Studies On Photo-induced Luminescence And Electrode Potentials.

STUDIES ON PHOTO-INDUCED LUMINESCENCE AND ELECTRODE POTENTIALS

BY

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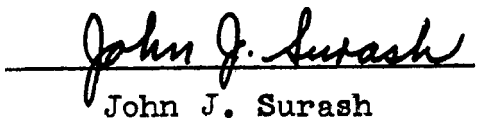

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ABSTRACT

The primary objective of this study was to investigate the cause of the photopotentials produced upon irradiation of absolute ethanol solutions of organic compounds. Negative photopotentials were recorded for the following compounds in this study: Acetophenone, 4-amino-, 4-bromo-, 4-hydroxy-, 4-methoxy-, 4-nitro-acetophenone, anthraquinone (9,10), anthraquinone 2,6 di sulfonic acid di sodium salt, benzaldehyde, benzoin, benzophenone, 4-bromo-, 4,4'-dimethyl-benzophenone, benzopinacol, p-benzoquinone, benzoyl peroxide, 2,2' bipyridyl, diphenylamine, fluorescein, tetrabromofluorescein, 1,4 naphthoquinone and phenazine. Earlier investigators reported positive potentials for several of the above mentioned compounds.

When the radiation was made incident on the nitrogen-flushed solution in the cell, the photopotential rose to a steady-state value and decayed slowly when the exciting radiation was extinguished. The following mechanism is proposed to account for the negative photopotential: Absorption of radiation by the compound to yield an excited state; formation of an intermediate species from the excited state; and interaction of the intermediate with the electrode to give a photopotential. The observed rise time was attributed to the formation of the intermediate and the decay time by reaction of the intermediate and diffusion of

the intermediate away from the electrode surface. Experimental observations on the intermediate, in the case of anthraquinone (9,10), are shown to be consistent with a free radical mechanism.

Positive potentials were observed only when oxygen was present, obscuring the primary process. The production of positive photopotentials has been shown to be due to peroxide formation.

Also, the photo-induced electrode potentials were investigated for oxygen-free solutions of metal oxalate complexes in water. A negative photopotential was observed in all cases.

The effect of variables was studied. Furthermore, it was determined that the photochemical production of the intermediate species did not require the presence of an electrode.

Attempts were made to determine the order of reaction of the rise and decay curves. Results indicated that complex equations are involved.

Absorption and fluorescence spectra of the intermediates at room temperature and luminescence spectra at liquid-nitrogen temperature are presented and discussed.

INTRODUCTION

The photovoltaic effect (sometimes called the Becquerel Effect) refers to the production of an electromotive force when two electrodes, immersed in a suitable electrolyte, are unsymmetrically illuminated. This phenomenon was first reported by Becquerel in 1839 (1). Since that time, numerous investigators have been concerned with the photovoltaic effect and several baffling, and sometimes conflicting, reports have been published. The photovoltaic effect has been observed for different types of electrode systems and electrolytes. Six experimental arrangements have been described in a review article (2):

I. Metal electrodes immersed in a suitable electrolyte.

II. Metal electrodes immersed in a fluorescent solution.

III. Metal electrodes immersed in an organic, non-fluorescent solution.

IV. Metal electrodes coated with an inorganic compound and immersed in a solution of an electrolyte.

V. Metal electrodes coated with a dye and immersed in a solution of an electrolyte.

VI. Metal electrodes separated by a semi-conductor.

Most of the studies reported in the literature have been concerned with experimental arrangements IV, V, and VI. A summary of work on equilibrium processes to 1930 can be obtained from Hughes and DuBridge (3). More recently Levin and co-workers published a series of articles which summarized previous experimental work and extended investigations in this field (4,5,6). Their work involved metal electrodes immersed in organic fluorescent and non-fluorescent solutions. The first paper dealt with experimental variables as they affect photopotentials. The other two papers were concerned with: (1) an attempt to correlate the absorption spectrum of a compound and the photopotential produced as a function of wavelength of radiation, and (2) an investigation of certain anomalies, which in the case of benzaldehyde, were attributed to peroxide formation.

Results of some of Levin's work concerning photopotentials of various compounds are shown in Table I. These data were obtained using the following experimental setup:

(1) A cubical glass cell, 5 x 5 x 5 cm., opened to the atmosphere.

(2) Two platinum electrodes - the irradiated electrode was 0.5 mm in diameter and 2 mm long, and the reference electrode was 2 x 6 cm. x .035 cm. thick.

TABLE I

PHOTOPOTENTIALS OF VARIOUS COMPOUNDS ACCORDING TO LEVIN

Substance	Conc. (Molality)	Photopotential (Millivolts)
Acetophenone	0.10	+ 22.0
Anthraquinone (9,10)	0.003	+ 38.5
Benzaldehyde	0.12	+ 49.5
Benzoin	0.06	+117.7
Benzophenone	0.07	+ 77.0
p-Benzoquinone	0.12	+ 66.0(transient)
Benzhydrol	0.07	none
Hydroquinone	0.12	none

(3) Absolute ethanol as solvent.

(4) Excitation wavelengths longer than 3000 Å supplied by a General Electric 100 watt clear glass-covered Mercury Lamp.

(5) An Electrometer in conjunction with a galvanometer as the detector.

Except for benzaldehyde, no mention is made of the purity of the compounds.

Since Levin and his co-workers failed to determine the cause of the photopotential, the present investigation was begun to establish the nature of the physical processes giving rise to the photo-induced electrode potentials for equilibrium systems (those in which no material transfer occurs at the electrode surface). In addition, the effect of irradiation on systems involving mass transfer across a concentration gradient, as in polarography, was investigated. The results of this work are presented in Part I of this thesis.

In the course of the above investigations photo-induced luminescence was observed in the solutions. The nature of the photo-induced luminescence was investigated as described in Part II of this thesis.

PART I

STUDIES ON PHOTO-INDUCED ELECTRODE POTENTIALS

INTRODUCTION

The initial title of this thesis was to be "Studies on the Photovoltaic Effect for Equilibrated and Mass Transfer Controlled Electrodes". However, the present work has shown that the effect referred to as a "photovoltaic effect" is not really a true photovoltaic effect but a change in electrode potential caused by a photochemically-produced intermediate species.

A broad definition of a photovoltaic effect was given on Page 3. However, practically all of the recent work relating to this effect has involved coated electrode-electrolyte systems (7,8,9,10) and semi-conductor-electrolyte systems (11,12,13,14) in which it has been definitely shown that the photovoltaic effect resulted from a chemical change of the irradiated electrode. This, then, is to be considered the criterion for a true photovoltaic effect.

In this present work it has been shown that the observed effect is due to photo chemical production of an intermediate species which occurs without the presence of an electrode. An electrode was used simply to indicate the change in potential due to the new intermediate species. Therefore, on this basis, the author felt that the observed effect should not be called a photovoltaic effect and subsequently chose the title of "Studies on Photo-Induced Luminescence and Electrode Potentials" for this thesis.

EXPERIMENTAL

Reagents and Solutions

The best available grades of chemicals were used and where necessary they were further purified by methods indicated in Table II. (The purification methods are described immediately following Table II). The uncorrected melting points versus those recorded in the literature are shown in Table III.

The source and quality of solvents used are listed in Table IV.

Solutions used were flushed with oxygen-free Nitrogen for ten minutes prior to use. Oxygen-free Nitrogen was obtained by passing Nitrogen (Airco Dry Nitrogen) through a purification train consisting of separate containers of vanadous chloride solution (15), water, Ascarite and calcium chloride.

Apparatus and Procedures

Photopotential-Time Curves

The instrument used in this investigation is described in detail in Appendix A. It consisted of:

(1) A Vycor "T" shaped cell.

(2) A platinum point electrode as the irradiated electrode and a silver-silver chloride electrode as the dark or reference electrode.

TABLE II

SOURCE AND METHOD OF PURIFICATION FOR COMPOUNDS

Compound	Source	Purification Method
1. Acetophenone	DuPont	Vacuum distillation
2. 4-Aminoacetophenone	Eastman Kodak	a
3. 4-Bromoacetophenone	Eastman Kodak	a
4. 4-Hydroxyacetophenone	Eastman Kodak	a
5. 4-Methoxyacetophenone	Eastman Kodak	Vacuum sublimation
6. 4-Nitroacetophenone	Aldrich Chemical Company	a
7. Anthraquinone (9,10)	Eastman Kodak	a (repeated twice)
8. Anthraquinone 2,6 DiSulfonic acid DiSodium Salt	K & K Laboratories, Inc.	b
9. Ascorbic Acid	Eastman Kodak	None
10. Benzaldehyde	J. T. Baker	Vacuum distillation 69.5°C at 20 mm.
11. Benzhydrol	Lehigh Stock	c
12. Benzoin	Eastman Kodak	a
13. Benzophenone	Eastman Kodak	a
14. 4-Bromobenzophenone	Aldrich Chemical Company	a
15. 4,4'-Dimethylbenzophenone	Eastman Kodak	c
16. 2 Hydroxy, 5 Chloro Benzophenone	DuPont	None

TABLE II (Cont.)

Compound	Source	Purification Method
17. Benzopinacol	Lehigh Stock	Recrystallization from Ethanol
18. p-Benzoquinone	Eastman Kodak	a (repeated twice)
19. Benzoyl Peroxide	Matheson Coleman & Bell	None
20. 2,2' Bipyridyl	The G.Frederick Smith Chemical Co.	a
21. Diphenylamine	Merck & Co.,Inc.	c
22. Fluorescein (Water Soluble-Uranine C.I.766)	Allied Chemical & Dye Corp.	None
23. Tetrabromofluorescein (Easin Y C.I.768)	Allied Chemical & Dye Corp.	None
24. Methyl Methacrylate (Monomer)	Rohm & Haas Co.	Vacuum Distillation 37.5°C at 75 mm.
25. 1,4 Naphthoquinone	Eastman Kodak	a (repeated twice)
26. Phenazine	Lehigh Stock	a
27. Tetraphenylhydrazine	DuPont	None
28. Styrene	Matheson Coleman & Bell	Vacuum Distillation 48°C at 20 mm.

Purification Methods

Method a - The compound was dissolved in hot absolute ethanol, treated with decolorizing carbon, boiled for five minutes, filtered and then crystallized from

TABLE II (Cont.)

absolute ethanol. After drying in a desiccator, the compounds were then vacuum sublimed.

Method b - The compound was heated with charcoal in aqueous solution and recrystallized from aqueous ethanol.

Method c - Same as Method a, except the compound was recrystallized from water following the boiling ethanol with decolorizing carbon treatment.

TABLE III

COMPARISON OF MELTING POINTS FOR COMPOUNDS

Compound	Melting Point in °C	
	Literature (16)	Found (Uncorrected)
1. Acetophenone	20.5	20.5
2. 4-Aminoacetophenone	106	105.5-106
3. 4-Bromoacetophenone	50-51	50-51
4. 4-Hydroxyacetophenone	109	109
5. 4-Methoxyacetophenone	38-39	38-39
6. 4-Nitroacetophenone	80-81	80
7. Anthraquinone (9,10)	286	285.5-286
8. Benzhydrol	69°	67.5-68.5
9. Benzoin	137	136-137
10. Benzophenone	form 48.5	47.5-48.5
11. 4-Bromobenzophenone	82	81.5-82
12. 4,4' Dimethyl-benzophenone	95	94.5-95
13. Benzopinacol	186 decomp.	186.5 decomp.

TABLE III (Cont.)

Compound	Melting Point in °C	
	Literature (16)	Found (Uncorrected)
14. p-Benzoquinone	115.7	115-116
15. 2,2' Bipyridyl	69.5	69-70
16. Diphenylamine	54	54
17. 1,4 Naphthoquinone	125	124.5
18. Phenazine	171°, 173-4°	172-173

TABLE IV

SOLVENT INFORMATION

Solvent	Source	Grade
1. Benzene	Brothers Chemical Co.	Reagent ACS
2. Chloroform	J. T. Baker Chemical Co.	Analyzed Reagent
3. Di Ethyl Ether (anhydrous)	Mallinckrodt	Analytical Reagent
4. N,N-Dimethylformamide	Matheson Coleman & Bell	Spectro-Quality
5. Etharol, Absolute	U. S. Industrial Chem. Co.	Pure, 100%
6. Glycerol	Matheson Coleman & Bell	Spectro-Quality
7. 2-Methyl Butane	Eastman Kodak	Practical
8. Propanol, Iso	Matheson Coleman & Bell	Spectro-Quality
9. Pyridine	J. T. Baker Chemical Co.	Analyzed Reagent

(3) A Hanovia high pressure D.C. Xenon Compact Arc Lamp, air cooled, as a source of radiation.

(4) A double convex quartz lens in the incident light beam.

(5) A Corning No. 7-54 filter between the lens and iris diaphragm.

(6) A detection system of a D.C. electrometer (17) in conjunction with a Brown recorder.

To obtain a photopotential-time curve 25 ml. of sample were added to the Vycor cell. The cell with sample was then flushed for 10 minutes with oxygen-free nitrogen. An atmosphere of Nitrogen was maintained above the sample after the initial flushing. With the recorder running, the ultraviolet radiation was made incident on the cell by means of a cable control on the iris diaphragm and the photopotential-time curve was recorded.

Photopotential-Time Curves as a Function of Wavelength

The instruments and calibration procedures used in this part of the investigation are described in detail in Appendix A, Tables XXII and XXIII. The only difference in operating procedure for obtaining a photopotential-time curve involved the use of a monochromator inserted between the radiation source and cell.

Absorption Spectra

Absorption Spectra were obtained using a Warren Spectracord with matched 1 cm. glass-stoppered, fused-silica cells.

Polymerization Studies

Polymerization initiated with Anthraquinone (9,10) were carried out in a 15 cc. Pyrex test tube at room temperature (25°C) using absolute ethanol as the solvent and 2400-4200 Å radiation from a Xenon lamp, 56 cm. from the cell, as the activator. The monomers, Methyl Methacrylate and Styrene, were distilled at reduced pressure immediately prior to use. In the polymerization of Methyl Methacrylate, equal volumes of a 5×10^{-4} Molar ethanol solution of Anthraquinone (9,10) and Methyl Methacrylate were added to the test tube, flushed with nitrogen, sealed with a cork and paraffin, and irradiated for 1 hour, unless otherwise specified. A similar polymerization procedure was used for Styrene except that a nitrogen atmosphere was maintained over the sample throughout the 2 hours of irradiation. Changes in viscosity and appearance of precipitates were noted.

