# A STUDY OF THE 2700A ABSORPTION

# OF MOLECULAR IODINE

by

# KENNETH JOSE MINTZ

B. Sc. (Hon.), University of British Columbia, 1965

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

CHEMISTRY

We accept this thesis as conforming to the required standard

# THE UNIVERSITY OF BRITISH COLUMBIA

DECEMBER, 1967

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of hemestry

The University of British Columbia Vancouver 8, Canada

Der Date

### ABSTRACT

A weak absorption in iodine vapour was reported by earlier workers to not obey Beer's Law, and was attributed to the dimer  $I_A$ . The ultraviolet spectrum of iodine vapour was reinvestigated in this study on a more quantitative basis. The extinction coefficients have been found to be independent of concentration of iodine  $(10^{-5} \text{ to } 10^{-2} \text{ M})$ , pressure of an inert gas (up to 1 atm), and temperature (25 °C to 220 °C, except for the usual temperature broadening). The absorption continuum (maximum 2694± 3 A; oscillator strength  $4.98 \pm .05 \times 10^{-4}$ ) must be due to a transition in the free molecule to a repulsive state correlating with either  $P_{3/2} + P_{3/2}$ or  ${}^{2}P_{3/2} + {}^{2}P_{1/2}$  atoms. The identification of the upper state involved and of the mechanism allowing the transition to occur were not possible with the available evidence. The previous identification of  $I_4$  in solution and of  $Br_4$  in the vapour phase, determined by similar ultraviolet continua, are discussed in relation to the lack of evidence for  $\mathbf{I}_{A}$  in the vapour phase found in this study.

ii

# TABLE OF CONTENTS

	INTRODUCTION Electronic Absorption Spectrum of Iodine Vapour 2700A Continuum of Iodine Vapour Iodine in Solution Purpose of this Study	Page . 1 . 4 . 6 . 9
	EXPERIMENTAL Optical Cells Chemicals Spectroscopy Slit-width Corrections Measurement of Concentration	.10 .13 .14 .17 .20
	RESULTS Visible Spectrum	.23 .32
	DISCUSSION Interpretation of the 2700A Continuum Comparison with Solution Comparison with Bromine	,.44 ,.52 58
	BIBLIOGRAPHY	•• 62
·		

# TABLE OF FIGURES

	Page
1.	The Visible Absorption Spectrum of Iodine Vapour24
2.	Log Absorbance versus ( $\nu - \nu_{o}$ ) <sup>2</sup> for the Visible Absorption
3.	Absorbance versus Absorbance at 4400A for the Visible Spectrum
4.	The Ultraviolet Spectrum of Iodine Vapour
5,6	Absorbance in the Ultraviolet versus Concentration at 63°C
7,8	Absorbance in the Ultraviolet versus Concentration at 220 °C
9.	Apparent Extinction Coefficient versus Concentration40
10.	Construction of Potential Energy Curve
11.	Extinction Coefficient versus Concentration
12.	Difference between Ultraviolet Spectra Measured at Different Concentrations
13.	Potential Energy Diagram of Iodine

# ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to Dr. E. A. Ogryzlo for his patient and knowledgeable direction of this research.

The author would also like to express his appreciation to Dr. A. V. Bree and Dr. D. P. Chong for advice and assistance during Dr. Ogryzlo's Sabbatical Leave.

#### INTRODUCTION

The absorption spectrum of iodine in the gas phase and in solution has been extensively studied since the early days of spectroscopy. The low-energy electronic spectrum encompassing the near infrared and visible are, by now, well understood mainly due to the theoretical studies by Mulliken.<sup>1-3</sup> On the other hand, there is still disagreement regarding the interpretation of the ultraviolet spectrum. Contradictions are most apparent with respect to a weak absorption continuum with its maximum at about 2700A.

A brief survey of the electronic absorption spectrum of iodine vapour will be presented first for background information.

# Electronic Absorption Spectrum of Iodine Vapour.

(a) Near Infrared.

Brown<sup>4</sup> has observed and analyzed a very weak band system from 9300 to 8360A, leading to a continuum with its maximum at 7320A at 50 °C. According to Mathieson and Rees<sup>5</sup>, this continuum has its maximum extinction coefficient of 30 l mole<sup>-1</sup> cm<sup>-1</sup> at 6950A at 120 °C. This system has been assigned to the A  ${}^{3}\Pi$   $(l_{u}) \ll X {}^{1}\Sigma^{+}(0_{g}^{+})$  transition.  ${}^{3,4,5,}$ (b) Visible

This system, which gives iodine its characteristic violet colour, consists of discrete bands ranging from about 7500A to its convergence limit at 4990A, with the continuum extending down to about 4000A. The rotational structure has been resolved and partially analyzed by Steinfeld at al.<sup>6</sup>

Values of extinction coefficients given by early workers were in error, partly because of nearly 100% absorption at the maxima of the rotational lines at the low pressures used. This error was eliminated by later workers by using a high pressure of an inert gas to broaden the lines.<sup>7,8</sup> Rabinowitch and Wood<sup>7</sup> have presented extinction coefficients in the range 4400-6000A, finding a maximum extinction coefficient of 820 1 mole<sup>-1</sup> cm<sup>-1</sup> at about 5200A at 20°C.

There is no doubt that the band system is due entirely to the B  ${}^{3}\Pi(0_{u}^{+}) \ll X^{1}\Sigma^{+}(0_{g}^{+})$  transition. There is some question about a possible underlying

- 2 -

continuum, however. Mulliken<sup>3</sup> has estimated, from extrapolation of the chlorine and bromine absorption spectra, that the transition  ${}^{1}\Pi(1_{u}) \leftarrow X^{1}\Sigma_{g}^{+}(0_{g}^{+})$ would have a maximum near that of the B  $\leftarrow X$ transition and with an intensity of less than 1% of it. Transitions to other states in this region  $({}^{3}\Pi(0_{\bar{u}}, 2_{u},))$  are expected to be much more forbidden.<sup>3</sup>

(c) Ultraviolet

Various weak discrete bands have been reported from about 3500A to shorter wavelengths. These bands can be observed only below 2200A at temperatures below 200 °C., but with increasing temperature they spread toward longer wavelengths until at 1100 °C they converge to an apparent continuum at 3413A.<sup>9</sup> This "continuum" is actually a series of overlapping bands. No extinction coefficients have been reported for this system. These bands and the "continuum" must involve high vibrational levels of the ground state.

(d) Vacuum Ultraviolet

Iodine vapour shows strong banded absorption from 2000A to shorter wavelengths rising to a maximum at about 1850A. Cordes<sup>10</sup> measured a large number of bands in the

range 1950-1540A at low temperatures and pressures. These bands may be part of the same system as the weak ultraviolet bands discussed above as suggested by Cordes, <sup>10</sup> Mulliken,<sup>2</sup> and Nobs and Wieland.<sup>11</sup> However, Mathieson and Rees,<sup>5</sup> and Venkateswarlu<sup>12</sup> claim that it is a separate band system and analyze it on that basis.

# The 2700A Continuum of Iodine Vapour

Butkow and Wojchiechowska<sup>13</sup> apparently were the first to observe this absorption continuum and to note that it did not obey Beer's Law. Kortum and Friedheim<sup>14</sup> have measured the extinction coefficients for three different concentrations of iodine at 340 °C. They confirmed that the extinction coefficients increased with increasing concentration and postulated that the absorption was due to a transition involving the dimer  $I_4$ . They did not attempt to observe the spectrum at different temperatures to determine whether the  $I_4$ was actually a bound complex or not. The absorption maximum was reported as 2670A by both groups of workers.

