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Collisions of the Second Kind Between Magnesium and Neon

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The relative intensities of a group of lines in the spectrum of Mg II as excited by a low voltage arc in a mixture of magnesium vapor and neon have been measured at various pressures of neon. Marked effects due to collisions of the second kind between magnesium atoms and neon ions and metastable atoms are found. The ratio of intensities at 2.0 and at 0.017 mm of neon was taken as a measure of the enhancement or the relative collision cross section for the excitation of the initial level. The results show a decrease of cross section with increase of energy-discrepancy, a finite cross section for exact resonance, and a definite dependence on the L value of the term excited by the collision. Approximate calculation places the cross section at about 10^{-11} cm^2 for collisions between neon ions and magnesium atoms.

I. Introduction

Since the initial experiments of Franck and Cario on energy transfer in collisions of the second kind, many types of experiments have revealed this phenomenon and yielded ideas of the efficiency of the process. The present study is that of a particular type of collision, one in which a normal atom is both ionized and excited by a metastable atom or an ion. Considerations of lifetime and concentration eliminate all but these two forms of atoms as active agents. The process may be represented by the reaction

$$E_i+F_i\rightarrow E_f+F_f+\sigma, \qquad (1)$$

where E_i is the initial energy of one atom, F_i that of another, the subscripts f refer to the final energies, and σ is thus defined as the energy-discrepancy between the initial and final states of the system. By analogy the effects have been called those of "resonance," and consequently σ measures the exactness of resonance.

The efficiency of energy transfer in these collisions will be measured by the yield of the reaction, that is, the number of excited atoms N—energy E_f—per cubic centimeter per second, and this number, considered as the result of a collision between two types of atoms of concentration N_1 and N_2 moving with a relative velocity v and having a certain action cross section q, is given by

$$N=qN_1N_2v. \qquad (2)$$

If the probability of transfer $P(r)$ at a distance of approach r is used instead of the concept of a cross section (2) becomes

$$N=2\pi N_1N_2v\int_0^\infty P(r)dr. \qquad (3)$$

The past investigations of the problem, both experimental and theoretical, have been concerned with the functional dependence of cross section on energy-discrepancy, and it has been found in all cases that the cross section decreases with increasing σ. There is, however, a distinct difference in point of view between the theoretical and the experimental work. The theoretical work has shown a variation of the cross section for the excitation of *one* state with energy-discrepancy, which is not possible of observation except in the utilization of the magnetic quantum levels where the energy can be varied by the magnetic field as in the experiment of Hanle.[1] In all other cases the consideration has been to measure the cross section for the excitation of *different* states as a function of their unperturbed energy-discrepancy from resonance. The measurements of Duffendack and Thomson[2] indicate a general agreement of the two views—a monotonic decrease of cross section with increase of energy-discrepancy—but some anomalies point to a dependence of cross section on the particular term excited. The present work was undertaken in order to determine not only the cross section for the excitation of levels of various energies but also to investigate other factors influencing the action cross section in these collisions of the second kind.

II. Experimental Method

By the use of the methods of spectrographic photometry[3] it is possible to measure the relative

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[1] Hanle, Zeits. f. Physik **85**, 548 (1933).

[2] Duffendack and Thomson, Phys. Rev. **43**, 106 (1933).

[3] Duffendack and Thomson, J. O. S. A. **23**, 101 (1933).

intensities of lines excited under conditions favorable for collisions of the second kind or under purely electronic impacts. The relative intensities in these two cases may be taken as a measure of the population of the initial state for a particular line, and that, in turn, as an indication of the relative efficiency of population by collisions of the second kind and by electron impact. The ratio thus obtained is designated as the enhancement of the line or of the level from which the line originates. It is, of course, essential that other effects be excluded. In general one may write the measured enhancement

$$E=\frac{J_r^n}{J_e^n}=\frac{N_e^n+N_r^n+f_\alpha(N_e^\alpha+N_r^\alpha)}{N_e^n+f_\alpha N_e^\alpha}\quad n<\alpha<\infty. \qquad (4)$$

J_r^n = intensity of a line, initial state n, under conditions for excitation by collisions of the second kind.

