THE PHOTOISOMERIZATION OF AZOBENZENE AT 77°K IN A RIGID SOLVENT AND AT ROOM TEMPERATURE

Thesis by

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ABSTRACT

The photoisomerization of azobenzene has been studied at room temperature in ethanol and P.Me.H., and at 77°K in a P.Me.H. rigid solvent. At room temperature, the photostationary state composition is 74 % trans (and 26 % cis) in ethanol and 77 % trans in P.Me.H.; it is 98 % trans in P.Me.H. at 77°K. It has been shown that both the trans to cis and the cis to trans photoisomerizations occur in the rigid solvent at liquid nitrogen temperature.

The spectra and molar extinction coefficients have been determined at room temperature for trans azobenzene in ethanol and P.Me.H. Other spectra were taken of azobenzene: at the photostationary state, at room temperature in ethanol and P.Me.H., and at 77°K in P.Me.H.; at 77°K of 100 % and 77 % trans in P.Me.H.

It has been shown that the photoisomerization occurs more readily by irradiation in the visible, than in the ultraviolet region. A new low temperature cell has been designed and used.

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I. INTRODUCTION

In recent years, free radicals and unstable species have been studied by means of low temperature techniques. Liquid nitrogen, hydrogen, and helium temperatures are used. Two general methods are employed. One is to form the radicals in the vapor phase, and then trap them on a suitable cold surface. The other is to form the radicals in a trapped condition in a rigid solvent. The latter is of interest in this work.

A number of free radicals have been made (by photolysis of suitable substrates) and trapped in rigid solvents or glasses (1, 2, 3). A rigid solvent, or a glass, is a transparent, amorphous material used in this type of investigation. However, a number of substances which can be photolyzed at room temperature do not photodecompose in the rigid solvents (3). It is thought that this is due to the effect of the low temperature solvent on the free radical particles.

It is the purpose of this project to study the effect of a rigid solvent on an intramolecular rearrangement. This is to be done by investigating the possible photoisomerization of azobenzene in a rigid solvent at liquid nitrogen temperatures ($77^{\circ}K$). Azobenzene exists in a cis and trans form. The two species are distinguishable via their different spectral characteristics. It is believed that the photoisomerization will occur because G. N. Lewis et al. reported the cis to trans change of stilbene in E.P.A. (ether, isopentane, ethanol; 5:5:2, parts by volume). This was effected by mercury irradiation at $77^{\circ}K$ (4).

II. MATERIALS

The azobenzene was "laboratory grade", made by Mathieson, Coleman, and Bell. It was recrystallized twice from n-hexane to give orange crystals. This was done in darkness because of the photosensitivity of azobenzene in solution. The m.p. range is 68-70°C. The m.p. of pure trans azobenzene is 68°C, that of pure cis is 71°C. There is a eutectic which melts at 41°C (5, 6). The colors of trans and cis are orange and red, respectively (5, 7). So, the melting point and color indicate the azobenzene is primarily in the trans form. This was also shown by preliminary photoisomerization experiments with the original material. Microanalytical data of the twice recrystallized material show C 79.1 wt. %, H 5.56 %, and N 15.4 % (theoretical, C 79.0 %, H 5.48 %, and N 15.4 %). In order to assure the sample being all trans, it was heated in a dry nitrogen atmosphere at 100°C for 14 minutes in darkness. The half-life for the thermal cis to trans change is 1.8 minutes at 100° C (6). It was found that two recrystallizations of the "laboratory grade" azobenzene from 92.5 % ethanol do not result in a pure product.

Two mixtures were used for the formation of the rigid solvents, E.P.A. and P.Me.H. The former is ethyl ether, isopentane, and ethanol; 5:5:2, parts by volume. P.Me.H. is isopentane and methylcyclohexane; 3:2. The ethanol was the absolute grade. The methyl cyclohexane was purified by Ronald G. Sowden by washing with H_2SO_4, drying over sodium wire, and passing it through activated silica gel. The isopentane was Phillips 66 pure grade (99 mole % minimum). The ether was from Mallinckrodt. It contained about 0.01 % H_2O and 5×10^{-6} % preservative (sodium diethyldithiocarbamate).

III. APPARATUS

The room temperature irradiation apparatus is depicted in fig. 1. It consists of a mercury or tungsten light source (C), a running water filter (B), (to remove the infrared light) and a water cooled cell holder (A). One light source was a General Electric AH4, 100 watt, mercury arc. The outer Pyrex bulb of the arc was removed. The tungsten irradiation was from a 500 watt Westinghouse projection lamp (shown in the figure). The aluminum masks (D) removed extraneous light. Each contains a hole which collimates the radiation from the light source. The solution was contained in a Cary spectrophotometer cell (E), which has quartz windows with a one centimeter light path. The water bath kept the cell at room temperature. A support, not shown in the figure, was used to hold the cell at a fixed distance from the light source. The spectra were made using a Cary model 11M recording spectrophotometer.

The low temperature irradiation apparatus is the same as that in fig. 1, except that the low temperature can replaces the water cooled cell holder. The low temperature can, hereafter to be called the can, is shown in fig. 2. It is similar to that of Sowden and Davidson (3). The bottom part is cylindrical and is made of aluminum. It makes a light tight fit in the spectrophotometer, with the quartz windows (A) in the light path. The steel lid has metal ground joints. The center one holds the liquid nitrogen reservoir; the side joint supports the evacuation connection. The lid is held to the can by two bolts. An O-ring (B) assures a vacuum tight fit. The can was evacuated by means of a Welch "Duo Seal" pump.

The windows on the reservoir and cell are quartz, all other glassware is Pyrex. The light path of the cells (fig. 3) is 13 to 14 mm. Cell (A) was found to be quite prone to cracking upon warming after a run, probably because of the reduced volume above the window. Cell (B) avoids big constrictions. At liquid nitrogen temperature, the top level of the meniscus is about 1.5 cm. above the top of the windows. Because the newer cell has only been used a few times, it is not possible to comment on its resistance to cracking. However, the preliminary results look good. A cell was held in the reservoir by means of a two holed rubber stopper. The hole on the side served as an outlet for the nitrogen vapors.

