Regularity Along a Series in the Variation of the Action Cross Section with Energy Discrepancy in Impacts of the Second Kind

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The enhancement of the intensities of lines in the spark spectrum of lead when excited by impacts of the second kind with neon ions relative to their intensities in electron impact excitation was measured. When the values of the enhancements are plotted against the energy discrepancies of the spectral terms in which the lines originate, smooth characteristic curves can be drawn through the points belonging to the same spectral series. The curves for different series, while similar in form, exhibit marked differences in details. Measurements were made on terms of negative as well as on terms of positive energy discrepancy. Maxima appear in the curves on the side of positive energy discrepancy, i.e., on the side where the energy values of the terms are less than the ionization potential of neon. The form of the curves beyond the maxima indicates that they may be of the form $q=A/\sigma^x$ where the value of both A and x vary with the particular series. The terms of the D series are most strongly enhanced. A calculation fixes the cross section for these collisions at approximately 15×10^{-11} cm^2.

I. INTRODUCTION

THE term "collision of the second kind," since first introduced, has come to have a broader meaning than that given it by Klein and Rosseland. In the present study we are concerned with a special type of such a collision, namely, one in which a normal lead atom collides with a neon ion, and, as a result, the lead atom becomes both ionized and excited, while the neon ion returns to its normal state. The reaction may be represented in the following manner:

$$Pb+Ne^+\rightarrow Pb^{+\prime}+Ne+\sigma, \qquad (1)$$

where σ, the energy discrepancy, represents the difference between the initial energy of the Ne ion and that of the final excited state of the Pb ion formed in the collision.

Although collisions may also occur between neon atoms in a metastable state and normal lead atoms, these, as will be shown, will not affect the results obtained.

The probability of an energy transfer as the particles approach each other is measured in terms of an action cross section which may be defined as follows. If we have in unit volume N_1 excited atoms of type A in state E_j and N_2 normal atoms of type B in state F_k, and if their relative velocity is u, then the number of collisions, n, which result in raising the type B atoms to the excited state F_j is given by

$$n=qN_1N_2u, \qquad (2)$$

where q is the action cross section for that particular type of collision. The action cross section may be expressed in terms of the probability of energy transfer, upon approach to a distance r, in the following manner. Let $P(r)$ represent this probability. If, as above, we have N_1 atoms of one kind and N_2 of another per cc, the number of the N_1 kind which approach one of the N_2 atoms to within a distance between r and $r+dr$ will be $N_2u\cdot 2\pi rdr$ and the total number of such approaches will be given by $N_1N_2u\cdot 2\pi rdr$. Hence the total number of such approaches resulting in energy transfer will be given by

$$n=N_1N_2u\int_0^\infty P(r)2\pi rdr \qquad (3)$$

and, comparing with the above, we have

$$q=\int_0^\infty P(r)2\pi rdr. \qquad (4)$$

Early investigation of collisions of this type were largely of a qualitative nature. Only recently have quantitative results been published[1, 2] in which action cross sections were calculated in terms of measured intensities of spectral lines. It has been found that the action cross section in these cases, as well as in those of a related nature, such as the quenching of resonance radiation, diminishes as σ increases and that the probability of an energy transfer is high only when σ is small.

[1] Duffendack and Thomson, Phys. Rev. **43**, 106 (1933).
[2] Duffendack and Manley, Phys. Rev. **47**, 56 (1935).

In these previous studies no attempt was made to determine any relationship between action cross section and energy discrepancy as a function of the different series of energy levels in a colliding atom. The work of Duffendack and Manley[2] on collisions between neon ions and magnesium atoms appeared to indicate that such a relationship did exist and a prediction was made that a definite regularity would be found for any one series, which might differ widely from one series to another. The prediction was based on the relatively small number of levels in each series that could be excited.

It was the purpose of the present investigation to determine whether such regularity exists and, if possible, to determine its nature. To do this it was necessary to observe at least three or four levels of each series and in as many series as possible.

II. Experimental Method

Experimentally the action cross section cannot be determined directly, but has been expressed in the usual manner in terms of an "enhancement" of those energy levels affected by the reaction. The enhancement of the energy level is expressed as the ratio of the intensity of a line originating in that level when excited principally by impacts with Ne ions to the intensity of that line when its initial level has been excited by electron impact. This is quite justified, since the intensity of a line is directly proportional to the number of atoms in a particular state and the number of atoms in that state is directly proportional to the efficiency of the process producing that state. Hence, we may consider:

$$\text{Enhancement} = \frac{\text{Eff. of energy transfer by collision of 2nd kind}}{\text{Eff. of energy transfer by electron impact}} = \frac{\text{Action cross section for collision of 2nd kind}}{\text{Action cross section for electron impact}}. \quad (5)$$

Since the investigation was one to determine series regularities, the first essential was to find a combination of particles such that the one should have many energy levels near the ionization level of the other. The most favorable combination was found to be lead and neon. At least four levels in each of four series for the lead ion are near enough the lowest level for the neon ion to be affected. The lines coming from these levels whose intensities were measured are listed in Table I. Lead had the further favorable properties of relatively low boiling point, making it easy to obtain in vapor state, and the lines involved were within the spectral region where good intensity measurements were possible.

