Concentration Dependence of the $T_1 \leftarrow S_0$ Transition in 1-bromonaphthalene: The External Effect of Neighboring Molecules.

(Chemistry 80 report on work conducted during the summer of 1963)

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Submitted: December 11, 1963

I. Abstract

The absorption coefficient of the lowest $T_1 \leftarrow S_0$ transition of 1-bromonaphthalene is investigated at several different concentrations. It is shown that there is a decrease of oscillator strength as the concentration is decreased indicating that there is an inter-molecular spin-orbit coupling between 1-bromonaphthalene molecules. It is thus indicated that past reports of the strength of the $T_1 \leftarrow S_0$ transition for 1-bromonaphthalene were too high since these reports were based on highly concentrated solutions and did not account for an external heavy atom perturbation between molecules of the same species. Also experiments show that past reports of oscillator strength of $T_1 \leftarrow S_0$ for the pure liquid 1-bromo- and 1-iodonaphthalenes may be too high.

II. Introduction

It has been previously noted that the $T_1 \leftarrow S_o$ transition of organic molecules may be enhanced by the introduction of either paramagnetic substances such as O_2[1] or heavy-atom containing molecules such as alkyl halides[2] and gases like Xe[3]. This paper is primarily concerned with the heavy-atom perturbation: efforts were made to exclude all types of perturbations (except those of an internal, structural nature) from the systems studied.

Heavy-atom (an atom of large atomic number) perturbation is due to increased spin-orbit coupling induced by the field of the heavy-atom nuclei. This perturbation may be either an internal effect caused by a heavy atom which is chemically bonded to the organic molecule or an external effect caused by the presence of a heavy atom in the chemical structure of the neighbors of the organic molecule in question. The nearest neighbors are most likely to cause this external effect and are, in fact, the only probable cause if a collisional nature of the perturbation is accepted. Of course, orientation of the various molecules (i,e. the relative positions of the heavy atoms) should be important.

The concern of this work is the separation of external perturbation effects from internal perturbation effects. A non-perturbing solvent was used to reduce external interactions between 1-bromonaphthalene molecules.

III. Experimental

A. Chemicals:

1. 1-bromonaphthalene: Matheson, Cole, & Bell reagent (Originally used without further purification; passed through an alumina column for final experiments.)
2. 1-iodonaphthalene: Eastman White Label (Alumina column purification.)
3. Hexane: Matheson, Cole, & Bell spectroquality reagent
4. Nitrogen: Matheson, Cole, & Bell prepurified (max. O_2 = 8 ppm.)

B. Techniques:

1. Measurement of the $T_1 \leftarrow S_0$ transition:

   a. Low concentration experiments: 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 a constant voltage transformer. A voltmeter which monitered the output from the transformer indicated if manual adjustments of a Variac leading to the imput to the transformer were necessary.

   The cell used was pyrex with a path length of 62.8 cm. It was determined that lamp intensity could be duplicated over a long period of time far more readily than could two cells of similar dimensions

be accurately matched. The technique was first to measure the intensity(I) of the lamp in the region being studied after the light had passed through the sample cell. The cell was then thoroughly rinsed and filled with pure solvent to determine the "blank" spectra (I_o). From this data the optical density (O.D.) of the sample solution could be determined. (O.D. = $\log I_o/I$)

b) Pure liquid experiments: Absorption spectra of the pure liquid 1-bromo- and 1-iodonaphthalenes in the $T_1 \leftarrow S_o$ region were measured on the Cary 14 recording spectrophotometer using 1 cm., matched quartz cells. The O.D. of these transitions was thus obtained.

c) Treatment of data: All of the data is interpreted in terms of the absorption coefficient, ϵ. The formula is, of course,

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

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

2. Concentration determination: To determine the concentration of the sample solution, a small portion of the solution was taken directly from the 62.8 cm. cell after the $T_1 \leftarrow S_o$ spectra had been taken. This portion of the solution was diluted appropriately and the O.D. of the strong $S_1 \leftarrow S_o$ transition was measured using 1 cm., matched quartz cells in the Cary 14 recording spectrophotometer. A pre-

liminary calibration of this transition in the desired concentration range was made by preparing solutions of known amounts of 1-bromonaphthalene with an analytical balance. The absorption of these solutions, using 1-cm. cells, was used to calibrate the $S_1 \leftarrow S_0$ transition. A similar calibration of the $S_1 \leftarrow S_0$ transition of 1-iodonaphthalene was made but hasn't been used yet.

