

ISOTOPE SHIFTS BETWEEN EVEN ISOTOPES Zn 64, 66, 68 AND 70 IN THE VISIBLE Zn II LINES

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The isotope shifts between all four even stable isotopes of zinc, *i. e.* 64, 66, 68 and 70, have been measured in three visible Zn II lines, λ 5894.35 Å, λ 6214.59 Å and λ 7478.79 Å corresponding to $3d^{10}4p \ ^2P_{1/2,3/2}^0 - 3d^94s^2 \ ^2D_{5/2,3/2}$ transitions. Enriched isotopes were used. The light source was a Schüller lamp cooled with liquid nitrogen.

The paper gives a discussion on the relative isotope shifts calculated on the basis of obtained data. The influence of the volume effect on the magnitude of the isotope shift in the Zn II spectrum is considered.

Introduction

In the range of elements of medium atomic masses both the mass effects (normal mass effect and specific mass effect) and the volume effect are usually very small. The values of the measured shifts are often even smaller, because the directions of shifts due to the normal mass effect and the volume effect are oppositely oriented, hence, their action is at least partially cancelled out. The accuracy of such measurements is ordinarily too low to be able to draw any more general conclusions on their basis. An exception are lines associated with two-electron transitions, when one of the jumping electrons is a *d*-electron; unexpectedly large isotope shifts were found to occur on such lines; frequently exceeding ten times (or even more) the value of shifts observed in a normal (*i. e.* one-electron) spectrum of the same atom or ion. Although there are experimental difficulties caused by the relative weakness of this type of lines, they are, of course, especially advantageous in studies on isotopic structure of spectral lines.

One of the elements for which the two-electron transitions in mention here are known is zinc. Namely, particularly large value of isotope shifts have been found in the Zn II spectrum for the transitions

$$3d^{10}4p \ ^2P_{1/2,3/2}^0 - 3d^94s^2 \ ^2D_{5/2,3/2}$$

and

$$3d^94s^2 \ ^2D_{5/2,3/2} - 3d^{10}5p \ ^2P_{1/2,3/2}^0.$$

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Isotope shifts measured on spectral lines belonging to the first group of transitions (visible region of the spectrum) average about 90 mK (Schüler, Westmeyer 1933), whereas for the other group of transitions (the ultraviolet region of the spectrum) about 115 mK (Leś, Leś 1963).

Zinc, in its natural composition, contains four stable even isotopes and one odd isotope. The abundances are (Frisch 1958):

isotope	64	66	67	68	70
abundance	48.89%	27.81%	4.11%	18.56%	0.62%

As far as we know, all measurements of isotope shifts in the spectrum of zinc caused by a change in the number of nucleons in the nucleus by two performed up to now treated only three of the most abundant isotopes, *viz.* 64, 66 and 68. The relative position of the component corresponding to the isotope 70 is unmeasurable when zinc of natural composition is used, owing to the too small content of this isotope relative to the remaining ones (Schüler, Westmeyer 1933).

The aim of this work was to measure the isotope shifts in the three mentioned visible Zn II lines: $\lambda 5894.35 \text{ \AA}$, $\lambda 6214.59 \text{ \AA}$ and $\lambda 7478.79 \text{ \AA}$ for all four even isotopes with the use of enriched isotopes. The inclusion of the next even isotope in measurements is of particular importance in this case, for thanks to this we have to our disposal three (instead of two) values of isotope shift for a given line, what in turn lets us calculate two values (instead of one) of relative shifts. As is known, changes in the relative isotopic shifts are the data which lead to the most impartial conclusions regarding the nature of isotopic effects responsible for the measured values (Kuhn, Ramsden 1956, King *et al.* 1966).

Experiment

Light source. The light source was a Schüler lamp, described in the paper on isotope shifts in the ultraviolet lines of Zn II (Leś, Leś 1963). Now, however, a lens of larger focal length ($f = 135 \text{ mm}$) was mounted inside the lamp, what decreased losses of light energy inside the lamp even more and at the same time enabled achievement of a more uniform illumination of the spectrograph slit. The lamp cathode was provided with an easily exchangeable pure aluminium cylindrical insert precisely fitted to the internal walls of the cavity (Leś 1964). Special mixtures of zinc isotopes were evaporated onto this insert. The cathode was cooled with liquid nitrogen. Only helium was used as the carrier gas owing to the multitude of Ne, Ar and Kr lines in the spectral region. The exposure times range from 5 minutes to one hour; the current was 8 mA.

