ABSORPTION BANDS IN THE SPECTRA OF MIXTURES OF METALLIC VAPORS

By R. K. Waring

Abstract

Evidence of the existence of HgTl molecules in the vapor state.—It is shown by experiment that at a given temperature the amount of thallium in the vapor state is increased by adding mercury vapor. This indicates definitely that thallium-mercury molecules are formed.

Absorption bands of HgTl molecules.—In a mixture of thallium and mercury vapors a number of bands appear in absorption which are to be attributed to the HgTl molecule. In no case was the resolving power sufficient to show structure. Asymmetric broadening of the atomic Tl lines and of the Cd line 2288 due to Hg vapor has been observed. Two possible explanations are discussed: broadening due to a superimposed molecular band, and broadening due to transfer of kinetic energy by collisions.

Absorption bands of InCd molecules.—Absorption bands due to InCd molecules were observed in mixtures of In and Cd vapors at temperatures of 400°, 500° and 800°C. Their short wave-length limits are tabulated. A few showed traces of their structure but the resolving power was not sufficient to make measurements possible.

IN 1908 Wood and Guthrie[1] studied the ultra-violet absorption spectra of mixtures of metallic vapors. They found that the spectrum of a mixture of thallium and mercury contained bands which were not present in the spectrum of the vapor of either pure metal. They also found that the presence of mercury vapor caused the atomic lines of thallium and of cadmium to broaden asymmetrically. In addition, there appeared to be evidence that the presence of mercury vapor permitted the vaporization of thallium at temperatures lower than any at which its presence could be detected by its optical absorption when mercury was not present, but the absorption bands seen under this condition, which do not appear with mercury vapor alone, must be attributed to a molecule (probably HgTl), and not to atomic thallium. The effect alluded to above might perhaps be classified as a solution of thallium in mercury vapor, analogous to similar phenomena described by Wood in the case of potassium iodide and alcohol vapor.[2]

The question now presents itself as to whether the mercury atoms attach themselves to thallium atoms in the vapor state (for a few must be present even at the low temperatures), and by thus lowering the partial pressure of the thallium vapor, permit more vapor to leave the metal which, in its turn, unites with the mercury, or the mercury atoms unite with the thallium atoms at the surface of the metal, the amalgam molecule then going into the vapor phase. The present investigation was undertaken for the purpose of con-

[1] Wood and Guthrie, Astrophys. J. **29**, 211 (1909).
[2] Wood, Phil. Mag. **41**, 423 (1896).

firming and extending these results, and studying the observed phenomena from the viewpoint of the theory of band spectra, which has been developed in recent years.

Preliminary Experiment

As a preliminary experiment an investigation was made to see whether it could be shown by non-optical methods that the volatilization of thallium was assisted by the presence of mercury vapor. Two identical Pyrex U-tubes of 15 cc capacity were evacuated, baked, and sealed off. One U-tube contained a piece of thallium in one branch, and a small amount of mercury in the opposite branch. The other U-tube contained a piece of thallium in one branch, and nothing in the opposite branch. The tubes were placed together in a vertical furnace with their ends down, and heated to 600°C. When equilibrium had been reached, a blast of cold air was directed against the branches which had not originally contained thallium, causing an immediate condensation of the contents. The blast was kept on for 30 seconds, after which the tubes were removed from the furnace and allowed to cool. The tubes were then opened and an analysis for condensed thallium was made.

Tihe branch which had contained mercury yielded one-half a milligram of thallum, while the branch which had been empty yielded no thallium. The experiment was repeated, using larger tubes and an improved method of analysis. This time the branch which had contained mercury yielded 5.3 mg of thallium, and the branch which had been empty yielded 0.5 mg of thallium.