Sumner<sup>15</sup> also observed the 2700A continuum but at

somewhat lower temperatures. He used saturated vapour and therefore was unable to change the concentration independently of the temperature. The absorbance at 2700A was then found to be proportional to between the first and second power of the concentration. (It should be noted that in his experiments higher concentration also corresponded to higher temperature.) Since the absorbances were measured at different temperatures, he assumed that the absorbance was actually proportional to the square of the concentration, and the deviation from the square dependency was due to the dissociation of I, at higher temperatures. This method yielded a bond energy for  $I_{4}$  of 6.2 Kcal/mole. However, Sumner also obtained evidence which seemed to contradict his hypothesis. After heating the iodine above its boiling point, the 2700A continuum did not change upon further heating up to the maximum temperature obtained (380 °C). No explanation of this last effect was given.

McConnell<sup>16</sup> has suggested that the 2700A continuum is due to a transition in a "selfintermolecular charge-transfer complex with the

- 5 -

formula I4." The existence of intermolecular charge-transfer complexes between iodine and various electron donors is well established in both gas phase<sup>17</sup> and in solution.<sup>18</sup> Unique absorption continua due to charge-transfer transitions are observed in the ultraviolet. A semi-empirical equation given by McConnell, Ham and Platt<sup>18</sup> predicts that the charge-transfer absorption of  $I_4$  should occur at about 2820A (assuming IA will follow the same rules as iodine donor complexes.) This prediction is actually for I<sub>4</sub> in solution; in the gas phase the absorption would be slightly further into the ultraviolet. The predicted value for the absorption maximum agrees reasonably well with the experimental results of Kortum and Friedheim.

On the other hand, Mathieson and Rees,<sup>5</sup> again on the basis of Kortum and Friedheim's semiquantitative work, claimed that the absorption arises from a very weak transition in the free molecule which is extremely sensitive to external perturbations.

Iodine in Solution.

Iodine, as is well known, forms violet solutions in some solvents and brown solutions in others. The brown colour is usually attributed to 1:1 complexes

- 6 -

of iodine with the solvents. The solvents that yield violet solutions (such as aliphatic hydrocarbons, carbon tetrachloride) are usually referred to as "inert" solvents, since the visible spectrum closely resembles that of gaseous iodine and presumably no complex is formed between the iodine and solvent molecules.

Doubt has been cast on this interpretation by Evans.<sup>19</sup> He found a definite difference between the ultraviolet spectrum of iodine dissolved in n-heptane and that in two fluorinated solvents: perfluoroheptane (PFH) and di-perfluorohexyl ether. Assuming that PFH was truly an inert solvent towards iodine, he was able to indicate the existence of an intermolecular charge-transfer transition below 2600A due to either a weak or collisional complex between iodine and n-heptane. Even if the visible spectrum of iodine in a particular solvent resembles closely that of gaseous iodine (i.e. a "violet" solvent), that solvent may still form charge-transfer complexes with iodine, and have a considerably different ultraviolet spectrum from that of gaseous iodine.

Evans<sup>19</sup> also found a low absorption maximum

at about 2800A for iodine dissolved in chloroform and a smaller maximum at 2850A for iodine in n-heptane. Both peaks did not obey Beer's Law and nearly vanished at high dilution. These were attributed to the  $I_4$  dimer.

Keefer and Allen<sup>20</sup> and deMaine<sup>21</sup> have independently proven the existence of the dimer  $I_4$  in carbon tetrachloride. deMaine, deMaine and McAlonie<sup>22</sup> have extended this work to include as solvents n-hexane, n-heptane, c-hexane, and chloroform. The results for iodine dissolved in carbon tetrachloride are in fairly good agreement between the two workers. Both decompose the apparent (observed) molar extinction coefficient, according to the equation:  $\varepsilon_{\rm app} = \varepsilon_2(I_2) + \varepsilon_4 \kappa (I_2)^2$ 

where:  $\epsilon_2$  is the extinction coefficient of  $I_2$  $\epsilon_4$  is the extinction coefficient of  $I_4$ K is the equilibrium constant  $I_4$ 

The extinction coefficients of  $I_2$  and  $I_4$  have maxima close together:

 $(I_2)^2$ 

Keefer and Allen<sup>20</sup>:  $\epsilon_2$  at 2800A,  $\epsilon_4$  at 2880A; deMaine<sup>21</sup>:  $\epsilon_2$  at 2775A,  $\epsilon_4$  at 2925A.

8 -

The decrease in  $K \in_4$  with increasing temperature was interpreted as evidence for a bound species  $(I_4)$  as opposed to a colliding pair of molecules. The heat of dissociation of  $I_4$  was calculated to be 1 - 2 Kcal/mole, depending on the solvent.

## Purpose of this Study

The extinction coefficients in the ultraviolet region of iodine vapour are to be determined accurately as a function of concentration and temperature. This should clarify the nature of the transition at 2700A. It should then be possible to correlate the vapour phase spectrum with the solution spectra with some degree of certainty. It is also of some interest to determine whether  $I_4$  exists in the gas phase as well as in various solvents.

#### EXPERIMENTAL,

## Optical Cells.

The 2700A continuum, as mentioned above, is very weak. In order to be able to work at low temperatures where iodine has a low vapour pressure, and still have sufficient absorbance to obtain accurate results, a three meter path length cell was constructed.

The exact path length was 298.5 cm. The major part of the cell consisted of a pyrex tube joined through a graded seal on each end to a short length of fused silica tubing. This was blown onto a 5 cm. fused silica spectroscopic cell, which was then sealed under vacuum. This achieved two purposes. First, the cell could be heated beyond the inner optical windows in order to maintain the entire cell at a constant temperature. Secondly, the double windows prevented convection cooling of the inner windows. Therefore, iodine could not condense on these windows, thus interfering with absorption measurements.

An earlier cell used fused silica windows cemented onto a pyrex tube. However, the cement appeared to fluoresce when ultraviolet light was shone on it; also the cement discoloured upon heating the cell containing iodine. Therefore, results obtained using this cell could not be used.

An inlet about midway in the cell consisted of a Fischer-Porter teflon needle valve. Although the stem turned pink from absorbing iodine vapour, it did not leak appreciably during a series of measurements (lasting up to a few days). No chemical reaction occurred between the teflon and iodine as was shown by reproducible results on heating and cooling the cell.

Tygon tubing was used to connect the needle valve with a small vacuum system. Flexible tubing was used for this connection to make the alignment with the spectrophotometer easier, and also to isolate the cell from the vacuum pump vibrations. Iodine discoloured the tygon tubing rather quickly. Therefore, it was necessary to be certain that the cell was not contaminated by any impurity. Iodine was always introduced directly into the cell, never through the tygon tubing. The concentration of iodine in the cell was changed by pumping out some of it. When inert gases were added to the cell, new tubing was used. Therefore, the iodine whose absorption was being studied at any time

- 11 -

had never been in contact with the tygon tubing, and the possibility of contamination of the sample was eliminated.

The cell was painted black to eliminate reflections and thus prevent an error in effective optical path length. Aluminum foil was wrapped around the cell to prevent temperature variations along the cell. A layer of asbestos paper, nichrome wire for heating the cell, and more layers of asbestos for insulation were then wrapped around the cell. A voltage from a variable transformer was applied through the nichrome wire (120 volt model for temperatures up to 65 °C, 240 volt model for temperatures up to 160 °C).

The temperature of the cell was measured at various places using copper-constantin thermocouples cemented onto the glass tubing. At lower temperatures (below 50°C), all the thermocouples yielded the same temperature within about 1 °C. On the other hand, at higher temperatures there was a temperature drop along the cell with the ends up to a few degrees warmer than the middle. Temperatures for the high temperature measurements are given as those measured half-way between the middle and ends. In all cases, the cell could be maintained at constant conditions for as long as necessary (about two hours).

For higher temperature and concentration measurements, a shorter path length cell had to be used because the absorbance in the 2700A region was too high to measure in the three meter cell. Originally constructed for other purposes, this 11.8 cm. cell was designed to fit into the Cary 14 spectrophotometer cell compartment. The cell, made entirely of fused silica, had a double jacket, the outer one being a vacuum. The cell was wrapped and heated in the same way as the three meter cell described above. In this case, however, iodine was sealed in the cell under vacuum. A small sidearm was left unwrapped and the concentration could be varied at constant temperature by varying the temperature of the sidearm by varying the amount of insulation on this sidearm.