The experimental technique employed was, with slight modification, that used by Duffendack and Manley[2] in the study of collisions between magnesium and neon. The method of excitation was that of the low voltage arc in neon in the presence of lead vapor. For a diagram of the tube see the paper by Duffendack and Manley.[2] The electrode assembly consisted of a quartz crucible, in which the lead was vaporized by means of a spiral heating coil of 12-mil tungsten wire. The crucible was enclosed in a nickel cylinder to reduce radiation losses. A flat, spiral filament of isovolt alloy placed near the mouth of the crucible served as the hot cathode for the arc, while the anode consisted of a nickel hood completely covering the filament and the crucible. The anode was provided with a rectangular side tube about 15 mm long and 2.5×5 mm in cross section, which was placed directly above the heated crucible and about 2 mm in front of the filament. This tube was lined up with the quartz window of the discharge tube and with the slit of the spectrograph. This arrangement greatly reduced the diffusion of the lead vapor and still permitted light from the arc to reach the spectrograph.

The measurements covered a range of wavelengths from about 2400A to 5074.6A. Two spectrographs were used during the course of the investigation. Both were quartz instruments made by Hilger. For the range $\lambda3451.7$ to $\lambda5074.6$ the type E-1 was used and for the shorter wavelengths, the smaller one, type E-2. Eastman polychrome plates were found quite satisfactory for both instruments.

Excitation by neon ion collisions was readily obtained. Measurements of intensities at a number of neon pressures from 5.5 mm to 1.6 mm indicated that the intensity was independent of the pressure. This would be expected since the low voltage arc, characterized by a neutral space charge, requires a constant concentration of positive ions for a given current.

At least two other methods of excitation were theoretically possible. Excitation by electron impact might be expected to some extent and, to a less extent, excitation due to the fact that the initial levels may be populated by transitions from above. That both of these effects are negligible appears clear from the following observations. The lines could not be obtained at all when the Ne pressure was reduced to a few hundredths of a millimeter. The arc was operated at about 24 volts, only a little above the ionizing potential of neon, and when the Ne pressure was reduced to 0.05 mm a sixteen-hour exposure at 150 volts failed to excite a single one of the lines. Thus the effect of electron impacts must certainly be negligible at the low voltage. Concerning the effect of transitions from above, it appears reasonable to assume that if the levels with which we were concerned could not be measurably excited by electron impacts, those levels still higher were even less likely to be thus excited. No lines from the higher levels were observed and thus the populations of such levels must have been extremely small and transitions from them negligible. We thus assume that the excitation observed is due entirely to collisions of the second kind.

To obtain the normal or electron excitation for comparison, much higher voltages were necessary. A spiral filament of 12-mil tungsten wire was used instead of the isovolt alloy as the latter broke down rapidly under the severe positive ion bombardment at the higher voltages. In order to prevent too rapid diffusion of the lead a small amount of He was admitted into the discharge tube. The He pressure was made such that the mean free path of the electrons was approximately 3 mm, the distance from the filament to the portion of the arc photographed. This required a He pressure of about 0.33 mm.[3] The potential necessary to excite the levels by electron impact was about 450 volts. Under these conditions an exposure of 30 minutes was sufficient to bring out the lines.

That the spark lines thus obtained are purely electron excited may be assumed for the following reasons. They could not have been due to impacts of the second kind with He ions, since the ionizing potential of He is 3 volts above that of Ne. Further, if any were due to such impacts, it would have been evident at the lower voltages. Conceivably it might have been due in part to collisions of the second kind with He metastable atoms whose excitation potential is only one volt below the ionizing potential of Ne. Again, if such effects were present, they would have occurred as well at lower voltages. Measurements also show that the levels in closest resonance with the metastable He were not appreciably enhanced. These facts, together with the high voltage necessary for the excitation, would appear to exclude all possibilities except that of electron impact.

The method of measuring the intensities of the lines was that developed by Thomson and Duffendack[4] in which a step diaphragm was used to place a calibration pattern on each plate that was measured.

