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ON THE DETERMINATION OF THE INTEGRAL INTENSITY OF VERY STRONG ABSORPTION BANDS IN THE INFRARED RECORDED BY THE METHOD OF MULTIPLE ATTENUATED TOTAL REFLECTION

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A determination of the absorption curve of very strong bands in the infrared and optical parameters in the region of the examined band is given. This was accomplished by approximating the anomalous dispersion curve, making use of a natural source of radiation when recording spectra by the MATR method. The applicability of this method is checked by recording the absorption bands of H_2O, D_2O and HDO. A comparison of the results of recordings and calculations with those of other authors who used both the reflection and the transmission techniques showed them to be in good agreement.

1. *Introduction*

Multiple attenuated total reflection — MATR — applied as a technique of recording absorption bands, supplements the deficiencies of the transmission method in the infrared. It enables very strong absorption bands to be recorded and the spectral parameters of the substance to be determined in this spectral region. A detailed description of this method is given in the monography by Harrick [1] and a number of other papers [2–6].

Although MATR does enable very strong absorption bands in the infrared to be recorded (*e. g.* those of water), complicated computations are necessary to be able to plot the absorption curve and find the integral intensity of the band from the recorded results. In the transmission method the magnitude of transmitted radiation T is recorded, whereas in MATR the quantity recorded in the reflectivity $R(\theta, n_{21}^2, \kappa)$, which is a function of the angle of incidence of the radiation on the sample θ, the ratio of refractive indices $n_{21} = n_2/n_1$ of the sample and prism or platelet (the principal element of the MATR device made of, *e. g.*, germanium or KRS-5) and the attenuation index κ of the examined substance.

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The absorption index α of any substance and the integral intensity of its bands are linked with the optical constants by the following relations:

$$\alpha = \frac{4\pi n\kappa\nu}{cN} \tag{1}$$

$$I = \int_{\nu_1}^{\nu_2} \alpha d\nu \tag{2}$$

where c is the molar concentration of the sample, N is the number of reflections, and ν the wave number.

The relations between the optical constants n_2 and κ and the reflectivity for the radiation components polarized perpendicularly and parallelly falling on the sample are described the known Fresnel equations

$$R_{\perp} = \frac{\xi - \eta}{\xi + \eta}, \qquad R_{||} = \frac{u - v}{u + v}, \tag{3}$$

where $R_{\perp} = \frac{R_{s\perp}}{R_{0\perp}}$ and $R_{||} = \frac{R_{s||}}{R_{0||}}$, R_0 being the reflectivity at the interface between air and the MATR platelet, and R_s that at the interface between the sample and the MATR platelet.

$$u = \delta^2[(\sin^2\theta - x)^2 + y^2] + (x^2 + y^2)^{1/2};$$

$$v = 2\delta\left\{\left[(n_{21}^2 - n_{21}^2\kappa)\frac{(x^2+y^2)^{1/2} - x}{2}\right]^{1/2} + y\left[\frac{(x^2+y^2)^{1/2} + x}{2}\right]^{1/2}\right\},$$

$$\xi = \delta^2 + (x^2 + y^2)^{1/2}, \qquad \eta = \sqrt{2}\,\delta[(x^2+y^2)^{1/2} - x]^{1/2}$$

$$x = \sin^2\theta - n_{21}^2 + n_{21}^2\kappa^2, \qquad y = 2n_{21}^2\kappa, \qquad \delta = \cos\theta.$$

By using the fixed-angle MATR device it is possible to calculate the values of n_2 and κ from Eq. (3), for $R_{\perp}$ and $R_{||}$ are measurable quantities directly obtained from the recording. As is seen, the system of Fresnel equations (3) is quite complicated and solving it is possible when electronic computer techniques are used. For bands weak enough ($\kappa \leqslant 0.05$) there is a justified possibility of using considerably simplified forms of Eq. (3), presented in papers [5, 6].

