Partial Selection Rule for Sensitized Fluorescence

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THE phenomena of sensitized fluorescence has in recent years received a much wider application than could have been foretold at the time it was discovered by Cario and Franck[1] about twenty years ago. The widespread use of electric discharges through mixtures of gases as light sources brings into practical application a class of phenomena for which no application was anticipated. The intensity distribution throughout the spectrum of the light emitted by a discharge through a gas mixture is largely determined by the same processes as those which take place in sensitized fluorescence.

It is the purpose of this discussion to describe experiments which provide information concerning the action of one of these processes, namely, the conditions under which excitation energy may be passed from one molecule to another on collision.

The original experiments of Cario and Franck, and many of those which followed, were performed with apparatus like that shown in Fig. 1.

Mercury and thallium were distilled into a quartz tube which was sealed off and mounted in furnaces, as shown. Under operating conditions for Tl, Cario and Franck used temperatures 800°C for O_1, 100°C for O_3, and a temperature to give 2 mm Tl pressure for O_2. The temperature of O_1 was kept high enough to prevent condensation of vapor on the walls of the tube.

Fluorescence was excited by light from a water-cooled, or air-cooled, and magnetically deflected quartz mercury arc. Fluorescence light emitted

FIG. 1. Apparatus similar to that of Cario and Franck for fluorescence.

from the vapor at the spot where the exciting light entered was focused on the slit of a small quartz prism spectrograph. The spectrum showed nine lines of the thallium arc spectrum. Experiments of this kind with the same type of apparatus have been carried out for mixtures of mercury vapor with vapors of Cd, Pb, In, Ag, Na, Zn, and Bi.[2] From these experiments the following information about sensitized fluorescence was obtained.

(1) A mixture of two monatomic gases, A and B, illuminated by light which only A can absorb, may emit as fluorescence light from atoms B. When the excitation energy of B was less than that received by A in absorbing the light, the intensity of B fluorescence was much greater than when the excitation energy of B was greater than the energy of light absorbed by A.

(2) The intensity of fluorescence of B depended upon the energy discrepancy, or energy difference, between that of excited atoms A and excited atoms B. The intensity was greater for smaller energy discrepancy. This effect was well demonstrated for sodium and mercury by Beutler and Josephy.[3]

(3) The intensities of lines in sensitized fluorescence followed a rule first stated by Wigner,[4] that those transitions are most probable for which the change in electron spin angular momentum for one atom is equal and opposite to that for the other atom.

Early experiments on sensitized fluorescence were carried out with mixtures of mercury and elements whose vapor pressures were sufficiently high at temperatures less than 1000°C for observation of fluorescence. The possibility of obtaining sensitized fluorescence for metals of much lower vapor pressure was first shown when it was found that a quartz tube, containing Hg
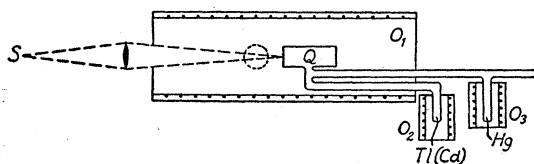
[1] G. Cario and J. Franck, Zeits. f. Physik **17**, 202 (1922).

[2] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms*, p. 65; Quenching, p. 202.

[3] H. Beutler and B. Josephy, Zeits. f. Physik **53**, 747 (1929).

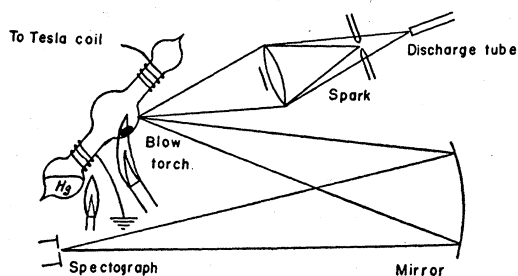[4] E. P. Wigner, Göttinger Nachrichten (1927), p. 375.

FIG. 2. Simplified fluorescence apparatus.

with tin as an impurity, showed tin lines in the spectrum of a Tesla discharge when the tube was heated at one spot by a blow torch. When, however, the arrangement of Cario and Franck was used in an attempt to observe the sensitized fluorescence of tin, there was no effect even though the temperature was raised until the quartz tube collapsed.

