

TEMPERATURE AND ENVIRONMENTAL EFFECTS ON THE PHOSPHORESCENCE
OF PYRAZINE, BENZOTRIFLUORIDE, AND BENZOTRICHLORIDE

by

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Chapter I

INTRODUCTION

The temperature dependence of the phosphorescence lifetime has been investigated for pyrazine, benzotrifluoride, and benzotrichloride. The dependence of the phosphorescence lifetime on emission wavelength for pyrazine and benzotrifluoride has been investigated. Lifetimes were measured from 77°K to approximately 150°K. The specific studies made were on the following samples: pyrazine in cyclohexane for slow and fast frozen samples, benzotrifluoride in methylcyclohexane for crystalline and glassy samples, and benzotrichloride in methylcyclohexane. A strong temperature dependence of the phosphorescence lifetime is observed for the pyrazine and benzotrichloride samples while a considerably weaker temperature effect is seen for benzotrifluoride.

Numerous investigations have shown that the phosphorescence lifetime of many molecules displays temperature dependence. Nieman¹ has stated that only the phosphorescence lifetimes of single ring aromatic molecules display strong temperature effects. Kilmer and Spangler² studied this dependence for benzene-h₆, benzene-d₆, and toluene in various polycrystalline solvents. Kilmer³ also made preliminary investigations of the temperature dependence of the phosphorescence of pyrazine in cyclohexane as well as environmental effects on the phosphorescence lifetimes of benzene in cyclohexane.

The studies reported in this thesis were originally designed to be part of an investigation of the effect on the temperature dependence of

the phosphorescence lifetime of single ring aromatic molecules with atoms other than C, H, and O present. A systematic study of molecules containing so called "heavy" atoms was to have been made. Further work is needed in continuing these studies.

Spangler and Sponer⁴ have investigated the effects of the two crystal forms of cyclohexane on the spectra of benzene. In the experiments discussed here, the phosphorescence lifetimes of pyrazine in cyclohexane and of benzonitrile in methylcyclohexane are measured as a function of temperature. Environmental effects due to the two crystal phases of cyclohexane are observed. These two crystal phases were made by slow freezing or fast freezing the samples, as discussed in Chapter III. Upon freezing, methylcyclohexane is glassy. Upon annealing, the sample could be made to go to a polycrystalline form. The effects of benzonitrile in both types of environment were studied. The temperature dependence of the phosphorescence lifetimes of benzonitrile was also studied.

The solvents used in these experiments were chosen in such a way that their geometry was similar to that of the molecules under study. In this way it was felt that the molecules would occupy unique sites in the mixed crystals.

Chapter II

THEORY

The subject of this thesis is the study of the effects of environment and temperature on the fluorescence and phosphorescence of pyrazine, benzotirfluorine, and benzotrichlorine. In order to understand the basic ideas, or general description of the absorption and emission of these molecules is needed. However, no detailed group theoretical presentation of the vibronic states of the molecules is made.

ELECTRONIC STATES

Aromated ring molecules of the type under consideration generally share the same type of absorption and emission characteristics. A generalized energy level diagram is presented in Fig. 1. Transitions between S_0 and S_1 and between S_0 and T_1 are observed. For benzotirfluoride the S_0 - S_1 energy difference is approximately 37500 cm^{-1} or 4.65 eV while the S_0 - T_1 energy difference is approximately 29200 cm^{-1} or 3.63 eV . In our experiments, the molecules under discussion are assumed to be

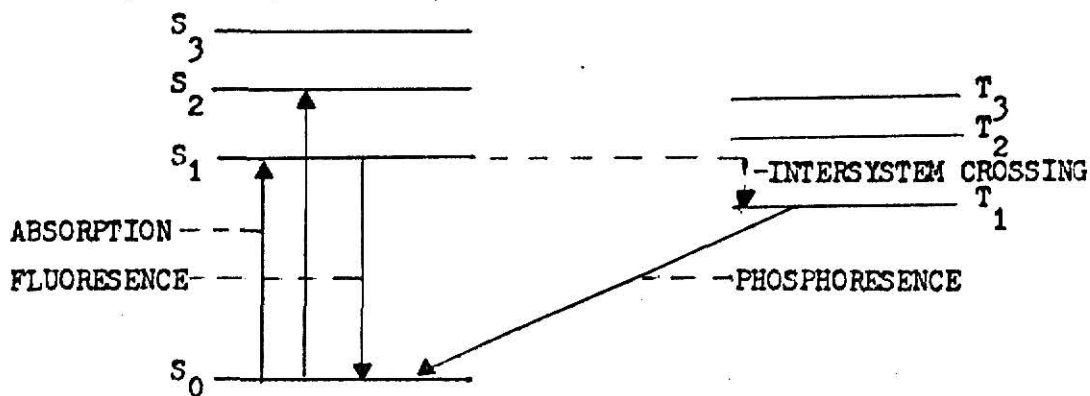


Fig. 1

distributed as guests in low concentration into the lattice of some other host molecules. For all host molecules used in our experiments, the first excited states are well above the guest excited states and are not directly involved in the processes being studied.

Because the atoms of the molecules are held together much more strongly than the van der Waals forces holding molecules together in the crystal, we are able to use, in first approximation, the molecular wave functions. Then, the guest molecules retain most of their free molecular properties, and the environmental influences are treated as perturbations on the free molecules. Thus, the guest molecule is treated in the regular way, applying the Born-Oppenheimer approximation to separate the electronic and nuclear components of the wavefunction. A good reference is Born and Huang⁵.

The type of molecule under discussion generally has an even number of electrons so that the total electron spin is an integral amount of angular momentum. Values of spin greater than one are not normally encountered. If the spin is zero, the state is called a singlet. If the spin is one, the state is called a triplet. In general, the energy difference (3-5 eV) between the ground state, a singlet state, and the first excited singlet state is such that absorption occurs in the ultraviolet. Transitions from a pure singlet to a pure triplet are forbidden and are generally not observed. However, it is possible for the triplet state to become populated. An excited singlet state may be spin-orbit coupled to the triplet state. This allows a non-radiative intersystem crossing to occur. Since a transition from the triplet to the singlet ground state is spin forbidden, the depopulation is very slow

and lifetimes on the order of seconds may be observed.

VIBRONIC STATES

As a result of the Born-Oppenheimer approximation, the nuclear component of the wave function gives the vibrational motion of the molecules. Associate with each electronic state is then a vibrational manifold. The energy of the vibrational states is of the order of 100 cm^{-1} to 3000 cm^{-1} or from $1.2 \times 10^{-2}\text{ eV}$ to $3.7 \times 10^{-1}\text{ eV}$. By using infrared, Raman, and the near ultraviolet spectra, it is possible to study in great detail the vibrational states associated with the electronic states.

JABLONSKI DIAGRAM

Figure 2 shows the electronic and vibrational energy level scheme for the molecules we are working with. The Boltzmann factor times the absolute temperature gives the approximate thermal energy of a particle at that temperature. At 77°K this gives an energy of approximately $6.6 \times 10^{-3}\text{ eV}$ or approximately 55 cm^{-1} . Thus, the molecules are generally in the lowest vibrational level of the ground state. When the molecule absorbs energy, it is excited to a higher electronic state and usually to a vibrationally excited state. Since the transition probability of excitation to the S_1 state from the S_0 state is on the order of 10^6 times that of transition to the T_1 state, the absorption is almost always S_0 to S_1 . Any vibrational energy which the excited state has will be lost to the host crystal within approximately 10^{-12} seconds. This vibrational relaxation is called internal conversion or Stokes' losses. At this

EXPLANATION OF FIGURE II

An energy level diagram for a mixed crystal showing the processes and their assigned rate constants.

k_f = transition probability per unit time for a fluorescence transition

k_{qr} = transition probability per unit time for a radiationless transition from $S_1 \rightarrow S_0$

k_{isc} = transition probability per unit time for intersystem crossing from $S_1 \rightarrow T_1$

k_p = transition probability per unit time for a phosphorescence transition

k_{qp} = transition probability per unit time for a radiationless transition from $T_1 \rightarrow S_0$

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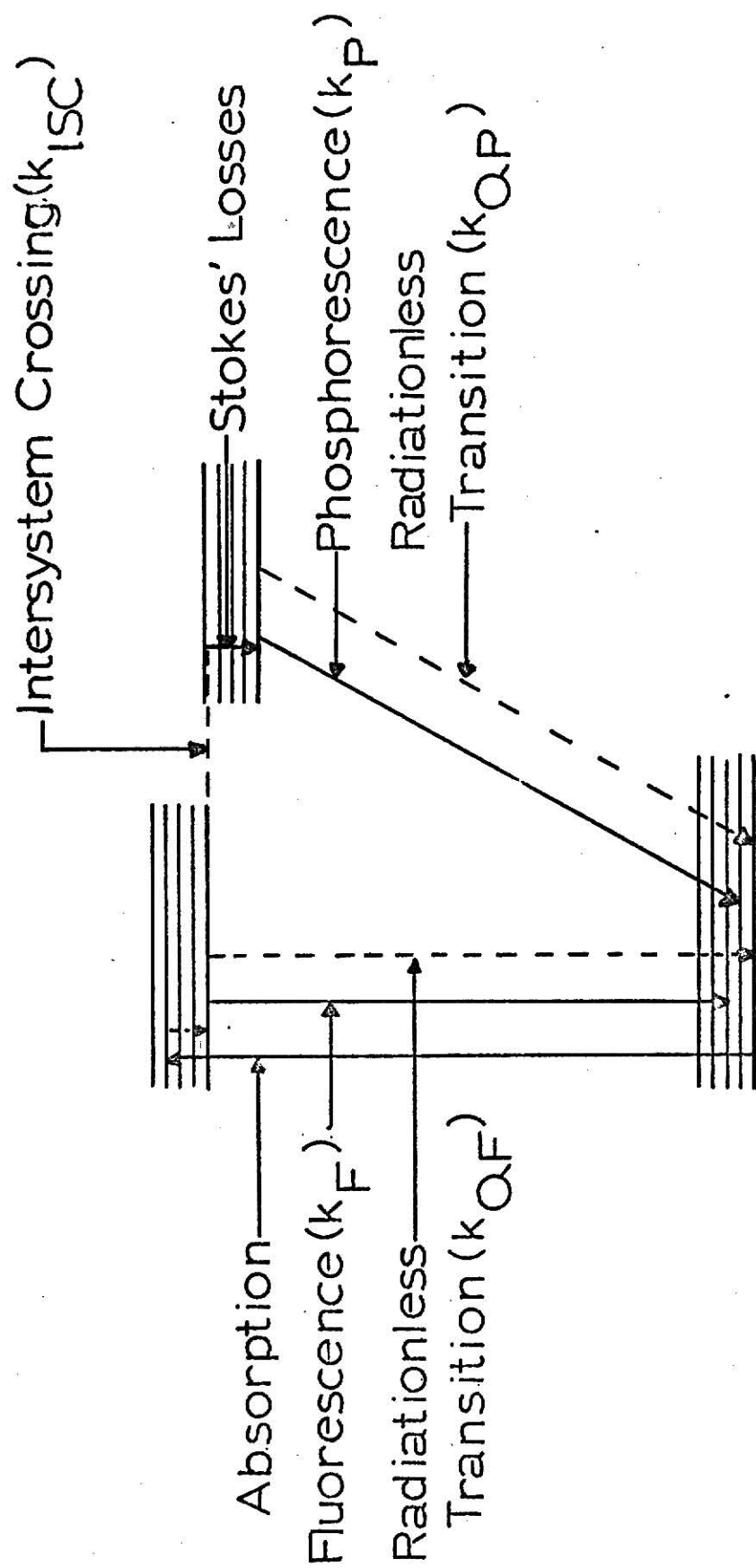


Figure II

point, the energy may go any of three routes: (1) fluorescence occurs if the S_1 state decays to the S_0 state by emitting a photon; (2) a radiationless transition occurs if the S_1 state decays to the S_0 state without emitting a photon; and (3) intersystem conversion occurs if the molecules spin changes from zero to one, at which time the molecule would be in the triplet manifold. Once the molecule gets into the triplet state, one of two paths may be taken: (1) phosphorescence occurs if the molecule decays to the ground state by emitting a photon; (2) a radiationless transition occurs if the spin changes from one to zero and no photon is emitted. The lifetime of the phosphorescence decay is long since the transition from the T_1 to the S_0 state is spin forbidden.

ENVIRONMENTAL EFFECTS

In general, placing a molecule of the type which we are discussing in a solvent shifts the spectrum to the red an amount on the order of $200\text{--}400\text{ cm}^{-1}$ when compared to the gaseous state. This is approximately $2.4 \times 10^{-2}\text{ eV}$ to $4.8 \times 10^{-2}\text{ eV}$. The total energy of the electronic transitions is on the order of 10^3 times greater than this shift. The vibrational spectrum is affected very little except for the overall shift. The amount of the shift is a function of the chemical nature of the solute and the crystal form of the solvent. Cyclohexane has two known crystal forms. A solid-solid phase change occurs at 186°K . Kilmer³ showed that for benzene in cyclohexane the low temperature phase has a slightly larger shift than the high temperature phase. When methylcyclohexane is frozen, one usually gets a glassy phase. Upon annealing, the sample can be made

to go to a crystalline phase. It would be expected that the spectra of benzotrifluoride in methylcyclohexane would be shifted by different amounts for each of these samples. Again, it should be emphasized, that the vibrational frequencies are not generally affected by the shift to the red of a few 10^{-2} eV.

It is observed in a wide variety of molecules that the low pressure gaseous spectra yield quite sharp vibrational spectra. In general, phosphorescence is not observed since collisional quenching of the long-lived triplet occurs. If the molecules are placed in a liquid environment, the vibrational spectra are not as sharp as that from the gaseous state and phosphorescence is still, in general, not observed. If one places the molecule in a rigid glass, where the molecules are randomly arranged, one sees a broad vibrational spectra and, in addition, phosphorescence can occur. If the molecules are now placed in a crystalline matrix, the spectra are quite sharp and many molecules display phosphorescence. Several investigators have reported a temperature dependence of the phosphorescence lifetime for molecules in solid matrices. There is little agreement as to the basic causes, although several theories have been advanced. These are discussed in some detail by Kilmer³.

Chapter III

EXPERIMENTAL

SAMPLES AND PREPARATION

Pyrazine ($C_4H_4N_2$), benzonitrile (C_6H_5CN), and benzotrichloride ($C_6H_5CCl_3$) were used in these experiments. The pyrazine, obtained from the Aldrich Chemical Company, was puriss grade. The cyclohexane was Matheson, Coleman and Bell spectroquality; the methylcyclohexane was Eastman spectrograde. The benzonitrile was obtained from PCR Incorporated, and the benzotrichloride from Matheson, Coleman, and Bell. All compounds except the benzonitrile were used without further purification. Exponential decays were obtained for these compounds, so it is felt that no interfering impurities were present. The purity of the benzotrichloride was checked by gas chromatography. A trace of $C_6H_5CHCl_2$ was indicated. Benzonitrile was distilled twice. The middle third of each distillation was retained. Decays using this benzonitrile were exponential. All samples were approximately .01 Molar solution and prepared the day of use. Cyclohexane was used as a solvent for pyrazine; methylcyclohexane was used as a solvent for benzonitrile and benzotrichloride. These solvents were chosen in order to insure with high probability that the solutes occupied unique substitutional sites. Since the spectra were sharp (except for the glassy phase of methylcyclohexane), it is fairly certain that this occurred.

Cyclohexane has a low temperature and a high temperature crystal form. Spangler and Sponer⁴ have shown that the spectra of benzene in

cyclohexane have different shifts for the two phases. The high temperature phase was prepared by quickly submerging the sample in a liquid nitrogen bath. The low temperature phase was prepared by placing the liquid sample several inches above a liquid nitrogen reservoir. After solidifying, the sample slowly cooled to liquid nitrogen temperature, resulting in a mixed crystal of cyclohexane in the low temperature phase. The spectra of all low temperature crystal phase sample prepared in this manner showed that some of the high temperature phase was also present. This was contrary to the case of benzene in cyclohexane, where Kilmer³ found that almost all samples froze readily into the low temperature crystal phase.

Methylcyclohexane has a glassy and a crystalline form. Glassy samples of benzotrifluoride in methylcyclohexane were normally formed when the samples were cooled to liquid nitrogen temperature. By careful annealing, the sample could be made to go into a crystalline form. Samples of benzotrichloride in methylcyclohexane were prepared by immersion in liquid nitrogen.

EXPERIMENTAL SET UP

A block diagram of the experimental set up is shown in Plate I. Plate II is a diagram of the optical system. Kilmer³ has described the experimental arrangements in detail. A Hanovia S38C9 900 watt Xe high pressure DC arc lamp was used as a light source. Light from the lamp was focused onto the entrance slit of a Bausch and Lomb quartz prism monochromator. The monochromator was adjusted to allow a 200 Å band pass at approximately 2600 Å. A mechanical shutter was used to shut off the illumination from the sample. For the benzotrifluoride and

EXPLANATION OF PLATE I

A block diagram of the experimental set up.

