Chemistry 80 Report II: The $T_1 \leftarrow S_0$ transition of 1-iodonaphthalene at a low concentration

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I. Abstract: An investigation was made of the $T_1 \leftarrow S_0$ transition of 1-iodonaphthalene at a low concentration. It was hoped that evidence could be obtained for this molecule which indicated inter-molecular spin-orbit coupling perturbations between 1-iodonaphthalene molecules. This effect would be evidenced by a decrease in the oscillator strength of this transition with concentration. However, such a decrease was not observed. This experiment was subject to large errors, however, and suggestions for further work are at the end of the report.

II. Introduction: The present work is a continuation of the work reported in "Concentration Dependence of the $T_1 \leftarrow S_0$ Transition in 1-bromonaphthalene: The External Effect of Neighboring Molecules" a Chemistry 80 report of the work done by the author during the summer of 1963. The present work is concerned with the separation of external perturbations from internal perturbations of 1-iodonaphthalene caused by heavy-atom spin-orbit coupling.

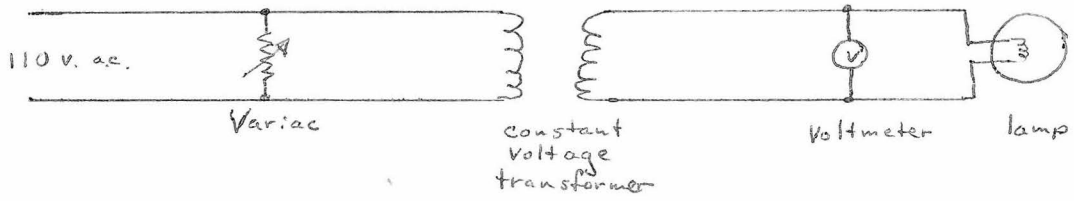
III. Experimental:

A. Chemicals:

1. 1-iodonaphthalene: Eastman White Label (Alumina column purification)
2. Hexane: Matheson, Cole, & Bell spectroquality reagent
3. Nitrogen: Linde Hi purity dry

B. Techniques:

1. Measurement of the $T_1 \leftarrow S_0$ absorption: Absorption spectra of the $T_1 \leftarrow S_0$ transition were measured on a Jarrel- Ash model 82-000 spectrophotometer using a Brown recorder. The light source was a 500 watt tungsten lamp whose intensity was kept constant by using the following circuit:



The voltage to the lamp was kept constant by the transformer. Minor deviations in lamp voltage, detected by the voltmeter, were corrected by variations in the voltage supplied to the transformer by slightly varying the Variac.

The lamp intensity, especially below 3600 Å, had to be kept at a low level to prevent decomposition of the 1-iodonaphthalene while spectra were being taken since this compound decomposes with a fairly high quantum yield at higher energies.[1] Therefore 12 neutral density filters with a transmission of 50% and a neutral density filter with a transmission of 10% were placed between the lamp and the sample. Also a cutoff filter (Corning No. 7380) which cuts off at about 3600 Å and transmits negligibly below 3400 Å was likewise positioned.

The cell used was pyrex with a path length of 62.8 cm. The cell was wrapped in black cloth during the experiment, and the room was darkened except for the lamp used for taking the spectra.

The technique was to first measure the intensity (I) of the light from 5600 Å to 3500 Å after it had passed through the sample. This procedure was carried out for three different runs to determine if the spectra were reproducible. The sample cell was then rinsed thoroughly with solvent (spectroquality hexane) and filled with pure solvent to determine the blank spectra (I_0) for three runs. Therefore the optical density (O.D.) of this solution could be determined.(O.D.= log I_0/I)

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[1] Wilkinson, J. Phys. Chem. , 66, p. 2569-74 (1962)

Naturally ϵ, the absorption coefficient, could be obtained from this data, since:

$$\epsilon = \frac{O.D.}{(c)\ (L)}$$

where c is the concentration in moles/ liter and L is the path length in cm.