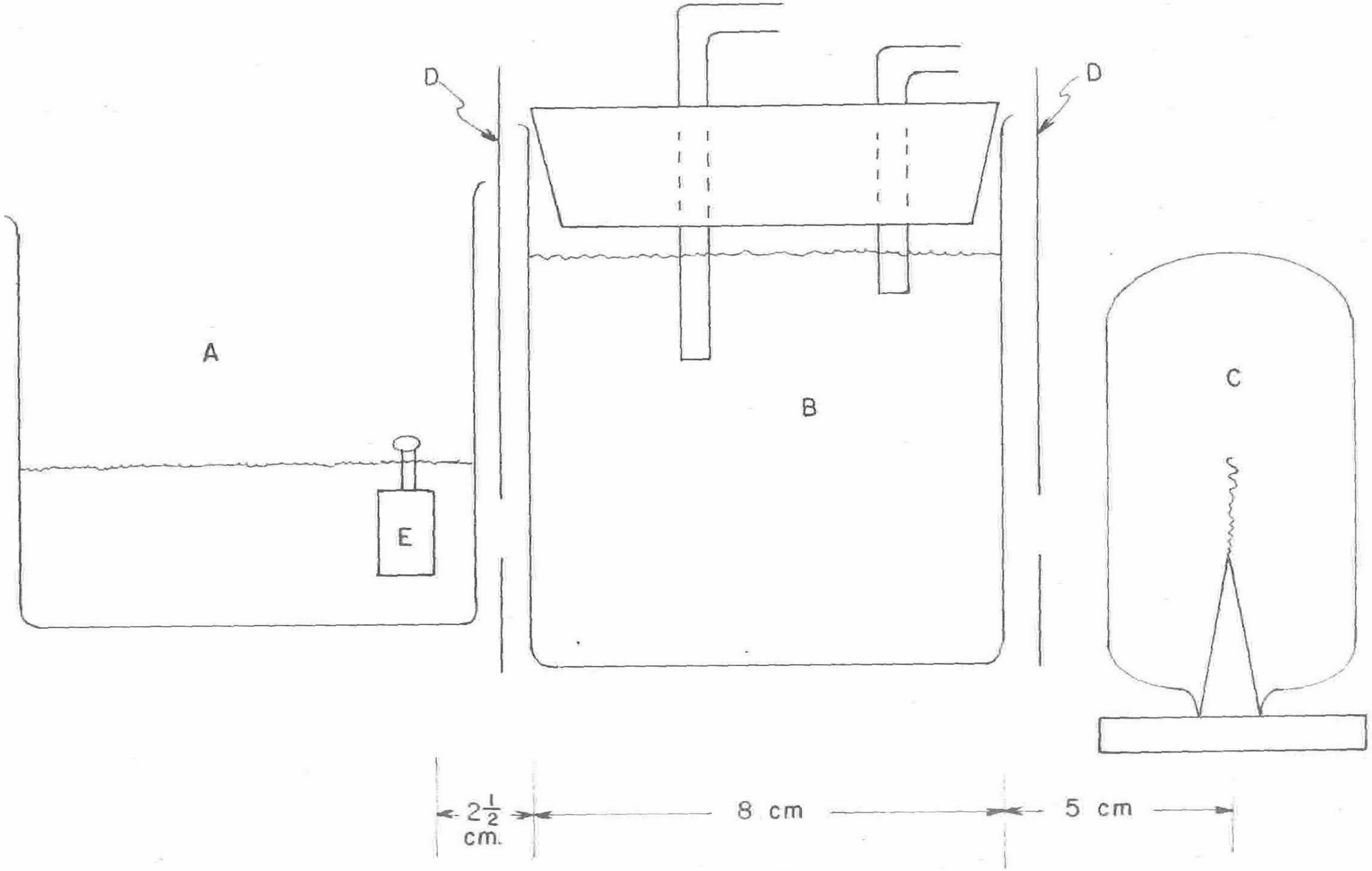


Figure 1. ROOM TEMPERATURE IRRADIATION APPARATUS

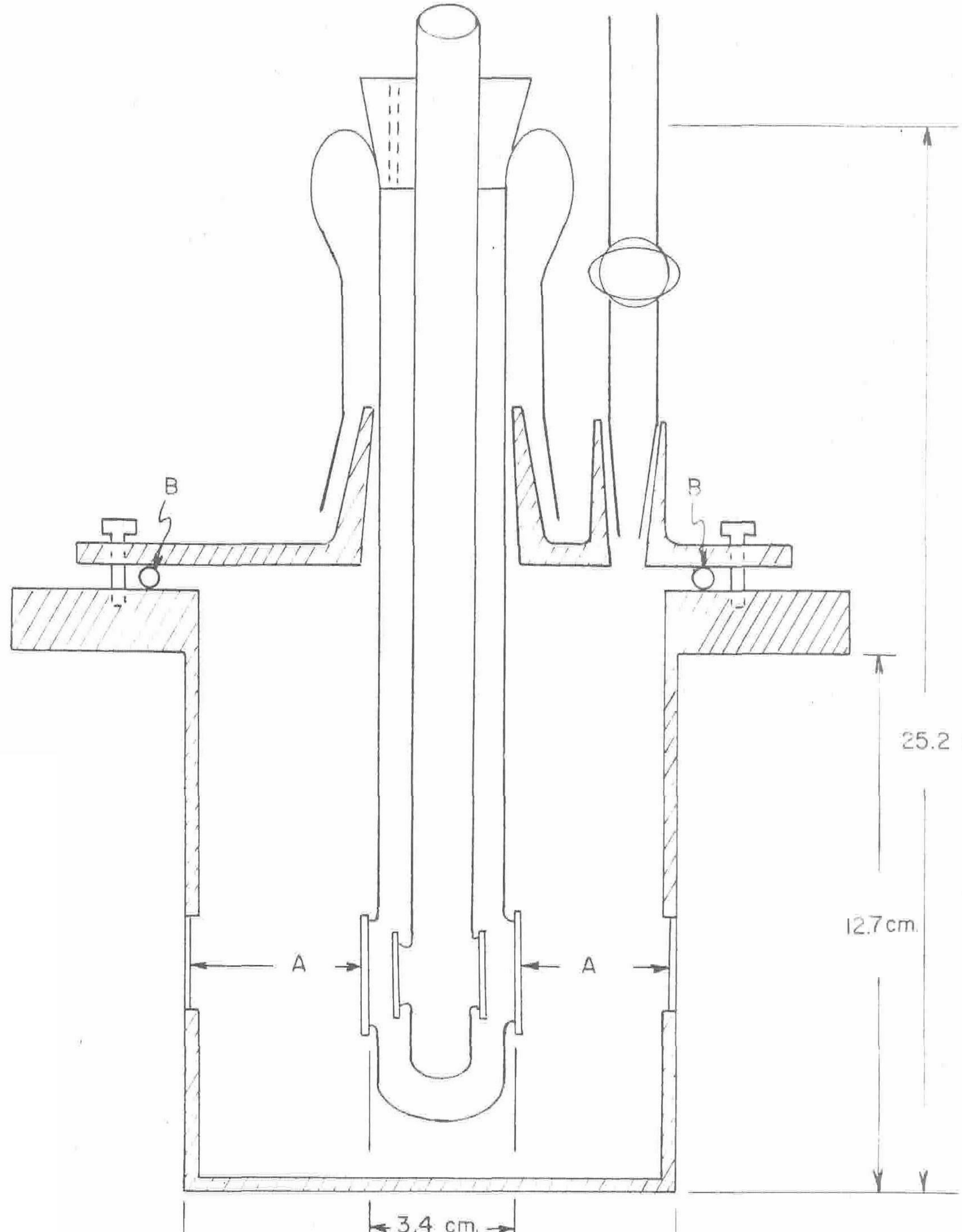
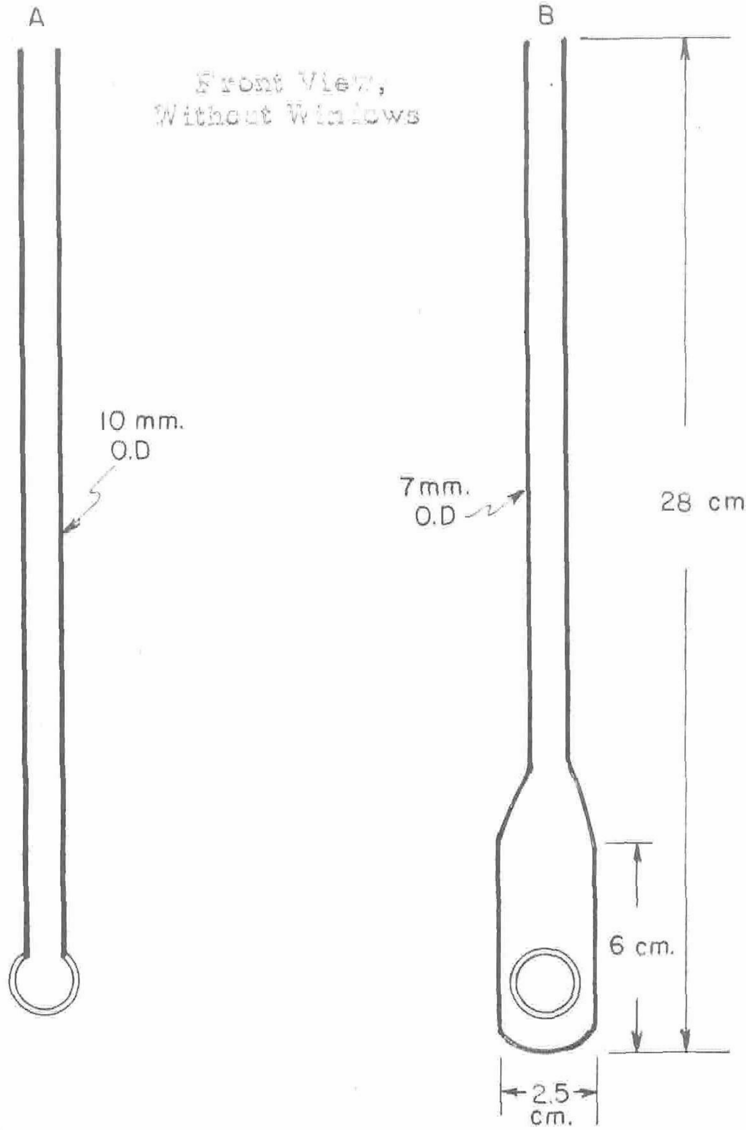


