Collision Induced Emission

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(Received November 15, 1935)

A new continuous spectrum, associated with the weak forbidden mercury line λ2269.80A, has been found in a low pressure mercury discharge with a few centimeters pressure of argon or helium added. The continuum lies on the short wave-length side of the line, rising steeply to maximum intensity at about 2259A, and then falling more slowly to 10 percent near 2237A. It is attributed to radiation from excited mercury atoms in the $^3P_2$ metastable state, perturbed by the close approach of rare gas atoms, at which time the thermal energy may be added to the energy of excitation to give a larger quantum. Since the total intensity of the continuum is many times that of the line, although the time during which an excited atom is appreciably perturbed is much less than the time between collisions, we must assume that during a collision the probability of emission is enormously increased. The j selection rule, which normally inhibits the transition $^1S_0-{}^3P_2$, evidently breaks down in the field of the colliding atom. This is shown to be reasonable on theoretical grounds.

Introduction

When an excited atom is perturbed by the close approach of a colliding neutral atom or molecule, it might be supposed that, in some cases, its probability of emission would be momentarily increased. This effect may be called "collision induced emission," and distinguished from the case in which a stable molecule, with quantized energy states, is formed. The halogens, for example, show intense band spectra due to transitions between molecular levels derived from atomic states between which transitions cannot take place. The time of interaction or the "duration" of a collision is very short, and we are chiefly interested in comparing the emission probability of the excited atom in the perturbed and unperturbed conditions.

It has, of course, been suggested before that a collision might increase the emission probability of an excited atom, but experimental evidence bearing on the question has never been satisfactory. Hamos,[1] for example, looked for this effect in a study of the intensity of the sodium D lines in fluorescence, with and without the addition of foreign gases. He decided that the changes he observed could be adequately explained by ordinary collision broadening of the absorption line, without the additional hypothesis of induced emission.[2] More recently, a diffuse helium band at 600A was investigated by Nickerson.[3] This seemed to be associated with the forbidden line λ602.418, $1\,^1S_0-2\,^1S_0$, although the connection was not very well established. Nickerson first suggested that the band might be due to induced emission during the close approach of a normal to an excited helium atom, since this would account for its location and comparatively great intensity relative to the line. However, he was forced to decide against this interpretation because the potential curves, which are known for the lower states of the helium molecule with considerable accuracy, indicated that no radiation could be emitted in this transition, of frequency greater than that of the atomic line itself.[4]

In the course of work on diffuse bands of the type, first reported by Oldenberg,[5] and in more detail by Kuhn and Oldenberg,[6] which accompany certain strong metallic lines in a discharge when a considerable pressure of one of the rare gases is added, a short continuum has been observed which is believed to give definite indication of collision induced emission. This continuum occurs on the short wave-length side of the weak forbidden mercury line λ2269.80, and

[1] Hamos, Zeits. f. Physik **74**, 379 (1932).

[2] There was no disproof of this hypothesis. Hamos's results were difficult to interpret, because only the *total* intensity of the fluorescent D lines was directly measured. A collision able to modify substantially the emission probability must also modify the interaction potential curves and hence, ordinarily, the frequency radiated. The total intensity, on the other hand, may remain unchanged.

[3] Nickerson, Phys. Rev. **47**, 707 (1935).

[4] That is, the potential curves for the ground state, $2p\sigma\,^1\Sigma_g$ and the upper state, $2s\sigma\,^1\Sigma_u$, are further apart at infinite nuclear separation than at any other time. Nickerson suggested that two somewhat similar diffuse bands, at 647A and 662A, may be due to transitions from the first two *vibration* levels of the $2s\sigma\,^1\Sigma_u$ state, and the possibility remains that the band at 600A comes similarly from a vibration level of some higher state.

[5] Oldenberg, Zeits. f. Physik **47**, 184 (1927).

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

has been obtained when a few centimeters of helium or argon were added to a low pressure mercury discharge.

Experimental

The simple Pyrex discharge tube had a capillary 5 mm in diameter and 10 cm long, and was supported within an electric furnace which maintained a temperature just sufficient to give a weak mercury discharge with a 0.5 kw, 15,000-volt transformer. Observations were made with a medium-sized quartz prism Hilger spectrograph.

