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THE NATURE OF ELEMENTAL MERCURY IN SOLUTION

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THE NATURE OF ELEMENTAL MERCURY IN SOLUTION

by

Grace Chunhae Kim

A Thesis Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

In the Graduate College

THE UNIVERSITY OF ARIZONA

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ABSTRACT

The nature of mercury in solution was studied by means of spectroscopic measurements - absorption, fluorescence and atomic absorption. The solvents used for the preparation of mercury solutions were alcohols (ethanol and methanol) and hydrocarbons (pentane, hexane and 3-methylpentane). The spectral results obtained from our work indicate that the dimer molecules of mercury exist predominantly in solution: this has not been reported previously. The large positive value of entropy of dimerization calculated (101.79 JK^{-1}) indicates that the dimerization process is an entropy driven process.

CHAPTER 1

INTRODUCTION

Spectroscopic studies are carried out both in vapor and in solution. Solution spectroscopy, particularly of large molecules, is investigated more frequently than in the vapor phase because of the convenience and the need to understand solution properties. In contrast, theoretical calculations involving energy levels and transition moments are performed exclusively on gas phase molecules since the quantum calculations on solvated molecules are very difficult. One of the major concerns in spectroscopic measurements of solutions has been the correct interpretation of the solvent effects on spectral results. The characteristic bands or lines are often shifted to higher or lower wavelength, depending on the type of solvents. Changes in band shape are also observed with changes in the solvent system. Therefore, in order to obtain better understanding of spectroscopic measurements in solution, one needs to investigate the effects of various solvent systems on solute spectra and compare these data with vapor phase data.

The best system for the study of solvent effects are the solutions of atomic elements in any solvent. Solutions made with non-polar solutes (elements) are assumed not to differ much from ideal

gas solutions. In this type of solution, enthalpy of solute - solvent
mixing is expected to be negligible ($\Delta H_{mixing} = 0$). Thus at constant
temperature, the free energy change (ΔG) will be composed solely of the
entropy term:

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

$$\Delta G = -T\Delta S \quad (\text{for } \Delta H = 0) \qquad (2)$$

The entropy of mixing of a solution of this type is

$$\Delta S = -R(n_A \ln X_A + n_B \ln X_B) \qquad (3)$$

where X_A and X_B are the mole fractions of solute and solvent. Equation
(3) is the thermodynamic equation that governs ideal solutions
including the solubilities of solutes.

Most of the elements that were used in solubility studies have
been the gaseous elements. Pierotti(1965) developed the scaled
particle theory to calculate the reversible work required to dissolve
gas molecules in liquid (i.e. the solubility of gases in liquid). De
Ligny and van der Veen(1972) tested Pierotti's theory with the aid of a
large amount of literature data on solubility and entropy of solution.
Among the solutes involved were He, Ne, Ar, Kr, Xe, Rn gases and Hg
vapors. Solubilities and thermodynamic properties of gaseous elements
were further studied by Wood and De Laney(1968), by McGowan(1971), and
by Brueckl and Kim(1981).

In contrast to gaseous elements, the solubilities of solid and
liquid elements have not been investigated. Elemental mercury, the
only common metal that is liquid at ordinary temperature due to its

unusally low melting point (-38.84°C), was the only exception.
Mercury, because of its unique properties, is slightly soluble at room
temprature and pressure. Thus it offers a good possibility for the
investigation of solvent effects and thermodynamic properties.

Kuntz and Mains(1964) believed that the solubility of mercury
in hydrocarbon solvents is of interest to the solution
thermodynamicists and tried to understand the nature and extent of
solvent - solute interactions. Spencer and Voigt(1968a) also stated
that the low solubility of mercury metal offers an excellent system for
the appraisal of solute - solvent interactions.

The solubility of metallic mercury in various solvents has been
studied by many researchers since the 1930's. The first attempts to
determine the solubility of mercury were made by Reichardt and
Bonhoeffer(1930) using a gravimetric method in which the soluble
mercury was amalgamated on a gold foil. They reported that the
absorption spectrum of the mercury solution showed the characteristic
resonance line of mercury at 253.7 nm, broadened considerably and split
into two peaks. The splitting of 253.7 nm line was explained as a
consequense of Stark effect (i.e. the interaction of the atomic
quadrupole moment of mercury atoms with electric field of solvent
molecules). This interpretation was based upon the assumption that the
mercury dissolved in the solvent exists as monomers, due to its
extremely low solubility, and that the mercury has an electric (as
distinct from nuclear) quadrupole moment. It should be noted, however,
that there is no evidence for the existence of electric quadrupole

moments for atoms. Reichardt and Bonhoetter claimed that the mercury in solution is monatomic and unionized with a ground state of $^1S_0$.

Several other attempts to determine the solubility of elemental mercury have been made. Stock and co-workers(1934) tried the method of electrodeposition of the dissolved mercury on a copper wire. Moser and Voigt(1957), Klehr and Voigt(1962), and Spencer and Voigt(1968a, 1968b) measured mercury solubility by determining directly the specific activity of a solution using a radioactive tracer Hg^{203}. Kuntz and Mains(1964) determined the solubility of mercury by combining optical data with known mercury solubilities. Neutron activation analysis was used by Choi and Tuck(1962), and by Rook and co-workers(1972) to measure the solubility in water. More recently atomic absorption spectrophotometry has been used by Glew and Hames(1971), by Onat(1974), by Vogel(1974), and by Okouchi(1981).

Table 1 shows the solubility data obtained from various methods mentioned above. There seemed to be an inconsistency among the results obtained from different methods and by different groups as Gerrard(1980) and then later Clever(1986) pointed out.

In addition to the studies on solubility and related thermodynamic properties, investigations were carried out on fluorescence and photosensitization. Phibbs and Darwent(1950), Bremer et al.(1975) and Brown(1977) made attempts to measure the fluorescence of mercury by photosensitization. They studied the wavelength region between 260 and 300 nm because they also assumed that mercury in

Table 1: Solubility of Mercury in Different Solvents[a]

| Solvent | Solubility (μmoles/ℓ) at temp(°C) of | | | | | |
	20	25	30	35	40	Ref
Methanol	-	0.78	-	-	3.0	(1)
	-	1.52	-	-	-	(2)
	2.1	2.94	3.5	4.7	-	(3)
Pentane	-	5.8	-	-	-	(2)
	6.4	9.4	12.8	-	-	(4)
Hexane	-	6.4	-	-	-	(2)
	-	-	-	-	13.5	(1)
	6.8	9.6	13.	-	22.	(4)
	7.3	9.6	12.6	16.1	-	(5)
3-methyl-pentane	-	5.1	-	-	-	(2)

[a]These solubilities were obtained from the previous work done by designated references.

Ref

(1) Moser, H.C. and Voigt, A.F., U.S.A.E.C. Rept. ISC-892, P. 65 (1957)

(2) Kuntz, R.R. and Mains, G.J., J. Phys. Chem. 68, 408-410 (1964)

(3) Spencer, J.N. and Voigt, A.F., J. Phys. Chem. 1913-1917 (1968)

(4) Okouchi, S. and Sasaki, S., Bull. Chem. Soc. Jpn. 54, 2513-2514 (1981)

(5) Spencer, J.N. and Voigt, A.F. Phys. Chem. 72, 464-470 (1968)

solution is a monatomic species. Within the region they studied, no fluoresecnce signal corresponding to mercury was observed. Fluorescence of mercury in solution has not yet been reported. The spectroscopic measurements of mercury in solution are limited mostly to absorption measurements.

Spectroscopy of mercury vapor, on the other hand, has attracted great interest with its applications in laser spectroscopy and photochemistry of excited states. Through various spectroscopic measurements such as absorption, fluorescence, and flash photolysis, it was confirmed that a small concentration of dimer molecules of mercury exists in the vapor phase and their fluorescence spectrum showed a band maximum at 335 nm.

