which happened to be the first near which collision bands were found, is the only one thus far which has associated with it two separate maxima, and the only one with discrete vibration bands on the long wave-length side. Molecular theory shows that both the upper and lower states of many of the bands which have been studied should be represented by more than one potential curve; as a rule these must so nearly coincide that observation of separate maxima is impossible. The absence of vibration bands in Cd and Tl may be due simply to the high temperature necessary to obtain an adequate metal vapor pressure in a discharge tube, but it is strange that none were found near other Hg lines.

In conclusion the author wishes to acknowledge his deep gratitude to Professor Otto Oldenberg, under whose direction and inspiration this work was done.

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A Spectroscopic Study of the Magnetron Discharge

Overton Luhr and Frank J. Studer
Union College, Schenectady, New York
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The spectra from magnetron discharges in various gases have been studied with the aim of investigating the efficiency of this type of source in producing the higher states of ionization. The study of helium was of particular interest since in a mass-spectrograph study of this type of discharge made by one of the writers, it was impossible to distinguish the He^{++} from the H_2^+ ions which were always present. The discharge between a tungsten filament and a nickel cylinder was operated at widely varying voltages, currents and gas pressures. The most satisfactory results were obtained at about 250 volts, 0.5 ampere and pressure of 0.1 mm of mercury. A magnetic field of the order of 150 oersteds parallel to the axis of the cylinder greatly intensified most of the lines in the region of the spectrum investigated between 7000 and 2000A. Higher members of the series in both the He I and He II spectrum were brought out with good intensity compared to results obtained with other types of discharge. The magnetron should thus be an efficient source of He^{++} ions. In the case of nitrogen and mercury many lines of the N II, N III, N IV and Hg II spectra were identified.

Introduction

The products of ionization from a magnetron type discharge designed to produce doubly ionized helium by multiple electron impact has been investigated with a mass spectrograph by one of the writers.[1] Such a source, consuming moderate power, would be of use in nuclear studies where alpha-particles were desired for bombardment. There was some doubt about the results because of the continued presence of H_2^+ ions as an impurity which could not be differentiated from He^{++} with the mass spectrograph used. There was evidence that at least two percent of the ion current was due to He^{++} but spectroscopic corroboration of this result seemed desirable. The present investigation was therefore undertaken primarily to obtain spectroscopic evidence for the presence of He^{++} ions by a study of the intensity of the He II spectrum.

In addition the magnetron discharge seemed to offer some advantages as a spectroscopic source. Due to the axial magnetic field, the electrons spiral close to the cathode, and make many impacts in a small region. It is therefore to be expected that the intensity of the radiation would be great in this region and since the electrons attain their maximum energy (given by the full discharge voltage) in passing through the thin positive ion sheath surrounding the cathode, it should be possible to study the excitation of weak lines with electrons of known energy. Furthermore, with intense ionization close to the cathode there should be a relatively high probability that an electron would strike an atom which had already been ionized and thus produce excitation or highly ionized atoms by multiple electron impact. So a second purpose in this investigation was to find out whether such a source might be of use to spectroscopists for the

[1] Luhr, Phys. Rev. 49, 317 (1936).

purpose of exciting ionized spectra. Most of the experiments were concerned with helium, but some investigation was made of the spectra of hydrogen, nitrogen and mercury in such a discharge.

Apparatus and Experimental Procedure

The discharge tube which was finally adopted as most satisfactory was of simple design and is shown in Fig. 1. The anode A was a cylinder of 10 mil sheet nickel, 4 cm long and 4 cm in diameter. A tungsten filament was used so that the discharge voltage could be controlled, and it was found that a piece of 16 mil wire 12 cm long wound into the form of a small spiral was satisfactory. To avoid shorting of the filament and cylinder leads due to sputtering, they were brought into the tube through separate stems. The quartz window B was located 10 to 15 cm from the discharge so that it would not be darkened by sputtered metal. In later tubes this window was pointed directly at the filament as it was found that the spectral lines were most intense in that region of the discharge. The continuous spectrum from the filament was of negligible intensity in the ultraviolet, though it gave trouble in the visible region. For work in the visible region tubes were built with the window pointing to one side of the filament, and in one tube end-plates were placed over the cylinder, with a slit cut in front of the window. However, some continuous radiation from the filament was always present, though the stronger lines stood out well against this background.