High purity of conditions in the discharge was essential, because of the comparative weakness of the phenomena to be observed. Clean mercury was distilled into a side arm attached to the discharge tube, which was previously baked out carefully. The argon and helium were purified for several days in a misch metal arc, until a spectrogram of long exposure showed no lines or bands due to impurities.

The addition of a rare gas over a wide range of pressures makes a discharge through mercury vapor of low pressure run smoothly and without much heating. The ionization voltage of mercury is 10.38, while the lowest excited levels of both helium and argon lie higher. For this reason, even with 10 cm of rare gas and only 0.01 mm of mercury vapor, the spectrum obtained is that of the metal alone, neither lines nor continua of the rare gases appearing.

Description of the Continuum

A microphotometer trace of the new continuum is shown in Fig. 1. It extends from the forbidden line to short wave-lengths, reaching a maximum near 2259A, 200 cm^{-1} from the line. From that point it falls uniformly, reaching 10 percent of its maximum intensity at about 2237A. To long wave-lengths, the continuum falls steeply to 10 percent at the line, and fades out near 2272A. No trace of structure can be made out. The ratio of the intensity of the line λ2269.80 to that of the maximum of the continuum is close to 0.50, in the case of 10 cm of added argon. This ratio is arbitrary, of course, since it depends on the width of the slit[7] of the spectrograph. The latter was kept constant throughout the experiment, so that the above ratio will be useful for purposes of comparison. It was estimated that the *total* intensity represented by the continuum was about 100 times that of the line.

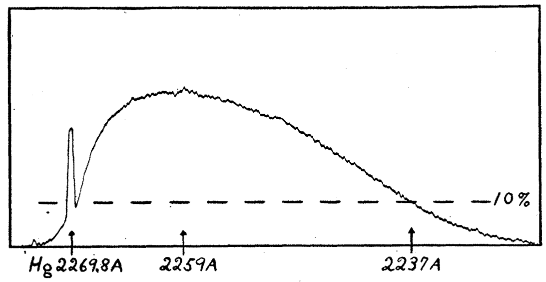

FIG. 1. Densitometer trace of the mercury-argon continuum associated with the forbidden line Hg λ2269.80A. The dotted line indicates the level at which the intensity is 10 percent of that at the maximum. Mercury v.p. 0.02 mm, argon pressure 10 cm, exciting current 1 ma a.c., exp. 24 minutes, medium sized Hilger.

The addition of 10 cm of helium in place of the argon gave rise to a similar continuum with its maximum in the same place, as closely as could be measured. In this case, however, the line was more intense than the maximum, in the ratio 1.4 to 1. When the pressure of helium was reduced to 11 mm, the continuum grew relatively weaker, and the ratio was measured roughly as 28, by comparing the exposure times necessary to give equal densities. For low densities and large intervals, this method is very inaccurate, and the above figure is not to be relied upon. It appears to indicate a variation of intensity with pressure more nearly linear than second power.

Careful measurements were made in an attempt to determine any change in the line-to-maximum ratio with variation of the exciting current. Exposures were made with 1.0, 0.25, and 0.05 amp. primary current, giving currents through the discharge tube of from 11 to less than 1 ma. In all three cases, the ratio remained constant at 0.50.[8]

[7] The intensity of a continuum varies directly as the slit width, while that of a line is independent of slit width if the latter is considerably greater than the spacing of the diffraction pattern of the collimating lens. In this experiment, the slit was kept at 0.05 mm, while the diffraction pattern spacing was less than 0.01 mm. In determining the line-to-maximum ratio, no correction was made for dispersion or plate sensitivity variation, because of the small range involved.

[8] The maximum experimental error in this measurement was probably less than 10 percent. The fact that all three determinations coincided is certainly accidental.

Discussion

It is of primary importance to make certain that the continuum is really due to a mercury-rare gas association, and not to either alone, or to an impurity. As stated above, great care was taken in the preparation of pure gases. Argon and helium have no lines or bands in this region, and in any case were not excited under the experimental conditions. The spectrum of mercury is well known, and although the molecule has a great number of diffuse bands and continua, none have been found in this region. The present structure was found only in the mixture of mercury and a rare gas, and with an intensity roughly proportional to the pressure of the latter. While similar in appearance, it was, for equal pressures of argon and helium, distinctly different in intensity relative to the line.