Polarographic Studies

The cell and irradiation system were the same ones used for the photopotential-time studies. A dropping mercury electrode in the form of an "L" was used as the

cathode and a mercury pool was used as the anode. The polarograms were recorded on an automatic recording polarograph constructed by Dr. E. J. Serfass at Lehigh in 1953.

All apparatus was turned on for fifteen minutes to a half hour prior to use. This was found to be sufficient time for the instruments and lamp to reach stability.

RESULTS

The photopotentials observed for various organic compounds in absolute ethanol are given in Table V. These were obtained using 2400-4200 Å radiation from a Xenon lamp 56 cm. from the cell and a nitrogen atmosphere above the sample, unless otherwise specified. A typical photopotential-time curve is shown in Figure 1. Photopotentials for the potassium metal oxalate complexes are presented in Table IX.

The effects of variables such as air, solvent, product, solute concentration, viscosity, and wavelength of incident radiation, on photopotentials are presented in Tables VI, VII, XI, XII, XIII, and XIV to XVI, respectively. The effect of Cobaltous ions on the photopotential of potassium cobaltioxalate Complex in water is shown in Table X.

The correlation between the photopotentials and absorption spectra for Anthraquinone (9,10), Benzoin and Benzophenone in absolute ethanol, as a function of wavelength of radiation are shown in Figures 6, 7 and 8, respectively.

The effect of 2400-4200 Å radiation on the absorption spectrum of Anthraquinone (9,10) in absolute ethanol is shown in Figure 2. Comparison of absorption spectra of Anthraquinone (9,10) in concentrated sulfuric acid, (non-irradiated solution), absolute ethanol, (irradiated and

non-irradiated solutions), and alkaline (KOH) absolute ethanol, (irradiated solution), are shown in Figures 3 and 4.

The effects of unfiltered radiation from a Xenon lamp on the absorption spectra of separate nitrogen flushed ethanol solutions of Benzophenone, Benzopinacol and Benzhydrol are shown in Figure 5.

Results of the polymerization of Styrene and Methyl Methacrylate using ultraviolet radiation as the activator and Anthraquinone (9,10) as the initiator are listed in Table VIII.

Half wave potentials for various quinones in different solvents containing Lithium Chloride as the supporting electrolyte are summarized in Tables XVII and XVIII.

TABLE V

PHOTOPOTENTIALS OF ORGANIC COMPOUNDS IN ABSOLUTE ETHANOL AT 0.01 M CONCENTRATIONS UNLESS OTHERWISE SPECIFIED

Compound	Photopotential in Millivolts
Acetophenone	- 434
4-Aminoacetophenone	- 43
4-Bromoacetophenone	- 210
4-Hydroxyacetophenone	- 62
4-Methoxyacetophenone	- 350
4-Nitroacetophenone	- 42
Anthraquinone (9,10) (.0005 M)	- 395
Anthraquinone 2,6 Di Sulfonic Acid Di Na Salt (.005 M)	- 250 (a)
Benzaldehyde	- 290
Benzhydrol	0
Benzoin	- 409
Benzophenone	- 400
4-Bromobenzophenone	- 350
4,4'-Dimethylbenzophenone	- 510
2 Hydroxy 5 Chloro Benzophenone	0
Benzopinacol (.005)	- 330 (b)

TABLE V (Cont.)

Compound	Photopotential in Millivolts
p-Benzoquinone	- 60
Benzoyl Peroxide	- 150
Bipyridyl (2,2')	- 240
Diphenylamine	- 465
Fluorescein	- 10
Tetrabromofluorescein (.0001 M)	- 200 (c)
Naphthoquinone (1,4) (.001 M)	- 95
Phenazine (.001 M)	- 345
Tetraphenylhydrazine	+ 130 (d)

(a) Solvent mixture used - 60% water and 40% absolute ethanol by volume.

(b) Used unfiltered radiation from Xenon lamp.

(c) Solution contained 0.001 M Ascorbic Acid. Also used unfiltered radiation from Xenon lamp.

(d) Solution used was the filtrate from a saturated solution of Tetraphenylhydrazine in absolute ethanol. A 0.01 M solution of Tetraphenylhydrazine in Chloroform gave a photopotential of + 155 millivolts.

TABLE VI

EFFECT OF AIR ON PHOTOPOTENTIALS

Compound	Molar Conc. in Absolute Ethanol	Photopotentials in Millivolts	
		Air (a)	Nitrogen
Acetophenone	0.01	+ 10	- 434
4-Bromoacetophenone	0.01	+ 60	- 210
4-Methoxyacetophenone	0.01	0	- 350
Anthraquinone (9,10)	0.0005	+ 70	- 395
Benzoin	0.01	+ 47	- 409
Benzophenone	0.01	+ 60	- 400

(a) Same experimental setup as for the Nitrogen flushed samples except that a 50 ml. Pyrex beaker was used as the cell and a 200 mesh screen with openings of .0029 inch was placed between the cell and iris diaphragm. Exclusion of air from the 50 ml. beaker, resulted in negative photopotentials for the above compounds.

TABLE VII

EFFECT OF SOLVENT ON PHOTOPOTENTIALS OF ANTHRAQUINONE (9,10)

Solvent	Anthraquinone (9,10) Molar Conc. X 10^3	Photopotential in Millivolts
Benzene	0.5	(a)
Chloroform	0.5	- 570
N,N-Dimethylformamide	1.0	- 370 (b)
Ethanol, Absolute	0.5	- 395
Ethanol, Absolute, Alkaline (c)	0.1	- 450
Isopropanol	0.5	- 215
Pyridine	0.5	(d)
Sulfuric Acid, Conc.	0.1	- 85

(a) Could not be measured due to low dielectric constant of benzene. However, no yellow intermediate was formed upon irradiation.

(b) Solvent had a residual photopotential of + 25 mv.

(c) Potassium Hydroxide added to alcohol before dissolving the Anthraquinone.

(d) Solvent reacted with the Anthraquinone before irradiation, therefore, no photopotential was determined.

TABLE VIII

POLYMERIZATION RESULTS

Trial No.	Activator	(By Weight) Initial Composition % Anthraquinone	% Monomer	% Ethanol (Absolute)	Irradiation Time	Remarks
1.	Ultraviolet	0.006	Methyl Methacrylate 55.0	45.0	(a) 5 minutes	Mixture very viscous after 24 hours standing. Considerable amount of insoluble material after 48 hours standing
2.	Ultraviolet	0.006	55.0	45.0	1 hour	Same as for 1
3.	None	0.006	55.0	45.0	None	Did not polymerize
4.	Ultraviolet	None	55.0	45.0	1 hour	Did not polymerize
5.	None	None	55.0	45.0	None	Did not polymerize
6.	Ultraviolet	0.006	Styrene 53.3	46.7	2 hours	Small amount of insoluble material after 2 hours irradiation
7.	None	0.006	53.3	46.7	None	Did not polymerize
8.	Ultraviolet	None	53.3	46.7	2 hours	Did not polymerize
9.	None	None	53.3	46.7	None	Did not polymerize

(a) Solution of Anthraquinone irradiated for 5 minutes with formation of yellow intermediate, Methyl Methacrylate was then added to this tube which was then sealed and placed in the dark without further irradiation

TABLE IX

PHOTOPOTENTIALS OF POTASSIUM METAL OXALATE COMPLEX 0.01 M IN WATER

Compound	Formula	Photopotential in Millivolts
Potassium Chromioxalate	$K_3Cr(C_2O_4)_3$	- 145
Potassium Cobaltioxalate	$K_3Co(C_2O_4)_3$	- 115
Potassium Ferrioxalate	$K_3Fe(C_2O_4)_3$	- 450

TABLE X

EFFECT OF COBALTOUS IONS ON THE PHOTOPOTENTIALS OF POTASSIUM COBALTIC OXALATE COMPLEX 0.01 M IN ACETIC ACID MODIFIED WATER

Molar Concentration of Cobalt Nitrate $Co(NO_3)_2 + 6H_2O$	Potential at Start	Photopotential Using 2400-4200 Å Irradiation
0	+ 245 mv	- 69 mv
0.1 (a)	+ 335 mv	- 135 mv
0.01	+ 310 mv	- 110 mv
0.001	+ 290 mv	- 90 mv
0.0001	+ 275 mv	- 75 mv

(a) A 0.1 M Co^{++} solution in acetic acid modified water without any $K_3Co(C_2O_4)_3$ gave a photopotential of + 80 mv. Acetic acid modified water without any $K_3Co(C_2O_4)_3$ gave no photopotential.

TABLE XI

EFFECT OF BENZOPINACOL ON THE PHOTOPOTENTIAL OF BENZOPHENONE 0.001 M IN ABSOLUTE ETHANOL

Molar Conc. of Benzopinacol in Absolute Ethanol X 10^3	Photopotential in Millivolts	
	Filtered light (2400-4200 Å)	Unfiltered light
0	- 200	- 305
1.0	- 204	- 310
0.5	- 196	- 305
0.1	- 200	- 300

TABLE XII

EFFECT OF SOLUTE CONCENTRATION ON PHOTOPOTENTIALS

Compound	Molar Concentration in Absolute Ethanol X 10^3	Photopotential in Millivolts
Anthraquinone (9,10)	0.5	- 395
"	0.1	- 285
"	0.05	- 225
"	0.01	- 200
"	0.005	- 195
"	0.001	0 (a)
Benzoin	30.0	- 500
	15.0	- 482
	7.5	- 308
Benzophenone	30.0	- 504
	15.0	- 427
	10.0	- 400
	7.5	- 355
	1.0	- 200
Diphenylamine	10.0	- 465
	1.0	- 465
	0.1	- 320
	0.05	- 160
	0.01	- 15

(a) Visual observation revealed the presence of a very small amount of yellow intermediate around the irradiated electrode but the detection system wasn't sensitive enough to show any photopotential.

TABLE XIII

EFFECT OF VISCOSITY ON PHOTOPOTENTIALS

Compound	Solvent Composition by Volume		Photopotential in Millivolts
	% Absolute Ethanol	% Glycerol	
Anthraquinone (9,10) (0.0001 M)	100	0	- 285
	90	10	- 275
	80	20	- 210
	70	30	- 165
	60	40	- 150
Benzophenone (0.01 M)	100	0	- 395
	80	20	- 265
	60	40	- 110
	40	60	- 80

TABLE XIV

EFFECT OF WAVELENGTH OF RADIATION ON THE PHOTOPOTENTIAL OF ANTHRAQUINONE (9,10) 0.0005 M IN ABSOLUTE ETHANOL

Wave Length in Å	Photopotential Uncorrected in Millivolts (A)	Xenon Lamp Relative Intensity (B) from Figure 47	Corrected Photo-Potential A/B Relative Units
2700	- 24.0	4.00	- 6.00
2800	- 31.2	4.05	- 7.70
2900	- 9.6	4.30	- 2.23
3000	- 27.2	4.65	- 5.85
3100	- 50.4	5.10	- 9.90
3200	- 60.0	5.70	-10.53
3300	- 43.2	6.30	- 6.84
3400	- 29.1	7.05	- 4.14
3500	- 3.5	7.80	- 0.45
3600	- 2.5	8.55	- 0.29

TABLE XV

EFFECT OF WAVELENGTH OF RADIATION ON THE PHOTOPOTENTIAL OF BENZOIN 0.005 M IN ABSOLUTE ETHANOL

Wave Length in Å	Photopotential Uncorrected in Millivolts (A)	Xenon Lamp Relative Intensity (B) from Figure 47	Corrected Photo-Potential A/B Relative Units
3100	- 141.0	5.10	- 28.0
3200	- 159.0	5.70	- 27.9
3300	- 121.6	6.30	- 19.3
3400	- 107.2	7.05	- 15.2
3500	- 94.4	7.80	- 12.1
3600	- 77.8	8.55	- 9.1
3700	- 20.8	9.40	- 2.2

TABLE XVI

EFFECT OF WAVELENGTH OF RADIATION ON THE PHOTOPOTENTIAL OF BENZOPHENONE 0.01 M IN ABSOLUTE ETHANOL

Wave Length in Å	Photopotential Uncorrected in Millivolts (A)	Xenon Lamp Relative Intensity (B) from Figure 47	Corrected Photo-Potential A/B Relative Units
2900	- 38.3	4.30	- 8.9
3000	- 33.6	4.65	- 7.3
3100	- 36.8	5.10	- 7.2
3200	- 38.4	5.70	- 6.7
3300	- 44.8	6.30	- 7.2
3400	- 49.6	7.05	- 7.1
3500	- 47.4	7.80	- 6.1
3600	- 41.6	8.55	- 4.9
3700	- 28.8	9.40	- 3.1

TABLE XVII

HALF-WAVE POTENTIALS FOR VARIOUS QUINONES 0.001 M IN N,N-DIMETHYLFORMAMIDE SOLUTIONS CONTAINING 0.1 M LITHIUM CHLORIDE

Quinone	Radiation 2400-4200 Å	$E_{1/2}$ (v) vs. Hg Pool	
		1st Wave	2nd Wave
p-Benzoquinone	None	—	- 0.25[a]
p-Benzoquinone	During run	—	- 0.25
p-Benzoquinone	Pre-irradiated 10 minutes	—	- 0.25
Naphthoquinone (1,4)	None	- 0.15	- 0.40
Naphthoquinone (1,4)	During run	- 0.15	- 0.40
Naphthoquinone (1,4)	Pre-irradiated 10 minutes	- 0.15	- 0.40
Anthraquinone (9,10)	None	- 0.34[b]	- 0.68[b]
Anthraquinone (9,10)	During run	- 0.34	- 0.68
Anthraquinone (9,10)	Pre-irradiated 10 minutes	- 0.34	- 0.68

(a) Reported in literature - 0.92 v; 0.1 M Tetrabutylammonium bromide used as supporting electrolyte.