The experiment was repeated with the simplified form of apparatus shown in Fig. 2. A quartz tube about 12 cm long with bulbs about 2-cm diameter was thoroughly outgassed and sealed off containing mercury and the metal to be studied. Mercury was evaporated away from the metal in the center bulb, and the drop of metal remaining was heated with a hydrogen-air blow torch. The mercury was heated with a Bunsen burner to provide Hg vapor pressures from 0.1 to 15+cm. The tube was illuminated by light from

FIG. 3. No. 1, spectrum of carbon arc containing tin; No. 2, Tesla discharge through mercury and tin vapors; No. 3, hydrogen air flame; No. 4, spectrogram with focal isolation of 2536 in the exciting light; No. 5, spectrum of the flame and scattered light when mercury pressure was too low for tin fluorescence.

a SC 2537 discharge tube or Al or Zn spark using a lens with central black spot for focal isolation of exciting wave-lengths.[5]

The spectrum obtained for a mixture of Hg and Sn is shown in Fig. 3. A total of 13 Sn lines were observed in sensitized fluorescence. These are shown on the energy level diagram Fig. 4. The spectrum of a carbon arc containing tin is shown in Fig. 3, No. 1. Figure 3, No. 2 shows the spectrum of a Tesla discharge through a tube containing Sn and mercury when the tube was heated at one point by a blow torch. The spec-
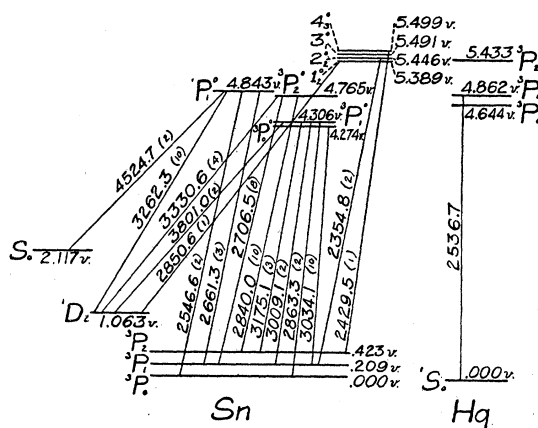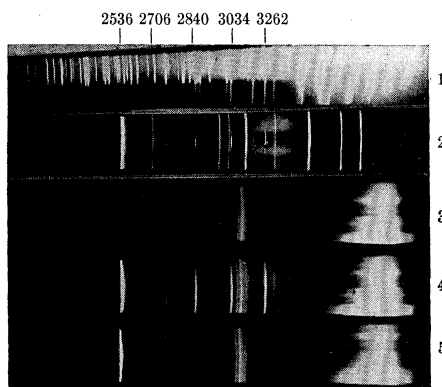

FIG. 4. Complete list of tin lines observed in sensitized fluorescence.

trum of the sensitized fluorescence of Sn is shown in Fig. 3, No. 4.

A comparison of intensities of Sn lines in Fig. 3, Nos. 1, 2, and 4 shows that in sensitized fluorescence and in Tesla discharge, the tin line 3034 ($^3P_1 \leftarrow {}^3P_0{}^\circ$) was much more intense than the tin line 3009 ($^3P_1 \leftarrow {}^3P_1$), but in the spectrum of the carbon arc containing Sn, the two lines were of approximately equal intensity.

If it is assumed that excitation of Sn $^3P_1{}^\circ$ and Sn $^3P_0{}^\circ$ is caused primarily by collisions with Hg $^3P_0$ rather than Hg $^3P_1$ (because of lower energy discrepancy and greater number for Hg $^3P_0$), it is seen that the intensities of the tin lines follow a simple selection rule. This rule states that for collisions between atoms A and B,

[5] J. G. Winans and R. W. Williams, Phys. Rev. 52, 930 (1937).

the probability for a transfer of excitation energy is greater if $J = J_A + J_B$ remains constant than if J changes. J_A and J_B are the resultant electron angular momenta for atoms A and B.