When recording spectra by the MATR method there occur some unavoidable losses in energy of the examined beam caused, among other things, by backward reflections off the "entrance slit" of the platelet or slit and by some self-absorption of the MATR platelet material. If, in addition, use is made of polarized radiation, the beam is weakened pronouncedly just by the extinction of one of the components, apart from other factors. When measurements are made with a double-beam spectrometer these losses may be compensated by selecting appropriate "compensational windows", but then the signal becomes weak and the signal-to-noise ratio drops considerably, what worsens the accuracy of measurements.

2. *Approximation of anomalous dispersion curve*

In this work a method is presented in which use is made of natural source radiation in measurements. By this energy losses stemming from polarization are avoided. At the same time an approximation of the anomalous dispersion curve in the region of the band under study is employed. In spectrometers, particularly of the double-beam type, the radiation reaching the receiver is always partially polarized because of the numerous reflections off guiding mirrors. The degree of polarization of this radiation can be strictly defined, namely

$$\gamma(\nu) = \frac{I_{\parallel}}{I_{\perp}}.$$

The reflection factor R of partially polarized (but measurable) radiation is

$$R = \frac{R_{\perp}+\gamma R_{\parallel}}{1+\gamma}. \tag{4}$$

Substituting the values $R_{\perp}$ and $R_{\parallel}$ from Eqs (3) into Eq. (4) yields

$$R = \frac{\frac{\xi-\eta}{\xi+\eta}+\gamma\frac{u-v}{u+v}}{1+\gamma}. \tag{5}$$

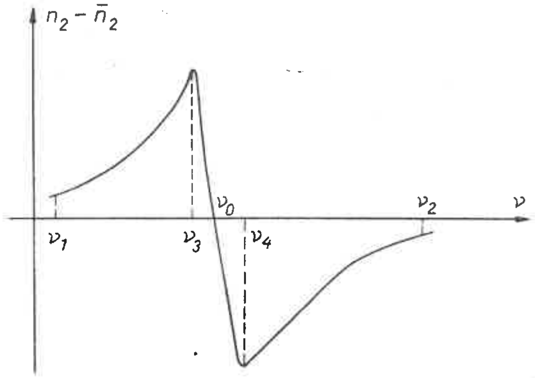

Fig. 1

From Eq. (5) we can compute the attenuation indices κ_i of the tested substance insofar as the shape of the anomalous dispersion curve is known. Figure 1 presents a schematic anomalous dispersion curve for a simple absorption band.

Let us notice that in the Fresnel equations (3) and (5) there is the square of the sample's relative refractive index n_{21}^2. It is therefore convenient to present the dispersion curve in a different reference frame than that in Fig. 1; this is shown in Fig. 2, where $\Delta n_2^2 = n_2^2-\bar{n}_2^2$.

It may be proved [7] that the maximum squared deviation of the refractive index n_2 is definable by the following equation with rather good approximation:

$$(\Delta n_2^2)_{\max} = (n_2^2)_{\max}(\kappa)_{\max}. \tag{6}$$

The value of n_2 at the maximum of the band is very close to the value of $\bar{n}_2$ of the "unperturbed" absorption band for any given spectral region. The index n_2 can be calculated by taking the average of the values of $n_2(\nu_1)$ and $n_2(\nu_2)$ from interference measurements at the flanks of the band (see Fig. 1) or even by interpolating or extrapolating experimental values of n_2 in the visible region and any value measured in the infrared (beyond the absorption regions). Substituting $\bar{n}_2$ (for the maximum) into Eq. (5) yields $\kappa_{\max}$ and $(\Delta n_2^2)_{\max}$ is

