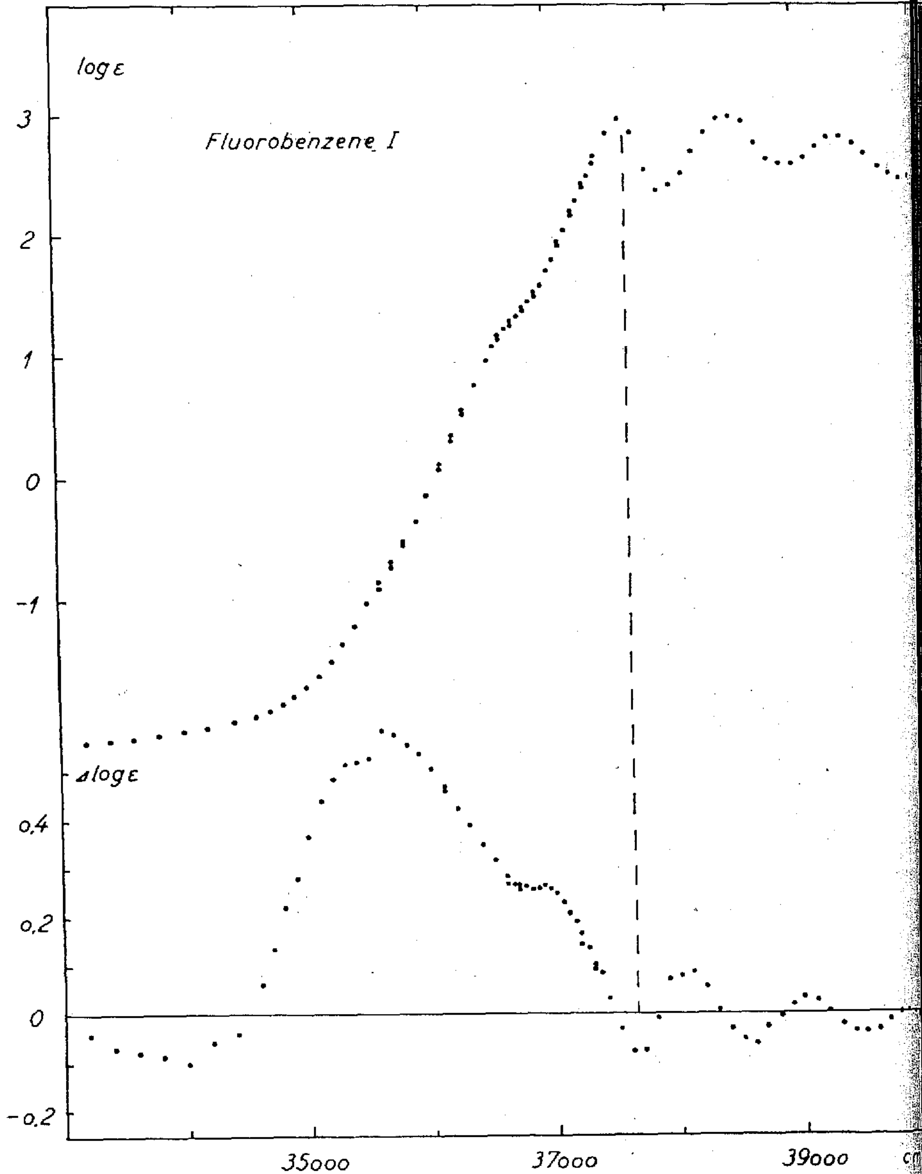

Fig. 15. log ε (25° C) and Δ log ε for fluorobenzene.

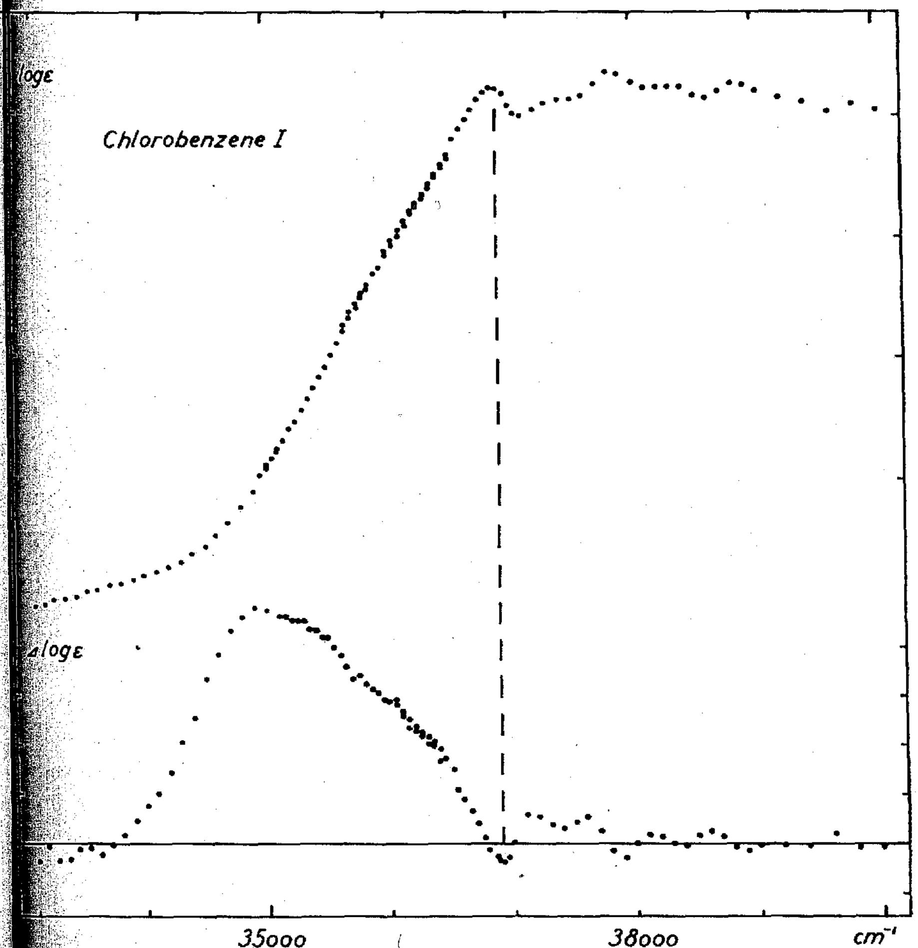

Fig. 16. log ε (25° C) and Δ log ε for chlorobenzene.

find the values of σ_1 and σ_2 estimated from our experimental extinction curves to be too uncertain even to allow us to settle if θ is bigger or smaller than 1, which is decisive for the sign of α. Nor the expression (54) for the maximal negative effect can be used to determine θ because the effect very seldom exceeds the absolute minimum value: 0.061 logarithmic units, which means that the conditions allowing (54) to be applied are not fulfilled. It seems to be fairly certain that the numerical value of α for group A never exceeds $200\ cm^{-1}$. This explains the good agreement with the simple curves.

It must be emphasized that the presence of a week, but constant back-ground absorption is a condition for the applicability of equation (16). This condition seems generally to be fulfilled, presumedly because traces of impurities will be present even in the most carefully purified substances. From our extinction curves we estimate the concentration—so far absorptive power is concerned—of impurities to be 10^{-4} to 10^{-5} times that of the main substance. In praxis any organic substance will contain minute traces of a very great number of different organic compounds whose absorption may be expected to add up to a quasi-continuous back-ground absorption. We should not expect any significant temperature effect due to the electronic lines of the different contaminating compounds, because these presumedly will be present in concentrations of the same order of magnitude (cp. Fig. 4, curve 0).