Figure 2. LOW TEMPERATURE CAN



Side View of Lower Section, With Windows
(Scale Enlarged)

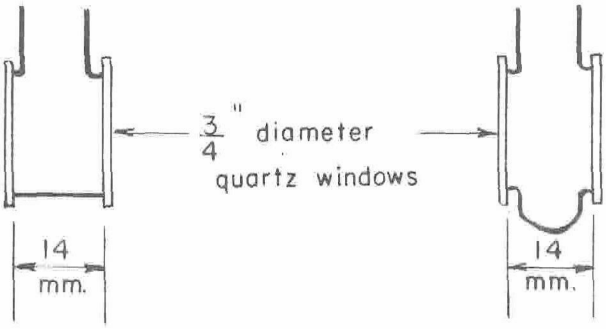


Figure 3. LOW TEMPERATURE CELLS

IV. PROCEDURE

Solution Preparation.

The solutions were prepared in the usual way. The azobenzene was weighed and put into a volumetric flask. This was filled to the mark with the solvent. The azobenzene weight ranged from 9 to 23 mg. Volumetric flasks of 50 and 100 ml were used. The preparation of solutions, as well as most of the other operations in this investigation, was done in subdued light. In the daylight hours, the shades were drawn and all lights turned off. The effect of the subdued light is small, compared to that obtained from the irradiation experiments. The concentrations were about 10^{-4} and 10^{-3} M. for the ultraviolet and visible, respectively, for room temperature experiments. The room temperature concentrations for the low temperature work were about 3.0×10^{-5} and 10^{-3} M. for the ultraviolet and visible ranges, respectively. The lower of the concentrations at room or low temperatures, were made by volumetric dilution with factors of 0.1 or 0.03, respectively.

Rigid Solvents.

In the course of this work three cooling techniques were used in making the rigid solvent. One was to slowly immerse the cell into the liquid nitrogen. The second technique is better in principle because it provides for uniform cooling of the entire solution. A quart Dewar is half filled with liquid nitrogen. The cell is immersed into the coolant and then removed to the cold vapors. This is done repeatedly until everything is at coolant temperature. This takes six minutes. The third technique is like the second, except that it reduces the number of up and down motions. The cell is immersed into the liquid nitrogen every 10 seconds. It is held in the coolant for 2 to 3 seconds, the other 7 to 8 seconds it is kept in the cold vapors with some shaking to insure a uniform temperature. After four minutes, more of the 10 second interval is taken up by the immersion position. This technique takes five minutes.

Two difficulties beset the preparation of a rigid solvent: the formation of voids and a deep meniscus. The former phenomenon was only observed with E.P.A. glasses. The voids are cracks which form in the rigid solvent. The large ones are one cm. long, one mm. wide, and 0.2 mm. across. At one instant the glass is clear; then, after a cracking noise, the entire window area is full of voids. The stem is usually free of them. E.P.A. is quite sensitive to their formation (1). Once it was possible to prepare a voidless E.P.A. sample, which stayed this way for two hours. Then it was removed from the liquid nitrogen into the room temperature air. Voids formed within half a minute. So, E.P.A. was not used as a rigid solvent because of its proneness to form voids.

The formation of a deep meniscus occurred with both E.P.A. and P.Me.H. It appears like a hollow bore, 2 to 3 mm. wide, and as much as two cm. long. It is a continuation of the meniscus which is normally present on top of a liquid. At times it extends 2 to 4 mm. below the top of the quartz window. For this reason an excess of solvent is used so that the bottom of the meniscus will be above the light path. The formation of the deep meniscus occurs shortly after all of the solvent is at 77°K. Excluding the void and deep meniscus formation, the E.P.A. and P.Me.H. glasses are clear.

As was mentioned in the apparatus section of this thesis, the cell design was changed because of the frequent formation of cracks in the Pyrex. The frequency of crack formation can be reduced by slowly warming the cell in a way analagous to the last two cooling techniques discussed above. Too slow warming should be avoided because the solvent may attack the Epibond. E.P.A. was found to dissolve through the Epibond seal on the cell in six or less hours at room temperature.

Use of Low Temperature Can.

Before the cell containing the rigid solvent was transferred to the can, a few steps had to be taken. First the liquid nitrogen reservoir was rinsed with ethanol to remove impurities and excess moisture. Drying was done by passing compressed air through it. (The cells were cleaned and dried in the same manner.) The can was evacuated for several hours to a pressure around 50μ. Then the evacuation stopcock was closed and the can disconnected from the vacuum aparatus. Next, the reservoir was filled with liquid nitrogen. At this point, the can is ready to receive the low temperature cell.

There are a few factors other than the azobenzene in the cell, which contribute to absorption of the spectrophotometer light beam. These are the factors mentioned earlier, which make it difficult to obtain accurate molar extinction coefficients. Frost can form on the cell window during the transfer from the Dewar to the liquid nitrogen reservoir. This is almost eliminated by the following technique. The Dewar and reservoir are filled with liquid nitrogen to within an inch of the rim. The Dewar is put next to the reservoir top. The ensuing vapors cool the path traversed by the cell windows in the transfer from Dewar to reservoir. With this technique, little frost forms on the cell windows.

The light absorption is also increased by bubbles and small ice crystals in the coolant. The bubbles are caused by the heat leakage to the reservoir. As the can loses its vacuum, the amount and size of the bubbles increases.

The presence of ice crystals in the liquid nitrogen causes two problems. First, most of them are kept in motion by the nitrogen bubbles and so remain in the spectrophotometer beam. The other difficulty is that of physical adsorption of the ice crystals on the cell windows. This may be due to a slight roughness on the cell windows after repeated use and to the presence of a very thin frost deposit. The bubbles and circulating ice crystals affect a constant light absorption during a spectrum determination. However, the amount of ice crystal adsorption on the cell windows increases with time. The latter effect is only of concern if the liquid nitrogen is unusually full of ice crystals and/or the cell window is very susceptible to adsorption.

The above problems can be minimized. The amount of bubbles can be reduced by having a better vacuum or by reevacuating the can during a run. The quantity of ice crystals can be cut down by starting with clear liquid nitrogen and removing the loose ice crystals from the rim of the reservoir and Dewar before transferring the liquid nitrogen. In rare instances, usually after a series of runs, the can gets cold. Consequently, moisture forms on the outside windows.

