THE EXCITATION OF THE Mg II SPECTRUM BY IMPACTS OF THE SECOND KIND WITH METASTABLE ATOMS AND IONS OF THE RARE GASES

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Abstract

The Mg II spectrum was excited in normal low voltage arcs in mixtures of magnesium vapor with hydrogen, argon, neon, and helium respectively in a tungsten furnace apparatus. The densities of the spectral lines were measured with a Moll microphotometer. The excitation is believed to be due to impacts of the second kind between normal magnesium atoms and metastable atoms or ions of the gas used. It is shown that a small amount of kinetic energy may be added to the inner energy available in the impacts of the second kind and that a larger amount of excess inner energy may be transformed into kinetic energy in such an impact. The probability of an impact of the second kind decreases after the excess energy reaches a certain value.

Introduction

THIS report covers an investigation of the excitation of the spectrum of Mg II by impacts of the second kind between normal Mg atoms and excited atoms and ions of the rare gases. The principal purpose of the investigation was to study the excitation of those levels of Mg^+ which lie just above and just below the levels of the metastable and ionized states of the rare gases in order to determine whether the levels excited were closely selected by "resonance" and to determine to what degree non-quantized kinetic energy may be added to quantized energy in impacts of the second kind to produce "anti-Stokes" radiation. Magnesium was selected for the experiments because the Mg II spectrum has many levels lying near those of the excited and ionized states of neon and helium. The Mg II spectrum converges at a level 22.5 volts above the normal state of Mg. This is only one volt above the ionizing potential of Ne and 2.7 volts above the metastable 2^3S state of He.

Method

The experiments were carried out with the use of the tungsten furnace apparatus described by Duffendack and Black,[1] the apparatus being regulated so as to effect the simultaneous ionization and excitation of magnesium atoms by the excited atoms or ions of the gas used in accordance with the method of Duffendack and Smith.[2] Normal low voltage arcs were maintained in mixtures of magnesium vapor with hydrogen, argon, neon, and

[1] Duffendack and Black, Phys. Rev. **34**, 35 (1929).
[2] Duffendack and Smith, Phys. Rev. **34**, 68 (1929).

helium respectively. In each case the pressure of the gas was about 2 mm. The vapor pressure of the magnesium in the furnace was controlled by regulating the temperature of the furnace so that the green arc lines of Mg appeared faintly in the spectrum of the arc viewed with a small hand spectro-

TABLE I.

Wave-length	Classification	Ex. pot. (volts)	Relative Densities H_2	A	He	Ne_a	Ne_b
2802.70	$3s\ S-\ 3p\ P$	12.02	8.28	8.10	8.58	7.43	
2795.52	$3s\ S-\ 3p\ P$	12.03	8.56	8.14	8.58	7.50	
3615.64	$4s\ S-\ 5p\ P$	19.64	—	—	Obs	3.20	
13.80	$4s\ S-\ 5p\ P$	19.64	—	—	by He	2.86	
2936.50	$3p\ P-\ 4s\ S$	16.23	6.22	8.14	8.57	7.48	
28.62	$3p\ P-\ 4s\ S$	16.23	4.50	7.91	8.57	7.34	
2797.99	$3p\ P-\ 3d\ D$	16.44	7.73	7.67	8.58	7.46	
90.77	$3p\ P-\ 3d\ D$	16.44	5.02	7.02	8.58	7.46	
4433.99	$4p\ P-\ 6s\ S$	20.35	—	—	—	5.21	
28.00	$4p\ P-\ 6s\ S$	20.35	—	—	—	Combined	
3553.51	$4p\ P-\ 7s\ S$	21.04	—	—	—	671	
49.61	$4p\ P-\ 7s\ S$	21.04	—	—	—	Comb.	
3175.84	$4p\ P-\ 8s\ S$	21.46	—	—	—	6.38	
72.79	$4p\ P-\ 8s\ S$	21.46	—	—	—	6.20	
2971.70	$4p\ P-\ 9s\ S$	21.72	—	—	—	—	
69.02	$4p\ P-\ 9s\ S$	21.72	—	—	—	—	
4390.59	$4p\ P-\ 5d\ D$	20.38	—	—	—	6.41	
84.64	$4p\ P-\ 5d\ D$	20.38	—	—	—	Comb.	
3538.86	$4p\ P-\ 6d\ D$	21.05	—	—	—	7.05	
35.04	$4p\ P-\ 6d\ D$	21.05	—	—	—	7.04	
3168.98	$4p\ P-\ 7d\ D$	21.45	—	—	—	6.25	
65.94	$4p\ P-\ 7d\ D$	21.45	—	—	—	5.14	
2967.87	$4p\ P-\ 8d\ D$	21.72	—	—	—	—	
65.19	$4p\ P-\ 8d\ D$	21.72	—	—	—	—	
3850.40	$3d\ D-\ 5p\ P$	19.64	—	—	3.70	3.40	
48.24	$3d\ D-\ 5p\ P$	19.64	—	—	6.89	6.74	
4481.33	$3d\ D-\ 4f\ F$	19.19	—	—	8.01	6.43	
81.13	$3d\ D-\ 4f\ F$	19.19	—	—	Comb.	Comb.	
3104.81	$3d\ D-\ 5f\ F$	20.41	—	—	7.00	9.49	
04.71	$3d\ D-\ 5f\ F$	20.41	—	—	Comb.	Comb.	
2660.82	$3d\ D-\ 6f\ F$	21.07	—	—	—	7.60	
60.76	$3d\ D-\ 6f\ F$	21.07	—	—	—	Comb.	
2449.57	$3d\ D-\ 7f\ F$	21.47	—	—	—	7.50	6.52
2329.58	$3d\ D-\ 8f\ F$	21.73	—	—	—	0.83	4.60
2253.87	$3d\ D-\ 9f\ F$	21.91	—	—	—	—	1.45
2202.68	$3d\ D-10f\ F$	22.04	—	—	—	—	0.22