Yet, in some cases we have observed a marked negative temperature effect in the back-ground absorption. In this group it is found for fluorobenzene I. From Fig. 15 it is seen that the $\Delta \log \varepsilon$ curve to the left of the proper temperature effect descends below the zero line. This effect can not be explained on the basis of the theory developed in this paper, but as it seems to play no important role for the proper temperature effect we have not as yet investigated it any further, and we shall therefore here desist from any attempt to explain it.

It will be seen from Fig. 4 that the parameter $\log (c_a K_a / c_b K_b)$ is of no importance for locating the electronic line. The values used are therefore simply adapted to fit the experimental points as closely as possible. For an eventual estimation of $\log (c_a K_a / c_b K_b)$ from the $\log \varepsilon$ curve, see pag. 39.

Group B.

The only representative for this group, amongst the substances investigated in this paper, is **benzene I** shown in Fig. 17.

The only important difference between this absorption system and those dealt with in group A is the forbidden electronic line, which in the spectrum of the vapour must be placed at $38090\ cm^{-1}$

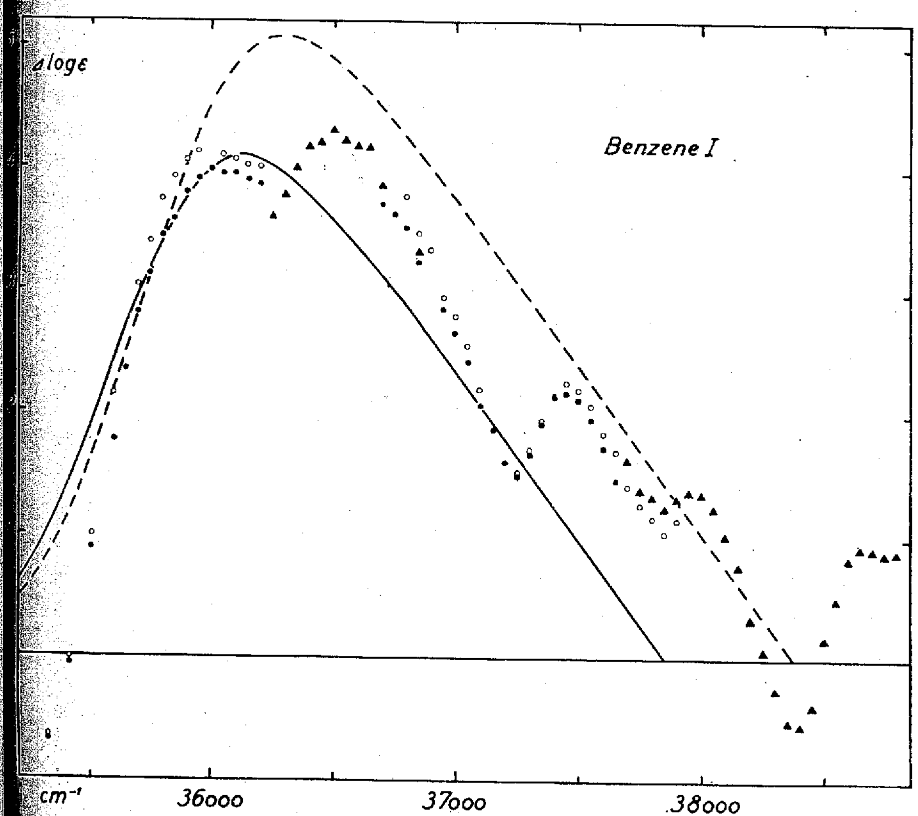

Fig. 17. $\Delta \log \varepsilon$ for benzene I. The different signatures for the observed points indicate six series of measurements. For theoretical curves see text.

corresponding to $37850\ cm^{-1}$ in ethanolic solution. The solid curve in Fig. 17 is drawn from this frequency. According to the theory the near-by prominent bands should give rise to a positive temperature effect at the place of the electronic line, whereas the negative effect arising from this line itself, which appears only as a consequence of the violation of the selection rules, must be expected to be small. The net effect should therefore be a positive one as observed (cp. Fig. 27, pag. 49).

It must be admitted that without any premature knowledge of the location of the electronic line, one might from the observed $\Delta \log \varepsilon$ curve perhaps be inclined to place ν_0 at ca. $38050\ cm^{-1}$, and hence be $200\ cm^{-1}$ in error. This indicates the magnitude of the error to be expected for substances belonging to this group. The most serious mistake would be to assign the strong band at 38380 cm^{-1} as the electronic line and on this basis adapt a theoretical curve as the one shown dotted in Fig. 17. However, if the known effect of the prominent bands is taken into account, as discussed above, this assignment seems to be rather unreasonable.

Group C.

For all absorption systems belonging to group C and D the simple equation (16) is no longer valid, but the broadening of the electronic line must be taken into account, as it is done in equation (38). Further, as already mentioned, we expect σ to be to a lesser degree dependent on the temperature than it is in the groups A and B. We should therefore expect to find $\Delta \log \varepsilon$ curves more like those given in Fig. 6 than like those in Fig. 7. As it seems impossible beforehand to tell what might be the exact temperature dependence of σ in a definite case we therefore have to deal with two more parameters σ_1 and σ_2 in establishing the theoretical curve. Obviously, we are therefore compelled to make use of the $\log \varepsilon$ curve as far as possible.

We might, as already discussed, try a comparison with the theoretical parabolas (51) in order to estimate the values of σ_1 and σ_2. However, the back-ground which is not taken into account in (51) is likely to make the result rather uncertain. A better method would be to calculate the electronic line plus back-ground according to equation (60) for different values of σ, $c_a K_a / c_0 K_0$ and $c_a L / c_0 K_0$. This would be a very tedious job, which we have not found it worth while doing on the basis of our present experimental results.

It is apparent from our experimental results as well as from theoretical curves computed from (60) and (61) that the maximum in the extinction curve corresponding to the electronic band is shifted considerably in frequency at rising temperature. Therefore this maximum can not be used for a closer localization of the electronic line. Far better is it to use the corresponding negative effect in the $\Delta \log \varepsilon$ curve, as it appears from Fig. 18. Here the experimental measurements for naphthalene II are compared with theoretical $\Delta \log \varepsilon$ curves calculated from (61) for different values of the parameters (as stated in the text under Fig. 18). It is seen that the minimum of the $\Delta \log \varepsilon$ curve with high precision corresponds to the location of the electronic line (marked by an arrow). It is better therefore to use this minimum for the exact localization of the electronic line in all absorption systems to be classified in group A or C (as well as some belonging

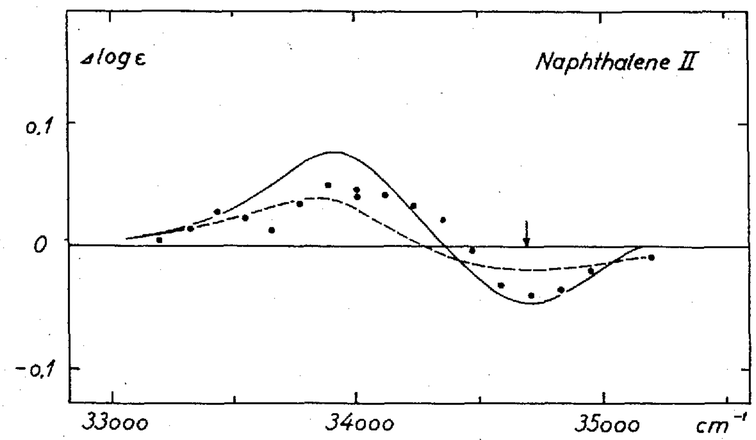

Fig. 18. $\Delta \log \varepsilon$ for naphthalene II. The theoretical curves are calculated from (61): ——— for $\sigma_1 = \sigma_2 = 300$ cm^{-1}; ---- for $\sigma_1 = 300$ cm^{-1} and $\sigma_2 = 325$ cm^{-1}.

to group B) instead of using the maximum in the extinction curve measured at a casual temperature.

