I. EFFECT OF GASES ON THE OPTICALLY EXCITED CADMIUM I SPECTRUM

By Paul Bender
Department of Physics, University of Iowa

(Received October 6, 1930)

Abstract

An apparatus producing intense optically excited cadmium radiation is used to study the effects of nitrogen, carbon monoxide, and hydrogen on the optically excited cadmium spectrum, which effects are compared to similar phenomena with mercury. Each gas produces a decrease in the intensity of each of the spectral lines; no increase occurs because of the lack of self-reversal in the lines of the exciting source. The quenching of the resonance line λ3261 A.U. is less than that of the remainder of the spectrum. Nitrogen quenches very inefficiently, while carbon monoxide is considerably more efficient: about 35 mm and 3 mm, respectively, of gas pressure are necessary to reduce the intensity of the resonance line to half value. Both of these gases transfer the excited cadmium atom from the 2^3P_1 to the metastable 2^3P_0 state by kinetic energy collisions. Hydrogen quenches the cadmium radiation very effectively; a collision between the excited 2^3P_1 cadmium atom and a hydrogen molecule produces a normal cadmium hydride molecule and a hydrogen atom.

Introduction

AFTER Wood's[1] first discovery of the quenching of the resonance radiation of mercury by the addition of foreign gases, Wood and numerous other workers have studied the rather remarkable changes occurring in the radiation from optically excited mercury vapor produced by the addition of foreign gases under various conditions. The cadmium spectrum exactly parallels in structure that of mercury, but shows decidedly different energy relations within the atom, which facts gave promise of interesting comparisons in the effects of foreign gases on the optically excited spectra of the two metals. Also, the hydrogen-filled, high-voltage discharge tube available as a source of the cadmium spectrum, with its intense radiation without self-reversal, offered a very satisfactory source of excitation for the spectrum of cadmium. Accordingly the present investigation was undertaken, studying the effect on the optically excited cadmium radiation of the addition of nitrogen, carbon monoxide, and hydrogen. This paper discusses the effect of these gases on the cadmium I spectrum; the succeeding paper discusses the cadmium hydride bands appearing in the optically excited radiation with the presence of hydrogen, together with zinc hydride and mercury hydride bands appearing under parallel experimental conditions.

Apparatus

The apparatus was constructed to produce intense optical excitation by the cadmium spectrum itself of cadmium vapor in the resonance tube R, as shown by the diagram in Fig. 1.

[1] Wood, Phys. Zeits. **13**, 353 (1912).

The source of illumination was a long hydrogen-cadmium discharge tube D, of a type first described by Ellett[2] and successfully used for exciting resonance radiation of various metals. It was operated with a 10 K.V.A. transformer with a 1 to 60 ratio from a 110-volt source with from 30 to 50 amperes in the primary circuit controlled by a water rheostat. A spirally arranged quartz section of the discharge tube, making two complete turns around the resonance tube R, and a side tube, containing cadmium metal from which cadmium vapor was distilled into the discharge tube, were constructed. The resonance tube was made entirely of quartz, one end being drawn out obliquely to form a light trap, the other end having a plane quartz window through which the optically excited radiation passed to the spectrograph. The passage of light from the discharge tube to the spectrograph was avoided by painting with lampblack the entire resonance tube excepting the central portion of the window and the portion of the tube adjacent to the spiral of the discharge tube. The resonance tube and the adjacent portion of the

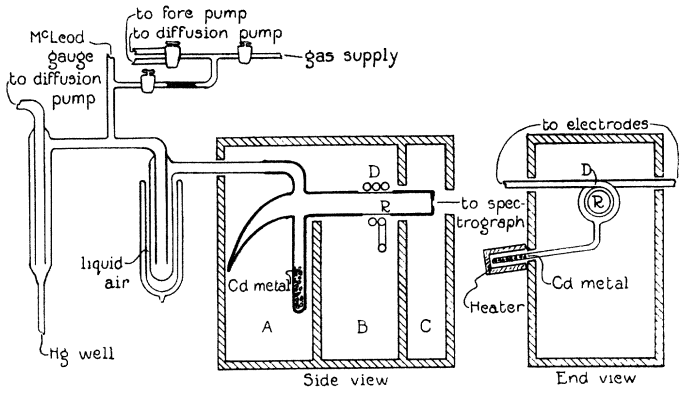

Fig. 1. Diagram of apparatus.