Since Mrozowski(1930) first assigned the 335 nm band to a $Hg_2(1_u)$ state, much work has been done to confirm and further investigate the properties of Hg_2. Stock and co-workers(1985) analyzed the decay of fluorescence in optically excited mercury vapor by a pump laser system. Drullinger, Hessel and Smith(1977) studied mercury molecules spectroscopically. They used absorption, fluorescence and a sequential two photon excitation technique. Theoretical calculations as well as experimental studies were performed. Hay, Dunning and Raffenetti(1976) approached a model calculation of Hg_2 using Zn_2 potential energy curves. Mies, Stevens and Krauss(1978) modeled their calculations on ab initio calculation of Mg_2 energy levels. They proposed a possible electronic structure of Hg_2. The electronic

absorption spectra of the optically excited mercury dimers was studied in the 230 - 600 nm range by Callear and Lai(1979). Stefanov, Iordanov and Zarkova(1982) estimated the enthalpy of dimerization in the vapor phase to be -10.8 ± 0.6 KJ from their study of the interaction potential between two ground state mercury atoms. Callear and Lai(1982) later employed the flash photolysis method for the study of mercury dimers. The quantum yield and lifetime of excited dimers of mercury vapors were reported by Callear, Devonport and Kendall(1982). The mass spectrometric identification of the Hg_2 molecule, its equilibrium partial pressure over Hg(1), enthalpy of evaporation and enthalpy of dissociation were studied by Hilpert(1982). Also, Rabbett and King(1985), and Atkinson, Niefer and Krause(1983) studied the formation of dimers by laser spectroscopic methods.

Problem Statement

In spite of all the efforts mentioned above, a great deal of uncertainties about the nature of mercury in solution still remains.

If mercury were to exist as monomers in solution as everyone has assumed for many decades, why is the mercury band observed from absorption spectrum so broad and why are there two peaks?

Our goals of this research are to study the spectra of mercury solutions to obtain the correct interpretation and also to observe a possibility of the presence of dimer molecules in solution.

The research described in this thesis is composed of the spectroscopic measurements of mercury solution. In particular, we will explore the fluorescence measurement since this has not been reported before.

CHAPTER 2

EXPERIMENTS AND RESULTS

This thesis reports experiments on absorption and fluorescence
of mercury in solution, and solubility of mercury by means of cold
vapor atomic absorption method.

Materials

Spectrophotometric grade pentane and hexane were obtained from
Aldrich Chemical Co. and were used without further purification.
Reagent grade pentane and hexane were obtained from EM Science. The
solutions made with these solvents produced black deposit on the
mercury surface. In order to avoid this blackening the solvents were
purified by washing them with concentrated sulfuric acid, distilling
and drying over potassium hydroxide pellets. This treatment was found
to be adequate to remove the impurities causing blackening of mercury
surface.

3-Methylpentane obtained from Phillips Petroleum Company was
described as a pure grade (99 Mol%). This solvent was also found to
blacken the mercury surface but the treatment mentioned above was found
to give satisfactory results.

Ethanol was obtained from the store room in Chemistry Department of the University of Arizona and was of 95 % purity. This solvent was used without further purification.

Methanol was a reagent grade solvent from EM Science and was used without further purification.

Triple distilled reagent grade mercury from Curtin Matheson Scientific Inc. was used without further purification.

The solutions were equilibrated by shaking each solvent with a drop of metallic mercury in a constant temperature water bath at 23°C controlled to within ± 0.5 C. It was found that the mercury concentration was constant after two days of shaking and remained constant over a period of several days.

Preparation of standard solution for atomic absorption: Mercuric chloride solution in dilute nitric acid (1000 ± 5 ppm) from Ricca Chemical Co. was used to prepare the standard solution. 1 ml of this solution was diluted to 100 ml with doubly distilled and deionized (DDI) water.

Methods

Absorption Measurements

The spectra of the mercury solution were taken with a Cary 219 Spectrophotometer, using two Beckman quartz cells of 5 cm path lengths. Dilutions of saturated solutions of mercury by factor of two, five, and ten were made and absorption spectra of these solutions as well as the saturated solutions were taken.

Fluorescence Measurements

Fluorescence measurements were made with a Perkin Elmer Fluorescence Spectrophotometer 204-A. A UV 30 optical glass filter was used to eliminate scattered light below 300 nm. Action spectra as well as emission spectra were obtained for each solution.

Cold Vapor Atomic Absorption

The measurements of the solubility of mercury in each solution were made with an Instrumentation Laboratory aa/ae Spectrophotometer. Two ml of each solution was analyzed by cold vapor atomic absorption method by passing nitrogen through the solution at a flow rate of 1.3 lmin^{-1}. The total volume of each sample in the sample vessel was made up to 20 ml with DDI water. Mercury concentration was determined from the integrated signal height at 253.7 nm. A calibration curve was constructed by analyzing a series of standard solution from 1 ppm to 5 ppm of mercury in 100 ml of DDI water. Mercuric ions in the standard solution were reduced to atomic mercury by 4N hydrochloric acid and sodium borohydride, and then analyzed by the cold vapor atomic absorption method mentioned above.

The addition of hydrocarbons and alcohols up to 10% by volume did not affect the calibration curve. This is consistent with Fujii's(1976) observations that these hydrocarbons have no effect on the analysis of mercury by cold vapor atomic absorption.

Results

Solubility

Solubility of mercury in various solvents has been studied for many decades by many researchers using several different methods. As Table 1 shows, there has been inconsistency in the results obtained by different methods and also by different groups. Solubility measurements, in our work, were carried out to verify already known values obtained by Okouchi and Sasaki(1981) and by Vogel(1974) who employed the cold vapor atomic absorption method.

Results obtained from our work are shown in Table 2.

Absorption

Figures 1 through 6 show the absorption spectra of the mercury solutions. All the spectra exibihit a broad band with twin peaks. Table 1 lists the wavelengths of the absorption peaks.

The absorbance of hexane , pentane and 3-methylpentane solutions are approximately three times greater than those of ethanol and methanol solutions.

The shape of the absorption spectrum is found to be independent of temperature. The spectra of diluted solutions showed a linear proportionality between concentration and absorbance.

Fluorescence

Figure 7 illustrates the fluorescence of mercury in a methanol solvent. Only the methanol solutions showed significant fluorescence.

Table 2: Solubilities of mercury in different solvents[a]

Solvents	Solubility in (μmoles/ℓ)				
	1	2	3	4	Avg.
Methanol	2.7	2.5	3.0	2.7	2.7
Ethanol	2.6	2.7	2.2	3.1	2.7
Pentane	4.0	4.1	4.1	-	4.1
Hexane	5.2	5.6	5.0	5.2	5.3
3-methyl- pentane	5.4	5.5	5.3	-	5.4

[a]These solubilities were obtained by cold-vapor atomic absorption method.

Figure 1. Absorption spectra of saturated solution of mercury in methanol and dilutions by factor of two, five and ten.

