

## Optical spectra of the complexes $[M(H_2O)_6]^{2+}$ and $MSO_3-(H_2O)_2$ ( $M = Ni^{2+}$ )

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In this work, the absorption spectra of complexes  $[M(H_2O)_6]^{2+}$  and  $MSO_3-(H_2O)_2$  ( $M = Ni^{2+}$ ) are measured in spectral region 360–800 nm. The energies of electron transitions in  $Ni^{2+}$  are calculated in both cases. The Lorentz curves of nickel complexes  $[Ni(H_2O)_6]^{2+}$  and  $NiSO_3-(H_2O)_2$  are presented. The refractive index of aqueous solution of  $MgSO_3 \cdot 6H_2O:Ni$  is calculated.

**Key words:** ions of transition metals, absorption spectra, electron transitions, Lorentz curves

### INTRODUCTION

The crystals of magnesium sulphite hexahydrate ( $MgSO_3 \cdot 6H_2O$ ) are related to the point group  $C_3$  (without symmetry center). They are anisotropic (uniaxial) and gyrotropic in accordance to the symmetry point group [1]. The pure crystals of  $MgSO_3 \cdot 6H_2O$  are colourless. An original method has been developed for single crystals of  $MgSO_3 \cdot 6H_2O$  growing. This method allows producing samples with linear sizes 40–50 mm [2]. The  $MgSO_3 \cdot 6H_2O$  crystals are still not enough investigated. The first investigation on the nonlinear optical properties of single crystals of  $MgSO_3 \cdot 6H_2O$  is reported in 1997. The appearance of the second harmonics is observed by illumination the crystal with Nd:YAG laser radiation [2]. The optical properties of  $MgSO_3 \cdot 6H_2O$  are investigated partially for separate spectral lines or in narrow spectral ranges in connection with its application of the crystals in the laser technique.

In this paper, we would like to discuss the Lorentz curves of the complexes  $[Ni(H_2O)_6]^{2+}$  and  $NiSO_3-(H_2O)_2$  which are the basic components of the crystal  $MgSO_3 \cdot 6H_2O:Ni$ . We are investigated the unsaturated solutions where the distance between the complexes is large. Thus, the  $Ni^{2+}$  ions do not interact each other. The results of our experiment demonstrate that nickel impurity can find future application in the laser technique.

### EXPERIMENTAL DETAILS AND RESULTS

The experimental set up for the measurement of the absorption coefficient in the visible region consisted of the following: a halogen lamp with a stabilized 3H-7 rectifier, a SPM-2 monochromator, a system of quartz lenses, a polarizer, a crystal sample holder, and a Hamamatsu S2281-01 detector. The thickness of the used cuvette is  $d = 0.995$  cm.

The absorption coefficient of the investigated samples has been measured between 360 nm and 800 nm (Figs. 1a, 2a). The first derivative of the absorption coefficient at photon energy is calculated in the 360–800 nm spectral region. The  $[d\alpha/d(h\nu)]$  determines only the number of electron transitions in  $Ni^{2+}$  ions and it does not give an exact information about the energy position of these transitions (Figs. 1b, 2b). This is the reason for the calculation of the second derivative of the absorption coefficient  $[d^2\alpha/d(h\nu)^2]$  (Figs. 1c, 2c). The absorption coefficient is calculated using the formula: (1)  $\alpha = (1/d)\ln(I_0/I)$ , where  $I_0$  is the intensity of the incident light,  $I$  is the intensity of the passing light and  $d$  is the sample thickness. The calculated Lorentz curves for  $[Ni(H_2O)_6]^{2+}$  and  $NiSO_3-(H_2O)_2$  complexes in the spectral regions 360–460 nm and 550–800 nm are presented in Figs. 3a, b. They are compared with the experimental Lorentz curves in the same spectral regions (Figs. 4a, b).