[3] K. T. Compton, Phys. Rev. **22**, 338 (1923).

TABLE I. *Lines of Pb II whose enhancement by collisions of the second kind with excited neon ions has been measured. Standard for lines λ3117.7 to λ2498.9 = Pb I, λ2476.4.*

		Intensity			Energy Discrepancy	
Line	Initial Level	Ne Impact	Electron	Enhancement	cm	volts
5074.6	7*g*	0.84	0.30	2.8	1879	0.23
5070.7	7*g*	0.91	0.30	3.0	1879	0.23
5042.0	7*d*	0.89	1.60	0.58	19825	2.44
4582.3	8*g*	1.24	.58	2.14	−237	.029
4579.1	8*g*	1.35	.66	2.05	−237	.029
4352.7	8*f*	2.19	.65	3.40	2116	.26
51.5	8*f*					
4296.6	9*g*	.43	.34	1.30	−1688	−.207
4293.8	9*g*	.52	.62	.85	−1688	−.207
4242.5	5*f*	2.12	2.50	.85	21580	2.66
4195.5	11*p*	.48	.12	4.00	1309	.17
3971.3	9*f*	1.02	.35	2.80	−41	−.0055
3785.9	5*f*	2.40	3.00	.80	21580	2.66
3784.0	10*p*	.37	.13	2.90	4258	.525
3718.2	9*s*	1.00	1.00	1.00	12763	1.58
3714.0	8*d*	2.24	2.17	1.03	9919	1.22
3665.6	8*p*	.85	.97	.88	17871	2.20
3451.7	6*f*	2.08	1.29	1.60	11229	1.39
3117.7	9*d*	1.14	.28	4.10	4763	.59
2986.9	10*s*	.067	.039	1.70	6179	.76
2914.5	11*s*	.17	.031	5.50	2535	.31
2887.3	7*f*	.102	.040	2.60	5580	.69
2840.6	10*d*	1.22	.108	11.40	1541	.19
2772.7	9*p*	.067	.045	1.50	9087	1.12
2728.4	12*s*	.110	.021	5.50	197	.024
2717.5	8*p*	.366	1.080	.342	17891	2.20
2693.6	11*s*	.120	.023	5.20	2535	.31
2684.9	11*d*	.322	.065	5.00	−398	−.049
2634.3	10*d*	1.20	.088	13.50	1700	.21
2526.7	7*f*	.96	.370	2.70	5580	.69
2498.9	11*d*	.183	.038	4.90	−357	−.044

[4] Thomson and Duffendack, J. Opt. Soc. Am. **23**, 101 (1933).

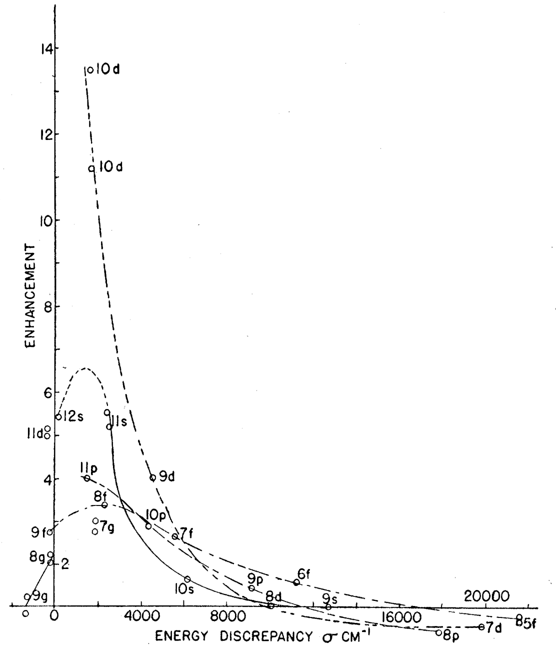

FIG. 1. Variation of enhancement with energy discrepancy.

All intensities were measured in terms of "standards" whose values were assumed to remain the same in the two types of excitation. Two such standards were necessary, one for each spectrograph. In the region of the E-1 spectrograph the line used as the standard was the Pb II line 9S→7P, λ3718.2. Its initial level was about 1.6 volts below the neon ion level and it would, therefore, not be expected to be enhanced by neon ions. The standard for the shorter wavelength region was the Pb I line λ2476.4 and one could be absolutely certain that this one was not affected by neon ions. The smooth curves obtained, when the measurements based upon the two standards were combined, indicate that neither standard was enhanced.

III. Experimental Results

The results of this investigation are presented in Table I and in the curves of Fig. 1.