The extinction curve may furthermore allow an estimate of $\log (c_a K_a / c_b K_b)$ in the following way. If one assumes the frequencies of the vibrations to be approximately the same for the ground state as for the exited state, it follows that the transition probability will vary approximately symmetrically with respect to the electronic line. We may now first extrapolate to the $\log \varepsilon$ for the impurities at the low-frequency side of the maximum in $\Delta \log \varepsilon$ (where we have the highest sensitivity to $\log (c_a K_a / c_b K_b)$), and then read the value of $\log \varepsilon$ for the substance itself at a frequency symmetric to the first with respect to the electronic frequency. The difference between these two $\log \varepsilon$ gives an approximate value for $\log (c_a K_a / c_b K_b)$.

If the low-frequency part of the experimental $\Delta \log \varepsilon$ curve is compared with the curves shown in Fig. 4 it should now be possible to estimate the values of the corrections α (33) and β (41)

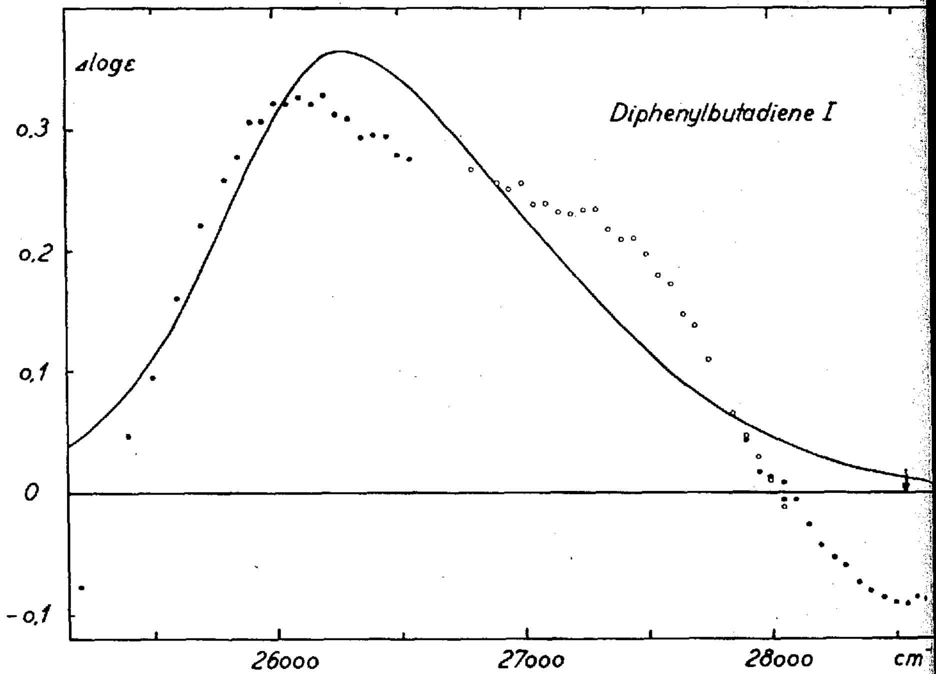

Fig. 19. $\Delta \log \varepsilon$ for diphenylbutadiene I. The different signatures for the observed points indicate three series of measurements. The theoretical curve is calculated from (38) for $\sigma_1 = \sigma_2 = 400 \text{ cm}^{-1}$ and $\log (cK/c_0K_0) = 4.5$.

assuming that the curve has attained to the asymptotical values discussed in the theoretical part (pag. 16). From α and β it is then possible to calculate σ_1 and σ_2 according to (33) and (41). We have found this method to give more probable results than those obtained by the direct comparison, as was discussed above.

If we solve the equations (33) and (41) with respect to σ_1 and σ_2 we get (by inserting numerical values):

$$\left.\begin{aligned} \sigma_1 &= 37.72\sqrt{138.9\,\beta - 0.2912\,\alpha} \\ \text{and} \quad \sigma_2 &= 37.72\sqrt{184.0\,\beta - 0.3351\,\alpha} \end{aligned}\right\} \quad (62)$$

As we furthermore claim that $\sigma_1 \leqq \sigma_2$, it follows that

$$\alpha \leqq 1026\,\beta \quad (63)$$

Fig. 19 illustrates how this method can be used in the case of diphenylbutadiene I. From the minimum in $\Delta \log \varepsilon$ we