#### Chemicals.

Mallinkrodt 1008 resublimed analytical reagent iodine was used in all experiments. The maximum limits of impurities specified by the supplier are: Cl and Br-0.005%, nonvolatile matter - 0.10%. Since all absorption measurements in this work were carried out on the gas phase, nonvolatile impurities are unimportant.

13 -

Therefore, no further purification other than degassing the solid was carried out. Commercial grade nitrogen, oxygen and carbon dioxide were used without purification.

### Spectroscopy.

Since the long path length cell obviously could not fit into the cell compartment of any automatic doublebeam spectrophotometer, a single-beam instrument had to be used. This was of course less convenient to use and involved more calculations.

A Beckmann DU spectrophotometer was used only as a monochromator. The cell compartment and the original electronics and photomultiplier tubes were removed from the instrument.

A holder for a RCA IP28 photomultiplier tube was constructed and attached to the monochromator against the exit slit. A Kepco regulated variable voltage DC power supply was used to apply a voltage to the photomultiplier tube. (900 volts gave optimum conditions). The current produced by the photomultiplier was measured by a Keithley micromicroammeter. Since the currents produced were small  $(10^{-6} \text{ to } 10^{-9} \text{ amp.})$ , it was necessary to use very short leads to eliminate stray currents.

The light sources used were a small tungsten lamp for the visible region of the spectrum, and the Beckmann hydrogen lamp (with its power supply) for the ultraviolet region. A constant voltage transformer was used to keep the light output from these lamps constant.

The monochromator was calibrated using a low pressure mercury lamp according to instructions given in the Beckmann DU instruction manual. The tolerance in wavelength ranges from 1A at 2000A to 6A at 6000A.

The intensity of light (as measured by the current produced by the photomultiplier tube) transmitted by the empty cell ( $I_0$ ) and by the cell containing iodine under varying conditions of temperature and concentration (I) must be measured separately. The absorbance at each wavelength was calculated by the equation:  $A = \log \frac{IO}{I}$ . Frequent remeasurements of  $I_0$  over the whole spectrum were made to eliminate the possibility of a change in the transmittance of the cell, emission intensity of the lamps or sensitivity of the photomultiplier tube.

The accuracy of absorbances varies considerably with wavelength, depending on three factors: emission of

- 15 -

the lamp used, photomultiplier response, and the dispersion of the monochromator. The tungsten lamp was used between 7000 and 3400A; the hydrogen lamp between 4000 and 2100A. This allowed some overlap in a region where iodine absorbs only very slightly.

The uncertainty in absorbances is about 0.008 at 0 absorbance in the wavelength region 7000-2200A. The uncertainty rises to about 0.02, at an absorbance of 2.5 in the wavelength range 6000-2500A, and at an absorbance of 1.0 at wavelength 2200A. Under conditions in which the absorbance is changing rapidly with wavelength (especially in the visible where the spectrum is compressed), there will be an increase of the uncertainty due to a slight uncertainty in the wavelength position.

As mentioned above, the Cary 14 double-beam recording spectrophotometer was used for the smaller cell operating at higher temperatures and pressures. This instrument yields absorbances directly, therefore reducing the number of calculations involved. It was only necessary to subtract off the absorbance due to the empty cell in order to obtain the iodine spectrum.

- 16 -

According to the manufacturer, the accuracy ranges from  $\stackrel{+}{-}$  .002 absorbance units at 0 absorbance to  $\stackrel{+}{-}$  .008 at 2.0 absorbance (the maximum that can be measured on this instrument). Errors in chart paper slippage and contractions will increase this error by about 0.005 absorbance units.

# Slit-Width Correction.

A slit width of 0.4 mm. was used for most of the measurements using the Beckmann spectrophotometer. This was the narrowest slit that could be used and still have sufficient light intensity on the photomultiplier tube to yield reasonably accurate results. Increasing the slit width gave considerably different absorbances in the visible (when high concentrations of iodine were used), but only slightly different absorbances in the ultraviolet. Since the visible absorption was used to measure the concentration of iodine in the cell, it was obviously of prime importance to know the true absorbances.

Errors due to using a finite slit width depend on the curvature of the light distribution curve across the slit rather than the slope. The equation for the true absorbance<sup>23</sup> is:

$$A(\lambda) = \log\left(\frac{\Phi_{o}(\lambda)}{\Phi(\lambda)}\right) = \log\left(\frac{F_{o}(\lambda) - \kappa \Delta^{2} F_{o}(\lambda) + L \Delta^{4} F_{o}(\lambda) + \dots}{F(\lambda) - \kappa \Delta^{2} F(\lambda) + L \Delta^{4} F(\lambda) + \dots}\right)$$

- 17 -

where: the subscript  $_0$  refers to no sample in the light beam.

 $\phi(\lambda)$  is the true light intensity at wavelength  $\lambda$ F( $\lambda$ ) is the observed light intensity at wavelength  $\lambda$ K and L are constants which depend on the relative values of the entrance and exit slit widths. When they are equal, as in the Beckmann spectrophotometer, K = 1/12, L = 1/90

 $\triangle^{2}F(\lambda) = F(\lambda + c) + F(\lambda - c) - 2F(\lambda)$ 

$$\Delta^{4} F(\lambda) = \Delta^{2} F(\lambda + c) + \Delta^{2} F(\lambda - c) - 2 \Delta^{2} F(\lambda)$$

c is the spectral band width (equal to one-half the spectral slit width) expressed in the same units as  $\lambda$ .

According to the Beckmann DU manual, the spectral band width for a mechanical slit width of 0.4 mm. varied from 200A at 7000A to 85A at 5000A and 4A at 2000A. These were the values used in the calculations.

Since measurements of light intensity were generally taken every 50A (for convenience), and since "c" varies with wavelength, it was not possible to measure F ( $\lambda$  +c) and F ( $\lambda$  -c) for each  $\lambda$ . Therefore F was approximated as a linear function of  $\lambda$  between two adjacent measurements (50A range) in the following manner:

$$\Delta^{2}F(\lambda) = \Delta^{2}F'(\lambda) + \operatorname{fract}(\frac{c}{50}) \left\{ \Delta^{2}F''(\lambda) - \Delta^{2}F'(\lambda) \right\}$$
  
$$\Delta^{2}F'(\lambda) = F(\lambda + 50 \operatorname{int}(\frac{c}{50})) + F(\lambda - 50 \operatorname{int}(\frac{c}{50})) - 2F(\lambda)$$
  
$$\Delta^{2}F''(\lambda) = F(\lambda + 50 \operatorname{int}(\frac{c}{50})) + 50) + F(\lambda + 50 \operatorname{int}(\frac{c}{50})) + 50) - 2F(\lambda)$$

where: int (c/50) means the integral part of that ratio fract (c/50) means the fractional part of that ratio. c and  $\lambda$  are measured in Angstroms,

A similar equation was derived for the  $\Delta^4$  F term. It was found that the  $\Delta^4$ F term was very small compared to the  $\Delta^2$ F term; therefore it was neglected.

The above equations were tested by measuring the same spectrum at three different (mechanical) slit widths: 0.4, 1.0, and 1.5 mm. The uncorrected absorbances were considerably different (for the visible absorption) for the different slit widths; the corrected absorbances agreed with each other within experimental error.

An alternate purely empirical method can be used to correct for slit-width errors. Absorbances can be extrapolated to zero slit width to obtain the true absorbance. This method would require that the light intensity be measured at each wavelength at a few slit widths, and would involve considerably more work. Therefore, the former method was used.