scope. Experience enabled us to determine the proper intensity of these lines so that the intensity of the Mg II spectrum would be great relative to that of Mg I in the photographed spectrum of the arc. In all cases the arc current was held between 45 and 55 milliamperes and the applied potential difference was 23 to 25 volts. The spectra were photographed with a Hilger E_2 quartz spectrograph.

The relative densities of the spectral lines on the plates were determined by means of a Moll microphotometer. The relative densities recorded in the table are those thus determined and corrected for the influence of continuous background and neighboring lines.

Results

Table I contains a list of the lines photographed and their relative densities in the spectrograms of the arcs in the various mixtures. The densities of the lines on one plate must not be compared with those on another plate, but some deductions are made as a result of comparing the relative densities of the lies of a series in the spectrum of one Mg-Ne mixture with their relative densities in the spectrum of another Mg-Ne mixture. The excitation potentials recorded in the table are computed relative to the normal state of the neutral Mg atom. The relative densities of the lines recorded in the column headed Ne_a are those for a spectrogram in which the intensity of the Mg II spectrum is great compared with that of the Mg I spectrum, while those recorded in the column headed Ne_b are for a spectrogram in which the lines of the Mg I spectrum are very strong, the ^3PS series being present to the eighth member and the ^3PD series to the ninth member. In the other spectrograms only the first one or two members of the series of arc lines were present.

Table II gives the critical potentials of the elements involved in this investigation. A consideration of these critical potentials in connection with the excitation potentials of the lines of the Mg II spectrum observed in each mixture affords the basis for the explanation of the results given in the following paragraphs.

TABLE II. *Critical potentials of elements.*

Element	Excited states	Ionization
Mg		7.61 volts
H_2		16.3–16.5
A	11.6 volts	15.69, 15.86
Ne	16.6	21.5
He	19.8, 20.5	24.5

Discussion

That the Mg II spectrum was excited by impacts of the second kind rather than by direct electron impacts is evidenced first of all by the great strength of the spark spectrum relative to the arc spectrum when the vapor pressure of magnesium is low. In all of the work in this laboratory and else-

where in a low voltage arc of the order of 25 volts, the arc spectrum of the gas has always been predominant. Furthermore, with the magnesium vapor constituting only a small percentage of the total gas in the region of the arc, the probability of an electron collision with a magnesium atom is small compared with the probability of an impact between a magnesium atom and metastable atom or ion of the rare gas.

Then too the distribution of intensity of the lines of a series in the spectrum of Mg II is quite different in this excitation than in a case of excitation by direct electron impacts. It will be noted from Table I that the Mg^+ ion was excited in each mixture only to a level corresponding to that of a metastable state or the ionized state of the gas molecule. It may be observed that each series is cut off suddenly. The intensity of the last line observed is much higher than one usually expects. There is no gradual diminution of intensity in the series until the lines fail except in the case of the ^2DF series in the neon mixture, Ne_b, in which the magnesium constituted a much larger percentage of the total gas, and excitation by direct electron impacts was an important factor.

The excitation can be accounted for by impacts of the second kind that may be represented by the following equations:

$$\begin{aligned} Mg+H_2^+ &= Mg^{+\prime}+H_2 \\ Mg+A^+ &= Mg^{+\prime}+A \\ Mg+Ne' &= Mg^{+\prime}+Ne \\ Mg+Ne^+ &= Mg^{+\prime}+Ne \\ Mg+He' &= Mg^{+\prime}+He \end{aligned}$$

These equations represent reactions in which a normal magnesium atom is simultaneously ionized and excited on contact with an excited molecule or ion of the gas with which the magnesium vapor is admixed. The inner energy of the excited molecule, or the energy of recombination of an ion with an electron as the case may be, is utilized in ionizing the magnesium atom and in simultaneously exciting the ion. In such a reaction the amount of energy available is limited to a quantity equivalent to the excitation potential or the ionization potential of the gas molecule. Thus the magnesium ion may be excited to the degree that the excitation potential, or the ionization potential, of the gas molecule exceeds the ionization potential of magnesium. Any remnant of energy remaining over must go into the kinetic energy of the reacting molecules.