Figure 2. Absorption spectra of saturated solution of mercury in ethanol and dilutions by factor of two, five and ten.
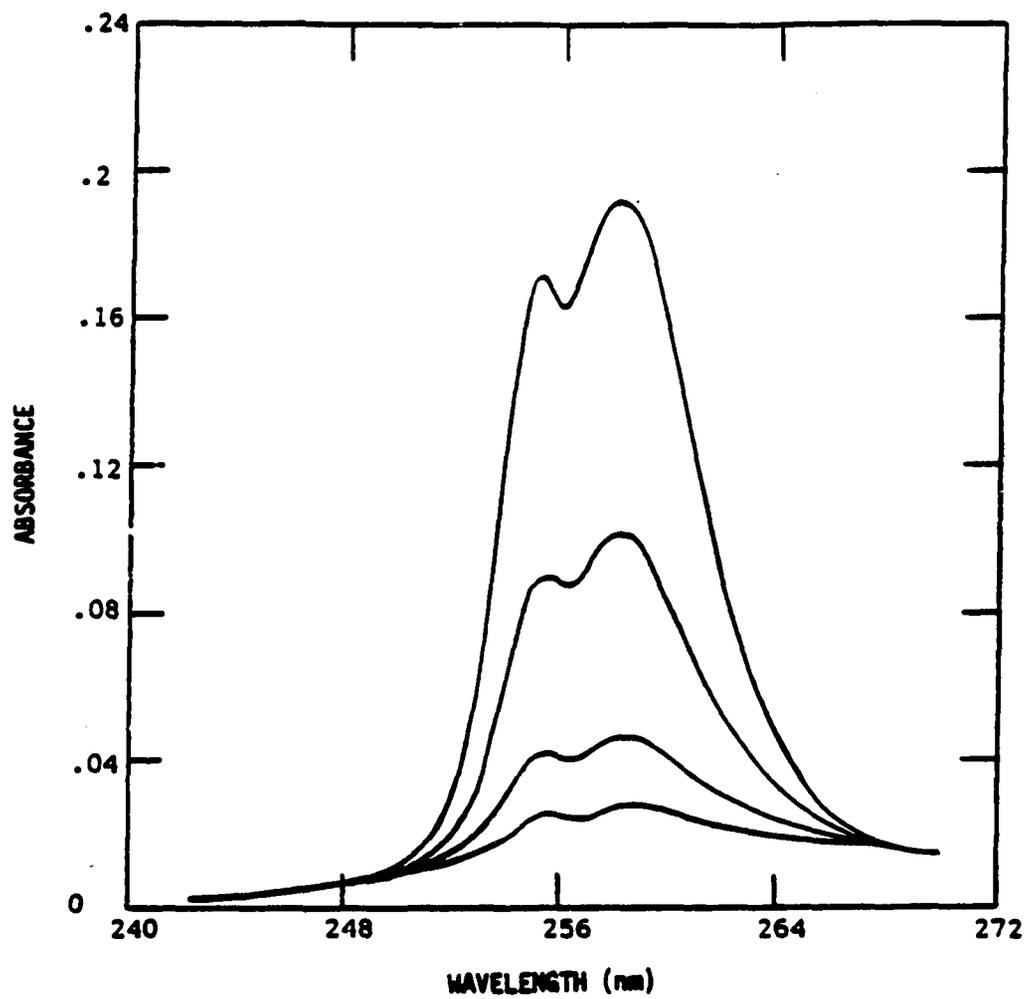
Figure 3. Absorption spectra of saturated solution of mercury in
pentane and dilutions by factor of two, five and ten.
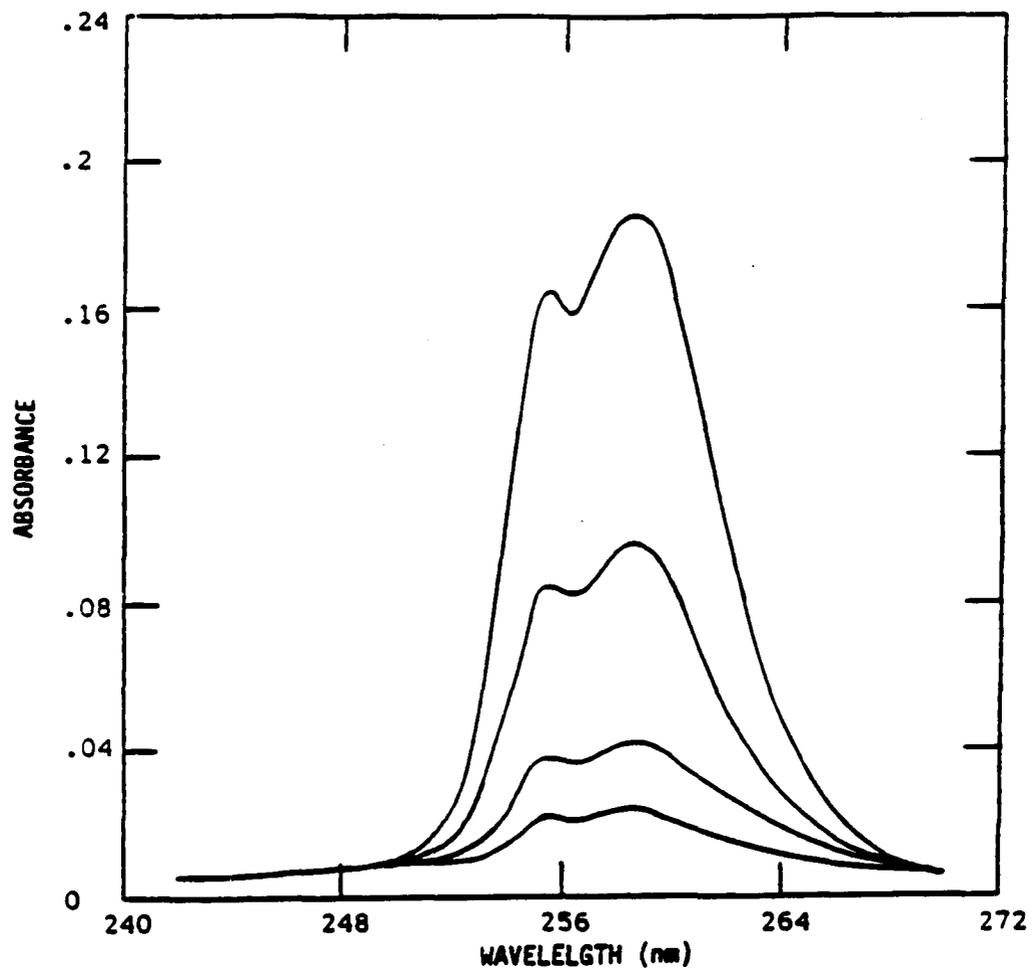
