Sensitized Fluorescence of Tin

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(Received August 23, 1937)

Several Sn lines have been observed in sensitized fluorescence and in a low voltage Tesla discharge. The fluorescence and the discharge were produced in a fused quartz tube containing Sn and Hg and heated by a blow torch and Bunsen burners. A Hanovia SC 2537 tube was used as a light source. The Sn lines observed in fluorescence with their estimated intensities are 4525 (2), 3801 (2), 3331 (4), 3262 (10), 3175 (3), 3034 (10), 3009 (2), 2863 (2), 2840 (10), 2851 (1), 2706 (8), 2661 (3), 2547 (2), 2430 (1), 2355 (0.2). The most intense Sn lines except 3034 are those of low energy discrepancy with excited Hg atoms. The abnormally high intensity of Sn 3034 which agrees with a corresponding effect in the sensitized fluorescence of Pb may indicate a new selection rule for collisions of the second kind.

It was first shown by Cario and Franck[1] that a mixture of Tl and Hg vapors would emit Tl lines in fluorescence when illuminated by the Hg resonance line 2536. Later experiments have demonstrated that this effect could be observed for mixtures of Hg vapors with the vapors of Cd, Ag, In, Na, Pb, Bi, and Zn.[2] Low vapor pressure metals such as Sn with a boiling point of 2270°C were not tried.

The present investigation has shown that sensitized fluorescence can be observed for a mixture of Hg and Sn at 900°C even though the vapor pressure of Sn at this temperature is less than 10^{-5} mm of Hg.

The possibility of obtaining sufficient Sn vapor for fluorescence in a quartz tube became apparent when the spectrum of a Tesla discharge through a tube containing Sn and Hg was found to give Sn lines.

Apparatus

The apparatus used for both discharge and fluorescence is shown in Fig. 1. A quartz tube 7 mm in diameter and 14 cm long containing some pure Sn metal was outgassed at 900°C for several days. Some mercury was then distilled into the tube and the tube sealed off. The tube was mounted in a nearly horizontal position as shown in the figure. Light from the tube was focused on the slit of a small Hilger spectrograph with an aluminum coated concave mirror. A discharge was excited through external electrodes by a small Tesla coil. Bunsen burners were used to heat the ends of the tube and a bead of tin at the center was heated by a hydrogen air blow torch.

For observations on fluorescence, light from a Hanovia SC 2537 tube was focused on the hot bead of tin. Some exposures were made using the method of focal isolation to eliminate all but 2536 from the exciting light. The use of a hydrogen air blow torch was necessary since the light from a gas air or gas oxygen flame covered such a wide spectral range that many of the fluorescence lines were obliterated. The Hg pressure required for Sn fluorescence was not critical and could be regulated sufficiently well by the Bunsen burners.

The temperature attained in the hydrogen air flame was determined by heating a chromel alumel thermocouple in a quartz tube of the same diameter as the fluorescence tube. It was

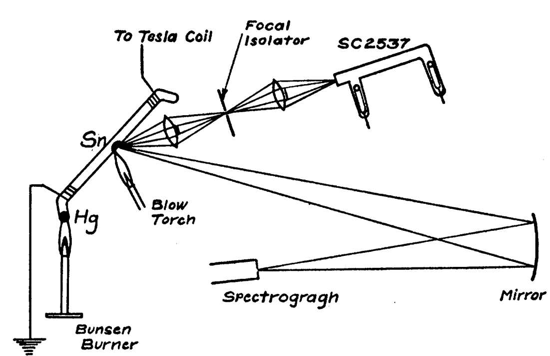


FIG. 1. Arrangement of apparatus.

[1] G. Cario, Zeits. f. Physik 10, 185 (1922).
[2] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms*, p. 59.

found that heating in a vacuum or in air gave the same temperature. The maximum temperature which could be reached was 900°C.

Results

The spectrum of a Tesla discharge through Hg and Sn vapors is shown in Fig. 2, No. 2. Fig. 2, No. 1 shows the spectrum of a carbon arc containing Sn metal. If the intensities of the Sn lines relative to each other in the carbon arc is considered normal, it is seen that some of the Sn lines are strongly enhanced relative to neighboring Sn lines in the Hg-Sn discharge. The wave-lengths of the enhanced Sn lines are 3262, 3034, 2840, and 2430.

