single crystals indicates the presence of absorption bands. The observations of A. H. Pfund[8] on sodium and potassium chloride crystals show such reflection maxima just to the long wave-length side of the bands observed by the transmission method. This displacement is to be expected on account of the change in the index of refraction in the neighborhood of a region of high absorption. Estimates of the positions of the absorption bands from the reflection maxima by Pfund agree well with those found by the transmission method.

In Fig. 4 the absorption structures of a number of halides of the alkaline earths and other elements are shown. These substances show little selective absorption, tending rather to a continuum with a relatively sharp edge at long wave-lengths. These results are similar to the observations of H. Fesefeldt[9] on a large group of compounds in the region above 1600A. Since the crystal systems of these salts are in general more complicated than that of the alkali halides, part of the difference in the absorption structure may be due to the lattice. The difference in valence may be another contributing factor. In all of this group of compounds the absorption coefficients were much smaller than those of the alkali halides, film thicknesses of 0.1 micron or greater being necessary to give measurable absorption.

In conclusion the authors wish to express their appreciation of the kindness of Professor G. P. Baxter of the department of chemistry for preparing several salts which are extremely rare, and to thank Professor T. Lyman for his continued interest in the progress of these experiments.

[8] Pfund, Phys. Rev. **31**, 315 (1938).

[9] Fesefeldt, Zeits. f. Physik **64**, 741 (1930).

MARCH 1, 1937 PHYSICAL REVIEW VOLUME 51

The Modification of Spectral Lines by Very Close Collisions[1]

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As a result of a survey of the spectra of Hg, Cd and Tl when a few centimeters pressure of a rare gas is added to a discharge through the vapor of these metals, it is concluded that bands of the type first reported by Oldenberg on the short wave-length side of the resonance line Hg 2536.7 probably occur with all metal lines, and with a total relative intensity of the same order of magnitude. The effect of collision induced emission seems in general to be negligible. The occasional appearance of diffuse maxima may be explained by a chance relationship between the potential curves which describe the interaction of the colliding atoms.

INTRODUCTION

CONSIDERABLE study has been devoted to the influence of surrounding atoms on the frequency of the radiation emitted from excited atoms of a gas, or absorbed by normal atoms.[2] A simple case of this general problem is that of a metal vapor at low pressure in the presence of a high pressure of some inert gas, under conditions of excitation such that only the former is excited. Any modification of the spectral lines of the metal must then be primarily caused by neighboring atoms in the normal state, and the effects of chemical binding forces and of resonance forces between excited atoms of the same species are eliminated. Under these conditions the metal lines show an asymmetrical broadening and shift, usually to long wave-lengths, which increase with the density of the inert gas. These pressure effects are due to perturbation of the emitting or absorbing atom by many comparatively distant foreign gas atoms, and must generally be studied at pressures of the order of atmospheres. This

[1] Extract from a thesis submitted to the department of physics of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] For a summary see Margenau and Watson, Rev. Mod. Phys. **8**, 22 (1936).

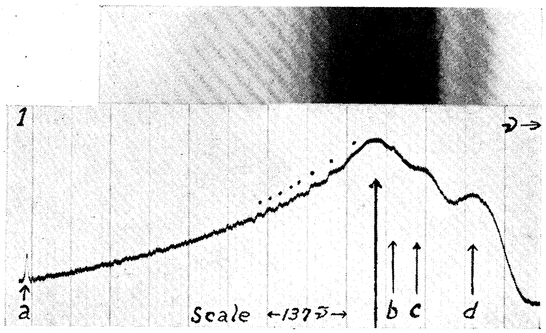


FIG. 1. Hg 2536.7, 10 cm A. On the short wave-length side of the line, whose center is indicated by the large arrow, are two diffuse maxima *c* and *d*; the latter has a relative intensity of 1/1800. *a* and *b* are weak Hg lines, λλ2576.3 and 2534, respectively. A few of the vibration bands superimposed on the long wave-length continuum are marked by dots.

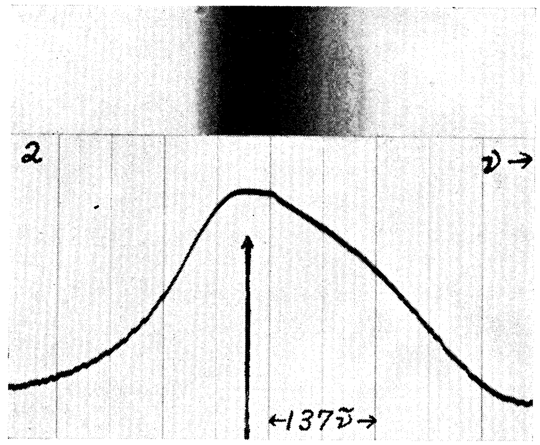


FIG. 2. Hg 2536.7, 10 cm He. There is a structureless continuum on either side of the line which can be traced further to short wave-lengths than in the case of Hg+A, but not so far to long waves.

paper is concerned with the less frequent very close collisions which modify the spectral lines emitted by unperturbed atoms in a more irregular manner. It will be shown that radiation emitted during these close encounters appears most commonly as a faint wing or diffuse band[3] close to the atomic line; it can often be observed, despite its relative weakness, at pressures as low as a millimeter of foreign gas.