discharge tube were mounted in an asbestos box which was heated by electric heaters and the heat generated by the discharge tube. Cadmium metal in a side tube supplied to the resonance tube the necessary cadmium vapor, the pressure of which was maintained at about 0.008 mm of mercury (corresponding to about 260° C) and controlled by regulating the temperature in section A of the box containing the side tube. Sections B and C of the box were always maintained at a considerably higher temperature than A to avoid condensation of the metal in the main part of the tube. A mercury diffusion pump served to evacuate the tube, and a mercury seal made it possible to seal the pump from the resonance system. The usual liquid-air trap prevented diffusion of mercury vapor to the resonance tube.

This set-up permitted a very intense illumination of the cadmium vapor in the resonance tube, causing it to radiate, but producing no effect when the hydrogen discharge tube was operated without cadmium vapor. The

[2] Ellett, Jour. Opt. Soc. of Am. **10**, 427 (1924).

optically excited radiation appeared as an intense bluish-green glow throughout the volume of the resonance tube with such strength that a ten-second exposure on a Hilger El quartz spectrograph sufficed to record all the strong lines in the cadmium spectrum.

The gases employed to modify the optically excited radiation were admitted into the resonance tube through a capillary tube and stop-cocks, as pictured in Fig. 1, which regulated the flow of gas, and which could be evacuated separately. The gas pressures up to 1 mm were measured on a McLeod gauge, and those above 1 mm were measured directly on the mercury seal.

To obtain pure gases for these experiments, the following methods of preparation were employed: Nitrogen was obtained from sodium azide, which was placed into a flask attached to the system and the entire system evacuated, after which the azide was gently heated to decompose it. Carbon monoxide was prepared from sodium formate and sulfuric acid: the formate was placed into a flask attached to the system, after evacuation the acid was admitted through a stop-cock, and the gas thus produced was passed through a liquid-air trap to freeze out any vapors. Hydrogen was prepared electrolytically and passed through a liquid-air trap.

To study the general effects of these gases on the optically excited radiation of cadmium, the radiation was photographed with a small quartz spectrograph having an average dispersion of about λ150 A.U. per mm over the range from λλ3000 to 5000 A.U., and the intensity relations of the spectral lines compared by matching, visually, equal densities on the photographic film for different exposure times. No accurate quantitative measurements of intensity were attempted.

Discussion

The gases used in the present investigation—nitrogen, carbon monoxide, and hydrogen—all produced a decrease in the intensity of the resonance radiation of cadmium, never an increase as observed by Wood[3] for mercury. There are two reasons for this difference: First, the lines in the source are free from self-reversal, insuring maximum absorption from the central portion of the line. Second, the absorbing vapor is at a temperature approaching that of the source, giving a Doppler broadening to the absorption line practically the same as that of the absorbed line. Thus any additional broadening of the absorption line, due to collisions with the foreign gas molecules, will tend only to decrease the absorption; hence, even apart from the actual quenching collisions, the only influence of a foreign gas will be to decrease the resonance radiation.

In the optical excitation of the cadmium spectrum, cadmium atoms are first brought to the 2^3P_1 state by absorption of the resonance line λ3261 A.U. ($2^3P_1 - 1^1S_0$), from which state they may either re-radiate the resonance line or absorb from the exciting light other frequencies corre-

[3] Wood, Proc. Roy. Soc. **A106,** 679 (1924).

sponding to transitions ending on the 2^3P_1 state to bring them to still higher excited levels. These more highly excited atoms will then radiate what might be termed the secondary portion of the cadmium spectrum, that is, the portion other than the resonance line and depending on two or more successive absorptions by the same atom and, hence, also depending on the second or higher power of the intensity of the exciting light. This part of the spectrum will include principally those lines ending on the 2^3P levels, the transitions from the 2^3S_1 and the 3^3D levels being the most intense. (See energy-level diagram in Fig. 2.)