Sensitized fluorescence of Sn was obtained with exposures of about 30 to 40 minutes. Fig. 2, No. 4 shows one of the spectrograms when focal isolation of 2536 in the exciting light was used. Fig. 2, No. 3 shows the spectrum of the hydrogen air flame and No. 5 is the spectrum of the flame and scattered light when the Hg pressure was too low for Sn fluorescence to be excited. The complete list of Sn lines observed in sensitized fluorescence with their estimated intensities is given in Fig. 3.

The Sn fluorescence lines of greatest intensity are those which were enhanced in the Hg-Sn discharge.

The spectra of the fluorescence with and without focal isolation of 2536 gave the Sn lines with the same intensities relative to each other except for 2429 and 2354. 2429 was much fainter and 2354 entirely absent when focal isolation of 2536 was used.

An attempt to observe the sensitized fluorescence of Sn in Hg with apparatus like that used for Zn[3] gave negative results up to 900°C. At 900°C the quartz tube reacted with its asbestos support to devitrify and crack the quartz. The transmission of quartz for the Al spark lines 1854 and 1862 was found to be very small at temperatures above 600°C.

Discussion

Previous experiments on sensitized fluorescence have demonstrated the rule that high intensities are associated with low energy discrepancies (energy difference between the excited states of the absorbing and fluorescing atoms). Fig. 3 shows the energy levels of Hg, and those of Sn as obtained by Sponer[4] and by Back.[5] The energy discrepancies are shown in Table I. The intensities of the Sn lines observed in sensitized fluorescence and in the Hg-Sn discharge are in agreement with the rule stated above except for 3034. In considering the energy discrepancies, account must be taken of the fact that the average thermal energy involved in a collision between two atoms at 900°C is 0.3 volts. Since thermal energy can be added to excitation energy to produce excited atoms, the energy discrepancy between Hg 2^3P_0 and Sn $^1P_1{}^0$ and $^3P_2{}^0$ can be considered as very small. The observed high intensities of 2840, 2706 and 3262 are to be expected. In the excitation of $^3P_1{}^0$ and $^3P_0{}^0$ of Sn by 2^3P_1 and 2^3P_0 Hg atoms the energy discrepancies are larger and the intensities of lines originating from these levels should be correspondingly less. The intensities of 3801, 3175, 3009, and 2863 are low as expected, but the intensity of 3034 is very high, contrary to expectations. The same relatively high intensity for 3034 was observed in the Tesla discharge spectra.

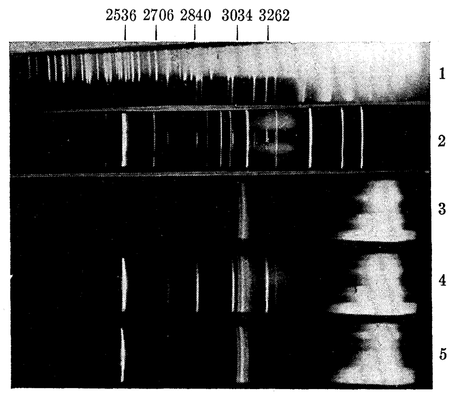


FIG. 2. No. 1, spectrum of carbon arc containing tin; No. 2, Tesla discharge through mercury and tin vapors; No. 3, hydrogen air flame; No. 4, spectrogram with focal isolation of 2536 in the exciting light; No. 5, spectrum of the flame and scattered light when mercury pressure was too low for tin fluorescence.

The possibility of an error in the classification of 3034 is slight since it checks measurements on the Zeeman effect[5] and the initial level for 3034

[3] J. G. Winans, Phys. Rev. **30**, 1 (1927).

[4] H. Sponer, Zeits. f. Physik **32**, 19 (1925).

[5] E. Back, Zeits. f. Physik **43**, 309 (1927); J. B. Green and R. A. Loring, Phys. Rev. **30**, 574 (1927).

