INTENSITY RATIOS OF SPECTRAL LINES IN THE VISIBLE TRIPLET OF ZnI IN THE TEMPERATURE OF LIQUID NITROGEN

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The effect of reabsorption on the intensity ratios of spectral lines is discussed.

The dependence of the intensity ratios of the spectral lines in the visible ZnI triplet ($4s5s\,^3S_1 - 4s4p\,^3P^\circ_{0,1,2}$: 4680, 4722, 4811 Å) on the current intensity in the liquid nitrogen-cooled Schüler type hollow-cathode lamp was determined.

The relative populations of the levels $^3P^\circ_{0,1,2}$ were evaluated.

Introduction

All light sources possess finite dimensions and light arising throuhg emission in the deeper layers of the source undergoes reabsorption. This affects the intesity and shape of the spectral lines observed. Since the absorption coefficient generally varies from one line to another, reabsorption is apt to modify their intensity ratios. The effect of reabsorption on the intensity and shape of the spectral line depends on the nature of the source. The problem was worked out in detail by Cowan and Dieke (1948).

Reabsorption is essential primarily in the case of resonance lines and of lines from transitions terminating in metastable states. The latter comprise the lines of the visible triplets of the sharp series of elements in the second column of the periodic system. As shown by Mrs. Leś and Niewodniczański (1958, 1961), the enormous divergences in the results of measurements of the intensity ratios of the respective triplets for ZnI, CdI and HgI are fully explained by the effect of reabsorption.

Fig. 1 brings a diagram of the energy levels for the lines of the visible ZnI triplet. The populations of the $^3P^\circ_{0,1,2}$ levels are decisive for the effect of reabsorption upon the intensity ratios of the lines.

In the papers by Mrs. Leś and Niewodniczański stress is laid on the effect of transitions between the $^3P^\circ_{0,1,2}$ levels deriving from inelastic collisions between atoms of the element under investigation and atoms of the inert gas on the relative populations of those levels. The transitions in question can play an essential role if the differences in energy between

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the $^3P^{\circ}_{0,1,2}$ levels, ΔE_1 and ΔE_2, are of the same order of magnitude as the thermal energy of the colliding particles. The energy gaps ΔE_1 and ΔE_2 are respectively: in ZnI, 0.023 eV and 0.048 eV; in CdI, 0.067 eV and 0.145 eV. The mean kinetic energy of the atoms at room temperature amounts to approximately 0.039 eV and, at the boiling temperature of liquid nitrogen under atmospheric pressure — to about 0.010 eV. Obviously, one should expect

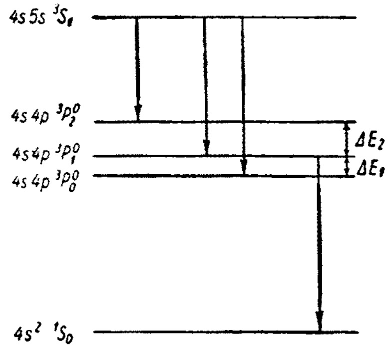

Fig. 1. Diagram of energy levels for the lines of the visible triplet of ZnI

the part played by inelastic collisions in establishing the populations of the $^3P^{\circ}_{0,1,2}$ levels to be the same in ZnI at the temperature of liquid nitrogen as in CdI at room temperature.

It was the aim of the present investigation to measure the intensity ratios of the spectral lines of the visible ZnI triplet at the temperature of liquid nitrogen and to compare the results obtained with those of measurements of the intensity ratios of the lines of the visible CdI triplet at room temperatures (Mrs. Leś, Niewodniczański 1958).

Theoretical

The effect of reabsorption on the observed intensity of a spectral line was discussed for the case of a homogeneous source of radiation by Ladenburg (Ladenburg, Levy 1930).

Let us consider a simple model of radiation source in the shape of a cylinder of length l and area of base s. Observation of the radiation occurs in the direction of the cylinder's axis, in a very small solid angle $d\Omega$. The volume element $d\tau$ of the source radiates the energy $\omega(\nu)d\nu\, d\tau$ per second in the frequency interval $(\nu, \nu+d\nu)$. Let us assume the source to be homogeneous *i.e.* the power of radiation $\omega(\nu)$ and absorption coefficient $k(\nu)$ to be functions of the frequency only.[1]

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[1] To some extent it is possible to free oneself from the assumption of a homogeneous source. Indeed, let $\omega(\nu)$ and $k(\nu)$ vary according to the same law along the axis of the source, *i. e.*

$$\omega(\nu, x) = \omega(\nu)\, f(x) \quad \text{and} \quad k(\nu, x) = k(\nu)\, f(x)$$

it is readily seen that this has no effect on the results of our considerations, apart from the fact that the geometrical thickness l of the source has now to be replaced in the formulas by the equivalent thickness $l' = \int_0^l f(x)dx$.