Thus, if before collision $J_{Hg} = 0$ and $J_{Sn} = 0$, and the value of J_{Hg} after collision is 0, that Sn transition is more probable which makes $J_{Sn} = 0$ after the collision. According to this rule, the Sn line 3034 should be more intense than 3009 as observed in Fig. 3.

In order to test the generality of this rule, the sensitized fluorescence of other substances was investigated.

LEAD

Lead has energy levels like tin, and the Pb levels $^3P_1^\circ$ and $^3P_0^\circ$ have nearly the same energy discrepancy with Hg $6\,^3P_0$ as have the corresponding levels of tin (0.35 volt for Sn and 0.30 volt for Pb). The energy levels of Pb are shown in Fig. 5.

The Pb lines whose intensities should demonstrate the selection rule have wave-lengths 3639 ($^3P_1 \leftarrow {}^3P_1^\circ$) and 3683 ($^3P_1 \leftarrow {}^3P_1^\circ$). Figure 6, No. 1 shows these two lines as obtained in sensitized fluorescence excited by light from a SC 2537 discharge lamp, while Fig. 6, No. 2 shows the lines as obtained in the spectrum of a carbon arc containing lead. It is easily seen that the relative intensities of these two lead lines are not noticeably different when excited in the arc and when excited in sensitized fluorescence. The
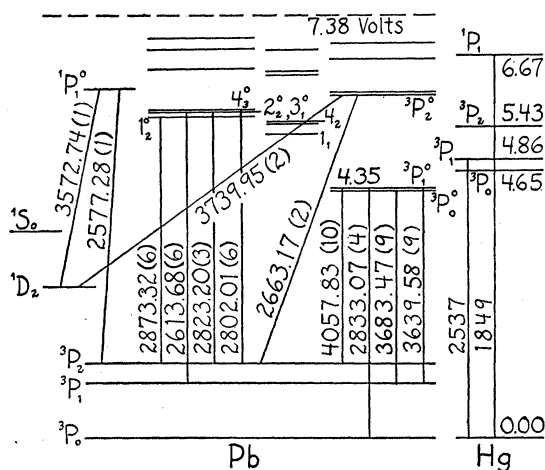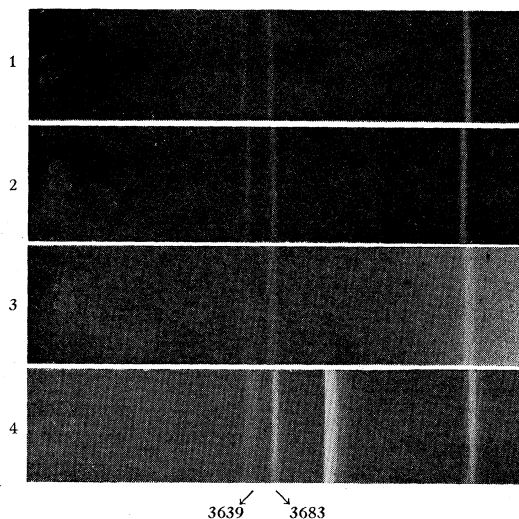

3639   3683

FIG. 6. Lead lines 3639 and 3683 excited by (1) Ordinary sensitized fluorescence (2) Pb in a carbon arc, (3) Sensitized fluorescence with time interval between excitation and emission, (4) Ordinary sensitized fluorescence in atmosphere of N_2 at 7 mm pressure.

relative intensities are, therefore, not the same as those observed for Sn, and the rule apparently does not apply to lead.

A comparison of the energy levels of Sn and Pb, however, shows an important difference. For Sn, there is a level at 4.84 volts of very low energy discrepancy with Hg $6\,^3P_1$ (4.86 volts). This means that practically all Hg $6\,^3P_1$ atoms colliding with normal Sn atoms would excite the Sn to states $^1P_1^\circ$ and $^3P_2^\circ$ and not to $^3P_1^\circ$ and $^3P_0^\circ$. Those Sn atoms which are excited to $^3P_1^\circ$ and $^3P_0^\circ$ must then have collided with Hg $6\,^3P_0$ only. For lead, as shown in Fig. 5, there is no level of low energy discrepancy with Hg $6\,^3P_1$ to receive all the energy of Hg $6\,^3P_1$, and, therefore, the $6\,^3P_1$ Hg atoms along with Hg $6\,^3P_0$ participate in the excitation of Pb $^3P_1^\circ$ and $^3P_0^\circ$. The selection rule applied to excitation by Hg $6\,^3P_1$ would predict a high intensity for the Pb line 3639, while for excitation by Hg $6\,^3P_0$, a high intensity for the Pb line 3683. Excitation by both Hg states would, therefore, tend to mask the action of the selection rule.