The measurements given are the average values from a number of plates. In the region of the E-1 spectrograph, the average of four exposures at four different pressures, varying from 5.5 mm to 1.6 mm of Ne, were taken as the Ne impact intensities. These intensities remain constant within the limits of experimental error. In this region two exposures for electron excitation were obtained and two microphotometer tracings made from each, giving again four measurements. In the region of the E-2 spectrograph three good exposures were obtained with each type of excitation. In these measurements the average deviation from the mean in nearly all cases was less than 10 percent. In a very few instances of either very weak or very strong lines it was between 10 percent and 15 percent. In all cases when the error was over 10 percent the levels were far removed from resonance and hence came on the flat portion of the curve.

IV. Discussion

An examination of the curves shows clearly that no regularity whatever exists in the relation between action cross section and energy discrepancy if we consider all the points as a whole. When we consider the levels of any one series, however, marked regularity is shown. Each series shows a decrease in action cross section with energy discrepancy, σ, and three of the series indicate a maximum value of the cross section on the side of positive energy discrepancy; that is, for the case in which the ion has an amount of energy greater than that of the level excited by collision. Such a maximum may also occur in the D series, but we cannot be certain since the two levels, $10D$ and $11D$, nearest resonance are on opposite sides of the zero energy discrepancy axis. These points cannot be joined because of the asymmetry which is present in all of the curves. In the case of the F series the $8f$ and the $9f$ were joined, even though on opposite sides, but only because the curve on the positive side indicated a maximum at about $8f$ and the curves on the two sides are expected to meet at the axis.

A comparison of the relative positions of the points representing $8f$ and $9f$, $7g$ and $8g$, and $10d$ and $11d$ shows clearly the asymmetry of the curves. Thus the cross section for $8f$ on the positive side where $\sigma = 2163$ cm^{-1} is greater than that for $9f$ at $\sigma = -41$ cm^{-1}.

The exact position of the maxima cannot be determined. They cannot be predicted since no theory has been developed for this type of impact. They depend in part upon the inter-

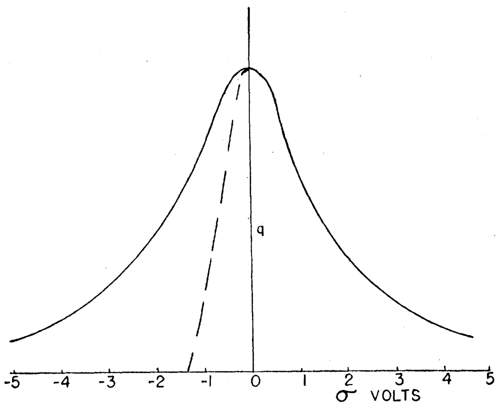

FIG. 2. Showing the relation between cross section and energy discrepancy. Solid curve, according to the theory of Kallmann and Rosen; dashed curve, as modified by taking account of the kinetic energy of the impacting atoms.

action potential curves of the colliding particles and these, at least at present, are outside the range of experimental observation.

The position of the maximum does not occur at the same value of σ for the different series, but in the case of the F series appears to be at about $\sigma = 2000$ cm^{-1} or roughly 0.25 volt. In the case of the S series, the position of the maximum is probably quite well determined, although its magnitude may be considerably in error. No attempt was made to construct a curve for the G series, since only one level, $7g$, was observed for positive values of σ.

As stated above, no theory has been developed for just this type of impact, so only qualitative comparisons are possible between these curves and those theoretically obtained for impacts of a somewhat different type.

In the theoretical treatment of Kallmann and London,[5] an equation is obtained which expresses the action cross section as a function of energy discrepancy for the excitation of *one* state only. In the derivation of the equation it was assumed that an atom had only a normal and one excited state. By neglecting the kinetic energy of the particles and by assuming, further, that, to a first approximation, the atoms upon approaching each other behave as dipoles, the following simple equation was obtained:

$$q\sigma^{\frac{2}{3}} = \text{constant}. \qquad (6)$$

The curve for this equation is symmetrical for values of $+\sigma$ and $-\sigma$ and indicates an infinite cross section for $\sigma = 0$. Since at close resonance the energy transfer proceeds so slowly it is not always completed, the authors, by taking this into account, find a lower limit for the cross section for $\sigma \to 0$. It must be remembered that in this treatment only excitation energy was transferred. There was no ionization and no electron transfer. Beutler and Eisenschimmel[6] show that the reverse reactions in collisions prevent the action cross section from going to infinity for zero energy discrepancy and calculate limiting values of the cross section for various conditions.

Kallmann and Rosen[7] have treated the case in which there was only electron transfer and obtained a curve similar in form to that of Kallmann and London except much broader. Its approximate form is shown in Fig. 2 (solid curve), and it will be noted that it, too, is symmetrical for $+\sigma$ and $-\sigma$.