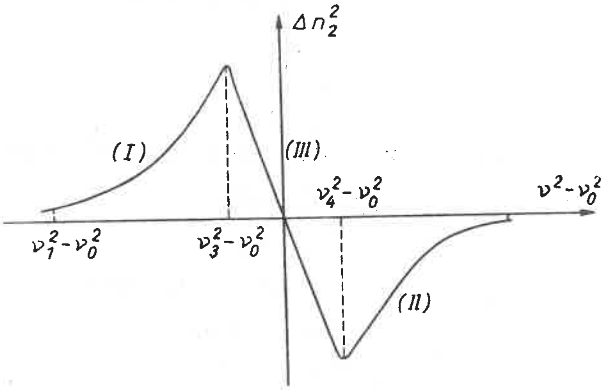

Fig. 2

found. The extreme values of refractive index for the given absorption band fall at the ends of the wave number interval defining the band half-width (in Fig. 1 the values ν_3 and ν_4). The shape of the anomalous dispersion curve can be approximated well by means of two branches of a hyperbole and a straight line segment in the region of large changes of n_2 (from ν_3 to ν_4), presented in the reference frame of Fig. 2 according to the formulae

$$\Delta n_2^2 = \frac{(\Delta n_2^2)_{\max}(\nu_3^2-\nu_0^2)}{\nu^2-\nu_0^2} \qquad \text{(for region I)}$$

$$\Delta n_2^2 = \frac{(\Delta n_2^2)_{\max}(\nu_4^2-\nu_0^2)}{\nu_0^2-\nu^2} \qquad \text{(for region II)}$$

$$\Delta n_2^2 = \frac{(\Delta n_2^2)_{\max}(\nu_0^2-\nu^2)}{\nu_0^2-\nu_3^2} \quad \text{and} \quad \Delta n_2^2 = \frac{(\Delta n_2^2)_{\max}(\nu^2-\nu_0^2)}{\nu_0^2-\nu_4^2} \qquad \text{(for region III).} \tag{7}$$

The value of κ_i for the various experimental points can be calculated from Eq. (5), whereas Eqs (1) and (2) provide the contour points of the dispersion curve and the integral intensity of the band. In the case of a complex band the approximation of the anomalous dispersion curve is harder to accomplish, although quite feasible. Here, the band $R(\theta, n_{21}^2, \kappa)$ is roughly separated into components and the approximate dispersion curve is found by the method described above for each component, and then superimposing the (usually overlapping) "components of the dispersion curve".

3. *Measurements and calculations*

To substantiate the applicability of the method described above, we measured the reflectivities R of the valence and deformation vibration bands of H_2O, HDO and D_2O. For measurements of the reflectivities R of the valence band of OH and the deformation vibration band of HOD in HDO use was made of a mixture of H_2O, HDO and D_2O; the molar concentrations of the components were $c_{H_2O} = 0.092$, $c_{HDO} = 0.418$ and $c_{D_2O} = 0.49$. In the reflectivity measurements of the OD valence and HOD deformation vibration bands the mixture of these substances in molar concentrations of $c_{D_2O}=0.092$, $c_{HDO}=0.418$ and $c_{H_2O} = 0.490$. Recordings were made with a UR-10 spectrophotometer employing a fixed-angle ($\theta = 45°$) MATR attachment with a germanium platelet for three reflections. Solutions of Eq. (5) and the integrals of the absorption curves were computed on an EMC Minsk-22 computer following our own program. Computations went along two paths: (1) by assuming the values of $n_2(\nu)$ calculated from Eqs (8), and (2) by assuming a single value of $\bar{n}_2$ for the entire absorption band.

4. *Results and conclusions*

Figures 3, 4, 5, 6 and 7 carry the plots of absorption curves of the ν_s and ν_δ bands for H_2O and D_2O and the ν_{val} band of the H_2O, HDO and D_2O mixtures of the molar fraction ratios given above. The dashed-line absorption curves are those for which a mutual averaged value of $\bar{n}_2 = 1.322$ was adopted for all of the bands considered, whereas the