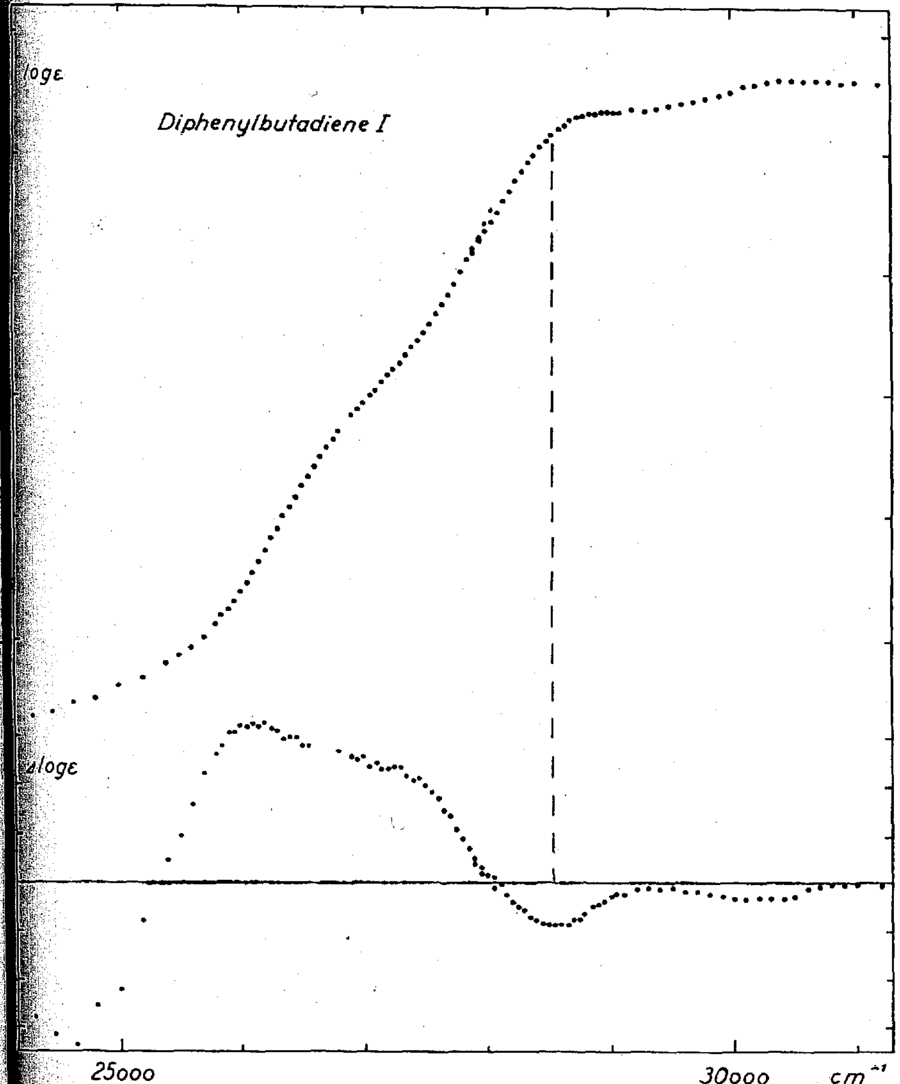

Fig. 20. $\log \varepsilon$ (25° C) and $\Delta \log \varepsilon$ for diphenylbutadiene.

immediately find $\nu_0 = 28550 \text{ cm}^{-1}$. This gives us $\alpha \simeq -700 \text{ cm}^{-1}$. Further, we estimate $\beta \simeq -1$ by comparing with Fig. 4 using $\log(c_aK_a/c_bK_b)$ determined from Fig. 20. From (63) it follows that $\alpha = -700 \text{ cm}^{-1}$ and $\beta = -1$ can not be fulfilled simultaneously. We get the best approximation using $\sigma_1 = \sigma_2 = 400 \text{ cm}^{-1}$, which

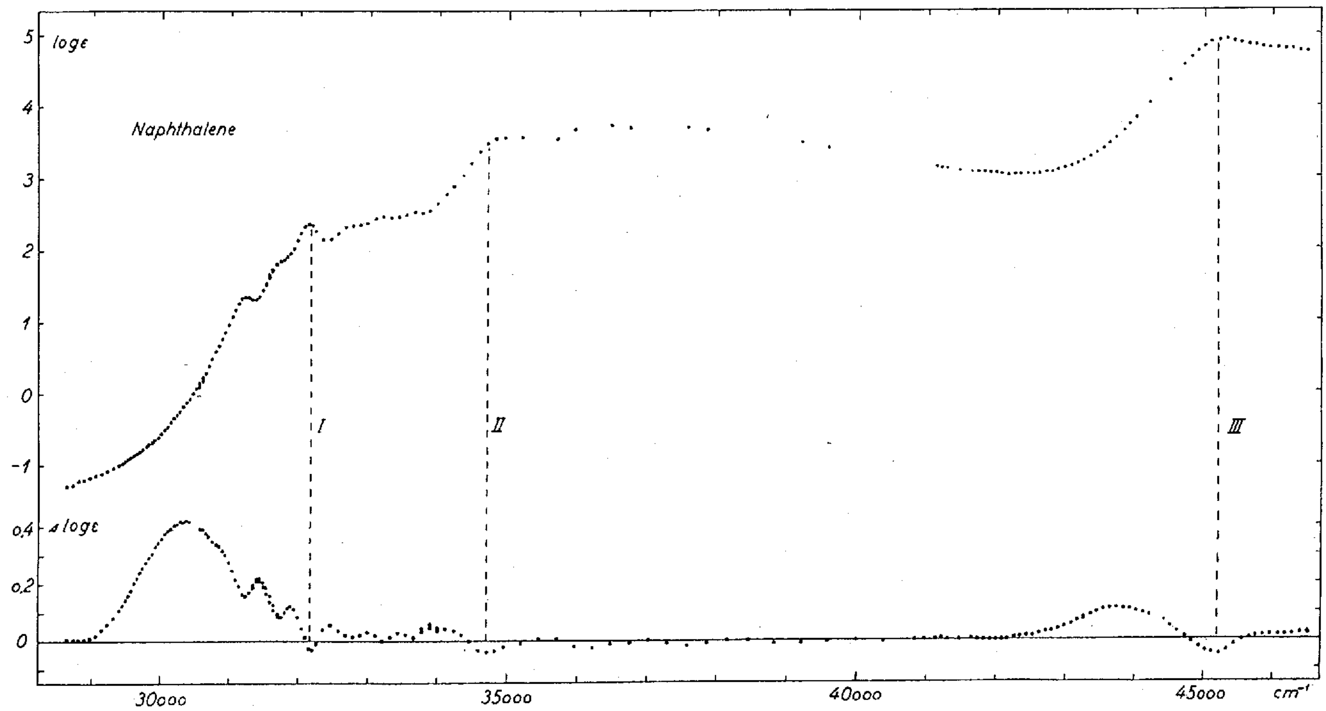

Fig. 21. log ε (25° C) and Δ log ε for naphthalene.

Nr. 3

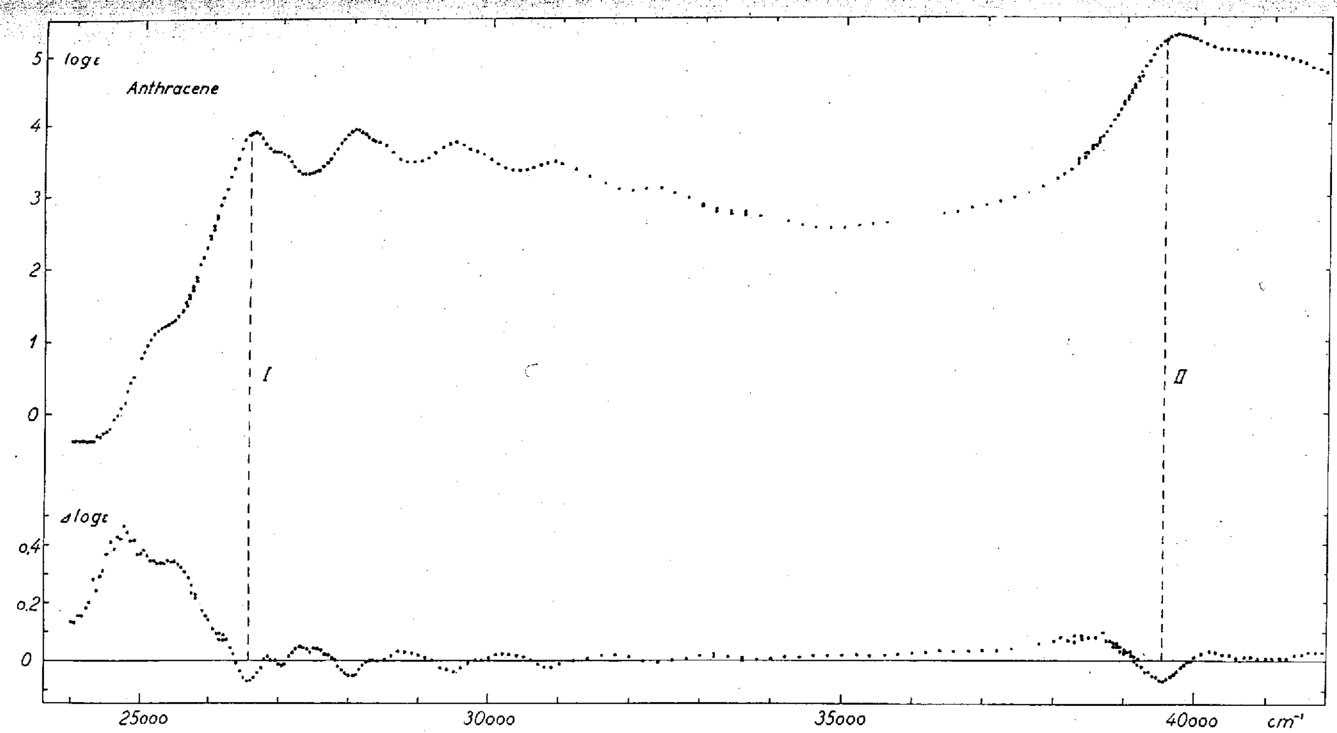

Fig. 22. log ε (25° C) and Δ log ε for anthracene.