Oldenberg[4] has shown that the resonance line Hg 2536.7, $1\,^1S_0-2\,^3P_1$, in fluorescence, with a few centimeters pressure of one of the rare gases added, is accompanied by certain peculiar spectra. With He a continuum extends on both sides of the line with continuously decreasing intensity (Fig. 2). With the heavier rare gases, one or two diffuse intensity maxima are found on the short wave-length side (Fig. 1), lying closer to the line the greater the atomic weight of the rare gas used. These maxima persist at high temperatures. According to Kuhn and Oldenberg[5] they represent radiation emitted from excited Hg atoms during collisions with normal rare gas atoms. At the turning point of a collision the kinetic energy of thermal motion in the internuclear direction has been transformed into potential energy, and part of this may be added to the excitation energy of the Hg atom to give a larger quantum provided emission takes place at this instant. Pairs of colliding atoms may be treated as molecules although they are in continuous states of "positive" total energy and will quickly separate unless transferred to a stable energy level as a result of radiation or a triple impact. Molecular theory indicates that two states arise from the approach of a $^3P_1$ atom and a normal $^1S_0$ atom of different species between which only weak attractive forces of the polarization type occur,[6] and Kuhn and Oldenberg supposed that the two bands near Hg 2536.7 arise in transitions from these two upper molecular levels to a common ground level.

Krefft and Rompe[7] showed that somewhat similar diffuse bands occur on the short wave-length side of a number of the strongest lines of different metals in the positive column of a discharge to which a rare gas has been added. They classified these bands according to visual judgment of their shape and suggested a number of empirical relations such as proportionality of the width of certain bands to $1/\sqrt{G}$, where G is the atomic weight of the particular rare gas used.

The present investigation of collision spectra was undertaken for two reasons. First, no intensity measurements had been made by previ-

[3] As a matter of convenience, the word "band" will be used rather loosely in this paper when referring to the modified portions of spectral lines believed to be caused by close collisions. These all appear to be *continuous* spectra, some distinctly separated from the actual line, others merely "wings" or marked asymmetries.

[4] Oldenberg, Zeits. f. Physik **47**, 184 (1928) and **55**, 1 (1929).

[5] Kuhn and Oldenberg, Phys. Rev. **41**, 72 (1932).

[6] Mulliken, Rev. Mod. Phys. **4**, 26 (1932).

[7] Krefft and Rompe, Zeits. f. Physik **73**, 681 (1932).

ous workers. Krefft and Rompe reported bands by only a few strong lines in the spectra of each of several metals, and without knowledge of the intensities of the bands relative to their associated lines it was possible that their absence by weak lines was due merely to insufficient exposure. All spectral lines show pressure broadening and shift and there was no apparent reason why they should not also be modified by very close collisions. Accordingly it was proposed to examine all the stronger lines in the spectra of three metals, Hg, Cd and Tl, in the range accessible with a quartz spectrograph, with the addition both of He and of A and with the longest possible exposures, and to measure the relative intensities of all bands found with sufficient accuracy to determine whether there was any considerable variation.

Second, the theory of the intensity distribution of collision radiation needed more careful examination. In explaining the diffuse maxima which appear near Hg 2536.7 in the presence of the heavier rare gases, Kuhn and Oldenberg made the assumption that all close collisions between excited and normal atoms are head on, thus reducing the problem to one dimension. It will be shown later that virtually their same argument extended to three dimensions does not predict any such intensity maxima, and that these require for their qualitative explanation some additional assumption. Kuhn and Oldenberg had suggested that a close collision might in some cases momentarily increase the emission probability of an excited atom, and that this might be a factor in the production of the bands near the mercury resonance line. Evidence of this process was later obtained[8] in the discovery of a small continuous spectrum near the weak forbidden line Hg 2269.8, $1\,^1S_0-2\,^3P_2$, with He or A added. This band has negligible intensity near the line, rises to a maximum near 2259A, and shades off more gradually to shorter wavelengths. With a 10 cm pressure of A the total integrated intensity of the band is over 100 times that of the line itself. Both the shape and the high relative intensity were satisfactorily explained by an enhanced transition probability from the metastable $^3P_2$ level during close collisions. It was desirable to obtain more experimental information about the modification of spectral lines by close collisions before deciding whether collision induced emission was of importance in other cases not involving metastable states.