(b) Reported in literature - 0.34 v 1st wave and - 1.10 v for 2nd wave.

TABLE XVIII

HALF-WAVE POTENTIALS FOR ANTHRAQUINONE (9,10) 0.0005 M IN ALCOHOL SOLVENTS CONTAINING 0.3 M LITHIUM CHLORIDE

Trial No.	Solvent	Radiation 2400-4200 Å	$E_{1/2}$ (v) vs. Hg Pool	
			1st Wave	2nd Wave
1	Isopropanol	None	- 0.68	None
1-A	Isopropanol	Soln. pre-irradiated 10 min. and during run	- 0.68	None
1	Absolute Ethanol	None	- 0.68	None
1-A	Absolute Ethanol	During run	- 0.95	None
1-B	Absolute Ethanol	Pre-irradiated 15 minutes	- 0.40	None
2	Absolute Ethanol	None	- 0.34	- 0.68
2-A	Absolute Ethanol	Pre-irradiated 1 minute	- 0.34	- 0.68
2-B	Absolute Ethanol	Pre-irradiated 3 minutes	- 0.34	- 0.68
2-C	Absolute Ethanol	Pre-irradiated 8 minutes	- 0.26	- 0.53
3	Absolute Ethanol	Pre-irradiated 15 minutes (a)	- 0.40	- 1.03
3-A	Absolute Ethanol	None	- 0.34	- 1.03
3-B	Absolute Ethanol	During run	- 0.34	≈ - 0.95
3-C	Absolute Ethanol	Pre-irradiated 10 minutes	- 0.34	None

(a) Pre-irradiation performed on sample solution in a large test tube prior to transfer to cell.

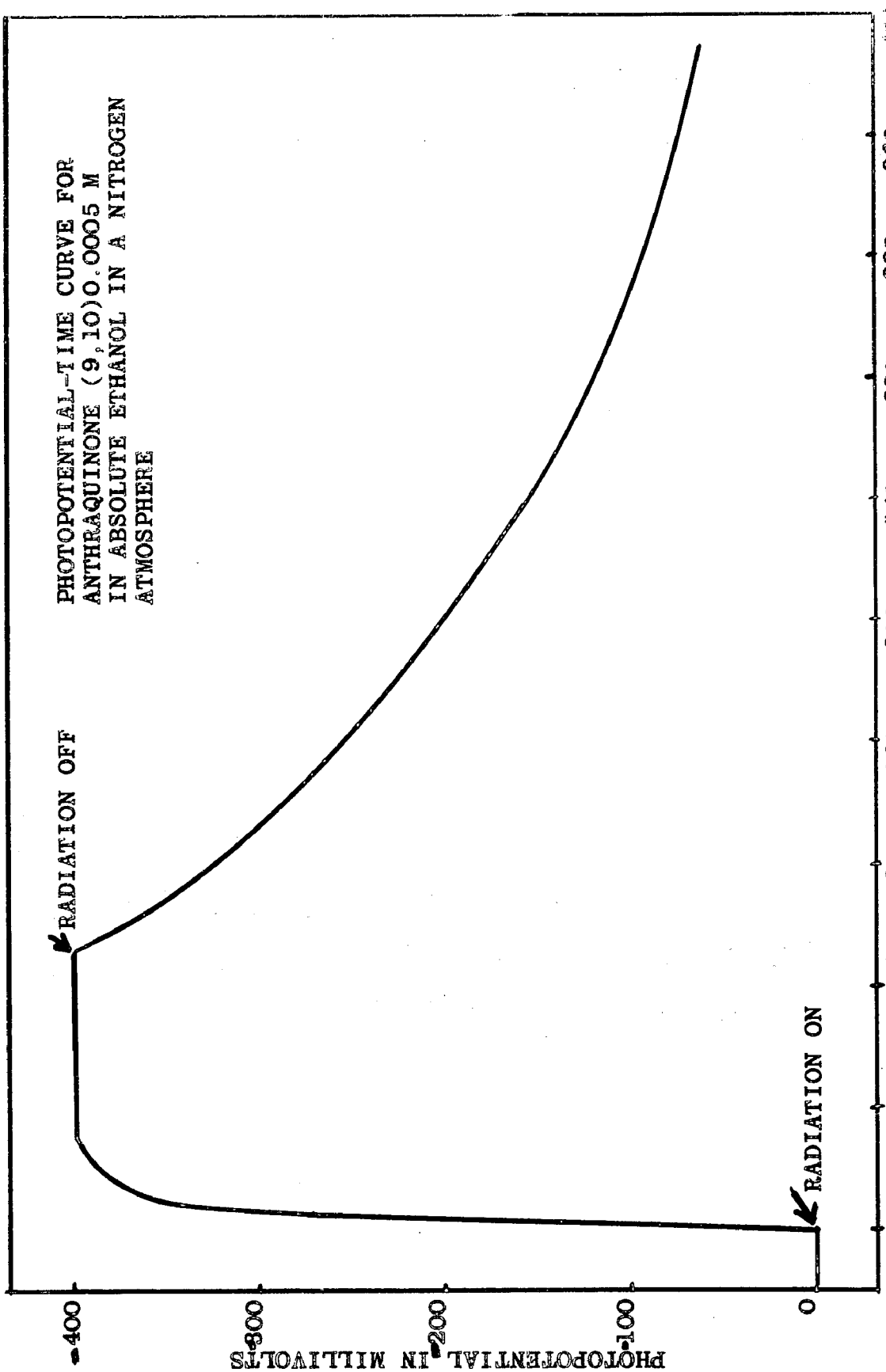
DISCUSSION OF RESULTS

Photopotentials for Anthraquinone (9,10)

Anthraquinone (9,10), AQ, was chosen as a model compound. Generally what has been found for AQ applies to the other compounds. AQ was selected because the AQ intermediate is easy to observe and is very stable.

A typical photopotential-time curve for 0.0005 M AQ in absolute ethanol in a nitrogen atmosphere is shown in Figure 1. It is clear from Figure 1 that the potential rapidly became more negative during illumination, reached a maximum negative potential, and slowly returned to a value near the initial point after the illumination was extinguished. The observed variation in the potential can be explained by the existence of an intermediate in the reduction of AQ. The initial rise in the photopotential-time curve occurs as the intermediate is photochemically produced at the electrode surface. As this product accumulates, a steady state is established between production, reaction and diffusion from electrode surface, causing the potential to remain constant as a function of time. When the radiation is shut off the potential changes to a value near the starting point. This is due to diffusion of the intermediate product away from the electrode surface combined with chemical reaction of the intermediate species. For long-lived intermediates such as the AQ

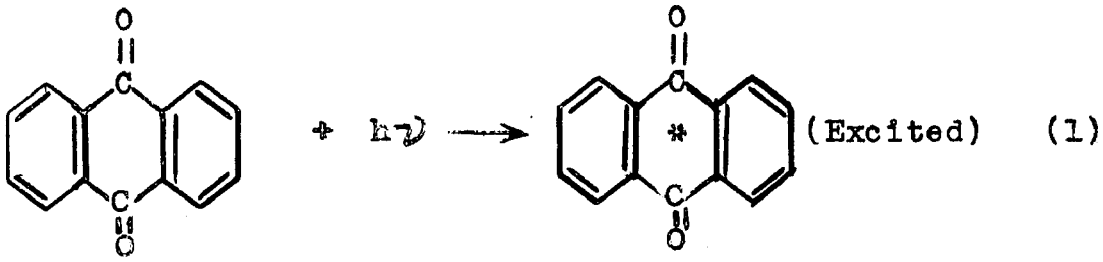
FIGURE 1


PHOTOPOTENTIAL-TIME CURVE FOR
ANTHRAQUINONE (9,10)0.0005 M
IN ABSOLUTE ETHANOL IN A NITROGEN
ATMOSPHERE
RADIATION OFF
RADIATION ON
PHOTOPOTENTIAL IN MILLIVOLTS
-400
-300
-200
-100
0
0
40
80
120
160
200
240
280
320
360
400
TIME IN SECONDS

intermediate, the former is the rate controlling process, whereas for short-lived species, the latter predominates.

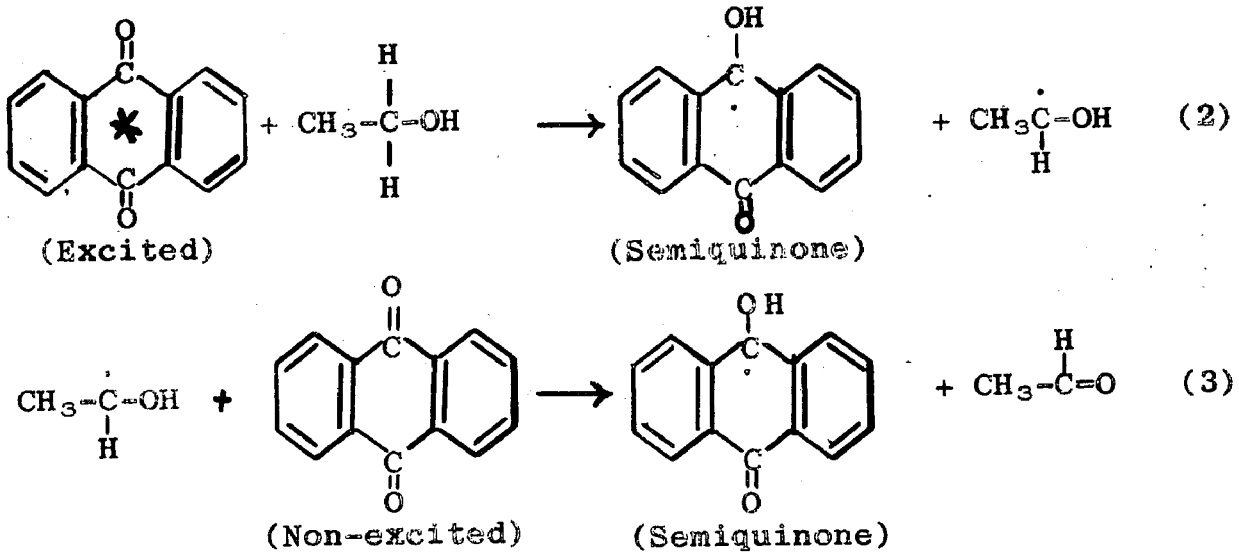
The following mechanism is proposed to account for the negative photopotential of AQ in absolute ethanol in a nitrogen atmosphere. Most of the compounds listed in Table V follow this mechanism. Exceptions to this mechanism are listed individually.

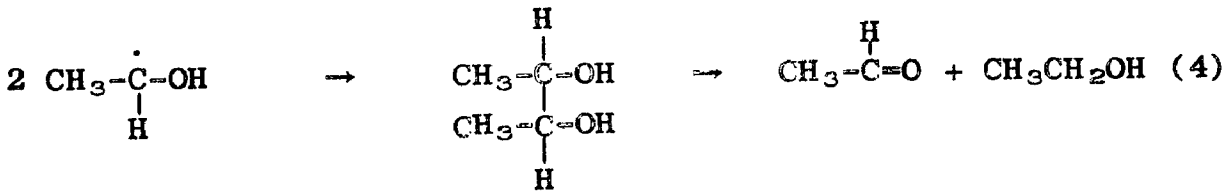
Primary Process

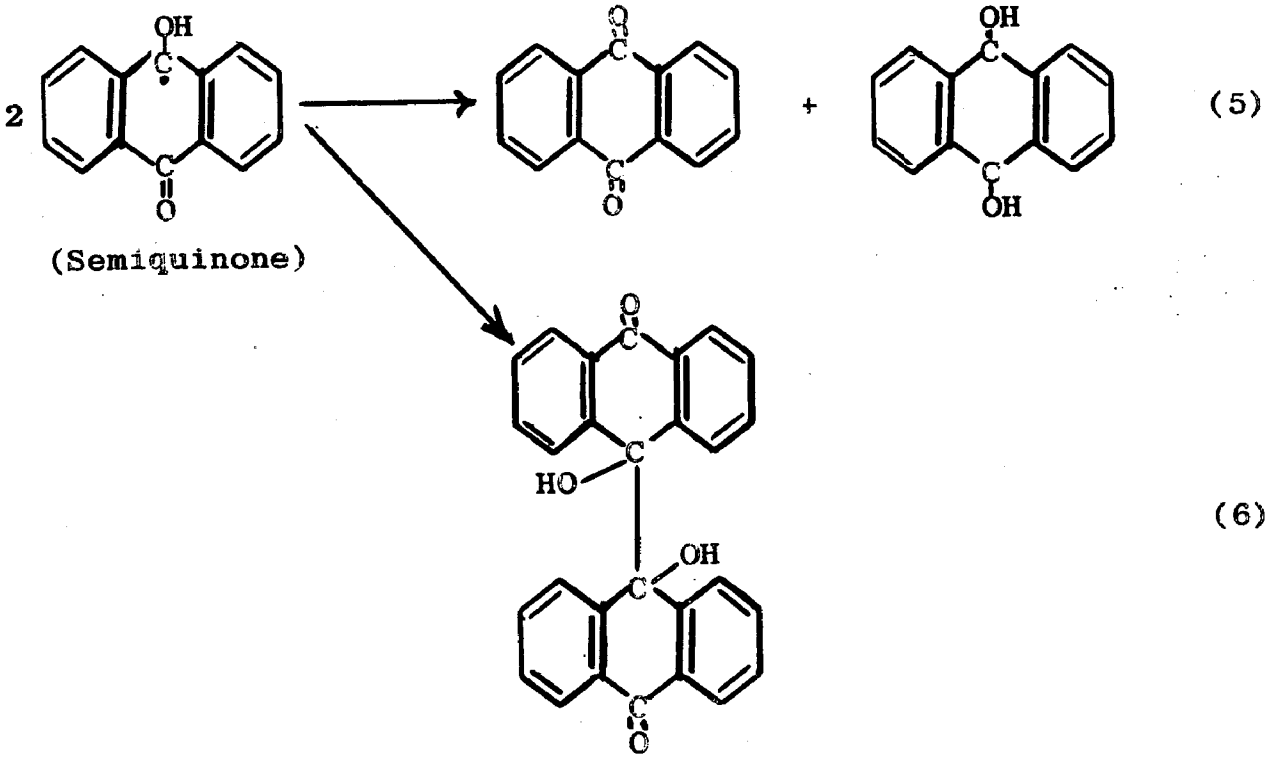


(1)

Since 2400-4200 Å radiation is effective in promoting this reaction, it is clear that the primary photochemical process must involve absorption of radiation by AQ (cf. Figure 2), rather than excitation of the absolute ethanol which is transparent above about 2200 Å. Since the $\pi \longrightarrow \pi^*$ transition seems to be as effective as well as the $n \longrightarrow \pi^*$ transition, interconversion between the excited states $^1\Gamma_{n,\pi^*}$ and $^1\Gamma_{\pi,\pi^*}$ probably occurs. Because the species involved is a radical, these must be converted to $^3\Gamma_{\pi,\pi^*}$.


