

## The Mechanism of Formation of Mercury Hydride and Mercury Deuteride. Optical Excitation of Cadmium Deuteride

Leonard O. Olsen

Citation: *The Journal of Chemical Physics* **6**, 307 (1938); doi: 10.1063/1.1750256

View online: <http://dx.doi.org/10.1063/1.1750256>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/6/6?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Diffusion mechanisms in mercury cadmium telluride](#)

*AIP Conf. Proc.* **235**, 1615 (1991); 10.1063/1.41087

[Diffusion mechanisms in mercury cadmium telluride](#)

*J. Vac. Sci. Technol. B* **9**, 1615 (1991); 10.1116/1.585433

[Ionization—Excitation Processes in Zinc, Cadmium, and Mercury](#)

*J. Chem. Phys.* **55**, 3642 (1971); 10.1063/1.1676640

[Optical Ionization Excitation Functions of Zinc, Cadmium, and Mercury by Electron Impact](#)

*J. Chem. Phys.* **53**, 754 (1970); 10.1063/1.1674054

[The Mechanism of Processes Initiated by Excited Atoms II. Photosensitization by Excited Mercury and Cadmium](#)

*J. Chem. Phys.* **10**, 43 (1942); 10.1063/1.1723620

---



# The Mechanism of Formation of Mercury Hydride and Mercury Deuteride. Optical Excitation of Cadmium Deuteride

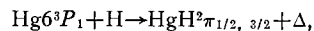
LEONARD O. OLSEN\*

State University of Iowa,† Iowa City, Iowa

(Received March 3, 1938)

An attempt has been made to secure resonance excitation of HgH by illuminating (1) a mixture of mercury, hydrogen and nitrogen, and (2) a mixture of mercury and water vapor, with the light from a mercury and hydrogen discharge. This discharge emitted a fairly intense HgH spectrum. Weak HgH band radiation was observed which was similar to that secured when the same mixtures were illuminated with a discharge tube which did not emit the HgH radiation. Inability to secure resonance is evidence that the weak band radiation is due to HgH

molecules formed in excited states which dissociate after emission. Experimental evidence is presented which indicates that the formation process is



where  $\Delta$  is an energy parameter. Essentially similar results were secured for HgD. Resonance excitation of CdD was observed when a mixture of cadmium and deuterium was illuminated with a cadmium and deuterium discharge.

## INTRODUCTION

GAVIOLA and Wood<sup>1</sup> secured the HgH band radiation from a mixture of mercury, hydrogen and nitrogen illuminated with a mercury vapor lamp. They presented indirect evidence indicating that the molecule is formed in an excited state and dissociates after emission. They also observed the molecular radiation when mercury and water vapor was illuminated with a mercury vapor lamp.

Similar experiments were performed by Beutler and Rabinowitch<sup>2</sup> and F. F. Rieke.<sup>3</sup> They assumed that the molecule is formed in the normal state and subsequently excited by a collision with an excited mercury atom. This was postulated because of the abnormal rotation of the HgH molecule excited in this manner.

It should be possible to determine which is the process occurring by comparing the band radiation secured when a source emitting the HgH radiation is used with that secured when a mercury discharge free of hydrogen is used.

If the HgH molecules were present in the normal state they would absorb molecular radiation from the source and produce a fairly intense

HgH spectrum. (This type process will be referred to as resonance excitation.) With the hydrogen-free source the only method of raising HgH molecules to excited states is by collisions of the second kind with excited mercury atoms. One would expect a much weaker band radiation to result from this process.<sup>4</sup>

On the other hand if the molecules do not exist in the normal state for an appreciable length of time because of their low energy of dissociation<sup>5</sup> (0.37 volts) resonance excitation and collision excitation would be impossible. Any band radiation observable should then be the same as excited by all sources emitting the atomic mercury spectrum with the same intensities. In addition, the band radiation would have to result from molecules formed in excited states which dissociate after emission.

## APPARATUS

The apparatus was essentially the same as that described by Bender<sup>4</sup> and consisted of a quartz resonance tube encircled by a spiral section of the discharge tube. Spectrograms of the fluorescence were secured with two instruments, one having an average dispersion of

<sup>4</sup> P. Bender (Phys. Rev. **36**, 1535 (1930)) has observed that resonance excitation of CdH is more than fifty times as intense as the weak band radiation which can be secured when the cadmium and hydrogen mixture is illuminated with a cadmium discharge not emitting the CdH spectrum. As the energies involved in the possible excitation processes are of the same order of magnitude as those obtaining for mercury and hydrogen, one would expect similar results for the optical excitation of HgH.

<sup>5</sup> E. Hulthen, Zeits. f. Physik. **50**, 319 (1928).