The further association of the continuum with the particular mercury line λ2269.80 is natural because of its proximity. It has the appearance of an unresolved rotation band coming to a head at the forbidden line. Unlike the case of helium, in which there are several other relatively distant unexplained molecular bands in the neighborhood of the λ600 band discussed by Nickerson,[3] in Hg+A the only diffuse bands which occur are close to atomic lines, namely, the one reported in this paper near λ2269.80, and those found near λ2536.5 by Oldenberg.[5] Even more conclusive is the constancy of the line-to-maximum ratio when the exciting current is varied twenty-fold. The three lowest excited states of mercury are ^3P levels. Of these, the $^3P_2$ (origin of λ2269.80) and the $^3P_0$ are metastable, and the associated lines are weak or missing in the ordinary discharge. Rayleigh[9] mentions that the intensity of both forbidden lines relative to the rest of the spectrum is greatly increased by lowering the exciting current.[10] In the present case, this effect was very marked. Relative to all surrounding lines, λ2269.80 increased in intensity several times when the current was lowered twenty-fold, so that in Fig. 1, taken with lowest current, only a trace of one other line appears in the 50A covered. Now if the continuum were close to the forbidden line only by chance, the current change would certainly produce a change in the line-to-maximum ratio. The constancy of this ratio allows us to conclude definitely that the two have a common origin, and our ability to establish this relationship gives particular interest to the continuum here reported.

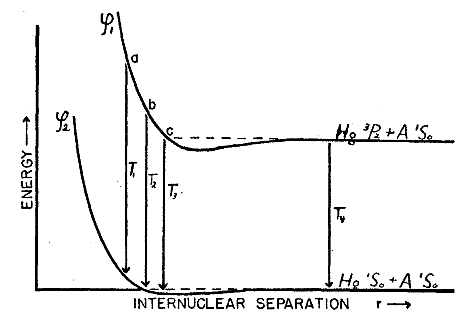

FIG. 2. Hypothetical potential curves, φ_1 for a $^3P_2$ mercury atom colliding with a normal rare gas atom, φ_2 for two normal atoms.

The occurrence of a continuum on the *short* wave-length side of the line may be explained if the interaction potential curves have the qualitative course indicated in Fig. 2. The attractive van der Waals force between two normal atoms will be very small. For Hg $^3P_2$+A $^1S_0$ the attraction will be somewhat greater, but for the present we are not concerned with the resulting minimum in the curve φ_1. At the position of closest approach, which coincides with the maximum of the wave function of nuclear motion, the thermal kinetic energy will be available as potential energy, as represented by some point between a and c on φ_1. If emission takes place, the corresponding transitions between T_1 and T_3 will give a continuous spectrum of shorter wave-length than the atomic line,[11] provided that the lower potential curve starts to rise at a smaller

[9] Rayleigh, Proc. Roy. Soc. **A114**, 620 (1927).

[10] However, Takamine (Zeits. f. Physik **37**, 72 (1926)) found that the intensity of λ2269.80 relative to surrounding lines was a maximum for a current density of about 0.2 amp./cm², decreasing for higher and lower currents. His more complicated branched arc is perhaps not comparable. It is to be noted that the variable intensity of this line under different conditions of excitation is due to changes in the density of population of the metastable state, rather than to the breakdown of selection rules in high ionic fields, as in the case of many ordinarily forbidden lines involving a change in the electronic angular momentum quantum number l other than ±1. High current density would be expected to remove a larger proportion of atoms from the $^3P_2$ metastable state, by secondary excitation and second kind collisions, to states from which transitions can readily occur.

[11] The idea of the addition of thermal to excitation energy at the moment of a collision was used by Oldenberg, reference (5) and Kuhn and Oldenberg, reference (6) to explain the mercury-rare gas bands near the resonance line, λ2536.5, without any suggestion of induced emission probability.

internuclear separation than the upper. This is reasonable, since the outer electron is on a higher orbit in the excited state and there are no strong attractive forces of valence or resonance type.[12]

There are now two reasons why it seems necessary to make the assumption that the probability of emission at close approach must be enormously increased. First, the mean free path of a mercury atom in argon at 10 cm pressure is about 5×10^{-5} cm, while the distance over which repulsive interaction extends is probably about 1×10^{-8} cm. Therefore we should expect that the vast majority of radiation processes would occur uninfluenced by the close approach of a neutral atom.[13] In other words, the intensity of the line proper should be very much greater than that of any accompanying continuous spectrum on the short wave-length side, if the emission probability remained constant. Actually, however, this continuum has a total intensity about 100 times that of the line.