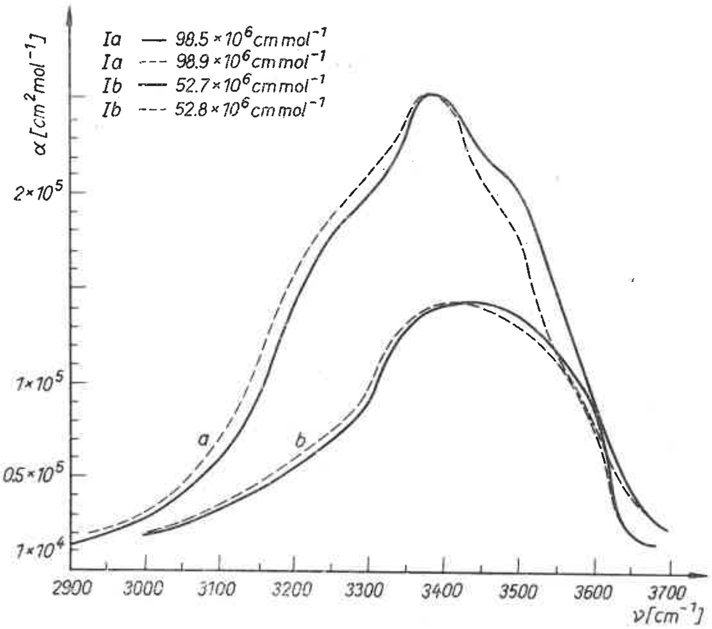

Fig. 3. *a*) Absorption curves of ν_s band for H_2O, *b*) absorption curves $\nu_{OH\ val}$ band of H_2O, HDO and D_2O mixture. Composition in molar fractions: $c_{H_2O} = 0.092$, $c_{D_2O} = 0.490$ and $c_{HDO} = 0.418$

continuous lines are absorption curves found by the method of dispersion curve approximation. Taking into account the participation of H_2O in the OH valence band of the H_2O, HDO and D_2O mixture of concentrations $c_{HDO} = 0.418$ and $c_{H_2O} = 0.092$, and the participation of D_2O in the OD valence band of the mixure of concentrations $c_{HDO} = 0.418$ and $c_{D_2O} = 0.092$, we calculated the integral intensities of the OH and OD bands in HDO.

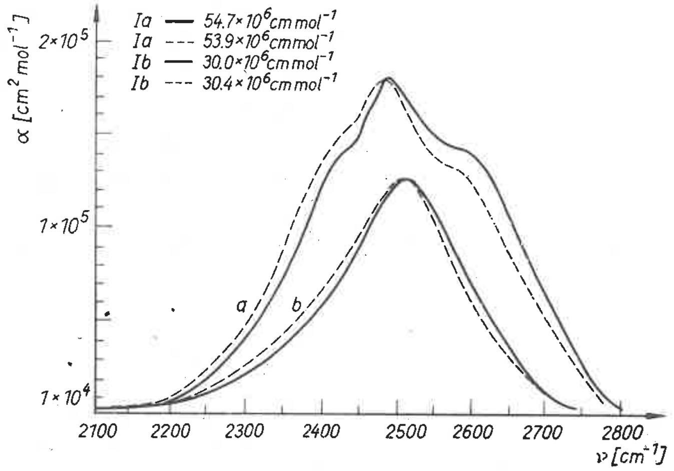

Fig. 4.*a*) Absorption curves of ν_s band for D_2O, *b*) absorption curves $\nu_{OD\ val}$ band of H_2O, HDO and D_2O mixture. Composition in molar fractions: $c_{H_2O} = 0.490$, $c_{D_2O} = 0.092$ and $c_{HDO} = 0.418$

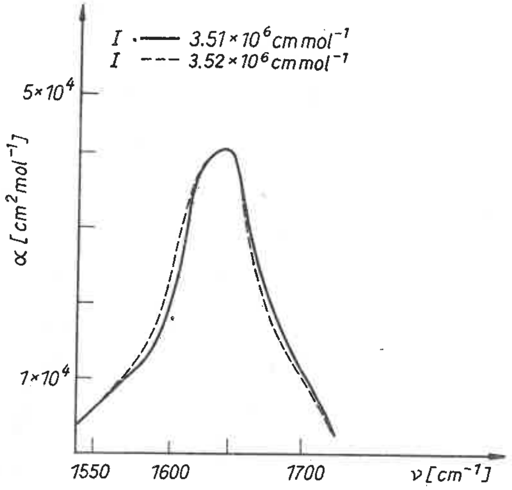

Fig. 5. Absorption curves of ν_{def} band for H_2O

Table I contains the obtained results of integral intensities for the examined absorption bands alongside the attenuation indices at the maximum of these bands. They are then compared with the data (though meagre as yet) to be found in the literature [8–10]. Zolotarev [8] measured the reflectivities $R_{\parallel}$ and $R_{\perp}$ with an H-800c spectrophotometer