[8] Preston, Phys. Rev. **49**, 140 (1936).

Experimental

The three metals studied, Hg, Cd and Tl, were readily purified by distillation in vacuum. The rare gases, He and A, were treated in a misch metal arc.[9] A high degree of purity was desirable because the whole spectral range from 2200A to 5000A was to be searched for weak new bands. The metal under investigation was distilled into a side arm attached to a simple capillary discharge tube supported within an electric furnace in order to obtain an adequate metal vapor pressure. The discharge was excited by means of a small transformer, using currents of about 10 ma through the capillary. In practice, a 10 cm pressure of rare gas was admitted to the discharge tube at room temperature and the furnace then turned on. While at first the spectrum of the rare gas was emitted strongly, when the metal vapor pressure reached the order of 0.01 mm only the metal spectrum was observed, since the lowest excitation potentials of both He and A lie above the ionization potentials of the metals studied. A quartz discharge tube and a temperature of about 700°C were necessary in the case of Tl. The exact metal vapor pressure was not known because there was some diffusion out into the cool tubing connecting the discharge tube to the vacuum system, but this process was retarded by the comparatively high pressure of the rare gas. It was desirable to have the metal vapor pressure as small as possible in order to keep the proportion of diatomic metal molecules present low. Cd_2 and Hg_2 emit a number of diffuse bands and extensive continuous spectra which can easily be confused with collision spectra.

Collision bands were invariably so weak relative to the lines which they accompany that extreme overexposure of the line was necessary in order to record the band on the photographic plate. A new medium sized quartz prism metal Hilger spectrograph was found to be far superior to older models for this work. Large dispersion

[9] Van Voorhis, Shenstone, and Pike, Rev. Sci. Inst. **5**, 367 (1934).

prism instruments require inconveniently long exposures for weak spectra and seem to produce an irregular diffraction pattern, probably caused by slight inhomogeneities in the optical system, when a line is greatly over-exposed. Diffraction grating spectrographs are unsuitable because ghosts are always too intense.

The photometric problem was that of comparing the intensity of a weak diffuse band with that of a neighboring line. Because the image of a spectral line is merely the central maximum of a diffraction pattern caused by the aperture of the camera lens, a long exposure will bring out many secondary maxima. For example, an exposure of 1000 times the minimum necessary to record a spectral line, which was frequently necessary in this work, will broaden the image to include the tenth diffraction maximum on either side. For this reason the weaker a band the greater the distance from its line to which it must extend in order to be observed experimentally. Most bands are partially and many wholly obscured by the overlapping diffraction pattern of the line.

Provided the slit width of a spectrograph is greater than the spacing of the diffraction pattern, the intensity of a continuous spectrum as measured on the photographic plate increases almost proportionally to the slit width, but a line simply broadens while its intensity remains constant. Hence the ratio of the intensity of a point in a continuous spectrum to a point in a line, as measured by a microphotometer, depends on the width of the spectrograph slit. The latter was kept constant in this work during all intensity measurements so that the results can be compared among themselves. A broad spectrograph slit was used throughout in order to have the photographic image wider than the microphotometer slit image, and also to reduce the necessary exposure time.

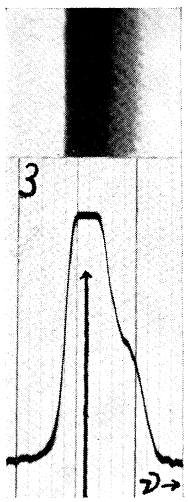
For the actual intensity measurements a line was recorded in a series of exposures of increasing time, using a gauze screen to reduce the intensity to the same order of magnitude as that of the neighboring band without a screen. The band was then photographed in a similar series of exposures without a screen. Comparing a line in the first series with some point in the associated band from the second series of the same density, as determined with a microphotometer, the relative intensity could be estimated from the known screen factor and the relative exposure times. Reciprocity law failure was thus neglected over small ranges. Only when a band is quite separate from its line can its intensity be defined unambiguously; it is then naturally taken at the band's maximum. When no maximum is observed the point at which to measure the band's intensity becomes somewhat arbitrary.