When the cell is in the liquid nitrogen reservoir, the can is ready for irradiation experiments. It is placed in position in the low temperature irradiation apparatus. The irradiation procedure is the same as that used at room temperature. During the irradiation the top of the can is covered with a black cloth to remove extraneous light. At the end of an irradiation, the can is transferred to the spectrophotometer in a light tight box. During the recording of a spectrum, the top of the can is again covered. In the course of a low temperature experiment, it was necessary to refill the liquid nitrogen reservoir every 30 minutes.

V. RESULTS

Light Absorption Characteristics.

The cis-trans photoisomerization was studied by means of the differences in the light absorption characteristics of the two forms. Following is a general discussion of the absorption behavior in ethanol. In the visible, the cis and trans maxima are both around 440 mμ, with the cis absorbing more strongly. The minima lie between 370-380 mμ, with both absorbing equally. In the ultraviolet, the maximum of the trans has the higher absorption value. So, in a change from the trans to cis, the peak will rise in the visible and fall in the ultraviolet.

The molar extinction coefficients of trans azobenzene in ethanol and P.Me.H. were obtained from spectra of the pure compound. The coefficients of the cis form were not determined. The values in an ethanol solvent are reported in Table 1, with the values of Hauser and Winkel & Siebert (8, 9). As can be seen from the table, the values obtained in this research agree more closely with those of Winkel and Siebert. It should be noted that there is some disagreement between the absorption values of the two literature sources. The reasons for the differences in the absorption results will not be discussed since their precise determination is not the purpose of this project, nor are they necessary for its results. The absorption characteristics of azobenzene in P.Me.H. at room temperature are in Table 2. The spectra of trans azobenzene in ethanol and P.Me.H. are shown in figs. 4, 5, 6, and 7, along with the photostationary state results.

It is difficult to obtain accurate molar extinction values of azobenzene at 77°K in a rigid solvent with apparatus and technique of this project. The factors bringing about this difficulty will be discussed later. However, the low temperature spectra of trans azobenzene in P.Me.H. can be seen in figs. 8 and 9, along with the photostationary state results.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF AZOBENZENE IN ETHANOL

molar extinction coefficient, $\left(\frac{\text{moles cm.}}{\text{lt}}\right)^{-1}$

wavelength, mμ	Hauser (8)	Winkel and Siebert (9)	Kraus
		trans azobenzene coefficients	
248	5×10^3	2.7×10^3	2.46×10^3
313	5.2×10^4	1.6×10^4	2.12×10^4
380	--	1.7×10^2	1.35×10^2
340	9×10^2	3.1×10^2	4.50×10^2
		cis azobenzene coefficients	
248	2.0×10^4	7.2×10^3	--
313	1.2×10^4	2.6×10^3	--
430	2.9×10^3	1.3×10^3	--

TABLE 2

MOLAR EXTINCTION COEFFICIENTS OF TRANS AZOBENZENE IN P.ME.H.

wavelength, mμ	coefficients from this research
260	3.39×10^3
316	2.24×10^4
380	1.08×10^2
430	3.87×10^2