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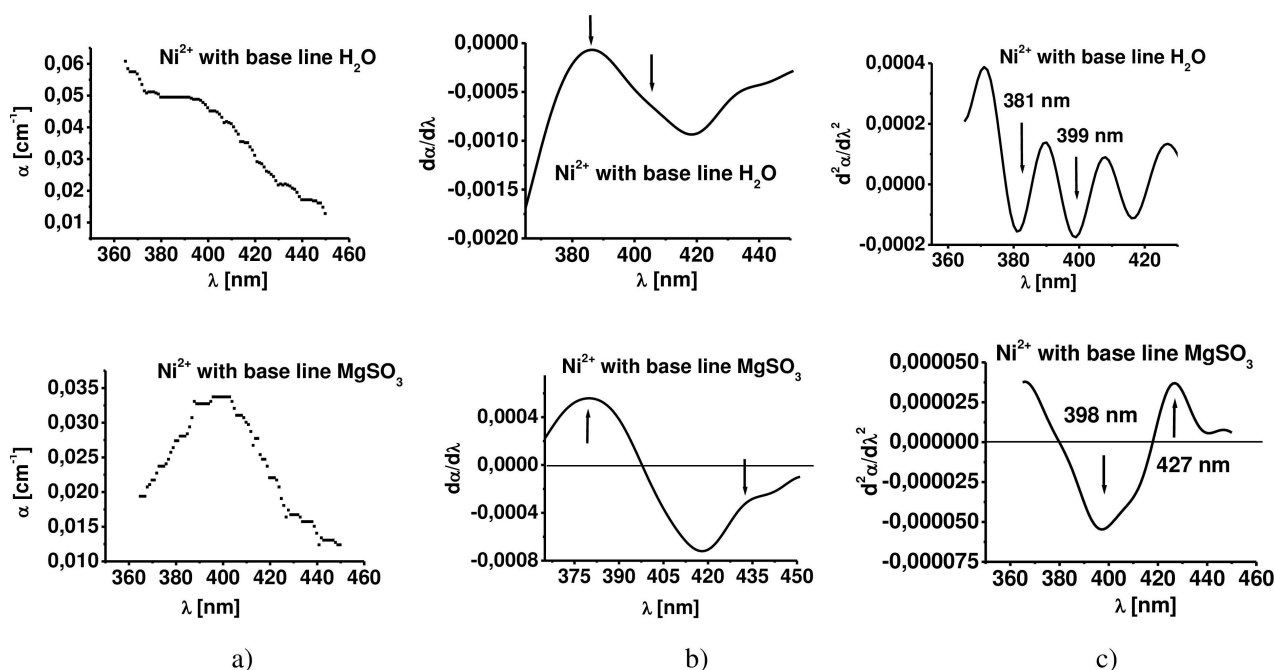


Fig. 1. a) Absorption spectrum of  $[Ni(H_2O)_6]^{2+}$  and  $NiSO_3-(H_2O)_2$  complexes in the spectral region 360–460 nm; b) Calculated first derivative of the absorption coefficient in the same spectral region; c) Calculated second derivative of the absorption coefficient.