It was suggested by Tyndall and Powell[8] that an asymmetry would be introduced by taking into account the kinetic energies of the colliding particles. For positive value of σ, there must be a liberation of energy upon impact to the kinetic energies of the particles, and for negative values of σ, energy must be absorbed from the kinetic energy. Thus, in the case of ions of slow speed, we would expect the electron transfer involving a given energy change to be more probable in the case where energy is liberated than where it is absorbed. For very slow speeds, there is no kinetic energy available for absorption and the curve must drop to zero for small negative values of σ. The modified curve would have the form indicated by the dashed curve in Fig. 2.

Morse and Stueckelberg[9] have treated the case where both ionization and excitation occur, but, due to their approximations, obtained values differing materially from those of Kallmann and London only in the region of very close resonance. Within this region, the curves show a maximum cross section for small positive values of σ for the case in which the transition is optically allowed. Since the difference introduced by

[5] Kallmann and London, Zeits. f. physik. Chemie **213**, 220 (1929).

[6] Beutler and Eisenschimmel, Zeits. f. physik. Chemie Abt. **B10**, 89 (1930).

[7] Kallmann and Rosen, Zeits. f. Physik **61**, 61 (1930).

[8] Tyndall and Powell, Proc. Roy. Soc. **A129**, 162 (1930).

[9] Morse and Stueckelberg, Ann. d. Physik **9**, 579 (1931).

Morse and Stueckelberg occurs only for values of σ much smaller than any involved in the present investigation, their curves are of less importance in this case.

A qualitative comparison of the experimental curves with those obtained by Kallmann and London shows that for the region beyond the maximum each of the experimental curves has the same general form as those theoretically obtained. The experimental curves obviously follow an inverse power law, though not as simple a one as that of Kallmann and London. Both the value of the constant and the power of σ must change from series to series, as is evident from the crossing of the curves. The action cross section has a finite value at $\sigma=0$, and the experimental curves are asymmetrical as suggested by Tyndall and Powell.

A striking effect indicated by the curves, but not predicted by the theory, is the marked preference shown for the D levels and a minor preference for the S levels. A tentative explanation of this preference was suggested to us by Dr. Hans Beutler, now at this laboratory. One may assume that at one phase of the impact, the neon ion and the lead atom are bound together into a quasi-molecule. The state of this molecule will be that of an odd spectroscopic term. This molecule dissociates into a normal neon atom and an excited lead ion. Since the normal state of the neon atom is that of an even spectroscopic term, the odd terms, D, S and G series, of the lead ion will be preferred over the even terms, P and F series.

Although it is not possible to calculate accurately the action cross section, one may, by use of Eq. (2), obtain its order of magnitude. Writing the equation as follows: $n=N_eNq_ev\cdots$ (2) where $N_e=$No. of electrons per cc, $N=$No. Pb atoms/cc, we may solve for q_e, the action cross section for electron impact.

Estimating the temperature to be 1300°K and the Pb vapor pressure as 0.02 mm we find $N=1.5\times10^{18}$/cc. N_e may be found from the measure of the arc current, remembering that the current is almost entirely an electron current. From a ratio of the mobility of the positive ions to the electrons and the total current, we may obtain the positive ion current and, from this, the value of n, the number of ionizing collisions per cc per sec. Substituting the values thus obtained we find:

$q_e=6\times10^{-18}$ cm², approximately = action cross section for ionization by electron impact.

Now to find q_{Ne}, the action cross section for Ne ion impact, we must write:

$$\text{Enhancement}=\frac{q_{\mathrm{Ne}}N_{\mathrm{Ne}}N_{\mathrm{Pb}}v_{\mathrm{Ne}}}{q_eN_eN_{\mathrm{Pb}}V_e}. \qquad (7)$$

From a measure of the currents in the two methods of excitation and from the respective particle velocities, we find that $N_{\mathrm{Ne}}/N_e=1/10$. For the Ne^+ excitation, the Pb vapor pressure is estimated to be 0.001 mm, and we thus obtain $N_{\mathrm{Pb}}/N_{\mathrm{Pb}}'=1/20$. For v_{Ne}/v_e we obtain 1/13000 and substituting these values in Eq. (7) we obtain for an enhancement of 10 the value $q_{\mathrm{Ne}}=15\times10^{-11}$ cm². The action cross section for Ne^+ impacts is thus seen to be very large compared to that for electron impacts.

We wish to express our appreciation to Professor S. A. Goudsmit for his interest in discussing with us the theoretical aspects of this research.