3. Purification techniques:

a. Procedure A: Oxygen was excluded from the solutions investigated in the $T_1 \leftarrow S_0$ absorption study. This was first accomplished by a process in which first nitrogen was bubbled through the solution, and then the solution was frozen at liquid N_2 temperature. Subsequently the gas over the solution was evacuated. Next the solution was allowed to warm up to room temperature, and hence the hexane boiled off until its vapor pressure at room temperature was reached. Also remaining dissolved gas came off during the thawing of this "freeze-thaw" process. Nitrogen was again bubbled through the solution and the "freeze-thaw" process repeated. The cell was then filled in vacuum with this solution and subsequently cut off and stoppered in a nitrogen atmosphere. The spectra was immediately taken, and the blank prepared as above.

b. Procedure B: The first step here was to purify the pure liquid of 1-halonaphthalene by passage

through an alumina column and subsequently store it in the dark. Solutions of 1-bromonaphthalene were also run through an alumina column into the 62.8 cm. cell and protected from light before their use. Oxygen was excluded in this technique by bubbling N_2 through the cell itself (ten minutes for pure liquid; thirty minutes for low concentration solutions.) In all cases the samples were protected from light until the actual determination of the $T_1 \leftarrow S_0$ transition was measured.

IV. Discussion

The Lambert-Beer law, $\epsilon(\nu) = \frac{O.D.}{(c)(l)}$, is quite easily derived assuming that each molecule has a constant absorption coefficient $a(\nu)$, where $\epsilon(\nu) = \frac{a(\nu)\,N}{(2.303)(1000)}$ and N is Avogadro's number and 2.303 is $\frac{1}{\log e}$. However, the assumption that $a(\nu)$ is a constant is not a valid one if the environment of the molecule under consideration is not identical to that of every other molecule with which it is compared. In many systems $a(\nu)$ does not change significantly with a change in environment, and thus the approximation is generally a good one. However, as has been indicated, the $T_1 \leftarrow S_0$ transition of organic molecules may show a pronounced change in $a(\nu)$ and thus $\epsilon(\nu)$ if paramagnetic[1] or heavy-atom containing molecules[2] are also introduced into the system in varying concentrations with the molecule being studied.

It seems reasonable that in the study of heavy-atom perturbation of 1-halonaphthalenes in high concentration experiments there are at least three different perturbation terms that contribute to the Hamiltonian and thus $a(\nu)$. One must consider first the internal perturbation of the transition by the halogen affixed to the organic molecule itself. Also, of course, one must consider the external perturbation of external heavy atoms. The external heavy-atom perturbation may, however have two sources. It may be due to, for example, another species such as an alkyl halide introduced in the solution.

It may also be due, however, to the presence of another 1-halonaphthalene in the immediate vicinity of the molecule whose $T_1 \leftarrow S_0$ transition is being perturbed. The last of these effects can be established by concentration studies, for the higher the concentration of 1-halonaphthalene in the sample, the greater the magnitude of this effect on $a(\nu)$ and subsequently the higher the apparent absorption coefficient, ϵ. The results indicate such a dependence.

In this study hexane was chosen as a solvent with no heavy atoms to give an external perturbation through spin-orbit coupling.

There are certain other problems in the meaningful measurement of the $T_1 \leftarrow S_0$ transition of 1-halonaphthalenes to determine if there actually is a decrease in the absorption coefficient. The main problem is the fact that the absorption coefficient is quite small for these transitions ($\epsilon = 10^{-1}$ for 1-iodonaphthalene, and $\epsilon = 10^{-2}$ for 1-bromonaphthalene.) In fact it is so small for 1-chloro- and 1-fluoronaphthalene ($\epsilon = 10^{-3}$)[2]. that only the two heavier 1-halonaphthalenes have thus far been considered in the present work. The problem is therefore since ϵ is so small, the measurements of differences in ϵ are even more difficult and are subject to error, these differences being quite small.

To facilitate the observation of these small ϵ and small differences in ϵ, relatively long path lengths were required for the measurements at low concentrations. No available spectrometer was designed to handle such cells, and thus the set-

up explained in the experimental section was devised and used.