Second, consider the distribution of intensity. The probability P of finding a rare gas atom in a spherical shell of radius r and thickness dr about an excited mercury atom will be proportional simply to the geometrical factor r^2 at large distances, while within the range of interaction there will be an additional factor $e^{-\varphi_1/kT}$, the Maxwell-Boltzmann distribution function. Thus P is a rapidly increasing function of r in the range of repulsion, and the corresponding chance of finding a colliding atom at a point on φ_1 of Fig. 2 decreases rapidly from c to a. As a result, were the probability of emission Q[14] independent of r, we should expect to find on the short wave-length side of the line, a "tail" with uniformly decreasing intensity. Suppose, however, that Q, while constant at large r, increases rapidly at small internuclear distances. Then the product PQ, which will be roughly proportional to the intensity of radiation, may have a maximum. In Fig. 2, the emission probability at a will be large, but few atoms will approach so closely, and transitions T_1 with large wave-length shift will be comparatively few. At c, there will be many more perturbing atoms, but a small emission probability, and transitions T_3 giving radiation only slightly shifted will also be rare. At some intermediate point, say b, the greatest number of transitions will occur, and the continuum will have a separate maximum, as is actually observed.

We may describe two colliding atoms as a molecule, keeping in mind that it is in a continuous positive energy state.[15] If the interaction is weak, as it certainly is in the present case in which the attractive force is of the van der Waals type and the thermal energy is limited to a few hundredths of a volt, the coupling will be of the type of Hund's case C. The number of molecular states is then determined by the possible values of the quantum number Ω, the sum of the projections of the j's of the individual atoms on the internuclear axis. Three molecular states arise from the combination of two unlike atoms in $^3P_2$ and $^1S_0$ levels, namely, 2, 1, and 0^-.[16] Two unlike $^1S_0$ atoms give only a 0^+ state. Since the selection rules are $\Delta\Omega=\pm1$, 0^- does not combine with 0^+, there is one and only one excited molecular state in the present case which can combine with the ground state.

If the unperturbed Hg $^3P_2$ atom had a zero transition probability, we could accordingly predict from molecular theory that it would acquire a chance of radiating during a collision with a neutral atom. The magnitude of this induced transition probability should be proportional to the perturbation, and from a knowledge of the Paschen-Back effect, we can say that it should not approach the transition probability of the $^3P_1$ state until the perturbation is of the order of the multiplet separation. The maximum of the continuum lies about 0.025 volt from the line,

[12] Finkelnburg, Zeits. f. Physik **96**, 699 (1935), discusses this matter from a qualitative theoretical point of view.

[13] All emission is of course *slightly* affected by neighboring atoms. In the different problems of collision broadening and Stark effect broadening, in which nearly all radiation is shifted by a very small amount, it is the combined effect of many distant atoms or ions which is important. Large shifts must arise from the rare close approach of single bodies, and it is only for such comparatively large perturbations that we should expect a considerable change in the emission probability, in the present case.

[14] Q here refers to electronic transitions, and is not to be confused with the transition probability derived from the wave functions of nuclear motion. The latter we ignore, in the absence of any accurate knowledge of the repulsive potential curves, except in so far as we assume that the Franck-Condon rule applies.

[15] This is sometimes called a "quasi molecule": Born and Franck, Zeits. f. Physik **31**, 411 (1925).

[16] Mulliken, Rev. Mod. Phys. **4**, 26 (1932), gives rules for determining the case C states arising from unlike atoms with given l, s, and j.

while the $^3P_2-{}^3P_1$ separation is 0.57 volt. Therefore we should expect that the intensity of the continuum at its maximum should still be far less than that of the line λ2536.5 $^1S_0-{}^3P_1$, and such is the case experimentally.

