INTENSITY RATIO IN THE "FORBIDDEN" DOUBLET λ 2958 AND λ 2972 Å. U. IN THE SPECTRUM OF ATOMIC OXYGEN

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The aim of the reported investigations was to discover in the O I spectrum the appearance of the "forbidden" electric quadrupole line λ 2958 Å. U. and afterwards to measure the ratio of the intensity of this line to that of the second line in the "forbidden" O I doublet, which is the previously observed magnetic dipole line λ 2972 Å. U.

This doublet was obtained in the radiation of a specially constructed discharge tube filled with a mixture of helium and oxygen. In the first part of this work optimum conditions of the discharges were found in order to obtain the much fainter component of the "forbidden" doublet, the line λ 2958 Å. U. which was never observed before. In the second part of the work the intensity ratio of these „forbidden" lines in the doublet was experimentally found to be $1:45 \pm 30\%$, which is in agreement in order of magnitude with the theoretically expected ratio $1:100$.

1. *Introduction*

The fundamental electron configuration of the neutral oxygen atom is $1s^2\ 2s^2\ 2p^4$. The four equivalent $2p$ electrons of this configuration determine five different energy states, all of the same even parity, namely ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, ${}^1D_2$ and ${}^1S_0$, of which the triplet state ${}^3P_2$ is the ground state of the atom. According to the selection rules no transition between these energy states is allowed for the electric dipole radiation.

Fig. 1 represents the diagram of the energy levels in O I, all belonging to the same ground electron configuration. Transitions which are forbidden for the electric dipole radiation but allowed for the magnetic dipole and the electric quadrupole radiation are shown by arrows, *MD* indicating the magnetic dipole and *EQ* — the electric quadrupole transitions. The figures designate the corresponding wave-lengths in Å. U., the figures in brackets give the theoretically evaluated transition probabilities in sec^{-1}. The green line λ 5577 Å. U. and the red triplet λ 6300, λ 6363 and λ 6292 Å. U. have been well known for many years in the spectrum of aurorae, Novae, planetary nebulae and night sky radiation. They were obtained much later under laboratory conditions. The line λ 5577 Å. U. was obtained for the first time in electrical discharges by McLennan and McLeod in 1927, the red triplet by Hopfield in 1931. The ultraviolet lines λ 2958 and λ 2972 Å. U. in the astrophysical light sources have not been observed thus far, since they are situated at the border of the spectral transmittance of the earth's atmosphere. The line λ 2972 Å. U. was obtained in laboratory conditions by Kaplan in 1939. The line λ 2958 Å. U. has been obtained for the first time in the present work. Hence all possible "forbidden" O I lines which correspond to the transition between energy states belonging to the ground electron configuration have now been obtained in the laboratory.

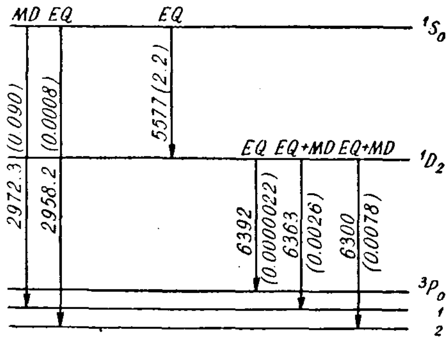

Fig. 1. Radiative transitions in the oxygen atom between energy levels belonging to the ground electron configuration $1s^2 2s^2 2p^4$.

The experimental determination of the ratio of intensities of the components of the ultraviolet O I "forbidden" doublet is of great importance, since both these lines are due either to the pure magnetic dipole or to the pure electric quadrupole radiation and correspond to the transitions starting from the same initial energy level.

In such measurements the theoretically expected ratio of the transition probabilities associated with radiations of different nature and polarity can be chequed.

2. *Apparatus and method used for obtaining the "forbidden" O I lines*

The method applied in the present work was not a repetition of any one previously used for similar purposes. The apparatus was designed to enable the discharge tube to work as well at high current density using the electrodes, as at high frequency electrodeless discharges, similar to the method developed by one of us in 1933 for the excitation of "forbidden" lines (Niewodniczański 1934).