It can be expected, however, that if the Pb could be excited by Hg $6\,^3P_0$ alone, an intensity distribution like that for Sn would result.

Partial isolation of Hg $6\,^3P_0$ was accomplished by the arrangement shown in Fig. 7. The exciting

FIG. 5. Energy levels of lead and mercury.
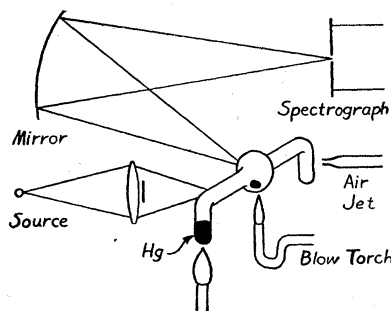
FIG. 7. Apparatus for isolation of Hg 6^3 Po.

light was admitted into a moving stream of Hg vapor at a point a short distance upstream from a region containing lead vapor. With the introduction of a time interval between excitation and sensitized fluorescence, the short-lived 6 $^3P_1$ mercury atoms are allowed to radiate their energy, leaving primarily the long-lived Hg 6 $^3P_0$. The spectrum obtained is shown in Fig. 6, No. 3. It is seen that the intensity of 3683 is much more than that of 3639, and the distribution of intensity between the two lines now resembles that observed for tin.

Figure 6, No. 4, shows the Pb lines as obtained in sensitized fluorescence of Pb and Hg in an atmosphere of N_2 gas at about 6 mm pressure and no time interval between excitation and emission. It is seen that the intensity of 3683 relative to 3639 is greater than in the carbon arc. N_2 is known to cause an increase in concentration of Hg 6 $^3P_0$ if temperatures are not too high. If the selection rule applies, N_2 should therefore cause an increase in intensity of 3683 in comparison to 3639, in agreement with experiment.

COPPER

The next element tried was copper. Here again a time interval between excitation and fluorescence caused intensities which agreed with predictions of the rule. Microphotometer curves of the resonance lines of copper at 3248 and 3274 are shown in Fig. 8. It is seen that the intensity of 3247 relative to 3273 is greater in sensitized fluorescence than in the carbon arc as predicted by the rule. The sensitized fluorescence was taken with a time interval between excitation and fluorescence.

THALLIUM

The energy levels of thallium are suitable for providing a check on the rule by a negative result. The energy levels of Tl are given in Fig. 9. Excitation of Tl 6 $^3D_{5/2}$ and 6 $^3D_{3/2}$ by Hg $^3P_0$ would favor neither state if $\Delta J = 0$, but excitation by Hg $^3P_1$ would favor Tl 6 $^3P_{3/2}$ over 6 $^3P_{5/2}$. For ordinary sensitized fluorescence excitation of Tl 6 $^2D_{5/2}$ and 6 $^2D_{3/2}$ would be expected to result primarily from Hg 6 $^3P_0$ since there is a Tl level of energy nearly equal to that of Hg 6 $^3P_1$. The effect should resemble that for Sn where Hg $^3P_1$ atoms were used in exciting the higher level and Hg $^3P_0$ was left to excite the lower ones. It is to be expected, therefore, that the relative intensity of 3519 and 3529 would be the same in the arc, sensitized fluorescence at all pressures of Hg and in remote excitation fluorescence. Figure 10 shows the spectrum of these two lines for Tl in a carbon arc, direct excited sensitized fluorescence and remote excited sensitized fluorescence. In all cases 3519 is stronger than 3529, and the relative intensities as judged visually are the same.

It should be noted that when a Tesla discharge was sent through Tl vapor alone, these two lines had approximately equal intensity, quite different from those shown in Fig. 10. This indicates a difference in process of excitation between the carbon arc in air and Tesla discharge in vapor at low pressure. Further study of this effect is needed before an explanation is apparent.