The isotopes. The enriched zinc isotopes were purchased in the Soviet Union by the Bureau for Isotope Distribution in Warsaw. The individual samples had the following degrees of enrichment:

isotope	64	66	68	70
percentage	91.6%	96.9%	95.7%	44.9%

Only the Zn 64 sample was in metallic form, the others being in the form of zinc oxide.

It is known from experiments that in electrodeless excitation the conditions of emission are better when the given substance is more volatile. Therefore, it is often worthwhile, even when a metal sample is available, to convert it into a more volatile compound before excitation (e.g. Corliss *et al.* 1957). However, in a Schüller lamp a major role in excitation is played by the cathode sputtering ability of the substance and its electrical conductivity. Preliminary research on the excitation of Zn II lines in the Schüller lamp with the use of ZnO, ZnCl₂ and metallic zinc revealed that in the case of ZnO and ZnCl₂ the emission efficiencies are comparable to each other, and much worse than when metallic zinc is used. Moreover, mixing ZnO or ZnCl₂ with silver dust in order to increase conductivity did not improve the results. Therefore, it was decided to reduce the oxides of the zinc isotopes to pure metal.

Zinc oxide reduction. It seemed that hydrogenation should be the best method for reducing small quantities of valuable oxides (oxides of enriched isotopes), for it does not give rise to any contamination of the sample during reactions with other substances. Unfortunately, application of this method for ZnO is very difficult, for on the one hand this reaction demands a high temperature ($t > 1000^{\circ}\text{C}$) because of the close affinity of zinc and oxygen and the durability of the ZnO compound, and on the other hand, metallic zinc at higher temperatures is extremely volatile. As attempts of reducing ZnO in a sealed quartz tube filled with hydrogen did not lead to positive results even at a temperature of 1300°C , reduction was carried out in the manner depicted in Fig. 1.

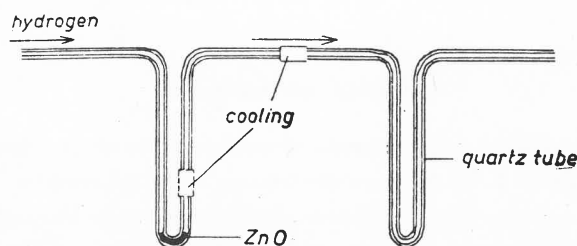


Fig. 1. Tube for the reduction of ZnO

A quartz tube of approximate diameter 5 mm was connected up *via* a number of washers and driers to a Kipp's apparatus generating hydrogen, and heated locally to over 1000°C by a gas burner. It was found that reduction has to be conducted very slowly and at the lowest possible temperature, for although the deoxidation process proceeds very slowly, the kinetic energy of the released metallic zinc is so high that just a slight transgression of a certain critical temperature causes unavoidable escape of zinc atoms out of the apparatus in the direction of the hydrogen stream. The excessively accelerated zinc atoms are extremely hard to "capture" somewhere along their path, even when very long labyrinths are used and hot barriers (heating the tube with another burner) or cold barriers (traps cooled by water with ice) are applied. Evidently, zinc atoms undergo elastic scattering in collisions with the quartz walls, for when the quartz tube is terminated with an Igelite tube the zinc atoms immediately conclude their migration, and become deposited on its walls. Hence, in order to prevent zinc atom acceleration cold water compresses were applied right next to the

heated area and moved along the tube as the reduced lot of metal deposited on the walls.

After the entire sample was reduced, the metallic zinc was easily localized on the walls of the tube under the cooling compress over a length of about 10 mm by means of a burner. This section of tube was then cut out, placed in a Mo sheet crucible matched earlier and, to avoid reoxidation, immediately inserted into the vacuum apparatus adapted for thermal evaporation of substances. Each sample contained from 0.5 to 2 milligrams Zn.

Other experimental details. The high resolution instrument used was a Fabry-Perot interferometer crossed with a medium-dispersion glass spectrograph. The interferometer plates of 5 cm diameter were overlaid with silver mirrors of $T = 6\%$ transparency in the yellow-red region and $T = 12\%$ in the infrared. The interferometer was placed in a thermostatic housing. Spacers of thicknesses from 10.70 to 26.15 mm were used.

The interference image of the $\lambda 5894 \text{ \AA}$ and $\lambda 6215 \text{ \AA}$ lines were recorded on ORWO WP1 plates, while I 750 plates were used in the infrared. The I 750 plates, before irradiation, were sensitized with a 5% ammonia solution for two minutes and then rinsed in methyl alcohol for 1.5 minute, all of this being done at a temperature lower than 9°C . The plates were developed in fine-grain Final Agfa developer.

All photographs were photometered by means of a self-recording Lirepho 2 microphotometer (C. Zeiss, Jena).