J_e^n = intensity of a line, initial state n, electronically excited.

N_e^n population of the state n by electron impact.

N_r^n = population of state n by collisions of the second kind.

f_α = fraction of state α populating state n by transitions from above (Kaskadensprünge).

It is evident that only if Kaskadensprünge are small and resonance effects large compared with electronic excitation is the measured enhancement that which the term usually denotes, namely, N_r^n/N_e^n. It is generally not possible to determine the f_α's because they are essentially transition probabilities for lines in the infrared, but since the number of transitions is proportional to the cube of the frequency, which is small, the effect is in most cases negligible. It is necessary, however, to check each result for the possibility of such population from above. Knowing the enhancement of a particular level under the proper conditions, the relative cross section follows immediately, for the enhancement is given by

$$E\simeq N_r^n/N_e^n=q_r^n N_1 N_2 v_r/q_e^n N_e' N_2' v_e', \qquad (5)$$

N_1 = concentration of metastable atoms or of ions,
N_2 = concentration of normal atoms,
N_e = electron concentration.

The case chosen as most favorable for study was the excitation of the magnesium spark spectrum by positive ions of neon. As is evident from Fig. 1, there is a large number of levels within a small range of energy-discrepancy, and so there is the possibility of determining the efficiency of excitation of terms of nearly the same energy-discrepancy. Furthermore, experimentally, the simplicity of the magnesium spectrum outweighs the difficulties due to the action of the vapor on glass, condensation on the electrodes, and the like.

The tube used to secure a low voltage arc in magnesium vapor and neon is illustrated in Fig. 2. A small quartz crucible A wound with a heater coil of 12 mil tungsten wire provided an easily controlled source of magnesium vapor. A nickel cylinder B surrounds the crucible to cut down radiation and convection losses. Electrons for the arc were supplied by a pancake filament F of Isovolt alloy located near the mouth of the crucible. In order to prevent excessive diffusion of magnesium vapor a cap C with a projecting observation tube T covers the crucible mouth and the filament. This cap was used as the anode of the arc. The observation tube was found to be very effective in cutting down diffusion of vapor to the quartz window of the large Pyrex bulb in which the whole electrode assembly was mounted. This particular arrangement for obtaining the spectrum of elements of moderate boiling points possesses the advantage of good temperature control, constancy of excitation, and ease of degassing and purification—important factors in intensity work. The low temperature emitter obviates continuous background which may be very troublesome. The tube and electrodes were thoroughly outgassed and the neon purified by continual circulation through charcoal and glass bead traps immersed in liquid air.

Although enhancement measurements have usually been made with a spark or an arc spectrum as the "normal" or electron-excited spectrum, this is not feasible in the case of magnesium because of the difficulty of securing the spectrum free from objectionable background. The intensities of the various lines were therefore measured at different neon pressures, the low pressure data thus approaching electronic excitation of the magnesium vapor. The ratio of intensities at high and low neon pressures may then be taken as a measurement of the enhancement