2. Concentration determination: To determine the actual concentration of the sample solution, 1.00 ml. of the solution was removed after the $T_1 \leftarrow S_0$ spectra had been taken. This portion of the solution was diluted to 100.0 ml. , and the O.D.'s of 4 peaks of the $S_1 \leftarrow S_0$ transition were measured using 1 cm., matched quartz cells in the Cary 14 recording spectrophotometer. Preliminarily the absorption coefficient, ϵ , of these peaks had been calculated by preparing solutions of known amounts of 1-iodonaphthalene using an analytical balance and measuring the O.D.'s of these peaks using the 1 cm. quartz cells and the Cary 14 spectrophotometer. Plots of concentration vs. O.D. for the 4 peaks of the $S_1 \leftarrow S_0$ transition are shown in Figures 1 and 2. The slopes of these plots give the absorption coefficients for these peaks.

3. Purification technique: The liquid 1-iodonaphthalene was purified by passage through an alumina column and subsequent storage in a brown bottle. After preparation of the 1-iodonaphthalene: hexane solution, the solution was also run through an alumina column into the 62.8 cm. cell. Oxygen was excluded by bubbling N_2 through the cell by means of a capillary tube for more than 8 hours. All steps were done in darkness.

4. Purity check: An attempt to check the purity of the 1-iodonaphthalene was made by running a v.p.c. of 2 microliters of the compound. However, meaningful data could not be obtained using a Loenco, Model 15B, Gas Chromatograph with a 6' Apiezon J column at 210° c and 20 lb. pressure of He.

IV. Discussion: This work, which was aimed at the same theory

as the author's previous work failed to show the hoped for concentration dependence of the $T_1 \leftarrow S_0$ transition in 1-iodonaphthalene as indicated in the results section. As indicated in that section, the possible errors in the experiment tend to indicate that these results are unreliable. It should be pointed out, however, that some of the problems of experimentation, encountered in previous work, were overcome in the present experiments.

For example, since the average error in the spectra of the 3 runs (described in the experimental section) with 1-iodonaphthalene was 0.44%, it is obvous that significant decomposition of the 1-iodonaphthalene does not occur during the period when spectra are being obtained. Therefore, the use of filters described in the experimental section does indeed permit meaningful spectra to be taken of the $T_1 \leftarrow S_0$ transition in 1-iodonaphthalene using these techniques.

V. Results: The results of this work are depicted in Fig. 3. Curve A was the $T_1 \leftarrow S_0$ absorption curve derived for 1-iodonaphthalene at 0.00805 moles/liter in hexane. It should be noted that this curve does exhibit a lower absorption coefficient at longer wavelengths (lower energies) than the pure liquid.

However, as is shown by the error bars for this experiment (due primarily to the fact that a solution with a low optical density was chosen for this study) the errors are rather large and become quite significant near the maximum of this transition. Also, an anomalous effect is noted in that the maximum for the low concentration experiment is actually higher than the high concentration experiment. It seems reasonable that errors in measurement could easily account for the anomalous behavior.

VI. Suggestions for further work: The concentration used was chosen since at this concentration less than 1% of the 1-iodonaphthalene molecules have nearest neighbors of other 1-iodo-

naphthalene molecules. (Assuming 12 nearest neighbors and using the formula:

$$P_N = \frac{N_S!\ \phi^N\ (1 - \phi)^{N_S - N}}{(N_S - N)!\ N!}$$

which gives the probability P_N that N of N_S given sites are occupied by solute molecules if ϕ is the mole fraction of solute.)[2] Although increasing the concentration by a factor of 10 would increse this probability to about 11%, were this tolerable, such an increase in concentration would reduce the errors by a factor of 10 wich would certainly improve the situation.

A better method of getting around these problems would be to increase the path length by using a multiple pass cell, providing that errors were not correspondingly increased. Probably a combination of these techniques with increased purification of the 1-iodonaphthalene should yield trustworthy results.