Results of measurements

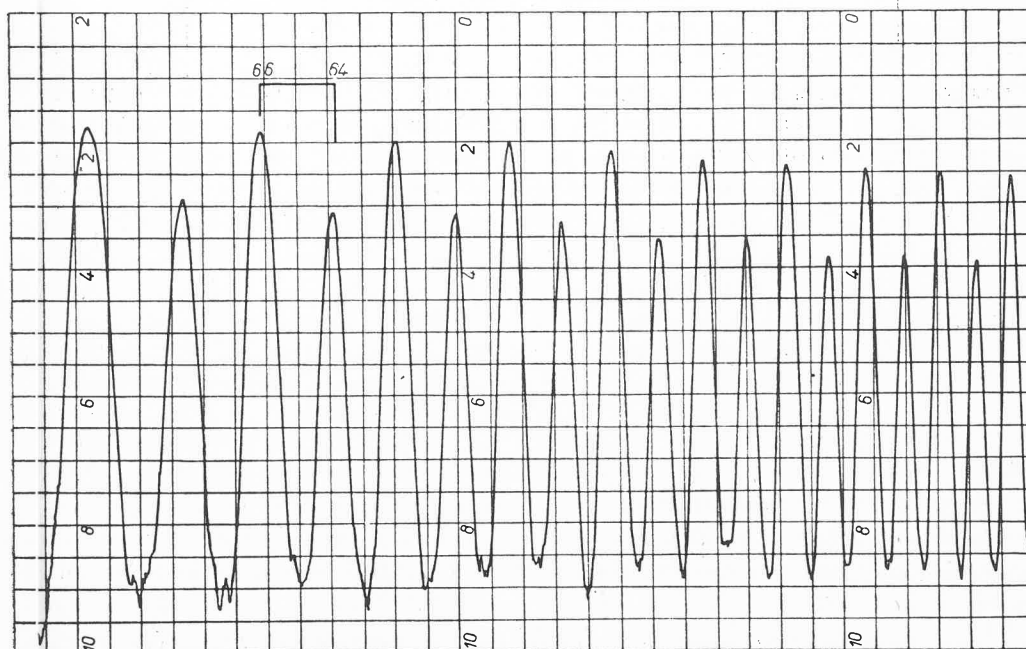
The results of immediate measurements of isotope shifts on the three examined Zn II lines are arranged in Table I. To measure the isotope shifts between the isotopes Zn 64, 66 and 68, a pair of these isotopes was placed successively in the lamp. The sample with the Zn 70 isotope contained all of the even isotopes, and there was 20.6% of the Zn 68 isotope. In order to improve the accuracy of the measurement, enough of the Zn 64 isotope was added to this sample for the intensity of the components corresponding to the 70 and 64 isotopes to be comparable and highest. It proved, however, that this was unnecessary, for in a majority of cases even the fringes corresponding to neighbouring isotopes were quite adequately separated. Typical microphotograms are shown in Figs 2 and 3. Both graphs depict the isotopic structure of the $\lambda 5894 \text{ \AA}$ line; in the first only the 64 and 66 pair of isotopes appear, whereas in the other all four even isotopes.

Table II gives the average values of the measured isotope shifts (column 4). The quoted error is the doubled mean error of the average value. The least accurate are results of measurements of the relative positions of fringes corresponding to the Zn 70 isotope, owing to the relatively low degree of enrichment. Another source of error on the $\lambda 7479 \text{ \AA}$ line issues from the rather large background of the I 750 plates, which were the only ones available, however.

For comparison, the results of measurements by Schüler and Westmeyer (1933) are given in column 3. It is seen that in some cases the discrepancies are quite large.

TABLE I

λ [Å]	Isotope pair	Dispersion region in 10^{-3} cm^{-1}	Number of fringes measured	Isotope shift (measured value) in 10^{-3} cm^{-1}
5894.35	64-66	191.20	20	95.7
	64-66	221.04	13	95.3
	64-68	467.29	17	184.0
	66-68	221.04	19	90.0
	64-70	382.85	14	269.7
	66-70	382.85	17	175.6
6214.59	64-66	221.04	16	96.0
	64-66	191.20	13	95.0
	64-68	467.29	14	185.8
	66-68	221.04	17	92.5
	64-70	382.85	17	266.0
	66-70	382.85	15	173.3
	68-70	382.85	3	79.2
7478.79	64-68	382.85	9	186.7
	64-68	467.29	7	186.6
	66-68	221.04	13	92.7
	64-70	382.85	6	269.5
	68-70	382.85	2	81.5