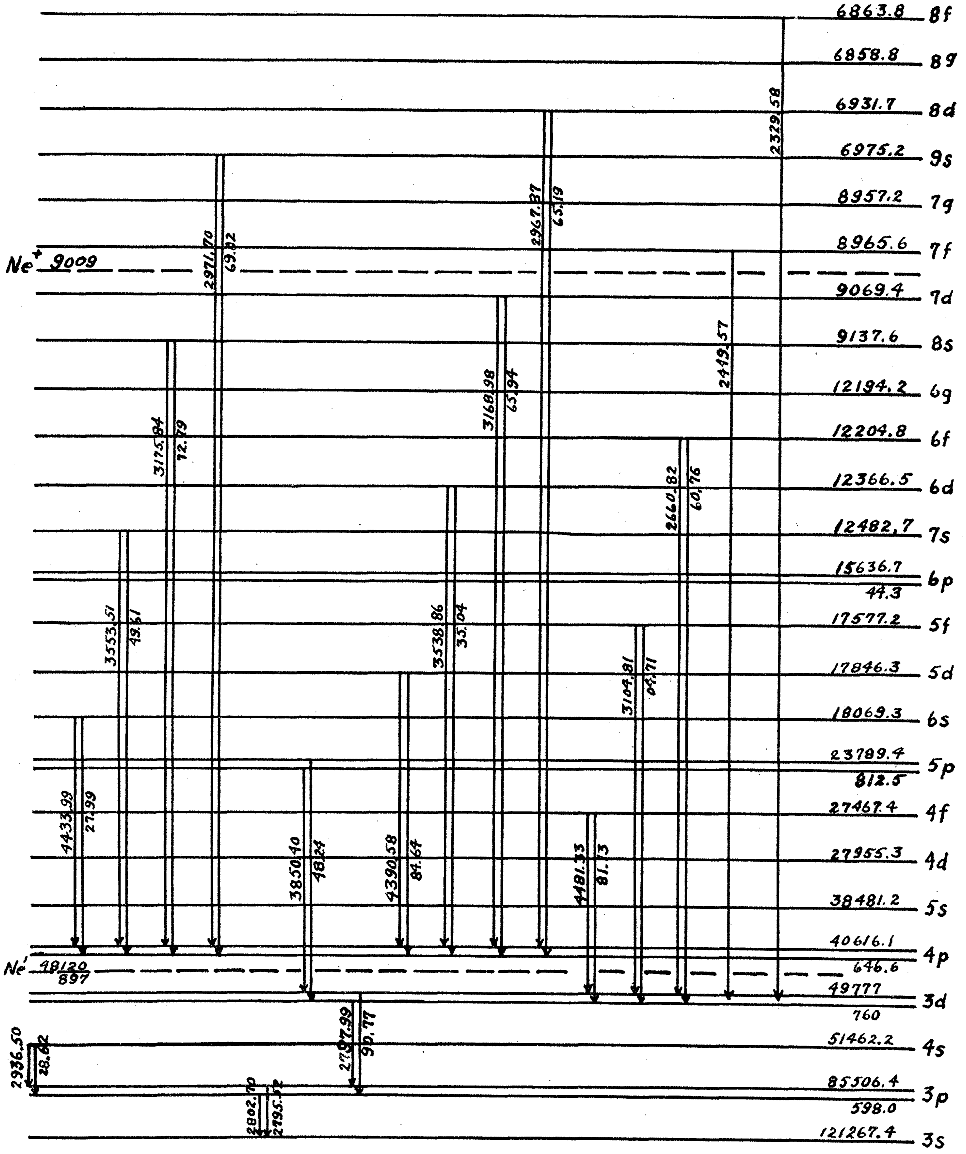

FIG. 1. Energy levels in magnesium.

due to neon ions. All intensity measurements were made relative to the intensity of the Mg I $4^3D \rightarrow 3^3P_2$, 3096 line. Such a choice of reference reduces the error from possible variation of direct electronic excitation of the Mg II terms. Although the final state of this line is the metastable $^3P_2$ and, therefore, is liable to a self-absorption varying with neon pressure as a result of the change of effectiveness of neon in creating or destroying $^3P_2$ atoms, it was found that the ratio of the 3093 ($^3D\ ^3P_1$) line, from which the relatively strong 4571 line originates, to the 3096 line was the same at various neon pressures. It is quite probable that the neon plays no essential role in the distribution of atoms in the $^3P_0$, $^3P_1$, $^3P_2$ states because of their small separation in energy. Neon pressure may, however, affect the electronic excitation of the ^3D initial state, and in order to investigate this point, the ratios of the intensities of the Mg II lines to the 3096 line were measured as a function of arc voltage at constant pressure as equivalent in electronic

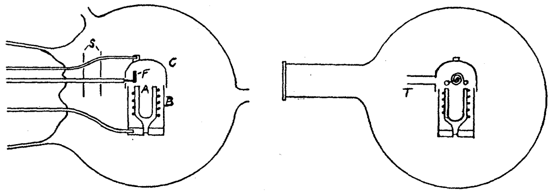

FIG. 2. Diagram of arc tube.

excitation to variable pressure at constant voltage.

