LOW VOLTAGE EXCITATION OF SODIUM

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Abstract

In an attempt to clarify the available data on excitation of atoms by low velocity electron impact, the author has studied the optical excitation function of the resonance lines in sodium vapor in the range from 1.8 to 4.2 volts. It is found that the excitation probability has three distinct maxima, corresponding to excitation to 3^2P, 4^2S and 5^2S states. Within two-tenths of a volt of the excitation potential the probability has dropped to zero and remains at that value until a new energy level is reached. No excitation to the 3^2D appears, possibly because of the existence of a selection principle in electronic excitation.

Introduction

About six years ago, Dymond, [1] in a study of critical potentials in helium, showed that the probability for the excitation of the 2^3S state of helium had a maximum at a quarter of a volt above the excitation potential. Hodges and the author[2] found that the assumption of maxima of excitation probability near the excitation potentials was the only way in which they could account for their observed intensity variations in the Geissler discharge in helium, and both Nottingham[3] and Glockler[4] came to similar conclusions working with the copper and helium arcs, respectively.

The first direct measurement of excitation probabilities was made by Brattain[5] who studied the number of electrons suffering energy losses in mercury, and found that the probability of excitation to the 6.7 volt state of mercury rose to a maximum when the impacting electrons possessed an energy slightly greater than that required for excitation. About a year ago the author published a study of the optical excitation function of helium,[6,7] in which the conclusion was reached that all states of the helium atom have very sharp peaks in excitation probability somewhere within 0.5 volts of the excitation potential.

The conclusions of Nottingham have been attacked by Ornstein and Vermeulen,[8] largely on the basis of the work of Elenbaas,[9] but Nottingham,

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[1] Dymond, Proc. Roy. Soc. **A107,** 291 (1925).
[2] Hodges and Michels, Phys. Rev. **32,** 913 (1928).
[3] Nottingham, Jour. Franklin Inst. **207,** 299 (1929).
[4] Glockler, Phys. Rev. **33,** 175 (1929).
[5] Brattain, Phys. Rev. **34,** 474 (1929).
[6] Michels, Phys. Rev. **36,** 604 (1930).
[7] Michels, Phys. Rev. **36,** 1362 (1930).
[8] Ornstein and Vermeulen, Zeits. f. Physik **64,** 657 (1930).
[9] Elenbaas, Zeits. f. Physik **59,** 289 (1930).

in subsequent work[10] has obtained further evidence of the excitation probability peaks. Hanle[11] and his students[12] have also failed to find these maxima, in general, but since they do not publish any velocity distribution curves for their electron beams, it is extremely probable that their resolution along the energy axis is not sufficient to show the existence of sharp maxima. Their data could be compared with that of other workers only if analyzed with the aid of a velocity distribution curve.

From the theoretical viewpoint equal confusion exists. Elsasser,[13] starting from Born's work, has calculated excitation probabilities for high electron energies, for the hydrogen atom, but Oppenheimer[14] has pointed out that the approximations involved are poor, particularly since no account is taken of the interchange which may take place between the exciting electron and one of the electrons in the atom. He shows, moreover, that this effect is probably most appreciable at energies near that required for excitation. More re-

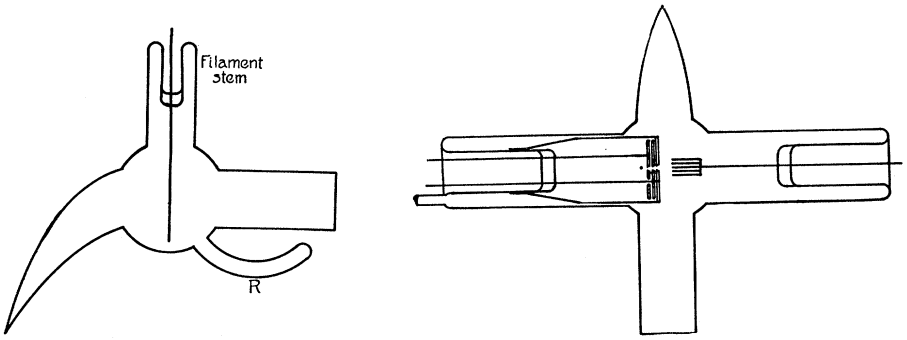

Fig. 1. Excitation tube.