• 1<u>9</u> -

The Cary 14 spectrophotometer has considerably better resolution in the visible region than the Beckmann DU. The automatic slit control was set such that the spectral band width at 5000A was about 1/50 of that used with the Beckmann spectrophotometer. Since slit width errors depend on the square of the slit width, no corrections were necessary for measurements using the Cary spectrophotometer.

## Measurement of Concentration

The means chosen in this study to measure the concentration of iodine was spectroscopic. Since the visible absorption obeys Beer's Law between 5000 and 4000A,<sup>7,14</sup> the concentration, c, can be determined from this equation:

$$c = \frac{A}{EI}$$

where: A is the absorbance at any particular wavelength

£ is the molar extinction coefficient at that wavelength.

I is the optical path length.

Extinction coefficients for the visible absorption of iodine are available in the literature. 7,14,23 Since it is

- 20 -

necessary that the extinction coefficients are accurate and that the visible absorption does indeed obey Beer's Law rigorously, a reinvestigation of the visible spectrum was carried out.

Three alternate methods could be used to measure the concentration of iodine in the cell:

(1) Saturated iodine vapour could be used and the concentration determined from the known vapour pressure curve of iodine. This method would require very rigid temperature control, especially at higher temperatures.

(2) The pressure of iodine in the cell could be measured directly. To prevent condensation, the pressure measuring device would have to be at the temperature of the cell. Because of the corrosive nature of iodine and the necessity of measuring very low pressures, such a measuring device would present major design difficulties.

(3) Iodine could be sealed into a cell, completely vapourized, later analyzed chemically. This method would require a separate sample for each different concentration. Also there would be difficulties transferring the iodine from the cell without loss. It would be very difficult to measure low concentrations accurately.

- 21 -

The spectroscopic method was used in this study because it is easiest and can be used with about the same accuracy at all temperatures and concentrations. Also, there is the most important factor of observing directly the concentration of iodine vapour in the light beam. There are no complications with adsorption of iodine on the walls, etc.

However, spectroscopically only the relative values of extinction coefficients can be determined. Therefore, the literature value of the iodine vapour pressure had to be assumed at some temperature in order to find the actual extinction coefficients. Room temperature was used because then there could be no errors involved with temperature control. The values used for the vapour pressure were calculated from the equation given by Gillespie and Fraser.

It is possible to determine the concentration by measuring the absorbance at only one wavelength in the visible continuum. However, over a wide range of concentration, the absorbance at any particular wavelength will become too large or too small to be accurately measured. In addition, the use of a number of points will reduce the random error involved.

- 22 -

#### RESULTS

## Visible Spectrum

Curves (a) and (b) of Figure 1 show the absorption spectrum of iodine vapour without and with added inert gas (1 atm.). Saturated vapour was used: the extinction coefficients represent an average of three measurements taken at different times with the 3-meter cell at a temperature of 25-27 °C (corresponding to a concentration of about  $2 \times 10^{-5}$  M). During any one of these spectra, the cell could be held to within 0.2 °C, corresponding to a maximum error of 2% in the concentration of iodine. The temperature was measured not only with the thermocouples, but also with a mercury thermometer outside the cell (since the cell was being held at room temperature). The temperatures measured agreed with each other within 0,2 °C. The average deviation in extinction coefficients was less than 2% in the range 4300-6500A.

The difference between curves (a) and (b) in the region 6350-4950A is due to more collisional broadening of the rotational lines at the higher pressures. The "true" spectrum is the high pressure spectrum, <sup>7,8</sup> curve (b). No difference

- 23 -



was found (or expected) below 4950A or above 6350A. The absorption near 6500A is probably largely due to the A  ${}^{3}\Pi_{IU} \leftarrow \times {}^{I}\Sigma_{g}^{*}$  transition.<sup>5</sup> The shoulders noticeable at about 5500 and 5750A are almost certainly due to transitions from the vibrational levels 1 and 2, respectively, of the ground state.

Curve (c) in Figure 1 is the high-pressure spectrum obtained by Rabinowitch and Wood at 20°C. They also presented a spectrum of the pure iodine vapour (not shown here). The difference between the high and low pressure spectra was considerably smaller than was found here. This is probably due to the difference in cell lengths. (12 cm. as opposed to 298.5 cm). A much more serious problem is the considerable (20%) difference in extinction coefficients. Rabinowitch and Wood state that their error was 2%, and that they obtained good agreement using two different instruments. Their concentration was determined in a manner similar to that done here at room temperature. Iodine was introduced into the cell at 20°C from a container held at 19°C. The

the temperature of the container, using the vapour pressure

pressure was assumed to be that of the saturated vapour at

- 25 -

curve given by Baxter, Hickey and Holmes.<sup>26</sup> This curve is within about 2% of that of Gillespie and Fraser<sup>25</sup> in this temperature range.

Curve (d) in Figure 1 represents the extinction coefficients calculated from the equation given by Sulzer and Wieland (see below). This curve lies generally closer to that obtained here than that obtained by Rabinowitch and Wood, especially near the absorption maximum.

Harris and Willard<sup>27</sup> found a value of  $780^+$  40 l mole<sup>-1</sup> cm<sup>-1</sup> for the extinction coefficient at the absorption maximum at 5200A. This value is within experimental error of that of Rabinowitch and Wood, but not of ours.

The extinction coefficients of iodine vapour (usually Rabinowitch and Wood's values) have been used to measure the concentration of iodine,<sup>7,27</sup>to compare the spectra of the different halogen molecules,<sup>3</sup> and to discuss differences between iodine in the gas phase and in solution.<sup>28</sup> Some results and arguments would have to be revised somewhat if the extinction coefficients found here are correct.

The large discrepancies in extinction coefficients between this study and others were quite unexpected. Very careful measurements were made here. A large excess of solid

- 26 -

iodine was left in the cell for several days to come to equilibrium with the vapour, but no change in absorbance was observed after about two hours. There does not seem to be any source of error that could falsify our results by 20%. Therefore, the extinction coefficients obtained here will be assumed to be correct.

As mentioned above, Sulzer and Wieland have derived an equation for a continuous absorption spectrum of a diatomic molecule. Under simplifying assumptions (such as a gaussian curve of constant area for the absorption), the extinction coefficient at temperature T and frequency  $\bar{\nu}$  is given by the equation:

 $\mathcal{E}_{\mathsf{T}}(\bar{\nu}) = \mathcal{E}_{\mathsf{o}}^{\max}\left[\tanh\left(\frac{hc\omega_{\mathsf{o}}}{2\,\mathsf{k}\,\mathsf{I}}\right)\right]^{\frac{1}{2}} \exp\left\{-\left[\tanh\left(\frac{hc\omega_{\mathsf{o}}}{2\,\mathsf{k}\,\mathsf{T}}\right)\right]\left[\frac{\bar{\nu}-\bar{\nu}_{\mathsf{o}}}{\Delta\,\nu_{\mathsf{o}}^{*}}\right]^{2}\right\}$ 

where:  $\omega_{o}$  is the fundamental vibrational frequency.

 $\mathcal{E}_{o}^{\max}$  is the extinction coefficient at the maximum at  $O^{o}K$ 

 $\Delta\bar{\nu}_{s}^{\star}$  is the half-width of the absorption continuum at  $0\,^{o}\text{K}$ 

 $\bar{\nu}_{o}$  is the frequency of the maximum. According to this equation, it is necessary to measure the spectrum at

- 27 -

only one temperature to find all three parameters;  $\epsilon_{\mu}^{\max}$  ,  $\Delta \bar{\nu}_{\nu}^{*}$ 

, and  $\vec{\nu}_{o}$ . For iodine, Sulzer and Wieland found that the frequency of the maximum of the visible absorption was not independent of the temperature, but varied from 19,250 cm<sup>-1</sup> at 423°K to 18,750 cm<sup>-1</sup> at 1325°K. For the calculation above for Figure i (d), the absorption maximum was estimated by extrapolation to be at 19,500 cm<sup>-1</sup> (5130A) at 25°C.