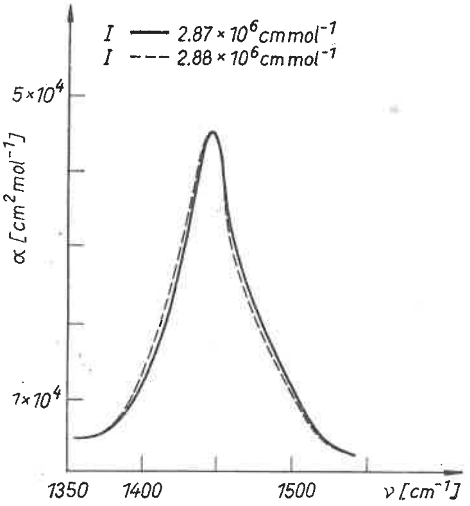

Fig. 6. Absorption curves of ν_{def} band for HDO

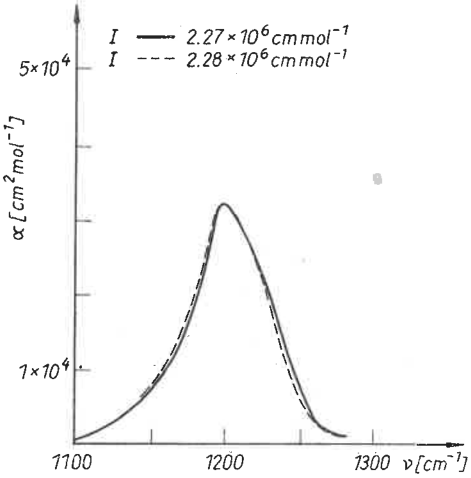

Fig. 7. Absorption curves of ν_{def} band for D_2O

employing a prism attachment for one reflection; his calculations were carried out with the use of very simplified forms of the Fresnel equations. In the studies described in Refs [9, 10] measurements were carried out by the transmission technique.

It follows immediately from the presented plots that the assumed dispersion curve approximation may be safely applied within a broad range of absorption bands, for single and complex bands alike, without any grave deformations of the absorption curve occurring. The considerable simplification used in version 2 brings about a slight deformation of the absorption curve, but does not visibly affect the value of integral intensity. For very strong absorption bands (ν_s for H_2O and D_2O) there is a more distinct effect, the shift of the band side-lines towards the lower frequencies (wave numbers); this, however, only alters

TABLE I

	$I_{\nu_s}(10^6\ \mathrm{cm \cdot mol^{-1}})$	$I_{\nu\delta}(10^6\ \mathrm{cm \cdot mol^{-1}})$	$\kappa_{\max\,\nu_s}$	$\kappa_{\max\,\nu\delta}$
H_2O	98.5 90.0 acc. [8]	3.51 —	0.254 0.31 acc. [8]	0.083 —
D_2O	54.7 60.0 acc. [8]	2.27 —	0.242 —	0.080 —

	$I_{\nu_{\mathrm{OH\,val}}}$	$I_{\nu_{\mathrm{OD\,val}}}$	$I_{\nu_{\mathrm{HOD\,def}}}$	$\kappa_{\max}\ \nu_{\mathrm{OH}}$	$\kappa_{\max}\ \nu_{\mathrm{OH}}$	$\kappa_{\max}\ \nu_{\mathrm{HOD}}$
HDO	43.6 44.9 acc [9]	24.9 23.6 acc. [10]	2.87 —	0.14 —	0.14 —	0.1 —

the symmetry of the band, not the position of possible local maxima and points of inflection of the band.

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