The life of a tube, barring accident, was limited by the sputtering away of the filament due to positive ion bombardment. With hydrogen and helium the walls of the tube became blackened in a short time, though the filament remained intact for at least 30 or 40 hours of operation. In the case of nitrogen and mercury the rate of sputtering was much higher, and 5 to 10 hours of operation would probably be the limit.

When the tube was operated as a magnetron it was surrounded by a water-cooled solenoid consisting of 800 turns of 45 mil enameled copper wire. After a number of trials it was found that maximum intensity of most lines was obtained with a field of 150 oersteds for a discharge voltage of 200.

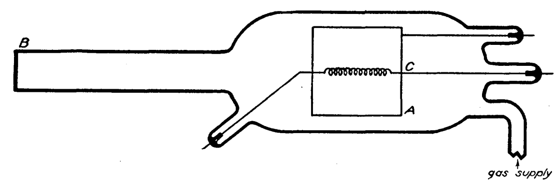

Fig. 1. Diagram of the experimental tube.

Photographs were taken with a small Bausch and Lomb quartz instrument whose dispersion was 125A per mm in the red, and 8A per mm at 2200A. Visual study was made with a constant deviation instrument.

Care was taken to obtain as high a degree of purity as possible in the gases used. The tube was baked out at 450°C for about two hours and the metal parts outgassed by electron bombardment from the filament. Tank hydrogen and nitrogen were purified by passage through hot copper, P_2O_5, and two liquid-air traps. The helium was obtained highly purified from the General Electric laboratories and was passed through a charcoal trap immersed in liquid air and two liquid-air traps before admission to the tube. Except in the case of mercury the tube was not sealed off and fresh gas was admitted after each exposure. Under these conditions lines due to impurities were always weak if there were any present at all; though in the case of helium, hydrogen was always present as indicated by the presence of several members of the Balmer series.

Results

Helium

Some twenty spectrograms, mostly of helium, were taken with the quartz spectrograph, in addition to observations in the visible region with the constant deviation spectrometer. The lines of ionized He were of special interest, but only in one or two cases could lines of the Pickering series be identified owing to the strong continuous spectrum in the region where the series is strong and also due to the continued appearance of the Balmer series. The λ4686 ionized series was quite intense, however, and was therefore employed as a qualitative measure of the concentration of He^{++} ions.

Typical spectrograms of the He magnetron are reproduced in Fig. 2, (a)–(f) inclusive, and a