Fig. 2. Microphotometric record of the λ 5894.35 Å line for the isotope pair 66-64

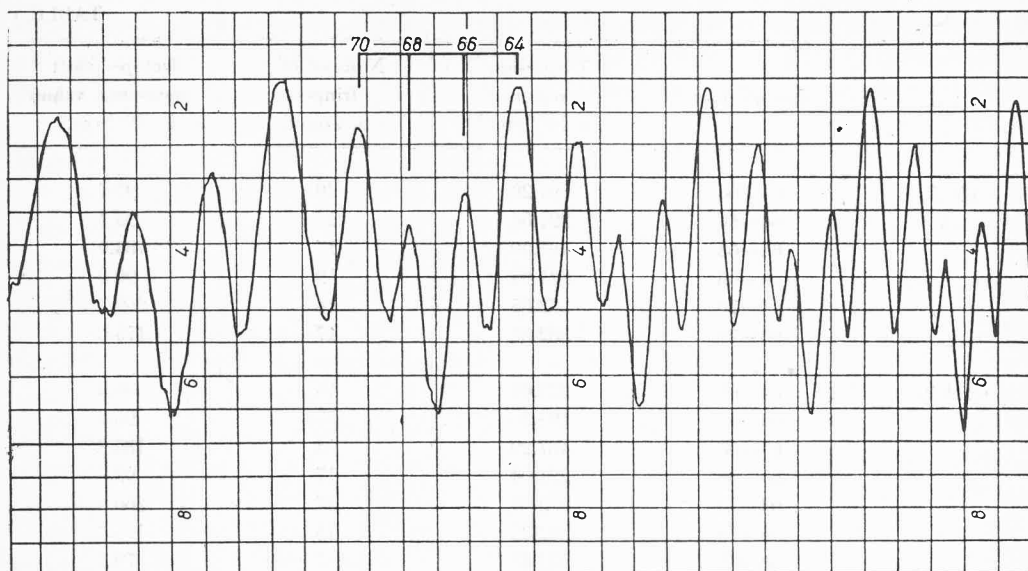


Fig. 3. Microphotometric record of the λ 5894.35 Å line for the isotopes 70-68-66-64

TABLE II

λ [Å]	Isotope pair	Schüler's and Westmeyer's measurements in 10^{-3} cm^{-1}	Present measurements (mean value) in 10^{-3} cm^{-1}	Calculated mass shift in 10^{-3} cm^{-1}	$\Delta\sigma_{\text{exp}} - \Delta\sigma_m$
5894.35	64-66	95	95.1 ± 0.8	4.38	90.7 ± 0.8
	66-68	94	89.7 ± 0.8	4.12	85.6 ± 0.8
	68-70		85.0 ± 1.0	3.88	81.1 ± 1.0
6214.59	64-66	95	94.8 ± 0.8	4.15	90.7 ± 0.8
	66-68	94	91.7 ± 0.8	3.91	87.8 ± 0.8
	68-70		80.5 ± 1.0	3.68	76.8 ± 1.0
7478.79	64-66	96	93.9 ± 1.0	3.45	90.5 ± 1.0
	66-68	92	92.7 ± 1.0	3.25	89.5 ± 1.0
	68-70		82.2 ± 1.2	3.06	79.1 ± 1.2

Discussion of results

It appears to be indisputable that the exceptionally large values of shifts observed at two-electron transitions with participation of a *d*-electron is primarily caused by the specific mass effect (*cf.* Elbel, Fisher 1961), for both the normal mass effect and the volume effect are very minute. Although there are still no formulae for calculating this effect for multi-electron atoms, general considerations imply that, as in the normal mass effect, the shift of the term induced by the specific effect is proportional to $1/M$, M being the mass of the

nucleus (Kuhn 1962). Hence, if the specific mass effect is responsible for the measured isotope shift, the shifts for three successive isotopes of the element in question differing from one another by the same number of nucleons should satisfy the relation (Kopfermann 1956)

$$\frac{\Delta\sigma_{12}}{\Delta\sigma_{23}} = \frac{M_3}{M_1} \quad (1)$$

Column 6 of Table II gives the values of isotope shifts observed in the examined Zn II lines after subtraction of the normal mass effect. With the use of these values the relative isotope shifts were calculated for the four even zinc isotopes; these are arranged in Table III, which also presents the theoretical values calculated from Eq. (1). This table shows that:

1) there is complete agreement between experimental data and theoretical predictions only for the $\lambda 5894 \text{ \AA}$ line;

2) for a fixed set of three isotopes the relative isotope shifts on both remaining lines are the same (the discrepancies lie within experimental error), but there are distinct differences for different sets of three isotopes (discrepancies lie beyond limits of error).

