DISPERSION CURVES OF MAGNETIC ROTATION AND OF THE REFRACTIVE INDEX OF THE La^{3+} ION IN AN AQUEOUS LaCl$_3$ SOLUTION

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R. M. SHUKUROVA, E. F. YAMSHCHIKOV

DISPERSION CURVES OF MAGNETIC ROTATION AND OF THE REFRACTIVE INDEX OF THE La^{3+} ION IN AN AQUEOUS $LaCl_3$ SOLUTION

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The dispersion curve of magnetic rotation (D.M.R.) and the dispersion curve of the refractive index (D.R.I.) are related to each other by relation (1), which differs from Becquerel' s formula (1) by the coefficient r:

$$V = r\,\frac{360}{2\pi}\,\frac{e}{2mc^2}\,\nu\left(\frac{\partial\mu}{\partial\nu}\right), \tag{1}$$

where V is the Verdet constant (in deg $\cdot$ cm^{-1} $\cdot$ G^{-1}); ν is the frequency in cm^{-1}; μ is the refractive index; e is the electron charge; m is the electron mass; c is the speed of light.

The coefficient r, introduced by Serber (2), is equal to unity for atoms having spherical symmetry, and to 0.5 for linear diatomic molecules. In all other cases r assumes an intermediate value from 1 to 0.5.

Relation (1), obtained for gases (3), whose ground state is $^1S_0$, is applicable in those cases where measurements are made far from absorption bands. It was shown experimentally (4) that in the case of noble gases the value of r is not exactly equal to unity, and moreover r varies somewhat within the wavelength range from 9000 to 3635 Å (the maximum change of r is observed for neon, $\sim 12\%$).

Relation (1) can be represented in a somewhat different form. Namely, dividing the right- and left-hand sides of equation (1) by ν and integrating, for example, from ν_1 to ν_2, we obtain

$$\int_{\nu_1}^{\nu_2} V'\,d\nu = r\,\frac{360}{2\pi}\,\frac{e}{2mc^2}\,\Delta\mu. \tag{2}$$

Fig. 1. Correction curve $\Delta\mu$ to formula (4) ($C_M = 0.04$ mol/l)

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The quantity $V' = V/\nu$ may be regarded as the rotation of the plane of polarization over a sample thickness equal to the wavelength of the incident light. The quantity $\Delta\mu$ is the difference between the values of the refractive indices $\mu_1(\nu_1)$ and $\mu_2(\nu_2)$ at the frequencies ν_1 and ν_2, respectively ($\mu_2 > \mu_1$, $\nu_2 > \nu_1$). The integral on the left-hand side of (2) is the area under the curve $V' = V'(\nu)$ in the frequency interval from ν_1 to ν_2. As can be seen, relation (2) differs advantageously from (1) in that it covers a broad frequency region simultaneously and is more convenient for experimental verification.

In the present work, using the example of the La^{3+} ion in an aqueous $LaCl_3$ solution, relations (1) and (2) are checked and the results obtained are compared. The choice of this object is due to the fact that the La^{3+} ion is diamagnetic, and its ground state, as in the noble gases, is ${}^1S_0$ (^{5}).

§ 1. **Preparation of the solution.** Solutions of lanthanum chloride were prepared in the usual way (^{6}, ^{7}), by dissolving freshly ignited La_2O_3 oxide in a solution of hydrochloric acid. For measuring the D.M.R. curve, a solution of relatively high concentration was prepared ($C_M = 1$ mol/l), since the observed Faraday effect from the La^{3+} ion in solution is small.

On the contrary, for measuring the refractive-index-dispersion curve the concentration of the solution was considerably lower ($C_M = 0.04$ mol/l), since only in this case was it possible to use method (7), which makes it possible to determine the refractive-index-dispersion curve of the La^{3+} ion with a high degree of accuracy. The solutions were prepared in 25-ml volumetric flasks at 20° and contained an excess of HCl acid amounting to 35% of the concentration of the solution.

§ 2. **Instruments.** Measurements of the refractive-index-dispersion curve were carried out on a Jamin-type interferometer coupled with an ISP-22 spectrograph. The interferometer cell, 0.5 cm thick, was closed with ground stoppers. The temperature difference between the solution under investigation and the compensating solution, monitored with a differential thermocouple, usually did not exceed 0.02°. The optical path difference arising when the solutions were introduced into the interferometer was determined by the method of rotating one of the interferometer plates. The measurement method and the design of the cell are described in detail in (7).

Fig. 1. Correction curve $\Delta\mu$ to formula (4) ($C_M = 0.04$ mol/l)

The refractive-index-dispersion curves were measured in the spectral region 15 400—37 300 cm^{-1}. The accuracy of measuring the dispersion was no worse than 1—$2 \cdot 10^{-6}$, and that of the absolute value of the refractive index was no worse than $\mu = \mu_{LaCl_3} - \mu_{HCl} \sim 2 \cdot 10^{-6}$. The magnetic-rotation-dispersion curves were measured on the apparatus (8), kindly made available by Yu. A. Sharonov, to whom the authors express their deep gratitude.

The improved model of the instrument made it possible to record the spectrum automatically; at the same time the influence of the solvent was excluded. Corrections connected with the replacement of solvent molecules were taken as negligibly small and therefore were not taken into account. The magnetic-rotation-dispersion curve of the La^{3+} ion was measured in the visible spectral region from 18 750 to 28 650 cm^{-1}. At a magnetic-field strength $H = 10\,000$ G and a layer thickness of 1 cm, the angle of rotation of the plane of polarization φ reached values of 0.056° (19 177 cm^{-1}) and 0.153° (28 637 cm^{-1}). The accuracy of measuring φ was 1—$2 \cdot 10^{-3}$ degrees. The Verdet constant was determined from the formula

$$V = \frac{\varphi}{lC_M}\frac{1}{H}, \tag{3}$$

where φ is the angle of rotation in degrees in the magnetic field H; l is the length of the light path in the solution in cm; C_M is the concentration of the solution in mol/l; H is the magnetic field in G.