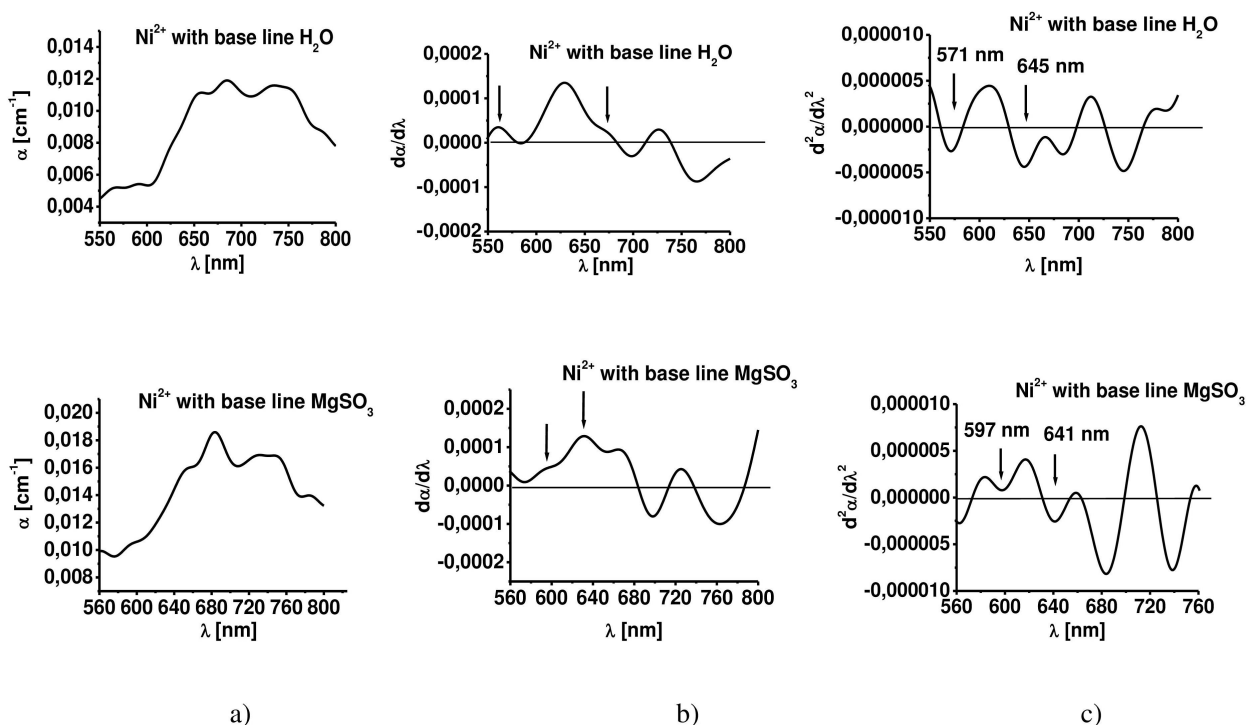


Fig. 2. a) Absorption spectrum of  $[Ni(H_2O)_6]^{2+}$  and  $NiSO_3-(H_2O)_2$  complexes in the spectral region 550–800 nm; b) Calculated first derivative of the absorption coefficient in the same spectral region; c) Calculated second derivative of the absorption coefficient.

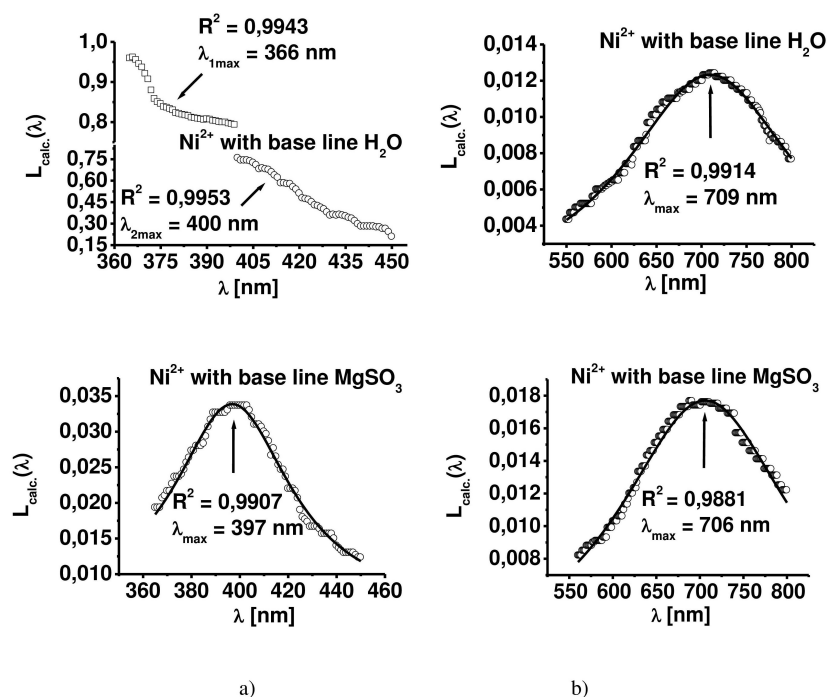


Fig. 3. The calculated Lorentz curves for  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $\text{NiSO}_3-(\text{H}_2\text{O})_2$  complexes in the spectral regions: a) 360–460 nm; and b) 550–800 nm.