Figure 4. Absorption spectra of saturated solution of mercury in hexane and dilutions of factor two, five and ten.
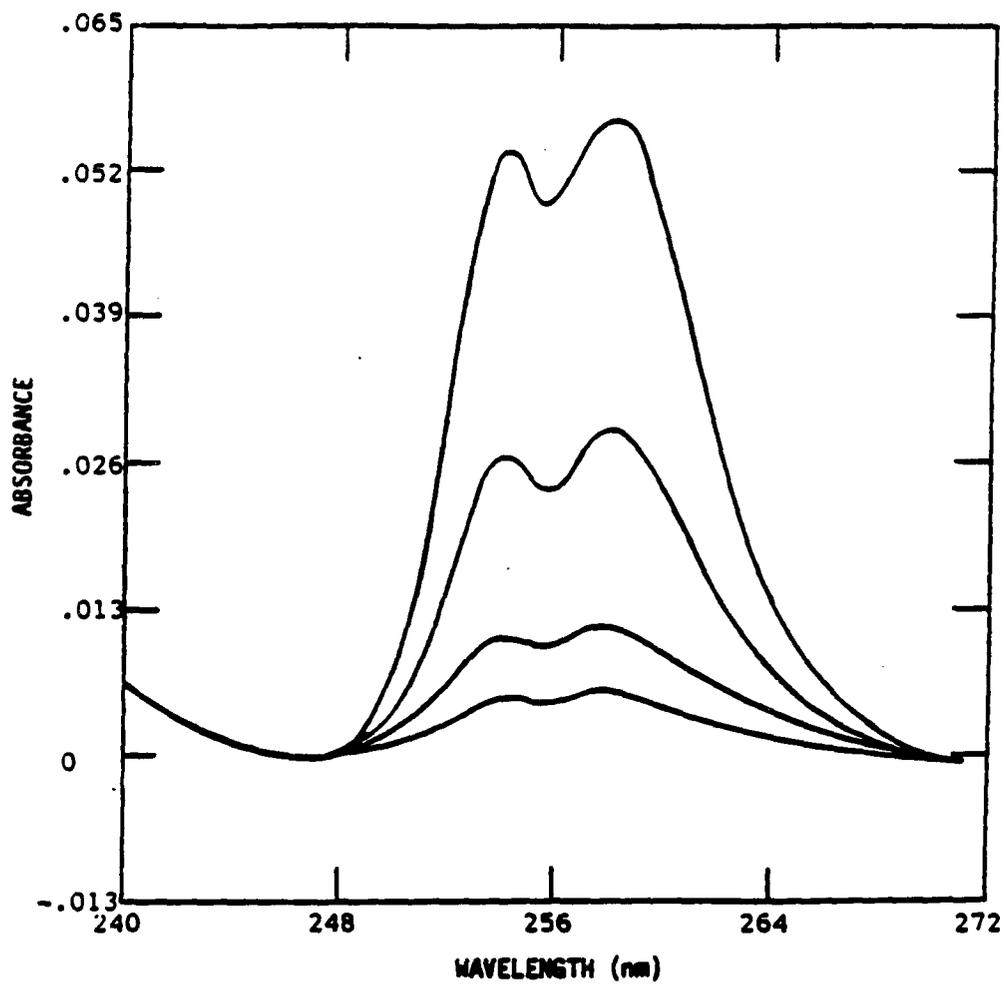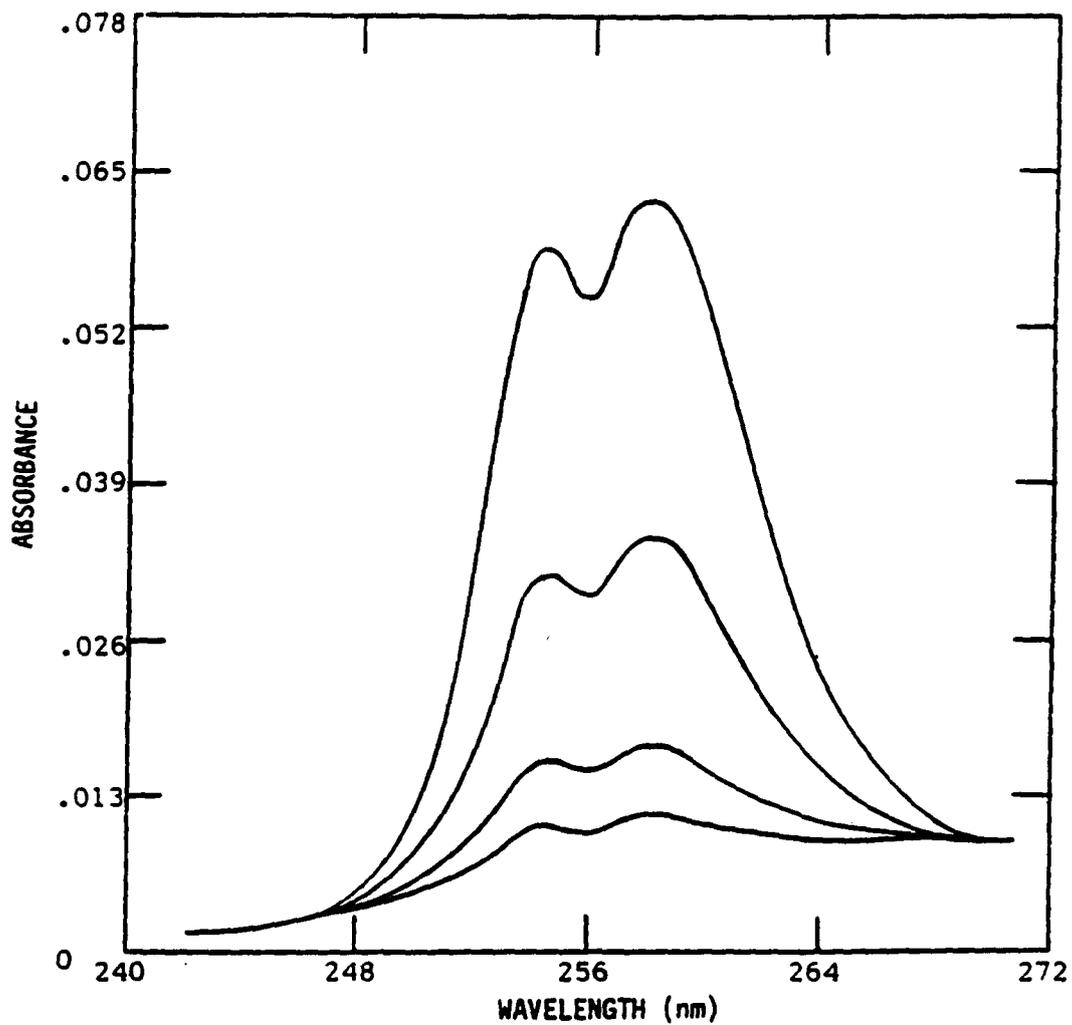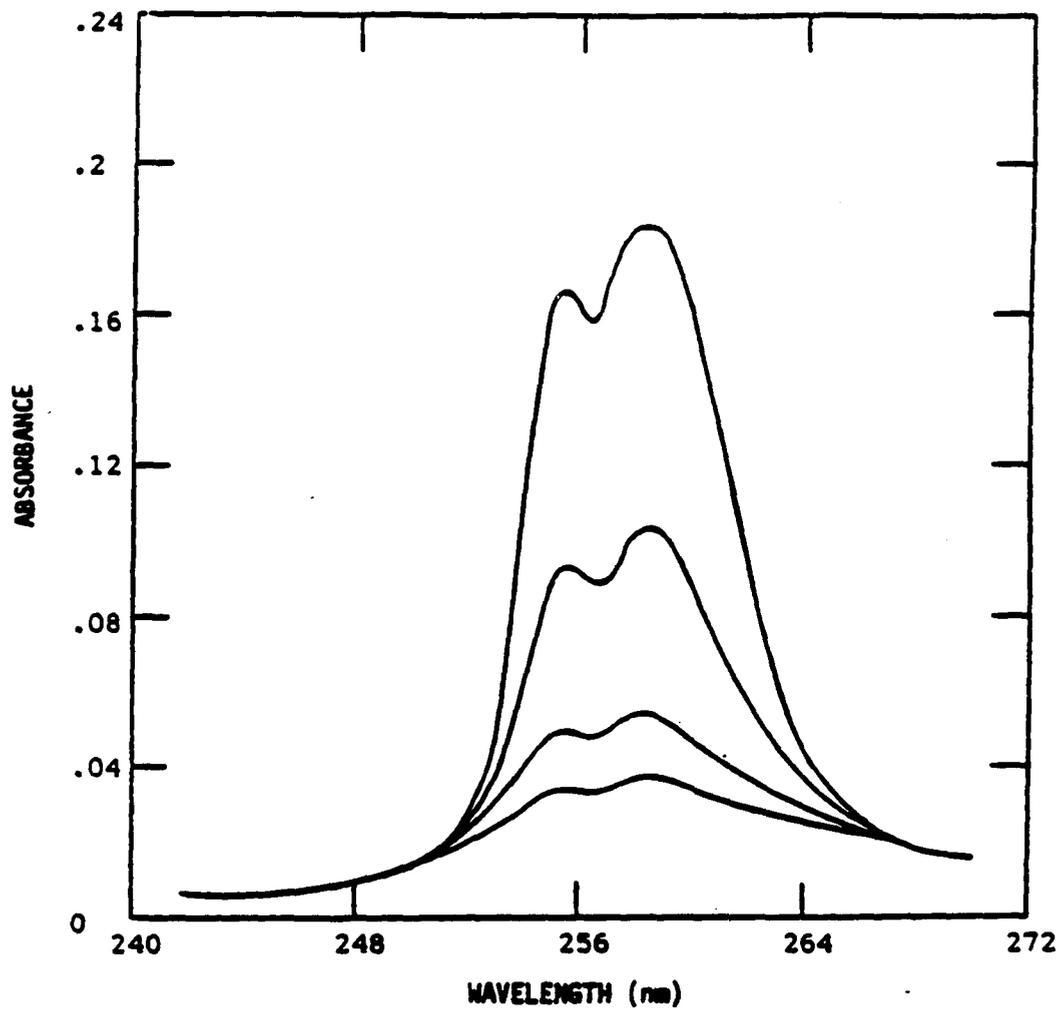
Figure 5. Absorption spectra of saturated solution of mercury in