(Excited)
(Semiquinone)
(2)
(Non-excited)
(Semiquinone)
(3)


(4)


(Semiquinone)
(5)
(6)

The yellow-colored semiquinone was found to be the cause of the negative potential. This can be explained by considering that some of the AQ molecules are converted to the yellow-colored semiquinone in the irradiated area. The platinum electrode is simply indicating the potential change due to the formation of the semiquinone, (•AQH). The following type of equation may be used to explain the potential changes

$$AQ + RH \longrightarrow \cdot AQH + R\cdot \qquad (7)$$

In terms of the Nernst equation

$$E = E^{\circ} + \frac{RT}{nF} \ell n \frac{[AQ][RH]}{[\cdot AQH][\cdot R]} \qquad (8)$$

The solvent molecule, RH, and solvent radical, •R, do not have much of an effect on the potential change since the concentration of RH is assumed to be constant and that the •R is very short-lived as shown in Equations 3 and 4. Therefore, the potential will be dependent upon the ratio of $\frac{[AQ]}{[\cdot AQH]}$. Since •AQH is being produced photochemically, this results in a smaller ratio of $\frac{[AQ]}{[\cdot AQH]}$ which in turn causes the potential to be more negative. In an alkaline medium the semiquinone radical is converted to the semiquinone radical ion.

$$\cdot AQH \rightleftharpoons \cdot AQ^{-} + H^{+} \qquad (9)$$

Therefore, in the Nernst equation, the ratio of $\frac{[AQ]}{[\cdot AQ^-]}$ is smaller during irradiation than the initial ratio and this should result in a negative photopotential. This was confirmed experimentally by addition of KOH to the alcoholic AQ solution which produced a more negative potential than the alcoholic AQ solution.

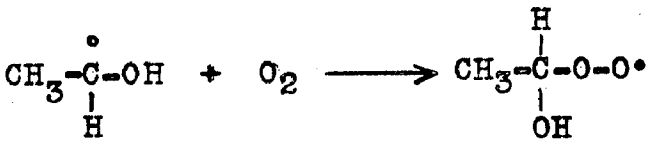
The need for the reactions to be carried out in an inert atmosphere was demonstrated by the irradiation of AQ in absolute ethanol in the presence of air. No yellow-colored intermediate was formed. The observed photopotential was positive as indicated for AQ and other compounds in Table VI. Levin obtained positive photopotentials and could not explain the cause of the potentials. These positive potentials are due to peroxide formation (19) which can be accounted for most satisfactorily in the terms of the mechanism detailed below:

$$AQ + h\nu \longrightarrow AQ^{*} \qquad (10)$$

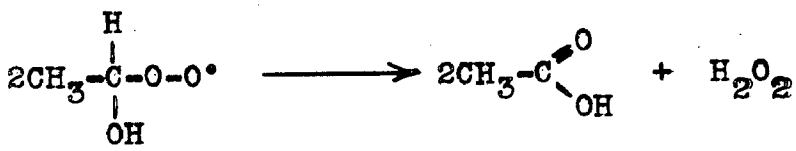
$$AQ^{*} + CH_3\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-OH \longrightarrow \cdot AQH + CH_3-\overset{\cdot}{\underset{H}{\overset{|}{\underset{|}{C}}}}-OH \qquad (11)$$

$$CH_3-\overset{\cdot}{\underset{H}{\overset{|}{\underset{|}{C}}}}-OH + AQ \longrightarrow \cdot AQH + CH_3-\overset{H}{\overset{|}{C}}=O \qquad (12)$$

$$\cdot AQH + O_2 \longrightarrow AQ + HO_2\cdot \qquad (13)$$

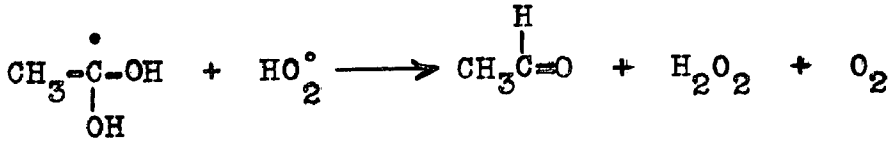


(14)



(15)

(16)



(17)

As can be seen from the above equations, there are several factors controlling the electrode reaction. One is the O_2/H_2O_2 couple, another is the $CH_3-\overset{H}{\underset{OH}{C}}OO^{\bullet}$ species and another is the oxidized alcohol. The net result of the above is a positive potential for the irradiated system. This was confirmed experimentally by addition of small amounts of a 3% hydrogen peroxide solution to an ethanol solution of AQ in the presence of air in the vicinity of the platinum point electrode. A potential more positive than the initial potential of AQ in alcohol was produced.

The need for the solvent to furnish a hydrogen atom to AQ was demonstrated by irradiation in various solvents as shown in Table VII. No yellow intermediate was obtained upon irradiation of AQ in benzene in a nitrogen atmosphere.

The potential of the AQ-benzene solution could not be measured due to the low dielectric constant of benzene. Negative photopotentials were obtained for AQ in tertiary butanol due to impurities. Gas chromatography showed the presence of primary and secondary alcohols in the tertiary butanol. The yellow intermediate of AQ was also produced in a tertiary fluoro-alcohol. This likewise was due to impurities in the fluoro-alcohol as shown by a UV absorption spectrum of the fluoro-alcohol.

Evidence for which atom of hydrogen is abstracted by the excited AQ molecule is cited in Reference 19. Bolland and Cooper (19) presented a detailed kinetic analysis of the reaction scheme involved in the photo-sensitized oxidation of ethanol. They used anthraquinone 2,6 disulfonic acid di sodium salt as the sensitizer. It was demonstrated that this sensitizer operated by an efficient cyclic mechanism and that it abstracted a hydrogen atom from the ethanol to give a semi-quinone radical which was rapidly converted to the original quinone by reaction with molecular oxygen. Bond-strength data indicated that the solvent radical produced by hydrogen abstraction by the excited sensitizer was $\left[CH_3-\dot{C}(H)-OH\right]$ and not the alkoxy form $\left[CH_3-C(H)-O^{\bullet}\right]$.

Equation (3) was postulated on the basis of the work of Pitts et al.(20) concerning the photochemical reactions

of benzophenone in Isopropanol. They postulated a reaction similar Equation (3) in order to account for the quantitative formation of benzopinacol. The absence of pinacols, mixed pinacols and benzhydrol indicated that the isopropyl free radicals $(CH_3)_2\dot{C}OH$ reacted very soon after they were formed in a manner similar to Equation (2) but not in recombination or disproportionation processes with the benzophenone radicals $\left[(C_6H_5)_2\dot{C}OH\right]$. The hydrogen transfer to form the more stable free radical $(C_6H_5)_2\dot{C}OH$ appeared to be rapid and in view of the strongly reducing nature of the $(CH_3)_2\dot{C}OH$ radical, (21,22), seemed quite reasonable to Pitts and co-workers.

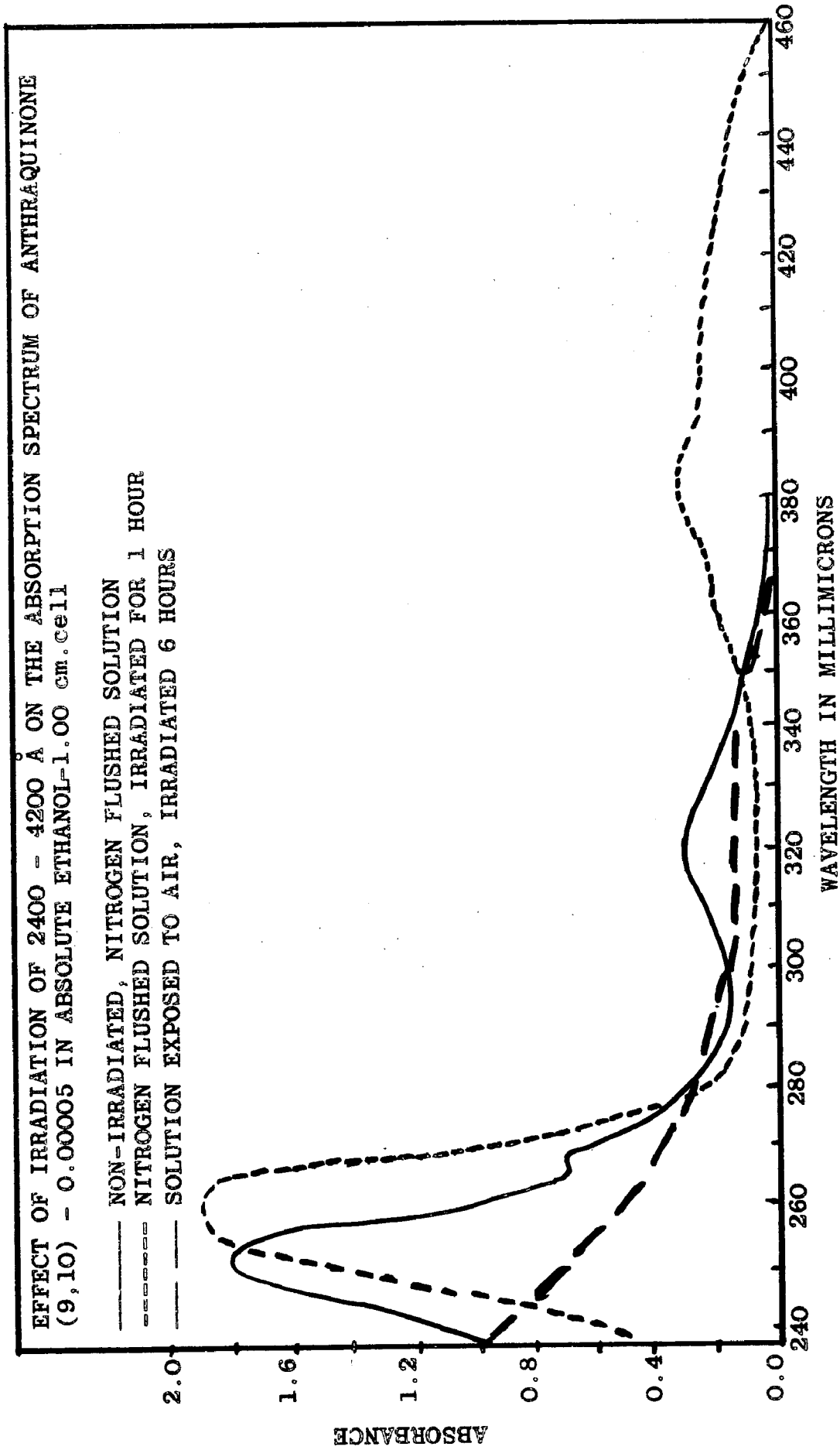
Equation (4) is another possible way the isopropyl radicals may combine and then be converted to the aldehyde and alcohol.

Equations (5) and (6) appear to be possible ways of explaining the reaction between two semiquinone radicals in the absence of oxygen.

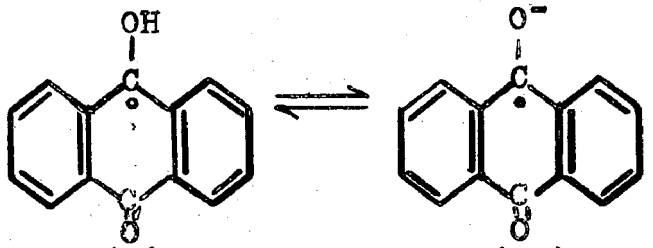
Nature of the AQ Intermediate Species

Direct evidence indicating that the yellow-colored intermediate is a semiquinone radical is supported by absorption studies. The absorption spectrum of an irradiated solution of AQ in absolute ethanol in a nitrogen atmosphere is shown in Figure 2. The formation of three new bands, two in the UV region at 360 and 383 millimicrons

FIGURE 2


EFFECT OF IRRADIATION OF 2400 - 4200 Å ON THE ABSORPTION SPECTRUM OF ANTHRAQUINONE
(9,10) - 0.00005 IN ABSOLUTE ETHANOL-1.00 cm. cell
NON-IRRADIATED, NITROGEN FLUSHED SOLUTION
NITROGEN FLUSHED SOLUTION, IRRADIATED FOR 1 HOUR
SOLUTION EXPOSED TO AIR, IRRADIATED 6 HOURS
ABSORBANCE
2.0
1.6
1.2
0.8
0.4
0.0
240
260
280
300
320
340
360
380
400
420
440
460
WAVELENGTH IN MILLIMICRONS

and a long band extending from 390 to 460 millimicrons is attributed to the yellow-colored intermediate, a semiquinone radical. Bridge and Porter (23) reported a group of bands at ca. 360 to 390 millimicrons due to the semiquinone radical in their flash photolysis study of AQ in solution. In addition they indicated the presence of a strong band at 480 millimicrons which they attributed to the semiquinone radical ion. In Figure 3 it can be seen that irradiation of an alkaline (KOH) absolute ethanol solution of AQ in a nitrogen atmosphere resulted in production of two new bands, one at 395 and another at approximately 485 millimicrons. This is a normal spectral shift caused by ionization of the semiquinone radical as follows:



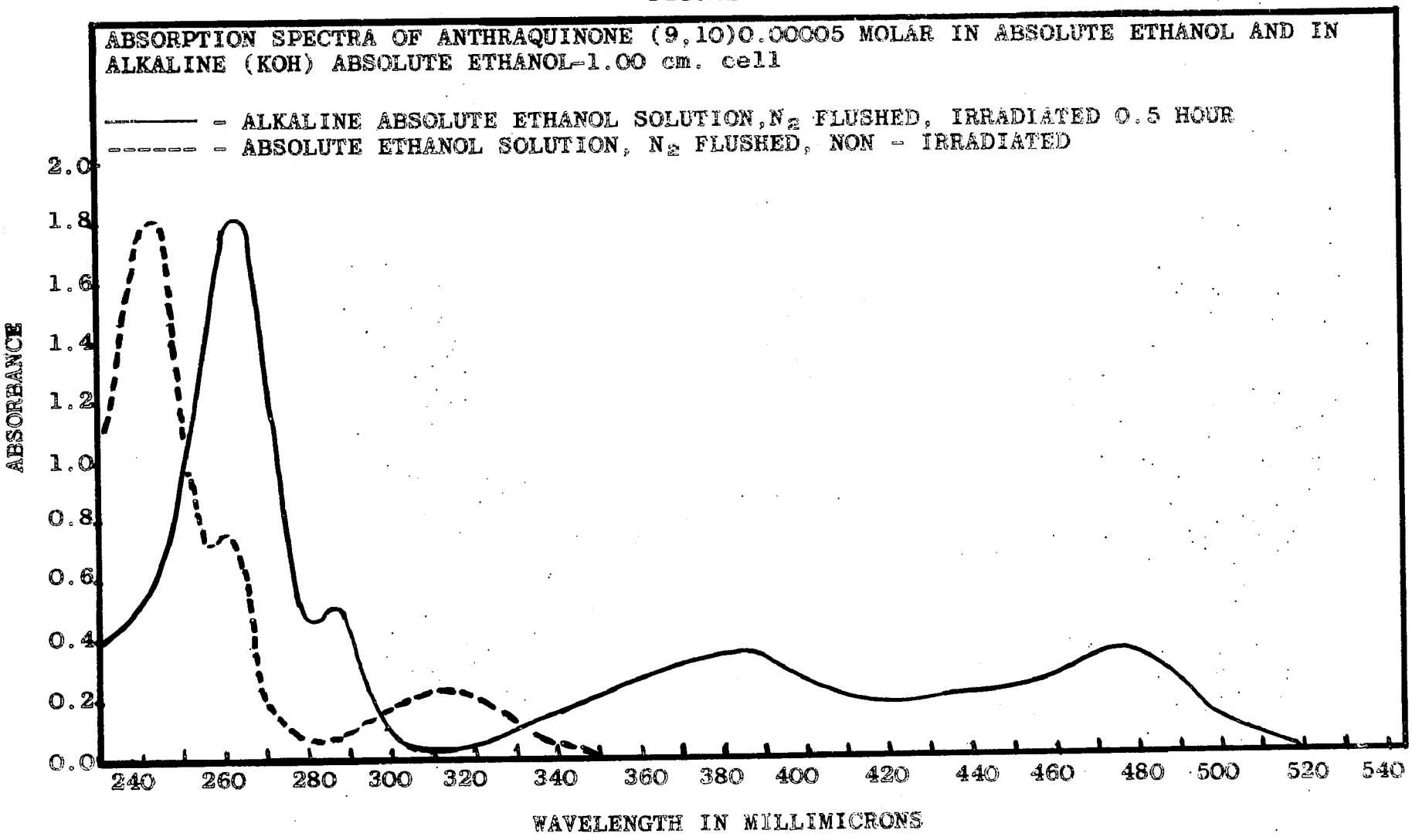
(18)

(I) Semiquinone Radical

(II) Semiquinone Radical Anion

(I) exists in an alcohol medium while (II) predominates in an alkaline alcohol solution. The entire spectrum was shifted to the red region with no apparent change in the shape of the spectrum. The most intense band shifts from 257 to 272 millimicrons. The small band shifts from 395-430 millimicrons. The large band shift corresponds to

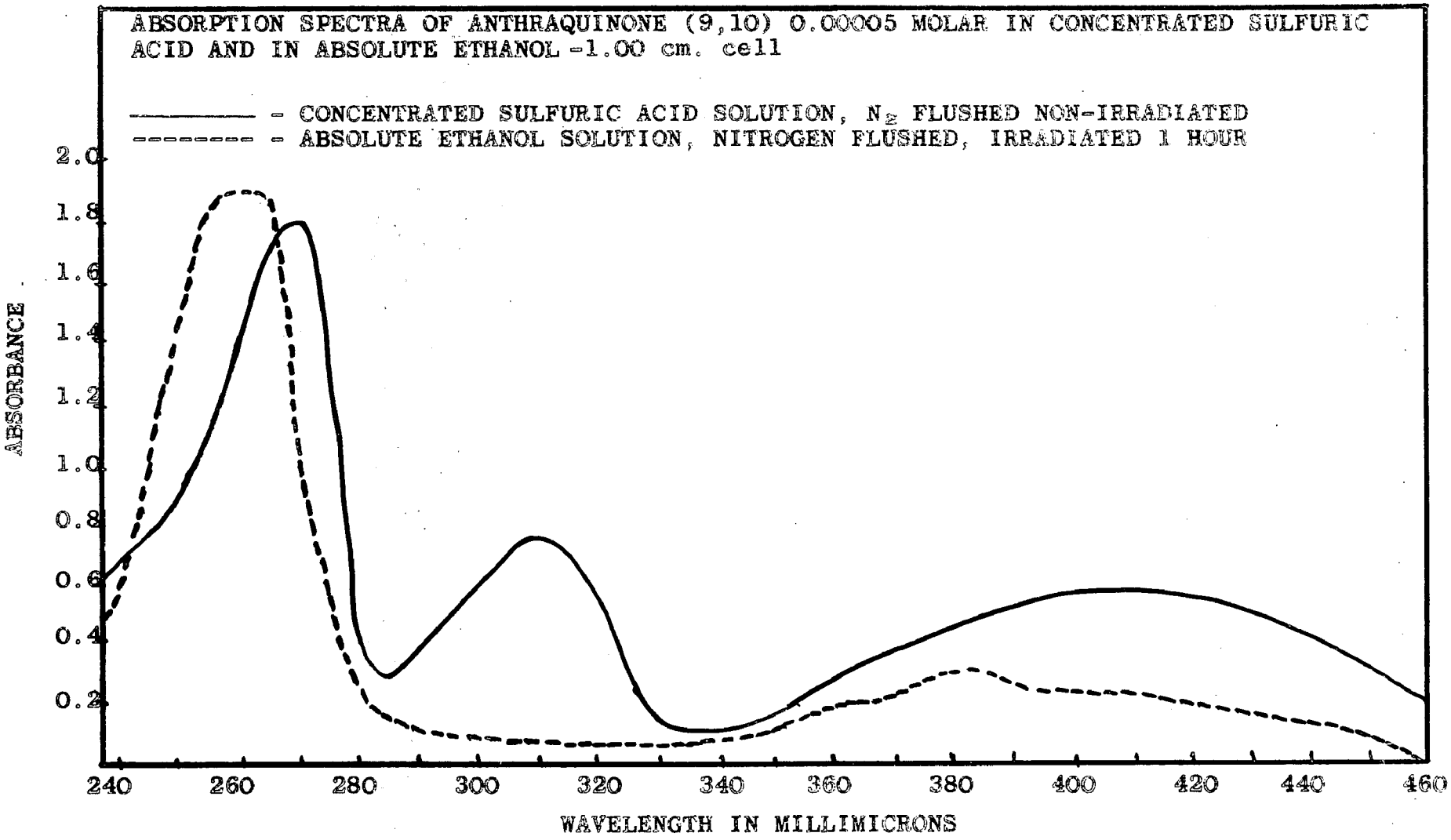
FIGURE 3


ABSORPTION SPECTRA OF ANTHRAQUINONE (9,10)0.00005 MOLAR IN ABSOLUTE ETHANOL AND IN ALKALINE (KOH) ABSOLUTE ETHANOL-1.00 cm. cell
——— = ALKALINE ABSOLUTE ETHANOL SOLUTION, N_2 FLUSHED, IRRADIATED 0.5 HOUR
------ = ABSOLUTE ETHANOL SOLUTION, N_2 FLUSHED, NON - IRRADIATED
ABSORBANCE
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
240
260
280
300
320
340
360
380
400
420
440
460
480
500
520
540
WAVELENGTH IN MILLIMICRONS

2300 cm.$^{-1}$ and the small band shift corresponds to 2100 cm.$^{-1}$ which indicates that the shifts are comparable shifts. This indicates that the transition involved a $\pi \rightarrow \pi^*$ transition. Additional characteristics of a $\pi \rightarrow \pi^*$ transition are: fine structure present even in polar solvents; failure of the absorption band to disappear in acid and a large molar absorptivity. In Figure 4 it is seen that the absorption spectrum of the irradiated solution of AQ in a nitrogen atmosphere is similar to the absorption spectrum of AQ in concentrated sulfuric acid.

Spectroscopic evidence suggests the presence of free radicals for other compounds listed in Table V. Pitts and co-workers (20) reported formation of a highly colored, oxygen-sensitive intermediate from the irradiation of a nitrogen flushed solution of benzophenone in isopropanol. They attributed this to the formation of benzophenone free radicals, $\left[(C_6H_5)_2\dot{C}\text{-}OH\right]$. In addition, they attempted to generate the "intermediate" by irradiation of solutions of benzhydrol in acetone. No trace of an "intermediate" similar to that found in the benzophenone-isopropyl alcohol was observed. Apparently, the benzopinacol-alcohol system was overlooked or else it was not considered due to the UV intensity of radiation source being too low below 3000 Å. Figure 5 clearly indicates the presence of an intermediate in the irradiated solution of benzopinacol in ethanol which absorbs in exactly the same region as the

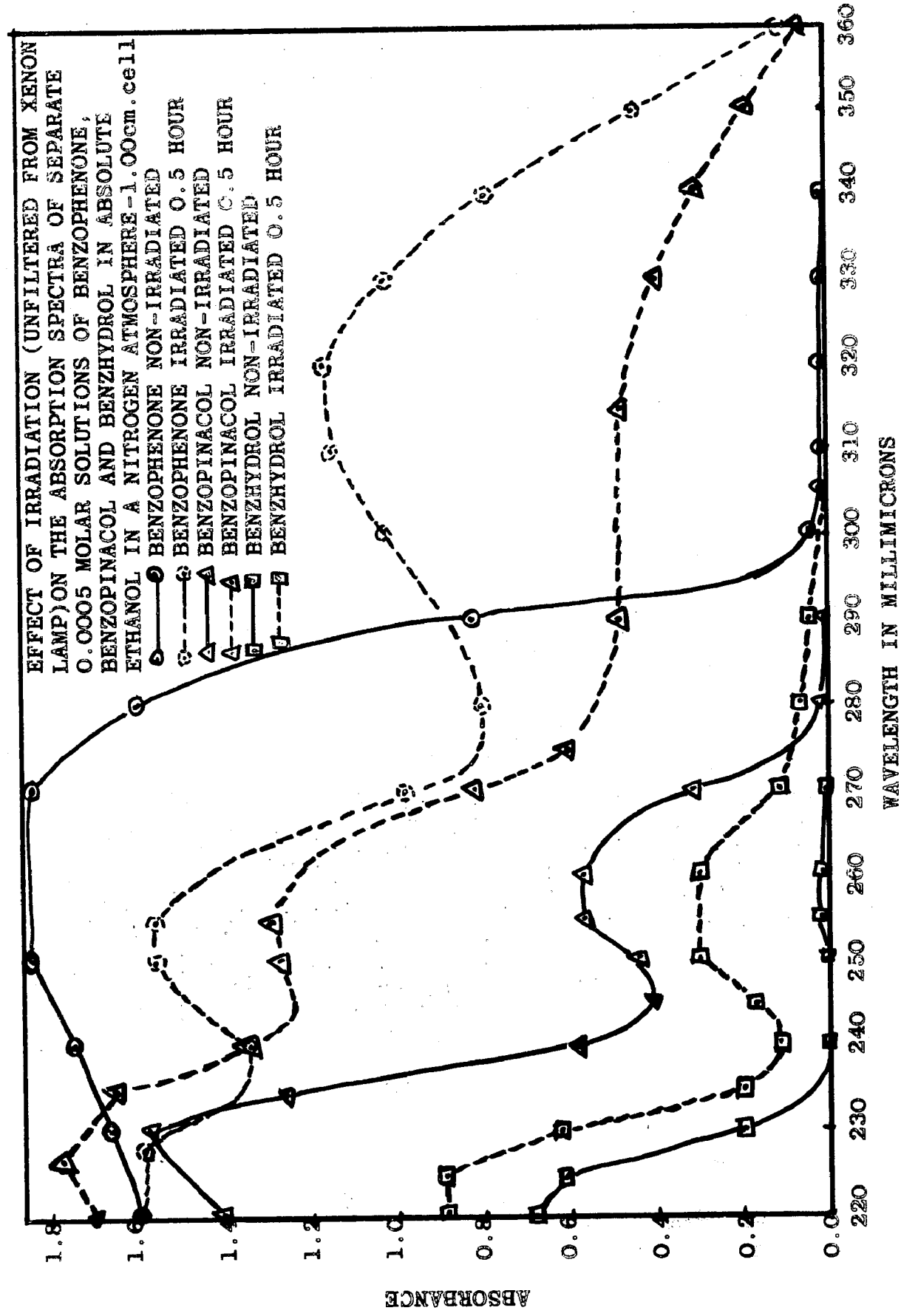
FIGURE 4


ABSORPTION SPECTRA OF ANTHRAQUINONE (9,10) 0.00005 MOLAR IN CONCENTRATED SULFURIC ACID AND IN ABSOLUTE ETHANOL -1.00 cm. cell
——— = CONCENTRATED SULFURIC ACID SOLUTION, N_2 FLUSHED NON-IRRADIATED
– – – – – = ABSOLUTE ETHANOL SOLUTION, NITROGEN FLUSHED, IRRADIATED 1 HOUR
ABSORBANCE
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
240
260
280
300
320
340
360
380
400
420
440
460
WAVELENGTH IN MILLIMICRONS

proposed benzophenone free radical in the benzophenone-alcohol system. This is explained on the basis of benzopinacol first being photodecomposed into benzophenone and benzhydrol. Prolonged irradiation results in the photoreduction of benzophenone to the benzophenone free radical. Irradiation of an ethanol solution of benzhydrol produced no "intermediate" as seen in Figure 5 and likewise did not produce a photopotential.