UV - ultraviolet light source

M - monochromator

F - filter

PM - photomultiplier

HV - high voltage power supply

A - picoammeter

TC - temperature controller

OSC - oscilloscope

C - camera

R - recorder

DVM - digital volt meter

P - digital printer

CR - cryostat

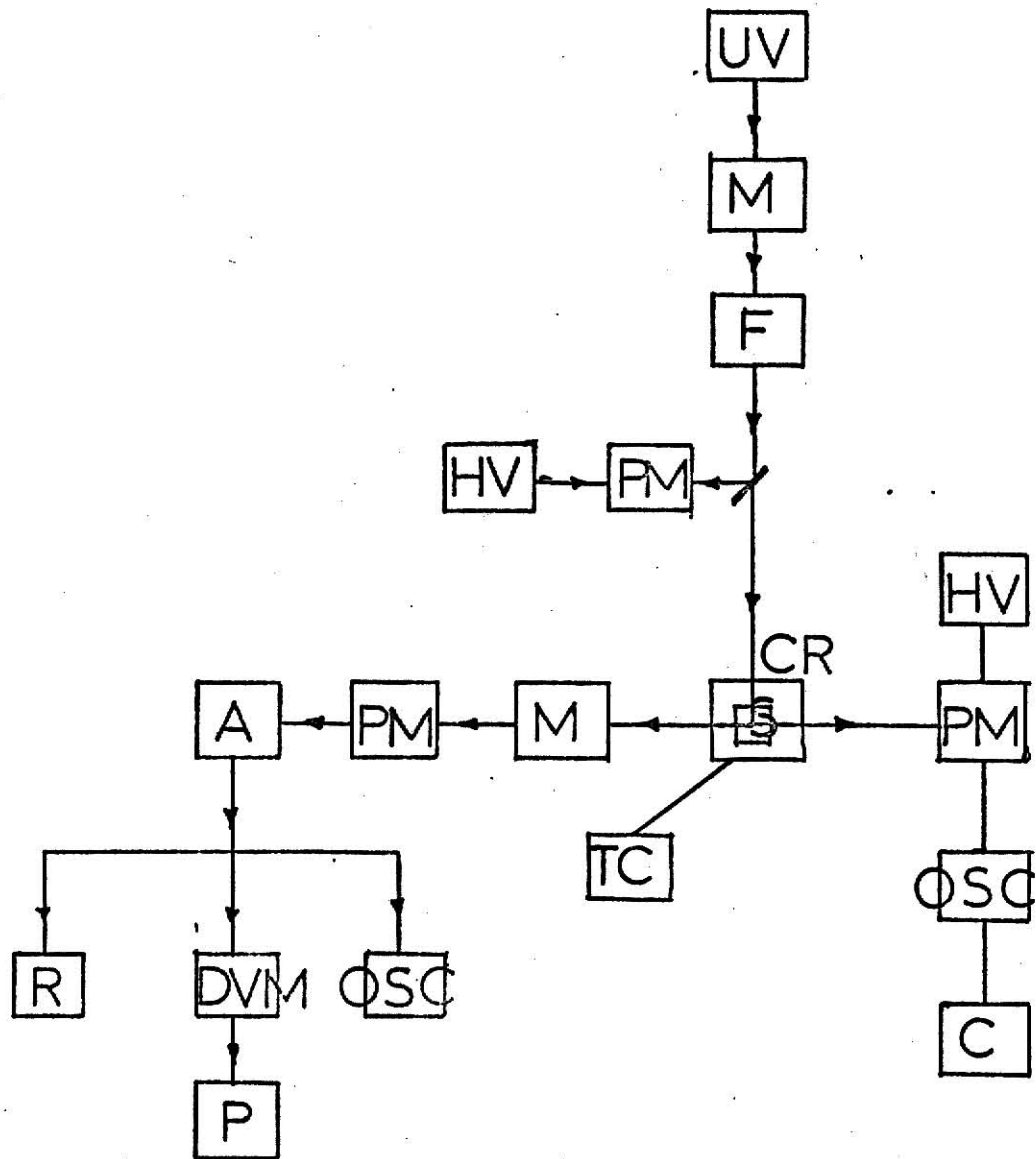
S - sample

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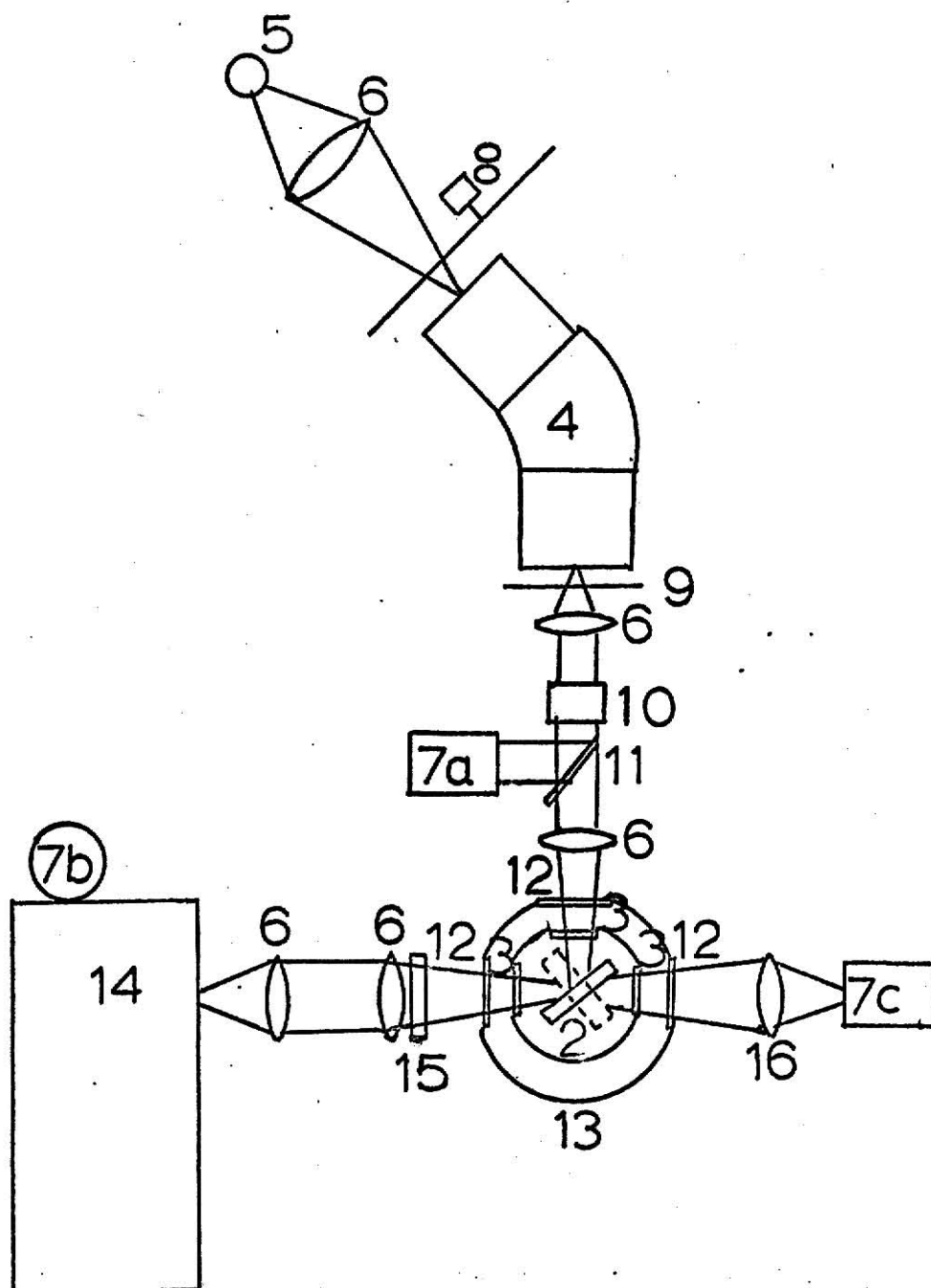
PLATE I



EXPLANATION OF PLATE II

1. Setting A of the sample holder.
2. Setting B of the sample holder.
3. Sapphire windows.
4. Bausch and Lomb small quartz prism monochromator.
5. Hanovia 53809 900-watt Xe DC high pressure arc lamp.
6. Quartz lenses.
7. 1P28 photomultiplier tubes. (b) and (c) were used to record lifetimes and spectra as described in the text; (a) was used to monitor the source intensity.
8. Chopper (used for measurements of phosphorescence lifetimes smaller than 0.1 sec).
9. Fast mechanical shutter.
10. 5-cm quartz cell filled with an aqueous solution of 24.0 g/liter $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 4.5 g/liter $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$.
11. Quartz plate.
12. Quartz windows.
13. Dewar tail.
14. Bausch and Lomb 0.5 m grating monochromator.
15. Corning CS 7-54 (9869) filter, used when recording fluorescence spectra.
16. Glass lens.

PLATE II



benzotrichloride samples, a manual shutter was sufficient. For the pyrazine samples a rotating wheel sector driven by an AC motor served as the shutter. Using a variac, the speed of the motor could be adjusted until the intensity decay would fall to approximately 1/4 of the initial value. A light sensitive diode was used to synchronize the oscilloscope and the shutter.

A Janis Research Company cryostat with temperature controller was used. The sample was located in an exchange gas which was in thermal contact with the liquid nitrogen surface.

Light emitted from the sample was focused using quartz lenses onto the entrance slit of a half meter Bausch and Lomb grating monochromator. A 1P28 photomultiplier was mounted at the exit slit. The PM was operated at 1000 V using a John Fluke 413C high voltage power supply. A Keithley 407 high speed picoammeter measured the output current from the PM. The output from the picoammeter was connected to an oscilloscope and a digital voltmeter. A Tektronix 561A oscilloscope along with a Hewlett Packard oscilloscope camera using Polaroid film were used to photograph traces of the decays. The digital voltmeter was a Beckman Model 4014. It was connected to a Computer Measurements Company digital printer in order to get a printout of the intensity decay.

PROCEDURES

Initially, the dewar was cooled and filled with liquid nitrogen. The sample chamber was filled to one atmosphere of pressure with gaseous helium. The prepared sample on the sample holder was then placed inside

the dewar. The helium gas was then pumped and the dewar maintained at a pressure of 10 to 100 microns.

Before any lifetime or spectra measurements were made, the sample was allowed to reach temperature equilibrium. This was done by monitoring the temperature indicated by the copper-constantan thermocouple. Approximately one half hour was sufficient time for temperature equilibrium.

Lifetimes were measured by closing a mechanical shutter which blocked the exciting radiation. The phosphorescence intensity was recorded as a function of time. The technique used to close the shutter is explained above. A base line was recorded showing zero intensity by closing the exit slit of the monochromator between the PM and the monochromator.

The phosphorescence lifetimes as a function of temperature were obtained in the following manner. A recording of the intensity versus time using the digital printer or the oscilloscope was made. Then the temperature was increased to a higher value using the temperature controller. After approximately one hour the temperature had stabilized at the higher value and another decay was recorded. This process was continued until the phosphorescence intensity became too weak to measure. At this point the temperature was lowered and, after being allowed to stabilize another decay would be recorded. This up and down process was used to determine whether any thermal hysteresis effects were present.

The phosphorescence lifetime as a function of wavelength was obtained as follows. The sample temperature was allowed to stabilize at 77°K. By adjusting the exit wavelength of the monochromator which viewed the emitted light from the sample, a decay could be taken at any desired wavelength. The exit wavelength of the monochromator was systematically adjusted across

the phosphorescence region. The slit width of the monochromator was set at 2mm, which is approximately 64 \AA bandpass.

A spectrum of each sample was taken using procedures described by Kilmer³.

CALIBRATIONS

A copper constantan thermocouple was used to measure the temperature. This thermocouple was embedded in the sample. Distilled ice water was used as a reference. A Keithley guarded differential voltmeter, whose quoted uncertainty was 5 microvolts, was used to measure the thermocouple voltage. The thermocouple calibration was taken from a paper by Powell, Burch, and Corruocini⁷. In order to correct for the deviation of our thermocouple from the values of the calibration paper, the fixed temperature points of the bp of N_2 and melting point of water were used to determine the deviation.

A Bausch and Lomb medium quartz prism spectrography was used to record the emission spectra. Comparison with the spectra of a Pfund iron arc operated at 220 volts DC and 5+ amps allowed the wavelengths of the emission spectra to be measured.

The spectrometer and oscilloscope were calibrated as described by Kilmer³.

Chapter IV

RESULTS

CALCULATION OF LIFETIMES

The decays of phosphorescence intensity were measured and recorded directly from the recording device. A weighted least squares fit for the decays was done on the computer. The data points were weighted as the inverse of the square of the individual uncertainties as discussed by Bacon⁸. There is 90% confidence that the true lifetime value will fall inside the uncertainty limits of the calculated lifetime, assuming that the measured values of the data points are drawn from a normal distribution of possible values. The program for those decays fitted using the IBM 360 is given by Kilmer³. The program for the lifetime calculations made on the desk top computer (Hewlett Packard 9100 B with extended memory) is given in the Appendix. Plots of the logarithm of the intensity with time yielded straight lines and were plotted using the desk top computer or the Cal Comp plotter.

LIFETIMES OF PYRAZINE IN CYCLOHEXANE

Samples of pyrazine in cyclohexane were prepared by slow freezing and by fast freezing. This yielded samples which were mainly low temperature phase or high temperature phase mixed crystals respectively, are described above. Plates III and IV show typical plots of the logarithm of phosphorescence intensity versus time for fast frozen and slow frozen

samples, respectively. The decays were fitted using the programs described above. These decays were recorded from the oscilloscope since the longest lifetime was approximately 20 milliseconds. For all the decays measured, the slits on the monochromator were 2mm, which allowed approximately 64 Å of bandpass.

Plates V and VI show the lifetime versus emission wavelength data for fast frozen and slow frozen samples, respectively. Tables I and II present the measured lifetimes for the two types of samples. A microphotometer traces of each type of spectrum is present in Plate VII.

Plates IX and X show the lifetime versus temperature data for the fast frozen and slow frozen samples, and Tables III and IV present the corresponding lifetimes. These decays were taken at 3780 Å set on the monochromator with a bandpass as stated above. This wavelength corresponded to the maximum intensity of the emitted phosphorescence. Experimental studies on several different molecules by Hadley, Rast, and Keller⁹, Jones and Calloway¹⁰, Hatch and Nieman¹¹, and Kilmer and Spangler² indicated the lifetimes can be fit by an expression of the form

$$\frac{1}{\tau} = k_0 + k_1 \exp(-\Delta E/k_B T) \quad (1)$$

where k_0 , k_1 and ΔE can be varied and k_B is Boltzman's constant. For very low temperatures,

$$\frac{1}{\tau} = k_0 \quad (2)$$

El-Sayed has reported that for very low temperatures the phosphorescence lifetime of pyrazine is not constant since the individual triplet state

components will not be equally populated. The lifetimes for both types of samples which are presented here appear to be constant for temperatures below approximately 90°K. An average value for these lifetimes was obtained, and from them k_0 was calculated. Williamson¹⁴ gives a scheme for calculating weighted least squares fits where there are uncertainties in both x and y variables. Using this scheme as described by Kilmer³ the values of k_1 and ΔE were found. These are presented in Table V for both samples. The solid curves of lifetimes as a function of temperature shown in Plates IX and X represent the least squares fit of equation (1) with the calculated values of k_0 , k_1 and ΔE .

LIFETIMES OF BENZOTRIFLUORIDE IN METHYLCYCLOHEXANE

Samples of benzotrifluoride were of two types. Upon freezing, the samples were glassy in appearance. If the sample was warmed almost to melting and then cooled again, it would change to a polycrystalline form. Plates XI and XII show typical plots of the logarithms of the phosphorescence intensity versus time. The straight line fits were made using the desk top computer as described above.

For both types of samples the phosphorescence lifetime versus emission wavelength was measured. Plate XIII shows a plot of lifetime versus emission wavelength for a crystalline sample. These data for a glassy sample are presented in Plate XIV. Tables VI and VII present the measured lifetimes for crystalline and glassy samples, respectively.

Plates XV and XVI show plots of lifetime versus temperature for the crystalline and glassy samples respectively. Tables VIII and IX present the measured lifetimes which yield these plots. All these decays were

taken with a 64 Å bandpass centered at 3775 Å. At this wavelength, the samples gave the maximum emitted phosphorescence intensity. No attempt was made to fit these data to an Arrhenius plot since measurements were not made at low enough temperatures to determine a realistic value of k_0 .

