APRIL 15, 1931 PHYSICAL REVIEW VOLUME 37

THE ENERGY OF DISSOCIATION OF MERCURY MOLECULES

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(Received March 5, 1931)

Abstract

The absorption spectrum of mercury vapor in the Schumann region showed three apparently continuous bands with maxima at wave-lengths 1849, 1808, and 1692. The 1849 and 1692 bands appeared without the 1808 band in the emission from an electrodeless discharge through mercury vapor. The absorption spectrum in the region 1900–1804 is correlated with a pair of potential energy curves for Hg_2. From these curves, the energy of dissociation of Hg_2 is 0.15 volts.

Introduction

The problem of the energy of dissociation of mercury molecules is particularly interesting because, as far as chemical evidence is concerned, mercury molecules do not exist. For example c_p/c_v for mercury vapor is 1.666, the value for a purely monatomic gas. Also the molecular weight of mercury vapor equals that of liquid mercury.[1] Nevertheless mercury molecules exist in both the excited and unexcited states as evidenced by the presence of bands in the absorption and emission spectra of mercury vapor.[2]

The binding force between two mercury atoms must be similar to that between two helium atoms since both have a closed outer shell containing two paired s electrons. So far three types of binding for diatomic molecules have been proposed; ionic as in NaCl, exchange forces as in H_2, and polarization or van der Waal's forces. The binding between neutral mercury atoms can not be ionic, and Heitler and London[3] have shown that the exchange forces between helium-like atoms must be repulsive if the Pauli exclusion principle holds. There remain only the polarization forces to hold the mercury molecule together. The analysis of Eisenschitz and London[4] has shown that the polarization forces may, at large separations be greater than the exchange forces and produce a definite equilibrium when the exchange forces are repulsive. Mercury molecules are probably of this type.

Values for the energy of dissociation of mercury molecules have been obtained by Koernicke[5] and Mrozowski.[6] Koernicke, following the work of Franck and Grotrian,[7] measured the change in total intensity of the mercury

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[1] Summary by J. W. Mellor, Treatise on Inorganic and Theoretical Chemistry, vol. 4, p. 766.

[2] R. W. Wood, Astphys. J. **26**, 41 (1907); Rayleigh, Proc. Roy. Soc. **A116**, 702 (1927); F. L. Mohler and H. R. Moore, J.O.S.A. **15**, 74 (1927).

[3] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[4] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 515 (1930).

[5] E. Koernicke, Zeits. f. Physik **33**, 219 (1925).

[6] S. Mrozowski, Zeits. f. Physik **55**, 338 (1929).

[7] J. Franck and W. Grotrian, Zeits. f. Tech. Physik **3**, 194 (1922).

band at 2540 with superheating and calculated the energy of dissociation of Hg_2 as 1.4 kg. cal./mol. or 0.06 volts. Mrozowski measured the total intensity of fluorescence in mercury vapor at different positions along the direction of the exciting light. He obtained the absorption coefficient of saturated mercury vapor at different temperatures for several exciting wave-lengths. Assuming this coefficient proportional to the number of Hg_2 molecules, he calculated D for Hg_2 as 17 kg. cal./mol. Koernicke's and Mrozowski's values differ by a factor 12. The two methods will be discussed in detail in a later paper.

The results of the present investigation give a value for D for Hg_2 which lies between the two above mentioned but is quite different from either. The method is the same as that used to obtain D for Zn_2 and Cd_2.[8] The value of D comes from an interpretation of the absorption region in the vicinity of the resonance line 1^1S-2^1P. This line comes at wave-length 1849 for mercury.

Apparatus and Procedure

The absorption spectrum of mercury in the region 3000–1550 was photographed with a small vacuum fluorite spectrograph on Schumann plates. The absorption cell, shown in Fig. 1, was made of fused quartz. The windows were very thin to give increased transparency and hemispherical in shape to withstand atmospheric pressure. The cell was heated in an electric furnace. A hydrogen discharge tube served as a source of continuous light.

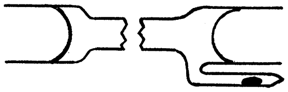

Fig. 1.