It is easily proved (Frish 1951) that the total energy emitted in the frequency interval $(\nu, \nu+d\nu)$ in the direction of the axis within the solid angle $d\Omega$ amounts to

$$dW(\nu) = \frac{\omega(\nu)\, d\nu\, s d\Omega}{4\pi\, k(\nu)} (1-e^{-k(\nu)l}). \tag{1}$$

Assume the source to be emitting a spectral line of frequency ν_0. A measure of the intensity $I_{\nu_0}^0$ of the line is given by the energy emitted per second by a unit volume of the source within the interval of frequencies corresponding to the line. Not taking into account the existence of other spectral lines, its true intensity is

$$I_{\nu_0}^0 = \int_0^\infty \omega(\nu) d\nu. \tag{2}$$

The intensity of a line is determined by measuring the energy emitted by the source into the solid angle $d\Omega$ within the frequency range corresponding to the line. From Eq. (1), the observed intensity of the line amounts to

$$I_{\nu_0}^l = \int_0^\infty \frac{\omega(\nu)}{k(\nu)l} (1-e^{-k(\nu)l})\, d\nu. \tag{3}$$

The shape of the line is the same for emission and absorption:

$$\omega(\nu) = \omega(\nu_0)\ \varphi(\nu) = \omega_0\ \varphi(\nu), \quad k(\nu) = k(\nu_0)\ \varphi(\nu) = k_0\ \varphi(\nu).$$

Hence,

$$I_{\nu_0}^l = \frac{\omega_0}{k_0 l} R_{\nu_0}(k_0 l)$$

or

$$I_{\nu_0}^l = \frac{I_{\nu_0}^0}{l \int_0^\infty k(\nu) d\nu} R_{\nu_0}(k_0 l), \tag{3a}$$

where the function

$$R_{\nu_0}(k_0 l) = \int_0^\infty (1-e^{-k(\nu)l}) d\nu$$

is the so-called equivalent width of the absorption line. The explicit form of this function depends on the shape of the line.

Let the latter be of the Doppler type at the centre of the line and let its edges, far from the centre, be of the natural shape. Van der Held (1931) published curves of the increase in equivalent line widht as a function of the optical thickness of the source, $R_{\nu_0}(k_0 l)$, for various ratios of the natural and Doppler half-widths. For intermediate values of $k_0 l$ of the order of 10^1-10^2, even for sources at low temperatures, it is the Doppler shape of the line that is decisive for the form of the function $R_{\nu_0}(k_0 l)$. On the other hand, for very

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considerable optical thickness of the source upward of 10^3—10^4, the equivalent width of the line is determined by the natural shape of the line. The form of the function $R_{\nu_0}(k_0 l)$ for the Doppler and natural shapes of the line are due to Ladenburg (Ladenburg, Levy 1930).

In the case of the ZnI and CdI lines under consideration $k_0 l$ attains but small values in the Schüler lamp. Hence, we shall restrict ourselves to taking into account the Doppler shape only. This yields

$$R_{\nu_0}(k_0 l) = a\nu_0 k_0 l\ S(k_0 l), \tag{4}$$

wherein

$$a = \frac{1}{c}\sqrt{\frac{2\pi RT}{M}}$$

and c is the velocity of light, M — the atomic mass of the atoms emitting the line under consideration, R — the constant of the equation of gases and T — the temperature of the source.

Fig. 2 shows the function $k_0 l\ S(k_0 l)$ as plotted from the calculations of Landenburg.

Let us compare the observed intensities of two spectral lines of frequencies ν_1 and ν_2. The corresponding absorption coefficients are $k_1(\nu)$ and $k_2(\nu)$. From Eq. (3a), by (4), we have

$$\frac{I^l_{\nu_1}}{I^l_{\nu_2}} = \frac{I^0_{\nu_1}\int\limits_0^\infty k_2(\nu)d\nu}{I^0_{\nu_2}\int\limits_0^\infty k_1(\nu)d\nu}\cdot\frac{\nu_1 k_{01}\, lS(k_{01}l)}{\nu_2 k_{02}\, lS(k_{02}l)}, \tag{5}$$

where k_{01} and k_{02} are the values of the absorption coefficient at the centres of the respective lines.