3-methylpentane and dilutions by factor of two, five and ten.
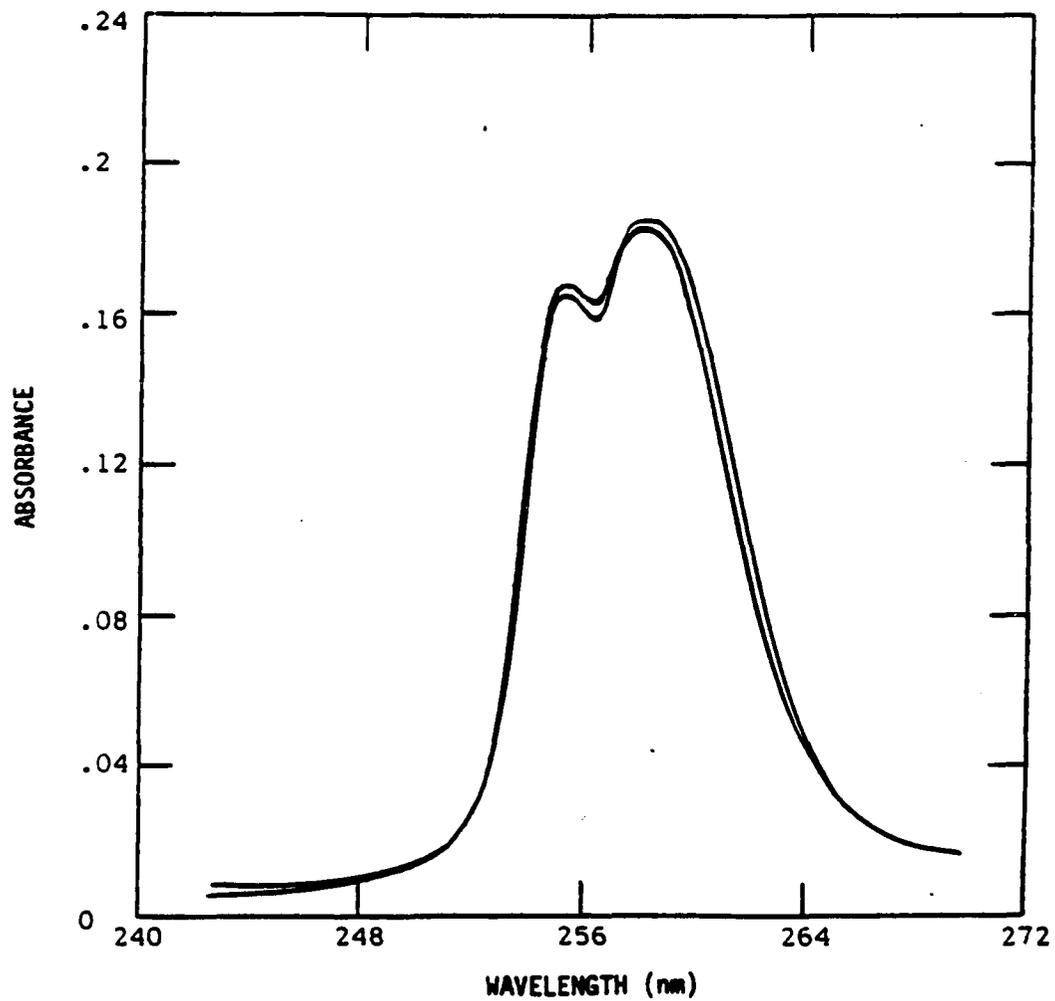
Figure 6. Absorption spectra of saturated solution of mercury in
3-methylpentane at 30, 40 and 50°C.
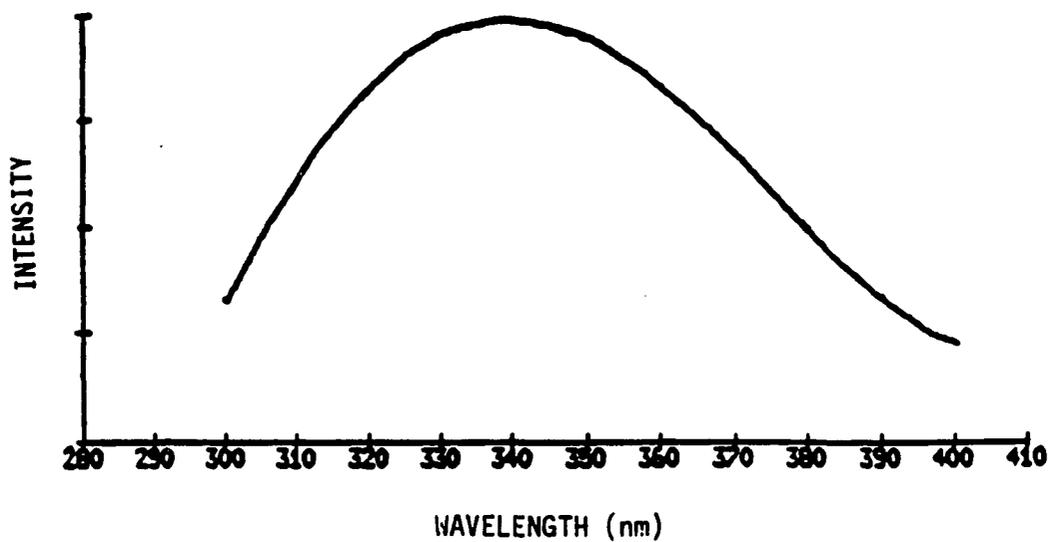
Figure 7. Fluorescence of saturated solution of mercury in methanol.
Excitation wavelength: 254 nm