CHROMIUM

With the form of apparatus used in these experiments, it was possible to obtain the sensitized fluorescence of chromium. The energy levels of chromium are such that of the six resonance lines of Cr to be expected in sensitized fluorescence, the selection rule predicts that the line from
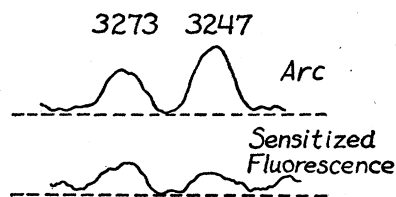

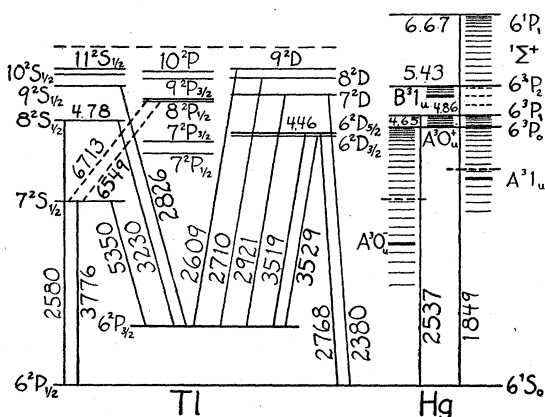FIG. 8. Microphotometer curves of copper resonance lines.

FIG. 9. Energy levels for thallium and mercury.

Cr $^7P_3$ should be especially strong if excitation is by Hg $6\,^3P_0$ and that all three $^7P_3$ levels should be about equally produced if excitation is by Hg $6\,^3P_1$. The selective excitation by Hg $^3P_0$ would be masked by the action of Hg $^3P_1$ and for directly excited sensitized fluorescence, the result should be negative as for thallium. The fluorescence spectrum obtained is shown in Fig. 11, No. 2, and the spectrum of Cr in a carbon arc in Fig. 11, No. 3. There is no apparent difference in intensity distribution among the six resonance lines of chromium for arc and fluorescence excitation. This agrees with the predictions of the rule. It has not yet been possible to obtain sensitized fluorescence of Cr with remote excitation.

One surprising thing about these experiments is the fact that fluorescence of metal vapors may be excited in a quartz tube which would collapse at a temperature greater than 1100°C, while the vapor pressure of the metals being tested was less than 10^{-5} mm of Hg at 1100°C. It happens, however, that because of the method of heating by directing the flame of a blowtorch on the tube and because of the state of fine division of the metal powder used, small specks of metal stick to the walls of the quartz tube and reach a temperature greater than 1100°C. The heat flows through the wall to cooler parts with sufficient rapidity to prevent collapse of the quartz wall. An optical pyrometer showed that specks of Cu or Cr considered as black bodies reached a temperature of 1400°C without having the walls of the quartz tube collapse. The walls were dented, however.

Microscopic examination of the Cr powder showed the grains to have a very rough surface and, therefore, resemble closely a black body.

DISCUSSION

Having now seen that sensitized fluorescence follows the partial selection rule $\Delta J = 0$ where $J = J_A + J_B$, we next seek to understand what molecular processes could give rise to such a rule. The mechanism of sensitized fluorescence is recognized as being very similar to the mechanism of predissociation in molecules. These processes are described by the potential curves shown in Fig. 12. In a collision of the second kind, an excited atom A' may approach a normal atom B following the curve A'+B. After collision it may recede from B along the curve A+B' separating as normal A and excited B'. The phenomena of predissociation is described by a change of the molecule from one curve to another when the vibrational energy is greater than that corresponding to the crossing point of the two curves. Since the processes of sensitized fluorescence and predissociation are so much alike, it is to be expected that the selection rules which apply to one should also apply to the other. The selection rules for predissociation are $\Delta S = 0$, $\Delta J = 0$, $\Delta \Lambda = 0$ or ± 1, $+ \leftrightarrow +$ $s \leftrightarrow s$, $a \leftrightarrow a$.