If the optical thickness of the source augments, and the ratio k_{01}/k_{02} of the absorption coefficients remaining constant, the expression $\frac{k_{01}l\ S(k_{01}l)}{k_{02}l\ S(k_{02}l)}$ tends to unity the faster the smaller is the difference between the absorption coefficients of either line. Fig. 2 shows $\frac{3k_0 l\ S(3k_0 l)}{k_0 lS(k_0 l)}$

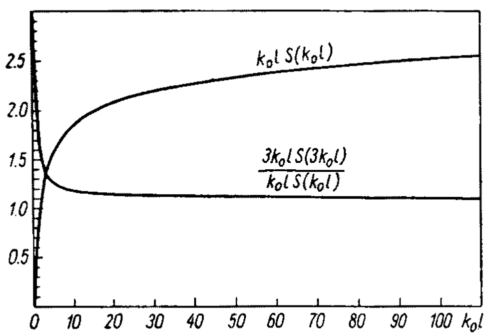

Fig. 2. Diagrams of the functions $k_0 l\ S(k_0 l)$ and $\frac{3k_0 lS(3k_0 l)}{k_0 l\ S(k_0 l)}$ as derived from calculations by Ladenburg (Ladenburg, Lévy 1930)

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as a function of $k_0 l (k_{01} = 3k_{02})$. It will be noted that the function approaches unity already in the neigbourhood of $k_0 l = 20$ and varies thereafter but insignificantly with higher values of $k_0 l$. Thus, saturation of reabsorption appears. The intensity ratio of the two lines attains a value that is approximated by the expression

$$\frac{I^l_{\nu_1}}{I^l_{\nu_2}} \approx \frac{I^0_{\nu_1}\nu_1 \int\limits_0^\infty k_2(\nu)d\nu}{I^0_{\nu_2}\nu_2 \int\limits_0^\infty k_1(\nu)d\nu} \tag{6}$$

and does not vary as $k_0 l$ increases.

It will be remembered that the intensity of a spectral line emitted in transition of an atom from the state m to a lower state n is given by the formula

$$I_{m,n} = N_m h\nu_{m,n} A_{m,n},$$

where N_m is the population of state m, $A_{m,n}$ — the probability of transition from state m to state n and $\nu_{m,n}$ — the frequency of the emitted line.

It is readily shown (Mitchell, Zemansky 1961) that

$$\int\limits_0^\infty k(\nu)d\nu = \frac{c^2 g_m N_n A_{m,n}}{8\pi\, \nu^2_{m,n}\, g_n}.$$

Here, g_m and g_n are the statistical weights of the states m and n and N_n is the population of state n. On substitution of the above quantities, Eq. (6) becomes

$$\frac{I^l_{\nu_1}}{I^l_{\nu_2}} \approx \frac{N_{1m} N_{2n} g_{2m} g_{1n} \nu_1^4}{N_{2m} N_{1n} g_{1m} g_{2n} \nu_2^4}. \tag{6a}$$

Consequently, for values of $k_0 l$ such that saturation of reabsorption occurs and at the same time the equivalent line widths are given by the Doppler shape, the intensity ratios observed are roughly independent of the ratios of the respective transition probabilities.

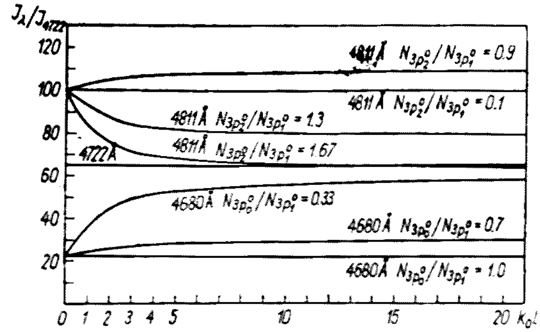

Fig. 3. Theoretical intensity ratios of the spectral lines of the visible ZnI triplet *versus* the optical thickness of the source, for various values of the population ratios of the levels $^3P^0_{0,1,2}$.

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With the aim of showing that reabsorption had no effect upon the intensity ratios measured, various authors carried out measurements varying the optical thickness of the source, though failing to take into consideration the possibility that saturation of reabsorption occurred at the optical thicknesses they were utilizing.

From Eqs (5) and (6) and the values of $S(k_0 l)$ computed by Ladenburg and Levy it is possible to predict the dependence of the observed intensity ratios of spectral lines on the optical thickness of the source. The curves of Fig. 3 illustrate the above relation as computed for the lines of the visible triplet of ZnI, for various ratios of the populations of the levels ${}^3P^\circ_{0,1,2}$. The intensity of the central line 4722 Å was assumed constant and the intensities of the other two lines were referred to it. The assumption was made that the lines fulfil the sum rule strictly *i.e.* that on taking the factor ν^4 into account the intensity ratios of the lines, for $k_0 l = 0$, are given by 100:65:22. The axis of abscissae gives the optical thickness of the source for the central line.