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[2] G. W. Robinson, J. of Mol. Spectroscopy, 6, (1961), p. 63, (footnote 6)

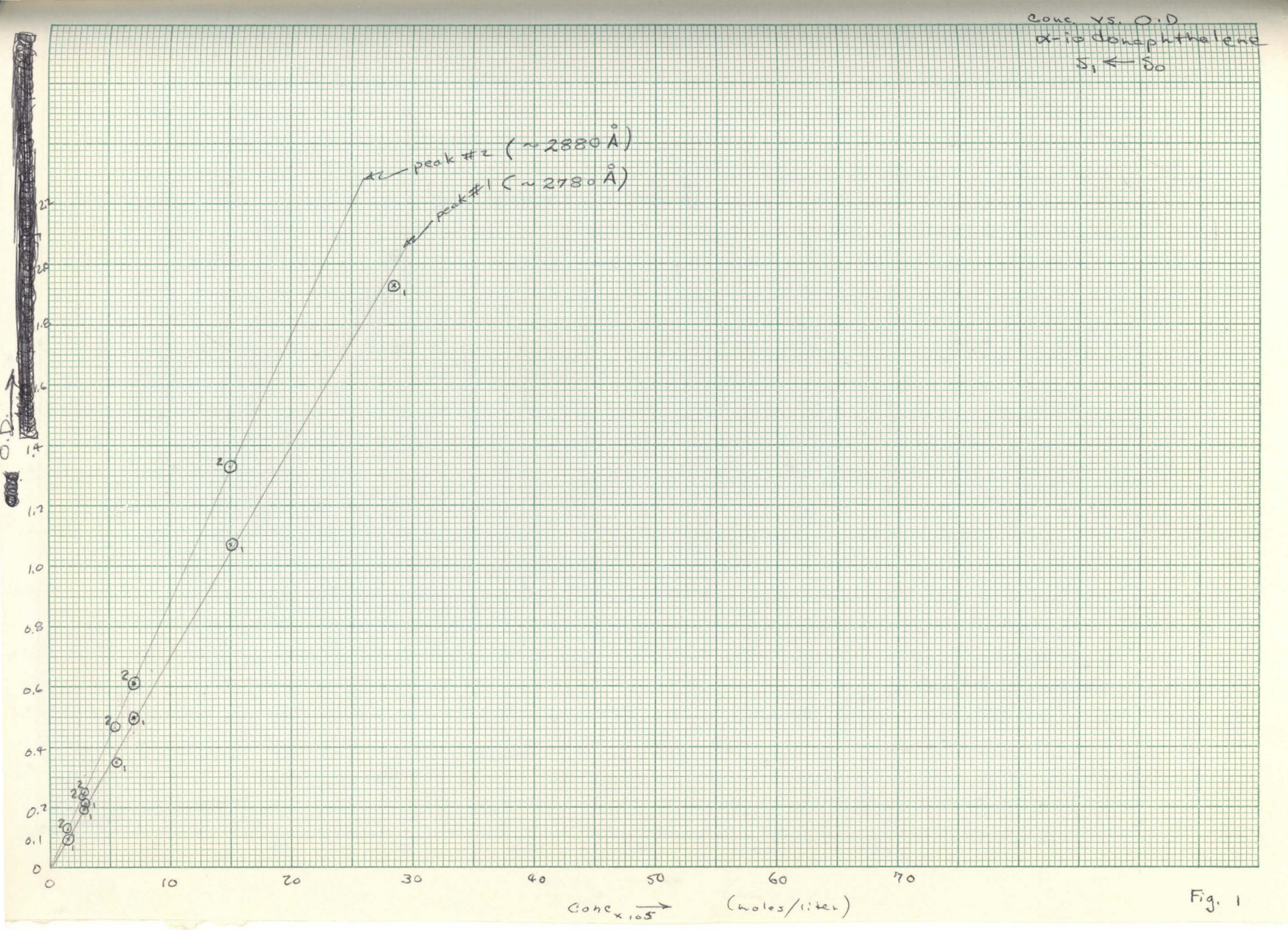
Conc. vs. O.D
α-iodonaphthalene
$S_1 \leftarrow S_0$
peak #2 (~2880 Å)
peak #1 (~2780 Å)
O.D.
Conc. ×10⁵ → (moles/liter)
0
0.1
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
0
10
20
30
40
50
60
70