Near constancy of the intensity of the desired lines relative to the 3096 line for voltages as large as 50 volts indicated that any change of electron velocities has negligible effect on the intensity of lines from spark levels. This also suggests that direct electronic excitation of these levels is very small. All subsequent measurements were made with an arc current of 40 m.a. at 25 volts.

The crucible temperature, about 500°C, was chosen to give sufficient magnesium vapor for visible excitation of the strong arc lines but kept low enough to prevent more than a negligible amount of ionization of magnesium atoms by electron impact. This latter condition is easily checked, for there is a critical magnesium pressure above which the arc voltage drops sharply due to the neutralization of space charge by the easily ionized magnesium atoms. At the same time the neon lines disappear and the complete arc spectrum of magnesium is excited. The crucible temperature was kept constant at all neon pressures by resistance measurement.

III. RESULTS

The results for the pressure dependence of the intensity of the Mg II lines are given in Fig. 3, in which the logarithm of the intensity relative to the 3096 arc line is plotted against the logarithm of the neon pressure. Because of the spread at 0.017 mm some of the points are not shown, but the curves are drawn toward these points. Compared to the reference line, the 3175–73, $8^2S \rightarrow 4^2P$, shows a rapid decrease of intensity with decrease of neon pressure below 0.8 mm; the 3104, $5^2F \rightarrow 3^2D$, a less rapid decrease; and the 2802–2795, $3^2P \rightarrow 3^2S$, scarcely any change. The conclusion follows that the excitation of the low terms is chiefly electronic whereas the terms near the energy of the neon ion owe

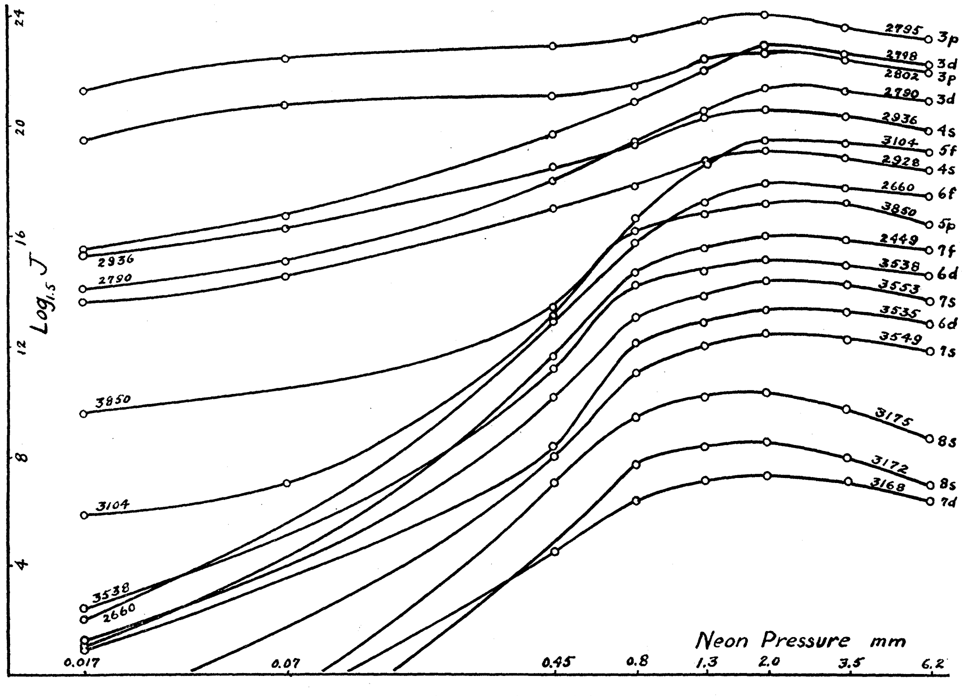

FIG. 3. Pressure dependence of intensities of Mg II lines.