Now, in the process of quenching the optically excited radiation by gas collisions, this secondary portion of the spectrum will be quenched more effectively than the resonance line, depending upon the second or higher power of the gas pressure according as the particular excited state involved is reached by two or more successive steps, while the quenching of the resonance line will depend only upon the first power of the gas pressure.

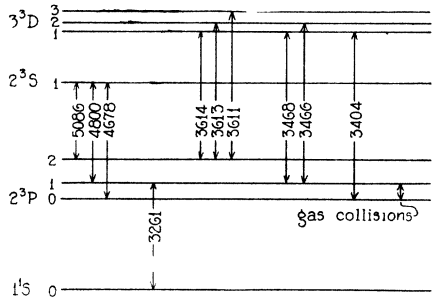

Fig. 2. Energy-level diagram for the cadmium atom.

This effect was observed in the cadmium spectrum with nitrogen and carbon monoxide, which produced a much greater decrease in the intensity of the secondary portion of the spectrum than of the resonance line. In the case of nitrogen, λ3261 A.U. persisted with only slightly diminished intensity to rather high gas pressures, its intensity at a pressure of 35 mm of nitrogen being roughly half that with no gas present. The secondary portion of the spectrum could readily be detected at 35 mm nitrogen pressure, although it had only a small fraction of its original intensity. Carbon monoxide was more effective in quenching the resonance line, 5 mm of the gas decreasing the intensity slightly more than did 35 mm of nitrogen. This difference in the effects of the two gases is similar to that reported by Stuart[4] in the case of mercury, although it seems to be considerably smaller. Stuart's method of excitation was such as to produce only the resonance line λ2537 A.U. with measurable intensity, and under these conditions the pressures necessary to reduce the intensity of the resonance line to one-half value were, for nitrogen 30 mm, and for carbon monoxide 0.4 mm.

[4] Stuart, Zeits. f. Physik **32**, 262 (1925).

Nitrogen and carbon monoxide also produced an increase in the relative intensity of the λ3404 A.U. line ($3^3D_1-2^3P_0$) over the remainder of the secondary spectrum observed, including the 3^3D-2^3P lines in the ultraviolet and the 2^3S-2^3P lines in the visible. (The two 3^3D lines ending on 2^3P_1 and the three 3^3D lines ending on 2^3P_2 were not resolved by the spectrograph used). This effect was first noticeable with about 0.01 mm pressure of nitrogen and with a slightly lower pressure of carbon monoxide, reaching its maximum at about 0.1 mm gas pressure in both cases and persisting with a relative intensity ratio between the λ3404 A.U. line and the remainder of the spectrum of about 2 to 1 throughout the whole range of pressures observed.

This phenomenon is apparently caused by an increased population of the metastable 2^3P_0 state of the cadmium atom, due to collisions of excited (2^3P_1) atoms with gas molecules. From the energy-level diagram (Fig. 2) it is evident that the 3^3D_1 level will be favored by an increase in the population of the metastable 2^3P_0 level, through absorption of λ3404 A.U. from the exciting light. On the other hand, the 3^3D_2 and 3^3D_3 levels will be decreased in population by the transfer of cadmium atoms from the 2^3P_1 level to the metastable 2^3P_0 level. Thus, in re-emission by transfer from the D to the P levels, λ3404 A.U. should show an increase in intensity as compared with the other two unresolved members of the D triplet.