cently, Morse and Stueckelberg[15] and Massey and Mohr[16] have computed theoretical excitation function curves. The former, without considering interchange, obtain curves similar to the triplet system experimental results of Hanle[11] rather than to his singlet system results although it is in the singlets that interchange is unnecessary and agreement might be expected. The latter authors have taken Oppenheimer's work into account and obtain a curve which shows behaviour intermediate between that found by Hanle and that found by the author.

In view of these difficulties, it seemed to be desirable to study the excitation of sodium by electron impact for three reasons

(1) The resonance lines are in the visible region where they may be conveniently studied.

[10] Nottingham, Zeits. f. Physik **68,** 824 (1931).
[11] Hanle, Zeits. f. Physik **56,** 94 (1930).
[12] Larche, Zeits. f. Physik **67,** 440 (1931).
[13] Elsasser, Zeits. f. Physik **45,** 522 (1930).
[14] Oppenheimer, Phys. Rev. **32,** 361 (1928).
[15] Morse and Stueckelberg, Ann. d. Physik **9,** 579 (1931).
[16] Massey and Mohr, Nature **127,** 234 (1931).

(2) The great relative spacing of the low energy levels offers promise of good resolving power along the energy axis.

(3) The atom is sufficiently hydrogen-like to offer more interesting theoretical possibilities than helium does.

With these points in view, a new apparatus has been designed and measurements of the optical excitation function have been made.

Apparatus and Method

A sketch of the tube used for the excitation is shown in Fig. 1. The electron gun consists of a 15 mil tungsten filament and three nickel slits, each filed to a knife edge and having an opening of one by ten mm. The potential on the first slit was always kept a few tenths of a volt higher than that on the second and third slits which were permanently connected together. Observations were made in the field free space between the last slit and the "black cavity" plate.

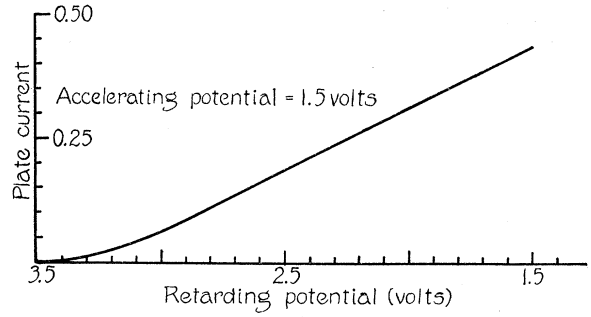

Fig. 2. Velocity distribution curve.

The purification and handling of the sodium presented some difficulty. It was found that dry sodium, if heat-treated in vacuo at gradually increasing temperature, up to 380°C, for a period of 24 to 36 hours, gave up all but a minute fraction of its gaseous impurities. This sodium was then introduced into the reservoir, *R*. During each run this reservoir and the observation window were maintained at a constant temperature of about 350°C, while the main body of the tube and the light trap were held at 280° and 170° respectively. This resulted in a jet of sodium vapor directed through the observation region and away from the window, so that the blackening effect on the latter was small. After several months of intermittent operation, the transmission of the window has decreased to about 50 percent of its initial value, but this change has been sufficiently slow to cause no trouble during a single run.

The extreme ease with which an arc is struck and maintained in sodium vapor caused considerable difficulty. It was found that an arc could exist when no measurable part of the electrons had energies sufficient to ionize, apparently because of cumulative effects started by a very few fast electrons. This difficulty was met by enclosing the entire filament and accelerating system by two nickel cylinders which fitted tightly over the glass stems. This kept the discharge from taking place in the observation region, but, even with

this precaution, it was impossible to work at potentials greater than 4.2 volts, as conditions then became unsteady.