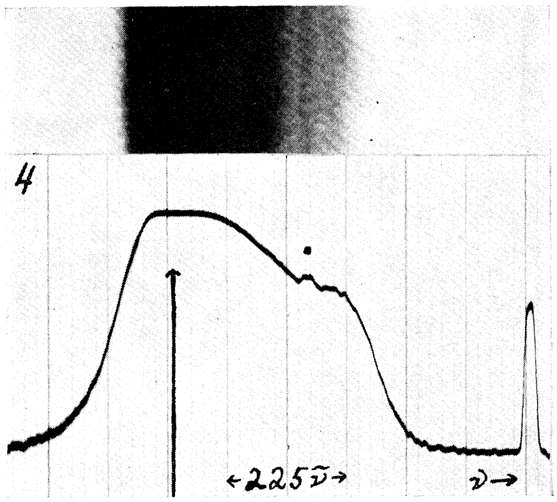
Experimental Results

Fig. 1 shows the line Hg 2536.7 in a discharge containing a 10 cm pressure of A. Below the photograph, on the same scale and in register, is a microphotometer trace. To short wave-lengths from the line can be seen a pronounced intensity maximum at 2526.0A and another, less clearly resolved, at 2530A. The outer maximum has a relative intensity of 1/1800; that of the inner appears to be somewhat greater, but is uncertain because of the overlapping line. No trace of fine structure can be observed in either of these diffuse bands. The position of the outer maximum was measured at three different temperatures, 55, 130, and 400 C; it was unchanged within a limit of error of about 0.3A.[10] There was likewise no observable shift when the argon pressure was reduced to 1 mm. The maximum was still clearly visible with as little as 0.1 mm of argon but its intensity relative to the line was enormously less than at 10 cm. In order to avoid errors caused by self-reversal, the intensities of all resonance lines like Hg 2536.7 were measured with a special discharge tube having a vertical quartz capillary 3 mm in diameter, viewed from the side through the capillary wall. At the low metal vapor pressures used the absorption must have been small under these conditions. Correction for residual error from this cause would lower slightly the above figure for the relative intensity of the Hg 2536.7 maximum.

On the long wave-length side of the line Hg 2536.7 in Fig. 1 may be seen a series of narrow bands, the first three with a distinct step-like form, superimposed on a continuous spectrum. These bands were reported by Oldenberg and explained as transitions from *stable* vibration levels of Hg $^3P_1-$A $^1S_0$ molecules to a normal

[10] Oldenberg (reference 4) found a slight shift to shorter wave-lengths over a somewhat larger temperature range.





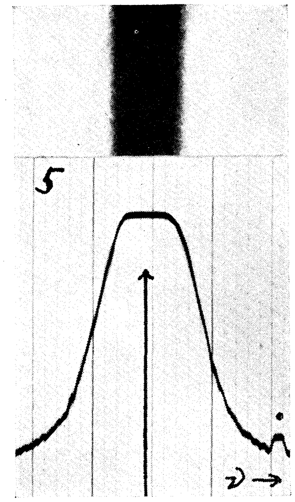


FIG. 3. Tl 3775.7, 10 cm A. There is a narrow band on the short wave-length side of the line, relative intensity 1/350.

FIG. 4. Tl 3775.7, 10 cm He. The broad band on the short wave side appears to have an intensity maximum, but it is confused by the line Zn 3740, which is marked by a dot. This band has a relative intensity of 1/3000.

FIG. 5. Tl 3775.7, 0.05 cm A. This shows the unmodified Tl line with the same exposure as in Fig. 4, namely about 10,000 times that just sufficient to record the line on the photographic plate. With only a trace of rare gas, added merely to make the discharge run smoothly, the line is accurately symmetrical.

state with unresolved vibration levels. Confirming Oldenberg's results, these bands disappear completely at temperatures of a few hundred degrees, a fact which is not surprising in view of the small binding energy to be expected in such polarization molecules. In the present work, similar bands were sought near other lines of Hg, Cd and Tl, but in no other case were they found.

Fig. 2 shows the corresponding band obtained with He. It is apparent that the intensity falls continuously away from the line on the short wave side without any indication of a maximum. The intensity fall is rather gradual, and with long exposures the band can be traced for at least 25A. On the long wave side of the line there is no trace of vibration bands and the continuous tail is relatively much weaker than with A.

Figs. 3, 4 and 5 illustrate the line Tl 3775.7, $2\,{}^2P_{\frac{1}{2}}-2\,{}^2S_{\frac{1}{2}}$. Fig. 3 shows the effect of the addition of 10 cm of A. There is a narrow band which to the eye appears to have a step-like form with a well defined edge 120 cm^{-1} from the line. The microphotometer shows that the intensity fall is continuous, but with a point of inflection which may indicate a maximum obscured by the overlapping overexposed line. The relative intensity of the band at the point of inflection in the microphotometer trace is about 1/350.