\* Now at Case School of Applied Science, Cleveland, Ohio.

† The main content of a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the department of physics, in the Graduate College of the State University of Iowa, August, 1937.

<sup>1</sup> E. Gaviola and R. W. Wood, Phil. Mag. **6**, 1191 (1928).

<sup>2</sup> H. Beutler and E. Rabinowitch, Zeits. f. physik. Chemie, **B8**, 231 (1930).

<sup>3</sup> F. F. Rieke, J. Chem. Phys. **4**, 513 (1936).

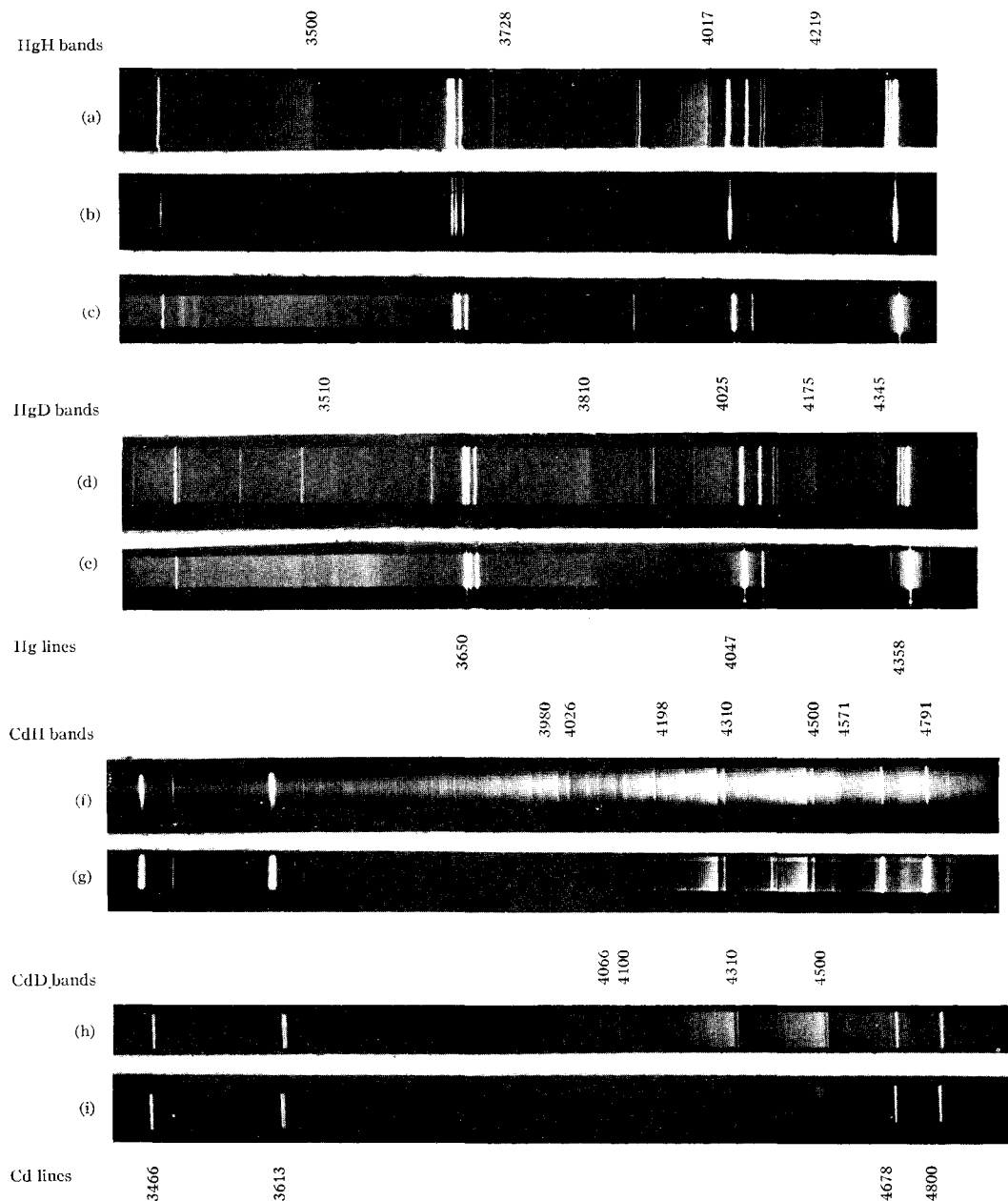


FIG. 1. (a) HgH source, (b) radiation excited with  $H_2$ -Hg discharge, (c) radiation excited with He-Hg discharge, (d) HgD source, (e) HgD radiation excited with He-Hg discharge, (f) CdH source, (g) CdH resonance, (h) CdD source, (i) CdD resonance.