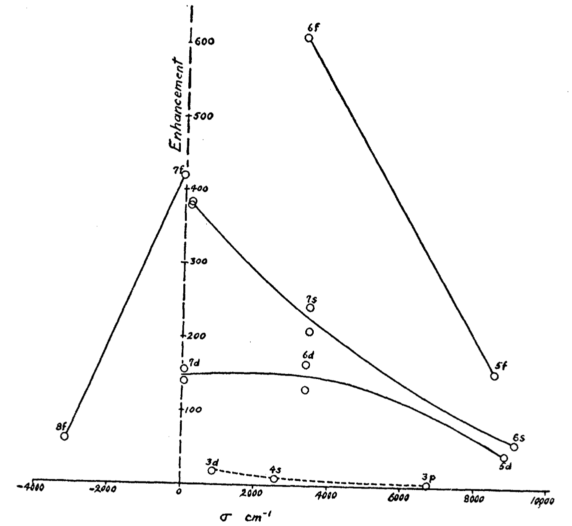

FIG. 4. Enhancement of lines for various energy-discrepancies (σ).

their excitation chiefly to collisions of the second kind. Since the arc is operated at constant current and a region of practically neutral space charge is photographed, the positive ion concentration should be independent of pressure and thus also the intensity of those lines excited by positive ions. Calculation shows, however, that at the current used there is insufficient gas concentration at pressures below about one millimeter to keep a constant positive ion concentration, and therefore the intensity of the lines excited by positive ions drops off at lower pressures. From the trend of the curves at a pressure of 0.017 mm of neon it is evident that positive ion excitation of some of the high terms is still considerable for the characteristic constant value attributed to electronic excitation is not yet reached. This low pressure limit is placed experimentally, however, because of the excessive diffusion of magnesium vapor to the leads and observation window when the neon pressure is further decreased. Not only is this a serious factor, but the electronic excitation of these levels is evidently so slight that the time of exposure becomes impractically long.

The ratio of the intensity of a line at 2.0 mm of neon to the intensity at 0.017 mm may be taken, nevertheless, as a measure of the enhancement of the initial level due to collisions of the second kind, and, if other methods of population of this level can be shown to be small, the results can be interpreted as the relative action cross section for excitation. Fig. 4 gives the points thus obtained, and curves are drawn through points belonging to the same series to illustrate the regularity. The 3^2D, 4^2S and 3^2P levels are placed with an energy-discrepancy (σ) measured from the neon level on the supposition that they are too far distant from the ion energy for enhancement, but that excitation by collisions of the second kind with neon metastable atoms is responsible for the enhancement.

IV. DISCUSSION

As pointed out above, for enhancement measurements to have a definite meaning, it is necessary that electronic excitation be small compared to resonance excitation and population from above be negligible. The form of the intensity-pressure curves indicates that electronic excitation of high series members is practically negligible, so Kaskadensprünge remain as the only possible cause of ambiguity.

The small enhancement of the 3^2D level, even though it is a terminal state for several strong lines from higher levels which show large enhancements, can only be interpreted to mean that population from above is far smaller than population due to collisions with neon ions. Since the number of transitions is proportional to the cube of the frequency of the radiation emitted, any transitions among the higher terms which are all within one volt of each other, must be much fewer in number than the mentioned transitions to the 3^2D. The empirical result of Bleeker[4] may be used to calculate a typical case, the $7^2D \rightarrow 6^2F$ and the $7^2D \rightarrow 5^2F$ transitions. It is found that there should be six times as many transitions to the 5^2F as to the 6^2F. That the enhancement of the 5^2F level is only about one-fourth that of the 6^2F is therefore evidence that the total population of these levels is, at most, only very slightly influenced by transitions from above. It should be mentioned that since no transitions are observed from high P-terms, the curve for the s-series certainly cannot be falsified by population from above.