Fig. 4 shows the same line with the addition of 10 cm of He. Because the resulting band is considerably weaker, the line is more overexposed and therefore broader than in Fig. 3; the longer exposure brings out a neighboring line Zn 3740 due to a trace of impurity, and this is marked by a dot. The relative intensity near the center of the He band is about 1/3000 and its short wave-length edge is approximately 375 cm^{-1} from the line.

Fig. 5 shows Tl 3775.7 in the absence of rare gas and with an exposure nearly the same as that in Fig. 4. By subtracting the intensity relative to the center of the Tl line at a number of points on the short wave wing of Fig. 5 from the intensity at corresponding points of Fig. 4, Fig. 6 is obtained. Although the accuracy of this procedure is small, Fig. 6 shows that the Tl 3775.7 He band has a definite maximum which in Fig. 4 was obscured by the overexposed Tl line and by Zn 3740.

Figs. 7 and 8 illustrate Hg 2967.3, $2\,{}^3P_0-3\,{}^3D_1$, the former with A and the latter with He. They show that diffuse maxima may also occur on the long wave-length side of metal lines in the

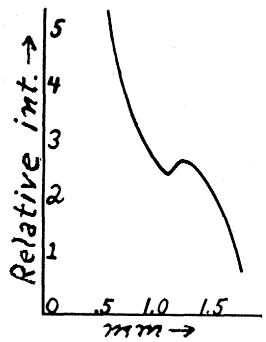


FIG. 6. Result of subtracting the short wave-length portion of Fig. 5 from that of Fig. 6, in terms of relative intensities, thus effecting a correction for the overlapping of the band by the over-exposed line. The ordinates give the relative intensity in units of 0.0001 of the intensity at the center of the line, the abscissae distances towards short waves from the center of the line, in millimeters on the plate.

presence of rare gases. Here the He band lies closer to the line than the A band.

Collision spectra were identified near 13 lines of the spectrum of Hg, 12 of Cd, and 6 of Tl. The majority of these resembled that shown in Fig. 3, having roughly defined short wave edges and no resolved maximum. Only three definite cases of maxima on the short wave side of lines were encountered, all lying fairly close to and definitely associated with an atomic line. Several examples were found of maxima like those in Figs. 7 and 8, at varying distances on the long wave side of lines, some at such great distances that they could not be definitely connected with any particular line.

It was pointed out in remarks concerning Figs. 3 and 4 that the band on the short wave side of Tl 3775.7 with He extended considerably further than that with A. It was found to be quite generally true that when a band with a fairly sharp short wave limit occurred by the same line with both He and A, the He band was roughly three times as wide as the A band. There was considerable variation in the ratios of these widths, however, and some bands had so gradual an intensity fall that no edge could be measured. For this reason it seems unlikely that any significant numerical relationship can be established between these band widths and the properties of the particular rare gas added to the discharge. The observations of Krefft and Rompe in this connection, which have been referred to previously, appear to be illusory.

It would be of interest to measure the ratio of the total energy represented by a band to that of its line. This total integrated relative intensity would afford a measure of the proportion of the total emission occurring during collisions, but it is usually impractical to obtain because of the overlapping of lines and bands. The most that can be said is that the broader bands (in frequency units) were always weaker than the narrow bands, and it is probably true that in all examples studied the total integrated relative intensity was of the same order of magnitude.

A survey of all bands observed indicated definitely that those associated with the lines of a particular spectral multiplet are much more alike in form and width than those belonging to unrelated lines. For example, diffuse maxima occur on the long wave side of several of the $2\,^3P-3\,^3D$ lines of Hg and Cd, and not by any other lines in the spectra of these metals; no bands were found on the short wave side of any members of this multiplet. Similarly, the three Hg lines $2\,^3P_{2,\,1,\,0}-3\,^3S_1$ and the line Cd $2\,^3P_1-3\,^3S_1$ all had a narrow He band without resolved maximum and with an edge approximately 60 cm^{-1} on the short wave side (the Cd lines $2\,^3P_{2,\,0}-3\,^3S_1$ happen to be in unfavorable positions for observation). A tendency was apparent for bands to become narrower in passing to the higher members of a spectral series; no

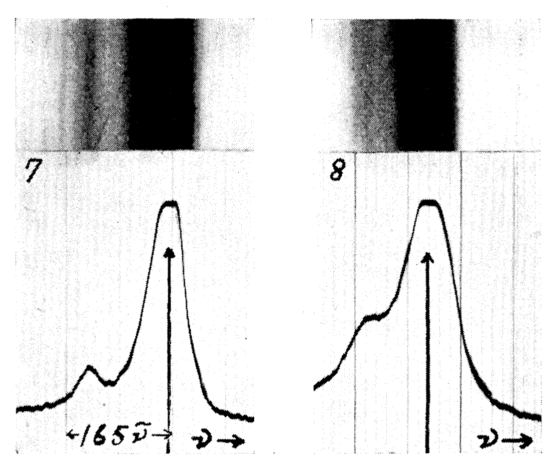


FIG. 7. Hg 2967.3, 10 cm A. This is an example of a clearly resolved maximum on the long wave-length side of a line; the separation is 125 cm^{-1}.