Since O_2 must be excluded from the system to prevent paramagnetic perturbations of the $T_1 \leftarrow S_o$ transition, procedures were used to assure its exclusion. The "Procedure A" described in the experimantal section was decided to be the "ideal" method of excluding O_2. However, it was later decided that such a complete procedure was perhaps unnecessary, especially since the vacuum system was quite vulnerable to the strains caused by the "freeze-thaw" process. Procedure B on the other hand was a much easier way of removing O_2 from the samples and was probably sufficient for the work.

Another problem, whose extent was not obvious until several experiments produced results which left much to be desired, was that of purity of the 1-halonaphthalenes. This is certainly a problem since the long path length used would necessarily imply that a very small amount of a high absorbing impurity would cause significant errors in the data. "Procedure B" was devised in the hope of excluding impurities of this nature. It is certainly probable that this helped, however even if all impurities were thus excluded, photodissociation of 1-bromo- and 1-iodonaphthalene during the measurement of $T_1 \leftarrow S_o$ could still change the results significantly.

If more extensive and reliable results were available, it would probably be significant to compare the average number of nearest neighbors containing a heavy atom with the apparent absorption coefficient. Since, however, the results of only

two different concentrations are reliable, such a comparison is impossible.

V. Results

1-bromonaphthalene: The original experiments with this compound were somewhat inconclusive. The method of purification was "Procedure A." Originally, experiments were attempted at a concentration as low as 3.8×10^{-2} moles/ liter. However, this concentration was so low that it was very difficult to measure the O.D. with the path length that was used. Plots of ϵ vs. kK for two other experiments in this category are shown in Fig. 1. One will note that the measurement of the more highly concentrated sample (i.e. Curve B) has a higher absorption coefficient than the other. However, comparison with others work, as plotted in Fig. 2, shows that both of these samples probably were contaminated since the very highly concentrated experiments shown in Fig. 2 have an absorption coefficient in some cases even smaller than these low concentration experiments. In all cases the sharp rise in absorption at higher kK is due to the tail of the $S_1 \leftarrow S_0$ transition.

Subsequent experiments using "Procedure B" for purification of the 1-bromonaphthalene proved to be more useful. These are given in Fig. 3. One will note that there is a reasonable correlation between the pure liquid curve and Evan's data (2.5 moles/ liter) as far as it goes. It is possible that the data of McGlynn et. al. is subject to error due to impurities. Also, however, the results of Fig. 3 are quite significant in that they show the predicted decrease of oscillator strength with

concentration. Curve A (0.1319 moles/ liter) indicates an absorption coefficient less than any previously found.

Thus it is probable that the effect originally reasoned does in fact exist. The only possible error that could cause such an experimental phenonmenon, other than something quite unreasonable, would be an error in the concentration determination. It is possible that some impurity absorbs very strongly in the $S_1 \leftarrow S_0$ region and not in the $T_1 \leftarrow S_0$ region. However, such a possibility is not very likely since it would have to be a quite large impurity to produce this effect. Also the actual calculations of the concentration from the O.D. and ϵ, of the $S_1 \leftarrow S_0$ transition, since the concentration was determined from 9 different bands of the $S_1 \leftarrow S_0$ transition over the region of 2600-3200 $\mathring{A}$ and were averaged, were quite accurate. Also the standard deviation of this concentration calculation was 0.0008 moles/liter, or an error of less than 1%. These facts indicate that the concentration determination was not subject to the aforementioned error.

1-iodonaphthalene: Fig. 4 illustrates the preliminary data on 1-iodonaphthalene. It is noted that the absorption coefficient of the pure liquid of this compound is lower than previously reported when "Procedure B" was used for purification. Also an experiment conducted at a low concentration similar to those conducted with 1-bromonaphthalene indicated that the compound photodissociated while the $T_1 \leftarrow S_0$ transition was being measured, and hence a better technique is needed.

VI. Conclusion

Although initial experiments indicated an oscillator strength too high, the evidence derived using more careful techniques of purification indicates that there is an external perturbation effect on the oscillator strength of the $T_1 \leftarrow S_0$ transition of 1-bromonaphthalene due to concentration effects. With better methods of purification as suggested in this paper, it is hoped that further experiments will indicate an absolute value of f, without external perturbation, for the 1-halonaphthalenes.

VII. Acknowledgements

The author would like to thank Dr. G. W. Robinson for suggesting this problem and his further suggestions and encouragement throughout the course of the work. Several of his students also provided helpful advice, especially Mr. R. P. Frosch. The author would like to thank Dr. R. M. Badger for loaning the Jarrel-Ash spectrophotometer and suggesting ways of solving problems of instrumentation.