LIFETIMES OF BENZOTRICHLORIDE IN METHYLCYCLOHEXANE

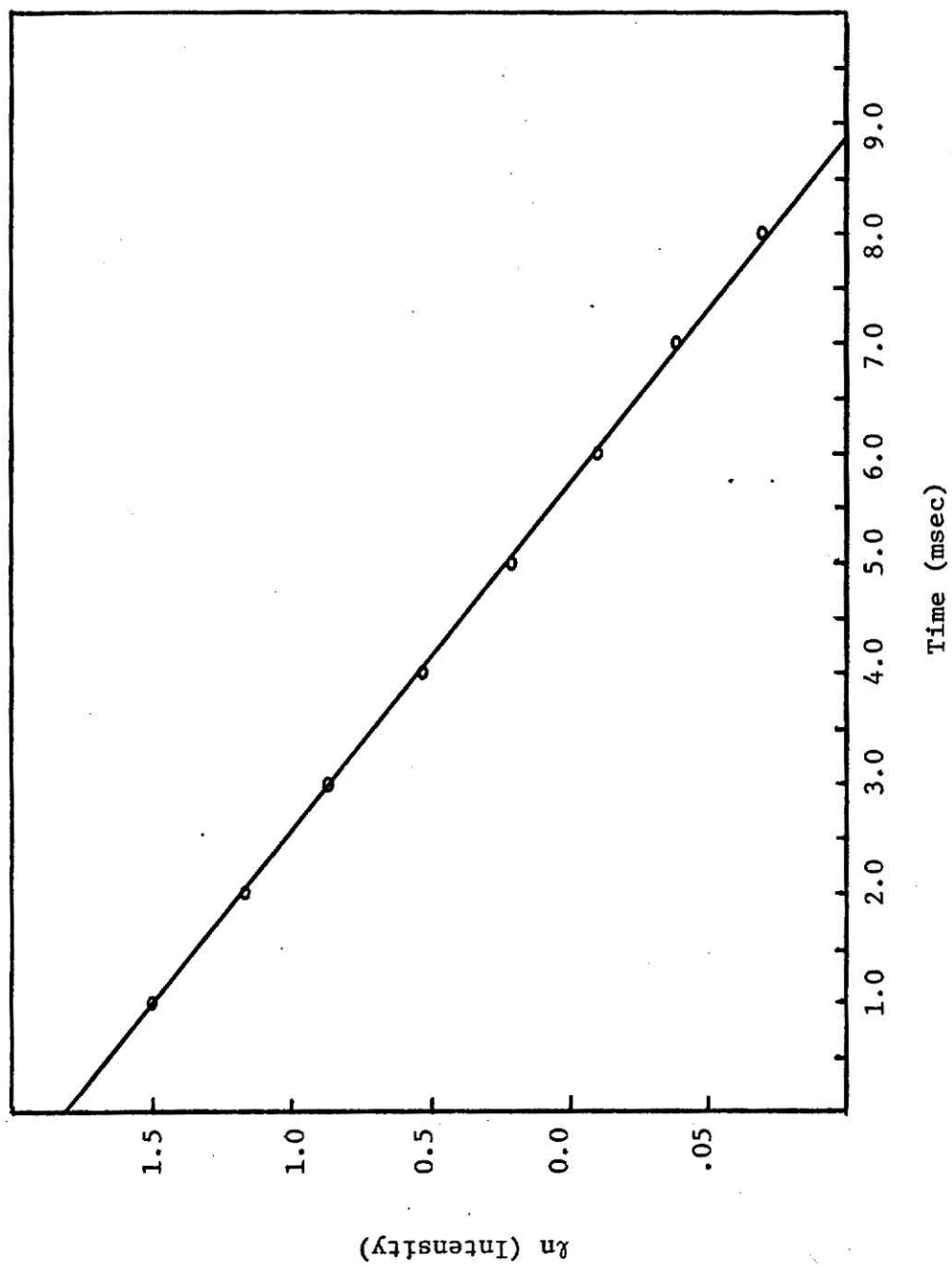
Plate XVII shows a plot of lifetime versus temperature for benzotrichloride in methcyclohexane. The measured lifetimes are presented in Table X. Using techniques described in Chapter III, the oscilloscope was used to record these decays.

Explanation of Plate III

This graph shows a typical plot of the decay of the phosphorescence intensity for fast-frozen pyrazine in cyclohexane.

<u>Decay</u>	<u>Temperature ($^{\circ}$K)</u>	<u>Lifetime (msec)</u>	<u>Uncertainty (msec)</u>
P125	136.89	3.15	.21

Plate III

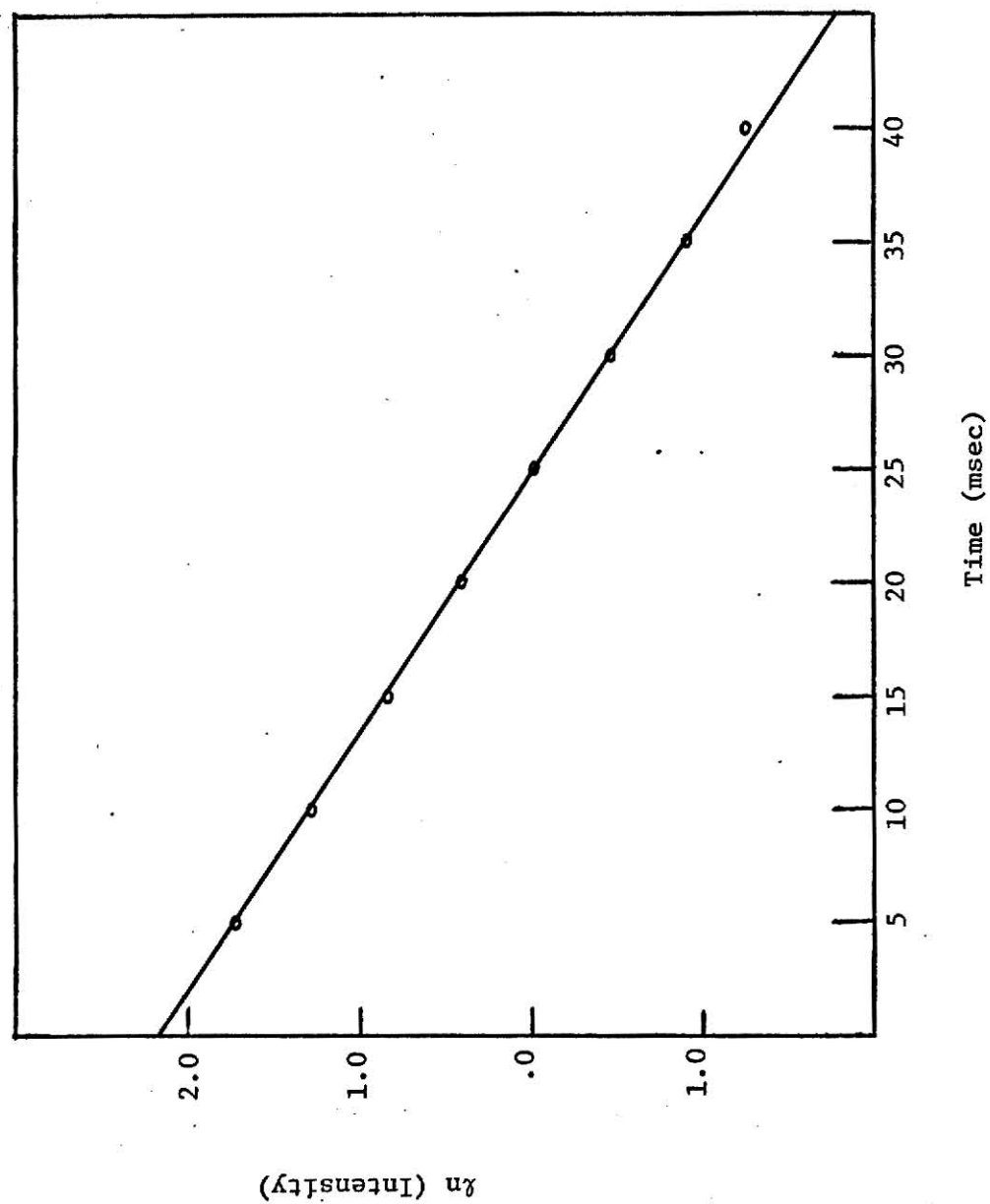


Explanation of Plate IV

The graph shows a typical plot of the decay of the phosphorescence intensity for slow frozen pyrazine in cyclohexane.

<u>Decay</u>	<u>Temperature (°K)</u>	<u>Lifetime (msec)</u>	<u>Uncertainty (msec)</u>
P102	129.52	11.48	.07

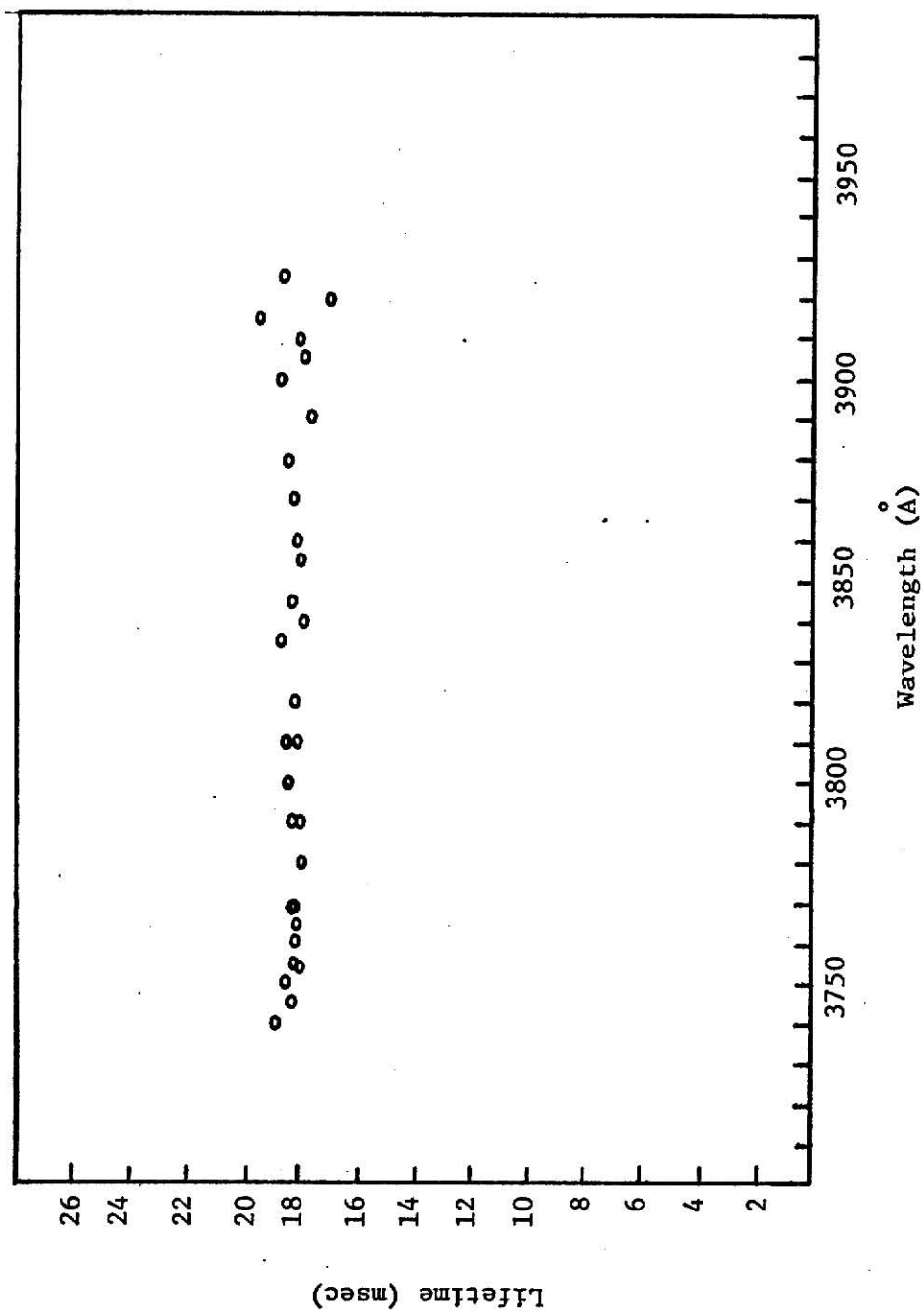
Plate IV



Explanation of Plate V

Graph shows a plot of phosphorescence lifetime versus emission wavelength of fast frozen pyrazine in cyclohexane.

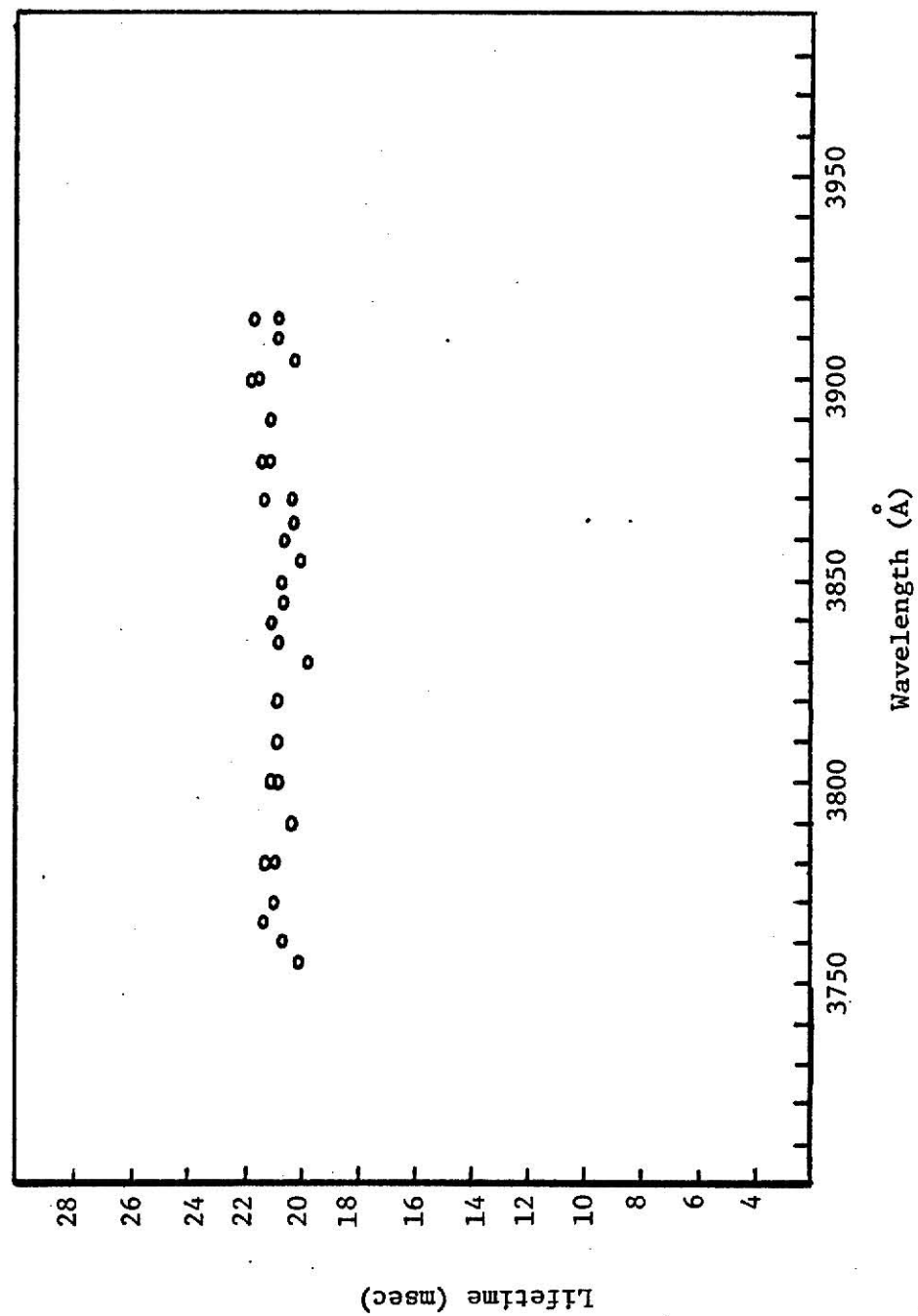
Plate V



Explanation of Plate VI

Graph shows a plot of phosphorescence lifetime versus emission wavelength of slow frozen pyrazine in cyclohexane.