FIG. 8. Hg 2967.3, 10 cm He. Here the maximum is not clearly resolved from the line, since the separation is only 90 cm^{-1}.

connection was observed between band shape or width and the inner quantum number j of either the initial or the final term characterizing the associated line.

It is now possible to answer at least partially the question of the occurrence of collision spectra. It must be emphasized that many lines in the range considered are not suitable for observation, either because they lie close to other lines of greater intensity or because the region about them is covered in long exposures by the extensive continua belonging to diatomic molecules of the metal being studied. Suppose, however, that a distinct band was observed first by one line of a Hg multiplet, in the presence of A. From the foregoing general results we should expect to find approximately similar bands by other members of this multiplet, and wider bands (hence easier to observe) by the same lines when He is added. This was always verified for as many lines as were favorable for study, that is, a band was always found when one of observable width was predicted and the region was not obscured. The evidence therefore suggests that every spectral line of a metal is modified in a characteristic manner by the addition to the discharge of a small pressure of He or A. In addition to the familiar pressure broadening and shift, which are very small under these conditions, a marked asymmetry appears which in extreme cases takes the form of a separate intensity maximum at a considerable distance from the center of the line. The position of these maxima appears to be independent of the pressure of foreign gas while their intensity is probably proportional to it.

Theory

Consider a single excited metal atom under the conditions specified at the beginning of this article. At any instant and for a given foreign gas density the probability of finding a normal atom of the foreign gas in a spherical shell of radius r and thickness dr about the excited atom is proportional to $r^2e^{-\varphi_1(r)/kT}dr$, where $e^{-\varphi_1(r)/kT}$ is the Maxwell-Boltzmann distribution function and $\varphi_1(r)$ the potential energy of interaction between the excited atom and a normal atom of the foreign gas. We will limit ourselves to a region so small that at ordinary pressures the chance of finding two or more foreign gas atoms within it at one time is negligible.[11] At small distances, $\varphi_1(r)$ increases rapidly as r decreases due to the strong repulsive forces between colliding atoms, and hence the probability of finding a foreign gas atoms decreases rapidly.

Suppose we now make the following assumptions:

(a) Let the Franck-Condon rule apply strictly, so that to each internuclear distance r there corresponds a frequency ν which will be emitted if a radiative transition occurs while a perturbing atom is at this distance. This frequency will be given by $h\nu(r)=h\nu'+\varphi_1(r)-\varphi_2(r)$, where ν' is the unperturbed frequency $=\nu(\infty)$, and $\varphi_1(r)$ and $\varphi_2(r)$ represent the interaction between a foreign gas atom and a metal atom in the initial and final states respectively which correspond to the particular transition.

(b) Let the curves φ_1 and φ_2 be nearly similar in their repulsive portions, but the former displaced slightly towards larger values of r. Since the atom in the state of higher excitation may be expected to have a larger collision cross section, repulsion should occur at larger internuclear distances,[12] and for any given value of r in this range we will have $\varphi_1>\varphi_2$ and $d\varphi_1/dr>d\varphi_2/dr$.

(c) The intensity $I(\nu)$ at the frequency ν is proportional only to the number of excited atoms which at any instant are so perturbed by colliding atoms that they can, according to the Franck-Condon rule, radiate this frequency. That is, $I(\nu)d\nu\propto e^{-\varphi_1(r)/kT}dr$ where ν and r are related by $h\nu=h\nu'+\varphi_1-\varphi_2$.

As a consequence of these assumptions the radiation emitted during collisions should appear as a tail on the short wave-length side of the unperturbed line, since $h\nu-h\nu'=\varphi_1-\varphi_2>0$. Its intensity should decrease continuously with distance from the center of the line because of the increasing rarity of the closer collisions which produce the larger shifts, and it should everywhere be small because of the relatively small probability of emission taking place during a close collision. This is indeed what was observed experimentally in a considerable number of cases, such as that illustrated in Fig. 2. However,

[11] Kuhn, Phil. Mag. **18**, 987 (1934).

[12] This assumption was made by Kuhn and Oldenberg, reference 4.