§ 3. **Measurement results.** The obtained refractive-index-dispersion curve ($C = 0.04$ mol/l) was interpolated by a formula of the Sellmeier type

$$\mu = A + \frac{B}{\nu_0^2 - \nu^2}, \tag{4}$$

where $\mu = \mu_{\mathrm{LaCl_3}} - \mu_{\mathrm{HCl}}$; A, B, and ν_0 are constants.

The deviation of the experimental points from formula (4) is given in the form of the correction curve in Fig. 1. The magnetic-rotation-dispersion curve was interpolated by the one-term formula (9)

$$V = \nu^2 b/(\nu_0^2 - \nu^2)^2, \tag{5}$$

where V is the Verdet constant (in $\mathrm{deg} \cdot \mathrm{cm}^{-1} \cdot \mathrm{mol}^{-1} \cdot \mathrm{l} \cdot \mathrm{G}^{-1}$), and b and ν_0 are constants. The term $4\nu_L^2\nu^2$ in formula (5) has been neglected because of its smallness in comparison with the term $(\nu_0^2 - \nu^2)^2$.

Figure 2 presents the correction curve for formula (5). As is seen from Fig. 2, the scatter of the experimental points lies within the limits of the measurement errors. Table 1 summarizes the results of interpolation of the M.R.D. and R.I.D. curves.

Table 1

Figure 2

Figure 2: Figure 2

Constants	Formula (4)	Formula (5)
A	$9.64 \cdot 10^{-4}$	–
B	$2.8528 \cdot 10^{5}$	–
b	–	$7.8938 \cdot 10^{4}$
ν_0^2	$2.6194 \cdot 10^{9}$	$6.7185 \cdot 10^{9}$
Interpolation limits, cm^{-1}	15 400	19 200
Interpolation limits, cm^{-1}	37 300	28 550

If the R.I.D. curve is interpolated by the formula $\mu = B'/(\nu_0'^2 - \nu^2)$ over the same limits as the M.R.D. curve, then the following values of the constants are obtained: $B' = 1.6763 \cdot 10^7$, $\nu_0'^2 = 1.5797 \cdot 10^{10}$. The effective oscillator strengths $f = 7.8$ and $f' = 7.8$, calculated from the coefficients b and B', are equal and close to the number of electrons in the closed shell $5s^2 5p^6$ of the La^{3+} ion. However, the absorption region of the La^{3+} ion, found from the M.R.D. and R.I.D. curves, differs noticeably.

§ 4. **Verification of Becquerel' s formula.** a) **Relation (1).** The value of the term $(\partial\mu/\partial\nu)$ in formula (1) was found graphically with the aid of a small mirror. This mirror was placed on the graph $\mu = \mu(\nu)$ so that the reflected R.I.D. curve was a continuation of the curve drawn on the graph, i.e., so that the actual and reflected curves lay on one line and did not form a break. The line drawn along the edge of the mirror is perpendicular to the tangent to the R.I.D. curve. The cotangent of the angle of inclination of this perpendicular is the required quantity $(\partial\mu/\partial\nu)$. Three frequencies were chosen: $\nu_1 = 19\,177$ cm^{-1}, $\nu_2 = 23\,656$ cm^{-1}, and $\nu_3 = 28\,027$ cm^{-1}, for which relation (1) was checked; in this case it turned out that $r_1(\nu_1) = 0.29 \pm 0.04$, $r_2(\nu_2) = 0.19 \pm 0.02$, and $r_3(\nu_3) = 0.20 \pm 0.02$. The mean value is $r_{\text{avg}} = 0.23 \pm 0.03$.

Fig. 2. Correction curve ΔV to formula (5), ($C_M = 1$ mol/l)

b) **Relation (2).** The integral in formula (2) was calculated graphically, using the trapezoidal rule. The entire area under the curve $V' = V'(\nu)$ in the frequency interval $\nu_1 = 1.8750$ cm^{-1} and $\nu_2 = 28\,750$ cm^{-1} was divided into 20 intervals at every 500 cm^{-1} (the area under the curve $V'(\nu)$, calculated by the more accurate Simpson formula, turned out to be smaller by 0.5%). The value of the integral found in this way is $3.8556 \cdot 10^{-6}$, $\Delta\mu = \mu_2(\nu_2) - \mu_1(\nu_1) = 9.50 \cdot 10^{-4}$ at a solution concentration of 1 mol/l*. Consequently, the coefficient r in formula (2) is equal to 0.24 ± 0.03.

Conclusion. The M.R.D. and R.I.D. curves of the La^{3+} ion in an aqueous solution of lanthanum chloride have been measured. A check of Becquerel' s differential (1) and integral (2) formulas has been carried out; it was found that the coefficient r in both formulas is, within the limits of the measurement errors (10-15%), the same and equal to 0.24. It is shown that formula (2) is more convenient for experimental verification and gives a more reliable result in determining the coefficient r. A discussion of why r is significantly less than unity, we consider premature, since it has not been established experimentally whether the course of the magnetic-rotation dispersion curves and refractive-index dispersion curves of the La^{3+} ion changes with changes in the concentration of the solution in the range $0.04 \div 1$ mol/l.

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Institute of General and Inorganic Chemistry
named after N. S. Kurnakov

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* Here it is assumed that the refractive index μ is directly proportional to the concentration of the solution.

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