Experimental

The Schüler type hollow-cathode lamp that provided the light source was essentially the same as the one described in the paper by Mrs. Leś and Niewodniczański (1961). Within the cavity of the iron cathode of diameter 6 mm and length 40 mm a zinc cartridge of inner diameter 4.5 mm was placed. The voltage was derived from a *DC* stabilized power supply. The inert gas consisted of spectrally pure helium, which, was

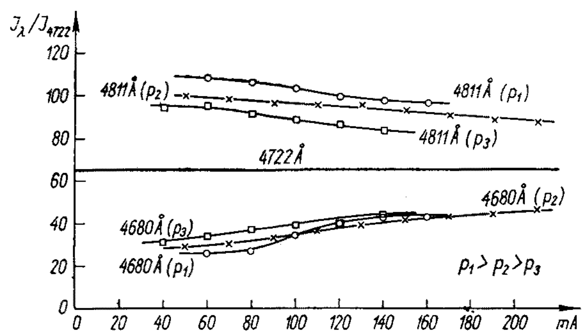

Fig. 4. Intensity ratios of the spectral lines of the visible ZnI triplet *versus* the intensity of the current in the Schüler lamp cooled with liquid nitrogen, for three different values of the helium pressure

introduced into the lamp by means of a dosimeter. The measurements were effected using a universal *VSU*-1 spectrophotometer made by Carl Zeiss, Jena. The relative sensitivity of the photocell for the wavelengths of the lines under investigation was determined with a normal lamp, taking account of the monochromator dispersion.

The dependence of the intensity ratios of the lines on the current was investigated for three values of the helium pressure $p_1 > p_2 > p_3$. The results are shown in Fig. 4. The intensity of the central line of wavelength 4722 Å was assumed constant and equalling 65.

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The background was evaluated for each measurement and was in most cases found equal to zero. Multiple measurements allowed to assess error at 1—3%. In the case of low current intensities the error is higher owing to the low intensity of the lines of ZnI in such conditions. Additionnally, account has to be taken of the error in determining the sensitivity of the photocell, which is of the order of 3% and is the same for all measurements.

Moreover, measurements were made with a zinc cartridge of diameter 3.8 mm as well as with a zinc layer deposited electrolytically directly on the iron cathode (with diameter 6 mm). The results, however, were found not to differ essentially from those obtained with the zinc cylinder of internal diameter 4.5 mm.

Discussion of results

The Schüler type hollow-cathode lamp fails to satisfy strictly the assumptions made as to the light source in the theoretical part of this paper. The aperture of the emerging beam amounted to about 3.5°. The discharge in the hollow cathode cannot be said to be homogeneous, unless we are making a gross approximation. Thus, the quantitative conclusions derived from a comparison of the experimental results and those of theoretical considerations may be controversial. On the other hand, the qualitative conclusions seem to be fully justified.

The shape of the dependence of the optical thickness of the source and of the ratios of the populations of the levels $^3P^\circ_{0,1,2}$ on the current intensity in the lamp can indeed be of an involved nature and can vary according to the pressure of the inert gas. Moreover, it is by no means sure whether the lines under investigation stricly fulfil the sum rule. That is why the interpretation of the experimental results is to some extent controversial.

Clearly, the optical thickness of the source increases with growing current intensity. This is corroborated by the experimental curves. The points of inflection of the latter can be interpreted as resulting from a change in the population ratios of the levels $^3P^\circ_{0,1,2}$ at a given value of the current intensity, or as resulting from a sudden increase in optical thickness of the source when a given value of the current is reached. The fact that the relative intensity I_{4811} of the line 4811 Å at a pressure of p_1 changes from a value of $I_{4811} > 100$ to one of $I_{4811} < 100$ in the vicinity of the point of inflection and that the curves representing the relative intensities of the line 4680 Å for the pressures p_1 and p_2 intersect one another are as many arguments in favour of our first interpretation.

From the shape of the experimental curves giving the dependence of the intensity ratios of our lines on the current it is possible to assess the relative populations of the levels $^3P^\circ_{0,1,2}$. At low current intensities, the population of the level $^3P^\circ_2$ would seem to differ but little from that of the level $^3P^\circ_1$, with $N_{^3P^\circ_2} < N_{^3P^\circ_1}$ at sufficiently high pressures of the gas and $N_{^3P^\circ_2} > N_{^3P^\circ_1}$ at lower pressures. The population of the level $^3P^\circ_0$ is less than that of the level $^3P^\circ_1$; at low current intensity and high pressure, the ratio $N_{^3P^\circ_0}/N_{^3P^\circ_0}$ is near unity and decreases with falling pressure and growing current intensity. At high values of the current, the dependence of the relative populations of the levels $^3P^\circ_{0,1,2}$ on the pressure is of an involved nature.