120 A/mm and the other, a Hilger *E1*, having an average dispersion of 8 A/mm (measured in the vicinity of the HgH 3500A band).

#### RESULTS FOR HgH AND HgD

A mixture of mercury vapor (approximately 40°C), about one-hundredth of a millimeter of

hydrogen and several millimeters of nitrogen<sup>6</sup> was illuminated with a mercury and hydrogen discharge. Spectrograms of the optically excited radiation show weak excitation of the HgH bands belonging to the  ${}^2\Pi_{1/2, 3/2} \rightarrow {}^2\Sigma_{1/2}$  system

<sup>6</sup> Nitrogen was produced by the decomposition of sodium azide in a vacuum. Hydrogen and deuterium were produced by electrolytic decomposition of water and deuterium oxide.

with a rotational structure differing from that of the source but similar to that observed by previous experimenters.<sup>1-3</sup> The same structure was also observed when the source was operated with helium in place of hydrogen. Frequent spectroscopic examinations of this source were made to be sure no hydrogen contamination was present. Excitation of the HgH band radiation was thus observed to be independent of the presence of HgH in the source.

The failure to secure resonance must mean that HgH is not present in the normal state. Hence, the HgH band radiation observed was produced by molecules formed in excited states. Fig. 1 (a), (b) and (c) shows spectrograms of the source and of the optically excited radiation.

Wood and Gaviola<sup>1</sup> assumed that the excited HgH molecules were formed from mercury atoms in  $6^3P$  states and atomic hydrogen. The large energy discrepancies involved in such reactions are rather unsatisfactory and an attempt was made to establish definitely which excited states are responsible for the formation of the molecules.

A consideration of the energy levels of mercury shows that the  $Hg7^3S_1$  state possesses the requisite amount of energy to form  $HgH^2\Pi_{1/2, 3/2}$  by means of an energy exchange with a hydrogen molecule. Interactions of atomic or molecular hydrogen with mercury atoms in other states of rather high probability involve larger discrepancies than encountered for  $Hg7^3S_1$  or  $Hg6^3P$  and thus need not be considered.

As the  $Hg7^3S_1$  state is populated principally by absorption of  $\lambda 4047$  by  $Hg6^3P_0$  and  $\lambda 4358$  by  $Hg6^3P_1$ , the HgH band radiation should disappear when these wave-lengths are filtered out of the exciting radiation if the HgH molecules are formed by these atoms.<sup>7</sup> When the filtered source was used the *HgH fluorescence still occurred* and it must be concluded that mercury atoms in the  $6^3P_{0, 1}$  states are responsible.<sup>8</sup>

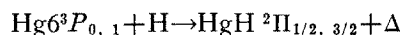
The energy above that required for formation in a low rotational state must be divided between energy of rotation, and energy of translation of the molecule and a third body. Classical

<sup>7</sup> A bromine and chlorine cell absorbs effectively in this region.

<sup>8</sup> F. F. Rieke (reference 3) also secured the molecular radiation using a filtered source. His filter was used for a different purpose, however.

considerations of an approximate character show that almost all of this energy could appear as energy of rotation of the HgH molecule. This would account for the abnormal rotation which has been observed.

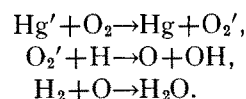
It will be observed that the process



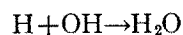
demands the presence of free atomic hydrogen whereas the process



suggested for formation in the normal state involves molecular hydrogen. The effect of oxygen on the optically excited radiation presents indirect evidence that it is necessary to have atomic hydrogen to secure the band radiation. Admission of a small amount of oxygen extinguishes the HgH radiation and causes the OH band in the vicinity of  $\lambda 3070A$  to shine out immediately. Wood and Gaviola<sup>1</sup> performed this experiment but it has been repeated because of its significance. In addition it has been observed that the intensity of the OH band falls off rapidly after the admission of the oxygen. Wood and Gaviola<sup>1</sup> proposed the reaction



The extinction of the OH band would indicate that the reaction



was also occurring. The water vapor formed was frozen out in the dry ice and acetone trap.

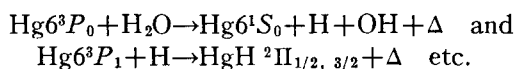
It would be of interest to know which  $Hg^3P$  atoms were uniting with atomic hydrogen to form  $HgH^2\Pi_{1/2}$  and  $HgH^2\Pi_{3/2}$ . From considerations of conservation of angular momentum about the axis of symmetry,<sup>9</sup>  $Hg6^3P_0$  plus hydrogen can produce only  $HgH^2\Pi_{1/2}$  whereas  $Hg6^3P_1$  plus hydrogen can produce both  $HgH^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$ .