Mercury in other solvents showed no fluorescence through the wavelength

range of 300 nm to 500 nm. Mercury dissolved in methanol showed a

broad band with a peak at 337 nm. The methanol solvent, with the UV 30

filter placed before emission monochromator, showed no significant

fluorescence. A small fluorescence signal was observed from the empty

cell over the wavelength range. It was subtracted from the larger

fluorescence signal of the mercury solution.

Figure 8 illustrates the action spectrum of mercury in

methanol. The action spectrum was taken by setting the emission

wavelength at 337 nm and scanning the excitation wavelength from 230 to

290 nm. As shown in Figures 1 and 8, the action spectrum matches the

absorption spectrum quite well.
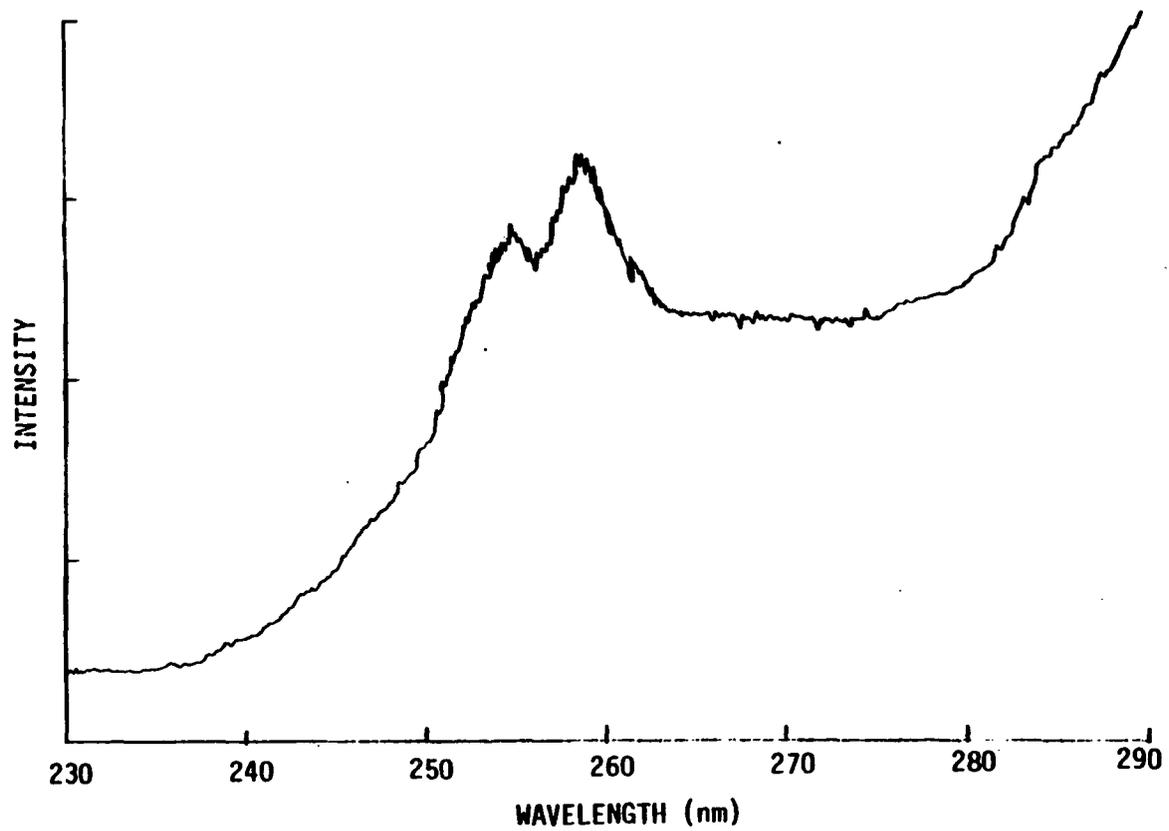
Figure 8. Action spectrum of saturated solution of mercury in methanol.
Emission wavelength: 337 nm

CHAPTER 3

EVIDENCE FOR DIMERIZATION

The solubility of mercury in organic solvents and water is in
the micromolar range so that one would expect the mercury to be
monatomic. Indeed elemental mercury in solution has been assumed to be
monatomic species as was described earlier.

From the experimental results, however, we are convinced that
the elemental mercury in solution exists predominantly as diatomic
molecules rather than as monomers.

Figure 7 shows the florescence of mercury in methanol. The
emission spectrum of mercury in solution has not been reported before.
However, the emission of mercury in the vapor phase has been known for
many years. This subject has been investigated to a great extent by
the researchers who were interested in the laser spectroscopy and
photochemistry of excited states. Broad band molecular fluorescence
from optically excited mercury vapor was studied in the early 1900's by
Wood and co-workers (1961) and by Lord Rayleigh(1927,1932) who excited
the mercury vapor using the 253.7 nm $6^1S_0 - 6^3P_1$ mercury resonance
line. Mrozowski (1930) first assigned the 335 nm band to a $Hg_2(1_u)$
state which correlates with $Hg(6^3P_1)$. A great amount of work has been
done since then to study the emission band at 335 nm. In the recent

years, the fluorescence of laser excitation and flash photolysis

techniques were applied for further studies of the 335 nm emission band

and the dimer molecules of mercury. Figure 9 shows the emission band

at 335 nm observed by Drullinger, Hessel and Smith(1977). This was

assigned to dimer molecules of mercury in the vapor phase. The

fluorescence of the mercury solution matches the fluorescence shown in

Figure 9. The emisson peak is at 335 nm in the vapor phase and is

observed to be at 337 nm in the solution. As mentioned in the results,

the solvent has no measurable fluorescence in this region. The small

fluorescence signal observed from the empty cell was subtracted from

the fluorescence of mercury solution to obtain the true fluorescence

signal of mercury. The absorption spectra of the solution before and

after fluorescence measurements are identical; this eliminates the

possibility that the observed emission is due to photogenerated

species. Furthermore, the action spectrum shown in Figure 8 matches

the absorption spectrum (Figure 1) very well. This confirms that the

emission peak is due to the same species that was observed from the

absorption spectrum (Willard et al. 1981). Therefore, we assign the

fluorescence signal in Figure 7 to Hg_2 species in solution.

Besides methanol, we tried ethanol, pentane and hexane solvents for

fluorescence measurements. However, the mercury solutions prepared

with these solvents showed fluorescence signals that were about the

same magnitude as the signals observed from the solvent and the cell

alone. The fluorescence of methanol solution shown in Figure 7 was
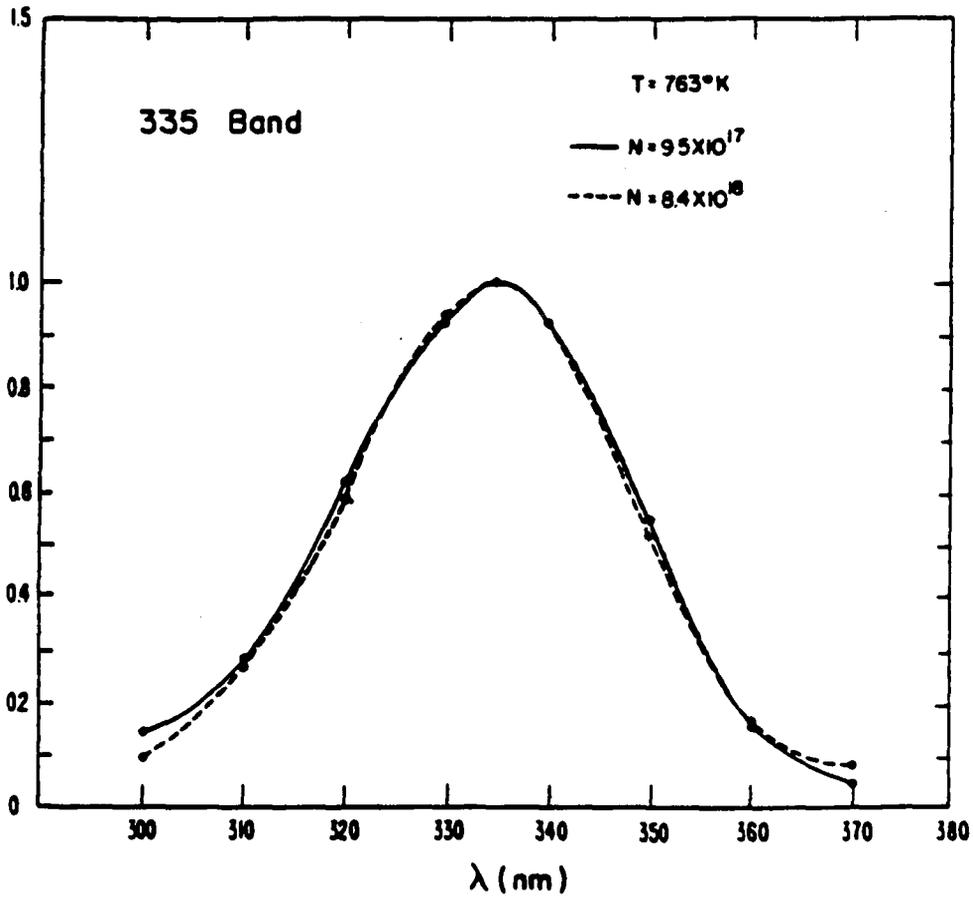
Figure 9. Fluorescence of dimer molecules of mercury vapor measured by
Drullinger, Hessel and Smith (1977).

taken with the maximum sensitivity of the instrument since the solution was very dilute. The fluorescence intensities of mercury in solvents other than methanol are below the detection limits of the instrument available to us.