The current vs. retarding potential curves, one of which is shown in Fig. 2, were obtained by applying the retarding potential between the last slit and the plate. In the figure the curve has been continued only to two volts below the potential required to stop completely the electrons, since this was the only region used in the measurements. The contact potential between the filament and the slit-plate system was found to be about 2.0 volts, the slits being positive with respect to the filament. This potential was slightly variable, probably due to the composite nature of the sodium on nickel surfaces, and required frequent checking. Velocity distribution curves were therefore taken for each photographic measurement.

The intensity measurements were made in a manner similar to that used for the work on helium. An F 3.3 spectrograph, built in the laboratory shops, was used, with Wratten and Wainwright hypersensitive panchromatic plates. These plates were found to be remarkably uniform in sensitivity, particularly when used with the Watkins thermo elon-hydrochinon developer recommended by Neblette.[17] A small amount of scattered and reflected continuous light from the filament was observed, but correction was made for this by running densitometer contours of the exposures and by subtracting the interpolated intensity of this light from the total observed at 5890A to obtain the intensity of the sodium radiation. The combined effect of the resonance lines $(3S-3D)$ was the only radiation measured.

The test for linearity of intensity with current density, which indicates the existence of simple excitation conditions, was made in the range used (up to 0.03 m.a. per mm^2) and the relationship nowhere departed from linearity by more than 5 percent of the total observed intensity (continuous plus resonance lines). This quantity was therefore chosen as the magnitude of the estimated limit of error of a single observation. Because of the use of a vapor jet the relationship of intensity with pressure could not be tested.

Intensity and Excitation Function

A small residual intensity below the excitation potentials was observed on all plates, probably because of a small drift of ions through the slits, but, since this seemed to be quite constant, its value was subtracted from all intensities to determine the intensity due to pure excitation. This is shown on the plot of intensity vs. maximum electron energy in Fig. 3, on which all intensities are reduced to unit current density. The centers of the circles represent experimentally observed points, while their radii are equal to the estimated uncertainties. From these points the relative excitation probabilities were calculated. Since the equation:

$$I_{V_m} = \int_{V_0}^{V_m} F(v)\, i(V_m, v)\, dv,$$

[17] Neblette, Photography, Principles and Practice, 2nd Ed. 309.

where I_{Vm} is the observed intensity with maximum potential V_m, V_0 is the excitation potential and $F(v)$ and $i(V_m, v)$ are the excitation and current distribution functions, cannot be solved rigorously for the $i(V_m, v)$ curve obtained in this work, it was replaced by the equation:

$$I_{V_m} = 0.1 \sum_{0}^{m} \overline{F(v)}\,\overline{i(V_m, v)}$$

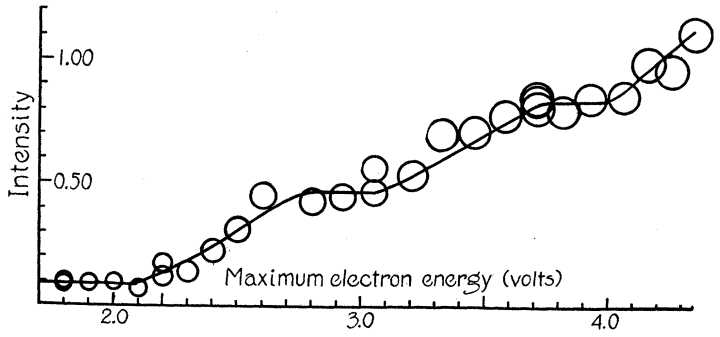

Fig. 3. Intensity curve.

where m is the number of 0.1 volt intervals between V_0 and V_m and $\overline{F(v)}$ and $\overline{i(V_m, v)}$ are the average values within the intervals. This summation was solved step by step with adjustments being made within the experimental error. In this way the best fitting points as shown in Fig. 4 were obtained.