Recently, Russian investigators reported on studies pertaining to the photoreduction of eosin (tetrabromo-fluorescein) employing ascorbic acid as the reducing agent and pyridine as the solvent. The first study pertained to potentiometric measurements of the intermediate reduction product of eosin; Tsepalov et al (24) obtained a photo-potential-time curve which was different from Figure 1 due to use of a low concentration of eosin. However, when the concentration of eosin was increased to about 10^{-4} M, a curve similar to Figure 1 was obtained. The second study employing spectral methods established that the photo-reduction proceeds in stages with formation of an intermediate product (25). The detailed study of the kinetics of the reaction which was conducted in these investigations led to the assumption that the relatively stable intermediate product is a free radical - semi-quinone of eosin. The kinetics of the reaction were described by the scheme:

FIGURE 5


EFFECT OF IRRADIATION (UNFILTERED FROM XENON LAMP)ON THE ABSORPTION SPECTRA OF SEPARATE 0.0005 MOLAR SOLUTIONS OF BENZOPHENONE, BENZOPINACOL AND BENZHYDROL IN ABSOLUTE ETHANOL IN A NITROGEN ATMOSPHERE-1.00cm.cell
BENZOPHENONE NON-IRRADIATED
BENZOPHENONE IRRADIATED 0.5 HOUR
BENZOPINACOL NON-IRRADIATED
BENZOPINACOL IRRADIATED 0.5 HOUR
BENZHYDROL NON-IRRADIATED
BENZHYDROL IRRADIATED 0.5 HOUR
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
WAVELENGTH IN MILLIMICRONS

$$E^{*} \xrightarrow{k_1} E^{\circ}H \xrightarrow{k_3} E H_2 \qquad (19)$$
$$\downarrow k_2$$
$$E$$

where E^{*} and E are eosin in the excited and ground states, respectively; $E^{\circ}H$ is the semiquinone of eosin and $E H_2$ is the leuco compound. The third study involved the electron paramagnetic resonance method (26). Results of the EPR method proved that it detected the same intermediate product detected earlier by the spectral and potentiometric methods. An analysis of the EPR spectrum permitted them to conclude that the free valence of the semiquinone form of eosin was localized on the carbon atom in position 9.

Hantzsch (27) in 1916 suggested a free radical structure for the reduced phenazine in view of the presence of two absorption bands in the UV, a phenomenon which is observed neither in the fully reduced nor in the fully oxidized form, and is absent in compounds of bimolecular structure. Irradiation of phenazine in absolute ethanol in a nitrogen atmosphere gave a negative photopotential as shown in Table V and also produced a new absorption band in the UV region at 270-275 mu in addition to the one present at 250 mu before irradiation.

Additional direct evidence indicating that the yellow-colored semiquinone of AQ is a radical is supported by polymerization results given in Table VIII. It is known that a photosensitizer of polymerization should absorb UV radiation and with the energy so acquired form free

radicals which have sufficient energy to initiate polymerization. It was demonstrated that the yellow-colored intermediate could initiate the polymerization of methyl methacrylate. This was done by first irradiating an ethanol solution of AQ in a nitrogen atmosphere until a sufficient quantity of yellow-colored intermediate was present. Irradiation was shut off and freshly distilled methyl methacrylate was added to the yellow-colored solution. The tube was immediately sealed and placed in the dark. A very viscous solution resulted in 24 hours indicating that polymerization of methyl methacrylate had occurred. An additional 24 hours resulted in the complete precipitation of polymethyl methacrylate. Identical results were obtained when a mixture of AQ in absolute ethanol and methyl methacrylate were irradiated for one hour in a nitrogen atmosphere. Comparison of the infra red spectra of polymethyl methacrylate and polystyrene with those presented in the literature (28) confirm the presence of the polymers.

Other compounds listed in Table V which gave negative photopotentials have also been reported as photosensitizers in polymerization processes. Benzaldehyde and benzophenone were used as initiators in the photo-polymerization of isoprene and styrene (29). Photopolymerizations of styrene, butyl acrylate, methyl acrylate, methyl methacrylate, and numerous vinyl compounds were initiated by benzoin (30,31,32).

Benzoyl peroxide has been employed as initiator in the photopolymerization of allyl methacrylate (33) and vinyl acetate (34). Phenazine has been reported as a sensitizer for film formers such as rubber hydrochlorides and nitrocelluloses, under the action of ultraviolet radiation (35).

Nuclear magnetic resonance studies (made by an outside laboratory) of an irradiated chloroform-ethanol solution of AQ in a nitrogen atmosphere showed a shift in the chloroform proton resonance band indicating the presence of a paramagnetic species in solution. Adams et al (36) have observed the paramagnetic resonance spectra of a number of semiquinone free radicals which included the AQ semiquinone intermediate. These were observed in alkaline solution (water, ethanol, acetone or mixtures thereof) while undergoing oxidation by atmospheric oxygen or after reduction with metallic zinc. An electron spin resonance study of the AQ radical ion produced by controlled potential electrolysis of AQ in 0.1 N tetraethylammonium iodide in dimethylformamide has been reported (37). Positive results were obtained only when the electrolyzed sample was chilled in liquid nitrogen and the ESR spectrum was run at liquid-oxygen temperatures. These same workers could not observe any hyperfine structure for the AQ radical at room temperature, owing to the lack of homogeneity in the magnetic field under the conditions that were used. Repeating the

controlled electrolysis experiments, the characteristic color of the proposed radical was produced.

Mechanisms for the Production of Photopotentials Different from that for AQ

The negative potential obtained upon illumination of a nitrogen flushed solution of benzoyl peroxide in absolute ethanol is attributed to the formation of benzoyloxy radicals as follows (38):

$$\phi COO - OOC\phi \xrightarrow{h\nu} 2\ \phi COO^{\bullet} \qquad (20)$$

$$\phi COO^{\bullet} + CH_3CH_2OH \longrightarrow \phi COOH + CH_3\overset{H}{\underset{\bullet}{C}}OH \qquad (21)$$

$$CH_3\overset{H}{\underset{\bullet}{C}}OH + \phi COO - OOC\phi \longrightarrow CH_3-\overset{H}{\underset{OCO\phi}{C}}OH + \phi COO^{\bullet} \qquad (22)$$

followed by $CH_3-\overset{H}{\underset{OCO\phi}{C}}-OH \longrightarrow CH_3-\overset{H}{C}=O + \phi COOH$ (23)

Electrochemically benzoyl peroxide may be reduced as follows:

$$\phi-\overset{O}{\overset{\|}{C}}-\ddot{\underset{\times\times}{O}}-\ddot{O}-\overset{O}{\overset{\|}{C}}-\phi + e^- \longrightarrow \underset{\text{Ion}}{\left[\phi-\overset{O}{\overset{\|}{C}}-\ddot{O}\right]^{\ominus}} + \underset{\text{Radical}}{\phi-\overset{O}{\overset{\|}{C}}-\ddot{O}\cdot} \qquad (24)$$

$$\therefore E = E^{O} + \frac{.06}{1}\log\frac{\left[\phi\overset{O}{\overset{\|}{C}}-OO\overset{O}{\overset{\|}{C}}-\phi\right]}{\left[\phi-\overset{O}{\overset{\|}{C}}-O^-\right]\left[\phi-\overset{O}{\overset{\|}{C}}-O^{\bullet}\right]} \qquad (25)$$

Therefore, any reaction that tends to form benzoyloxy radicals will result in the above ratio being smaller and thus the potential will be more negative. This is confirmed experimentally since radiation decomposes each benzoyl peroxide molecule into two benxoyloxy radicals and a potential more negative than the starting potential is observed.

The observed photopotentials for diphenylamine and tetraphenylhydrazine (39) cannot be explained by their obvious reactions

$$\phi_2NH \xrightarrow{h\nu} \phi_2N\cdot + \cdot H \qquad (26)$$

$$\begin{matrix}\phi & \phi\\ :N\text{-}N: \\ \phi & \phi\end{matrix} \xrightarrow{h\nu - e^-} + \begin{matrix}\phi & \phi\\ \cdot N\text{-}N: \\ \phi & \phi\end{matrix} \longrightarrow \phi_2N^{(+)} + \phi_2N\cdot \qquad (27)$$

On the basis of the above reactions and the Nernst equation, diphenylamine should have given a positive potential and tetraphenylhydrazine, a negative potential. But the observed photopotentials were reversed, therefore, some other mechanisms are involved which cannot be explained here.

Photopotentials for Complex Oxalates

The negative photopotentials obtained by irradiation of the complex oxalates shown in Table IX are probably due to the photoreduction of the metal complexes resulting in

the formation of the next lowest oxidation state of the metal and conversion of the oxalate ion to carbon dioxide. The most recent work done on the photodecomposition of ferrioxalate indicates the following stages in the reaction (40):

1. Absorption of radiation by a trioxalate ferric iron ion to yield an excited ion.

2. Conversion of the excited trioxalate ferric iron ion to a mestable state which may be a free radical, a quartet or a ferro-oxalate ion attached to an oxalate radical.

3. Dissociation of the metastable state to give a dioxalate ferrous iron ion and an oxalate radical.

4. Reaction of the oxalate radical with a trioxalate ferric iron to give an oxalate ion and a dioxalate ferric iron attached to the oxalate radical which in turn decomposes to a dioxalate ferrous iron ion and carbon dioxide.

The effect of Co^{++} on the photopotential of potassium cobaltioxalate complex in water is shown in Table X. During radiation, the formation of a white precipitate was observed in the irradiated area. Actually the Co^{+3} is reduced by the oxalate to Co^{+2}. The oxalate is being released from the complex and, therefore, results in precipitation of cobaltous oxalate. This makes a quantitative analysis of the photopotential data via the Nernst equation impractical

without further investigation. Author cannot conclude from this whether photopotential is due to accumulation of Co^{+2} or oxalate radical.

Effect of Variables on the Photopotential

1. Effect of Air. This already has been mentioned in discussing the proposed mechanism responsible for formation of the AQ yellow-colored intermediate. Photopotential results are listed in Table VI.

2. Effect of Benzopinacol on the Photopotential of Benzophenone. Results of this study are shown in Table X. This investigation was conducted in order to show the effect of a product on the photopotential of a particular system. Benzopinacol was selected since it was definitely shown to be a product obtained in the irradiation of benzophenone in alcohol in a nitrogen atmosphere. Table XI indicates that benzopinacol had no significant effect on the photopotential of benzophenone. This can be explained by consideration of the absorption spectra of the compounds as shown in Figure 5. Benzophenone probably absorbs all of the radiation, thus preventing the benzopinacol from being photodecomposed into benzophenone and benzhydrol. Table XI also indicates the precision of the measurement of photopotentials to be approximately $\pm$ 2% as shown by the photopotentials obtained using filtered radiation.

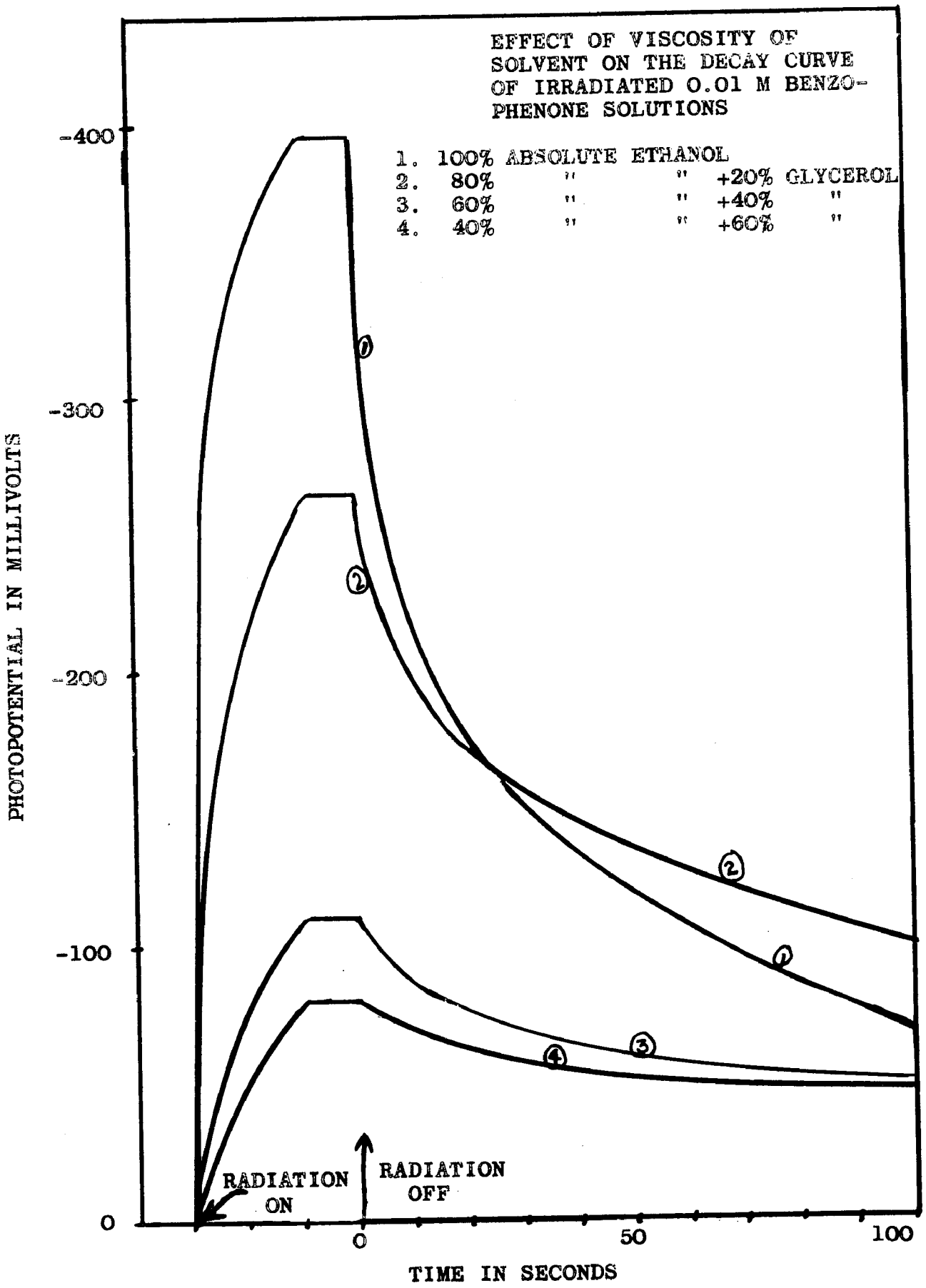
3. Effect of Concentration of Solute on Photopotentials. The results of this study are presented in Table XII. It is

seen that increasing the concentration of the solute produced a higher negative photopotential. An increase in concentration of solute leads to increased absorption of radiation and, in general, has the same effect on the kinetics of the process as an increase in the intensity of radiation. A higher initial concentration of solute results in the production of an increased concentration of intermediate, thereby, changing the potential to a more negative value.