The discharge tube has the shape of an inverted letter *Π* (see Fig. 2). The vertical branches of the tube are closed by glass containers enclosing cylindrical electrodes E_1 and E_2 made of pure aluminium foils. One side surface of each electrode has an area of 120 cm^2. In order to ensure more efficient cooling of the electrodes their outer surfaces are in close contact with the glass walls of containers. The horizontal part of the discharge tube consists of a tube 45 cm long and with an inner diameter of 0.6 cm. It has a quartz window Q at one end in front of which the slit of the spectrograph was placed. Owing to the strong heating during the discharges the whole tube was made of hard Jena glass and was placed in a metal vessel with flowing water. Such a shape of the discharge tube is convenient, since with a gas mixture of properly chosen pressure and composition one can see in the spectrum of the discharges in the horizontal tube the spectral lines of atomic oxygen and helium without any stronger molecular oxygen bands. The dissociation of oxygen molecules takes place mainly in the vertical tubes connecting the cylindrical electrode containers with the horizontal part. Spectroscopically

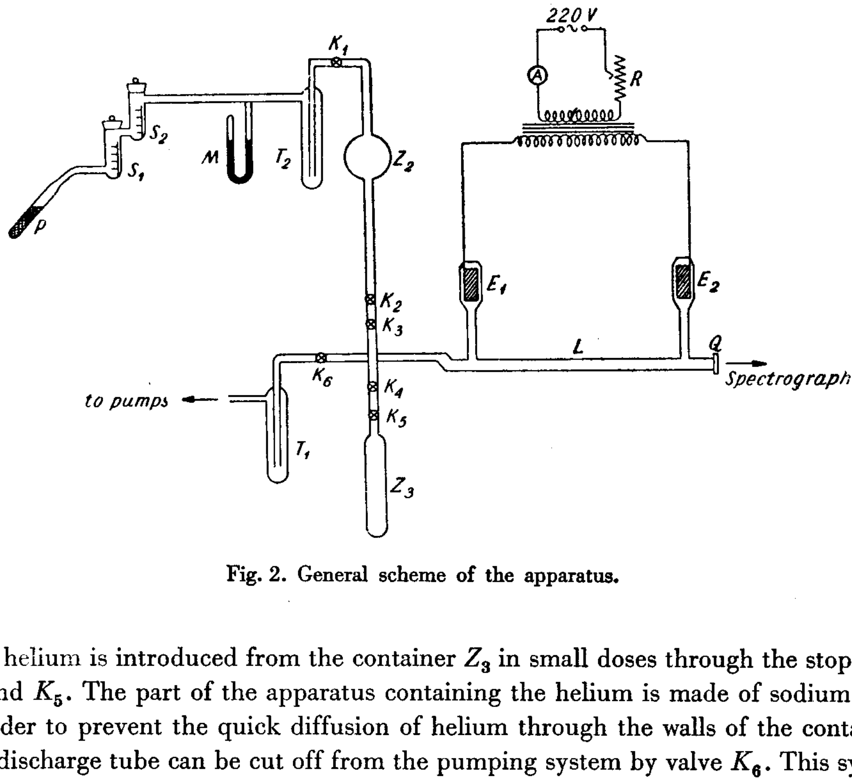

Fig. 2. General scheme of the apparatus.

pure helium is introduced from the container Z_3 in small doses through the stopcocks K_4 and K_5. The part of the apparatus containing the helium is made of sodium glass in order to prevent the quick diffusion of helium through the walls of the container. The discharge tube can be cut off from the pumping system by valve K_6. This system is situated behind a liquid air trap T_1 and consists of a 3-stage mercury diffusion pump and a 2-stage rotary oil pump. The vacuum obtained was always better than 10^{-4} mm Hg. Oxygen was introduced from the container Z_2 in small doses using the stopcocks K_2 and K_3. The container Z_2 is filled after opening the stopcock K_1 connecting it with the system for oxygen production. The oxygen is obtained by heating $KMnO_4$ in a test tube made of resotherm glass and connected by a ground glass joint. The produced oxygen is transmitted through dryers S_1 and S_2 containing KOH and through the trap T_2 cooled by a mixture of solid CO_2 and acetone. The pressure of the oxygen in the container was measured with a mercury manometer M.