Plate VI



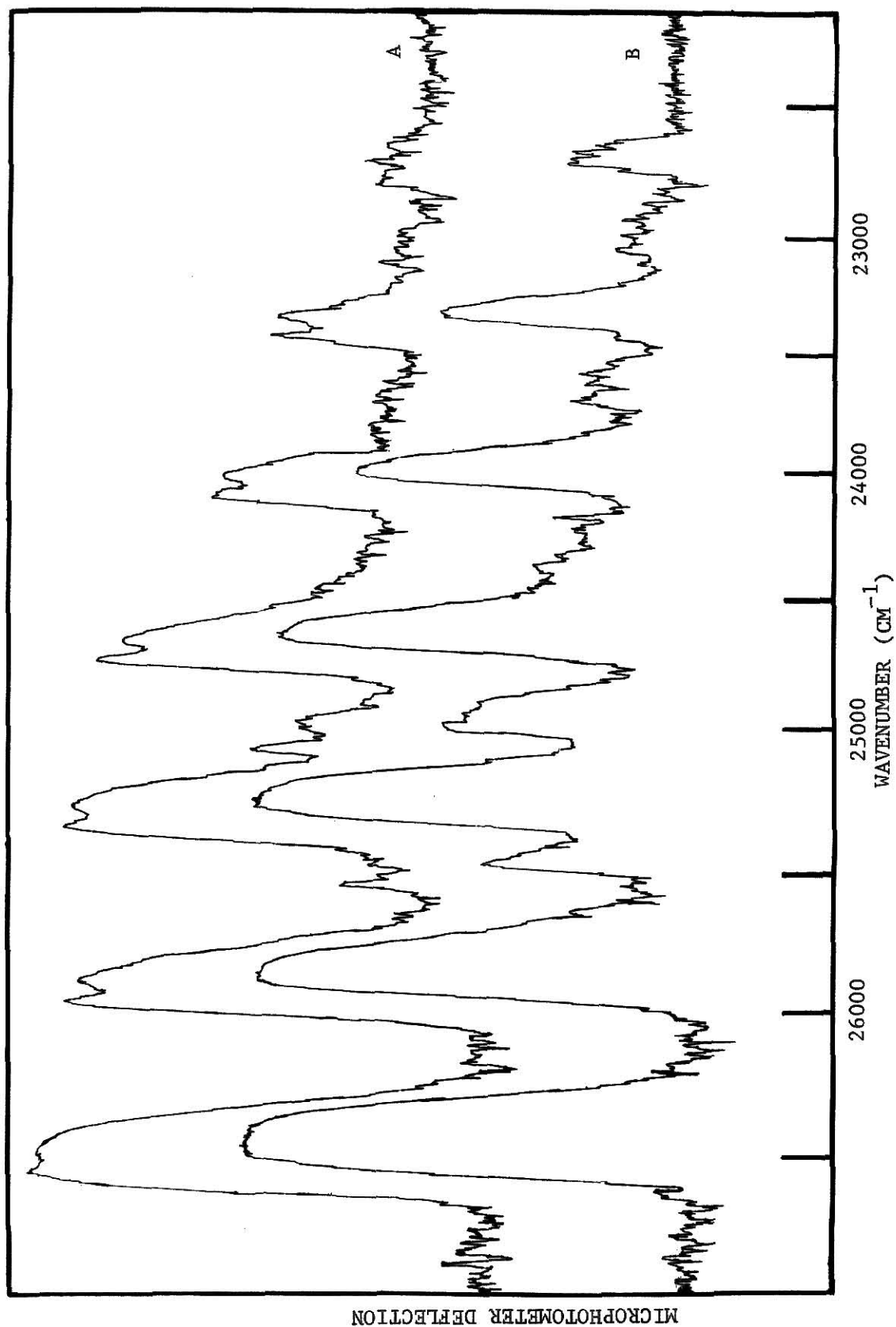
EXPLANATION OF PLATE VII

This plate was made from densitometer tracings of the spectrum of pyrazine in cyclohexane.

A - Plate P-7 fast frozen sample

B - Plate P-8 slow frozen sample

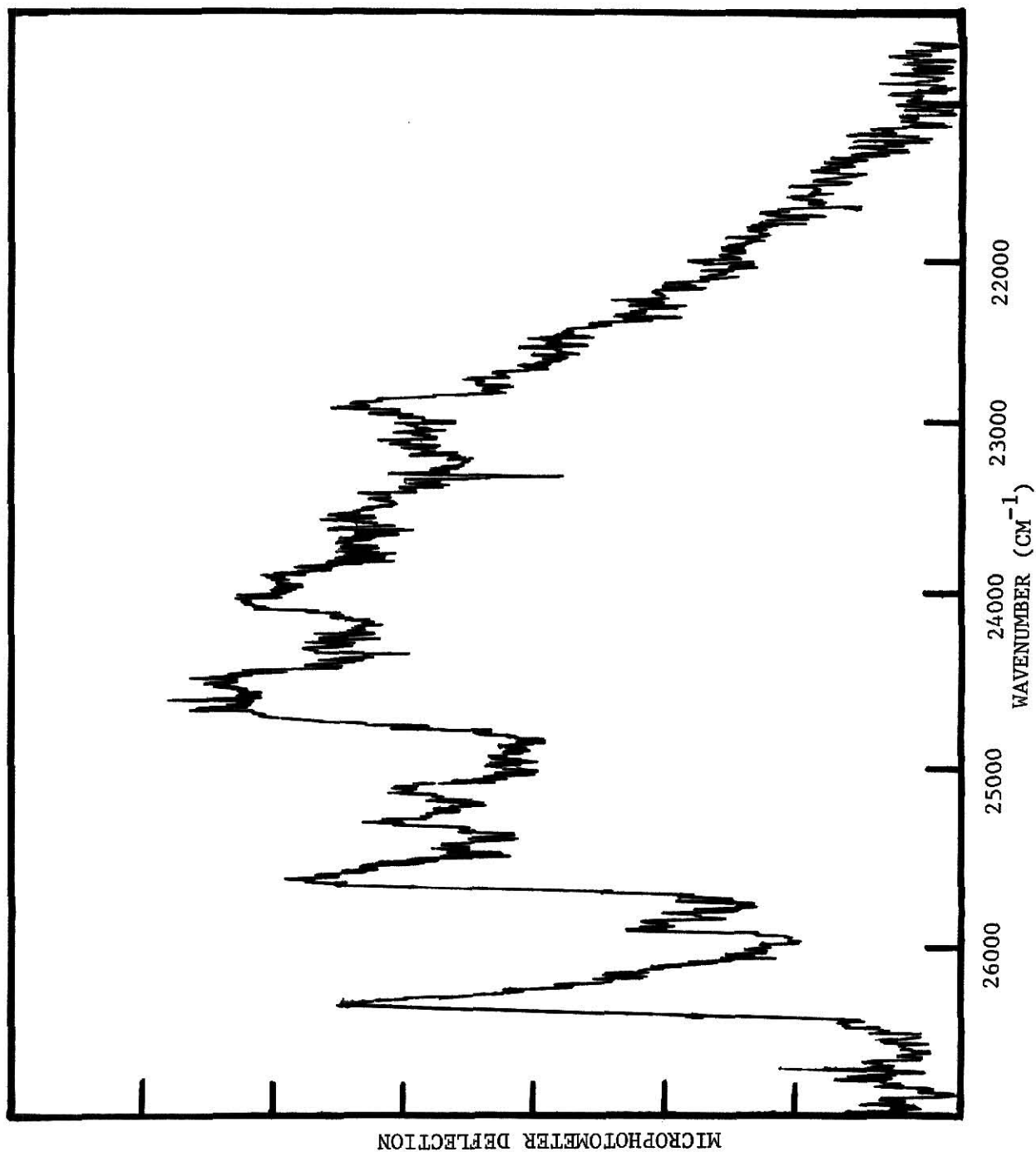
PLATE VII



EXPLANATION OF PLATE VIII

This plate was made from densitometer tracings of the spectrum of benzotrifluoride in methylcyclohexane.

PLATE VIII



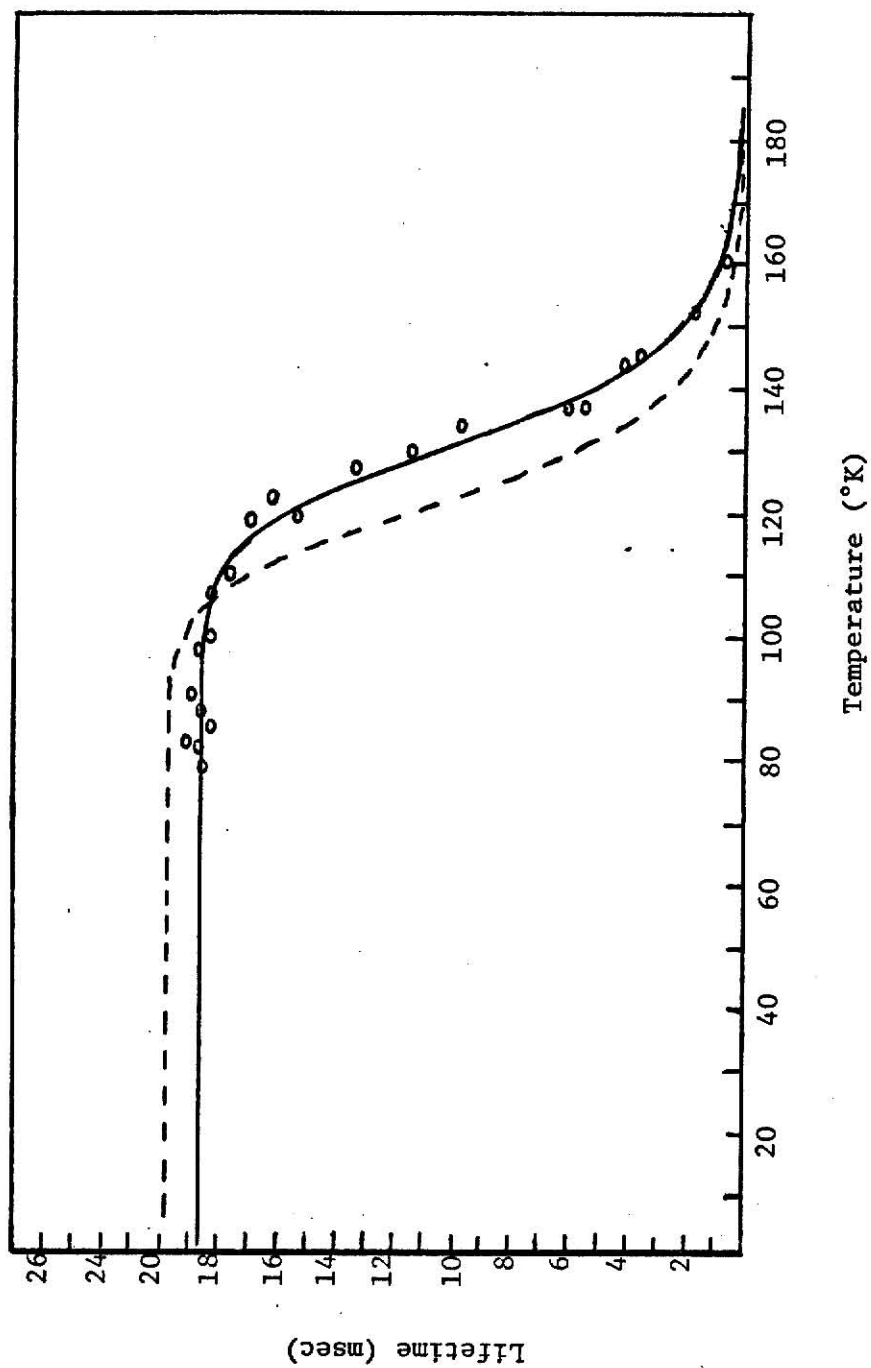
Explanation of Plate IX

A graph showing the temperature dependence of the phosphorescence lifetime for fast frozen pyrazine in cyclohexane.

solid curve - fast frozen

broken curve - slow frozen

Plate IX



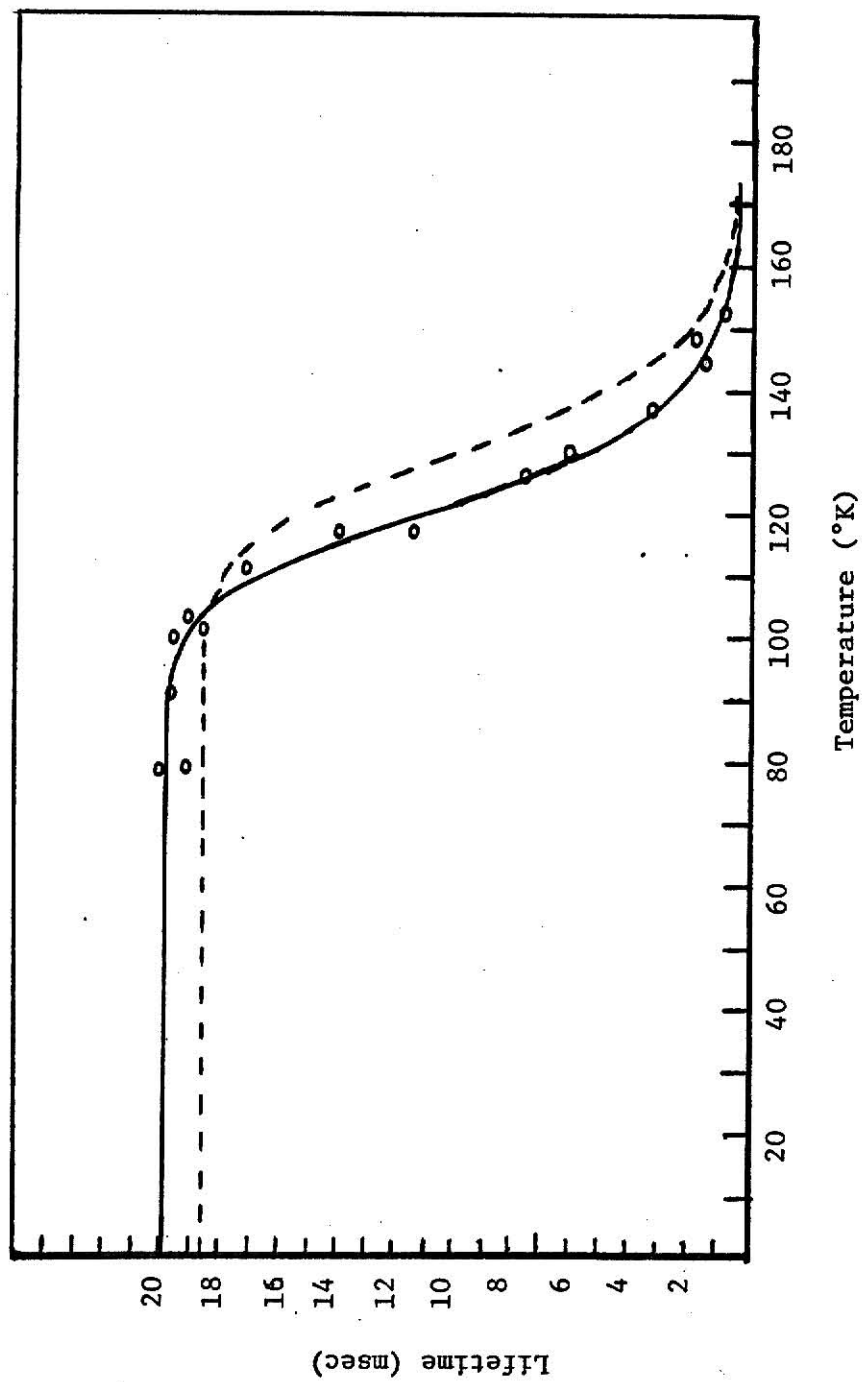
Explanation of Plate X

A graph showing the temperature dependence of the phosphorescence lifetime for slow frozen pyrazine in cyclohexane.

solid curve - slow frozen

broken curve - fast frozen

Plate X

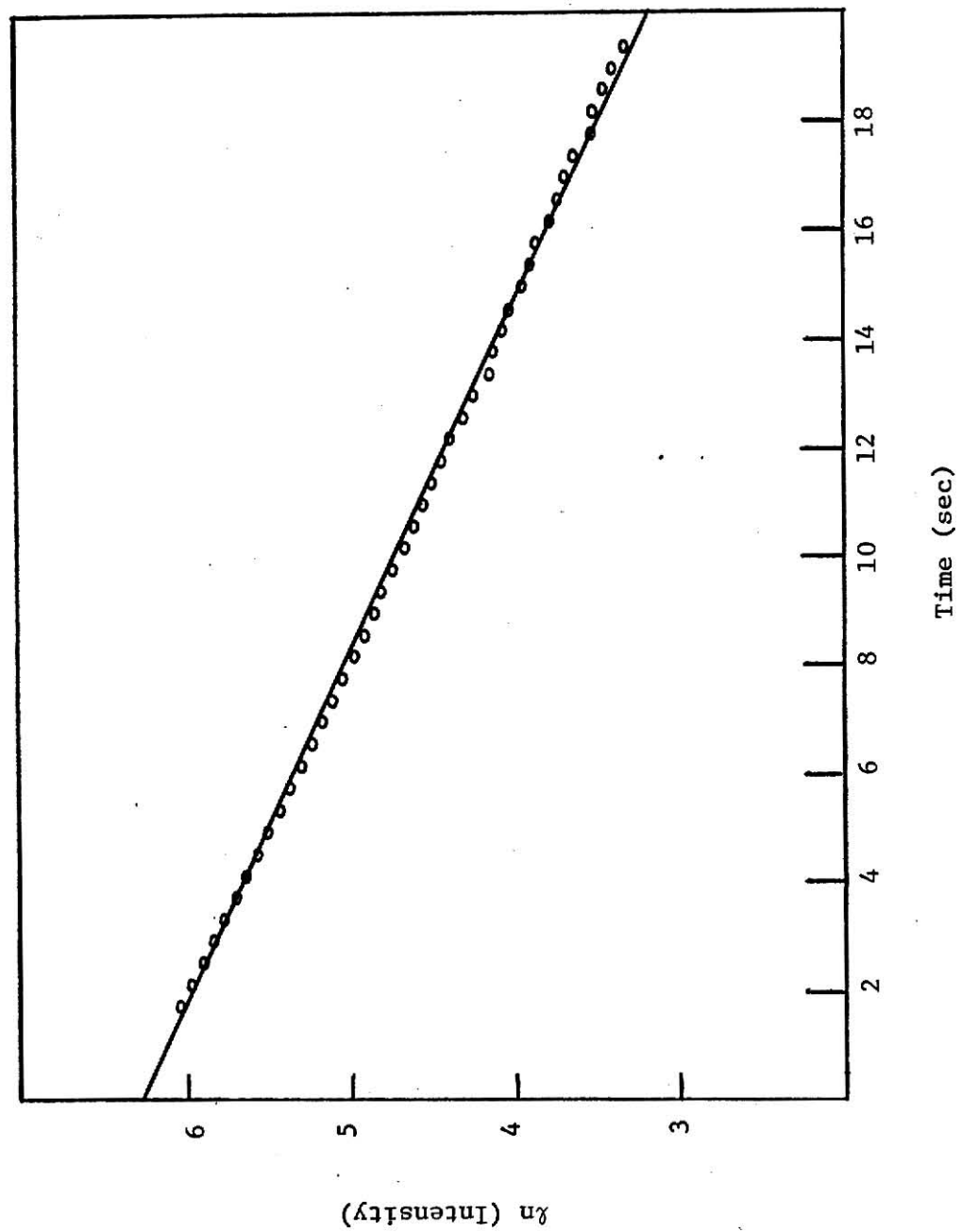


Explanation of Plate XI

The graphy shows a typical plot of the decay of the phosphorescence intensity of benzotrifluoride in glassy methycyclohexane.