For photographing the emission spectrum of mercury, the cell of Fig. 1 was waxed to a tube leading to the spectrograph, a wire wrapped around each end, one wire grounded and the other connected to a low-voltage Tesla coil (leak chaser). When the tube was heated by a bunsen burner, a brilliant mercury discharge was obtained. CO bands from a discharge through air were used as standards for wave-length measurements.[9]

Results

The absorption spectra taken with increasing pressures of mercury vapor (Fig. 2) show first the atomic line 1849 which broadens rapidly, then a continuous band with a maximum intensity at 1808 A (Fig. 2 No. 1) and finally another continuous band with maximum at 1692 (Fig. 2, No. 2), Fig 3 is a microphotometer record of Fig. 2 showing the 1692 band. Fig. 2, No. 2 shows how, at increased pressure the 1808 band is broadened principally toward

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[8] J. G. Winans, Phil. Mag. **7**, 555 (1929).

[9] T. Lyman, Astrophys. J. **23**, 204 (1906); "The Spectroscopy of the Extreme Ultraviolet," p. 114.

longer wave-lengths and the absorption region surrounding 1849 broadened toward shorter wave-lengths as far as the 1808 band but no farther, and toward longer wave-lengths beyond 2200 A. The lack of intensity below 1690 in No. 1 Fig. 2 was due to short exposure and not to absorption.

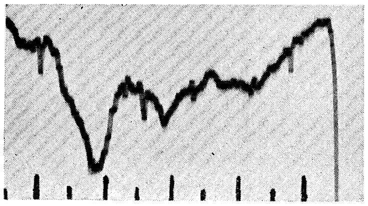

Fig. 2.

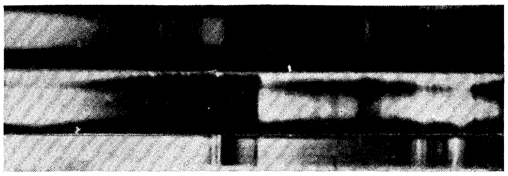

Fig. 3.

In the emission spectrum from the electrodeless discharge (Fig. 2, No. 3), the band surrounding 1849 and the one at 1692 were observed but not the one at 1808. The distribution of intensity in the 1692 band was the same in emission and absorption (Fig. 3).

TABLE I.

Description	Wave-length	Vacuum wave-number
Absorption maximum	1691.4	59123
Emission maximum	1692.1	59097
average	1691.8	59110
Absorption maximum	1808.0	55311
*Short wave limit	1804.2	55427

* The wave-length was measured at the point where the photographic blackening from the source had been reduced to one half.

Table I gives a summary of results. Wave-lengths previously given (Phys. Rev. **36**, 1020(1930) should be corrected to agree with Table I.

DISCUSSION

The continuous bands at 1808 and 1692 do not coincide with atomic transitions and are observed only at pressures much greater than that needed to show the atomic line 1^1S-2^1P. They are therefore attributed to molecules of mercury and these molecules are assumed to be diatomic. The characteristics of these bands as described above can be correlated with a set of potential energy curves for the Hg_2 molecule.

The band at 1808 was observed in absorption but not in emission in the electrodeless discharge. In the spectra of atoms, absorption lines are sometimes missing in emission because they are absorbed by the vapor surrounding the source. This can not be the case for the 1808 band; since, from the order of appearance of the bands with increasing pressure, the absorption coefficient of the missing band 1808 lies between that of the two bands at 1849 and 1692, both of which were observed in emission. A probable reason for the non-appearance of 1808 in emission is that the Hg_2 molecule is dissociated upon absorption of this wave-length. If this is true, the curves of potential energy as a function of nuclear separation must have definite relative positions. According to the Franck-Condon principle, the nuclei of a molecule do not change their separation appreciably during an electron transition. If curves of potential energy and nuclear separation are plotted for the excited and normal molecule, allowed transitions are represented by vertical lines connecting the two curves. For interpreting absorption spectra, one assumes a Boltzmann distribution of molecules in the vibrational states of the normal molecule, so that the lowest vibrational state with 1/2 quantum of energy is the most thickly populated. The most intense part of an absorption band should be represented by vertical lines through the points of the normal molecule curve, corresponding to this lowest energy. If absorption of the 1808 band results in dissociation of an Hg_2 molecule, the potential energy curves must have relative positions like either *c* and *a* or like *c* and *b* in Fig. 4. If positions *c* and *a* are correct, after absorption of 1808, (transition B) the nuclei find themselves with sufficient potential energy to dissociate into one excited and one normal atom. This is the usual interpretation given to a photo-chemical dissociation. If curves *c* and *b* are correct, the nuclei simply lose all attraction for each other upon absorption of 1808, and find themselves free to drift apart. In either case the band 1808 should be observed in absorption but not in emission.