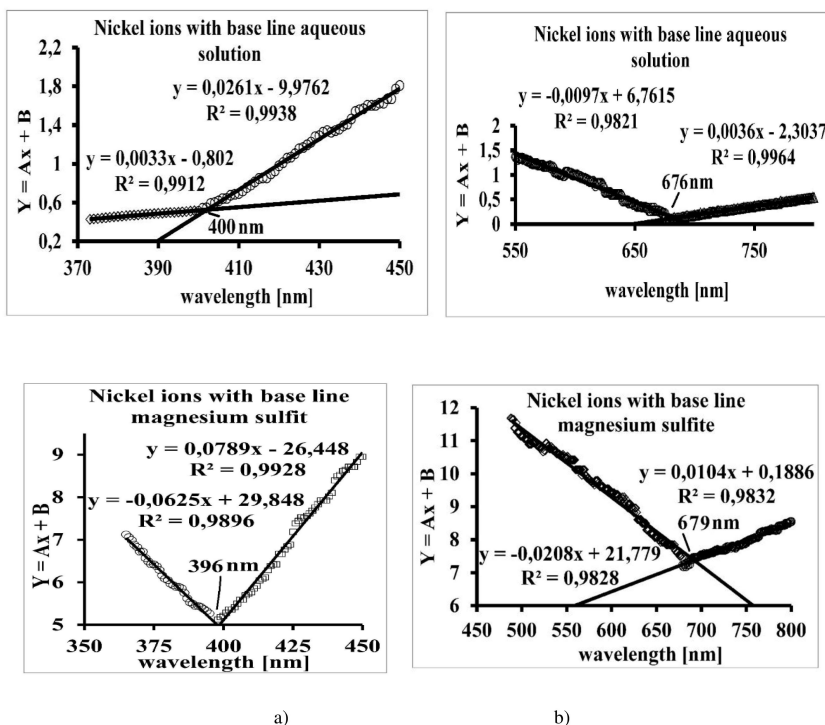


Fig. 4. The linearized experimental Lorentz curves for  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $\text{NiSO}_3-(\text{H}_2\text{O})_2$  complexes in the spectral regions: a) 360–460 nm; and b) 550–800 nm.

## DISCUSSION

The theory [3] shows that:

The absorption spectrum of impurities in the crystals, glasses and thin films consist of phonon and non-phonon part in low electron-phonon connection. The phonon part of spectrum consists of quasi-Lorentz curves. In harmonic approximation, these curves have intensity and half-width which depend on the electron-phonon interaction and temperature. The phonon part of spectrum manifests as structureless band. The separate maxima can be observed on the background of this band.

The form of the curve of first-order derivative consists of two maxima (positive and negative (Fig. 1b) or two positive (Fig. 2b)) [4]. Therefore, the enveloping Lorentz curve of absorption nickel structures includes two Lorentz components.

The ground state of  $Ni^{2+}$  in the octahedral coordination is  ${}^3A_{2g}(t_{2g})^6(e_g)^2$ . The ion  $Ni^{2+}$  has two unpaired spins in this coordination. Thus, we can observe three absorption bands connected with the transitions  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  [5–7]. In our case the electron transitions in  $Ni^{2+}$  are two as follow:  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  (Fig. 1c) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  (Fig. 2c). Therefore, we can solve the system of the next equations  $\nu_1 = 14793 \text{ cm}^{-1} = 15Dq + 1.47B$  and  $\nu_2 = 25000 \text{ cm}^{-1} = 15Dq + 13.53B$  for the complex  $[Ni(H_2O)_6]^{2+}$ . The values of  $\nu_1$  and  $\nu_2$  present the cross point of two Lorentz curves which are included in the complex spectral structure of nickel (Figs. 4a, b). When the impurity spectral structures are very wide, we can present only the experimental Lorentz curves, because the difference between their cross point and  $\lambda_{\max}$  of the calculated Lorentz curve is very large (Figs. 3b and 4b).