Figures 1 through 6 illustrate the absorption spectra of elemental mercury in solution. The twin peaks shown in the figures were noted in the earlier work and assigned to monatomic mercury. However, no satisfactory explanation was given for this unusal structure of the spectra. Reichardt and Bonhoeffer(1930) explained the splitting by Stark effect. According to this theory, in a homogeneous constant electric field the peak at 253.7 nm is split into sigma and pi components and the splitting should increase with increase in electric field strength of the solvent molecules, since the stark effect is proportional to the square of the electric field strength. However, as shown in Table 3, the splitting is relatively insensitive to the nature of the solvents. Also, later studies have failed to prove the existence of electric quadrupole moments for atoms. Hence the splitting cannot be attributed to Stark effect.

The splitting observed between two peaks is approximately 3 nm apart which is much too small to be assigned to the three ^3P terms of atomic mercury. The wavelenghs of triplet terms are 265.64($^1S \rightarrow {}^3P_0$), 253.73($^1S \rightarrow {}^3P_1$) and 227.05 nm($^1S \rightarrow {}^3P_2$). These separations are much larger than the 3 nm splitting observed in mercury solution spectra. Therefore, we assign the two absorption peaks in the 250 nm region to

Table 3: Absorption Peaks of Mercury in Different Solvents

Solvents	wavelengths(nm)	
	$^1\Sigma_g^+ \rightarrow {}^1\Pi_u$	$^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$
Methanol	254	258
Ethanol	254	258
Pentane	255	258
Hexane	255	258
3-methylpentane	254	257

Hg_2 species. This assignment is also consistent with the vapor phase experiments and the results of theoretical studies.

Mies, Stevens and Krauss(1978) attempted the model calculation of Hg_2 based on ab initio calculation of Mg_2. As shown in Table 4, from the ground $^1\Sigma_g^+(0_g^+)$ state there are spin-orbit induced electric dipole transitions possible with three triplet states, the $^3\Sigma_u^+(1_u)$, $^3\Sigma_u^+(0_u)$ and $^3\Pi_u(1_u)$, which correlates with the $^3P_1 + {}^1S$, $^3P_1 + {}^1S$, $^3P_2 + {}^1S$ asymptotes respectively. The $^3\Sigma_u(1_u)$ state which correlates with $^1S + {}^3P_2$, however, has no transition probability asymptotically. Thus as illustrated in Figure 10, the transition between only the $^3\Sigma_u^+(1_u)$ and $^3\Pi_u(0_u^+)$ states and the ground state are allowed and transition peaks are observed at 257.2 nm and 254 nm respectively, in the vapor phase (Drullinger et al. 1977, Smith et al. 1977, mies at al. 1978). The two peaks in the solution spectra represented in Table 3 match these values very well: hence we assign the long wavelength peak to the $^1\Sigma_g^+(0_g^+) \rightarrow$ $^3\Sigma_u^+(1_u)$ transition and the short wavelength peak to the $^1\Sigma_g^+(0_g^+) \rightarrow$ $^3\Pi_u(0_u^+)$ transition. The potential curve for the ground state $^1\Sigma_g^+(0_g^+)$ and $^3\Pi_u(0_u^+)$ state are shallow and very similar in curvature. Hence the transition between these two states is expected to be a narrow band which is in agreement with the absorption spectra. The potential curves for the ground state and $^3\Sigma_u^+(1_u)$ state, on the other hand, are quite different in shape with $^3\Sigma_u^+(1_u)$ state has a deep potential well, thus leading to a rather broad band which agrees well with the peak in the 257 nm region.

Table 4: Catalogue of Electric dipole transitions involving the ground and excimer states.[a]

States	Asymptote
$0_g^+(X^1\Sigma_g^+)$	$^1S+^1S$

States	Asymptote
$1_u(^3\Sigma_u^+); 0_u^+(^3\Pi_u)$	$^3P_1+^1S$
$1_u(^3\Pi_u)$	$^3P_2+^1S$
$0_u^+(^1\Sigma_u^+); 1_u(^1\Pi_u)$	$^1P_1+^1S$
$0_u^+, 1_u(^3\Pi_u); 1_u(^1\Pi_u)$	Ion-Pair
$0_u^+(^1\Sigma_u^+); 1_u(^3\Sigma_u^+)$	$1,3S^*+^1S$

0_g^-	0_g^+	1_g	$2_g(^3\Pi_g)$	Asymptote $^3P+^1S$
$0_u^-(^3\Sigma_u^+)$				$^3P_0+^1S$
	$1_u(^3\Sigma_u^+)$	$0_u^+(^3\Pi_u)1_u(^3\Sigma_u^+)$		$^3P_1+^1S$
0_u^-	1_u		$1_u,2_u(^3\Pi_u)$	$^3P_2+^1S$
	$1_u(^1\Pi_u)$	$c_u^+(^1\Sigma_u^+)$	$1_u(^1\Pi_u)$	$^1P_1+^1S$
0_u^-	1_u	0_u^+	$1_u,2_u(^3\Pi_u)$	Ion-Pair
	1_u		$1_u(^1\Pi_u)$	Ion-Pair
0_u^-	1_u		$1_u(^3\Sigma_u^+)$	$3S^*+^1S$
		$0_u^+(^1\Sigma_u^+)$		

0_u^-	1_u $(^3\Sigma_u^+)$		Asymptote $^3P+^1S$
$0_g^-(^3\Pi_g)$			$^3P_0+^1S$
	1_g	$0_g^+(^3\Pi_g)$	$^3P_1+^1S$
0_g^-	$1_g(^3\Sigma_g^+)$	$2_g(^3\Pi_g)$	$^3P_2+^1S$
	$1_g(^1\Pi_g)$	$0_g^+(^1\Sigma_g^+)$	$^1P_1+^1S$
	1_g	$0_g^+(^3\Sigma_g^-),2_g(^1\Delta_g)$	$^3P+^3P$

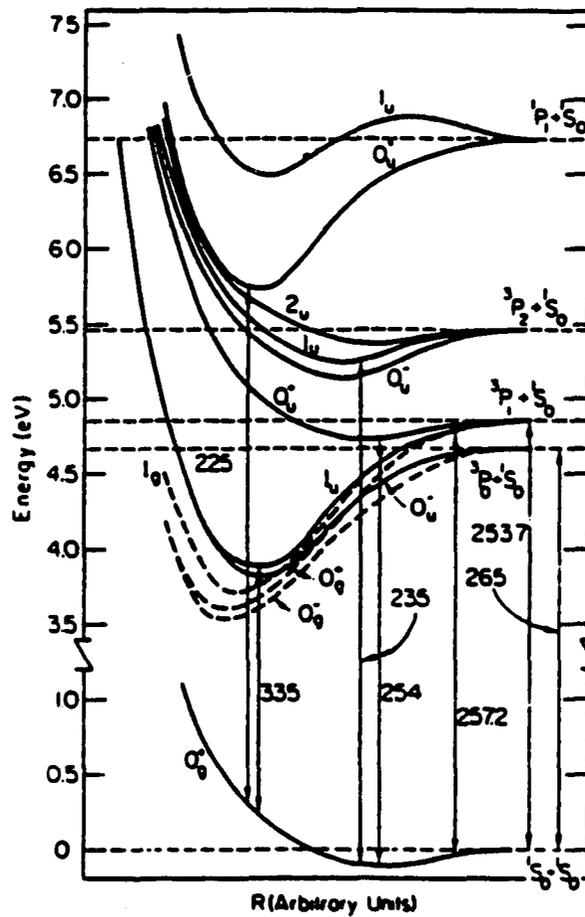[a]This table is obtained from Mies, Stevens and Krauss' publication(1978)

Figure 10. Qualitative potential energy diagram of several excited
states in Hg₂. This figure is based on the Mg₂ calculations
as well as various absorption, fluorescence and two photon
induced spectra. (Drullinger, Hessel and Smith 1977)