<u>Decay</u>	<u>Temperature (°K)</u>	<u>Uncertainty (°K)</u>	<u>Lifetime (sec)</u>	<u>Uncertainty (sec)</u>
B260	79.0	.5	6.30	.02

Plate XI

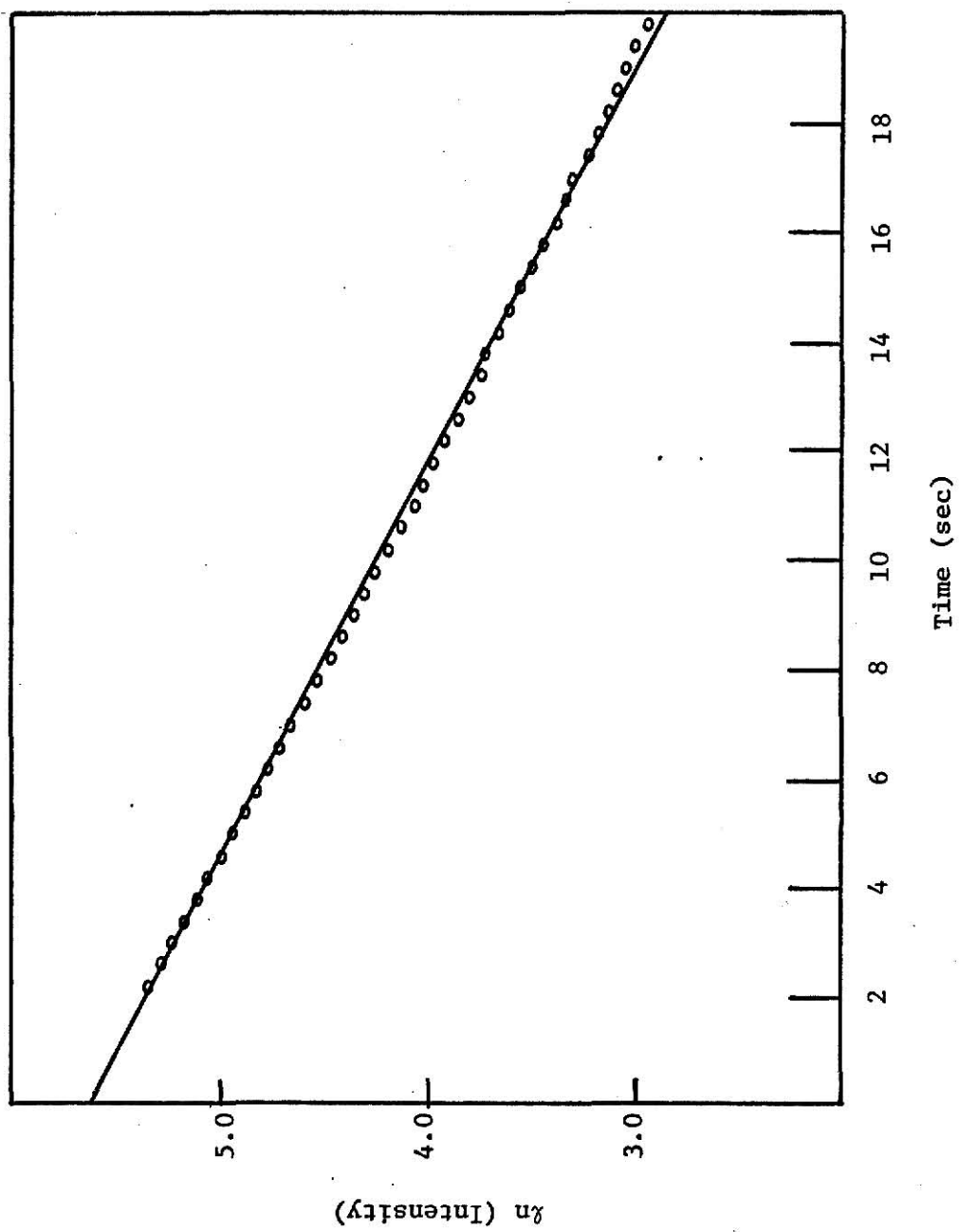


Explanation of Plate XII

The graph shows a typical plot of the decay of the phosphorescence intensity of benzonitrile in crystalline methycyclohexane.

<u>Decay</u>	<u>Temperature (°K)</u>	<u>Uncertainty (°K)</u>	<u>Lifetime (sec)</u>	<u>Uncertainty (sec)</u>
B207	77	.5	6.83	.02

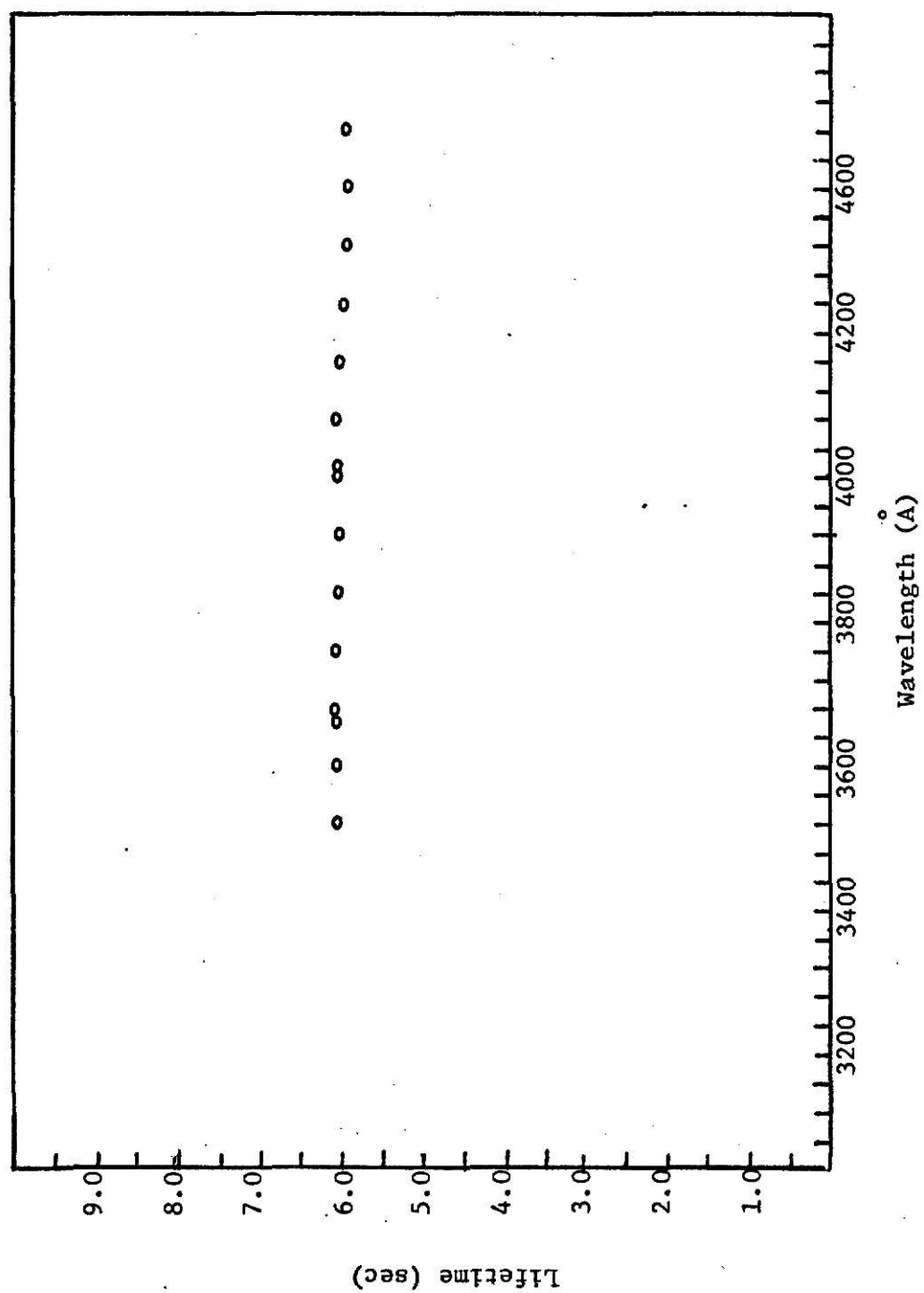
Plate XII



Explanation of Plate XIII

Graph shows a plot of phosphorescence lifetime versus emission wavelength of benzotrifluoride in crystalline methycyclohexane.

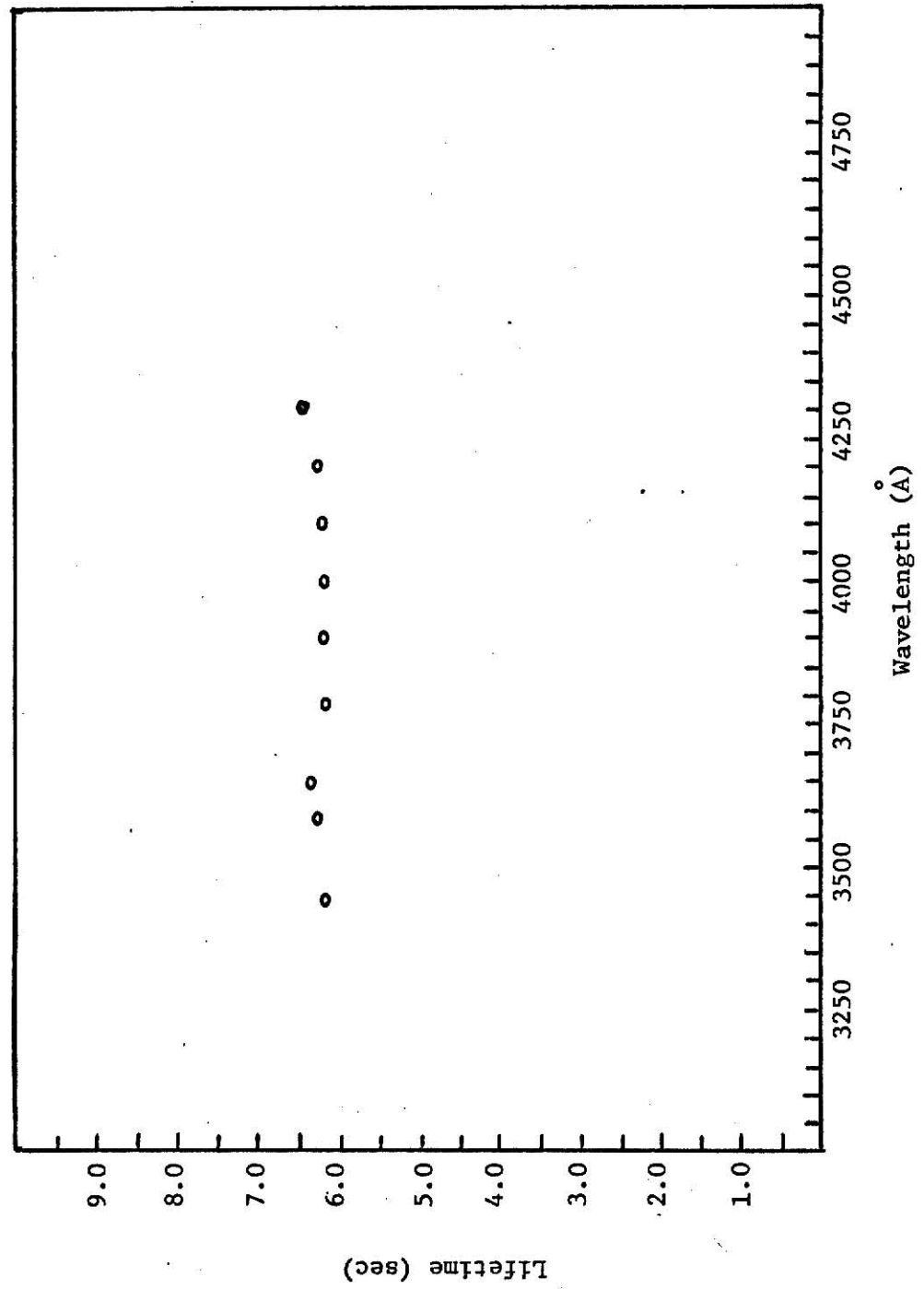
Plate XIII



Explanation of Plate XIV

Graph shows a plot of phosphorescence lifetime versus emission wavelength for benzotrifluoride in glassy methylcyclohexane.

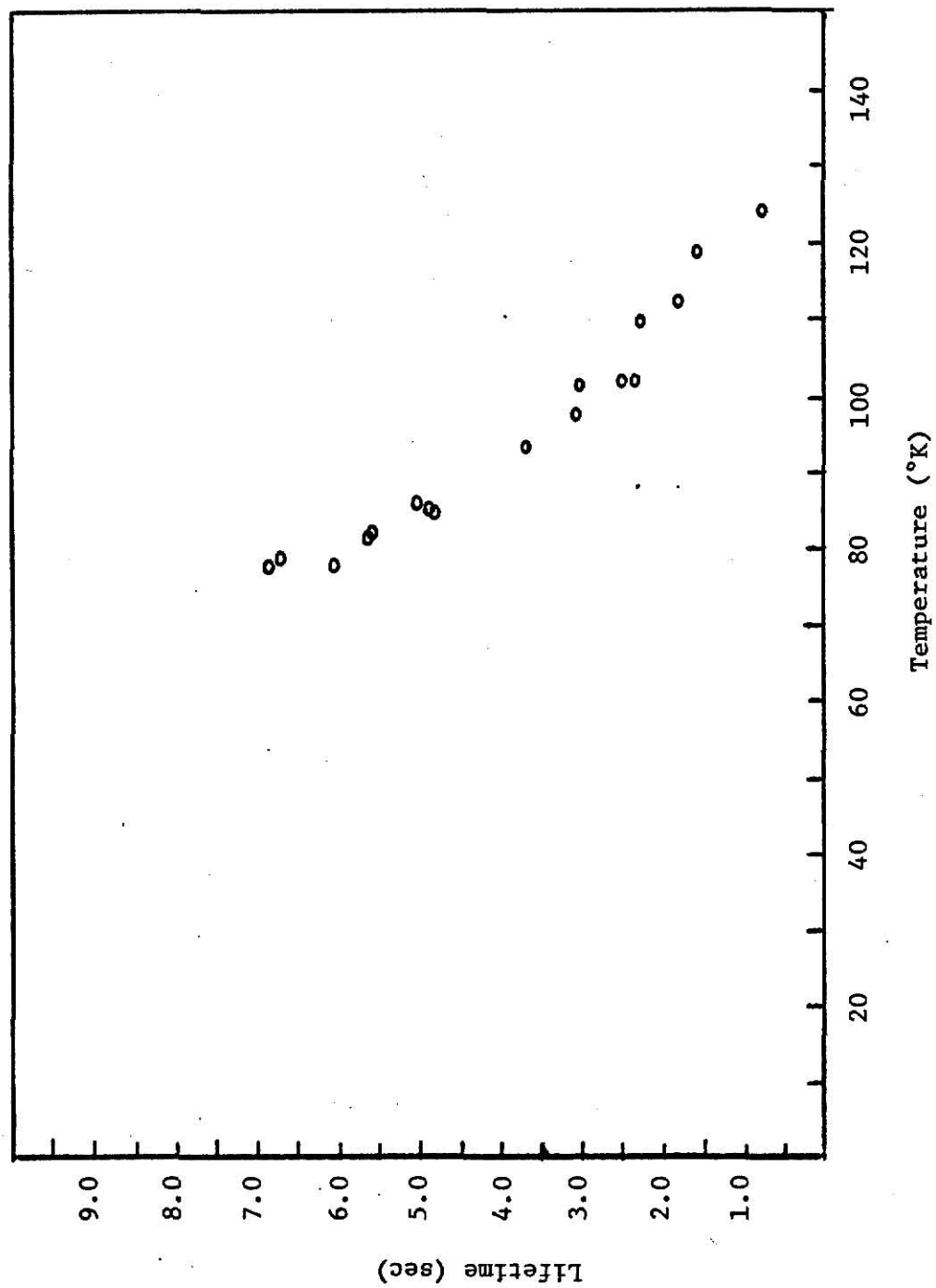
Plate XIV



Explanation of Plate XV

A graph showing the temperature dependence of the phosphorescence lifetime for benzotrifluoride in crystalline methylcyclohexane.