Fig. 1

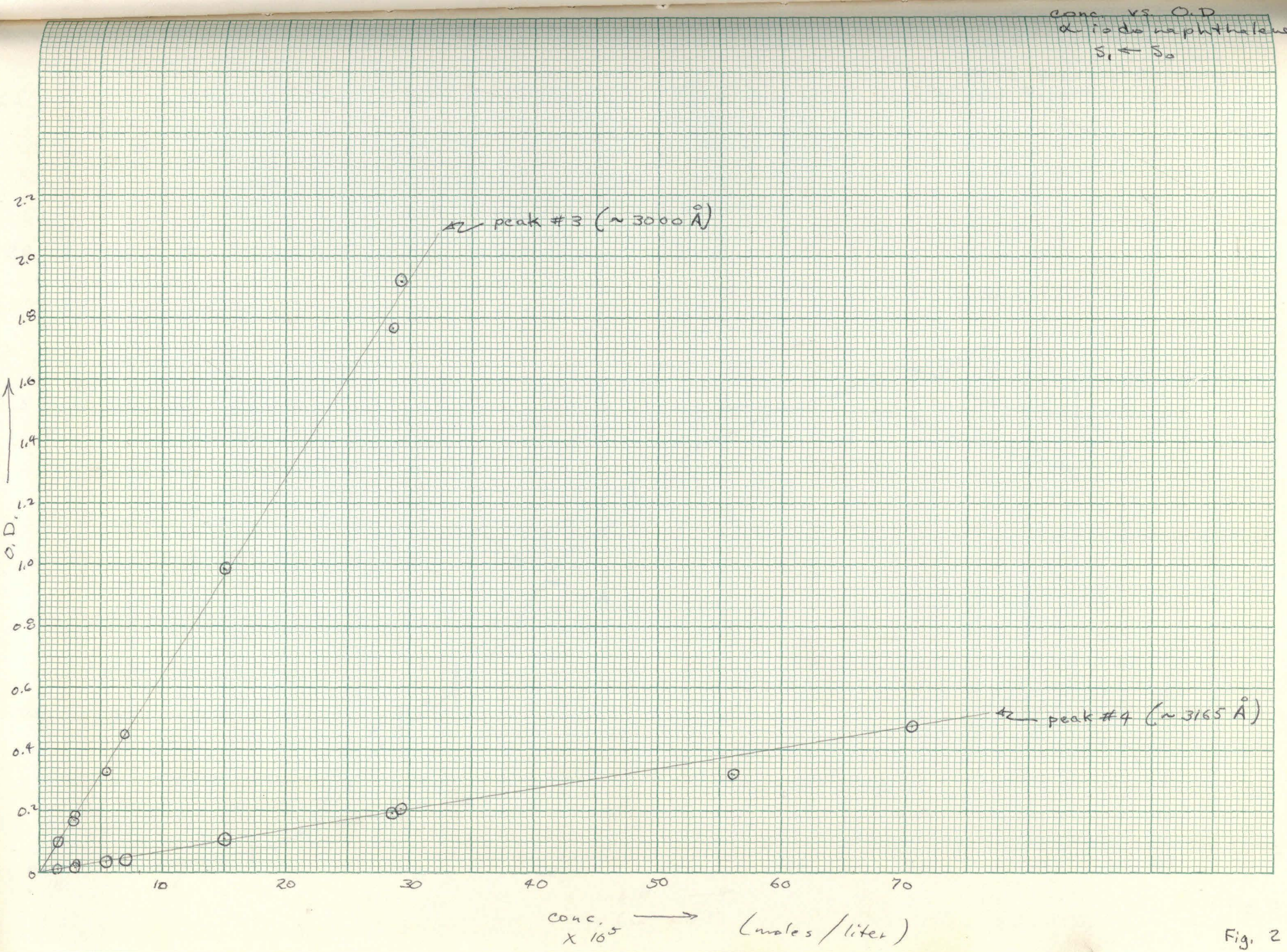
conc. vs. O.D
α iodo naphthalene
$S_1 \leftarrow S_0$
peak #3 (~ 3000 Å)
peak #4 (~ 3165 Å)
O.D
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
10
20
30
40
50
60
70
conc. x 10^5 (moles/liter)