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[4] Bleeker, Zeits. f. physik. Chemie **120**, 63 (1926).

The enhancement curves certainly indicate a finite cross section at $\sigma = 0$ in accord with the work of Hanle[1] and the theory of Stueckelberg.[5] The finite cross section and the asymmetry of the curves negate the resonance interpretation of the older theory of Kallman and London[6] which gives an infinite cross section at $\sigma = 0$ and a symmetry cut-off for negative values of σ by the temperature of the gas.

The variation of the enhancement with the nature of the term is a result to be expected theoretically but not heretofore observed experimentally. Since the cross section depends on the square of the matrix element of the interaction potential V, $|\int \psi_i V \psi_f d\tau|^2$, one might inquire why any regularity exists, since presumably both V and ψ_f will be characteristic of the state excited. The regularity is, therefore, necessarily interpreted as a similarity of interaction potentials and wave functions for states with the same L-value, and the difference between series as due to a variation of either or both of these quantities with azimuthal quantum number. The present status of the theory, particularly the lack of knowledge of the wave functions of these states and of the interaction fields, prevents more detailed conclusions.

From the experimental results it is possible to obtain, by use of Eq. (5), an idea of the order of magnitude of the cross section in these collisions. At a pressure of 2.0 mm we may assume that the positive ion and electron concentrations are equal in the region photographed and therefore the ratio N_1/N_e' becomes the ratio of the electron concentration at the two pressures. Since the current was kept constant $N_1/N_e' = N_e/N_e' = v_e'/v_e$ and this ratio may be calculated from the mobility of electrons at 2.0 mm and from the field acceleration at 0.017 mm for in the latter case the mean free path is several times the length of the arc space. This ratio is approximately 1 : 20. Due to the constant magnesium pressure, $N_2/N_2' = 1$. For neon ions we may take a velocity slightly above that corresponding to the gas temperature, say 10^5 cm/sec., and in the low pressure case the electron velocity may be computed from the field and was about 2×10^8 cm/sec. Strictly, these velocities should be relative to the magnesium atoms, but from the geometry of the tube their motion is nearly at right angles to the current flow, and therefore the approximation of the magnesium atoms at rest should be correct in order of magnitude. Combining these factors with a measured enhancement of 400, for example, yields $q_r^n \simeq 2 \times 10^7 q_\epsilon^n$. It has been found that the electronic cross section for inelastic collisions is of the order of 3×10^{-18} cm^2, whence $q_r^n \simeq 6 \times 10^{-11}$ cm^2. This cross section, some 10^5 times the kinetic theory value is characteristic of collisions of the second kind where the energy-discrepancy is small. Stueckelberg has calculated cross sections of 2×10^{-13} cm^2 with an assumed interaction potential.

V. CONCLUSIONS

From intensities of the lines of the Mg II spectrum in the presence of neon the form of the cross section *vs.* energy-discrepancy curve has been found for the *s*, *d* and *f* series, and the following information concerning the cross section for collision between neon ions and magnesium atoms has been obtained: (a) The cross section has a maximum, finite value for $\sigma = 0$. (b) There is a sharper decrease of cross section for increasing negative values of σ than for positive. (c) The cross section depends on the L-value of the state excited by collision. (d) The order of magnitude of the cross section in this case is 10^{-11} cm^2.

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[5] Stueckelberg, Helv. Phys. Acta **5**, 370 (1932).

[6] Kallman and London, Zeits. f. physik. Chemie **B2**, 220 (1929).