The chemical analysis offered difficulties because of the small amount of thallium involved. The method finally adopted consisted in introducing some mercury into the branch of the tube to be tested for thallium, and then oxidizing the thallium with air under a known volume of standardized sulphuric acid. The thallic hydroxide formed is immediately dissolved by the acid so that the amount of thallium can be calculated from the amount of acid used, which, in turn, is determined by titration. The process may be represented as follows:

$$4Tl + 3O_2 = 2Tl_2O_3$$
$$2Tl_2O_3 + 6H_2O = 4Tl(OH)_3$$
$$4Tl(OH)_3 + 6H_2SO_4 = 2Tl_2(SO_4)_3 + 12H_2O$$

The method was tested with known amounts of thallium, and it was found that for small amounts of thallium the test consistently showed less thallium than was really present. For example, when 10 mg of thallium was used, and air was bubbled through the acid for 15 hours, the test showed 7 mg of thallium. While this seems very rough, it is sufficient for the purpose since, in the last actual experiment, the yields of condensed thallium from the two branches of the two U-tubes were 0.5 mg, and 5.3 mg, respectively.

This result indicates that more thallium exists in the vapor condition when mercury is present. It was realized that such a result might be due to lack of uniform temperature throughout the furnace, so care was taken to

obtain a uniform temperature. The amount of mercury present was so small that it was entirely volatilized at 600°. When the mercury was condensed by means of the air blast it might have swept the thallium vapor along with it to such an extent as to increase the amount of thallium which was condensed, but this process could not possibly increase the amount of condensed thallium from 0.5 mg to 5.3 mg. Thus, the experiment seems to indicate quite definitely that thallium-mercury molecules were formed.

Winans[3] has found bands in the absorption spectra of vapor freshly distilled from a mercury-zinc amalgam which do not appear in the spectra of the stagnant vapor. He attributes the bands to a zinc-mercury molecule, and it would seem likely that the molecule is formed in the amalgam and soon dissociates when in the vapor state. In the case of thallium there is no evidence as to whether the molecule is formed at the surface of the solid thallium or in the vapor.

Experimental Procedure

The metals to be studied were placed in a quartz tube which was then evacuated, baked, and sealed off. Tubes were used from 10 to 15 cm long, and from 1 to 2 cm in diameter. At first flat quartz windows were sealed on the ends of the tube, but later it was found that quite satisfactory results were obtained by blowing a bulb on each end of the tube. If the quartz was blown rather thin the transmission was good. In the ultra-violet a quartz spectrograph of one meter focus was used, while in the visible a one meter concave grating, and a 21 foot plane grating spectrograph were employed. Hammer Special plates were used for the photography of the ultra-violet, and Panchromatic for the visible. The source of light in the ultra-violet was the continuous background of the cadmium spark, while in the visible the carbon arc was used. The usual procedure was to place the source of light about 50 cm from the slit of the spectrograph, and focus on the slit by means of a quartz lens placed about 10 cm from the source. The light then passed through the absorption tube, which was contained in a platinum wound furnace. The furnace was fitted with auxiliary heating units at each end in order to prevent condensation on the windows of the tube. The maximum temperature attainable was 1200°C.

Absorption Spectra of Mixtures of the Vapors of Thallium and Mercury

The ultra-violet absorption of pure thallium was photographed at temperatures between 200°C and 800°C. The following lines appeared: $2^2P_1 - 3^2S_1$ (2316A); $2^2P_1 - 2^2S_1$ (2580A); $2^2P_1 - 1^2S_1$ (3776A); $2^2P_1 - 4^2D_2$ (2380A); $2^2P_1 - 3^2D_2$ (2768A). The first three of these lines appeared at 700°C, and the last two at 600°C. In addition a very faint trace of a line at about 3230A appeared at about 400°, but its intensity did not increase at higher temperatures. Later on in the work, with a different tube and a different sample

[3] Winans, Phys. Rev. **31**, p. 710 (April, 1928).

of thallium, this line again appeared, and in addition, two very faint lines at about 3221 and 3241. These lines were also observed by Wood and Guthrie.