The free $^3P_2$ mercury atom has actually always a slight chance of radiating, since we observe the sharp atomic line in the discharge, so the most we can say is that it is theoretically reasonable that a collision should *increase* its transition probability, in accordance with our interpretation of the experimental facts. If we consider a Hg $^3P_1$ atom, on the other hand, we should not suppose that a collision would greatly modify its already large transition probability. The rare gas bands found by Oldenberg,[5] on the short wave-length side of λ2536.5, have a total intensity very much less than that of the line proper, and perhaps they must be explained without collision induced emission.

Other forbidden lines ought to be accompanied by continua like that found near Hg λ2269.80, in particular, the corresponding cadmium line, λ3141.01. Investigation showed that unfortunately the neighboring cadmium resonance line has an intense tail, when rare gases are added to the discharge, which covers the region of the forbidden line and makes observation of weak spectra impossible. It is interesting to note that the $^3P_0$ metastable state of cadmium and mercury gives only a 0^- state in combining with a foreign $^1S_0$ atom. Transitions from this to the 0^+ ground state are excluded, and therefore no collision induced emission should be found near these lines, if the theory is correct. Experimentally, they are both obscured by the resonance line tails. In the case of pure mercury, no bands have been found to accompany the line λ2269.80 on the short wave-length side, although a series of what appear to be vibration bands commences at 2345A and gradually merges into a continuous spectrum extending to the long wave-length side of the line.[17] Corresponding vibration bands appear to be lacking in mercury-rare gas mixtures (see below), and we can suppose that the larger binding energy of Hg_2 results in the shift of the repulsive portion of the upper state potential curve to smaller internuclear distances, so that transitions to the ground state liberate *less* energy than the atomic line.

Mention should be made of a paper by Finkelnburg,[18] in which he discusses two diffuse bands at 2285A and 2365A, found by Kessel in a discharge through mercury vapor at 4 mm pressure with 1 mm of argon added.[19] Finkelnburg proposed that these bands came from the lowest vibration levels of states $\Omega=1$ and $\Omega=0$ of stable Hg $^3P_2-$A $^1S_0$ molecules with a considerable binding energy. He further suggested that two bands of some sort should be found on the short wave-length side of the forbidden line λ2269.80, due to collision induced emission at the moment of closest approach. These latter were not found by Kessel.

On some early plates, the author found a faint band at 2365A which was almost certainly that described by Kessel. It has never appeared under conditions of high purity in the discharge. Moreover, one such early plate showed an exposure taken with 2 mm of added argon beside one taken with 90 mm of argon, and in each the 2365A band was of nearly the same intensity. If due to Hg+A molecules, it would surely have been much more intense at the higher pressure. Possibly Kessel's bands were caused by some impurity. Theoretically, as we have said, the $\Omega=0$ excited molecular state cannot combine with the ground state because one is 0^- and the other 0^+. It is also most unlikely that Hg+A should have a larger binding energy than Hg_2, in similar molecular states.[20] Since the author found no trace of spectra on the long wave-length side of λ2269.80 in Hg+A, it is probable that the binding energy of Hg $^3P_2+$A $^1S_0$ is very small. The continuum on the short wave-length side, however, corresponds in principle to Finkelnburg's prediction.

In conclusion, the author wishes to express his deep gratitude to Professor Otto Oldenberg, who directed this work, for his unfailing interest and helpful advice; also to Professor Van Vleck for a discussion of the theoretical aspects of this paper.

[17] Rayleigh, Proc. Roy. Soc. **A116**, 702 (1927); Kuhn, Zeits. f. Physik **76**, 50 (1932).

[18] Finkelnburg, Zeits. f. Physik **81**, 781 (1933).

[19] Kessel, Zeits. f. Physik **70**, 623 (1931).

[20] For mercury, the polarizibility $\alpha=5.2\times10^{-24}$, for argon $\alpha=1.6\times10^{-24}$. In addition, mercury will show resonance attraction. Kuhn calculates a dissociation energy of about 0.1 volt for Hg $^3P_2+$Hg $^1S_0$, while Finkelnburg obtained a dissociation energy of 0.2 volt from Kessel's bands, for Hg $^3P_2+A$ $^1S_0$.