The rule stated by Wigner for sensitized fluorescence is the same as $\Delta S = 0$ where S is the total spin angular momentum for the quasi-molecule formed by the two atoms on collision.
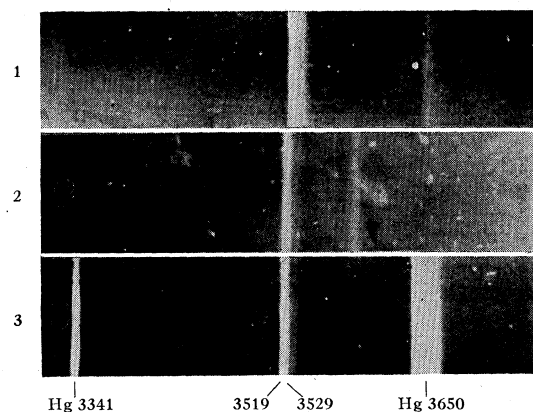

FIG. 10. Thallium lines—(1) Sensitized fluorescence with time interval between excitation and emission, (2) Carbon arc spectrum of Tl, (3) Sensitized fluorescence with no time interval between excitation and emission.
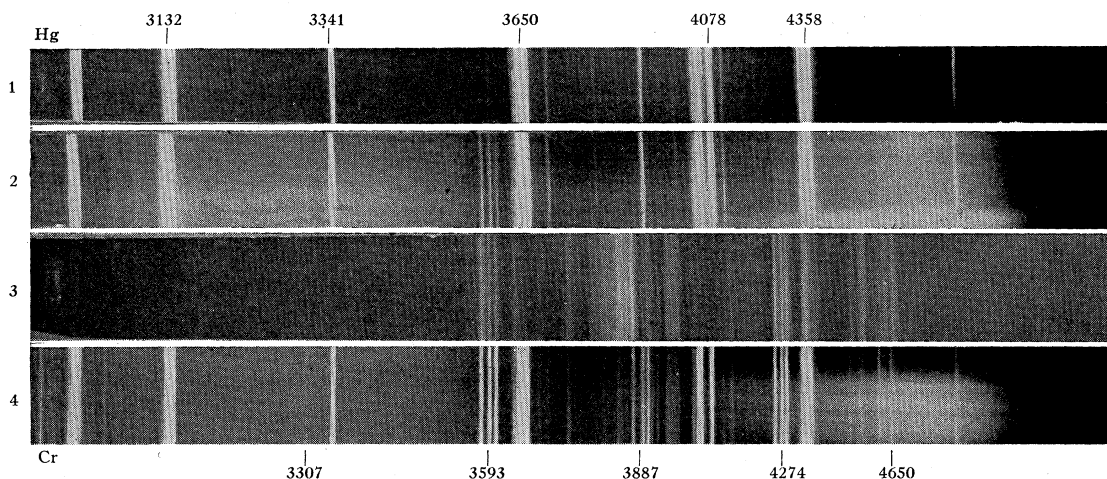
FIG. 11. Fluorescent spectrum of chromium. (1) Scattered light—Hg arc. (2) Sensitized fluorescence of chromium. (3) Carbon arc spectrum of Cr. (4) Spectrum of Tesla discharge through Cr and Hg vapor.

The rule which we have just been considering is the equivalent of $\Delta J = 0$ where J is the resultant angular momentum for the quasi-molecule.

In a stable molecule, the value of J is the vector sum of the component of electronic orbital angular momentum parallel to the internuclear axis (Λ), the component of spin angular momentum parallel to the same axis (Σ), and the angular momentum of the nuclei (N). The individual atomic angular momenta J have been split by the strong internuclear electric field and no longer have any significance. In sensitized fluorescence, however, we have a partial selection rule which is determined by a resultant J which is made up as the vector sum of $J_A + J_B$. How can this have meaning if the internuclear electric field would destroy J_A and J_B? The meaning can be understood when it is recognized that most of the collisions between atoms are non-central collisions, and the P.E. curves followed in these collisions are the same as those for molecules in a state of high energy of rotation. Such curves are shown in Fig. 13.