A number of tubes were next tried which contained 20 parts thallium to one part mercury, and one tube which contained 15 parts thallium to one part mercury. In every case the amount of mercury was 8 mg. Considerable difficulty was encountered because of the corrosive action of the thallium on the quartz windows which would eventually become opaque to ultra-violet light. It is interesting to note that this effect was always encountered when mercury was present, but never caused any trouble when the tube contained only thallium. With these tubes it was found that all the thallium lines came out at a lower temperature (roughly 100°) than with pure thallium. This is caused, at least in part, by the broadening of the lines due to the presence of the mercury vapor. The extremely faint lines observed with thallium at 3221, 3230 and 3241 now appeared at about 400°, as bands about 3A wide, sharp on the side of short wave-length, and shaded toward the visible. They broadened slightly with increasing temperature. Two other bands also appeared, one at about 3100 and one at about 2510. Both bands were somewhat faint but quite broad.

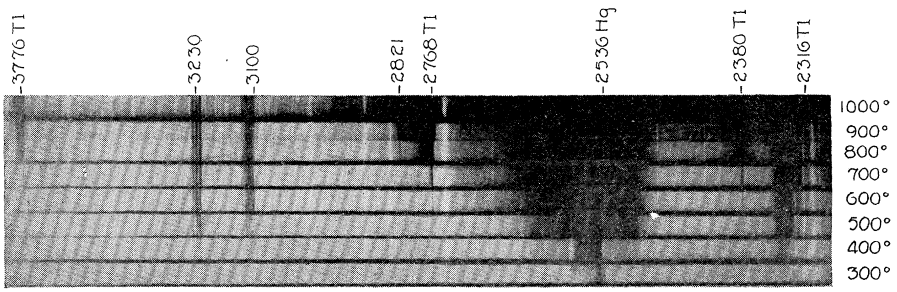

Plate I.

A tube was next prepared containing 132 mg of thallium and 100 mg of mercury. (It may be mentioned that in all cases the mercury was completely volatilized at temperatures, above 600°, while in no case was much of the thallium volatilized.) In this case all of the absorption lines and bands came out much stronger than in previous cases, and a number of new lines and bands appeared (Plate I). Table I gives a list of the absorption with this tube (temperature 900°C) omitting the absorption bands due to pure mercury vapor. The wave-lengths are accurate to a few tenths of an Angstrom,except where a question mark follows the recorded value. In no case was the resolving power sufficient to show the structure of any of the bands. All of the unclassified lines are faint and will probably not be visible in the reproduction included in this article. It is thought probable that many, or all, of the "unclassified lines" are very narrow bands. Wood and Guthrie observed a number of narrow bands in this region when they used very high vapor pressures.

TABLE I. *Wave-lengths of absorption bands and lines in a mixture of thallium and mercury vapors.*

Bands		Thallium Lines	
3244?	(diffuse limit)	$2^2P_1-3^2S_1$	(2316)
3240.3	(sharp limit)	$2^2P_1-1^2S_1$	(3776) very broad
		$2^2P_1-4^2D_2$	(2380) very broad
3235?	(diffuse limit)	$2^2P_1-3^2D_2$	(2768) very broad
3231.7			
3230.5	(sharp limit)	$2^2P_1-3^2D_2$	(3519) narrow
		$2^2P_2-3^2D_2$	(3539) narrow
3226.1?	(diffuse)	$2^2P_2-4^2D_3$	(2918) narrow
3221.3	(sharp)		
		Unclassified lines	
3127?	(diffuse)	3382.9?	3280.9
3098?	(diffuse)	3323.7	3279.7?
		3311.4	3270.5
2822.4?	(diffuse)	3309.2	3263.9
2819.3?	(diffuse)		
		3300.1	3252.0?
2510?	(a broad band which merges with the mercury band at 2536)	3298.4	3205.9?
		3292.3	3193.8?
		3290.0	

The band from 3230.5 to 3235 has a very narrow region at 3231.7 where the absorption is not as strong as in the rest of the band. From the appearance of the plate it seems probable that there are in reality two superimposed bands in this region.

At 700° a faint band appeared, extending from the short wave-length side of the atomic thallium absorption line 2380 to about 2375. As the temperature was raised this band rapidly became stronger and extended toward the long wave-lengths. At 800° it had attained a width of about 20A. It was sharp on the side of shorter wave-lengths and shaded towards longer wave-lengths. A similar effect was noted in the case of the line 3776 except that the band first appeared on the long wave-length side of the atomic line. Still greater broadening was observed at 2768, this band attaining a width of 40A at 900°C. No information is available as to the broadening of the lines 2580 and 2316 as they were masked by mercury absorption.