VIII. References

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2. S. P. McGlynn, R. Sunseri, and N. Christodouleas; Journal of Chemical Physics, 37, pp. 1818 - 1824 (1962)
3. A. Grabowska, Spectrochimica ACTA, 19, pp. 307 - 313 (1963)

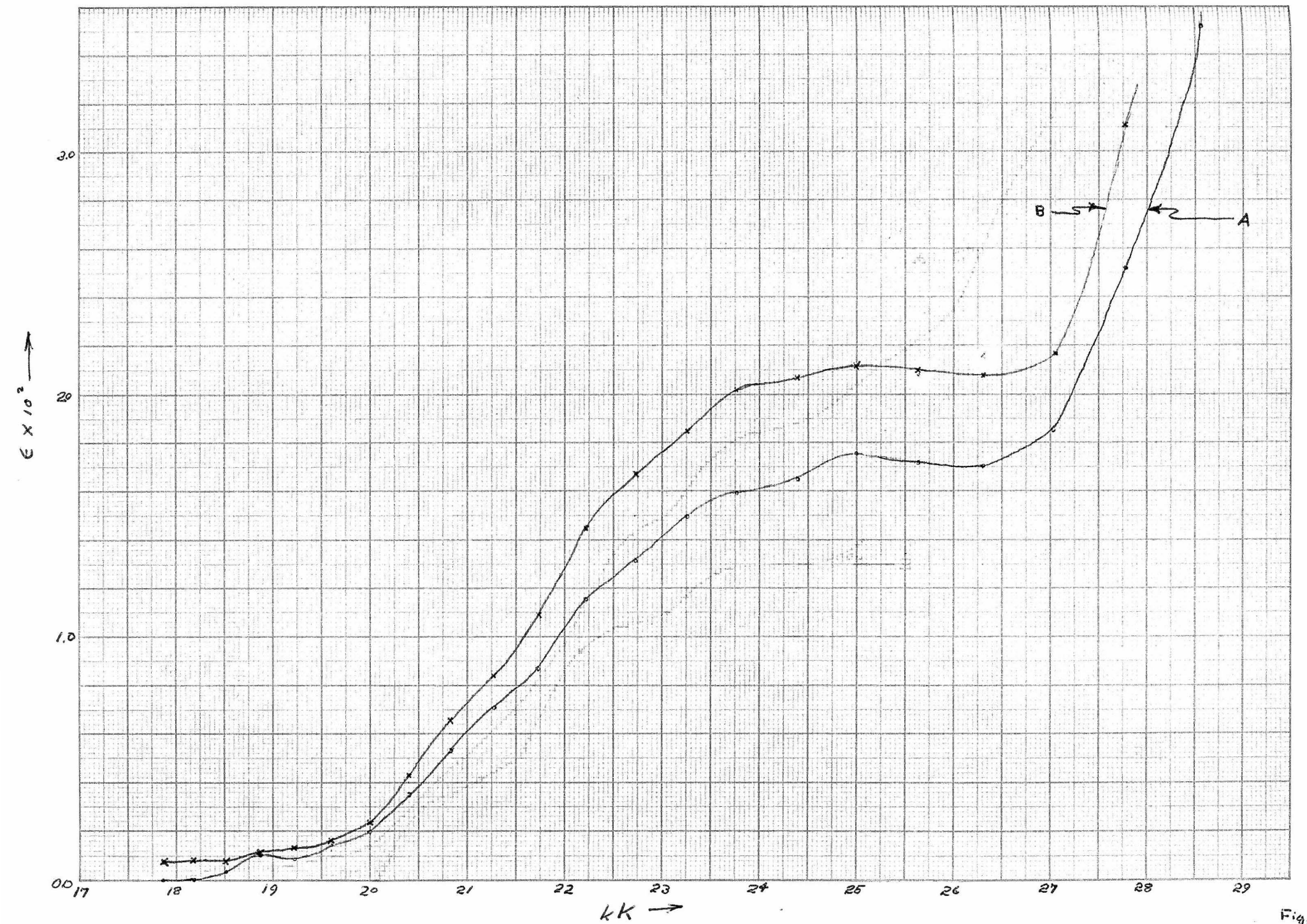

Fig. 1

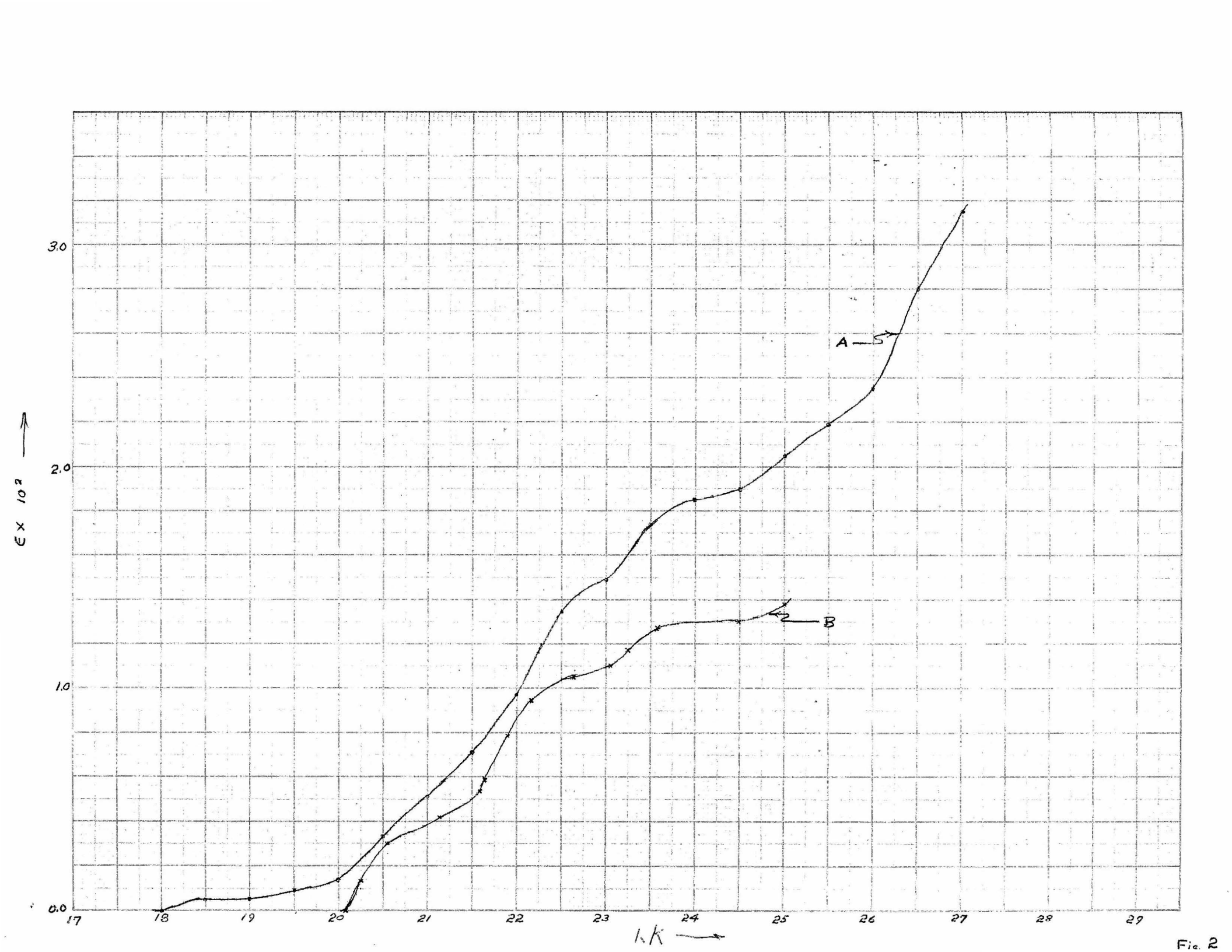

Fig. 2

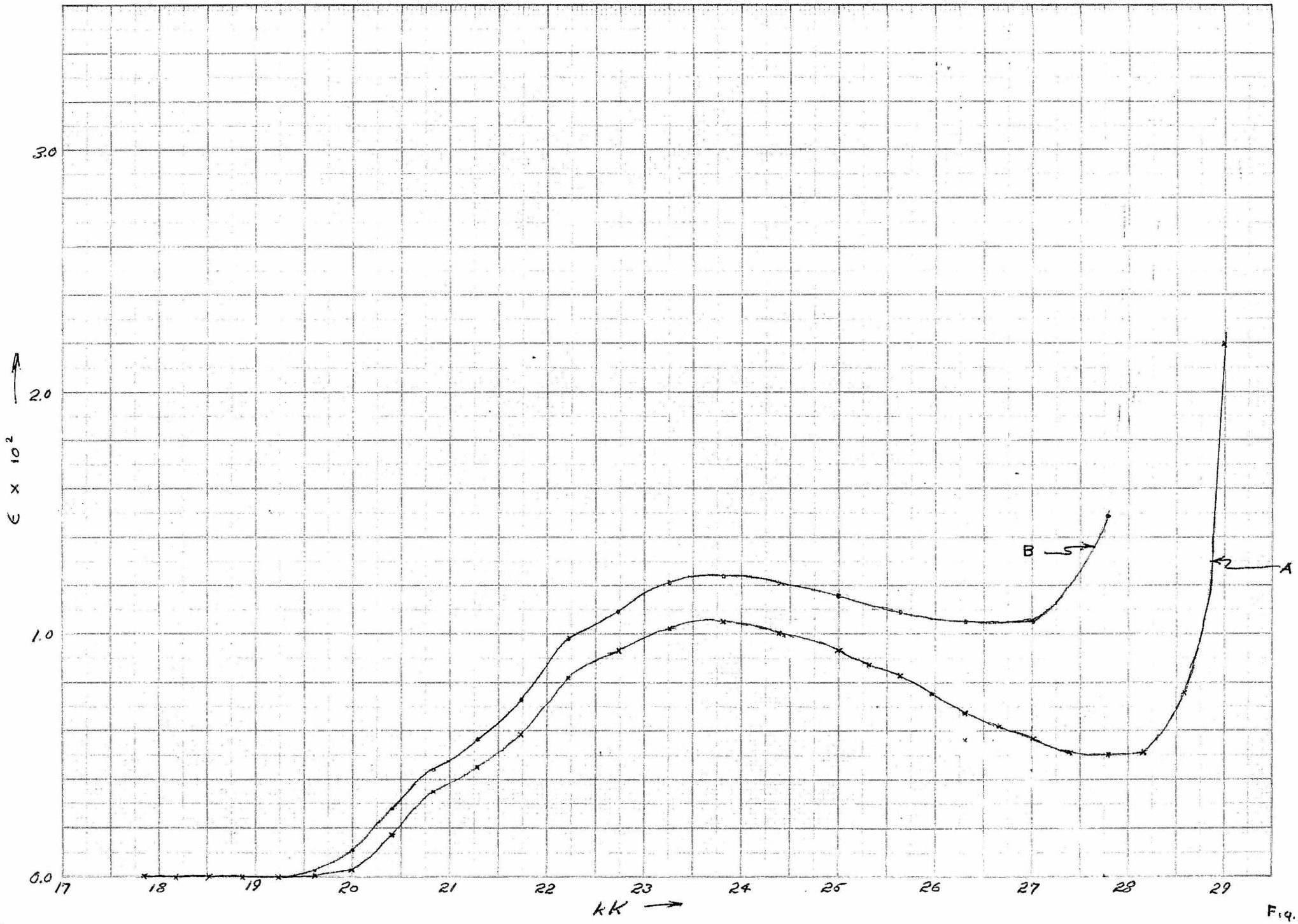

Fig. 3