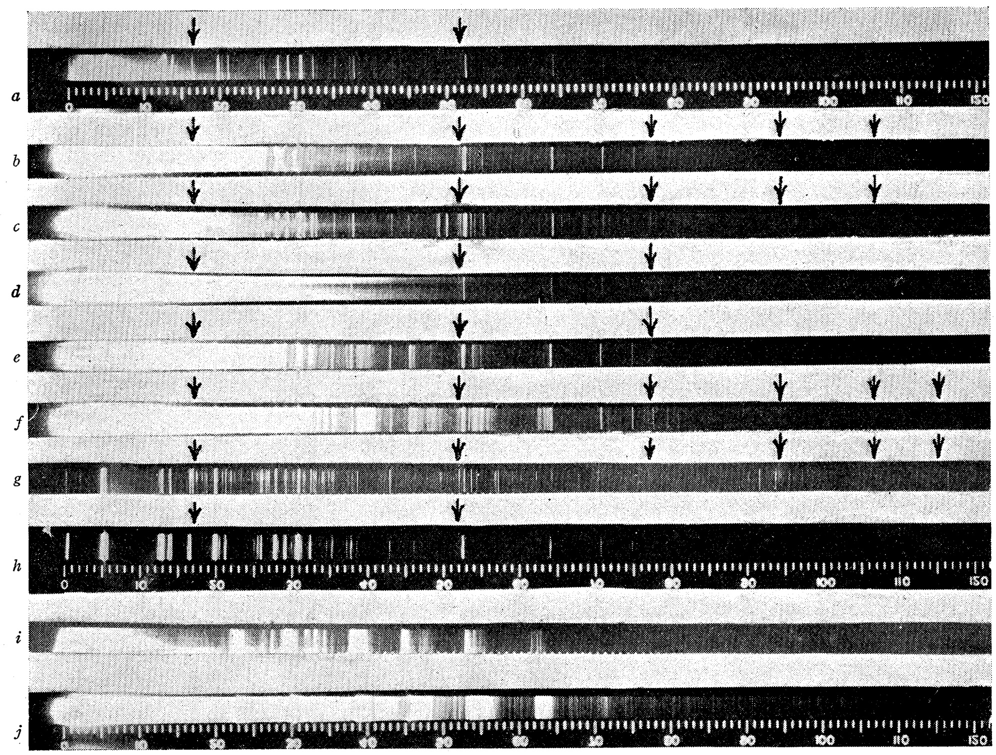

FIG. 2. Typical spectrograms. Arrows indicate position of 4686 series lines of ionized He visible on the original plates. Principal triplet series starts with λ3889 at 30.8 on the scale and ends at about 83 on the scale at λ2645.

summary of the experimental conditions and results are given in Table I.

The intensity of the higher series members in the magnetron seemed to compare favorably with that obtained in other types of discharge, but in order to get some direct comparison a capillary tube was constructed and the He spectrum photographed. The condensed capillary discharge in particular has been employed[2] to obtain ionized spectra. Fig. 2(*g*) shows the results obtained with an hour exposure using a 10,000 volt transformer and a 4.0 mm spark gap. Similar results for the uncondensed capillary discharge are shown in (*h*).

Hydrogen, nitrogen and mercury

In order to investigate the possibility of employing the magnetron discharge to obtain the higher series members and ionized spectra of other gases, the spectra of hydrogen, nitrogen and mercury have been observed. As might be expected, the source did not prove satisfactory in bringing out the Balmer series in hydrogen as the concentration of atomic hydrogen in such a discharge is small.[1] Only six or seven Balmer lines were identified in an hour exposure. The secondary spectrum was relatively strong. The presence of continuous radiation in the ultraviolet was suggested by a violet fluorescence observed on the quartz window, and this showed up on the plates rather strongly throughout the whole region down to 2200A.

Results for nitrogen are shown in Fig. 2(*i*) and (*j*). The strong bands present could probably be suppressed and the nitrogen lines brought out more strongly by employing mixtures of helium and nitrogen[3] but this was not tried.

The mercury spectrum was observed only in the visible region with the constant deviation spectrograph and no photographs were taken. The pressure, though not carefully controlled,

[2] Evans, Phil. Mag. **29**, 284 (1915).

[3] Duffendack and Wolfe, Phys. Rev. **34**, 409 (1929); Merton and Pilley, Proc. Roy. Soc. **A107**, 411 (1925).

TABLE I. *Summary of experimental conditions and results for spectrograms shown in Fig. 2. (a) Window pointed to one side of filament. All other spectrograms shown were taken with window pointed directly toward filament. (b) About the most favorable conditions of operation for bringing out higher members of the series. (c) High pressure gives greater intensity of lower series members, but higher members less intense. Many faint unidentified lines. (d) All lines much less intense without magnetic field. (e) Lower voltage results in weakening the ionized series and higher members of the unionized series. (f) Larger current and longer exposure brings out a few more high members of the series. (g) Only 5 of 4686 series observed in spite of high relative intensity of 4686 itself. He I partially suppressed. (h) Higher series members of He I weaker than in the magnetron.*

Plate No.	Gas	Discharge Voltage	Discharge Current (ma)	Magnetic Field (Oersteds)	Pressure (mm)	Exposure Time	No. Members Prin. Trip Series	No. Members 4686 Series
a	He	220	500	150	0.08	1 hr.	6	2
b	He	220	500	150	0.10	1 hr.	10	5
c	He	260	500	150	1.0	1 hr.	6	5
d	He	260	500	0	0.14	1 hr.	6	3
e	He	100	500	150	0.14	1 hr.	8	3
f	He	220	800	160	0.08	2 hr.	12	6
g	He	condensed capillary discharge			0.7	1 hr.	7	5
h	He	uncondensed capillary discharge			0.7	1 hr.	8	2
i	N	150	500	350	0.06	1 hr.	50 lines due to N II 10 lines due to N III 6 lines due to N IV	
j	N	220	500	160	0.3	1 hr.		

was of the order of a few thousandths of a mm; discharge voltage was 250 and current 0.30 ampere. Application of the magnetic field brought out many lines that were not visible otherwise, about sixty being recorded in the region 7000 to 4000A. Of these, 23 were identified as being due to Hg I, 25 to Hg II, and the remainder have not been identified.