The visible spectrum was now examined for absorption, the only result being the observation of the thallium line $2^2P_1-1^2S_1$ (5350A) (Plate II-a). This line appeared at about 800°, and broadened more toward the long wave-lengths than toward the short in the same manner as the lines previously discussed. The fact that the line did not appear at a lower temperature is to be expected since 2^2P_2 is about 0.9 volts above the normal orbit of thallium 2^2P_1.

The question of the broadening of the atomic lines seems most worthy of discussion, but in this paper it will only be treated briefly since the available data are not sufficient to give a definite explanation of the phenomenon. It seems fairly certain that thallium-mercury molecules of some sort exist and that the absorption bands previously mentioned, that do not coincide with atomic lines, are the result of absorption by these molecules.

In the case of the broadening of the atomic lines, two explanations present themselves. The first is that the apparent broadening is really a superimposed molecular band, the molecule having a weak bond so that the band is not much displaced from the position of the atomic line. The fact that no fine structure appears is not surprising since both mercury and thallium atoms have very large mass.

The chief objection to the explanation is that Frayne and Smith[4] and others have observed with pure thallium a similar broadening of the atomic lines which originate on the 2^2P_1 orbit. All the lines observed in the present investigation, except $2^2P_2-1^2S_1$ (5350) originate on this level. Frayne and Smith heated thallium in a tube with open ends and could reach a temperature of 2000°C.

It has been suggested by Oldenberg[5] that, if an atom absorbs a light quantum at the instant in which it collides with another atom, it may be possible for the quantum energy and part of the kinetic energy of the colliding atoms to act together to excite the absorbing atom. This would mean that a light quantum of smaller energy than the excitation energy would be absorbed; that is, the atomic line would broaden toward longer wave-lengths as the temperature of the vapor is increased. If it is further postulated that a quantum of greater energy than the excitation energy can be absorbed at the instant of a collision, and the excess energy transferred to kinetic energy of the colliding atoms, a broadening towards the shorter wave-lengths will result. It follows that the short wave-length limit of the broadening should be independent of temperature and pressure, that the long wave-length limit should increase with increasing temperature, and that the intensity of the absorption should increase with the number of collisions, that is, with the pressure.

Under the conditions used in these experiments the pressure increases with the temperature. Hence, it should be expected that with increasing temperature (and pressure) the line would broaden steadily towards the long wave-lengths, but that on the short wave-length side the broadening would be constant, the intensity of the entire absorption increasing. This is just the effect which is actually observed.

In order to choose between the two alternatives, molecular band or collision broadening, additional data are needed. If the temperature should be increased at constant density, the absorption should get fainter if it is molecular in origin, since the molecules would dissociate more rapidly at a higher temperature, while, if the effect is due to collisions, the intensity should be proportional to the number of collisions, that is, to the square root of the absolute temperature. Photographs were actually taken under these conditions, but the temperature range at constant density was not sufficient to cause noticeable changes in the intensity of absorption.

[4] Frayne and Smith, Phys. Rev. **27**, p. 23 (1926).

[5] Oldenberg, Zeits. f. Physik **47**, p. 184 (Feb., 1928).

INDIUM-CADMIUM

In using a tube containing indium with cadmium present as an impurity a series of bands was observed (Plate II-b). It seems probable that these bands are due to indium-cadmium molecules. A few of the bands showed

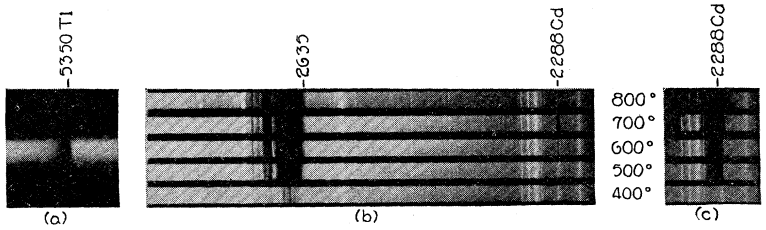

Plate II.