A similar but much larger effect is observed in the case of mercury by Wood[5] and Klumb and Pringsheim,[6] nitrogen and carbon monoxide producing a very large increase in the population of the metastable 2^3P_0 state of the atom. Oldenberg[7] has suggested that this is due to a resonance phenomenon between the excited mercury atom and the gas molecules, pointing out that the energy difference between the 2^3P_1 and 2^3P_0 levels of the mercury atom (0.218 volt) is nearly the same as the energy required to excite the normal gas molecule to its first vibration level (0.29 volt for N_2 and 0.265 volt for CO). In cadmium, however, the difference in energy between the two P levels is only 0.07 volt; consequently the same resonance phenomenon could not occur. But with so low an energy difference one would expect a large transfer of the excited cadmium atoms to the metastable state by collisions of the second kind with gas molecules, in which the excess atomic energy appears as kinetic energy of translation of the colliding molecules. Again, at the temperatures employed (about 350°C), at which the average kinetic energy of translation of the gas molecules is about 0.08 volt, collisions with a metastable cadmium atom will have a large probability of bringing it back to the 2^3P_1 state. Now, in the absence of a gas, the concentration of the metastable atoms is relatively low since they are destroyed by rapid diffusion to the walls of the tube and are formed only by emission of λλ4678 and 3404 A.U. from the 2^3S_1 and 3^3D_1 levels, respectively, which in turn are reached only by two or more successive absorptions. With the addition of

[5] Wood, Phil. Mag. (7) **4,** 466 (1927).
[6] Klumb and Pringsheim, Zeits. f. Physik **52,** 610 (1928)
[7] Oldenberg, Zeits. f. Physik **49,** 609 (1928).

a gas, two effects will tend to increase the population of the metastable state: first, the presence of the gas will decrease the rate of diffusion of the metastable atoms to the walls of the tube, thus increasing their effective life; and, second, the kinetic energy collisions of the gas molecules with the atoms in the 2^3P_1 and 2^3P_0 states will produce more metastable atoms than they will destroy. The final equilibrium with gas present, therefore, should have a larger population of the metastable state than does the condition without the gas. As pointed out above, this favors the population of the 3^3D_1 level by absorption of λ3404 A.U. which in turn permits the observed increased re-emission of this same line.

Transfer of the 2^3P_1 cadmium atoms to the upper metastable state (2^3P_2) by collisions with gas molecules is highly improbable since the energy difference between the two levels (0.14 volt) is considerably in excess of the mean kinetic energy of the gas molecules (0.08 volt).

It is interesting to note here, also, in the cases of mercury and cadmium, a comparison of the pressures required to produce the first evidences of increased population of the metastable level by gas molecule collisions. For mercury the effect first appears at a gas pressure of about 0.1 mm, as stated by Pringsheim,[8] while for cadmium it is evident at 0.01 mm pressure. This is to be expected from the difference in the mean lives of the two excited atoms (2^3P_1). The mean life for mercury is 0.98×10^{-7} sec.[9] and for cadmium it is 2.30×10^{-6} sec.[10], giving a ratio of the mean lives of the same order of magnitude as the ratio of the collision times required to produce the effects observed.

Hydrogen produced a quenching of the whole optically excited cadmium spectrum, with only a slightly greater efficiency for the secondary portion of the spectrum than for the resonance line λ3261 A.U. The quenching was evident at pressures as low as 0.01 mm, and the resonance line was almost entirely extinguished at 4 mm gas pressure. Bates[11] and Hoffman[12] have observed this quenching effect of hydrogen. Bates attempted to produce the spectrum of cadmium by optical excitation of cadmium vapor in the presence of hydrogen, but found complete quenching. He failed to state the gas pressures employed, however. Hoffman studied the absorption of the $2^3S_1-2^3P$ lines (λλ5086, 4800 and 4678 A.U.) by electrically excited cadmium vapor in the presence of gases, and found varying degrees of absorption of these lines with nitrogen and the inert gases, but could detect no absorption in the presence of about 2 mm of hydrogen, which showed that the hydrogen very effectively destroyed the 2^3P atoms.

In the case of mercury, the excited atom has an energy (4.86 volts) only slightly greater than the dissociation energy of the hydrogen molecule

[8] Pringsheim, Fluorescenz und Phosphorescenz, p. 117

[9] Olson, Phys. Rev. **32,** 443 (1928).

[10] Ellett, Phys. Rev. **33,** 124 (1929).

[11] Bates, Proc. Nat. Acad. Sci. **14,** 849 (1928).

[12] Hoffman, Zeits. f. Physik **60,** 457 (1930).