Figure 4, Part 1. AZOBENZENE IN ETHANOL 1.03 x 10^{-4} M TRANS

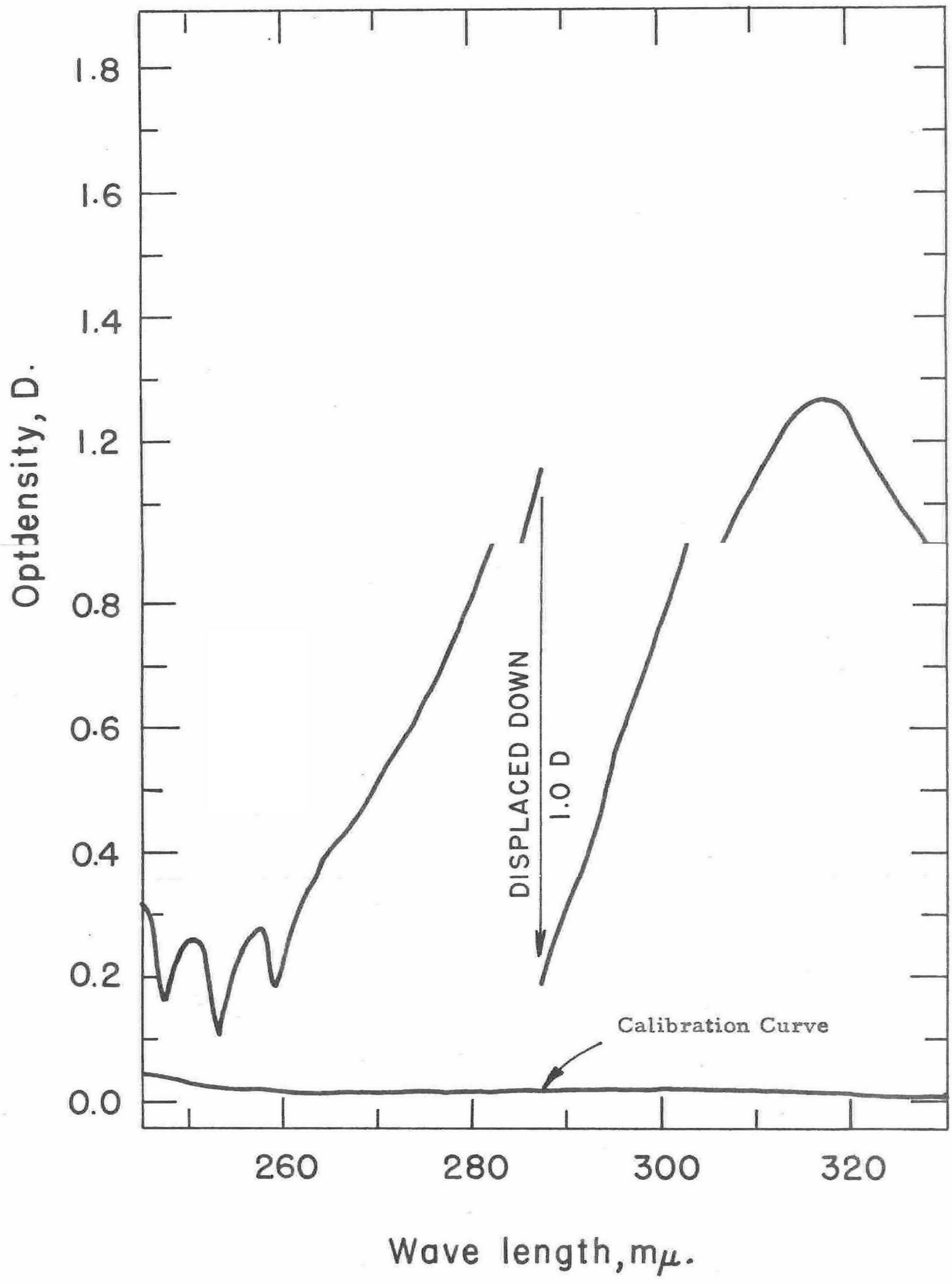


Figure 4, Part 2. SOLUTION OF PART 1 AFTER IRRADIATION

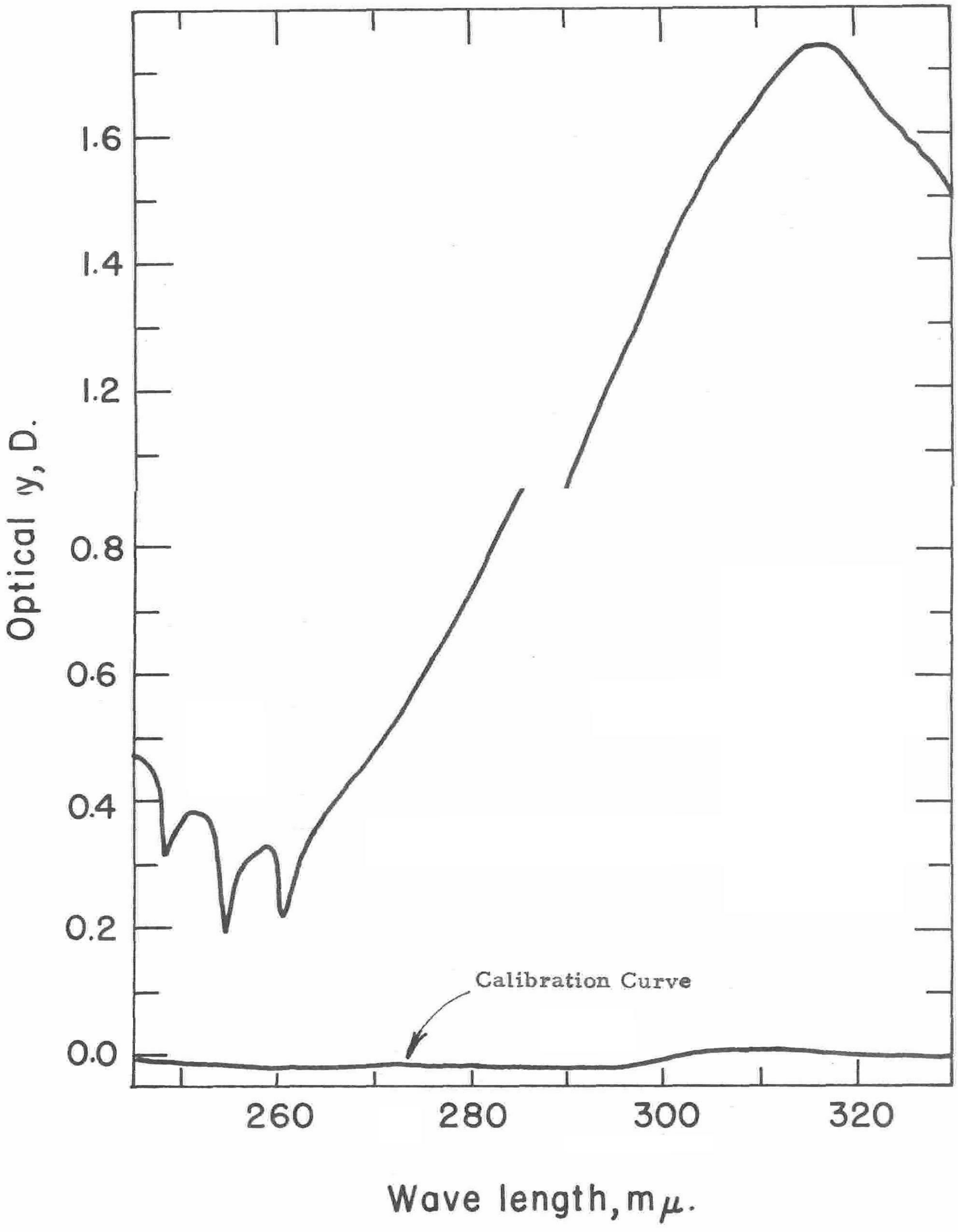


Figure 5. AZOBENZENE IN ETHANOL