Because these curves have a maximum at relatively large values of r, atoms may collide and be repelled away without having the nuclei make a close approach. At these large internuclear distances, the electric field may be expected to be small enough to preserve the identity of J_A and J_B. While the atoms are in the neighborhood of each other during part of one revolution, they

may form a resultant $J = J_A + J_B$ which remains constant during the collision, though atoms approach along one P.E. curve and separate along another. The time of near approach being less than the time for one revolution would result in only a partial quantization of J with the consequence that the selection rule $\Delta J = 0$ would not be a rigid rule but only a partial one. It serves only to indicate those transitions of greater intensity.

The significance of the rule as observed experimentally, therefore, turns out to be that collisions of the second kind with transfer of excitation energy from one atom to another may take place at distances which are large compared to the equilibrium distance between nuclei or to the diameter of the individual atoms.

This conclusion is in agreement with the results of experiments on the quenching of fluorescence by foreign gases.[2, 6] These experiments show that even with the assumption that every collision is a quenching collision, the effective radius of an excited atom for quenching is 3–10 times the kinetic theory radius. Such large effective radii are easily understandable in terms of the transfer of energy between atoms in non-central collisions at relatively large distances apart. Such transfers are indicated by the action of the partial selection rule $\Delta J = 0$.

These experiments also show an explanation for
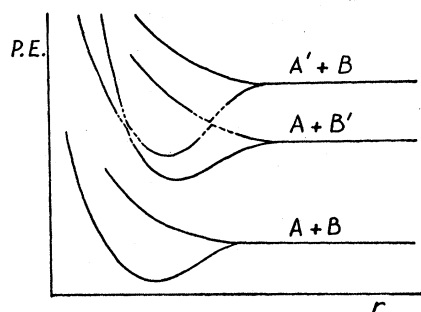
[6] J. G. Winans, Zeits. f. Physik 60, 631 (1930).

FIG. 12. Potential energy curves.

FIG. 13. Potential energy curves for non-central collision.

the increase in effective radius for collisions of the second kind with decrease in energy discrepancy. For lower energy discrepancy, the repulsion curve from $A+B'$ intersects the curve $A'+B$ at larger values of r. Figure 12 shows two curves $A+B'$ for different energy discrepancy with the curve for smaller discrepancy dashed. It is seen that the point of intersection between $A+B'$ and $A'+B$ occurs at larger r for smaller energy discrepancy. As the energy discrepancy approaches 0 the r for the intersection point goes to ∞.

As $\Delta E \rightarrow 0$, it will also be possible for an energy transfer to take place by radiation, but this will not occur until the energy discrepancy is less than the Doppler width of a spectrum line. Experiment shows that before the energy discrepancy is as small as the Doppler broadening, the effective radius has increased very greatly.[3] This large increase in effective radius can be accounted for by the crossing of the P.E. curves for a rotating quasi-molecule at large values of r.

In conclusion, the experiments on sensitized fluorescence show that, (1) atoms may transfer excitation energy on collision, the energy difference going to or coming from thermal energy; (2) the probability of transfer is greater for smaller energy discrepancy; (3) the probability of transfer is greater if $\Delta S=0$ where $S=$ vector sum of electron spin for all electrons in both atoms; and (4) the probability of transfer is
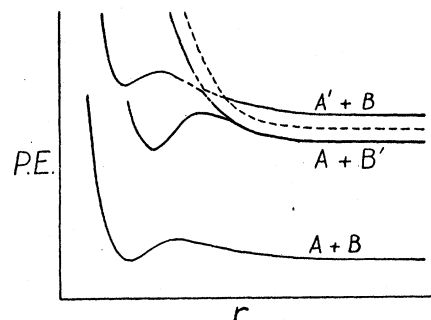
greater if $\Delta J=0$ where J is the resultant angular momentum for the quasi-molecule formed by the two atoms on collision.