An attempt was made to find new constants in the Sulzer-Wieland equation that would fit the experimental results closer. According to the equation, at any temperature the plot of log  $\notin$  versus ( $\bar{\nu} - \bar{\nu}$ , )<sup>2</sup> should yield a straight line of slope ( ${}_{\Delta}\nu_{\tau}^{*}$ )<sup>2</sup>. This plot is shown in Figure 2 for a spectrum of iodine at 65 °C (with 50 torr CO<sub>2</sub> added as an inert gas). The absorption maximum was found to be at 5115<sup>±</sup> 5A. It can be seen that the long wavelength side of the peak differs considerably from the short wavelength side. The experimental results obviously do not fall on a straight line. If lines are drawn approximately, as shown, "halfwidths" of 2050 and 2490 cm<sup>-1</sup>, respectively, are obtained in contrast to the 2060 cm<sup>-1</sup> calculated from the Sulzer-Wieland equation.

- 28 -

Obviously, the Sulzer-Wieland equation does not provide a good fit of the experimental data for the visible absorption of iodine. In contrast, Seery and Britton<sup>29</sup> were able to find a set of parameters that would adequately fit their experimental data on the visible absorption spectra of other halogens. The poor fit for iodine is at least partly due to the partial separation of absorption from the various vibrational levels, noticeable by the presence of shoulders in Figure 1(b).

Gibson and Bayliss<sup>29</sup> for chlorine, and Acton, Aicken, and Bayliss<sup>30</sup> for bromine, have separated the experimental absorption curve into contributions from the first two vibrational levels. This involves measuring the variation with temperature of the absorbance at each wavelength. However, iodine has its vibrational levels much closer together; even at room temperature, 12% of the molecules are not in the first two vibrational levels. This method would therefore involve such a long extrapolation as to make the results meaningless.

Since absorption continua change shape with temperature, it is not possible to calculate the concentration of iodine

- 29 -



(a) short wavelength side

(b) long wavelenght side
directly from the absorbance in the visible if the cell is not at the same temperature at which the extinction coefficients had been measured. The above attempts to fit the experimental absorption curve into an equation which is applicable at different temperatures were made so that a correction could be made for the variation in the absorption curve with temperature. Since the temperature range used in this study was not very large, it was possible to use a very crude method to estimate the necessary correction.

From the shoulders present on the long wavelength side of the peak, and the calculation of the relative population of the vibrational levels using the Boltzmann equation, the position of the first four vibrational maxima can be estimated to be 5100, 4700, 4400, 4200A, respectively. The Boltzmann distribution will then allow the calculation of the correction necessary to cancel out the effect of increasing temperature. Since at all temperatures the absorbance at a number of wavelengths was measured, the correction necessary was calculated at each wavelength. They yielded fairly consistent results.

It should be noted that the relative concentrations of iodine at any particular temperature are still accurate to

- 31 -

about 2%, but the absolute concentration may be in error by as much as 5% at the higher temperatures.

Figure 3 shows a plot of the absorbance at various wavelengths in the visible continuum versus the absorbance at 4400A at  $63^{\pm}$  2°C. Straight lines were obtained which show that the visible continuum is consistent with Beer's Law (as had been proven previously<sup>7,13</sup>). The maximum concentration used was that of the saturated vapour.

Absorption measurements in the visible at different concentrations were made at various other temperatures: 25°C, 160°C using the 3m. cell and the Beckmann DU Spectrophotometer and at 220°C using the 11 cm. cell and the Cary 14 spectrophotometer. In all cases, similar straight lines (with different slopes at different temperatures of course) were obtained when absorbances at various wavelengths were plotted against the absorbance at a particular wavelength.

#### 2700A Continuum

Figure 4 shows the ultraviolet spectrum of iodine vapour at various temperatures. The vertical axis is called the apparent molar extinction coefficient because these extinction

- 32 -



FIGURE 3: Absorbance versus Absorbance at 4400A for the Visible Spectrum.

coefficients have been reported to change with concentration.<sup>14</sup> At low temperatures, the 2700A continuum is virtually completely separated from any other peak. With increasing temperature, the main ultraviolet absorption spreads out to overlap the 2700A continuum.

The realative values of the extinction coefficients in curve (a) are accurate to about 0.5 1 mole<sup>-1</sup> cm<sup>-1</sup>; in each of curves (b), (c), (d) to about 0.2 1 mole<sup>-1</sup> cm<sup>-1</sup>. However, because of the uncertainty in concentration, the extinction coefficients in curves (c) and (d) may be all too high or all too low by an additional 5%.

The extinction coefficients near the maximum can be seen to decrease with increasing temperature. (The apparent increase at 220°C is probably due to overlap from the main ultraviolet peak.) This is no doubt due to the decrease in the percentage of molecules in the lowest vibrational level at higher temperatures. An increase in the tails of the continuum at higher temperatures can also be observed, but since this increase is spread over a larger range of wavelengths, it is not as noticeable. For the change in shape to

34 -



be due to temperature broadening, as we believe, the integrated absorption must remain constant. This is true within the error limits noted above.

The absorbance at various wavelengths in the ultraviolet was plotted against the concentration for measurements taken at  $63^+$  2°C. as shown in Figures 5 and 6. Quite good straight lines going through the origin were obtained. This seems to prove that Beer's Law is obeyed within experimental error at these concentrations. There appears to be some deviation from the straight line at the shorter wavelengths. The random error in this region is larger because the sensitivity of the photomultiplier decreases rapidly towards 2000A.

Similar results measured on the Cary 14 spectrophotometer at 220<sup>+</sup> 5 °C are shown in Figures 7 and 8. Again, fairly good straight lines were obtained, although there is somewhat more scatter. If the observed extinction coefficients were actually composed of linear and quadratic terms:

 $A = \mathcal{E}_{1} | (I_{2}) + \mathcal{E}_{2} | (I_{2})^{2}$ then a plot of  $\mathcal{E}_{app}$  versus  $(I_{2})$  would give a straight line of slope $\mathcal{E}_{2}$ . This plot is shown in Figure 9 for three

- 36 -



FIGURE 5: Absorbance in the Ultraviolet versus Concentration at 63 °C.

.



FIGURE 6: Absorbance in the Ultraviolet versus Concentration at 63 °C.

wavelengths. The scatter is sufficiently large so that it can not be decided definitely whether or not there is actually a positive slope. However, the slope would appear to be increasing towards shorter wavelength. An upper limit for  $\xi_2$  of 100 1<sup>2</sup> mole<sup>-2</sup> cm<sup>-1</sup> can be estimated for wavelengths between 3200 and 2800A, with a progressively higher upper limit below 2800A. This is an upper limit and certainly cannot be taken as evidence for a non-zero quadratic term.

The temperature of the cell containing iodine at less than its saturated vapour pressure was varied between 25 and 65 °C. By reference to the visible absorption, it was found that the concentration increased slightly with increased temperature. This was probably due to the Teflon needle valve stem absorbing less iodine at higher temperatures. When a correction was made for the change in concentration, no change in the 2700A continuum was observed except for a slight broadening of the peak at higher temperatures, as discussed above.

The effect of inert gas on the 2700A continuum was also studied. About 50 torr of carbon dioxide, nitrogen, and oxygen were each added to the cell containing iodine. The cell was heated to 63 °C and the spectrum taken. None of

• 39 -



39a



FIGURE 8: Absorbance in the Ultraviolet versus Concentration at 220 °C.



FIGURE 9: Apparent Extinction Coefficient versus Concentration at 220 °C.

- 40 -

these gases caused any observable effect on the ultraviolet spectrum. One atmosphere of air was also added to the cell containing excess solid iodine and extinction coefficients were measured at various temperatures up to 63 C. Virtually identical results were obtained using iodine with no air present. An upper limit of 20  $1^2$  mole<sup>-2</sup>cm<sup>-1</sup> can be estimated for the extinction coefficient of the term 1 (I<sub>2</sub>) (Inert gas).