4. Effect of Viscosity on Photopotentials. As can be seen in Table XIII, increasing the viscosity of the solvent resulted in lower photopotentials. The major viscosity effect is that of enhancing recombination of the AQ radical and solvent radical. This results in more AQ molecules being present in the irradiated area. Therefore, the ratio of the oxidized form (AQ)to the reduced form (•AQH) is greater in a more viscous medium. This causes the potential to be more positive. It should be noted that the viscosity of the solvent had a much greater effect on the decay curve than on the rise curve. More time was required for the potential to reach a value near the initial point as the viscosity of the solvent was increased. (See Figure 6). This definitely indicates that the decay curve is due to diffusion of products away from the platinum electrode provided it is a case of long-lived species as for AQ.

5. Effect of Para-Substitutents on the Photopotentials. The photopotentials obtained for the para-substituted

FIGURE 6


EFFECT OF VISCOSITY OF SOLVENT ON THE DECAY CURVE OF IRRADIATED 0.01 M BENZOPHENONE SOLUTIONS
1. 100% ABSOLUTE ETHANOL
2. 80% " " +20% GLYCEROL
3. 60% " " +40% "
4. 40% " " +60% "
PHOTOPOTENTIAL IN MILLIVOLTS
-400
-300
-200
-100
0
RADIATION ON
RADIATION OFF
0
50
100
TIME IN SECONDS

acetophenones and benzophenones are listed in Table V. Due to the strong absorption in the region of the exciting radiation, one might expect that all of the compounds should have produced high negative photopotentials. However, such was not the case. No explanation for the resulting photopotentials can be given at this time. Information regarding the electron densities of the excited states of these compounds would probably help explain these results.

6. Effect of Wavelength of Radiation on Photopotentials. Excellent results are presented in Tables XIII, XIV, and XV to demonstrate this effect. Figures 7, 8 and 9 show that the photopotentials definitely follow the absorption spectra for the investigated compounds. The $\pi \longrightarrow \pi^*$ band was chosen for the radiation studies since the $n \longrightarrow \pi^*$ band is very weak in these compounds. The results are reasonable since increased radiation absorption by a compound results in more molecules being excited. These in turn can then abstract hydrogen atoms from solvent molecules to form the free radicals which have been shown to be the cause of the photopotentials.

Effect of Presence or Absence of Electrode on Production of Intermediate Species. It is interesting to note that a homogeneous concentration of the yellow-colored semiquinone in a very viscous medium (80% glycerol and 20% absolute ethanol by volume) in a nitrogen atmosphere produced a negative photopotential which changed

FIGURE 7

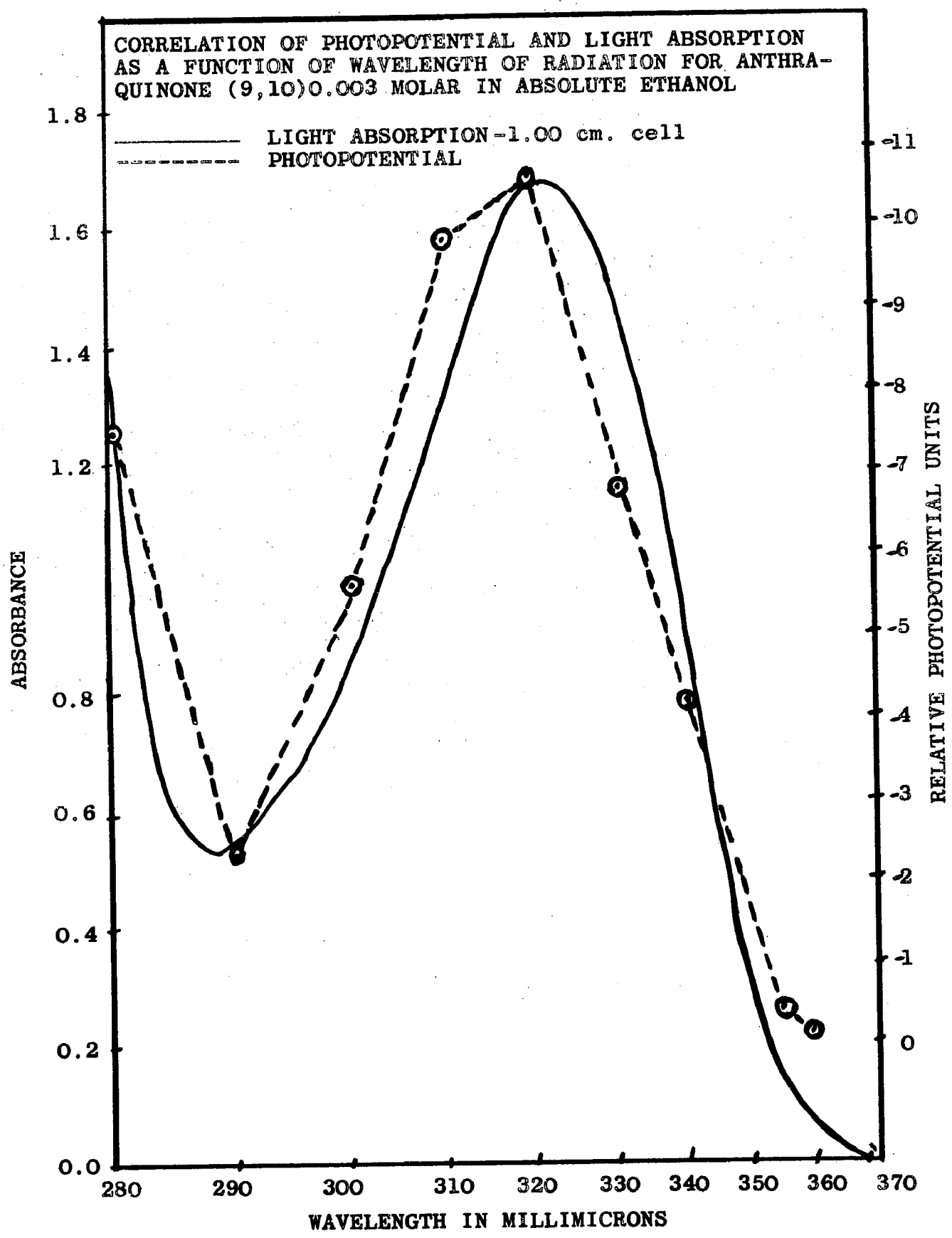

CORRELATION OF PHOTOPOTENTIAL AND LIGHT ABSORPTION AS A FUNCTION OF WAVELENGTH OF RADIATION FOR ANTHRAQUINONE (9,10)0.003 MOLAR IN ABSOLUTE ETHANOL
LIGHT ABSORPTION-1.00 cm. cell
PHOTOPOTENTIAL
ABSORBANCE
RELATIVE PHOTOPOTENTIAL UNITS
WAVELENGTH IN MILLIMICRONS
1.8
1.6
1.4
1.2
0.8
0.6
0.4
0.2
0.0
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
280
290
300
310
320
330
340
350
360
370

FIGURE 8

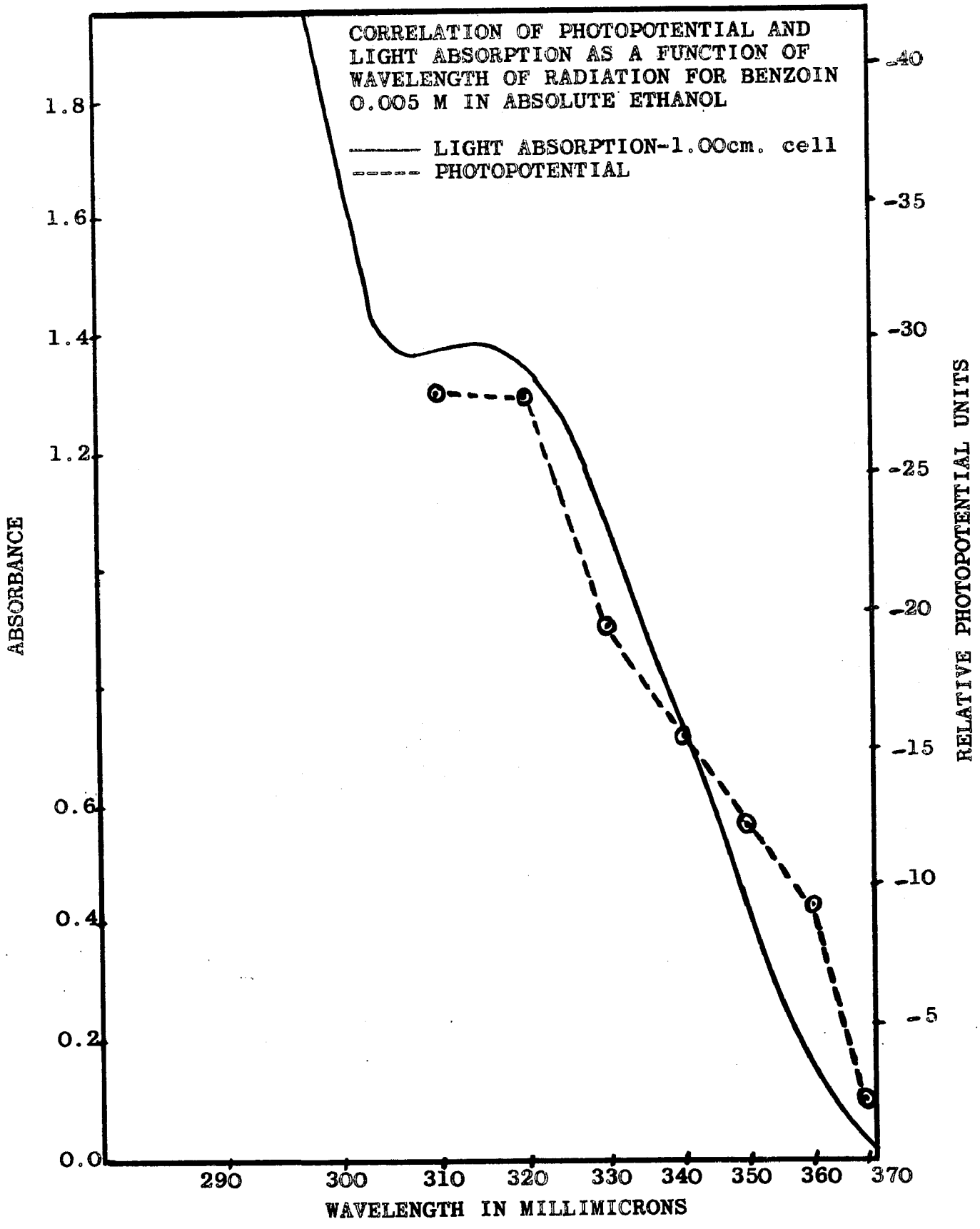
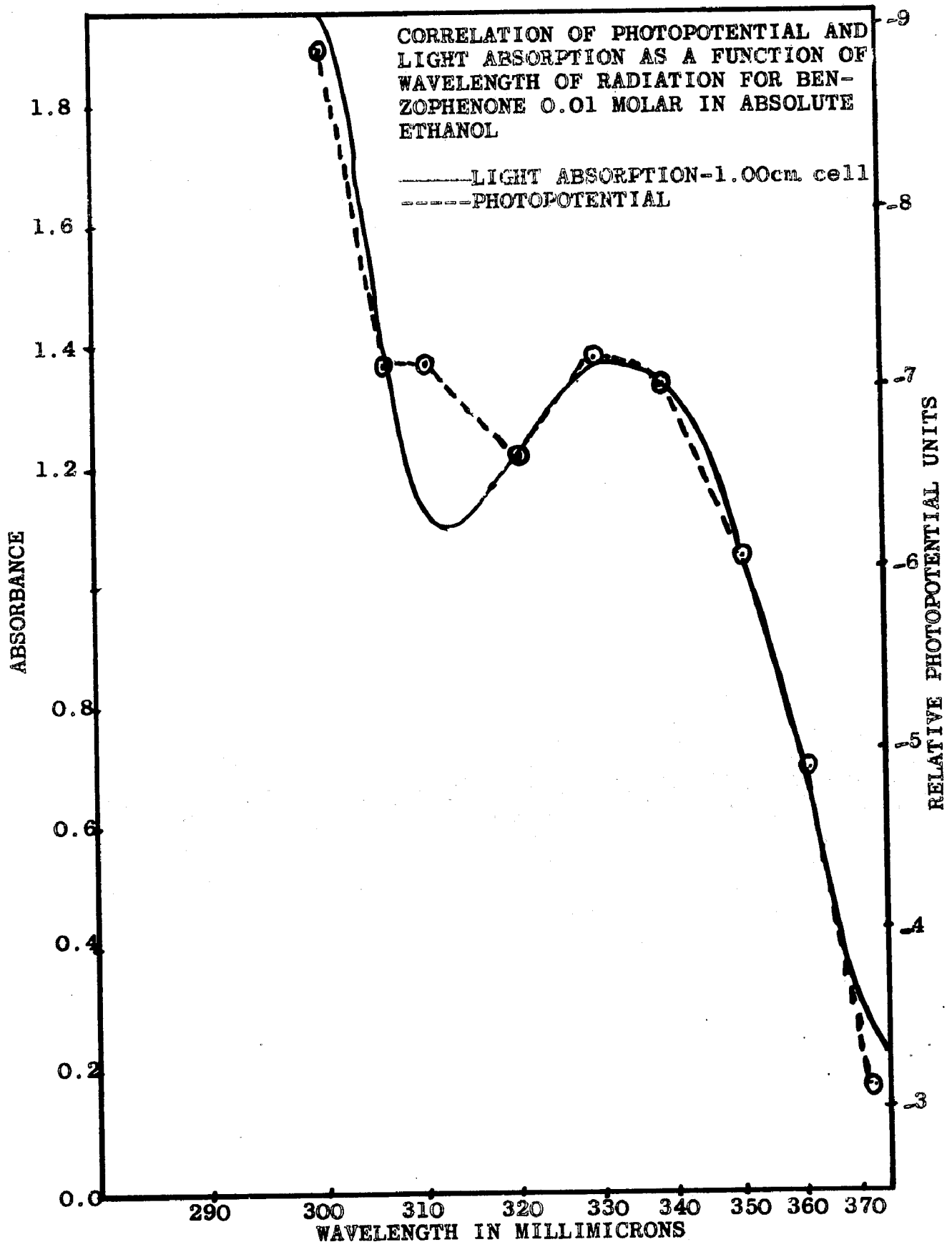