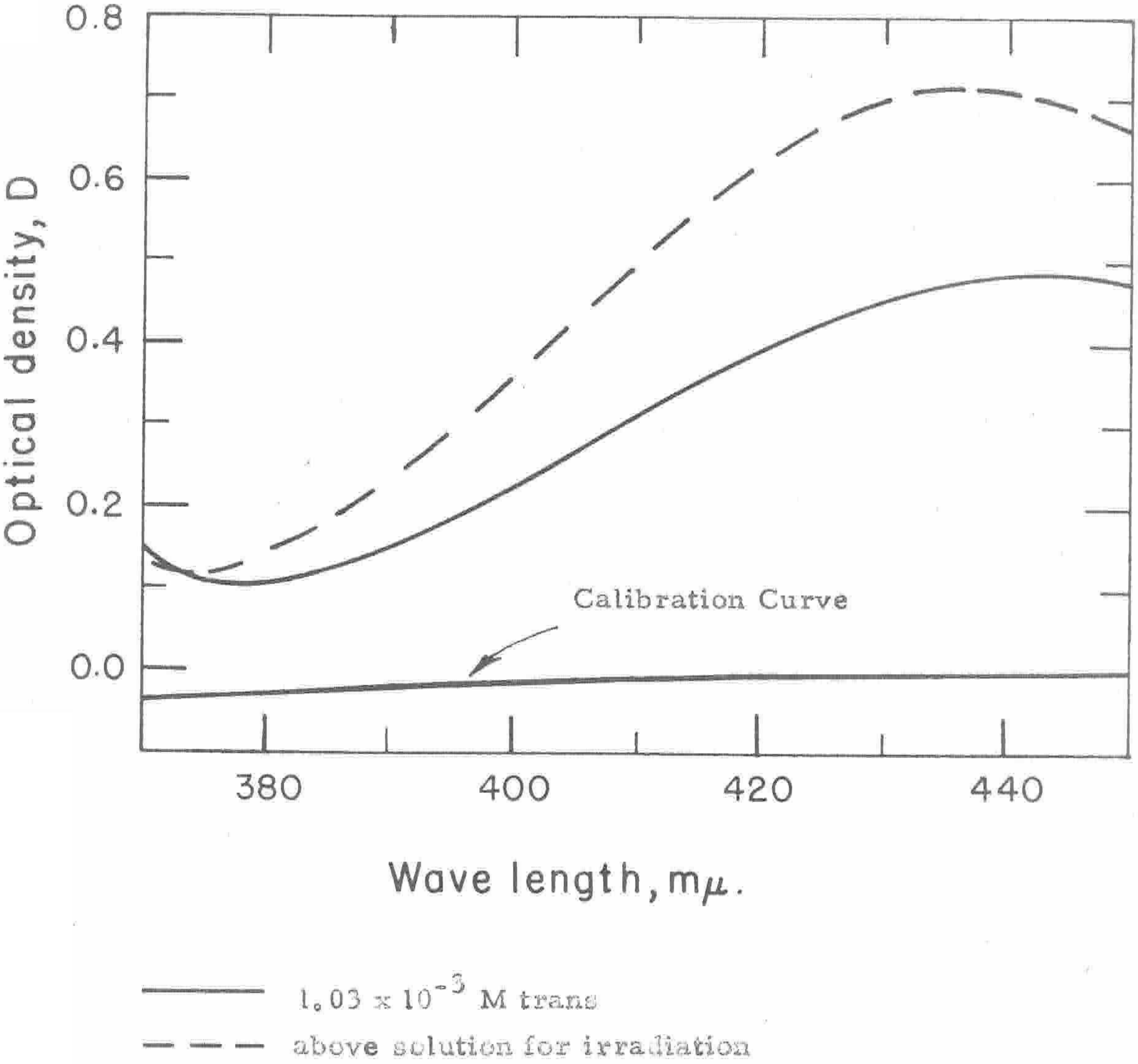


Figure 6. AZOBENZENE IN P.ME.H. AT 77°K

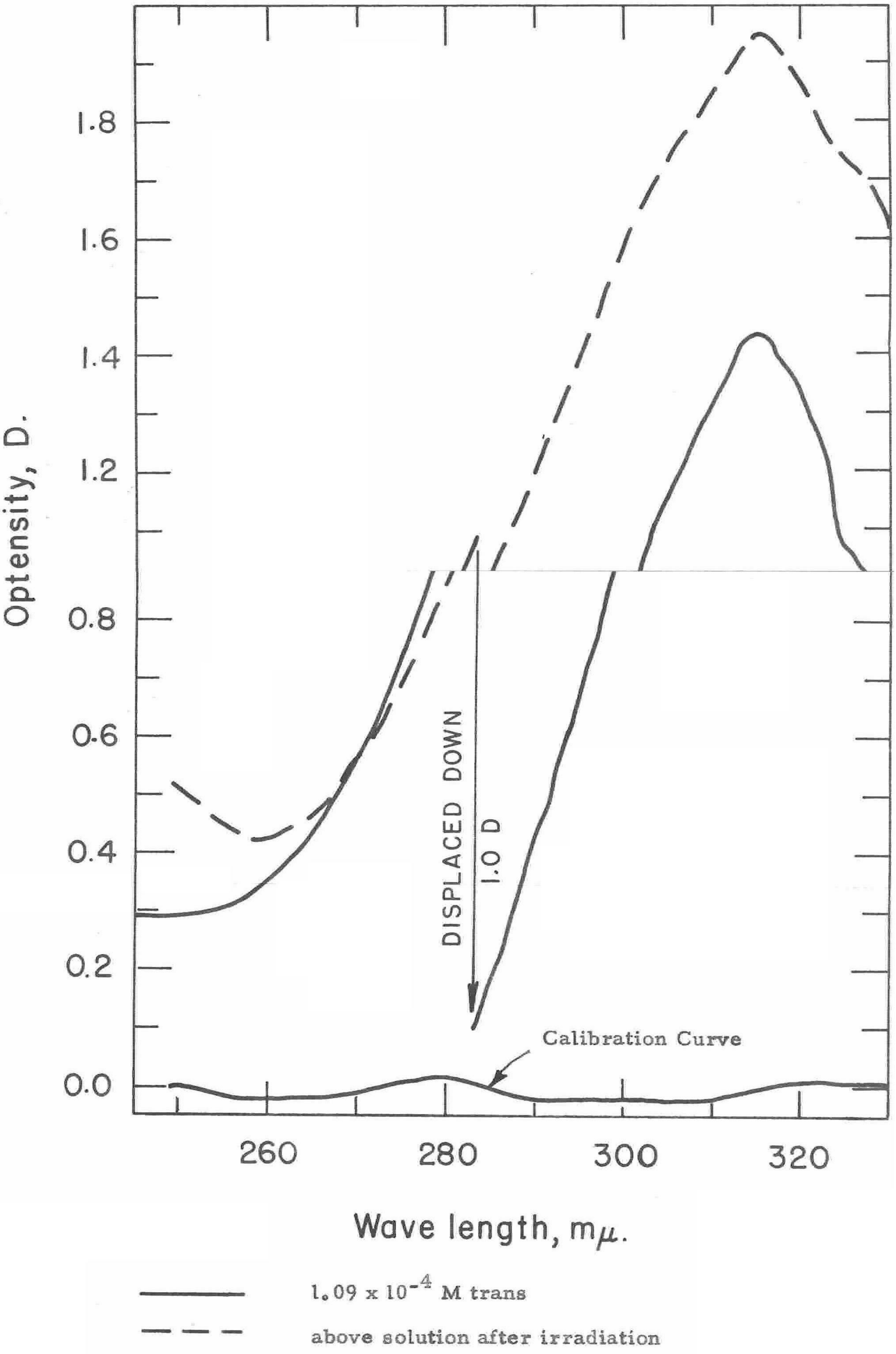


Figure 7. AZOBENZENE IN P.ME.H.

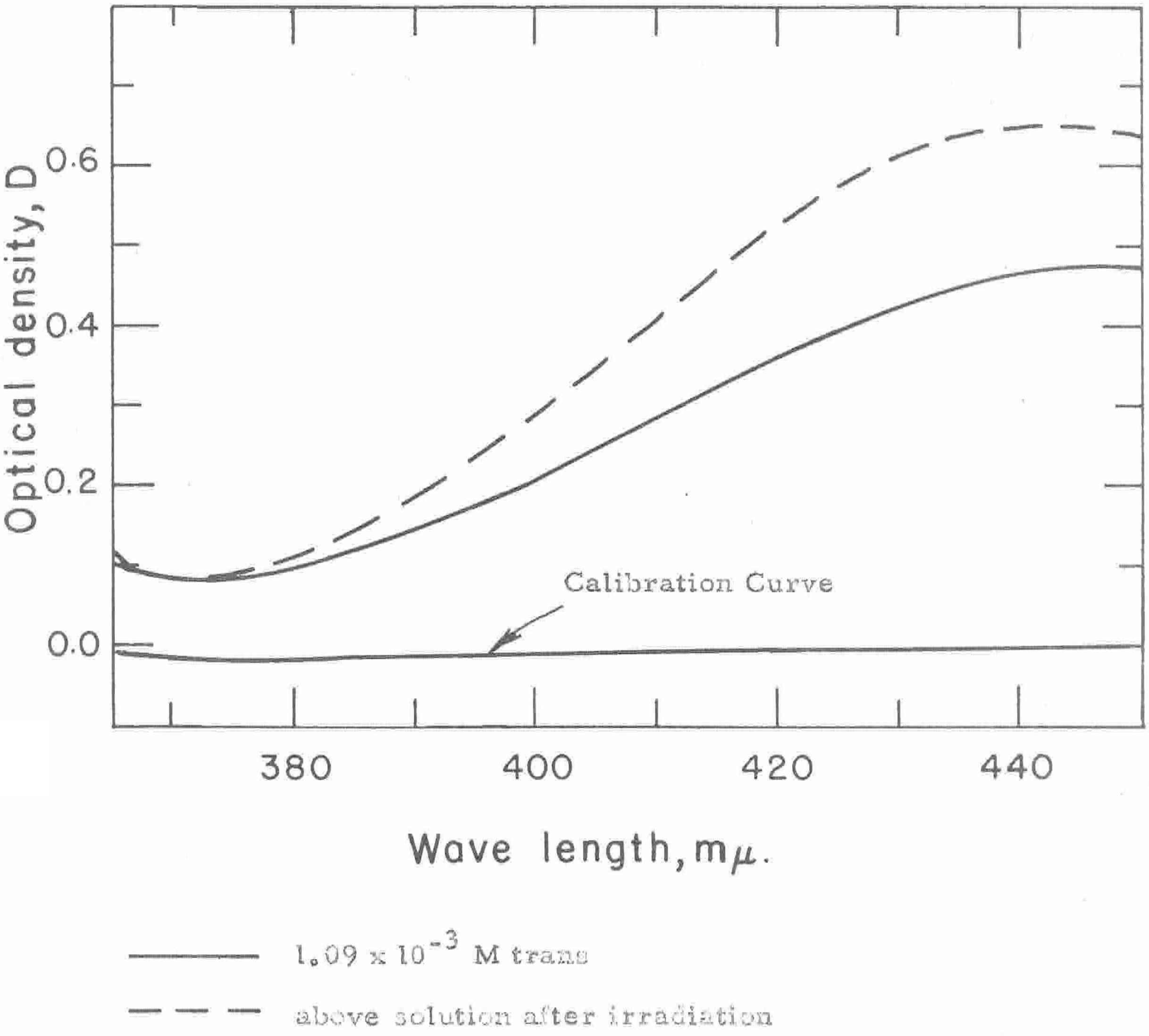
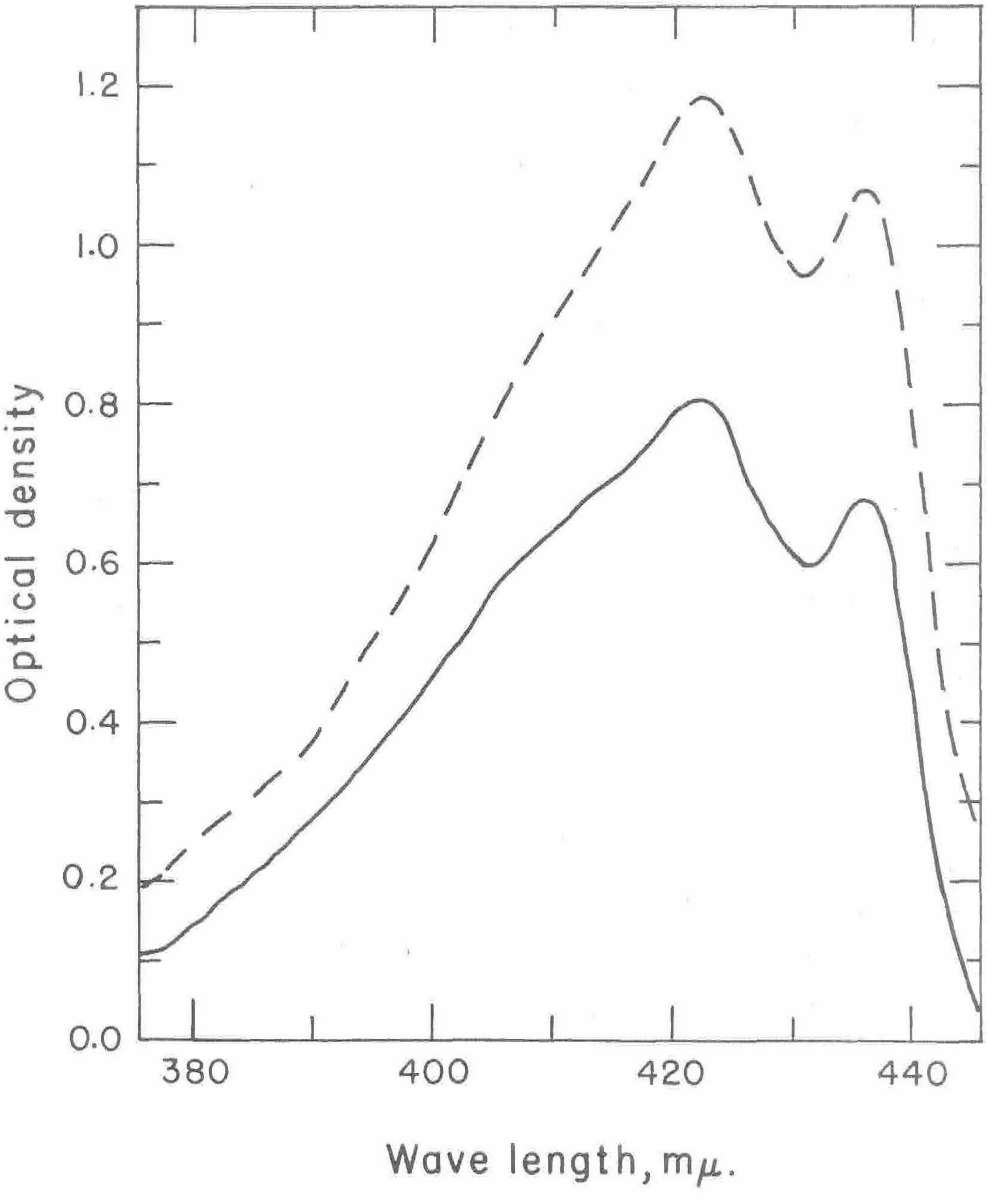