gives the curve shown in Fig. 19. The deviations between the experimental and the theoretical curves can be explained as effects due to the presence of prominent bands. This effect seems only to be a little more pronounced than normally because of the greater value of σ. For physical reasons σ_2 should be expected to be somewhat bigger than σ_1. Undoubtedly it would be possible by trial and error to approximate to values for σ_1 and σ_2 which satisfy this condition and at the same time give a closer agreement between theory and experiment.

The last two examples in this group: naphthalene III and anthracene II, are found in Fig. 21 and 22. The electronic lines have been located from the minima found in the $\Delta \log \varepsilon$ curves, and σ was estimated from the $\log \varepsilon$ curves. The numerical values are given in the Table III (pag. 52).

Group D.

This group encompasses absorption systems which show practically no traces of vibrational structure as can be seen from the extinction curves given in Fig. 24, 25 and 26. The theoretical treatment is therefore difficult. The absence of narrow bands excludes an estimation of σ by means of a comparison with the theoretical parabolas. Further, the electronic lines do not give rise to any negative effect in the $\Delta \log \varepsilon$ curves. This fact, together with the comparatively low values observed for the extinction, has induced us to classify these absorption systems as forbidden electronic transitions.

For the determination of the parameters of this group we are therefore compelled to make the outmost possible use of the $\log \varepsilon$ curve. We have for this purpose calculated some theoretical $\log \varepsilon$ curves, shown in Fig. 23, by plotting $\log G$ versus $\nu_0 - \nu$. This gives us the theoretical shape of the extinction curves so far as the transition probability can be considered as constant. Although this condition obviously is not fulfilled, we have still found a comparison of the observed curves with these theoretical curves to give a valuable help to a first estimation of the parameters.

In the case of diphenyl I, Fig. 24, we are lucky enough to find that the $\Delta \log \varepsilon$ curve attains to its asymptotic values a little

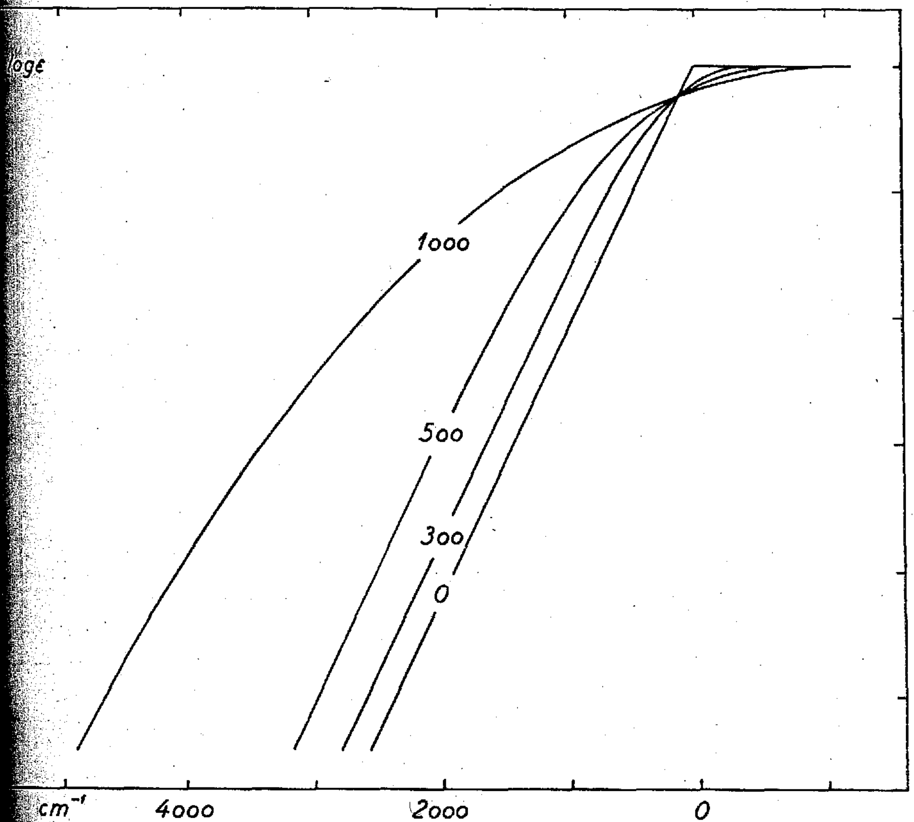

Fig. 23. Theoretical curves for $\log \varepsilon = \log G$ calculated for $T = 298° K$ and for different values of σ as indicated. The ordinate is given in logarithmic units.

before the maximum and from there follows the shape of the simple curves (Fig. 4). This gives us a fairly good estimate of β to be about -2. From this value it follows that $\alpha \leqq -2000\ \mathrm{cm}^{-1}$. Assuming $\alpha = -2000\ \mathrm{cm}^{-1}$ we calculate $\sigma_1 = \sigma_2 = 670\ \mathrm{cm}^{-1}$. If we take the shape of the $\log \varepsilon$ curve into consideration, and if we furthermore assume σ_2 to be a little greater than σ_1, we can improve the adaptation of the theoretical curve to the experimental one. In this way we have found $\nu_0 = 36000\ \mathrm{cm}^{-1}$, $\sigma_1 = 650\ \mathrm{cm}^{-1}$ and $\sigma_2 = 700\ \mathrm{cm}^{-1}$ to be reasonable values. This approximation may then be taken as starting point for further and more detailed calculations. We will, however, await more accurate measurements before we pursue these considerations any further. One