At optimum conditions the discharge tube was filled with helium at a pressure of about 4 mm Hg and a small quantity of pure oxygen so as to maintain the ratio of the partial pressures of oxygen and helium equal to about 1:10. Voltage up to 6000 V A. C. was applied to the electrodes of the discharge tube. The power of the discharge current could be altered by using a variable resistor R on the primary side of the transformer. The highest power applied to the discharge tube was 1.5 kW, which corresponded to a current density of 0.7 A/cm^2 in the horizontal tube.

A considerable disadvantage of the apparatus was the lack of possibility of measuring the partial pressure of gases in the discharge tube.

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3. *Results of the experiments*

After final adjustment of the apparatus various spectral exposures were taken. The discharge tube was filled either with pure oxygen or with helium and oxygen mixtures of different total and partial pressures. The exposures were made using a high luminosity (1:5) quartz spectrograph. In spite of all precautions the spectra contained, besides oxygen and helium, also some Hg, H, N and N_2. The source of these impurities was probably the $KMnO_4$ of insufficient purity that was used for producing the oxygen.

The best exposures containing the sought-for line λ 2958.2 Å. U. and the line λ 2972.3 Å. U. were obtained when the discharge tube was filled with helium at a pressure of about 3 mm Hg and oxygen at about 0.5 mm Hg and when the density of the current in the horizontal tube was about 0.5 A/cm^2. The exposures lasted from 1 to 3 hours. There was no reason to extend the time of exposures over that limit because after a longer discharge the "forbidden" oxygen lines gradually disappeared. This behaviour can be explained by the considerable diminishing of the amount of oxygen in the discharge tube owing to the oxidation of the strongly heated electrodes. This destroyed the optimum ratio of partial pressures of helium and oxygen. For this reason it would be more reasonable to apply electrodeless discharges or continuous circulation of oxygen.

In the close neighbourhood of the "forbidden" oxygen lines which were being searched 6 lines were identified which were used for constructing the exact dispersion curve in the spectral region under consideration. These lines were: Hg — λ 2967.5 and λ 2975.2 Å. U., He — λ 2945.1 Å. U. and the second positive series of N_2 bands λ 2953.2, λ 2962.0 and λ 2976.8 Å. U. Since as reference lines both molecular bands and atomic lines were used, visual determination of their positions by means of a comparator could not give satisfactory results. Therefore profiles of all reference lines as well as of the O I lines were measured with a microphotometer and the centres of gravity of all these lines were taken into consideration (see Fig. 3). The position of a spectral line determined in this manner contains an error of $\pm$ 0.003 mm which gives an error of $\pm$ 0.1 Å for the spectral region under consideration. The positions of the reference lines determined in this way were used to prepare the dispersion

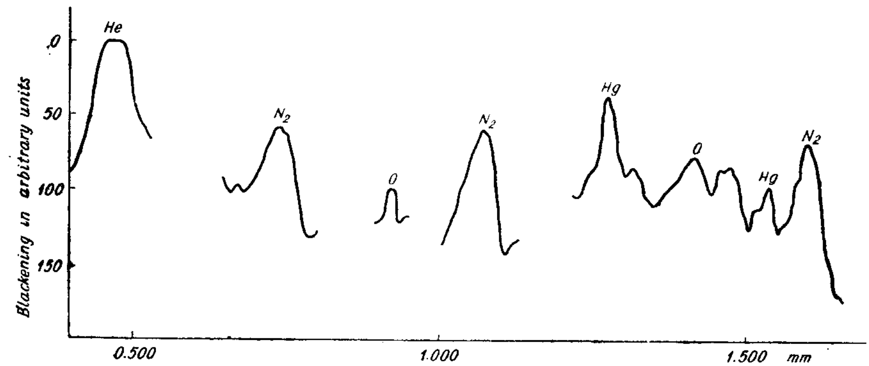

Fig. 3. Microphotometer records of profiles of the investigated and reference spectral lines.

curve (Fig. 4). Hence the wave-lengths of the two "forbidden" oxygen lines obtained are:

$$\text{Transition } {}^1S_0 - {}^3P_1: \quad \lambda = (2972.2 \pm 0.1) \text{ Å. U.,}$$
$$\text{Transition } {}^1S_0 - {}^3P_2: \quad \lambda = (2958.1 \pm 0.1) \text{ Å. U.}$$

These wave-lengths are in agreement with those evaluated from the values of terms given by Hopfield (1931): λ 2972.3 and λ 2958.2 Å. U.