The significance of these observations is that (a) sensitized fluorescence is similar to predissociation in molecules and follows the same selection rules and (b) the P.E. curves followed by most atoms on collision are like those for a molecule with high rotational energy and the curves cross at large values of r. This accounts for (1) the selection rule $\Delta J=0$, (2) the large effective cross section of excited atoms needed to account for the quenching of fluorescence by foreign gases, and (3) the increase in effective cross section for collisions of the second kind with decrease in energy discrepancy.
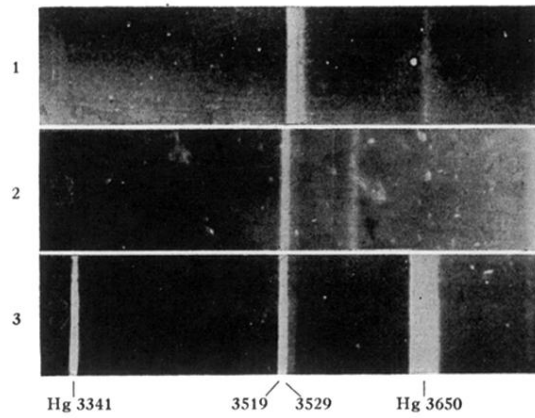
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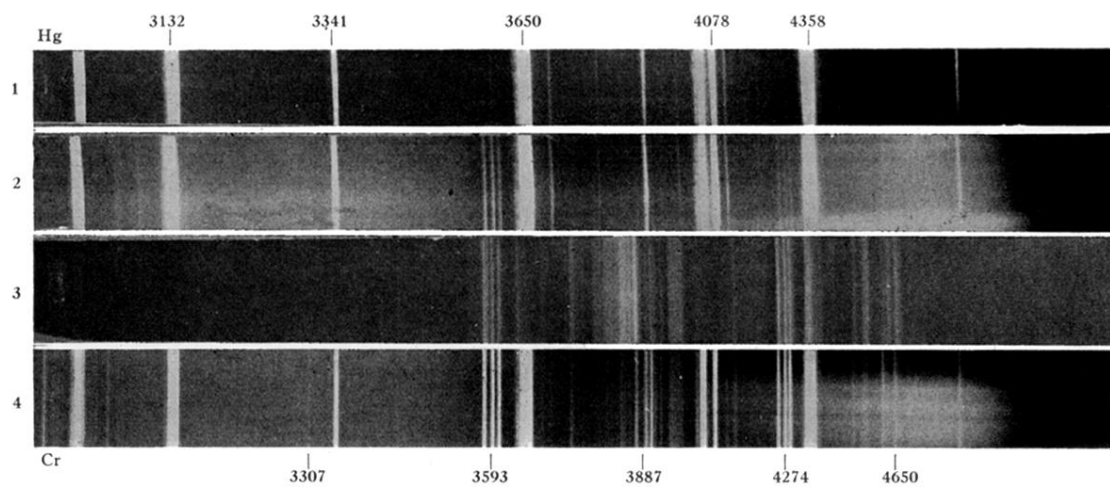
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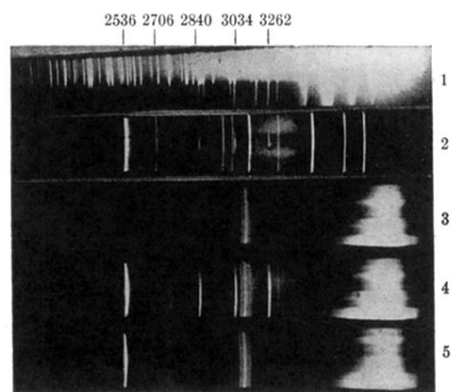
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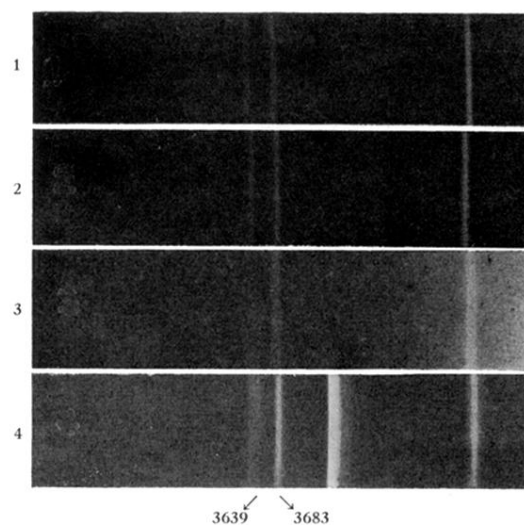
3639   3683

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