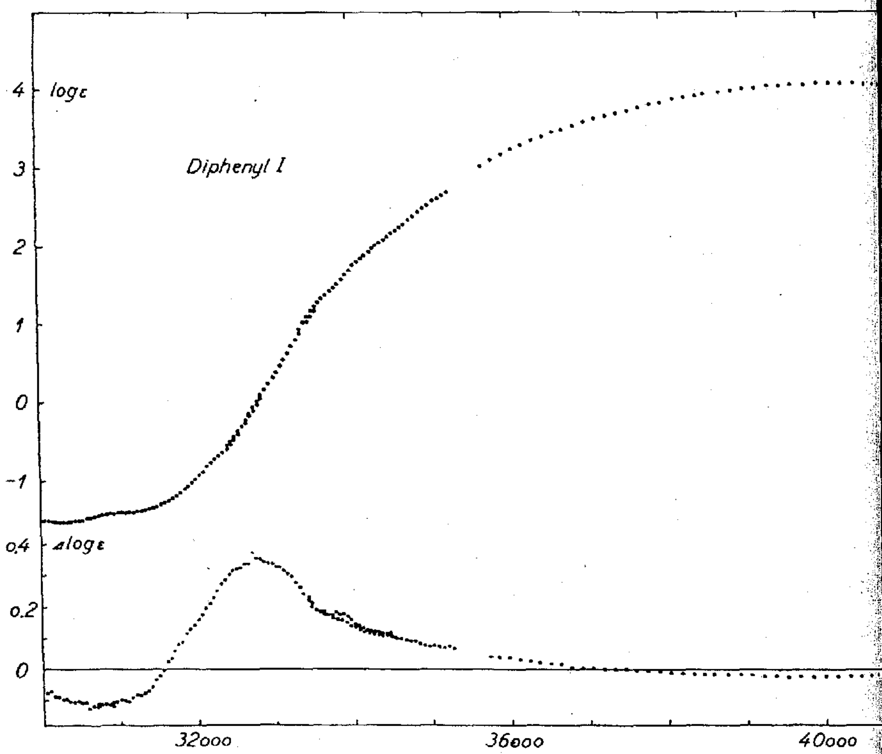

Fig. 24. log ε (25° C) and Δ log ε for diphenyl.

thing may though be established with certainty: the electronic line for diphenyl I must be located at a considerable lower frequency than that corresponding to its maximum of absorption.

For **acetone I** (Fig. 25) and for **cycloöctatetraene I** (Fig. 26) the theoretical treatment of our measurements is even more difficult. In neither case the observed $\Delta \log \varepsilon$ curves attain to the asymptotic values. The complete absence of structure in the absorption spectrum indicates large values for σ. Considering the shape of the observed curves it seems likely that acetone I has a σ value of about 1000 cm^{-1} and that its electronic line is to be found at ca. 33000 cm^{-1}. For cycloöctatetraene I σ seems to be still higher, probably about 2000 cm^{-1}, and its electronic line must then be placed somewhere around 27000 to 28000 cm^{-1}.

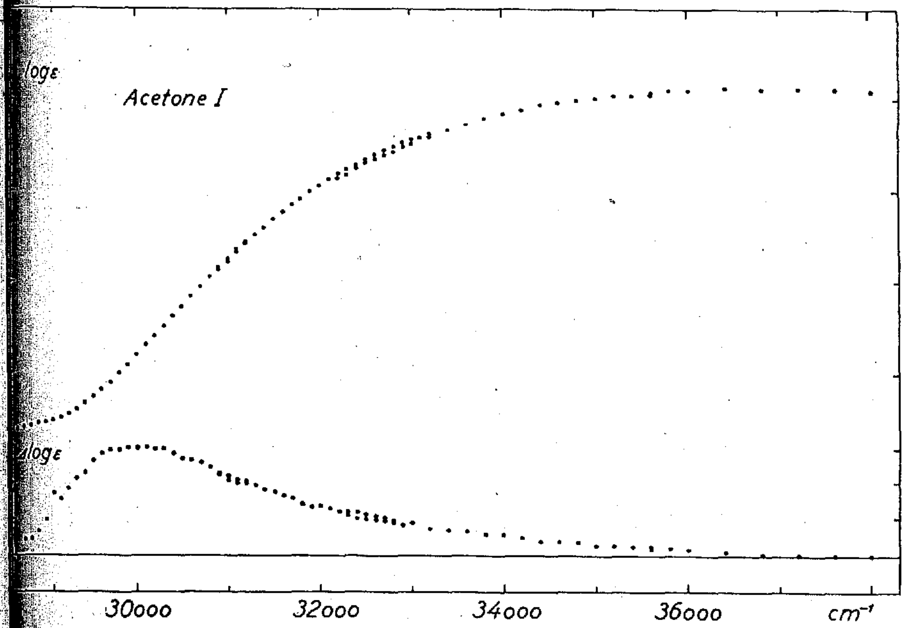

Fig. 25. log ε (25° C) and Δ log ε for acetone.

Finally, for **benzene II** (Fig. 27) our experimental results are not sufficient to allow us to decide if this system belongs to group C or D. If we tentatively assume $\nu_0 = 48000$ cm^{-1} on the basis of the extinction curve, we get by the method used in group C $\alpha = -900$ cm^{-1}, $\beta = 0.3$, $\sigma_1 = 660$ cm^{-1} and $\sigma_2 = 710$ cm^{-1} in good agreement with the shape of both of the curves.

From quantum-theoretical considerations it has been shown that benzene II most likely is due to the forbidden $A_{1g} \rightarrow B_{1u}$ transition[1]. It should therefore—in spite of its comparatively high intensity—belong to group D, in which case the electronic line is to be located at a somewhat lower frequency than 48000 cm^{-1}. We must await more experimental material before we can discuss benzene II any further.

[1] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938); G. Nordheim, H. Sponer and E. Teller, ibid. 8, 455 (1940).

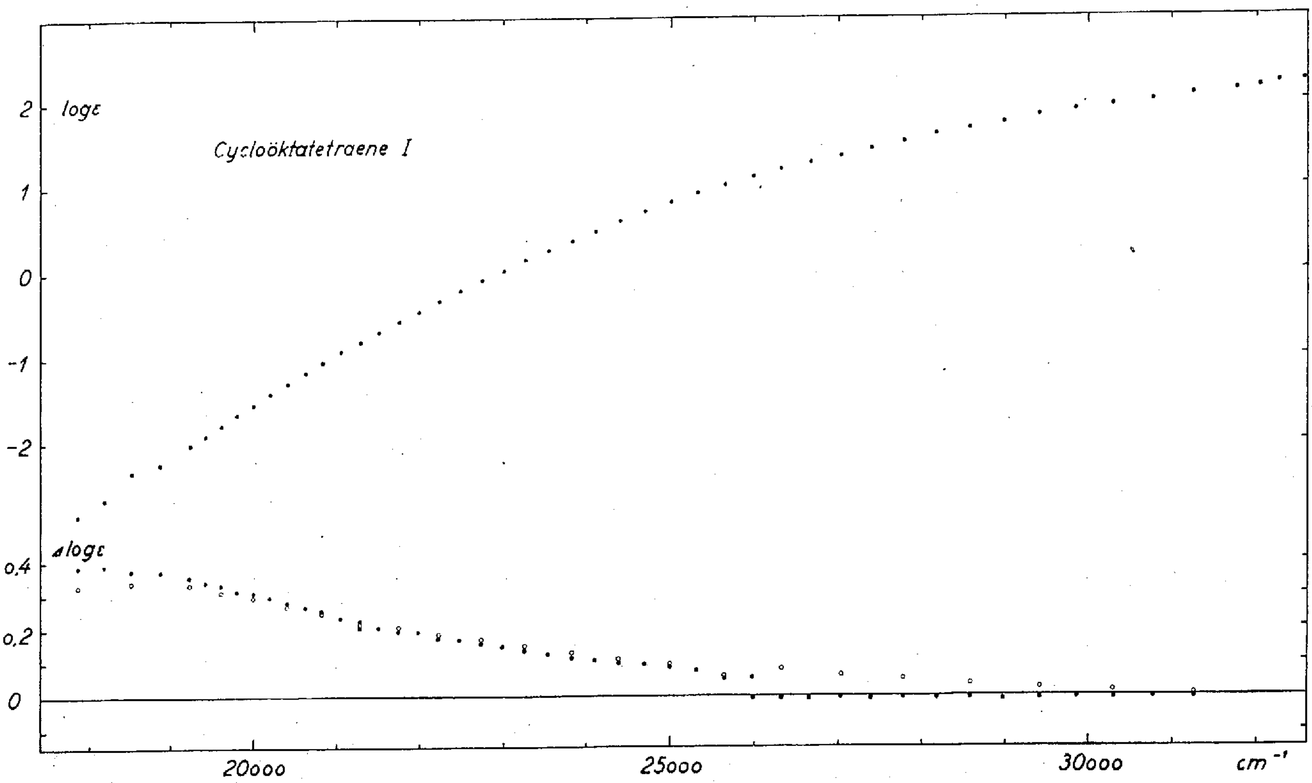

Fig. 26. log ε (25° C) and Δ log ε for cycloöctatetraene dissolved in decaline. Because of the instability of cycloöctatetraene the measurements at 25° C were repeated after those at the high temperature. The corresponding Δ log ε are indicated by open circles.