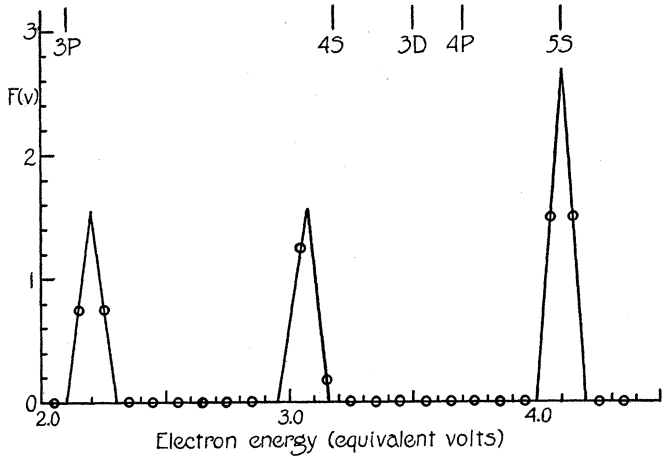

Fig. 4. The excitation function for sodium.

The justification for this procedure may be seen in the curve of Fig. 3, which was computed directly from the excitation functions of Fig. 4 and the experimental current distribution functions, similar to Fig. 2. It will be observed that this curve passes within the estimated error of the observed points with only three exceptions.

Discussion and Conclusions

The three peaks of excitation function found in sodium appear to be due to excitation of the 3^2P, 4^2S and 5^2S states. The peaks center at 2.2, 3.08 and 4.1 volts, while the excitation potentials of these states are at 2.10, 3.18 and 4.10 volts. The random differences between the peak centers and the excitation potentials are probably due to variations in contact potential, which were of the right order to account for these discrepancies, so it is still impossible to say for certain whether the maxima occur at or slightly above the excitation potential. Since the 2.2 volt peak is quite accurately placed by the definite break in the intensity curve, showing the start of excitation at the theoretical 2.1 volt level, it would seem to be most reliable, and would indicate that the probability of excitation reaches its maximum at about 0.1 volt above the excitation potential. Since the method of calculating the results can give only the area under the curves, the straight line interpolation is only a guess, and, for the same reason, the only statement which can be made in regard to the width of the peaks is that it is not greater than 0.2 volt. The fact that the 5^2S peak is higher than the other two may well be spurious, since either a mistaken assumption in regard to the shape of the peak or a small amount of ionization, which definitely started just above this point, might introduce errors in the magnitude of the probability. The location of the peak, however, is very definite, as the break in Fig. 3 at 4.0 volts shows.

Two entirely unexpected results were obtained. The first is the zero value of the excitation function between the relatively narrow maxima. The value of the probability in these regions can be definitely put at less than five percent of the height of the first two maxima, as any change greater than this would very appreciably affect the intensity curve. Finally, it is difficult to see why no traces of maxima due to excitation to 3^2D and 4^2P occur. The last may be accounted for if the transition from 4^2P to 3^2S is much more probable than to 4^2S and 3^2D. If the first is ten or twenty times as probable as the sum of the last two, the effect of 4^2P excitation on the 5890A lines might easily go undetected, as practically the entire effect of excitation to this state must be observed on the 3303A lines. But if excitation from 3^2S to 3^2D takes place, the electron must return through the 3^2P state. It therefore appears that the low voltage excitation of this transition is very improbable. If neither excitation to S or D occurred, we should expect that the optical selection rules applied, but it is now evident that if a selection rule holds in excitation it allows transitions for which $\Delta L = 0$ or 1. Elsasser[13] has shown that for high velocities, the transition from S to D is much less probable than that from S to P, in hydrogen, but his theory can not be applied to this case, both because of the energy values and because he is dealing with excitation from a 1^2S level.

In conclusion I wish to express my extreme gratitude to the staff of the Palmer Physical Laboratory for extending the facilities of the laboratory and for very helpful advice and assistance during the work.