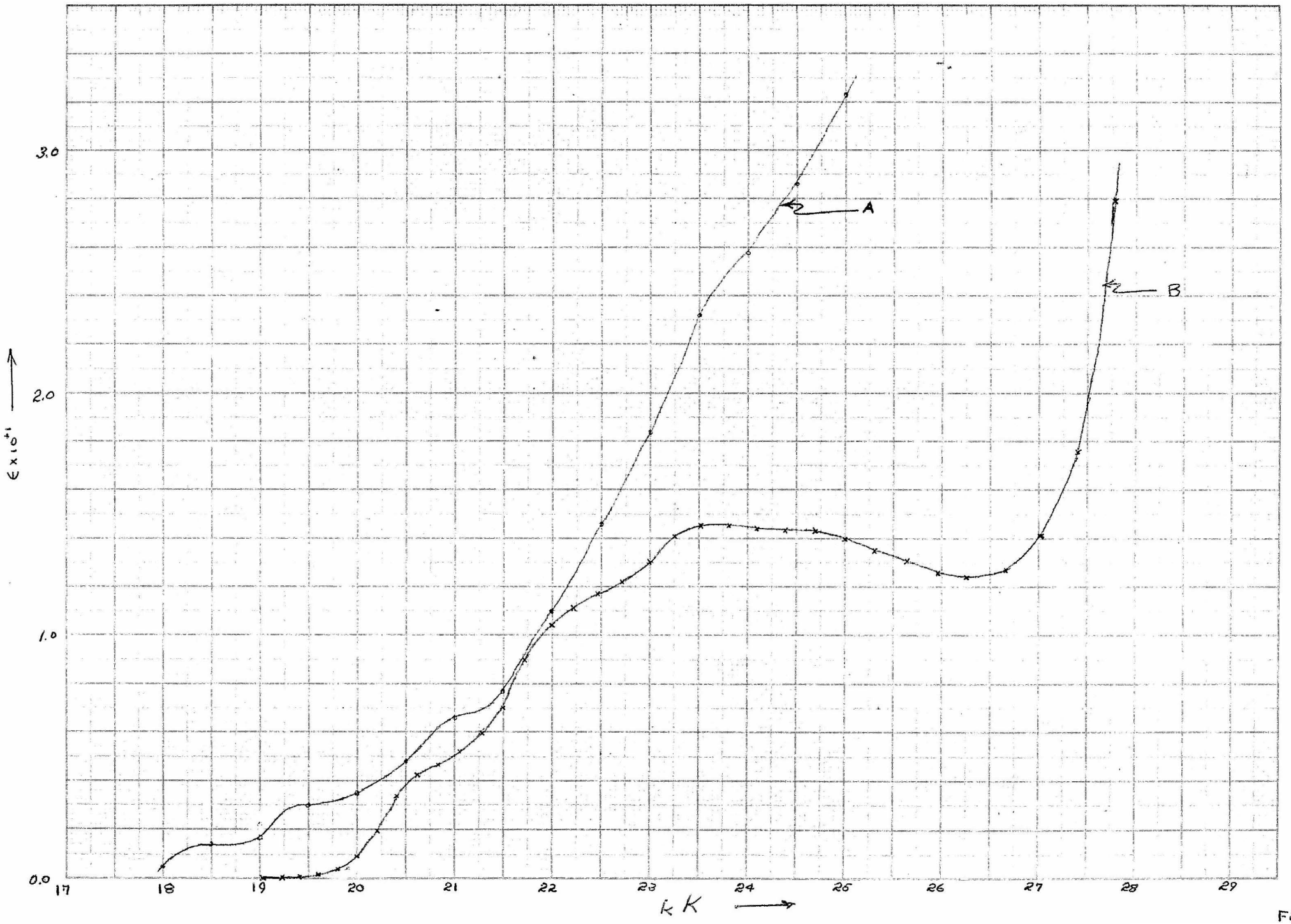

Fig. 4

Key to Figures

In all figures the abscissa is in kiloKaysers ($cm.^{-1} \times 10^{-3}$), and the ordinate is the absorption coefficient, ϵ, as explained in the introduction.

Fig. 1: Curve A: 1-bromonaphthalene in hexane (0.0866 moles/ liter)

Curve B: 1-bromonaphthalene in hexane (0.1507 moles/ liter)

The 1-bromonaphthalene used for these experiments was purified by "Procedure A."

Fig. 2: Curve A: 1-bromonaphthelene (pure liquid = 7.25 moles/ liter) Taken from: McGlynn, Sunseri, and Christodouleas; J. Chem. Phys., 37, p. 1823, (1962)

Curve B: 1-bromonaphthalene in chloroform, no O_2 (2.5 moles/liter) Taken from: Evans, J. Chem. Soc., 1957, p. 1354

Fig. 3: Curve A: 1-bromonaphthalene in hexane (0.1319 moles/ liter)

Curve B: 1-bromonaphthalene (pure liquid = 7.25 moles/liter)

The 1-bromonaphthalene used for these experiments was purified by "Procedure B."

Fig. 4: Curve A: 1-iodonaphthalene (pure liquid = 6.83 moles/liter) Taken from: McGlynn, Sunseri, and Christodouleas; J. Chem. Phys., 37, p. 1823, (1962)

Curve B: 1-iodonaphthalene (pure liquid = 6.83 moles/liter) The 1-iodonaphthalene for this experiment was prepared by "Procedure B."