The absorption at 2700A appears to be a true continuum. No structure could be observed when a slit width of 0.05 mm was used with the Backmann spectrophotometer. This corresponds to a spectral band width of 2.5A at 2500A. The absorption maximum is at  $2694^{\pm}$  3A. It would not be possible to determine the wavelength of the maximum much more accurately than this because of the broadness of the maximum.

The oscillator strength for the 2700A continuum was calculated from the equation:  $^{32}$ 

$$f = 4.31 \times 10^{-9} \int \varepsilon_{\nu} \, d\nu$$

to be $(4.98^{\pm}.05) \times 10^{-4}$ . The visible absorption, by contrast has an oscillator strength of about 9.5 x  $10^{-3}$  (according to our work).

. 4] -

If it is assumed that the absorption continuum at 2700A is due to a transition in the free iodine molecule, then the potential energy curve of the upper state involved in that transition can be constructed. The square of each vibrational wave function times the fraction of molecules in that level summed over all vibrational levels yields the distribution of molecules as a function of internuclear distance. Here, the harmonic oscillator wave functions<sup>33</sup> were used with only the first four vibrational levels taken into account for the calculation at 63°C. The resultant distribution is plotted on the horizontal axis as curve (a) of Figure 10. The experimental extinction coefficients divided by the frequency are plotted on the vertical axis as curve (b). According to Herzberg  $\overset{34}{,}$  a curve that will reflect one of these curves onto the other will be the potential energy curve of the upper state. In this case, since both curves are nearly gaussian in shape, the potential energy curve in this region is nearly a straight line.

- 42 -



FIGURE 10: Construction of Potential Energy Curve.

#### DISCUSSION

## Interpretation of the 2700A Continuum

The above results indicate that the 2700A continuum behaves very much like a "normal", although weak, transition in  $I_2$ . It does not seem to be affected by temperature, pressure, or concentration. However, previous workers have found quite different results. To make our results acceptable, it is necessary to show that the other results may have been interpreted incorrectly.

Kortum and Friedheim<sup>14</sup> measured the ultraviolet absorption spectrum at three concentrations (9.2 x  $10^{-4}$ , 5.6 x  $10^{-3}$ , 2.6 x  $10^{-2}$  M) at a higher temperature (340 °C). They observed that the extinction coefficients increased with increasing concentration. If the absorption were due partly to the monomer and partly to the dimer, then a plot of apparent extinction coefficient versus concentration would yield a straight line. This type of analysis was not done by Kortum and Friedheim. However, we made such a plot of their results as shown in Figure 11 for a few wavelengths. A straight line does not provide a good fit of the data. Therefore, this analysis does not appear to be true.

If the increase in extinction coefficients were actually

due to the 2700A continuum, then there should be a larger increase in the extinction coefficient with concentration at 2700A than at either higher or lower wavelength. Curve (a) of Figure 12 shows the difference in the extinction coefficients between the spectra measured by Kortum and Friedheim at 5.6 x  $10^{-3}$  and 9.2 x  $10^{-4}$ M; curve (b) that measured at 2.6 x  $10^{-2}$  and 9.2 x  $10^{-4}$ M. It is obvious from Figure 12 that the increase in extinction coefficients with concentration is not due to the 2700A continuum, but rather to some absorption further into the ultraviolet.

There has been little quantitative work done on the vacuum ultraviolet absorption spectrum of iodine. Bayliss and Sullivan<sup>35</sup> observed the spectrum between 46,500 and 54,000 cm<sup>-1</sup> (2150 to 1850A), and reported extinction coefficients of 29,000 at 49,000 cm<sup>-1</sup>, 130,000 at 51,000 cm<sup>-1</sup>, and 150,000 at 53,000 cm<sup>-1</sup>. An oscillator strength of 2.29 was also reported, although it is difficult to understand how this was measured since the maximum of the peak is beyond the limit of their measurements. Our extinction coefficients are about 1000 times smaller at 2150A. A more detailed comparison is impossible to made because the temperature at which their spectrum was taken was not specified.



FIGURE 11: Extinction Coefficient versus Concentration (from Kortum and Friedheim <sup>14</sup>).

46 -



# FIGURE 12: Difference between Ultraviolet Spectra measured at different Concentrations (from Kortum and Friedheim <sup>14</sup>).

Grover and Willard<sup>36</sup> measured the extinction coefficient of iodine vapour using the mercury line at 1849.68A close to the maximum of one of the most intense absorption bands at 1849.58A.<sup>10</sup> They found that the addition of 600 torr of argon increased the extinction coefficient from 50,000 to 200,000. This increase was attributed to the "pressure broadening of the iodine absorption bands in the region of 1849A, thus increasing the overlap between the iodine band and the 1849A mercury line." Actually it is the individual rotational lines that are broadened rather than the vibrational bands. The increase in extinction coefficient is probably not just due to the increased overlap but also to the elimination of 100% absorption at the centers of the rotational lines.

Although Grover and Willard's extinction coefficient would appear to be in fair agreement with those measured by Bayliss and Sullivan, it should be noted that the two groups were measuring different quantities. Grover and Willard were measuring very close to the maximum of an absorption band using, in effect, a very narrow slit. On the other hand, Bayliss and Sullivan were using a comparatively wide slit (10A) which covered several bands and yielded an average extinction coefficient over those bands. This should

- 48 --

be much smaller than measurements made near the band maximum. Therefore, Bayliss and Sullivan's extinction coefficients were not confirmed by Grover and Willard as these latter authors apparently believe. On the basis of both Grover and Willard's work and ours, Bayliss and Sullivan's extinction coefficients appear to be considerably too large.

An interesting point is the pressure broadening. It seems quite possible that the Cordes bands are affected by pressure in a similar manner to the visible bands. As shown by Rabinowitch and Wood,<sup>7</sup> the visible bands apparently do not obey Beer's Law because of virtually complete absorption at the rotational line centers. If this is indeed the case in the ultraviolet, Kortum's results can be easily explained. Figure 12, which shows an increasing departure from Beer's Law towards shorter wavelengths, supports our hypothesis. А test of this could easily be made. The addition of an atmosphere of inert gas to a cell containing iodine at a low - concentration at 340 C should broaden the individual rotational lines, thus markedly increase the absorption, and give a spectrum similar to that of Kortum's high concentration sample.

Sumner's results possibly can be explained in a similar

- 49 -

manner. He used a subjective method of subtracting off the absorption due to the main ultraviolet system. Since the 2700A continuum was, at the higher temperature, only a shoulder to this system, large errors can occur; especially when it is considered that this underlying absorption may be changing shape with both temperature and concentration. Sumner found about 10 to 20% quadratic dependency; this cannot be considered outside his limits of error.

The identification of the upper state involved in the transition does present some problems. Because the potential energy curve is almost linear in the range investigated, and because the absorption is continuous, it would seem most probable, on a qualitative basis, that the state correlates with either two ground state  $({}^{2}P_{3/2})$  atoms or one ground and one excited  $({}^{2}P_{1/2})$  state atom. The possible states (rejecting those of "g" symmetry and those which would lie at too low energy) are the following:

- (a)  $^{3}\Delta$  (1<sub>u</sub>, 2<sub>u</sub>, 3<sub>u</sub>)
- (b)  ${}^{3}\Sigma^{+}$  (1<sub>u</sub>, 0<sub>u</sub><sup>-</sup>)
- (c)  $\Sigma^{-}(0_{\rm u})$

All these states arise from the electron configuration  $\dots \sigma_{g}^{1} \pi_{v}^{3} \pi_{g}^{3} \sigma_{v}^{1}$ . The iodine molecule is fairly close to

- 50 -

Hund's case (c) (  $\Omega - \Omega$  ) coupling. Therefore both types of symbols for the states are given, with the ones in brackets (case (c) ) probably giving a better representation.