The molecular bands are very weak in the vapor phase compared to the atomic lines: the transition $^1\Sigma_g^+(0_g^+) \rightarrow {}^3\Pi_u(0_u^+)$ is observed as a wing on the much more intense atomic transition $^1S_0 \rightarrow {}^1P_1$ line as Rosen(1970) reported. This difference in intensity indicates the difference in probability: the atomic transition has much greater probability than the molecular transition. This observation is consistent with Hilpert's(1982) mass spectral results which show that the equilibrium constant(K) for $2Hg(v)=Hg_2(v)$ is 2.15×10^{-6} at 330K. In contrast to this result, the solution spectra indicate that the concentration of Hg atoms is insignificant compared to Hg_2 species. Due to the low solubility of mercury, uncertainties in the solubility data and insignificant atomic concentration in solution, we were not able to determine K, the equilibrium constant, for $2Hg(soln) = Hg_2$ (soln). Nevertheless, an order of magnitude estimate of K can be made from our data. Dilutions of saturated solutions of mercury by factors of two, five and ten show that Beer's law is obeyed at all wavelengths of the spectra. This is consistent with a previous report by Vinogradov and Gunning(1964).

When the dimers are in equilibrium with monomers, Beer's law is usually not obeyed. However, the consideration given below shows that if the equilibrium constant is large enough such that $4KC_T > 1$, where C_T is the total concentration expressed as a monomeric unit (twice the dimer concentration + monomer concentration), absorbance varies linearly with C_T.

Let X = dimer concentration, C_T = total concentration (= 2X + monomer concentration), then

$$K = \frac{\text{dimer concentration}}{(\text{monomer concentration})^2} \tag{4}$$

$$= \frac{X}{(C_T - 2X)^2} = \frac{X}{C_T^2 - 4XC_T + 4X^2} \tag{5}$$

From this equation, we obtain

$$KC_T^2 - (4KC_T + 1)X + 4KX^2 = 0, \tag{6}$$

which rearranged, gives:

$$\frac{C_T^2}{4} - \left(\frac{4KC_T + 1}{4K}\right)X + X^2 = 0 \tag{7}$$

If $4KC_T + 1 = 4KC_T$, then

$$\left(\frac{C_T}{2}\right)^2 - C_TX + X^2 = \left(X - \frac{C_T}{2}\right)^2 = 0 \tag{8}$$

Therefore we get,

$$X = \frac{C_T}{2} \tag{9}$$

The absorbance of the solution is given by

$$A = \varepsilon_M C_M + \varepsilon_D C_D \tag{10}$$

where A = absorbance,

ε_M = absorptivity of monomers,

ε_D = absorptivity of dimers,

C_M = concentration of monomers,

and C_D = concentration of dimers.

Substituting $C_M = C_T - 2X$ and $C_D = X$

$$A = \varepsilon_M(C_T - 2X) + \varepsilon_D X. \tag{11}$$

When $X = C_T/2$, we obtain

$$A = \varepsilon_D X = \varepsilon_D \frac{C_T}{2} \tag{12}$$

Equation (11) shows a direct proportionality between absorbance and total concentration. Therefore, if $4KC_T > 1$, even with the presence of dimers in solution, a linear relation of A with C_T will be observed. Since the solubility of mercury in solution is in micromoar quantity (1 x 10^{-6}M), combining this with the above assumption we estimate that K should be greater than 10^7 at 298 K, which is much larger than the estimated vapor phase value.

The large difference in the vapor and solution K values points to the importance of entropy in determining the nature of molecular species in solution. Hilpert(1982) and Stefanov and co-workers(1982) reported the enthalpy of vaporization in the vapor phase to be -8.5 ± 0.8 KJ and -10.8 ± 0.6 KJ. The enthalpy in solution should be in the same range as that in the vapor phase since the wavelengths of the absorption peaks of both vapor and solution are identical and are not affected by the nature of the solvents. A preliminary study of temperature effects on solution spectra showed that the spectra are insensitive to temperature variations, indicating a small enthalpy of dimerization.

The familiar thermodynamics equations relating enthalpy, entropy and the equilibrium constant are

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

$$\Delta G = -RT\ln K \qquad (12)$$

Dividing (1) and (12) by RT, we get

$$\Delta S = \frac{\Delta H}{T} + R\ln K \qquad (13)$$

Assuming the enthalpy of dimerization (ΔH) is the average of the two values from vapor phase mentioned above (ΔH = 9.6 KJ) and K = 1 x 10 , ΔS can be determined from equation (13).

The values of ΔS thus calculated is +101.79 JK^{-1}. This large positive change in entropy indicates that the formation of dimer molecules is spontaneous and the dimer species is favored over the monomer species. The ΔS of dimerization is usually negative since dimers are more structured thereby being less favored than monomers in terms of entropy of bonding (i.e. dimerization is a non-spontaneous process). The large ΔS value in our case thus should be attributed to the changes in the solvent structure upon dimerization of mercury rather than the bonding in Hg_2. The solvent molecules around atomic mercury are likely to be in an ordered environment. When two solvated mercury atoms combine to form a diatomic molecule, some of the solvent molecules will be displaced from the ordered environment to a relatively disordered environment of bulk solvents. This process can be explained by the concept of hydrophobic bonding approached by Kauzmann(1959). Kauzmann defined hydrophobic bonding as a non-bonded

interaction which affects the conformational stability of proteins in aqueous solution. Since the solution of a non-polar group in water is accompanied by an unfavorable entropy change, Kauzmann considered that there would be a tendency for the non-polar groups of the protein to come in contact with one another in solution, thereby lessening their area of contact with water. This tendency of the non-polar groups to come together in aqueous solution and thus minimize energetically unfavorable interactions with the water is termed "hydrophobic bonding". The well known micelle formation could be considered also as an example of hydrophobic bonding for here the non-polar residues of solute molecules (or ions) aggregate to form a non-aqueous environment, while the polar groups remain on the cluster surface and in contact with water. The entropy of micelle formation at ambient temperature is reported to be in the vicinity of 140 $JK^{-1}mol^{-1}$ by Atkins (1970). Further, Franks(1973) reported that the tendency of solutes to aggregate into dimers, trimers, etc. in aqueous solution, as evidenced by the work of Kozak(1968) and Kauzmann(1959), would appear to be a reflection of the hydrophobic bonding.

A rough idea of the changes in the solvent configuration around Hg caused by dimerization can be obtained by compairing the entropies of fusion of organic solvents with the entropy of dimerization of Hg. The average value of fusion for organic molecules was reported by Karapetyants(1978) to be in the range of 50 $JK^{-1}mol^{-1}$. Thus the entropy of dimerization for mercury calculated above (101.79 JK^{-1}) is

what one would expect if two molecules were displaced, for each dimer of mercury formed, from an ordered environment into the liquid phase.

Entropy driven processes have been studied and provided the mechanism for hydrophobic and solvophobic interactions (Lauffer 1975). We believe that the dimerization of mercury in solution offers the simplest and clearest example of entropy driven processes in chemistry.

CHAPTER 4

FUTURE WORK

Mercury in solution should be investigated further than what
was reported in this thesis. The concentration range and temperature
range of the solution should be extended beyond the regions we studied.
The study of lower concentration range can offer a direct measure of
the equilibrium constant between monomers and dimers. By extending the
temperature range, a reliable value of the enthalpy can be obtained.

Our work shows that an entropy driven process may be studied
with the elements in solution. Further investigation of this process
with other elements will be useful. Possible elements for continuous
study are cesium and gallium. Since these elements are liquid at
slightly above room temperature, 28.40°C and 29.78°C respectively, they
are comparable with mercury. Cesium belongs to the alkali metal group
and its spectrums relatively simple. Hence the spectrum for cesium in
solution could provide a valuble means for the continued investigation
of solution properties.

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