TABLE III

Relative isotope shifts	$M_3:M_1$	Experimental values		
		5894.35 \AA	6214.59 \AA	7478.79 \AA
$\frac{\Delta\sigma_{64-66}}{\Delta\sigma_{66-68}}$	1.06	1.06	1.03	1.01
$\frac{\Delta\sigma_{66-68}}{\Delta\sigma_{68-70}}$	1.06	1.06	1.14	1.13

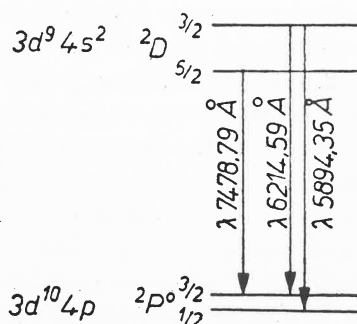


Fig. 4. Energy levels and transitions related to the visible triplet of Zn II

In consideration of the diagram of energy levels of the transitions in question (Fig. 4) and the character of these changes, the following explanation of the observed regularities, linked with the volume effect, presents itself:

Re 1) From considerations on the volume effect it is known that it appears in practice only for configurations having s and $p_{1/2}$ electrons, for it is only for these electrons that the

wave functions have non-zero values at the position of the nucleus (this is discussed in detail, for example, in the paper by Schawlow and Townes 1955). Hence, in the case of the $\lambda 5894 \text{ \AA}$ line the volume effect will shift both the upper energy level, corresponding to the $3d^9 4s^2$ configuration, and the lower one, corresponding to the $3d^{10} 4p_{1/2}$ configuration. Indeed, in the configuration of the ${}^2D_{3/2}$ level there are even two s -electrons, while in the ${}^2P_{1/2}^0$ case only one, and this not even being an s -electron but $p_{1/2}$. Notwithstanding, bearing in mind the fact that the energy levels of the $3d^{10} 4p$ configuration have a much lower corresponding energy than the levels of the $3d^9 4s^2$ configuration, it seems quite probable that the action of the volume effect on the upper and lower levels of the $\lambda 5894 \text{ \AA}$ line is at least reduced to a considerable extent, if not totally. (Isotope shift due to the volume effect diminishes with increasing principal quantum number like n^{-3} (Fradkin 1962), but the transitions considered here are two-electron ones and, thus, the energy values of the energy levels should be taken into account here, rather than quantum numbers labelling these levels). This is why the relative isotope shifts are in agreement with theoretical values.

Re 2) The lower level of the $\lambda 6215 \text{ \AA}$ and $\lambda 7479 \text{ \AA}$ lines corresponds to $3d^{10} 4p_{3/2}$ configuration, for which the shift induced by the volume effect is undoubtedly insignificant. Hence, in the case of both of these lines the volume effect of the ${}^2D_{3/2}$ and ${}^2D_{5/2}$ levels will decrease the isotope shift caused by mass effects, what in turn will affect the value of relative shifts. It is seen in Table III that the relative isotope shifts are practically identical for both considered lines, what is in accord with the assumption that the volume effect is responsible for deviations (Kuhn 1962). On the other hand, the directions of the observed deviations for each set of three zinc isotopes may be logically associated with experimental data on Coulomb excitation of these isotopes. Namely, experiments show that in line with the isotope sequence $64 \rightarrow 66 \rightarrow 68$ the deformation of these nuclei becomes smaller, whereas when going from Zn 68 to Zn 70 it increases again (Stelson, McGowan 1962).

Now, numerous general studies (Stacey 1966) have shown that increased deformation of a nucleus causes, as a rule, an increase in the volume isotopic effect. Therefore, as we go from Zn 64 to 68 the proportion of the volume effect influence on the lines under consideration should become smaller. Hence, the resultant isotopic effects should increase, in result relative shifts of the Zn 64, 66, 68 isotopes can be smaller than theoretically predicted, what actually is seen. Reasoning along the same lines made for the Zn 66, 68, 70 isotopes leads to the conclusion that in this case the relative shifts should be larger than the ratio M_{70}/M_{66} , what is also in complete agreement with the obtained results.

The considerations developed here are of course, only of a qualitative nature. For the purpose of improving the accuracy of the results obtained in this work, as regards isotope shifts, analogous measurements are to be performed in the nearest future with enriched isotopes on the ultraviolet lines of Zn II which have common $3d^9 4s^2 {}^2D_{5/2, 3/2}$ levels with the lines examined here.

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