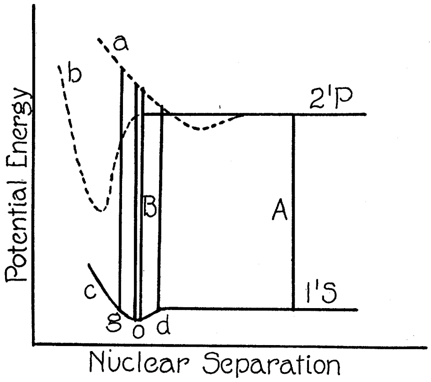

Fig. 4.

If the original assumption that absorption of 1808 means dissociation is correct, it is not difficult to decide which of the two relative positions shown in Fig. 4 must be right. From analogy with He_2, which is found to exist only when excited, the energy of binding in the excited mercury molecule is probably greater than that in the normal molecule. In practically all molecules which have been studied, greater energy of binding is associated with smaller nuclear separation at the minimum of the potential energy curve, so that curves *c* and *b* should be required for Hg_2. If curves *c* and *a* were correct, with increase of pressure and temperature and corresponding increase in the number of normal molecules in higher vibrational states, the 1808 band (*B*, Fig. 4) should broaden toward both longer and shorter wave-lengths corresponding to transitions from points *g* and *d*. This does not agree with the observation that the 1808 band broadened almost entirely toward longer wave-lengths. On curve *c* and *b*, however, we see that 1808 represents the longest vertical distance between the two curves and absorption from points *g* and *d* would give a broadening toward longer wave-lengths only.

Further we can also explain the very interesting fact that the absorption region surrounding 1849 reaches a short wave limit coinciding with that for the 1808 band, but reaches no definite long wave limit. Consider two mercury atoms making a collision. Their mutual potential energy would follow the curve for the normal mercury molecule (estimated as curve *c*, Fig. 4). If they absorbed light during a collision, the energy absorbed would correspond to vertical lines between the two potential energy curves of Hg_2, and since they come to rest at point *g*, Fig. 4, and move more slowly at point *d* than at *o*, the positions *g* and *d* would be more probable positions for the absorption of light. This would represent wave-lengths slightly greater and slightly less than that of the atomic absorption line 1849. Now suppose the number of colliding atoms which absorb light to be greatly increased, one should observe absorption from points *c* and *o*. This would mean a continuous broadening of the 1849 line toward both longer and shorter wave-lengths but it would reach a limit on the short wave side coinciding with the limit for the 1808 band. This exactly describes what was observed. Of course, it is not sure that the short wave limit of 1849 exactly coincides with that of 1808 since the observed limit comes from a superposition of both. It is, however, significant that the 1849 band does not broaden beyond 1804 on the short wave side but broadens beyond 2200 on the long wave side.

We have correlated a set of curves such as *b* and *c*, Fig. 4, with three observations; the appearance of 1808 in absorption but not in emission, the broadening of the 1808 band toward longer wave-lengths with pressure, and the peculiar broadening of the 1849 band with pressure.

From Fig. 4 it is easily seen that the energy of dissociation of the normal molecule is simply the difference in energy between the 1849 and the 1808 bands. This gives D for Hg_2 equal to 0.15 volts or 3.5 kg. cal./mol. This value is three times Koernicke's value and one-third of Mrozowski's. The three methods will be compared and discussed in a later paper.

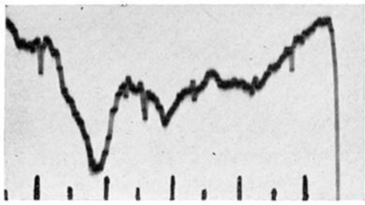

Fig. 2.

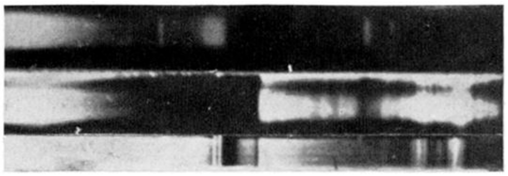

Fig. 3.