traces of their structure, but not clearly enough to enable measurements to be made. The bands were sharp at the short wave-length limit and shaded towards the visible. At temperatures above 400° the bands near the limit of the series merged so that the absorption appeared continuous. Table II gives the wave-lengths of the short wave-length limits of all the bands that could be measured at three different temperatures. It was impossible to

TABLE II. *Short wave-length limits of bands observed in mixture of indium and cadmium vapors.*

400°	500°	800°	800°
2652.8	[2640.1	[2634.6	2333.4
2661.4			2339.7
2672.1			2341.9
2684.2	[2685.8	[2690.6	2346.1
			2347.2
	2693.9	?	2352.9
			2353.4
2695.0	2694.6	[2694.2	
	2705.5		
2707.1	2711.6	[2712.4	
2718.1	2717.6	2717.0	
		2717.9	
	2728.2	2728.2	
2729.9	2729.8?	2729.8	
	2739.7?	2739.7	
	2741.1?	2741.1	
		2751.3	
	2752.8	2753.0	
		2776.3	
		2787.9	
		2800.2	

make very accurate measurements but the recorded values are correct to within a few tenths of an Angstrom. The approximate limits of the apparently continuous absorption are given in brackets. Another series of bands observed on the same plates (Plate II-b) is recorded in the last column in the table.

A band about 0.7A wide with both limits sharp appeared at 600°. It extended from 2333.6A to 2337.3A. A very faint diffuse band about one Angstrom wide appeared at 700°. The wave-length of the center of this band was about 2338.5A. With increasing temperature the intensity of both bands increased, but neither band broadened appreciably.

The cadmium line 2288 was absorbed and broadened symmetrically with increasing temperature (Plate II-b). The cadmium line 3261 also appeared at the higher temperatures, but was very faint. When a little mercury was added the line 2288 broadened more toward the long wave-lengths exactly as described by Wood and Guthrie (Plate II-c), while the line 3261 appeared stronger but did not broaden much. Further discussion of the results obtained with indium and cadmium will be postponed until more data are available.

I wish to take this opportunity of thanking Professor R. W. Wood for proposing this problem, and for offering many valuable suggestions while the work was in progress. I also wish to express my gratitude to Professor K. F. Herzfeld for the encouragement and valuable advice which he has given me.

THE JOHNS HOPKINS UNIVERSITY
May, 1928.

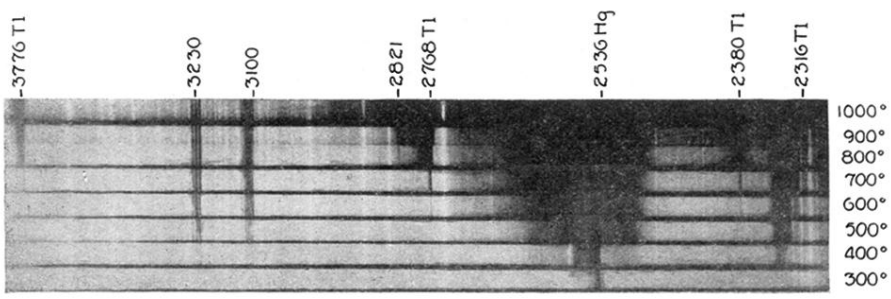
3776 Tl
3230
3100
2821
2768 Tl
2536 Hg
2380 Tl
2316 Tl
1000°
900°
800°
700°
600°
500°
400°
300°

Plate I.

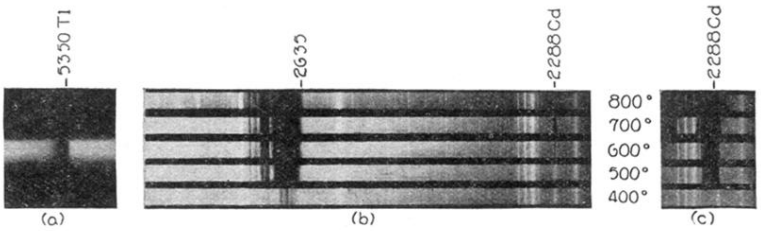

Plate II.