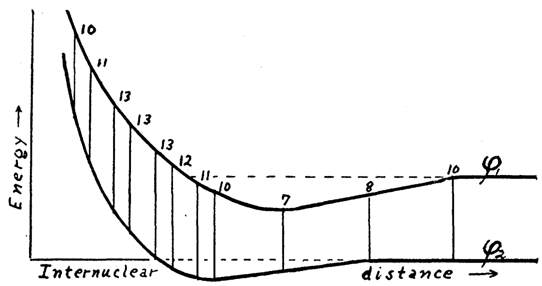


FIG. 9. Hypothetical potential curves illustrating the suggested explanation of diffuse collision spectra having the form of separate maxima. The upper and lower curves represent, respectively, the energy of an excited and of a normal metal atom colliding with a neutral rare gas atom. The lengths of the vertical lines, indicated by the accompanying numbers, are a measure of the energy available if emission takes place at the corresponding nuclear separation.

some modification of our assumptions is necessary to explain the occurrence of separate maxima.

(a) has been discussed by Kuhn and London.[13] It may be expected to apply the more closely the smaller the relative velocity of the colliding atoms, and slight departures from it will merely introduce a certain blurring.

We stated in the introduction that it had been suggested that collision induced emission might be a factor in the explanation of these intensity maxima. Our experimental results show, however, that collision radiation represents a very small[14] and at any given pressure a relatively constant fraction of the total intensity of the line proper. It is not possible to actually calculate this fraction without a quantitative knowledge of the course of φ_1 and φ_2, but estimates show that the intensity is of the right order of magnitude if we assume that (c) is true and that the emission probability of ordinary excited atoms is not markedly influenced by close collisions with normal atoms.

The assumptions under (b) are more arbitrary and possibly quite unnecessary. In Fig. 9, φ_1 and φ_2 have been drawn in such a manner that φ_1 has a somewhat smaller curvature than φ_2 in the region of repulsion[15] and hence the curves are approximately parallel over a short range of r; their vertical separation is here greater than at $r=\infty$. Radiation emitted from hypothetical colliding atoms whose interaction conforms to these potential curves will have a definite high frequency limit somewhere on the short wave-length side of the line, and near this limit the intensity will be large because perturbations over a considerable r range will produce approximately the same frequency shift. The blurring introduced by slight departures from the Franck-Condon rule will result in the formation of a rounded intensity maximum with rapid intensity fall on its short wave-length side.

Of course, these potential curves were devised for the express purpose of "explaining" intensity maxima like those shown in Figs. 4 and 6; almost any sort of band can be similarly accounted for because there is little independent information about the potential curves. Still, it is not unreasonable that there should be a considerable variation in the forces between foreign gas atoms colliding with metal atoms in different states of excitation and that occasionally this special relationship should exist between the potential curves.

In considering Fig. 9 once again, it is apparent that we have neglected radiation coming from the portion of the upper potential curve where the interatomic force is attractive. Since there is an increasingly large chance of finding a perturbing atom at these greater internuclear distances, the corresponding radiation must be more intense than that coming from the range in which repulsive forces predominate. In Fig. 9 the depth of the minimum has been greatly exaggerated; it is necessarily shallow when the attractive force is due only to polarization, as in the case of an excited metal atom colliding with a neutral rare gas atom. For this reason the radiation from this portion of the potential curve is shifted only slightly to long wave-lengths and is therefore obscured by the broadened overexposed atomic line. The weaker collision radiation can only be detected because of its larger frequency shift. The connection between radiation from excited atoms perturbed by close approaches of foreign atoms and the phenomena of pressure broadening and shift has also been discussed by Kuhn.[11]

It is rather surprising that the line Hg 2536.7,

[13] Kuhn and London, Phil. Mag. **18**, 983 (1934).

[14] Except in the case of the Hg 2269.8 band (reference 8), which originates in transitions from a metastable state.

[15] This particular relationship between potential curves was suggested by a diagram in an article by Kuhn (Zeits. f. Physik **72**, 462 (1931)), in which it was used to explain the position of certain TlI bands.

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

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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).

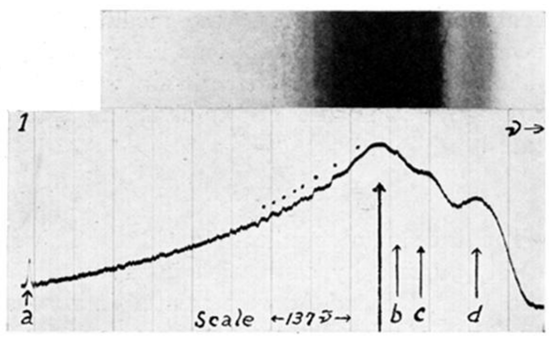

FIG. 1. Hg 2536.7, 10 cm A. On the short wave-length side of the line, whose center is indicated by the large arrow, are two diffuse maxima *c* and *d*; the latter has a relative intensity of 1/1800. *a* and *b* are weak Hg lines, λλ2576.3 and 2534, respectively. A few of the vibration bands superimposed on the long wave-length continuum are marked by dots.