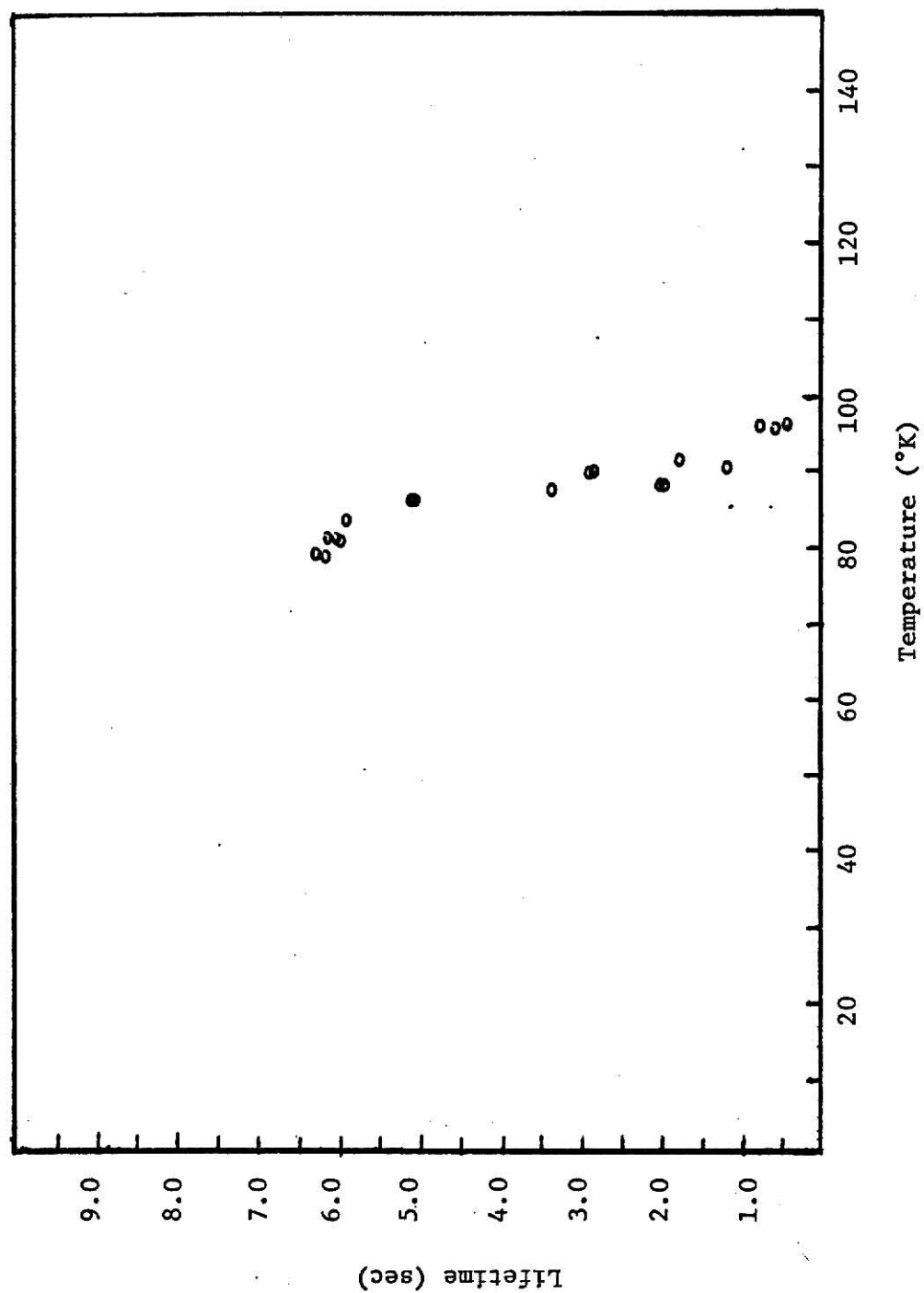
Plate XV



Explanation of Plate XVI

A graph showing the temperature dependence of the phosphorescence lifetime for benzonitrile in glassy methylcyclohexane.

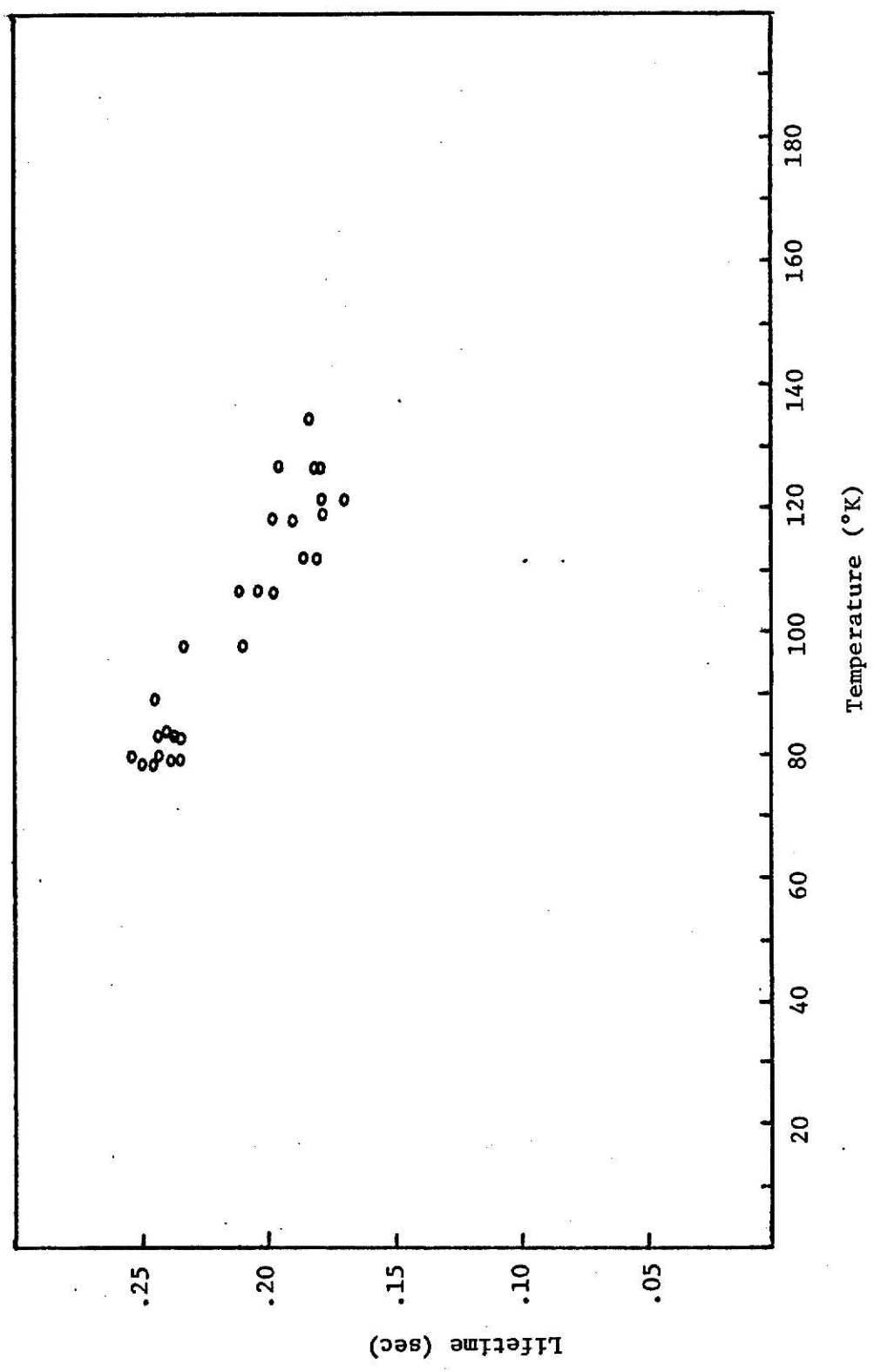
Plate XVI



Explanation of Plate XVII

A graph showing the temperature dependence of the phosphorescence lifetime for benzotrichloride in methylcyclohexane.

Plate XVII



EXPLANATION OF PLATE XVIII

This plate was made from densitometer tracings of benzotrifluoride in crystalline methylcyclohexane.

PLATE XVIII

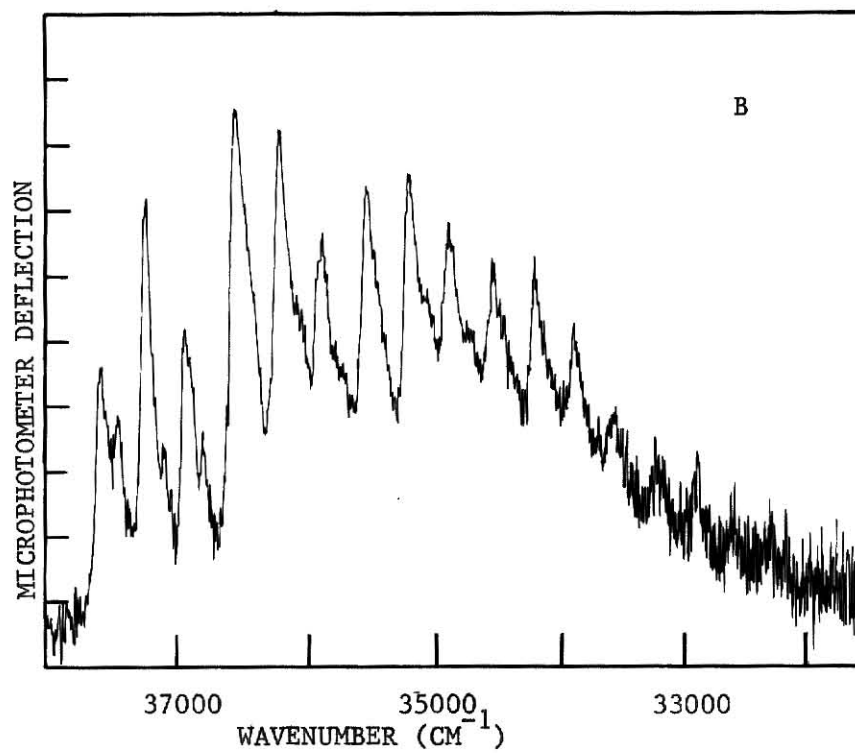
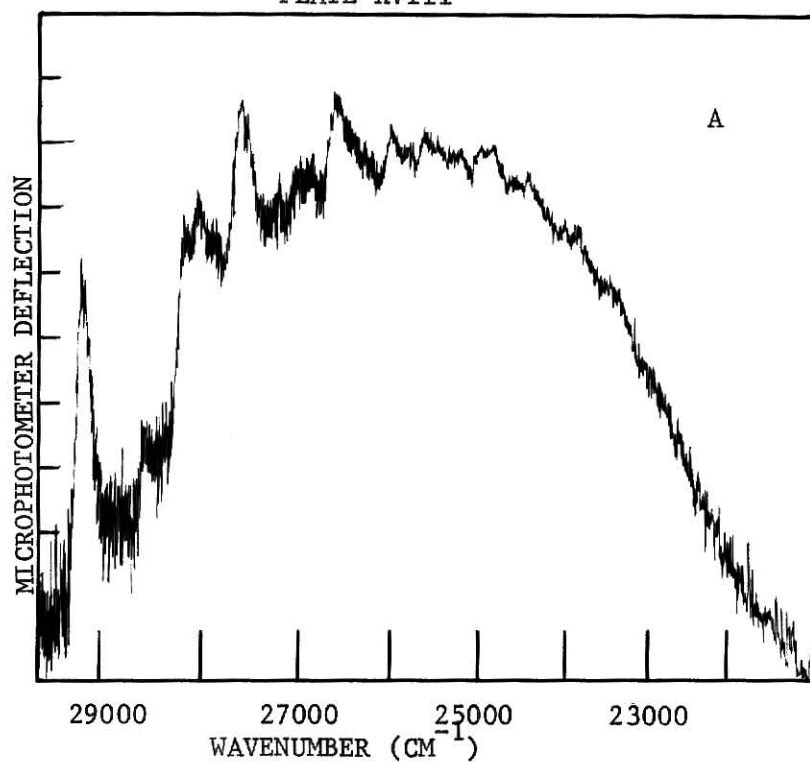


Table I

TABLE OF LIFETIMES OF PHOSPHORESCENCE AT VARIOUS EMISSION WAVELENGTHS OF PYRAZINE IN CYCLOHEXANE

FAST FROZEN

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (msec)	Uncertainty (msec)	Emission Wavelength (Å)
120A	77	.5	18.91	.12	3740
121	77	.5	18.28	.10	3745
122	77	.5	18.50	.13	3750
123A	77	.5	18.03	.08	3755
123B	77	.5	18.28	.08	3755
124	77	.5	18.18	.09	3760
125	77	.5	18.17	.06	3765
126	77	.5	18.27	.05	3770
127	77	.5	17.99	.07	3780
128A	77	.5	18.39	.11	3790
128B	77	.5	18.00	.08	3790
129	77	.5	18.45	.05	3880
130	77	.5	18.54	.07	3810
130	77	.5	18.11	.06	3810
133	77	.5	18.68	.09	3835
134	77	.5	17.92	.09	3840
135	77	.5	18.33	.08	3845
137	77	.5	18.04	.06	3855
138	77	.5	18.19	.07	3860

Table I

(continued)

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (msec)	Uncertainty (msec)	Emission Wavelength (Å)
139	77	.5	18.30	.06	3870
140	77	.5	18.50	.10	3880
141	77	.5	17.70	.11	3890
142B	77	.5	18.76	.11	3900
143	77	.5	17.94	.10	3905
144	77	.5	18.08	.09	3910
145	77	.5	19.54	.16	3915
146	77	.5	17.11	.13	3920
147	77	.5	18.73	.13	3925

Table II

TABLE OF LIFETIMES OF PHOSPHORESCENCE AT VARIOUS EMISSION WAVELENGTHS OF PYRAZINE IN CYCLOHEXANE

SLOW FROZEN

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (msec)	Uncertainty (msec)	Emission Wavelength (Å)
90	77	.5	18.85	.07	3780
91	77	.5	19.14	.13	3780
93	77	.5	17.99	.12	3755
94	77	.5	18.53	.13	3760
95	77	.5	19.23	.10	3765
96	77	.5	18.86	.10	3770
97	77	.5	18.77	.09	3780
98	77	.5	18.23	.07	3790
99A	77	.5	18.89	.08	3800
99A	77	.5	18.53	.07	3800
99A	77	.5	18.71	.07	3800
99B	77	.5	19.09	.18	3800
100	77	.5	18.69	.06	3810
101	77	.5	18.75	.05	3820
102	77	.5	17.87	.10	3830
102	77	.5	17.74	.10	3830
103	77	.5	18.73	.10	3835
104	77	.5	19.00	.11	3840
105	77	.5	18.53	.12	3845
106	77	.5	18.66	.16	3850
107	77	.5	17.95	.09	3855
108A	77	.5	18.60	.12	3860
108B	77	.5	18.47	.15	3860
109	77	.5	18.18	.09	3865
110A	77	.5	19.18	.08	3870
110B	77	.5	18.23	.09	3870

Table II

(continued)

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (msec)	Uncertainty (msec)	Emission Wavelength (Å)
110B	77	.5	17.71	.07	3870
111A	77	.5	19.39	.10	3880
111B	77	.5	19.02	.08	3880
112	77	.5	19.04	.12	3890
113A	77	.5	19.71	.14	3900
113B	77	.5	19.46	.12	3900
114	77	.5	18.17	.08	3905
115	77	.5	18.72	.11	3910
116A	77	.5	18.73	.13	3915
116B	77	.5	19.60	.12	3915

Table III

TABLE OF LIFETIMES OF PHOSPHORESCENCE AT VARIOUS TEMPERATURES FOR FAST FROZEN PYRAZINE IN CYCLOHEXANE

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (msec)	Uncertainty (msec)
P116	77.70	.5	19.77	.12
P117	78.60	.5	19.83	.09
P118	78.60	.5	20.15	.15
P119	81.61	.5	19.97	.15
P120	91.23	.5	20.07	.17
P121	99.86	.5	19.60	.12
P122	102.91	.5	19.00	.12
P123	117.39	.5	13.90	.08
P124	126.11	.5	7.56	.06
P124	126.11	.5	7.64	.04
P125	136.89	.5	3.15	.21
P126	144.75	.5	1.31	.02
P127	152.57	.5	0.76	.02
P128	161.99	.5	0.45	.01
P128	161.99	.5	0.53	.02
P134	79.21	.5	19.20	.22
P135	79.01	.5	20.05	.40
P136	78.90	.5	19.86	.09
P137	91.33	.5	19.64	.21
P138	101.16	.5	18.43	.23
P139	110.98	.5	17.11	.12
P140	110.98	.5	17.06	.13
P141A	117.39	.5	11.33	.05
P142A	130.22	.5	6.07	.08
P143	140.55	.5	2.37	.03
P144	148.46	.5	1.70	.12
P145	156.18	.5	1.35	.13