According to both cases (a) and (c),  $\Delta n = 0, \pm 1$  is a rigorous selection rule. Therefore, transitions to

 ${}^{3}\Delta$  (2<sub>u</sub>, 3<sub>u</sub>) states are forbidden.

Mathieson and Rees<sup>5</sup> suggest that the state involved must correlate with ground state atoms. The only state that will do so is one of the  $0_u$  states; which one is not yet certain. Again  $0^+ < 0^-$  is a rigorous selection rule for case (c) and  $\sum_{i=0}^{+} \sum_{j=0}^{-}$  for case (a). A transition to  $\sum_{j=0}^{+} (0_u^-)$ is forbidden for either case. Mathieson and Rees<sup>5</sup> consider that although the transition to  $3\sum_{j=0}^{+} (0_u^-)$ is rigorously forbidden for pure case (c) coupling, weak absorption may occur if the coupling is not complete.

A difficulty arises in this interpretation from the observed oscillator strength of the 2700A continuum being comparable to that of the A  ${}^{3}\Pi$  (1<sub>u</sub>) - x  ${}^{1}\Sigma^{+}$  (0g<sup>+</sup>) near infrared transition. This latter transition is allowed in case (c); therefore would be expected to be considerably

stronger than the  ${}^{3}\Sigma^{+}(0^{-}_{u}) \iff X \ \Sigma^{+}(0^{+}_{g})$  transition. Therefore, the possibility that a  $l_{u}$  state (a component of either  ${}^{3}\Sigma^{+}_{v}$  or  ${}^{3}\Delta_{v}$ ) correlating with  ${}^{2}P_{3/2} + {}^{2}P_{1/2}$  atoms is the upper state of the 2700A continuum appears not unreasonable.

Figure 13 shows the potential energy curve of the state in question in relation to the more established states. The dotted lines show the very approximate potential energy curves if the state were either a  ${}^{3}\Sigma_{\circ}^{+}$  (O<sub>u</sub><sup>-</sup>) or a l<sub>u</sub> state. The portion of the O<sub>u</sub><sup>-</sup> state at large internuclear distance is taken from the potential energy diagram of Steinfeld.<sup>37</sup> Because of a scarcity of data on these curves, a decision between the two choices for the identification of the state can not be made.

## Comparison With Solution Work

As mentioned in the Introduction, considerable work has been done on the ultraviolet spectrum of iodine in solution. Of interest especially is the work of Keefer and Allen<sup>20</sup> and deMaine<sup>21,22</sup> on the iodine dimer. It should be noted first of all that deMaine makes a gross error throughout a number of papers when presenting the extinction coefficients of  $I_4$ .

- 52 -



They are all a factor of  $10^4$  too small.

- 54 -

## Monomeric Absorption

The extinction coefficient of monomeric I<sub>2</sub> in carbon tetrachloride is about 46 l mole<sup>-1</sup> cm<sup>-1</sup> at its maximum at 2800A, 20 compared with the gas phase value found here of 19 l mole<sup>-1</sup> cm<sup>-1</sup> at 2700A. If the difference in extinction coefficients were due to induction of the transition from two-body collisions between the iodine and solvent molecules, i.e.  $A = \varepsilon_1 (I_2) + \varepsilon_{I_2}$ - Solvent 1 (I<sub>2</sub>) (Solvent),  $\varepsilon_{12}$  - CCl<sub>4</sub> would have a value of about 2.5  $1^2$  mole<sup>-2</sup> cm<sup>-1</sup>. This is, of course, only a crude approximation since in solution higher-order collisions become important, but any better approximation would only lower the value of  $\epsilon_{I_2-CCI_4}$ . We previously estimated the upper limit of E I2-Inert gas. to be 20  $1^2$  mole<sup>-2</sup> cm<sup>-1</sup>. Since this upper limit is much greater than the corresponding value in solution, the absorption in the gas at 2700A and in solution at 2800A could arise from the same transition, with the difference in intensities due to the induction of the transition by the solvent. The 100A shift of the peak maximum going from gas to solution could be caused by a very small perturbation of

the iodine molecule by the solvent. The potential energy curve of the upper state is very steep at the equilibrium internuclear distance of iodine: a change of 0.02A would be sufficient to cause this shift.

Some confirmation on this hypothesis would be achieved if an inducing effect on the 2700A continuum by inert gases could be found in the gas phase. However, a very long path length high pressure cell inert to iodine that could be heated would be required.

Since much of the absorption of iodine in solution at 2800A is, according to our hypothesis, due to the solventinduced transition, the extinction coefficients should increase markedly with increasing density of the solvent. This could be achieved by using a cell which compresses the solution, similar to the cell constructed by Ham.<sup>38</sup>

deMaine<sup>22</sup> has studied the ultraviolet spectrum of iodine dissolved in other inert solvents. Unfortunately, his spectra of  $I_2$  are not of sufficient accuracy to make any comparisons. If the above analysis is correct, the intensity of the absorption of " $I_2$ " should vary with the solvent.

- 55 -

## Dimeric Absorption

The evidence seems fairly clear that in solution, at any rate, there is a weakly bound  $I_4$  complex which has a transition about 2880A. Because of the close coincidence in wavelength between this peak and that due to the "free" iodine molecule, it seems quite probable that they are due to the same transition. If so, the  $I_4$  transition cannot be a simultaneous or self-intermolecular charge-transfer transition, but is simply an induced transition.

Experimentally only " $\epsilon_4$ K" could be determined (see Introduction). However, K is believed to be small (i.e.  $(I_4) < < (I_2)$ ), and therefore  $\epsilon_4 > \epsilon_4$ K. Since  $\epsilon_4$ K = 2000  $1^2 \text{ mole}^{-2} \text{ cm}^{-1}$  at 25°C<sup>20,21</sup>, iodine would appear to be at least 1000 times more effective at inducing the transition than the solvent. However the interactions between two iodine molecules in the dimer and iodine and the solvent are somewhat different in nature. An iodine molecule in a dimer will cause a stronger perturbation to its partner than will a solvent molecule. Therefore a direct comparison of the effectiveness at inducing the transition between the

- 56 -

dimer and the solvent is not strictly valid.

It would be of interest to compare the effectiveness of colliding pairs of iodine molecules to that of inert gas molecules (in the gas phase). Unfortunately, at the extremely high temperatures and concentrations required, the main ultraviolet system would spread out and not allow the 2700A peak to be observed.

The problem of the quadratic extinction coefficient found in solution being much larger than the upper limit found in the gas phase can be explained in one of two ways: (1) Only in solution is the I<sub>4</sub> complex formed in a large enough concentration to be observed.

(2) Both in solution and in the gas phase  $I_4$  exists. However, because the transition observed at 2800A is forbidden for  $I_4$ , the interaction of the solvent is necessary for the transition to occur.

Again, compressing the solvent may help decide this question. If possibility (2) is correct, then the extinction coefficients of  $I_4$  should increase markedly; if possibility (1) is correct, not as great a change would be expected.

- 57 -

We have assumed above, in common with all other authors, that CCl<sub>4</sub> acts as an "inert" solvent. This assumption may not be valid. Evans<sup>19</sup> has shown that perfluoroheptane (PFH) and diperfluorohexyl ether are considerably more "inert" towards iodine than are chloroform or the paraffin hydrocarbons. This is shown by the ultraviolet spectrum of iodine in PFH being closer to that of vapour phase iodine than is iodine in chloroform. Since deMaine<sup>22</sup> has found that iddine in chloroform has a similar ultraviolet spectrum to that of iodine in carbon tetrachloride, CCl<sub>4</sub> may not be the ideal inert solvent for studying the iodine spectrum. Evans noted that the absorption of iodine in the gas phase was slightly different from that in the fluorinated solvents, but apparently did not study it in detail. It would be of considerable interest to determine whether there is any  $\mathbf{I}_{\mathcal{A}}$  absorption in these solvents or whether all absorption obeys Beer's Law as in the gas phase.