Thus the presence in the spectrum of atomic oxygen of the "forbidden" electric quadrupole line λ 2958.2 Å. U. has been proved.

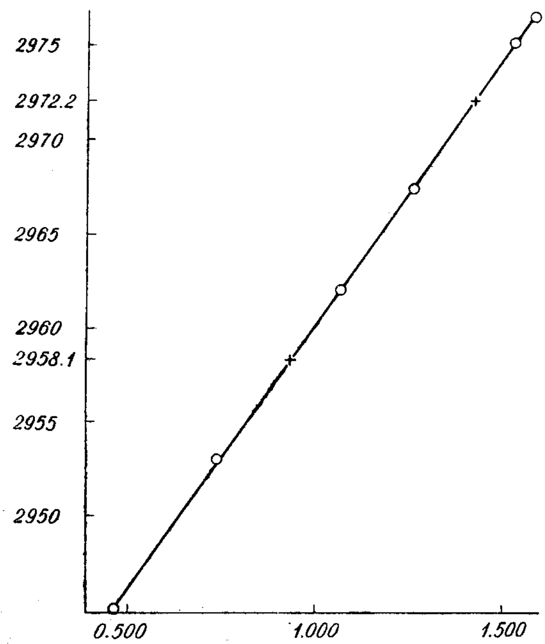

Fig. 4. Dispersion curve of the spectrograph in the region of the "forbidden" O I lines λ 2972.2 and λ 2958.1 Å. U.

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4. *Measurements of the intensity ratio in the "forbidden" ultraviolet* O I *doublet*

In the experiments reported above the newly discovered electric quadrupole line λ 2958 Å. U was considerably fainter than the previously known magnetic dipole line λ 2972 Å. U. Subsequent experiments were undertaken in order to measure the ratio of the intensities of these two lines in the "forbidden" O I doublet.

For this purpose more than 60 spectral exposures were taken using a rhodiumised seven-step filter giving in the investigated spectral region the following weakening ratios: 1:2.6:4.6:7.3:12.5:20.0. Since the measured lines have sufficiently close wave-lengths it was possible to apply the method of monochromatic photographic spectrophotometry. This was chequed by the parallelism of the density curves drawn for both these lines.

For the determination of the intensity ratio of these lines only 3 spectrograms could be used. These had an exposure time of 3 hours and a current density in the horizontal tube of 0.6 A/cm^2, the partial pressures of helium and oxygen being 3 mm Hg and 0.5 mm Hg, respectively. Under these conditions the fainter line λ 2958 Å. U. could be seen on the photographic plate in 4 steps of the filter, which made possible the measurement of the ratio of intensities. The mean value of the intensity ratio obtained in these measurements is:

$$I_{2958} : I_{2972} = 1:45$$

Owing to the very small intensity of the fainter component of the doublet this result contains a rather high statistical error of about ± 30%. The order of magnitude of the obtained ratio is in accord with the theoretically expected value of 1:100.

The relatively somewhat higher intensity of the electric quadrupole line may be caused by the specific conditions in the discharge tube. The possibility of the electric enhancement of some transitios in the oxygen atoms cannot be excluded.

КРАТКОЕ СОДЕРЖАНИЕ

Л. Лишка и Г. Неводничанский, *Отношение интенсивностей в запрещенном дублете λ 2958 и λ 2972 Å в спектре атомного кислорода.*

Целью работы было открытие в спектре OI наличия запрещенной электрической квадрупольной линии λ 2958 Å и измерение отношения интенсивностей этой линии и другой в запрещенном дублете атомного кислорода магнитной дипольной линии λ 2972 Å, которая наблюдалась раньше. Этот дублет был получен в спектре излучения специально построенной разрядной трубки, наполненной смесью гелия и кислорода. В первой части работы были найдены оптимальные условия разряда с целью получения весьма слабой составляющей запрещенного дублета линии λ 2958 Å, которая раньше не наблюдалось. Во второй части работы было экспериментально получено отношение интенсивностей этих запрещённых линий 1 : 45±30%, которое по порядку величины сходно с теоретически предвиденным отношением 1 : 100.

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