(4.46 volts);[13] the excited mercury atom is very effective, therefore, in dissociating the hydrogen molecule, losing, of course, its own energy of excitation in the process, as pointed out by Cario and Franck.[14] Thus, only a small amount of hydrogen gas is necessary to quench the mercury resonance radiation. In cadmium, however, the energy of excitation of the first excited state (3.78 volts) is less than the dissociation energy of hydrogen, hence the same quenching process can not occur. Nevertheless, the quenching effect of hydrogen seems to be about as strong for cadmium as for mercury.

The present investigation, however, reveals the formation of the unexcited cadmium hydride molecule in the excited cadmium-hydrogen mixture (evidence for this is discussed in the succeeding paper), which leads directly to the explanation of the quenching of the cadmium radiation by hydrogen: an excited cadmium atom in the 2^3P_1 state collides with a hydrogen molecule, forming an unexcited cadmium hydride molecule and an atom of hydrogen,

$$Cd(2^3P_1) + H_2 \rightarrow CdH + H. \quad (1)$$

Svensson,[15] in his analysis of the cadmium hydride band system, gives for the dissociation energy of the normal CdH molecule the value 0.67 volt.[16] In the collision represented by Eq. (1), therefore, the total energy available is the sum of the excitation energy of cadmium (3.78 volts) and the dissociation energy of the CdH molecule, which sum amounts to 4.45 volts. This is practically the same as the required dissociation energy of the hydrogen molecule (4.46 volts), which fact makes the process highly probable.

The present experiments gave evidence, also, of the formation of atomic hydrogen in the optically excited cadmium-hydrogen mixture, which is further verification of the process of molecule building represented by Eq. (1). With commercial (chemically pure) cadmium metal in the side tube of the resonance tube, optical excitation of the cadmium-hydrogen mixture in the resonance tube caused a large decrease in the hydrogen pressure, which decrease did not occur without optical excitation even when the mixture stood for a long period at the high temperature employed. The lost hydrogen was found as water frozen out by the liquid-air trap, which had been formed, presumably, through a reduction by atomic hydrogen of some oxide present in the cadmium supply. This was further verified by using in the resonance tube cadmium which had first been distilled in an atmosphere of hydrogen to reduce any oxide present; whereupon only a very small decrease in the hydrogen pressure occurred on operation of the tube.

[13] Richardson and Davidson, Proc. Roy. Soc. **A123,** 54 (1929).

[14] Cario and Franck, Zeits. f. Physik **11,** 161 (1922).

[15] Svensson, Zeits. f. Physik **59,** 333 (1930).

[16] The spacing between the vibration levels of the normal CdH molecule does not follow the empirical rule stated by Condon and Morse (Quantum Mechanics p. 159) as holding for many diatomic molecules. Applying this empirical rule to the three highest vibration levels recorded by Svensson yields the value given (0.67 volt) for the dissociation energy. Higher values are obtained when it is applied to other levels. This value must be considered, therefore, merely as a rough approximation.

In contrast with the effects of nitrogen and carbon monoxide, the spectrograms of the present investigation showed no evidence of an increased population of the metastable state with hydrogen present, which agrees with the observations of Klumb and Pringsheim[6] for mercury. The reason in the present case of cadmium is obvious when we consider that a collision of the excited cadmium atom with a hydrogen molecule produces the CdH molecule, as described above, and hence will not transfer the cadmium atom to the metastable state.

In addition to the cadmium spectrum, cadmium hydride bands appear in the optically excited radiation from the cadmium-hydrogen mixture. This interesting phenomenon is discussed in the succeeding paper.

Conclusions

Nitrogen and carbon monoxide have a low quenching efficiency on the optically excited cadmium radiation, and are less effective in quenching the resonance line λ3261 A.U. than the remainder of the spectrum.

Kinetic energy collisions of gas molecules with excited cadmium atoms transfer them from the 2^3P_1 to the metastable 2^3P_0 state.

Hydrogen is very effective in quenching the optically excited cadmium radiation, collisions with the 2^3P_1 cadmium atoms forming CdH molecules and atomic hydrogen.

To Professor A. Ellett, who suggested the present investigation and rendered valuable assistance in its execution, the writer wishes to express his appreciation.