The crystal field parameter  $Dq$  is  $903 \text{ cm}^{-1}$  and Racah's parameter  $B$  is  $846 \text{ cm}^{-1}$  for the same complex. The other system of equations is:  $\nu_1 = 14728 \text{ cm}^{-1} = 15Dq + 1.47B$  and  $\nu_2 = 25253 \text{ cm}^{-1} = 15Dq + 13.53B$  for the complex  $NiSO_3-(H_2O)_2$ . The crystal field parameter and Racah's parameter for this complex are respectively  $Dq = 896 \text{ cm}^{-1}$ ,  $B = 873 \text{ cm}^{-1}$ . The Racah's parameter  $C$  for the complexes  $[M(H_2O)_6]^{2+}$  and  $MSO_3-(H_2O)_2$  ( $M = Ni^{2+}$ ) has values respectively  $3985 \text{ cm}^{-1}$  and  $4112 \text{ cm}^{-1}$ .

When the plane electromagnetic wave propagates in the absorbing isotropic medium, the absorption coefficient is presented as:

$$\alpha(\lambda) = \frac{Ne^2(\gamma/2)}{2cn\epsilon_0m(\lambda_0 - \lambda)^2 + (\gamma/2)^2}. \quad (1)$$

The normalized curve of the absorption coefficient has the form:

$$L(\lambda) = \frac{\alpha(\lambda)}{\alpha_{\max}} = \frac{(\gamma/2)^2}{(\lambda_0 - \lambda)^2 + (\gamma/2)^2}, \quad (2)$$

where

$$\alpha_{\max} = [Ne^2]/[2en\epsilon_0m(\gamma/2)]. \quad (3)$$

We can calculate the refractive index  $n$  of the solution, when the equation (3) is transformed into

$$n = \frac{N_d q_d^2}{2c\alpha_{\max}\epsilon_0m_d(\gamma/2)} = 1.3721, \quad (4)$$

where  $N_d = 1.02 \times 10^{31} \text{ m}^{-3}$  (number of  $Ni^{2+}$  ions per unit volume),  $q_d = 44.8 \times 10^{-19} \text{ C}$ ,  $c = 3 \times 10^8 \text{ m/s}$ ,  $\alpha_{\max} = 96.14 \text{ m}^{-1}$ ,  $\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$ ,  $m_d = 0.9941 \text{ kg}$ ,  $\gamma/2 = 294$ .

If the curve is Lorentz curve, it should be checked as follows: The dependence  $L(\lambda)$  is reduced to a linear and a linear correlation analysis is used.

Thus, the equation (2) is transformed into the equation

$$[(1/L(\lambda)) - 1]^{1/2} = [\lambda_0/(\gamma/2)] - [1/(\gamma/2)]\lambda. \quad (5)$$

$\lambda_0$  is the own wavelength of vibration of oscillators per unit volume and  $\gamma$  is the damping ratio takes into account the loss of energy of the oscillators. If  $Y = [(1/L(\lambda)) - 1]^{1/2}$ ,  $B = [\lambda_0/(\gamma/2)]$ ,  $A = -[1/(\gamma/2)]$  and  $x = \lambda$ , then  $Y = Ax + B$ .

If the coefficient of correlation is  $R^2 = 0.98$ , then the probability  $P$  is 0.95. Therefore, the relationship between  $Y$  and  $x$  is linear and the curve is Lorentz curve.

## CONCLUSIONS

The different coordination of  $Ni^{2+}$  gives different energy positions of electron transitions in this ion. The methodology for the experimental Lorentz curves gives opportunity for determination of the refractive index of the solutions. The calculated Lorentz curves are used in well expressed sharp maxima and their  $\lambda_{\max}$  coincides with the cross point of experimental Lorentz curves.

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ОПТИЧНИ СПЕКТРИ НА  $MSO_3$  И  $[M(H_2O)_6]^{2+}$  ( $M = Ni^{2+}$ )

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(Резюме)

В тази работа са измерени спектрите на поглъщане на комплексите  $NiSO_3$  и  $[Ni(H_2O)_6]^{2+}$  в спектралния диапазон (400–600) nm. Изчислени са енергиите на преходите на електроните в  $Ni^{2+}$  и в двата случая. Представени са и са дискутирани напречните сечения на поглъщане  $\sigma_a^1$  и  $\sigma_a^2$  на никела съответстващи на комплексите  $MSO_3$  и  $[M(H_2O)_6]^{2+}$  ( $M = Ni^{2+}$ ). Определени са големините на спин-орбиталното взаимодействие и Зеemanовото разцепване.