The kinetic energy of the reacting particles in impacts of the second kind may serve not only as a sink but also as a source of energy. The excitation of the $8\,f^2F$ level in the neon mixture Ne_a must involve the addition of nonquantized kinetic energy to the energy of recombination of the neon ion and electron during the impact. The amount of kinetic energy needed in this instance is 0.23 volts, a quantity certainly available in a gas mixture at a temperature of about 1000°C. The higher F levels reached in the neon mixture Ne_b were probably reached by direct electron impact, as the percentage of magnesium vapor in this mixture was large. The variation in the

relative intensities of the ^2DF series lines in these two neon mixtures is typical of the difference between excitation by impacts of the second kind and excitation by direct electron impacts. Of course, impacts of the second kind are effective also in the case of the Ne_b mixture but are responsible for only a part of the excitation. The excitation of the $4s\ ^2S$ and $3d\ ^2D$ levels in the argon mixture would not be expected to result from impacts of the second kind of argon ions with normal magnesium atoms. The ionization potential of argon is less than the excitation potentials of these levels. The excess energy demanded (0.58 volt), furthermore, is larger than one would expect to come from the kinetic energy of the impacting particles at the temperature of the mixture, about 1000°C. These levels were probably excited by nitrogen ions for, unfortunately, the argon employed was badly contaminated with nitrogen. We regret that lack of time prevented our repeating the argon excitation with pure gas.

An interesting question that suggests itself is whether the amount of excess energy remaining over in an impact of the second kind and transformed into kinetic energy of the reacting particles is limited. Obviously the amount of energy that can be drawn from kinetic energy as a source is limited to that available and is determined almost wholly by the temperature of the gas. It is possible that there is a dissymmetry with respect to the amounts of kinetic energy that can be taken from this source and that can be put into this sink. The only level excited that required the addition of kinetic energy was the $8\ f^2F$ level in the neon mixture Ne_a when 0.23 volt energy was drawn from the kinetic energy of the gas. On the other hand the $5d\ ^2D$, $6s\ ^2S$, $5p\ ^2P$, and $4f\ ^2F$ levels in the neon mixture Ne_a must have been excited by impacts of the second kind with neon ions leaving excess energy of amounts 1.12, 1.15, 1.86, and 2.31 volts respectively to be absorbed as kinetic energy by the reacting molecules. A quantative study of the probability of such collisions of the second kind as a function of the excess energy to be disposed of would require very careful quantitative measurements on the intensities of the spectral lines. These measurements were not made, but, taking into consideration the change with the wave-length in the sensitivity of the photographic plates used as well as the transition probabilities, one can safely say that the probability of such a collision does decrease after the excess energy reaches a certain value.

One of the most striking results of this investigation is the demonstration that higher excited levels of the magnesium ion are reached in the neon mixture than in the helium mixture. This is evidently because in the neon mixture both metastable neon atoms and neon ions are effective, while only metastable helium atoms make impacts of the second kind with magnesium atoms. The ionization potential of helium is higher than the second ionization potential of magnesium. Consequently, if helium ions were to be effective, a considerable excess of energy would have to be disposed of. The highest level that did give a spectral line in our region of observation was the $10f\ ^2F$ level, and its excitation by helium ions would have required the disposal of 2.46 volts excess energy. Though this amount is not greatly in excess of

the maximum amount observed in the neon mixture, the $3d\ ^2D - 10f\ ^2F$ lines were not present in the spectrum of the helium mixture.

Excitation in Hollow Cathodes

Considerable evidence has accumulated recently to indicate that the types of impacts described above are effective in the excitation of the spark spectra of metals in hollow cathodes. Professor Sawyer and Dr. Lang[3] have used the hollow cathode method recently in this laboratory for the excitation of the spark spectra of gallium and indium. They find these spectra developed to the levels that can be reached by impacts of the second kind with metastable atoms and ions of helium which they used as the conducting gas. Very recently, too, Professor Takahashi visited this laboratory and reported that some experiments by Professor Paschen and himself revealed two maxima in the excitation of the spark spectrum of cadmium in a hollow cathode with helium. One maximum occurred at levels close to the minimum excitation potential of helium and the other close to the ionizing potential of helium. We believe this is the first instance where two maxima have been observed in a single spectrum excited in a mixture with a single gas. Other explanations[4] have been given for the excitation of spark spectra in hollow cathodes, but many of the cases on record can be accounted for solely by impacts of the second kind like those described above. The exceptions to this explanation occur in cases where the percentage of metallic vapor in the mixture is considerable, and hence excitation by direct electron impacts may be expected to be important.

[3] To be published soon.

[4] Frerichs, Ann. d. Physik **85,** 362 (1928). Paschen, Sitzungsberichten der Preuss. Akad. der Wiss. 1928.