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As noted in the Introduction, an essential part in establishing the relative populations of the levels $^3P^\circ_{0,1,2}$ is played by inelastic collisions of Zn atoms in the states $^3P^\circ_{0,1,2}$ with atoms of the inert gas in the lamp, which give rise to transitions between the $^3P^\circ_{0,1,2}$ levels. These collisions become particularly important when the current intensity in the lamp is small, and thus the influence of the inelastic collisions with electrons on the population ratios is not considerable. The number of collisions between atoms grows with increasing pressure. The results of measurements show that for small values of the current the population ratios $N_{^3P^\circ_2}/N_{^3P^\circ_1}$ and $N_{^3P^\circ_1}/N_{^3P^\circ_0}$ decrease with increasing pressure, Hence, the transitions $^3P^\circ_2 \rightarrow {}^3P^\circ_1$ and $^3P^\circ_1 \rightarrow {}^3P^\circ_0$ whih stand in relation to collisions of the second kind possess higher probability than the inverse transitions $^3P^\circ_1 \rightarrow {}^3P^\circ_2$ and $^3P^\circ_0 \rightarrow {}^3P^\circ_1$. In accordiance with the Klein-Rosseland law, the cross-section for collisions of the second kind between particles with mutual energy E is always greater than that for collisions of the first kind between particles of mutual energy $E+\Delta E$. In the inelastic collisions accompanied by transitions between the states $^3P^\circ_{0,1,2}$ the partners are primarily atoms whose thermal energy is not greatly different from the energy of transition ΔE. A collision of the first kind can occur only if the energy of the atoms in collision is not less than the energy of transition. If the transition energy is lesser than the mean thermal energy of the particles and lies within the region of the downward branch of the Maxwell distribution curve, the number of atoms with energy slightly lesser than the transition energy is much greater than that of atoms with energy slightly above that value. This enhances the asymmetry of transition deriving from the Klein-Rosseland law. The probability of a transition from a higher level to a lower level is now much greater than the probability of the inverse transition. In accordance with our introductory remarks, this is precisely the situation for transitions between the $^3P^\circ_{0,1,2}$ levels of ZnI at the temperature of liquid nitrogen and of CdI at room temperature. The results of measurements of the intensity ratios of spectrol lines of the visible CdI triplet carried out in a water-cooled Schüler lamp by Mrs. Leś and Niewodniczański (1958) allow to evaluate the ratios of the populations of the $^3P^\circ_{0,1,2}$ levels as a function of the gas in the lamp, yielding about 0.7:1:2.7 at lower pressures and 0.7:1:2.0 at higher pressures. Thus, unexpectedly, the population ratios of the $^3P^\circ_{0,1,2}$ levels for CdI at room temperature differ markedly from those of the $^3P^\circ_{0,1,2}$ levels of ZnI at the temperature of liquid nitrogen. It would seem that intercombination transitions $^3P^\circ_1 \rightarrow {}^1S_0$ are primarily responsible for this divergence. The transitions in question lower the population of the level $^3P^\circ_1$ with respect to that of the levels $^3P^\circ_{0,2}$. The probability for an intercombination transition is about 12 times greater for CdI than for ZnI. It may also be of some importance that the slope of the Maxwell distribution curve of the particles' energy is approximately 4 times steeper for an energy of 0.048 eV at 77°K than for one of 0.145 eV at 290°K. Hence, the asymmetry between the probabilities for collisions of the first and second kinds is greater for ZnI at the temperature of liquid nitrogen than for CdI at room temperature.

It might seem queer that the population of $^3P^\circ_1$ differs but so insignificantly from that of the levels $^3P^\circ_0$ and $^3P^\circ_2$ both for ZnI and CdI notwithstanding the fact that the last two levels are metastable. Although, one should keep in mind that the intercombination line $^3P^\circ_1 \rightarrow {}^1S_0$ is strongly absorbed within the source and hence its effect in lowering the population of the level $^3P^\circ_1$ is small. Since the density of radiation with wavelength corresponding to the intercombination line is greater within the source than in its outer layers, the population ratios of the $^3P^{\circ}_{0,1,2}$ levels vary from one point of the source to another. Consequently, all conclusions regarding the population ratios of the levels $^3P^{\circ}_{0,1,2}$ are valid for some kind of mean values of the ratios in question.

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