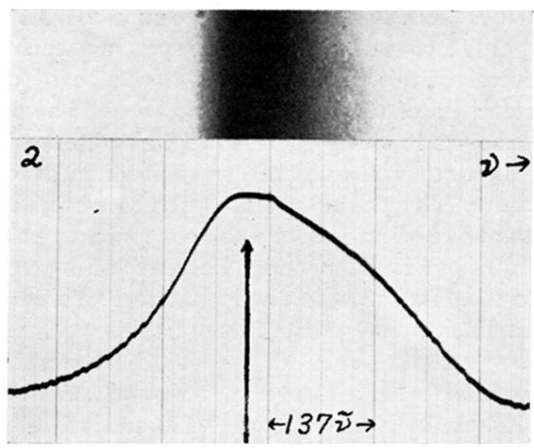

FIG. 2. Hg 2536.7, 10 cm He. There is a structureless continuum on either side of the line which can be traced further to short wave-lengths than in the case of Hg+A, but not so far to long waves.

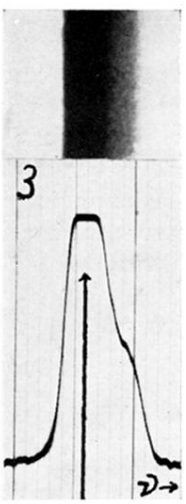

FIG. 3. Tl 3775.7, 10 cm A. There is a narrow band on the short wave-length side of the line, relative intensity 1/350.

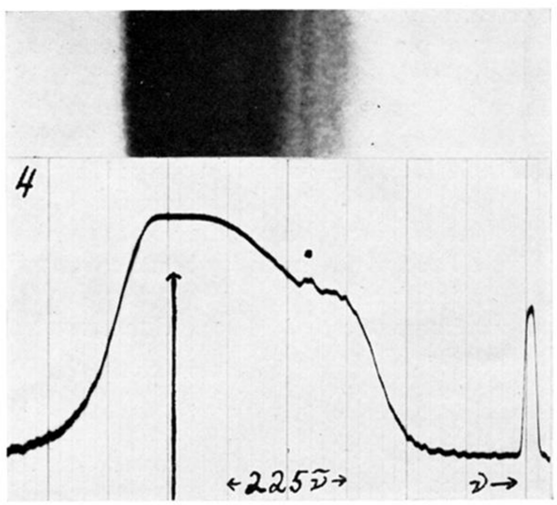

Fig. 4. Tl 3775.7, 10 cm He. The broad band on the short wave side appears to have an intensity maximum, but it is confused by the line Zn 3740, which is marked by a dot. This band has a relative intensity of 1/3000.

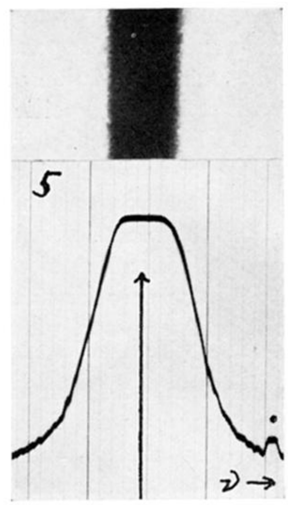

FIG. 5. Tl 3775.7, 0.05 cm A. This shows the unmodified Tl line with the same exposure as in Fig. 4, namely about 10,000 times that just sufficient to record the line on the photographic plate. With only a trace of rare gas, added merely to make the discharge run smoothly, the line is accurately symmetrical.

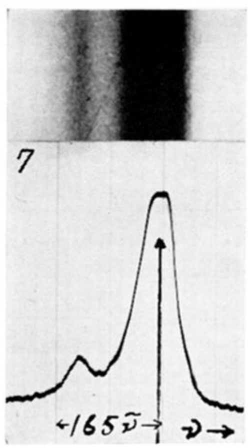

FIG. 7. Hg 2967.3, 10 cm A. This is an example of a clearly resolved maximum on the long wave-length side of a line; the separation is 125 cm^{-1}.

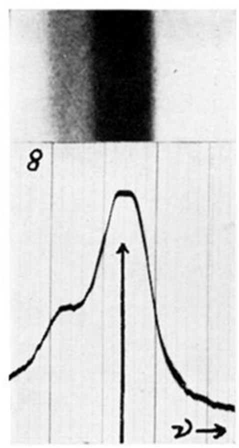

FIG. 8. Hg 2967.3, 10 cm He. Here the maximum is not clearly resolved from the line, since the separation is only 90 cm^{-1}.