Table IV

TABLE OF LIFETIMES OF PHOSPHORESCENCE AT VARIOUS TEMPERATURES FOR SLOW FROZEN PYRAZINE IN CYCLOHEXANE

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (msec)	Uncertainty (msec)
P89A	77	.5	18.04	.11
P89B	77	.5	18.31	.20
P90	77	.5	17.93	.12
P91	77	.5	18.13	.13
P92	77	.5	17.79	.13
P93	77	.5	17.76	.13
P94A	106.02	.5	18.22	.12
P95A	106.02	.5	18.36	.15
P95B	106.02	.5	18.38	.13
P96	78.20	.5	18.56	.06
P97	87.73	.5	18.68	.09
P98	84.52	.5	18.29	.11
P99	99.45	.5	18.38	.07
P100	108.92	.5	17.47	.10
P101	119.00	.5	15.34	.10
P102	129.52	.5	11.48	.07
P103	145.66	.5	3.64	.07
P104	136.24	.5	6.13	.07
P105	152.27	.5	1.63	.06
P106	143.65	.5	4.18	.09
P153	78.00	.5	18.60	.09
P154	82.21	.5	19.15	.13
P155	81.51	.5	18.51	.10
P156	81.41	.5	18.77	.06
P157	90.33	.5	18.84	.34
P158	97.35	.5	18.70	.13
P159	121.90	.5	16.24	.12

Table IV

(continued)

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (msec)	Uncertainty (msec)
P160A	109.44	.5	17.75	.08
P160B	109.47	.5	17.55	.07
P161	118.40	.5	16.99	.15
P162	126.91	.5	13.40	.19
P163	133.81	.5	9.82	.20
P164	136.89	.5	5.47	.15
P165	151.67	.5	2.05	.09
P166	151.67	.5	1.92	.10
P167	160.69	.5	0.85	.03

Table V

PARAMETERS TO FIT PHOSPHORESCENCE LIFETIMES VERSUS TEMPERATURE CURVES WITH A FUNCTION OF THE FORM
 $\frac{1}{\tau} = k_0 + k_1 \exp(-E/k_B T)$

Solute	Solvent	How Frozen	$\Delta E/hc$ (cm^{-1})	K_1^{-1} (sec^{-1})	τ_0 (sec)
pyrazine	cyclohexane	slow	1301	2.2×10^8	19.84
pyrazine	cyclohexane	fast	1521	8.5×10^8	18.60

Table VI

TABLE OF LIFETIMES OF PHOSPHORESCENCE AT VARIOUS EMISSION WAVELENGTHS BY BENZOTRIFLUORIDE IN
CRYSTALLINE METHYLCYCLOHEXANE

Decay	Temperature (°K)	Uncertainty (°K)	Uncertainty (sec)	Emission Wavelength (Å)
B240A	78.6	.5	6.17	3440
B241	78.6	.5	6.28	3585
B242	78.6	.5	6.35	3645
B243	78.6	.5	6.17	3785
B244	78.6	.5	6.20	3900
B245	78.6	.5	6.19	4000
B246	78.6	.5	6.23	4100
B247	78.6	.5	6.26	4200
B248	78.6	.5	6.46	4300

Table VII

TABLE OF LIFETIMES OF PHOSPHORESCENCE AT VARIOUS EMISSION WAVELENGTH FOR BENZOTRIFLUORIDE IN GLASSY

METHYLCYCLOHEXANE

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (sec)	Uncertainty (sec)	Emission Wavelength (Å)
B183	78	.5	6.04	.01	4220
B184B	78	.5	6.06	.01	4200
B186	78	.5	6.05	.01	3600
B187	78	.5	6.07	.01	3700
B188	78	.5	6.08	.01	3800
B189	78	.5	6.06	.01	3900
B190	78	.5	6.05	.01	4000
B191	78	.5	6.03	.01	4100
B192	78	.5	6.04	.01	4200
B193	78	.5	6.08	.02	4300
B194	78	.5	6.03	.01	4400
B195	78	.5	5.99	.02	4500
B196	78	.5	5.95	.03	4600
B197	78	.5	5.95	.04	4700
B198	78	.5	5.96	.04	4800
B199	78	.5	6.06	.01	3775

Table VIII

TABLE OF LIFETIMES OF PHOSPHORESCENCE AT VARIOUS TEMPERATURES FOR BENZOTRIFLUORIDE IN CRYSTALLINE
METHYLCYCLOHEXANE

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (sec)	Uncertainty (sec)
B199	77.9	.5	6.06	.01
B200	86.0	.5	5.04	.01
B201	101.4	.5	3.04	.01
B202	109.5	.5	2.29	.03
B223	78.6	.5	6.72	.01
B224	84.5	.5	4.80	.03
B225	84.9	.5	4.89	.01
B226	93.0	.5	3.70	.02
B227	97.4	.5	3.07	.02
B228	101.9	.5	2.35	.02
B229	101.9	.5	2.35	.02
B230	101.9	.5	2.51	.07
B231	112.2	.5	1.80	.06
B232	118.7	.5	1.58	.09
B233	124.0	.5	.78	.04
B234A	81.3	.5	5.64	.01
B234B	81.3	.5	5.59	.01
B235	81.3	.5	5.46	.01
B236	82.2	.5	5.58	.01
B237	82.2	.5	5.56	.01
B238	82.2	.5	5.52	.05

Table IX

TABLE OF LIFETIMES OF PHOSPHORESCENCE AT VARIOUS TEMPERATURES FOR BENZOTRIFLUORIDE IN GLASSY

METHYLCYCLOHEXANE

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (μsec)	Uncertainty (sec)
B249	81.6	.05	6.02	.02
B250	81.0	.05	6.04	.03
B251	81.0	.05	5.97	.04
B252	79.8	.05	6.00	.02
B253	79.8	.05	5.99	.02
B254	88.1	.05	2.00	.05
B255	88.1	.05	2.04	.03
B256	95.5	.05	.58	.03
B257	95.5	.05	.58	.03
B258	79.0	.05	6.31	.02
B259	79.0	.05	6.23	.05
B260	79.0	.05	6.30	.02
B261	79.0	.05	6.27	.02
B262	79.0	.05	6.28	.03
B263	80.8	.05	6.06	.02
B264	80.8	.05	6.05	.02
B265	87.6	.05	3.35	.02
B266	87.6	.05	3.37	.02
B267	91.3	.05	1.77	.02
B268	91.3	.05	1.77	.05
B269	96.04	.05	.76	.07
B270	96.04	.05	.47	.02
B271	81.0	.05	6.14	.02
B272	81.0	.05	6.14	.02

Table IX

(continued)

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (sec)	Uncertainty (sec)
B273	83.3	.05	5.90	.02
B274	83.3	.05	5.91	.02
B275	86.1	.05	5.08	.02
B276	86.1	.05	5.12	.03
B278	89.6	.05	2.87	.02
B279	89.6	.05	2.90	.03
B280	90.5	.05	1.17	.05
B281	90.5	.05	1.19	.03
B282	96.2	.05	.43	.02
B283	96.2	.05	.43	.02

Table X

TABLE OF LIFETIMES OF PHOSPHORESCENCE AT VARIOUS TEMPERATURES FOR BENZOTRICHLORIDE IN METHYLCYCLOHEXANE

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (sec)	Uncertainty (sec)
C-2	78.60	.5	.246	.003
C-3A	78.60	.5	.250	.420
C-3B	78.60	.5	.250	.002
C-5C	101.06	.5	.148	.003
C-7A	111.98	.5	.180	.001
C-8A	111.98	.5	.178	.003
C-8C	111.98	.5	.186	.005
C-8D	111.98	.5	.180	.003
C-9A	121.50	.5	.169	.003
C-9B	121.50	.5	.178	.004
C-11	83.01	.5	.239	.005
C-12A	80.01	.5	.254	.002
C-12B	80.01	.5	.243	.005
C-13A	79.51	.5	.246	.002
C-13B	79.51	.5	.235	.004
C-13C	79.51	.5	.238	.005
C-141A	79.41	.5	.242	.003
C-141B	79.41	.5	.249	.003
C-142A	89.03	.5	.244	.002
C-15	97.75	.5	.209	.002
C-16B	97.75	.5	.233	.004
C-16C	97.75	.5	.209	.001
C-16D	97.75	.5	.209	.002
C-17A	106.77	.5	.211	.002
C-17B	106.77	.5	.204	.003
C-17C	106.77	.5	.198	.002
C-18A	118.09	.5	.190	.003
C-18B	118.09	.5	.198	.002

Table X
(continued)

Decay	Temperature (°K)	Uncertainty (°K)	Lifetime (sec)	Uncertainty (sec)
C-19A	126.71	.5	.178	.004
C-19B	126.71	.5	.182	.002
C-19C	126.71	.5	.196	.003
C-20A	134.53	.5	.184	.006

Chapter V

DISCUSSION OF RESULTS AND CONCLUSIONS

The emission wavelength dependence of the phosphorescence lifetimes presented for pyrazine and benzonitrile in Chapter IV shows that no change in lifetime occurs with change in emission wavelength. In the case of pyrazine, this is independent of the type of crystal phase, although each crystal phase produces a different phosphorescence lifetime value. For benzonitrile, this result stands for both glassy and crystalline samples. Again, each type of sample gives a different phosphorescence lifetime value. It should be noted that the scatter of the data in both crystal phases is considerably greater for pyrazine than for benzonitrile in either of its sample phases. This probably is a result of the considerably lower intensity levels of the phosphorescence of pyrazine. The decays are exponential for both pyrazine and benzonitrile across the total emission wavelength region. This indicates that, in addition to there not being any impurities of consequence present, the origin of the phosphorescence decay is a single state. Since this single state is a triplet, whose three levels are very close together in energy, the thermal relaxation among the states must be much more rapid than the phosphorescence lifetime so that these states are equally populated.

The low temperature crystal form of cyclohexane was much more difficult to obtain with pyrazine than with benzene. Kilmer⁶ had very little difficulty in cooling the sample slowly enough to obtain solely the low

temperature phase. Further, in the present studies it was not possible to cool the samples rapidly enough to eliminate more than approximately one half of the low temperature phase crystals of cyclohexane. Kilmer⁶ found a lifetime of approximately 4 seconds for benzene in low temperature cyclohexane and approximately 1 second in the high temperature phase, both measured at 77°K. Nieman¹⁵ found approximately the same values. The present studies at 77°K give a value of approximately 19.9 milliseconds for the nearly pure low temperature phase and approximately 18.6 milliseconds from an approximately 50% sample of high temperature phase cyclohexane. Plate XVIII shows a comparison of the spectra of slow and fast frozen samples. Note that the fast frozen sample has a single spectra consisting of the lower energy component of the fast frozen samples' spectrum. Decays of both the fast and slow frozen samples were exponential, which indicates the lifetime of the high temperature phase is lower than 18.6 milliseconds, but not much lower, contrasting to the factor of approximately four which Kilmer⁶ and Nieman¹⁵ found for benzene. The results indicate that the total rate constant for triplet depopulation is quite strongly affected by a change in environment. The pyrazine phosphorescence lifetime is increased roughly 5% to 10% upon going from the slow frozen to the fast frozen sample. At this same time a shift of 400 cm^{-1} in the vibrational spectrum would amount to a shift of only approximately 5×10^{-2} eV in a total energy of approximately 4 eV. The data for benzotrifluoride suggest similar strong environmental effects when the phosphorescence lifetime is measured in the crystalline and glassy samples.

Kilmer and Spangler² have measured the temperature dependence of the phosphorescence lifetime of toluene in methylcyclohexane. They

were able to fit an Arrhenius curve to the data. The results of the present study of benzotrifluoride in methycyclohexane indicate that for the crystalline samples the temperature dependence is almost identical for the temperature values obtained. In addition, the temperature dependence of the phosphorescence lifetime of toluene d3 is essentially the same as for toluene h3 and benzotrifluoride. There appears then to be almost no effect on the phosphorescence rate constants by changing the methyl group hydrogen or deuterium atoms to fluorine atoms. In addition, the phosphorescence spectra of benzotrifluoride are almost identical to that of toluene in methycyclohexane except for a small frequency shift of the whole spectrum. This toluene 0,0 line is at 29019 cm^{-1} while the benzotrifluoride 0,0 line lies at 29184 cm^{-1} , giving a shift of 165 cm^{-1} . However, the fluorescence spectrum of benzotrifluoride is greatly changed from that of toluene, which Kilmer and Spangler² have recorded. Plate XIX shows spectra of benzotrifluoride in methycyclohexane. The glassy samples of benzotrifluoride in methycyclohexane displays a much faster decrease of the phosphorescence lifetime with increasing temperature than the crystalline samples. This is probably because the glass softens considerably while warming and the crystalline samples retain their structures upon warming. In addition, the glassy samples have much less sharp spectra. When the temperature dependence of the phosphorescence lifetime of benzotrifluoride is considered, we see that exchanging the fluorine atoms for chlorine atoms changes the dependence drastically. Also, the vibrational character of the benzotrichloride phosphorescence is much different as can be seen from Plate VIII the 0,0 line lies at 26294 cm^{-1} , so that the spectrum was shifted in excess of 3000 cm^{-1} from that of toluene. These effects are

most likely a result of the greatly increased spin-orbit coupling associated with the higher Z of chlorine. The benzotrichloride in methylcyclohexane samples display a much less rapid decrease of phosphorescence lifetime with temperature increase than did the benzotrichloride samples in methycyclohexane. Also, the benzotrichloride samples display no fluorescence spectra. Further studies of the benzotrichloride and benzotrifluoride system should be carried out.

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APPENDIX

Program 1

DRAW AXES

00 CLEAR	30 -	60 $x \supset y$
01 STOP	31 e	61 FMT
02 $\&n$ x	32 c	62 ↓
03 ROLL ↑	33 $x \supset y$	63 $x \supset y$
04 $\&n$ x	34 x	64 b
05 ROLL ↑	35 $y \rightarrow ()$	65 +
06 PRINT	36 c	66 d
07 STOP	37 $x \supset y$	67 If $y > x$
08 PRINT	38 b	68 7
09 Acc t	39 ROLL ↑	69 1
0a STOP	3a x	6a 0
0b $y \rightarrow ()$	3b $y \rightarrow ()$	6b $x \supset y$
0c c	3c b	6c GO TO
0d $x \rightarrow ()$	3d $x \supset y$	6d 5
10 b	40 d	70 7
11 PRINT	41 x	71 0
12 RCL	42 $y \rightarrow ()$	72 ↑
13 -	43 d	73 FMT
14 1	44 RCL	74 ↑
15 0	45 -	75 FMT
16 ÷	46 ↓	76 ↓
17 1	47 x	77 b
18 3	48 $y \rightarrow ()$	78 ↑
19 $x \supset y$	49 e	79 4
1a ROLL ↑	4a CLR x	7a ÷
1b $y \rightarrow ()$	4b ↑	7b c
1c d	4c FMT	7c ROLL ↑
1d ÷	4d ↓	7d FMT
20 5	50 c	80 ↓
21 0	51 ↑	81 ROLL ↓
22 0	52 4	82 $x \supset y$
23 $x \supset y$	53 ÷	83 FMT
24 ÷	54 0	84 ↓
25 $y \rightarrow ()$	55 ↑	85 ROLL ↓
26 -	56 b	86 $x \supset y$
27 f	57 FMT	87 FMT
28 5	58 ↑	88 ↓
29 0	59 ROLL ↑	89 c
2a 0	5a $x \supset y$	8a +
2b ROLL ↑	5b FMT	8b e
2c ÷	5c ↓	8c If $y > x$
2d $y \rightarrow ()$	5d ROLL ↑	8d 9

Program 1

Continued

```

90  5
91  0
92  GO TO
93  7
94  d
95  2
96  FMT
97  GO TO
98  END

```

Program 2

LOAD POINTS

```

00  CONTINUE
01  STOP
02  x+( )
03  -
04  d
05  y+( )
06  -
07  c
08  x-( )
09  -
0a  f
0b  ROLL ↑
0c  x
0d  y+( )

```

```

20  ROLL ↓
21  -
22  0
23  ROLL ↑
24  If x=y
25  2
26  c
27  ROLL ↓
28  x ⊃ y
29  GO TO
2a  1
2b  8
2c  ↓
2d  y+( )

```

```

40  ÷
41  ln x
42  ↑
43  x-( )
44  -
45  3
46  FMT
47  y+( )
48  x ⊃ y
49  1
4a  -
4b  ↓
4c  FMT
4d  y+( )

```

```

10  c
11  5
12  ↑
13  0
14  ↑
15  2
16  4
17  7
18  FMT
19  y+( )
1a  ROLL ↓
1b  1
1c  -
1d  x ⊃ y

```

```

30  -
31  3
32  STOP
33  y+( )
34  -
35  b
36  ROLL ↑
37  x+( )
38  b
39  x-( )
3a  -
3b  d
3c  -
3d  ↑

```

```

50  ↑
51  1
52  -
53  b
54  x ⊃ y
55  FMT
56  y+( )
57  IF FLAG
58  7
59  1
5a  ↑
5b  1
5c  -
5d  y+( )