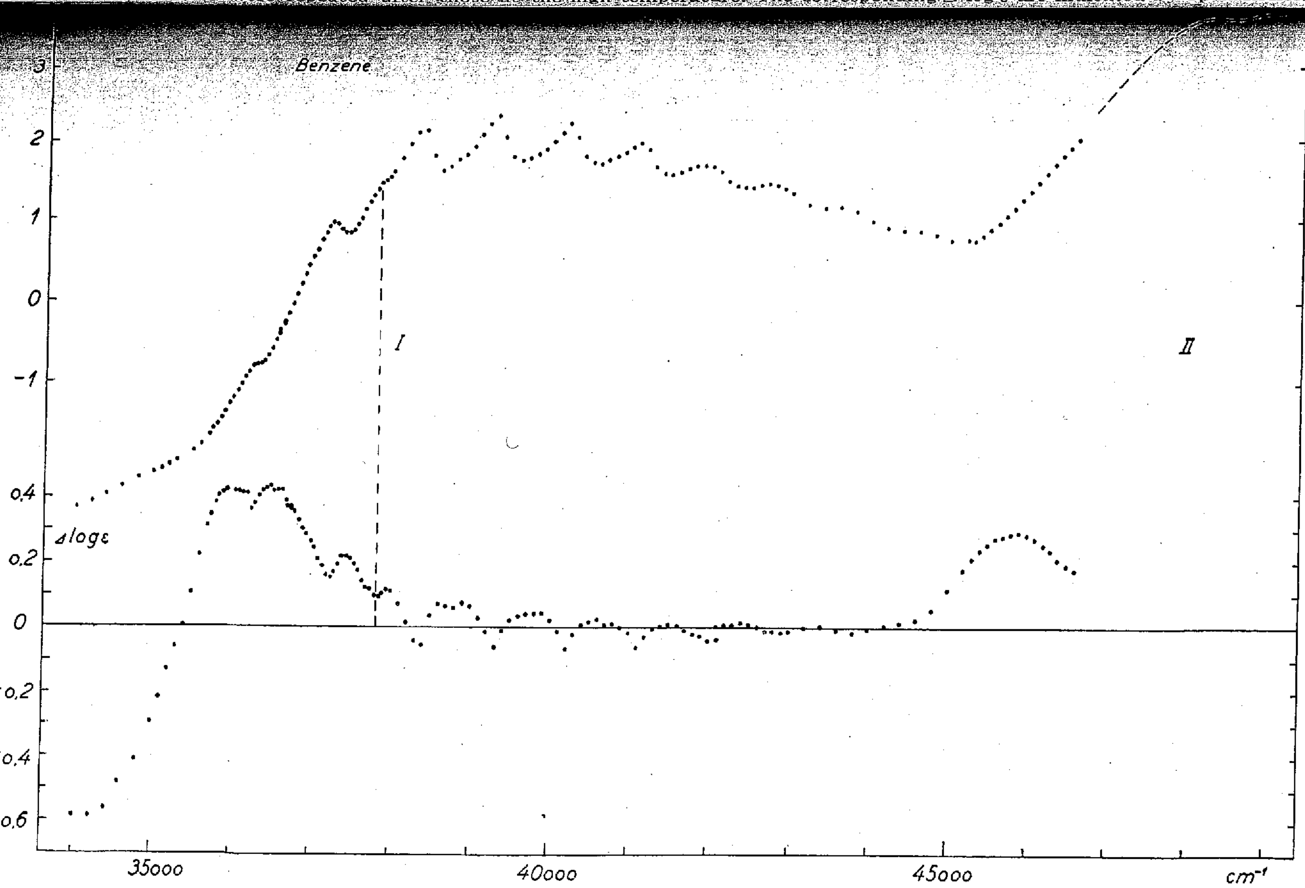

Fig. 27. log ε (25° C) and Δ log ε for benzene. The dotted part of the log ε curve (for n-heptane solution) is taken from Nat. Bur. of Standards Catalog of Ultraviolet Spectrograms. No. 172. Department of Physics, University of Chicago.

V. RESULTS

We may summarize the results obtained in this investigation by giving a survey of the procedure to be followed in order to localize the electronic line of an absorption spectrum. Often this can not be accomplished in a straight-forward manner, but rather as a result of successive approximations.

First the observed absorption system should be assigned to one of the four groups, *A*, *B*, *C* or *D* on the basis of the following characteristics:—

a) *Groups A and B*. The value of σ is 100—200 cm^{-1}, strongly increasing at rising temperatures. The spectra of the vapour show vibrational fine structure. The simple theoretical curves (Fig. 4) may be applied.
b) *Groups C and D*. The value of σ is greater than 300 cm^{-1}, slightly increasing at rising temperatures. The spectra of the vapour have no vibrational fine structure. Theoretical curves calculated from equation (38) are to be used.
c) *Groups A and C*. The electronic line asserts itself strongly in the extinction curve and gives rise to negative values for $\Delta \log \varepsilon$. The minimum of the $\Delta \log \varepsilon$ curve appears at the frequency of the electronic line.
d) *Groups B and D*. The electronic line is not—or only faintly—to be seen in the $\log \varepsilon$ as well as in the $\Delta \log \varepsilon$ curve. For these groups a close localization of the electronic line is difficult.

In order to obtain a reliable value for ν_0 a theoretical $\Delta \log \varepsilon$ curve should be calculated so as to fit the experimental curve as closely as possible. For this purpose the parameters σ_1, σ_2, α, β, and $\log (c_a K_a / c_b K_b)$ must be determined. This may be done in the following ways:—

1) ν_0: from the minimum in the $\Delta \log \varepsilon$ curve.
2) σ_1 and σ_2: by comparison of prominent, narrow bands with the theoretical parabolas (51), or in case of the electronic line itself, with curves calculated from (60).
3) σ_1, σ_2 and ν_0: by comparison of the $\log \varepsilon$ curve with the theoretical curves (Fig. 23).

4) $\log (c_a K_a / c_b K_b)$: directly from the experimental $\log \varepsilon$ curve.
5) β: by comparison of the asymptotic part of the $\Delta \log \varepsilon$ curve with the theoretical curves given in Fig. 4, provided that $\log (c_a K_a / c_b K_b)$ is known.
6) α: in the same way as β, provided that ν_0 is known.