Under the conditions of this experiment  $Hg6^3P_0$  atoms were more abundant than  $Hg6^3P_1$ , yet the  $\lambda 3500A$  ( $^2\Pi_{3/2} \rightarrow ^2\Sigma_{1/2}$ ,  $0 \rightarrow 0$ ) band was more intense than  $\lambda 4017A$  ( $^2\Pi_{1/2} \rightarrow ^2\Sigma_{1/2}$ ,  $0 \rightarrow 0$ ). (Refer to Fig. 1.) It has also been found that the

<sup>9</sup> R. S. Mulliken, Rev. Mod. Phys. 4, 26 (1932).

intensity of these bands increases somewhat less than linearly with increasing nitrogen pressure in the range from zero to three millimeters pressure. This has been determined by visual examination of a series of exposures for which the time of exposure was halved when the nitrogen pressure was doubled. An approximately linear relationship should exist if mercury atoms in the  $6^3P_1$  state were the combining atoms. On the other hand, if  $Hg6^3P_0$  were the reacting atoms the band intensity should be approximately a quadratic function of the nitrogen pressure. The first  $Hg6^3P_0$  atom produced by a collision of  $Hg6^3P_1$  with a nitrogen molecule would be used to dissociate a hydrogen molecule, a second nitrogen molecule would be used to form an  $Hg6^3P_0$  which would combine with one of the free hydrogen atoms. Thus the relationship between nitrogen pressure and band intensity, and the intensity of  $\lambda 4017A$  compared with  $\lambda 3500A$ , both indicate that  $Hg6^3P_1$  were the reacting atoms.

The energy relations obtaining for mercury and water vapor are more favorable for formation of  $HgH$  in the normal state.<sup>2, 3</sup> However, an attempt to secure resonance when mercury vapor in the presence of water vapor at a pressure of several millimeters of mercury was illuminated with a discharge emitting the  $HgH$  radiation gave negative results. Further, a weak  $HgH$  band radiation was observed which was similar to that secured when a mercury-helium discharge was used. It must therefore be concluded that the principal reactions which occurred were



That free atomic hydrogen is necessary for the formation of the molecules is further substantiated by comparing the  $HgH$  fluorescence secured when the water vapor in the resonance tube was circulated by pumping through a capillary tube during the exposure with that secured when the tube was shut off from the pumping system. The intensity of the fluorescence was much greater in the second case.

The rotational intensity distribution observed in this case was intermediate between that

secured for the mercury, hydrogen and nitrogen combination and that observed for the source. (This is in agreement with the results of F. F. Rieke.<sup>3</sup>) Other conditions being unchanged increasing the water vapor pressure shifted the rotational intensity distribution in the bands toward that of the source.

Substitution of deuterium for hydrogen in the combination mercury, hydrogen and nitrogen, and excitation with a mercury-helium discharge free of hydrogen produced an  $HgD$  fluorescence similar in most respects to the  $HgH$  fluorescence already described. Fig. 1 (d), (e) shows spectrograms of the source and optically excited radiation. Comparing these spectrograms with those of Fig. 1 (a), (b), (c) it will be observed that the  $HgD$  band heads are somewhat more prominent than the corresponding heads for  $HgH$ . Also, for  $HgD$ , the  $^2\Pi_{1/2} \rightarrow ^2\Sigma_{1/2}(1 \rightarrow 0)$  band is more intense than  $^2\Pi_{1/2} \rightarrow ^2\Sigma_{1/2}(0 \rightarrow 0)$  which is not true for  $HgH$ . The spectrograms of the source and fluorescence both show a peculiar band structure in the region of  $\lambda 3550A$  which has not been identified.

#### RESONANCE EXCITATION OF CADMIUM DEUTERIDE

Bender<sup>4</sup> observed that the effectiveness of hydrogen in quenching the cadmium resonance radiation is due to the fact that an excited cadmium atom in collision with a hydrogen molecule produces  $CdH$  in the normal state. He was also able to secure resonance excitation of these molecules.

This experiment was repeated and extended to include the optical excitation of  $CdD$ . Fig. 1 (f, g, h and i) shows typical spectrograms of the  $CdH$  source,  $CdH$  resonance,  $CdD$  source and  $CdD$  resonance. Considerable difficulty was experienced in securing a pure  $CdD$  source. The source was first operated with helium and then with deuterium. After continued operation and frequent changes of the deuterium the source emitted a practically pure  $CdD$  spectrum.

In conclusion, the writer wishes to express his sincere appreciation to Professor A. Ellett for his excellent guidance and inspiration during the period of this investigation.