```

Program 2

Continued

60	-	70	2
61	3	71	x→()
62	x←()	72	-
63	-	73	3
64	c	74	3
65	ROLL ↑	75	FMT
66	+	76	GO TO
67	x←()	77	END
68	-		
69	b		
6a	↑		
6b	0		
6c	GO TO		
6d	3		

Program 3

PLOT POINTS

00	2	1c	x	38	+
01	2	1d	y→()	39	↓
02	4			3a	x ⊃ y
03	2			3b	FMT
04	↑	20	b	3c	↑
05	FMT	21	x←()	3d	FMT
06	π	22	-		
07	GO TO	23	2		
08	7	24	x ⊃ y	40	↓
09	c	25	1	41	b
0a	-	26	-	42	-
0b	↓	27	y→()	43	-
0c	↑	28	-	44	↓
0d	c	29	2	45	x ⊃ y
		2a	↓	46	FMT
		2b	FMT	47	↓
		2c	π	48	x←()
		2d	↑	49	a
10	π			4a	ROLL ↓
11	y→()			4b	c
12	-			4c	-
13	2			4d	↓
14	ROLL ↓	30	x←()		
15	f	31	-		
16	-	32	f		
17	x←()	33	x		
18	-	34	b	50	FMT
19	e	35	ROLL ↑	51	↑
1a	x	36	x→()	52	FMT
1b	ROLL ↑	37	a	53	↓

Program 3

continued

54	↑	60	↑	70	↑
55	c	61	$x \leftarrow ()$	71	f
56	+	62	-	72	$x \rightarrow ()$
57	+	63	3	73	-
58	↓	64	If $x=y$	74	a
59	FMT	65	6	75	d
5a	↑	66	d	76	$x \rightarrow ()$
5b	$x \leftarrow ()$	67	1	77	-
5c	-	68	-	78	9
5d	2	69	↓	79	4
		6a	GO TO	7a	FMT
		6b	0	7b	GO TO
		6c	4	7c	↑
		6d	FMT	7d	1
80	CHG. SIGN	90	$x \supset y$		
81	If $x=y$	91	2		
82	8	92	+		
83	b	93	↓		
84	↑	94	If $x=y$		
85	$x \supset y$	95	6		
86	↑	96	d		
87	1	97	GO TO		
88	GO TO	98	0		
89	0	99	4		
8a	a	9a	END		
8b	$x \leftarrow ()$				
8c	-				
8d	3				

Program 4

SELECT POINTS AND MAKE FIT

00	Continue	0c	1	18	CHG. SIGN
01	STOP	0d	STOP	19	If $x=y$
02	↑			1a	2
03	3			1b	1
04	x	10	$x \leftarrow ()$	1c	GO TO
05	2	11	-	1d	2
06	4	12	1		
07	2	13	↑	20	8
08	$x \supset y$	14	FMT	21	↓
09	-	15	π	22	2
0a	y ()	16	↑	23	-
0b	-	17	1		

Program 4

continued

24	↓	50	2	80	GO TO
25	GO TO	51	↓	81	1
26	7	52	FMT	82	3
27	4	53	π	83	2
28	CHG. SIGN	54	x	84	4
29	ROLL ↑	55	ROLL ↓	85	7
2a	x ⊃ y	56	x ⊃ y	86	FMT
2b	-	57	2	87	π
2c	y→()	58	4	88	↑
2d	-	59	4	89	2
		5a	FMT	8a	4
		5b	+	8b	3
30	2	5c	f	8c	FMT
31	x ⊃ y	5d	ROLL ↑	8d	π
32	FMT				
33	π	60	x	90	x
34	÷	61	ROLL ↓	91	2
35	÷	62	x ⊃ y	92	4
36	2	63	2	93	6
37	4	64	4	94	FMT
38	7	65	6	95	π
39	FMT	66	FMT	96	↑
3a	+	67	+	97	x
3b	↓	68	↑	98	↓
3c	x	69	x	99	-
3d	x→()	6a	2	9a	y→()
		6b	4	9b	e
40	+	6c	3	9c	2
41	2	6d	FMT	9d	4
42	4				
43	5	70	+	a0	5
44	FMT	71	x←()	a1	FMT
45	+	72	-	a2	π
46	x←()	73	2	a3	↑
47	-	74	↑	a4	2
48	2	75	x←()	a5	4
49	↑	76	-	a6	3
4a	1	77	3	a7	FMT
4b	-	78	If x=y	a8	π
4c	y→()	79	8	a9	x
4d	-	7a	3	aa	2
		7b	1	ab	4
		7c	-	ac	6
		7d	↑	ad	FMT

Program 4

continued

b0 π
b1 \uparrow
b2 2
b3 4
b4 4
b5 FMT
b6 π
b7 x
b8 \downarrow
b9 -
ba e
bb \div
bc $y \rightarrow ()$
bd -

c0 7
c1 0
c2 $x \rightarrow ()$
c3 d
c4 $x \rightarrow ()$
c5 -
c6 8
c7 5
c8 FMT
c9 GO TO
ca END

Program 5

00 \uparrow
01 2
02 4
03 7
04 FMT
05 π
06 \uparrow
07 2
08 4
09 4
0a FMT
0b π
0c x
0d 2

20 \div
21 $y \rightarrow ()$
22 -
23 6
24 2
25 4
26 3
27 FMT
28 π
29 \uparrow
2a e
2b \div
2c \downarrow
2d \sqrt{x}

40 -
41 4
42 $x \rightarrow ()$
43 -
44 1
45 \uparrow
46 FMT
47 π
48 \uparrow
49 1
4a CHG. SIGN
4b If $x=y$
4c 5
4d 2

10 4
11 5
12 FMT
13 π
14 \uparrow
15 2
16 4
17 6
18 FMT
19 π
1a x
1b \downarrow
1c -
1d e

30 $x \rightarrow ()$
31 -
32 5
33 2
34 4
35 7
36 FMT
37 π
38 \uparrow
39 e
3a \div
3b \downarrow
3c \sqrt{x}
3d $x \rightarrow ()$

50 GO TO
51 5
52 a
53 \downarrow
54 2
55 -
56 d
57 $x \supset y$
58 a
59 0
5a CHG. SIGN
5b ROLL \uparrow
5c $x \supset y$
5d -

Program 5

continued

60 $y \rightarrow ()$
 61 -
 62 2
 63 $x \supset y$
 64 FMT
 65 π
 66 \div
 67 \div
 68 $y \rightarrow ()$
 69 f
 6a \downarrow
 6b $x \leftarrow ()$
 6c -
 6d 7

70 -
 71 $x \leftarrow ()$
 72 -
 73 2
 74 \uparrow
 75 1
 76 -
 77 $y \rightarrow ()$
 78 -
 79 2
 7a \downarrow
 7b FMT
 7c π
 7d \uparrow

80 $x \leftarrow ()$
 81 -
 82 6
 83 x
 84 \downarrow
 85 -
 86 \downarrow
 87 \uparrow
 88 x
 89 f
 8a x
 8b d
 8c +
 8d $y \rightarrow ()$

90 d
 91 1
 92 \uparrow
 93 $x \leftarrow ()$
 94 -
 95 8
 96 +
 97 $y \rightarrow ()$
 98 -
 99 8
 9a \downarrow
 9b $x \leftarrow ()$
 9c -
 9d 2

a0 \uparrow
 a1 $x \leftarrow ()$
 a2 -
 a3 3
 a4 If $x=y$
 a5 a
 a6 d
 a7 1
 a8 -
 a9 \downarrow
 aa GO TO
 ab 4
 ac 4
 ad \downarrow

b0 $x \leftarrow ()$
 b1 -
 b2 8
 b3 \uparrow
 b4 2
 b5 -
 b6 \downarrow
 b7 \div
 b8 \downarrow
 b9 \sqrt{x}
 ba \uparrow
 bb \uparrow
 bc $x \leftarrow ()$
 bd -

c0 5
 c1 x
 c2 \downarrow
 c3 $x \rightarrow ()$
 c4 f
 c5 $y \rightarrow ()$
 c6 e
 c7 6
 c8 FMT
 c9 GO TO
 ca END

Program 6

00 RCL	30 9	60 4
01 ↑	31 If y>x	61 7
02 x←()	32 5	62 FMT
03 -	33 9	63 y→()
04 4	34 x←()	64 ↑
05 ROLL ↑	35 -	65 1
06 x	36 6	66 -
07 x←()	37 ROLL ↑	67 2
08 -	38 x	68 4
09 7	39 x→()	69 2
0a Continue	3a c	6a If x=y
0b e^x	3b x←()	6b 7
0c ROLL ↑	3c -	6c 3
0d $x \ominus y$	3d 7	6d ↓
10 x	40 +	70 GO TO
11 $x \ominus y$	41 x←()	71 6
12 PRINT	42 -	72 2
13 PRINT	43 a	73 x←()
14 ↓	44 -	74 -
15 1	45 x←()	75 9
16 CHG. SIGN	46 -	76 x→()
17 ↑	47 e	77 d
18 x←()	48 x	78 x←()
19 -	49 ↓	79 -
1a 6	4a $x \ominus y$	7a a
1b ÷	4b FMT	7b x→
1c ROLL ↑	4c ↓	7c f
1d $x \ominus y$	4d c	7d π
20 ÷	50 ↑	80 ↑
21 ÷	51 x←()	81 8
22 ↓	52 -	82 FMT
23 PRINT	53 c	83 GO
24 PRINT	54 +	84 END
25 0	55 ↓	
26 ↑	56 GO TO	
27 ↑	57 2	
28 x←()	58 6	
29 -	59 0	
2a f	5a ↑	
2b x	5b FMT	
2c x←()	5c ↑	
2d -	5d 2	

Program 7

00	0	30	ROLL ↑	60	+
01	↑	31	$x \supset y$	61	↑
02	FMT	32	3	62	e^x
03	↑	33	-	63	ROLL ↑
04	STOP	34	$x \leftarrow ()$	64	e^x
05	IF FLAG	35	-	65	$x \supset y$
06	0	36	3	66	-
07	b	37	If $x > y$	67	↑
08	GO TO	38	4	68	$\ln x$
09	1	39	0	69	↑
0a	1	3a	↑	6a	$x \leftarrow ()$
0b	SET FLAG	3b	GO TO	6b	-
0c	8	3c	2	6c	2
0d	FMT	3d	5	6d	FMT
10	GO TO	40	0	70	$y \rightarrow ()$
11	↑	41	↑	71	↑
12	3	42	$x \rightarrow ()$	72	3
13	x	43	-	73	-
14	$y \rightarrow ()$	44	4	74	$y \rightarrow ()$
15	-	45	2	75	-
16	d	46	4	76	2
17	$x \leftarrow ()$	47	2	77	2
18	-	48	$x \rightarrow ()$	78	4
19	3	49	-	79	2
1a	↑	4a	2	7a	↑
1b	1	4b	$x \leftarrow ()$	7b	$x \leftarrow ()$
1c	-	4c	-	7c	-
1d	$y \rightarrow ()$	4d	2	7d	d
20	-	50	FMT	80	-
21	2	51	π	81	↑
22	2	52	↑	82	If $x > y$
23	4	53	$x \leftarrow ()$	83	9
24	2	54	-	84	5
25	↑	55	4	85	$x \leftarrow ()$
26	FMT	56	↑	86	-
27	π	57	$x \leftarrow ()$	87	c
28	ROLL ↑	58	-	88	↑
29	FMT	59	6	89	$x \leftarrow ()$
2a	$y \rightarrow ()$	5a	x	8a	-
2b	$x \supset y$	5b	$x \leftarrow ()$	8b	4
2c	1	5c	-	8c	+
2d	-	5d	7	8d	$y \rightarrow ()$

Program 7

continued

```

90  -
91  4
92  GO TO
93  4
94  b
95  1
96  CHG. SIGN
97   $x \subset y$ 
98  8
99  FMT
9a  GO TO
9b  END

```

Program 8

00 π	20 2	40 -
01 If $x=y$	21 4	41 4
02 5	22 2	42 $x \leftarrow ()$
03 a	23 $x \rightarrow ()$	43 -
04 IF FLAG	24 -	44 3
05 2	25 4	45 If $x>y$
06 0	26 $x \leftarrow ()$	46 5
07 \downarrow	27 -	47 0
08 ROLL \uparrow	28 3	48 $x \leftarrow ()$
09 FMT	29 \uparrow	49 -
0a $y \rightarrow ()$	2a 1	4a 5
0b \uparrow	2b -	4b GO TO
0c 3	2c $y \rightarrow ()$	4c 2
0d -	2d -	4d 9
10 $x \leftarrow ()$	30 5	50 STOP
11 -	31 \downarrow	51 IF FLAG
12 3	32 FMT	52 5
13 If $x>y$	33 π	53 7
14 1	34 \uparrow	54 7
15 a	35 $x \leftarrow ()$	55 FMT
16 \downarrow	36 -	56 GO TO
17 GO TO	37 4	57 1
18 0	38 FMT	58 FMT
19 9	39 $y \rightarrow ()$	59 GO TO
1a 3	3a \uparrow	5a STOP
1b FMT	3b 3	5b IF FLAG
1c GO TO	3c -	5c 7
1d CONT	3d $y \rightarrow ()$	5d 5

Program 8
continued

60	$x \leftarrow ()$	70	FMT	80	FMT
61	-	71	$y \rightarrow ()$	81	π
62	6	72	GO TO	82	$x \rightarrow ()$
63	\uparrow	73	8	83	-
64	8	74	5	84	7
65	4	75	8	85	STOP
66	FMT	76	4	86	IF FLAG
67	$y \rightarrow ()$	77	FMT	87	8
68	$x \leftarrow ()$	78	π	88	c
69	-	79	$x \rightarrow ()$	89	4
6a	7	7a	-	8a	FMT
6b	\uparrow	7b	6	8b	GO TO
6c	8	7c	8	8c	7
6d	5	7d	5	8d	FMT
					GO TO
					END

Program 9

00	CONT	20	5	40	8
01	STOP	21	FMT	41	5
02	-	22	$y \rightarrow ()$	42	FMT
03	8	23	8	43	π
04	4	24	4	44	x
05	FMT	25	FMT	45	\downarrow
06	$y \rightarrow ()$	26	π	46	$x \supset y$
07	$x \leftarrow ()$	27	+	47	\div
08	-	28	\downarrow	48	\downarrow
09	1	29	\uparrow	49	$\ln x$
0a	$x \rightarrow ()$	2a	$\ln x$	4a	\uparrow
0b	-	2b	\uparrow	4b	$x \leftarrow ()$
0c	2	2c	$x \leftarrow ()$	4c	-
0d	$x \leftarrow ()$	2d	-	4d	2
10	-	30	2	50	FMT
11	2	31	FMT	51	$y \rightarrow ()$
12	FMT	32	$y \rightarrow ()$	52	\uparrow
13	π	33	$x \supset y$	53	2
14	\uparrow	34	1	54	-
15	1	35	-	55	$x \leftarrow ()$
16	CHG. SIGN	36	$y \rightarrow ()$	56	-
17	If $x=y$	37	-	57	3
18	6	38	2	58	If $x>y$
19	3	39	\downarrow	59	6
1a	\downarrow	3a	FMT	5a	c
1b	e^x	3b	π	5b	$y \rightarrow ()$
1c	\uparrow	3c	e^x	5c	-
1d	8	3d	\uparrow	5d	2

Program 9
continued

60	GO TO	70	+()
61	0	71	-
62	d	72	f
63	x+()	73	x
64	-	74	y+()
65	2	75	c
66	↑	76	3
67	3	77	FMT
68	-	78	GO TO
69	GO TO	79	END
6a	5		
6b	5		
6c	STOP		
6d	↑		

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TEMPERATURE AND ENVIRONMENTAL EFFECTS ON THE PHOSPHORESCENCE
OF PYRAZINE, BENZOTRIFLORIDE, AND BENZOTRICHLORIDE

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ABSTRACT

The temperature dependence of the phosphorescence lifetime of pyrazine in both the high and low temperature crystalline phases of cyclohexane were measured from 77°K to approximately 150°K. This data was fit to a function of the form $\frac{1}{\tau} = k_0 + k_1 \exp(-\Delta E/k_B \tau)$ where k_0 , k_1 and ΔE have different values for each crystal phase. The temperature dependence of the phosphorescence was measured from 77°K to approximately 150°K for the following systems: benzotrifluoride in glassy and in crystalline methylcyclohexane and benzotrichloride in crystalline methylcyclohexane. The benzotrifluoride data for the crystalline sample agrees almost exactly the data which Kilmer and Spangler have measured for toluene in methylcyclohexane, while the benzotrichloride samples show a very different temperature dependence from that of the toluene or benzotrifluoride. This indicates that the increased spin-orbit coupling due to chlorine atoms severely alters the triplet-state depopulation scheme, while very little alteration occurs for the benzotrifluoride. The phosphorescence lifetime as a function of emission wavelength for the following systems at 77°K was measured: pyrazine in the high and low temperature crystal phases of cyclohexane and benzotrifluoride in glassy and crystalline samples of methylcyclohexane. For each sample the phosphorescence lifetimes is constant across the emission wavelengths, but this constant is different for each of the two crystal samples of pyrazine in cyclohexane and for each of the two sample types of benzotrifluoride in methylcyclohexane. It is concluded that environmental conditions of the solvent must be explicitly considered in any detailed scheme of phosphorescence.