Discussion

It has been shown by Bleakney and Smith[4] that a maximum of 0.55 percent of the ions in helium are He^{++} when ionization is produced by single electron impact. Therefore it would seem that an efficient source of He^{++} must depend on multiple electron impact. Very little is known about the process of ionization in successive stages, but it is usually assumed to be fairly efficient. In the case of helium the problem then resolves itself into one of obtaining as high a degree of ionization as possible, then removing the remaining electron from the He^{+} ions by a second impact. Rough calculations indicate that only about one or two percent of the gas is ionized in a magnetron discharge such as that described here. However, this percentage may be much higher in the intense region of ionization close to the filament. This conclusion is borne out by the increased intensity of the $\lambda 4686$ series when the window was pointed directly at the filament.

It is obviously impossible to make any quantitative estimate of the concentration of He^{++} ions from spectroscopic results. But these results do indicate the best operating conditions. Thus a fairly low pressure (about 0.1 mm) is evidently desirable since the higher series members are brought out best under those conditions. However, the pressure must not be too low or the electrons escape from the region of intense ionization without making any impact. At first it was surprising that the lower members of the 4686 series should be brought out stronger at much higher pressures (about 1.0 mm) since the percentage of gas ionized under these conditions is presumably smaller. But the intensity of those lines may be due principally to single electron impact, and at any rate, the fact that the higher members are weaker would indicate that high pressures are not desirable for the production of

[4] Bleakney and Smith, Phys. Rev. **49**, 402 (1936).

He^{++} ions. The spectroscopic results also indicate that the electrons should have an energy of two to three hundred volts, but higher energy does not seem desirable, especially if accompanied by a decrease of current. Mass-spectrograph experiments are now under way to study the products of ionization under the most satisfactory conditions of operation.

A consideration of other possible sources of He^{++} ions indicates, where calculation is possible, that the percentage of ionization of the gas would be no greater, and probably less in most cases than in the magnetron. The condensed capillary discharge seems to offer one of the best possibilities since the He II lines are very intense relative to those of He I. However, here again, the higher members of the series are relatively less intense than in the magnetron at low pressures, and the concentration of He^{++} ions may be small. Nevertheless, it would be worthwhile to study the products of ionization in the condensed capillary discharge with a mass spectrograph.

In regard to the excitation of ionized spectra in other gases, the magnetron seems to offer some possibilities. The intensity is high close to the filament, and its superiority over ordinary gas discharges was demonstrated strikingly in the case of mercury where many additional lines were brought out by the application of the magnetic field. Whether it can compete with the other devices employed by spectroscopists, such as the electrodeless discharge or the vacuum spark, could probably be determined only with a vacuum spectrograph as most of the strong lines of the highly ionized states lie in the far ultraviolet. It does, however, offer the possibility of intensity studies with electrons of known energy which is not possible with most other sources.

The writers are indebted to Dr. J. C. Boyce of Massachusetts Institute of Technology for a discussion of the manuscript.

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Low Electronic States of Simple Heteropolar Diatomic Molecules:

III. Hydrogen and Univalent Metal Halides

ROBERT S. MULLIKEN
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

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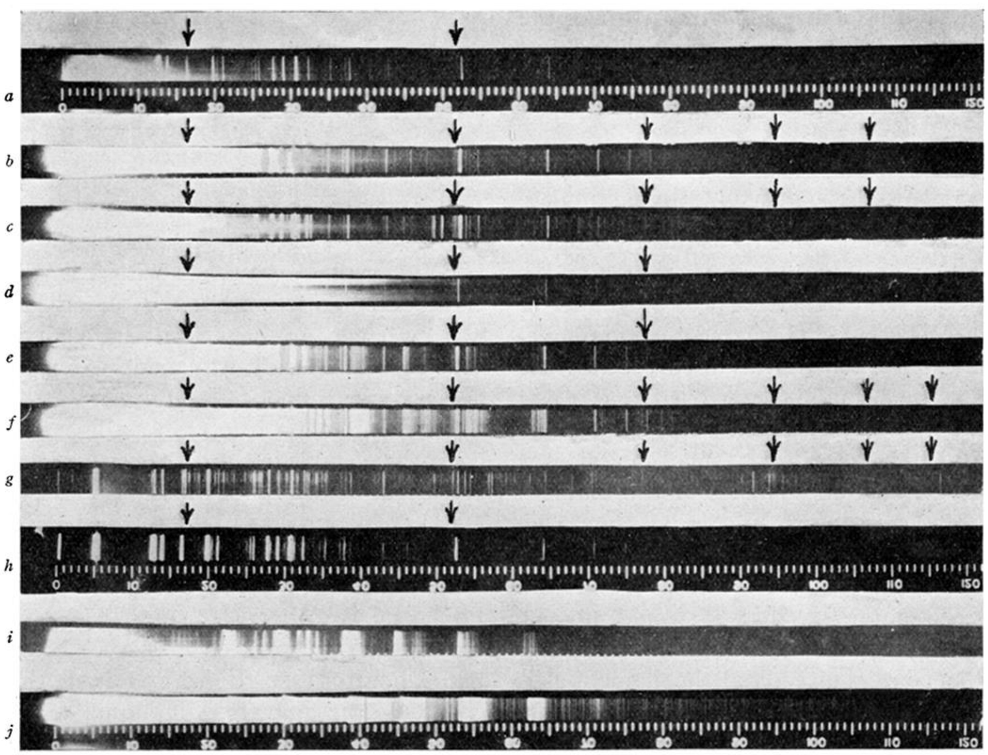
Electronic structures for the electronic states involved in the near ultraviolet spectra of AX are discussed (X = halogen, A = hydrogen or univalent metal). The upper electron levels involved are mostly among a set of levels $Q\ {}^1\Pi$ and ${}^3\Pi$, $T\ {}^3\Sigma^+$, $V\ {}^1\Sigma^+$, or their Ω-s or case c equivalents. Tentative potential energy curves for states Q, T and V of HI, AgI, and NaI are shown in Figs. 1–3. It is concluded that the observed HX absorption (continuous) involves the three Q levels corresponding to ${}^3\Pi_1$, ${}^3\Pi_{0^+}$, and ${}^1\Pi$, but with Ω-s coupling. It is further concluded (in contrast to what is found in the halogen spectra) that the observed absorption goes mainly to the ${}^3\Pi_1$ and ${}^1\Pi$ levels rather than the ${}^3\Pi_{0^+}$. The N and V potential energy curves of HX obtained here are compared (see text) with those given by Pauling; for HI there is good agreement, but for HBr, HCl, HF the V curves go increasingly higher than those of Pauling.

For AgX, it is concluded that the upper potential energy curve of the observed bands (curve B) contains a shallow minimum followed, as r is increased, by a maximum, beyond which it sinks to an asymptote about 1 ev lower. It is concluded that curve B is probably a resultant of an interaction of a stable ${}^1\Sigma^+$ curve, derived from a d^9s^2 excited silver atom and an unexcited X atom, with curves of the types $V\ {}^1\Sigma^+$ and especially $Q\ {}^3\Pi_{0^+}$; but that near its minimum state B is essentially $Ag(d^9s^2)\cdot X$ in character, corresponding to a stable union between an Ag atom with a d valence electron and an X atom. It is concluded that transitions to the three Q levels in AgX probably involve continuous absorption, as in HX and MX. The various band systems of CuX and AuX at long wave-lengths are ascribed to electron levels derived mainly from metal atoms in which a d electron has been excited (state d^9s^2, ${}^2D$).

For MX (M = alkali metal), it is concluded, in agreement with previous workers, that the process of light-absorption in the near ultraviolet has approximately the effect of transferring an electron from X^- of M^+X^- to the M atom, leaving two neutral atoms M and X which tend to fall apart (case c separate-atom coupling). The thus indicated lack of valence attraction between neutral M and X probably involves a thoroughgoing failure in MX of the additivity rule for homopolar bond energies. Possible reasons for this probable failure (mainly, highly unequal size and energy of valence orbitals of M and X) are



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