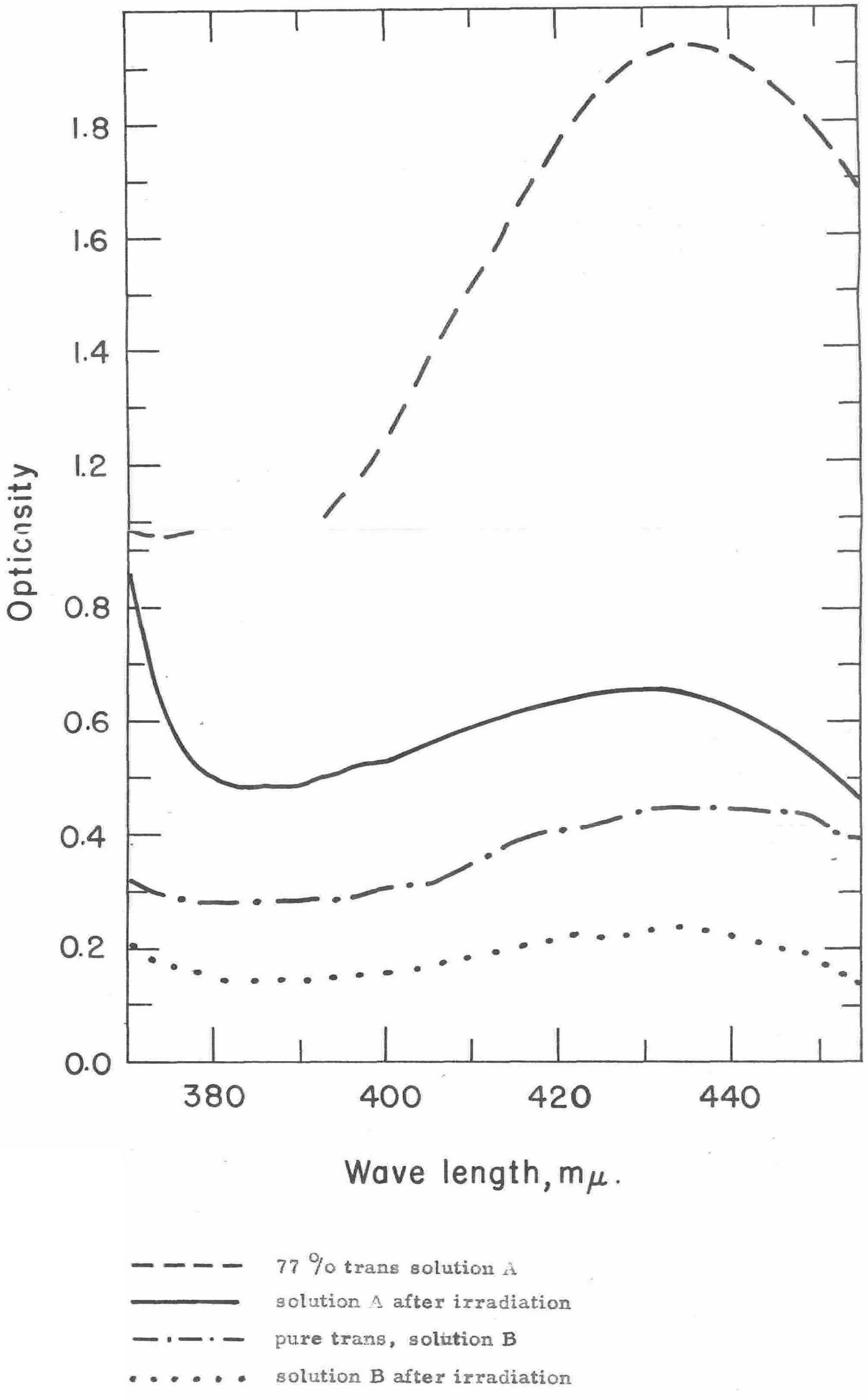
Figure 8. AZOBENZENE IN P.ME.H. AT 77°K



——— 77 % trans solution

— — — above solution after irradiation, and "pure" trans before and after irradiation (zero of optical density scale arbitrary for both curves

Figure 9. AZOBENZENE IN P.ME.H. AT 77°K



(zero of optical density scale is arbitrary for all curves)

Room Temperature Irradiation.