#### Comparison with Bromine

Recently two groups of workers  $^{39,40}$  have independently indicated the existence of  $Br_4$  in the gas phase by means of a weak absorption continuum at about 2100A. The apparent

- 58 -

extinction coefficient was found to be composed of a term independent of and a term linearly dependent on the concentration of bromine. The term independent of concentration did not vary appreciably with temperature; the other term decreased considerably with increasing temperature. The latter term was attributed to a transition in the Br<sub>4</sub> dimer, which would then have a bond energy of about 2 Kcal/mole. This transition was not identified, but must be a simultaneous, charge-transfer, or induced transition.

According to Ogryzlo and Sanctuary,<sup>39</sup> the peak due to Br<sub>4</sub> has a definite maximum at about 2100A. According to Passchier et al,<sup>40</sup> the Br<sub>4</sub> peak has its maximum about 2050A. However, examination of their data shows that the maximum may well lie below 2000A (their lower limit). The Br<sub>2</sub> peak appears to have its maximum between 2100 and 2300A. Both groups used spectrophotometers containing the RCA 1P28 photomultiplier tube. According to its specifications, the sensitivity falls off very rapidly below 2200A, and is virtually insensitive below 2100A. Therefore, the position of the maximum of the quadratic term of the extinction coefficient can not be stated to have been found. We believe only two features have been shown convincingly:

- 59 -

(1) a continuum of Br<sub>2</sub> at about 2200A

(2) Some absorption with its maximum further into the ultraviolet which does not obey Beer's law and which decreases with increasing temperature.

There is a good possibility that the  $Br_2$  absorption is due to the same transition as we found in iodine at 2700A. The extinction coefficient of  $Br_2$  at 2100A is about 1/6 of that of  $I_2$  at 2700A. (The ratio of the visible peaks is about 1/4.) On the other hand, the absorption attributed to the  $Br_4$  dimer cannot be identified as such until a careful study in the vacuum ultraviolet has determined the complete absorption continuum.

Evans<sup>41</sup> has noted that the ultraviolet spectrum of bromine dissolved in PFH is similar to the gas phase spectrum, although the deviation from Beer's Law is more marked. Unfortunately, no quantitative work has been done on the ultraviolet spectrum of bromine in inert solvents, so that we cannot compare the difference between bromine in the gas phase and in solution with that of iodine in the gas phase and in solution.

Earlier, we postulated that in the iodine dimer (in solution), the transition at 2800A due to  $I_4$  is actually

- 60 --

just the 2700A gas phase transition strongly induced by its partner. In gas phase charge-transfer complexes between iodine and donor molecules, the observed chargetransfer transition is not very far from 2700A. (diethvl sulphide-2900A, benzene-2680A, diethyl ether- 2340A). 17 The 2700A iodine transition would be expected to be induced in a charge-transfer complex. However the magnitude of the induced transition can not be estimated because of lack of data. The induced transition may occur as a separate absorption band, possibly too small to be observed since it would lie close to the strong charge-transfer band. Alternatively, the excited charge-transfer state may mix with the excited iodine state. In that case, there may be only one band observable having the character of both charge-transfer and induced transition. Further work on gaseous charge-transfer complexes between iodine and donor molecules and on iodine in inert solvents may help clarify this problem.

# BIBLIOGRAPHY

1.	R.	S. Mulliken, Phys. Rev. <u>36</u> , 1440 (1930)
2.	R.	S. Mulliken, Phys. Rev. <u>46</u> , 549 (1934)
3.	R.	S. Mulliken, Phys. Rev. <u>57</u> , 500 (1940)
4.	w.	G. Brown, Phys. Rev. <u>38</u> , 1187 (1931)
5.	L.	Mathieson and A. L. G. Rees, J. Chem. Phys. <u>25</u> 753 (1956)
6.	J.	I. Steinfeld, R. N. Zare, L. Jones, M. Lesk, and W. Klemperer, J. Chem. Phys. <u>42</u> , 25 (1965)
7.	Ε.	Rabinowitch and W. C. Wood, Trans. Farad. Soc. <u>32</u> 540 (1936)
8.	E.	A. Ogryzlo and G. E. Thomas, J. Mol. Spec. <u>17</u> , 198 (1965)
9.	D.	T. Warren, Phys, Rev. <u>47</u> , 1 (1935)
10.	H.	Cordes, Z. Physik. <u>97</u> , 603 (1935)
11.	Α.	Nobs and K. Wieland, Helv. Phys. Acta 39, 564 (1966)
12.	Ρ.	Venkateswarlu, Proc. Ind. Acad. Sci. A24, 473 (1946)
13.	к.	Butkow and Jr. Wojchiechowska, Z. Physik, Chem. Abt. <u>49</u> , 131 (1941)
14.	G.	Kortum and G. Friedheim, Z. Naturforschg. 29, 20 (1947)
15.	F.	M. Sumner, B. Sc. Thesis, University of British Columbia, April 1966.
16.	H.	McConnell, J. Chem. Phys. <u>22</u> , 760 (1954)
17.	Μ.	Tamres and J. M. Goodenow, J. Phys. Chem. <u>71</u> , 1982 (1967)
18.	Н.	McConnell, J. S. Ham, and J. R. Platt, J. Chem. Phys. 21, 66 (1953)
19.	D.	F. Evans, J. Chem. Phys. 23, 1424 (1955)
20.	R.	M. Keefer and T. L. Allen, J. Chem. Phys. <u>25</u> , 1059 (1956)

21.	P. A. D. deMaine, J. Chem. P <sub>h</sub> ys. <u>24</u> , 1091 (1956)
22.	M.M. deMaine, P. A. D. deMaine and G. E. McAlonie, J. Mol. Spec. <u>4</u> , 271 (1960)
23.	W. E. Forsythe, Measurement of Radiant Energy, McGaw-Hill, 1937, pp. 349-351.
24.	P. Sulzer and K. Wieland, Helv. Phys. Acta 25, 653 (1952)
25.	L. J. Gillespie and L. H. D. Fraser, J. Am. Chem. Soc. 58, 2260 (1936)
26.	J. P. Baxter, C. H. Hickey, and W. C. Holmes, Trans. Am. Chem. Soc. <u>29</u> , 127 (1907)
27.	G. M. Harris and J. G. Willard, J. Am. Chem. Soc. <u>76</u> 4678 (1954)
28.	R. S. Mulliken, J. Am. Chem. Soc. <u>72</u> , 600 (1950)
29.	D. J. Seery and D. Britton, J. Phys. Chem. <u>68</u> , 2263 (1964)
30.	G. E. Gibson and N. S. Bayliss, Phys. Rev. <u>44</u> , 188 (1933)
31.	A. P. Acton, R. G. Aicken and N. S. Bayliss, J. Chem. Phys. <u>4</u> , 474 (1936)
32.	R. S. Mulliken, J. Chem. Phys. 7, 14 (1939)
33.	G. Herzberg, Spectra of Diatomic Molecules, van Nostrand, 1950, p. 76
34.	Ibid, p. 392.
35.	N. S. Bayliss and J. V. Sullivan, J. Chem. Phys. <u>22</u> , 1615 (1954)
36.	T. A. Grover and J. E. Willard, J. Am. Chem. Soc. 82, 3816 (1960)
37.	J. I. Steinfeld, J. Chem. Phys. <u>44</u> , 2740 (1966)
38.	J. Ham, J. Am. Chem. Soc. <u>76</u> , 3881 (1954)

- 63 -

39. E. A. Ogryzlo and B. C. Sanctuary, J. Phys, Chem. <u>69</u>, 4422 (1965)

40. A. A. Passchier, J. D. Christian and N. W. Gregory, J. Phys. Chem. <u>71</u>, 937 (1967)

41. D. F. Evans, J. Chem. Phys. 23, 1426 (1955)