Fig. 2

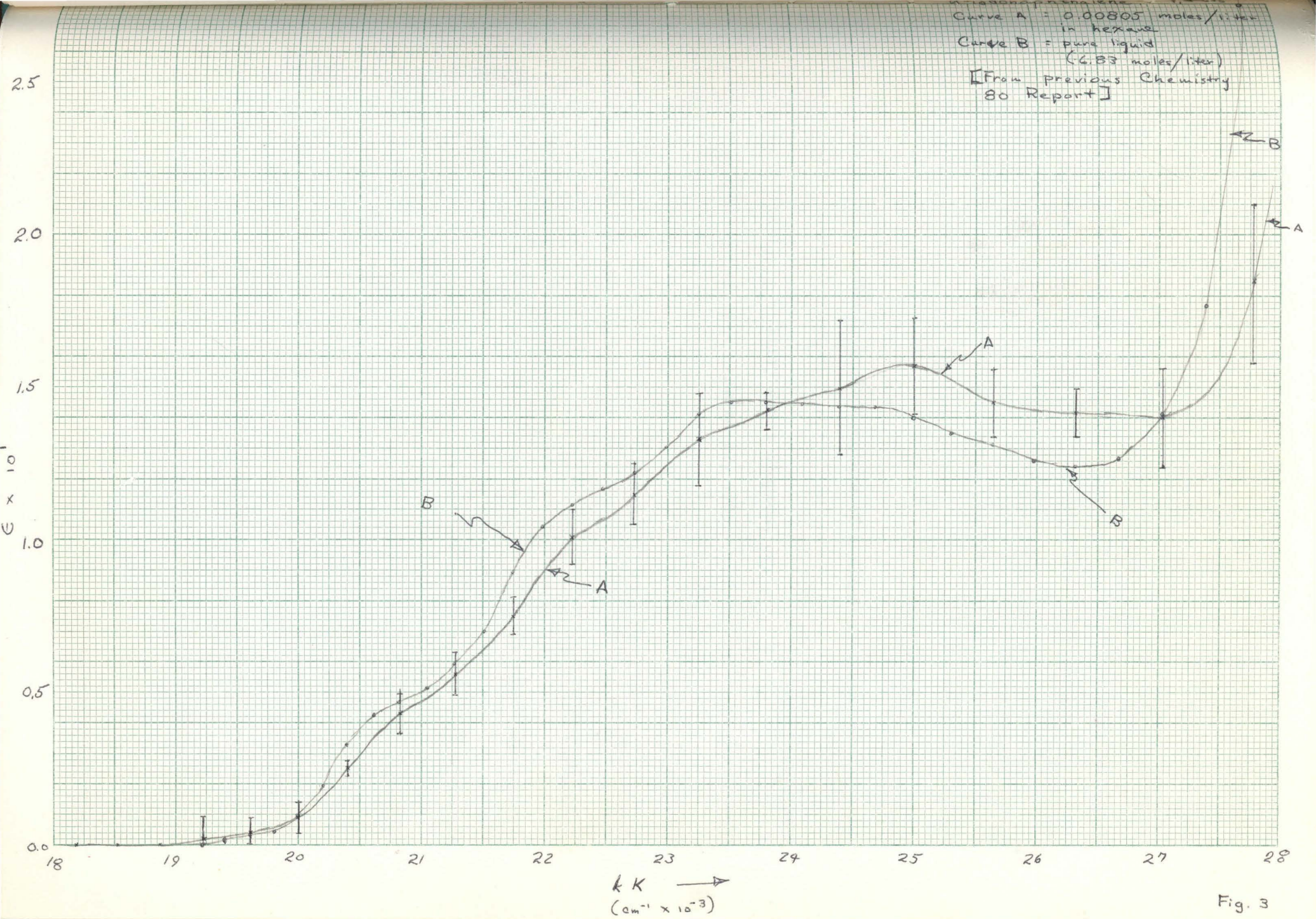
Curve A = 0.00805 moles/liter in hexane
Curve B = pure liquid (6.83 moles/liter)
[From previous Chemistry 80 Report]
2.5
2.0
1.5
1.0
0.5
0.0
18
19
20
21
22
23
24
25
26
27
28
B
A
A
B
B
A
k K
(cm⁻¹ x 10⁻³)

Fig. 3