Method 1) is very useful for the groups *A* and *C*, and with circumspection for group *B*. 2) can usually be applied for the groups *A*, *B* and *C*. 3) is usually bad, but is always helpful for approximate estimations. Similarly, method 4) can always be used for approximate estimations. Method 5) is of interest only for the groups *C* and *D*. It can only be applied if the observed $\Delta \log \varepsilon$ curve attains to the asymptotic values, i. e. if $\log (c_a K_a / c_b K_b)$ is large, and σ has a rather small value. Also 6) is only of interest for group *C* and *D*. For group *C* ν_0 is known from 1), but for group *D* a guess has to be made, and then by successive approximations a theoretical curve should tentatively be adapted to the observed one.

The equations (33), (41) and (62) give correlations between σ_1, σ_2, α, and β. Further, expression (63) gives a restriction for the value of α in relation to β.

Usually, by following the above procedure, a likely frequency for the electronic line can soon be obtained. However, in order to prove the correctness of this value, it is necessary to determine a set of parameters which allow the calculation of a theoretical curve showing a reasonable agreement with the observed one.

It will be apparent from the above discussion that the ease with which an electronic line may be localized on the basis of the observed temperature effect is highly dependent on the nature of the spectrum. For systems belonging to group *A* and *C* a good accuracy may be achieved. This should also be possible for group *B*, but here the risk for a confusion with group *A* exists. Group *D* is the most difficult to treat, but even if the inherent uncertainty of the estimation is taken into consideration, the obtained value is still a far better approximation to the electronic line than that constituted by the frequency of the absorption maximum, which is generally taken to represent the "frequency" of the absorption system. Finally, in case there are different electronic transitions for the same substance the method fails completely if the "remaining" intensity of a pre-ceding system is equal to, or even greater than, the intensity o the system whose electronic line is to be localized.

Further it might be mentioned that in addition to the locatio of the electronic line the method gives valuable information abou the nature of the absorption system as well as about the num erical values of the σ's, which are defining the sharpness o the electronic levels at the experimental conditions.

In the following Table III we give the numerical resul found for the nine substances investigated. As already mentione the values for σ_1 and σ_2 should only be considered as approx imative. The found frequency for the electronic line is—if possibl —corrected to the value for the gaseous state (given in column 3 by a direct comparison of the spectra in the two states. Th uncertainty in this correction increases rapidly with σ.

Table III.

Substance	ν_0 in ethanol cm^{-1}	ν_0 in vapour cm^{-1}	Group	σ_1 cm^{-1}	σ_2 cm^{-1}	log ε curve see page
Benzene I	(37,850)	(38,090)	B	100	110	49
— II*	—	—	C or D	660	710	„
Naphthalene I	32,170	32,455	A	130	180	42
— II	34,700	—	C	300	330	„
— III ...	45,100	—	C	430	500	„
Anthracene I	26,575	27,200	A	180	200	43
— II	39,550	—	C	300	370	„
Fluorobenzene I ...	37,650	37,816	A	120	150	34
Chlorobenzene I ...	36,900	37,052	A	140	200	35
Cyclooöctatetraene I.	ca. 28–29,000	—	D	ca. 2000	ca. 2000	48
Diphenyl I	ca. 36,000	—	D	650	700	46
Diphenylbutadiene I	28,550	—	C	400	400	41
Acetone I	ca. 33,000	—	D	ca. 1000	ca. 1000	47

* See text pag. 47.

In preliminary notes[1] we have stated values for ν_0 which i some cases are deviating slightly from those given in Table II

[1] A. Langseth and Svend Brodersen, Acta Chem. Scand. **3**, 778 (1949 *iidem:* Nature **165**, 931 (1950).

because we at that time did not take the diffuseness of the elec-tronic levels into consideration. Further we found it necessary to assume the presence of several near-by electronic lines in order to explain the shape of the $\Delta \log \varepsilon$ curve in the case of cyclooöctatetraene and diphenyl. However, the theory as it is presented in this paper doubtless gives a much more satisfying and unconstrained explanation of the observed temperature effects.

One of the authors (S. B.) wishes to express his thanks to Det teknisk-videnskabelige Forskningsråd for financial support. We also thank lektor K. P. Hansen for the preparation of a very pure sample of cyclooöctatetraene, Mr. P. Solgård for assistance in some of the measurements, and Mr. Rastrup Andersen for draw-ing the figures.

VI. APPENDIX

Numerical Values of the Function $F(x, y)$ for $T_1 = 298°\,K$ and $T_2 = 343°\,K$.

(Definition, see page 9.)

y in cm^{-1}	x					
	0	1	2	3	4	5
0	0.000	0.000	0.000	0.000	0.000	0.000
100	0.010	0.023	0.027	0.028	0.028	0.028
200	0.016	0.044	0.054	0.055	0.055	0.055
300	0.017	0.059	0.079	0.083	0.083	0.083
400	0.016	0.069	0.104	0.110	0.110	0.110
500	0.013	0.070	0.125	0.136	0.138	0.138
600	0.011	0.066	0.144	0.162	0.165	0.165
700	0.007	0.058	0.156	0.188	0.193	0.193
800	0.006	0.047	0.160	0.212	0.219	0.220
900	..	0.037	0.157	0.234	0.246	0.248
1000	0.003	0.028	0.143	0.251	0.273	0.275
1100	..	0.020	0.125	0.264	0.298	0.302
1200	0.002	0.014	0.102	0.269	0.323	0.329
1300	..	..	0.080	0.263	0.345	0.356
1400	..	0.007	0.060	0.247	0.364	0.382
1500	..	..	0.044	0.220	0.378	0.410
1600	..	0.003	0.031	0.187	0.386	0.434
1700	..	..	0.021	0.150	0.383	0.457
1800	..	..	0.015	0.116	0.368	0.478
1900	..	..	..	0.086	0.340	0.495
2000	..	..	0.007	0.062	0.300	0.506
2100	..	..	..	0.044	0.252	0.508
2200	..	..	0.003	0.030	0.202	0.498
2300	..	..	..	0.020	0.156	0.474
2400	..	..	..	0.014	0.115	0.435
2500	..	..	..	..	0.083	0.382
2600	..	..	..	0.006	0.058	0.321
2700	..	..	..	..	0.041	0.258
2800	..	..	..	0.002	0.027	0.199
2900	..	..	..	..	0.018	0.147
3000	..	..	..	..	0.013	0.106
3100	..	..	..	..	..	0.074
3200	..	..	..	..	0.005	0.051
3300	..	..	..	..	..	0.035
3400	..	..	..	..	0.003	0.024
3500	..	..	..	..	..	0.016

Note: For several of the numerical calculations occurring in this paper it is convenient use a table of addition logarithms giving $\log(1 + 10^x)$.

VII. SUMMARY

1. A method is proposed for localizing the electronic lines ($0 \rightarrow 0$ frequencies) in more or less continuous ultra-violet absorption spectra on the basis of quantitative measurements of the temperature effect.
2. A detailed theory based on the Boltzmann distribution law is given for this effect, making various simplifying assumptions.
3. Experimental results for nine different substances are compared with the theory and a satisfactory quantitative agreement is demonstrated.
4. It is concluded that the method in most cases gives valuable results. The accuracy obtained depends on the nature of the absorption system in question, which furthermore is disclosed in some detail.

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