In all experiments, the tungsten lamp and mercury arc irradiations were done in the same way. The light source was not preheated before a run. Because of this, the irradiation was not at top intensity during the initial time of irradiation.

Experiments were done to determine whether the visible or ultraviolet regions are more effective in absorbing radiation for isomerization. The "laboratory grade" azobenzene was used for this. It was done by observing the rise of the cis peak in the visible. The photostationary state is attained when the peak reaches a constant height, i.e. when further irradiation produces no change in the spectrum. The usual run with a sample consisted of a number of repetitions of taking the spectrum and irradiation, until a constant peak height was attained. With the tungsten lamp, the photostationary state was reached in less than two minutes. The time required with the mercury arc was between 10 to 15 minutes. A General Electric AH4 mercury arc radiates 5.0 % of the lamp watts in the range of 280 to 380 mμ and 10.4 % in the 380 to 760 mμ spread (10). No comparable information was available for our 500 watt projection lamp, so that of a 900 watt source was used (10). In the 280 to 380 mμ range 0.13 % of the lamp watts are irradiated, it being 14.6 % for 380 to 760 mμ. By calculating the joules of radiation necessary to attain the photostationary state, it is seen that the visible range is more effective.

The per cent trans at the photostationary state in ethanol was calculated using the data of fig. 4 at 313 mμ, the Beer-Lambert Law, and the Winkel and Siebert values (Table 1) for the molar extinction coefficient of cis azobenzene. By means of successive approximations, the photostationary state composition of azobenzene in ethanol was determined to be 74 % trans (and 26 % cis). Hartley reports 15 - 40 % cis depending on the solvent (6). Values up to 40 % cis were reported for the photostationary state by Blaisdell in isopropyl alcohol and isoctane solvents (11). The calculations for azobenzene in P.Me.H. were done in the same manner as above, using the data of fig. 6. The photostationary state composition is 77 % trans. With both solvents, the cis extinction coefficient of Winkel and Siebert was used because it was not determined in this project.

Low Temperature Experiments.

Two cis-trans compositions were used in the low temperature work. The first was with pure trans azobenzene, the other with 77 % trans. The latter composition was attained by irradiation of the azobenzene solution in P.Me.H. at room temperature until the photostationary state was reached.

Low temperature spectra of azobenzene in P.Me.H. were taken of the pure trans, and 77 % trans glasses in the ultraviolet and visible. Their general form is shown in figs. 8 and 9, along with their appearance at the photostationary state.

The low temperature spectra were taken with air as the reference. The P.Me.H. begins to absorb strongly below 270 mμ, thus making it necessary to study azobenzene at wavelengths greater than this. The absorption characteristics of azobenzene established the other wavelength boundaries. In the subsequent discussion, the ultraviolet region means from 275 to 345 mμ, the visible from 365 to 455 mμ.

With trans azobenzene, the results in the ultraviolet and visible differed. In the visible the photostationary state was attained in less than two minutes. Irradiation up to 30 minutes produced no change in the ultraviolet spectrum. Since the concentration of the azobenzene for the ultraviolet study was 0.03 that of the concentration in the visible, the effect of the slight amount of light present during the experiments would be more noticeable. Thus, the rigid solvent may have had the approximate low temperature photostationary state composition before irradiation.

With the 77 % trans azobenzene, the ultraviolet and visible results were identical. In both spectral ranges the photostationary state composition was the same as that attained by irradiation of trans azobenzene.

However, it should be noted that there is a small irregularity in the visible. The spectrum attained by the irradiation of 77 % trans azobenzene (fig. 9) differs somewhat, at the two ends of the curve, from that reached by irradiation of pure trans. The high absorption at 265 mμ is not consistent with the spectra of pure or 77 % trans. The anomalous nature of this one curve is not understood. It may be due to an impurity dissolved from the Epibond by the P.Me.H. during the room temperature irradiation in the low temperature cell.

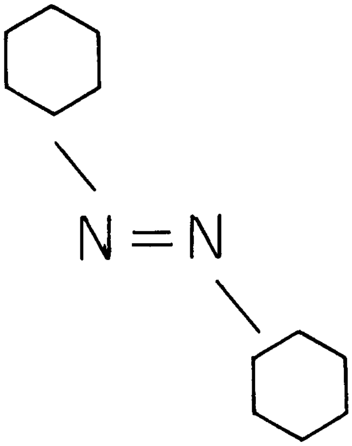
It is assumed that the cis-trans ratio of the 77 % trans azobenzene is the same at 77°K as at room temperature. At the low temperature photostationary state, the azobenzene is estimated to be 98 % trans. This value was obtained by successive approximations using the data of fig. 9. With the solution used for the visible range, the photostationary state was attained between 2 to 6 minutes.

So, the following conclusions can be made about azobenzene in a P.Me.H. rigid solvent at 77°K. Tungsten irradiation of pure trans and 77 % trans azobenzene give the photostationary state values of 98 % trans and 2 % cis. Thus, both the trans to cis and cis to trans photoisomerizations occur in a rigid solvent. The per cent trans in P.Me.H. at the photostationary state shifts from 77 % at room temperature to 98 % at 77°K.

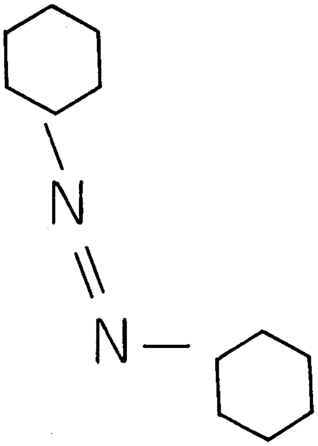
VI. DISCUSSION

The purpose of this work was to see if the photoisomerization of azobenzene occurs in a rigid solvent. As was shown above, it does take place. The other interesting result is that the cis-trans ratio at the photostationary state is lower at 77°K than at room temperature. This trend with lower temperatures is predicted theoretically by Olson's model (12). However, a brief literature search showed no good experimental evidence supporting it. But, it must be born in mind that the change in the cis-trans ratio may also be due to the differences in viscosity of the room temperature and rigid solvents.

Before going further, let us look at the nature of the isomerization. From the usual way in which the cis and trans forms are graphically depicted, it appears as though the benzene molecule flips from one side to the other, over the nitrogen-nitrogen axis. Actually, the benzene segments remain nearly fixed, and one of the nitrogen atoms flips from one position to the other.



Trans



Cis

There are a series of proposed experiments which would give more information on the effect of temperature and viscosity on the cis-trans ratio at the photostationary state. The effect of viscosity could be studied by varying it at 77°K by means of different solvents. A bigger effect could be obtained if one used a liquid solvent. It is very difficult to find a liquid solvent with the necessary properties for such a study.

It would be easier to use a different temperature at which both a fluid and a rigid solvent can be used. Propylene glycol has been used as a rigid solvent at -80°C (13). Azobenzene is soluble enough at room temperature to give this solvent a try. It is proposed that P.Me.H. be used as the fluid solvent. The results of this intermediate temperature study would be compared with the room and low temperature data of this thesis.

There is another way in which the viscosity effect could be studied. As reported by G. N. Lewis et al., stilbene is suitable for low temperature photoisomerization experiments in rigid solvents. With this compound, it is essentially the C-H group that flips in the isomerization. It would be interesting to study the effects of various substituents, in place of the hydrogen, on the photoisomerization in rigid media. Possible substituents would include the halogens, methyl groups, and larger alkyl groups.

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