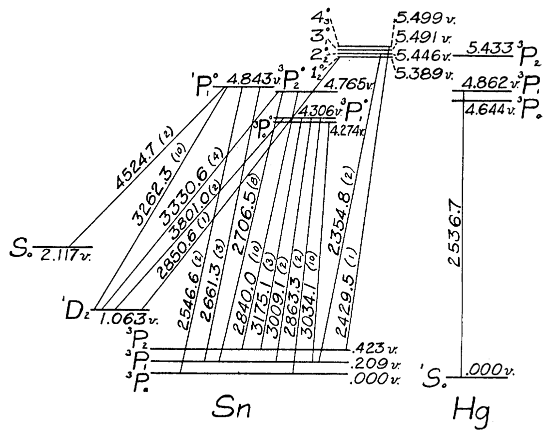


FIG. 3. Complete list of tin lines observed in sensitized fluorescence.

is the final level for three infrared lines classified by Randall and Wright.[6] Also 3034 can be reversed in the arc and must therefore have a final level of low energy.

The high intensity of Sn 3034 ($^3P_1-{}^3P_0{}^0$) in comparison to Sn 3009 ($^3P_1-{}^3P_1{}^0$) in fluorescence in Hg vapor or in the Hg-Sn discharge but not in an arc indicates a process which favors the excitation of Sn $^3P_0{}^0$ over $^3P_1{}^0$ in collisions of the second kind with Hg 2^3P_1 or 2^3P_0.

An effect similar to this seems to be shown by an experiment of Kopfermann on the sensitized fluorescence of Pb in Hg vapor.[7] Kopfermann observed Pb 3683 ($^3P_1-{}^3P_0$) and not 3640 ($^3P_1-{}^3P_1$) in fluorescence. The initial levels for these two lines have energies 4.60 and 4.36 volts. The line with the greater energy discrepancy is the stronger, in contradiction to the usual rule.

TABLE I. *Energy discrepancies in volts.*

Hg	Sn $^1P_1{}^0$	$^3P_2{}^0$	$^3P_1{}^0$	$^3P_0{}^0$
2^3P_1	0.019	0.097	0.556	0.588
2^3P_0	−0.199	−0.121	0.338	0.370

The relative abundance and effectiveness in collisions of the second kind of 2^3P_1 and 2^3P_0 Hg atoms and excited Hg_2 molecules is difficult to determine. Mrozowski[8] has recently obtained evidence that excited Hg_2 molecules may produce sensitized fluorescence. The action of Hg_2 molecules in the present investigation is probably very slight, since it has been shown that at the temperatures reached in a blow torch Hg_2 bands do not appear in a discharge.[9] The relative abundance of 2^3P_1 and 2^3P_0 Hg atoms can be expected to follow a Boltzmann distribution since Hg atoms under the conditions of this experiment would make 10^5 collisions with other Hg atoms while making one collision with a Sn atom. At 900°C there would be seven 2^3P_0 to one 2^3P_1 Hg atoms.

Assuming that 2^3P_0 Hg atoms produce the abnormal intensities of Sn 3034 and Pb 3863 in collisions of the second kind, it appears that the transition O−O normally forbidden in the Hg atom takes place more readily if producing a O−O transition in a colliding atom. Further experiments are needed before this can be accepted as a general rule.

The writers wish to acknowledge the assistance of Dr. S. Winston Cram in the preliminary work with the usual type of sensitized fluorescence apparatus, and of Professor J. E. Mack in checking classifications of Sn lines.

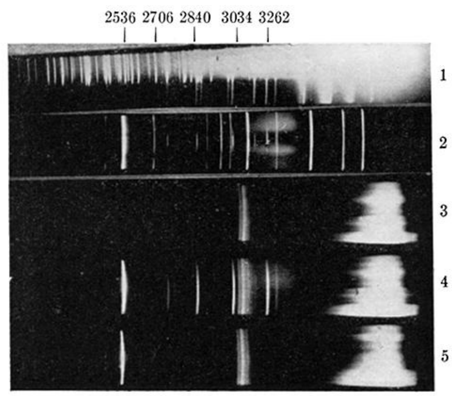
This investigation was supported in part by a grant from the Wisconsin Alumni Research Foundation.

[6] H. M. Randall and N. Wright, Phys. Rev. **38**, 457 (1931).

[7] H. Kopfermann, Zeits. f. Physik **21**, 318 (1924).

[8] S. Mrozowski, Acta Phys. Pol. **6**, 58 (1937).

[9] J. G. Winans, Phys. Rev. **45**, 125 (1934). Fig. 2, No. 2 shows how the Hg_2 band at 3300 is quenched by the heating necessary to bring out the Sn lines. This picture was taken with a reduced image of a vertical discharge tube focused on the spectrograph slit. The tube was heated at the center by a blow torch.



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