CORRELATION OF PHOTOPOTENTIAL AND LIGHT ABSORPTION AS A FUNCTION OF WAVELENGTH OF RADIATION FOR BENZOIN 0.005 M IN ABSOLUTE ETHANOL
LIGHT ABSORPTION-1.00cm. cell
PHOTOPOTENTIAL
ABSORBANCE
1.8
1.6
1.4
1.2
0.6
0.4
0.2
0.0
RELATIVE PHOTOPOTENTIAL UNITS
-40
-35
-30
-25
-20
-15
-10
-5
290
300
310
320
330
340
350
360
370
WAVELENGTH IN MILLIMICRONS

FIGURE 9


CORRELATION OF PHOTOPOTENTIAL AND LIGHT ABSORPTION AS A FUNCTION OF WAVELENGTH OF RADIATION FOR BENZOPHENONE 0.01 MOLAR IN ABSOLUTE ETHANOL
LIGHT ABSORPTION-1.00cm. cell
PHOTOPOTENTIAL
ABSORBANCE
1.8
1.6
1.4
1.2
0.8
0.6
0.4
0.2
0.0
RELATIVE PHOTOPOTENTIAL UNITS
-9
-8
-7
-6
-5
-4
-3
290
300
310
320
330
340
350
360
370
WAVELENGTH IN MILLIMICRONS

very little, hours after the irradiation was stopped. Introduction of air into this system resulted in a gradual disappearance of the yellow-colored semiquinone accompanied by a corresponding change in potential to a less negative value approaching the initial non-irradiated potential. At this point, an experiment was performed to determine whether or not an electrode was essential for production of the intermediate species. The platinum point electrode was rotated 90° so that it was not in the path of the radiation. With the recorder running, the radiation was made incident on the cell. During a period of several minutes of irradiation, no change in potential was noted even though the yellow intermediate was being formed. Then, simultaneously, the radiation was shut off and the platinum electrode rotated 90° so as to be against the cell wall in the area previously irradiated. The potential changed to a more negative value and then decayed to a point near the starting potential. This definitely indicated that the electrode is not necessary for the production of the yellow intermediate species of AQ.

Reaction Kinetics

The rise- and decay-curve data were employed in various equations in an attempt to determine the order of reaction. It was found that the decay data could not fit any simple equation due to several factors, such as reaction

of intermediate and diffusion of intermediate away from the electrode, controlling the decay rate. The rise-curve data gave a straight line when used in the following equation

$$E = m\,Cr + b \tag{28}$$

$$\frac{dE}{dt} = m\,\frac{d\,Cr}{dt} \tag{29}$$

If kinetics obey first order

$$-\frac{d\,Cr}{dt} = k\,Cr \tag{30}$$

$$\text{then } \frac{1}{m}\left(-\frac{dE}{dt}\right) = k\left[\frac{E-b}{m}\right] = kE - kb \tag{31}$$

Plot of $\frac{\Delta E}{\Delta t}$ vs. E is linear with slope = $k(t^{-1})$ and intercept = $-kb$.

However, there is no justification for assuming (28) to be correct since electrode potentials involve a log term for the concentration. This means that the rise curve is affected by several factors other than concentration of reactant.

Polarography

Half-wave potentials for p-Benzoquinone, Naphthoquinone (1,4) and Anthraquinone (9,10) in Dimethylformamide solutions containing 0.1 M lithium chloride are presented in Table XVII. Results indicate that irradiation

(2400-4200 Å) had no effect on the half-waves. The only observed effect was that of the diffusion currents being decreased when the solution was exposed to irradiation before and or during the run. The half-waves found for p-Benzoquinone and Anthraquinone (9,10) do not agree with those presented in the literature (41). The only difference was the use of lithium chloride as supporting inert electrolyte instead of tetrabutylammonium bromide. Apparently the fact that lithium chloride is very hygroscopic is a partial explanation for the shift of the half-waves of p-Benzoquinone and Anthraquinone (9,10). Wawzonek and co-workers (41) reported that the presence of 1% water in the solutions lowered the second half-waves approximately 0.35 volts in each case. Therefore, the presence of water could easily account for results listed in Table XVII.

Polarographic results of alcohol solutions of Anthraquinone (9,10) using 0.3 lithium chloride as supporting electrolyte are listed in Table XVIII. Inconsistent results were obtained as shown by the values for the second half-wave. In addition to the diffusion current being decreased, irradiation also resulted in a shift of the half-waves of 9,10 Anthraquinone in most cases and of the supporting electrolyte in some cases. The values for the half-waves found in this study do not agree with those presented in the literature (42). The only differences

were the use of a saturated calomel electrode as the reference electrode and the presence of a small amount of lithium hydroxide. In the cited reference (42) Anthraquinone exhibited half-waves at -0.83 v and -1.17 v vs. the saturated calomel electrode which was assumed to represent a reduction through the semiquinone to anthrahydroquinone. Apparently these authors overlooked the junction potential effect due to the use of a saturated calomel electrode in a non-aqueous medium. This would probably account for the major differences between the results obtained in the present study and the literature report.

These series of polarographic investigations were primarily of a qualitative nature and an accurate explanation for the compounds studied is impossible in view of the inconsistent results.

CONCLUSIONS

The investigation of the photo-induced electrode potentials can be summarized by the following conclusions:

1. The photo-induced electrode potentials have been shown to be due to intermediates produced by photochemical reduction. The experimental observations on the intermediate in the case of anthraquinone (9,10) are consistent with a free radical interpretation.

2. On the basis of the experiments with AQ, it can be concluded that the free radical is the active agent causing the negative potentials produced by radiation of other compounds.

3. Discrepancies in the literature pertaining to positive photo-induced electrode potentials have been explained on the basis of peroxide formation.

4. Variables affecting the photo-induced electrode potentials have been studied.

5. Photo-induced electrode potentials appear to be potentially, a useful tool for the detection of minute quantities of radicals and should prove useful in the investigation of the kinetics of reactions involving radicals.

PART II

PHOTO-INDUCED LUMINESCENCE

INTRODUCTION

Luminescence is a process whereby a molecule which has absorbed energy of a given frequency emits electromagnetic radiation to rid itself of the absorbed energy. Fluorescence and phosphorescence are examples of luminescent processes. These phenomena occur when electromagnetic radiation of one frequency (generally ultraviolet radiation) is absorbed and radiation of another frequency is emitted. The time delay between absorption and emission is extremely short (10^{-8} seconds) for fluorescence but may be on the order of minutes or hours for phosphorescence.

Normally, ketones do not fluoresce but phosphoresce due to $n \longrightarrow \pi^*$ absorption leading to a triplet state. This was reported by Lewis and Kasha (43) in their work concerning phosphorescence in rigid media at liquid-nitrogen temperature. During the studies pertaining to photo-induced electrode potentials most of the compounds listed in Table V exhibited fluorescence and showed the presence of colored intermediates. Therefore, this thesis was expanded to study the fluorescence at room temperature and luminescence at liquid-nitrogen temperature of these intermediates.

EXPERIMENTAL

Materials

All materials were purified and oxygen-free solutions were prepared, as described in Part I of this thesis. Absolute ethanol and EPA were used as solvents for room temperature and liquid-nitrogen temperature studies, respectively. These solvents showed no residual fluorescence at the level of the sensitivity used. EPA was prepared as follows:

EPA - Ether, isopentane and absolute ethanol (5:5:2) - Mallinckrodt reagent grade diethyl ether, Eastman Kodak technical grade isopentane and absolute ethanol were used without further purification.

Apparatus and Procedure

The apparatus used to obtain room temperature fluorescence and low-temperature luminescence spectra has already been described (18). In brief, for room temperature studies, radiation from a high-pressure mercury lamp was passed through a filter system and into a Vycor cell. Fluorescence was, in turn, passed through a Bausch and Lomb grating monochromator to a photomultiplier tube. The output of the photomultiplier was amplified and introduced into a Varian recorder. For liquid-nitrogen temperature studies, the only difference in the experimental

procedure was the placing of the sample cell in a liquid-nitrogen bath held in a Vycor Dewar flask.

All apparatus was turned on for fifteen minutes to a half hour prior to use. This was found to be sufficient time for the instrument and lamp to reach stability. Detailed operating procedures are given in Reference 18.

RESULTS

The absorption and fluorescence spectra for compounds listed in Table V are shown in Figures 10 through 27. The absorption spectra were obtained using non-irradiated, nitrogen flushed solutions. Radical bands which were found to be present in the absorption spectra of some of the irradiated, nitrogen flushed solutions are also shown in these Figures. The fluorescence spectra were obtained using nitrogen flushed solutions in stoppered Vycor cells at room temperature and are uncorrected for phototube response. Pertinent information for the fluorescence procedure is listed in Table XIX.

The luminescence spectra of compounds in EPA at liquid-nitrogen temperature are shown in Figures 28 through 45. These spectra were obtained using irradiated (for 1 minute with 3130 Å radiation) and non-irradiated, nitrogen-flushed EPA solutions. The solutions containing 5×10^{-4} M of solute were frozen to clear glasses in a liquid-nitrogen bath prior to placing in the Spectrofluorometer. The spectra are uncorrected for phototube response. The analyzer monochromator slit widths used to obtain the spectra are indicated on each Figure. Visual observations regarding the color and duration of phosphorescence of the EPA glasses, after removal from the exciting radiation, are noted in Table XX.

TABLE XIX

INFORMATION CONCERNING ROOM TEMPERATURE

FLUORESCENCE PROCEDURES

Compound	Molar Concentration X 10^4	Analyzer Monochromator Slit Widths in mm.
Acetophenone (a)	5.0	.18
4-Aminoacetophenone	1.0	.19
4-Bromoacetophenone	5.0	.18
4-Nitroacetophenone	5.0	.18
Anthraquinone (9,10) in alcohol	1.0	.10
Anthraquinone (9,10) in acid	1.0	.30
Anthraquinone (9,10) in alkaline alcohol	1.0	.30
Benzaldehyde	5.0	.18
Benzhydrol	5.0	.11
Benzoin (b)	10.0	.15
Benzophenone	1.0	.20
4-Bromobenzophenone	5.0	.05
4,4'-Dimethylbenzophenone	1.0	.19
Benzopinacol	5.0	.12
p-Benzoquinone (b)	1.0	.15
Benzoyl Peroxide	1.0	.15
2,2' Bipyridyl	2.5	.18
Diphenylamine	2.5	.09
1,4 Naphthoquinone (b)	10.0	.15
Phenazine	5.0	.25

TABLE XIX (Cont.)

(a) All of the above compounds were run using the following settings for the Spectrofluorometer: Voltage 800; Load 100 megohms; Amplifier Beckman Zeromatic; Filter System, 7-54 glass filter + $NiSO_4 \cdot 6H_2O$, 200g/ℓ of H_2O in a 5 cm. quartz cell.

(b) Same as (a) except an additional filter of K_2CrO_4, 0.2g/ℓ of H_2O, in a 1 cm. quartz cell was inserted in the filter system.

TABLE XX

VISUAL OBSERVATIONS OF PHOSPHORESCENCE OF EPA GLASSES AT LIQUID-NITROGEN TEMPERATURE

Compound	Color and Duration of Phosphorescence after Removal from Exciting Radiation
Acetophenone	None
4-Aminoacetophenone	Blue - approx. 4 secs.
4-Bromoacetophenone	Blue - approx. 2 secs.
4-Hydroxyacetophenone	Blue - approx. 4 secs.
4-Methoxyacetophenone	Blue - approx. 5 secs.
Anthraquinone 9,10	None
Benzaldehyde	None
Benzoin	Violet - approx.4 secs.
Benzophenone	None
4-Bromobenzophenone	None
4,4'-Dimethylbenzophenone	None
Benzopinacol	None
p-Benzoquinone	Blue - approx.10 secs.
Benzoyl Peroxide	(a) Blue-approx.6 secs.
2,2' Bipyridyl	Sky Blue-approx.5 secs.
Diphenylamine	Brilliant Blue-10 secs.
1,4 Naphthoquinone	None
Phenazine	(a) Green-approx.5 secs.

(a) Obtained on the EPA glass whose solution was irradiated before being frozen.

DISCUSSION OF RESULTS

Absorption and Fluorescence Spectra

Quinones

The quinone structure has been reported as not being conducive to fluorescence. Benzoquinone, naphthoquinone and anthraquinone (AQ) do not fluoresce in solution, although anthraquinones containing hydroxyl groups capable of forming hydrogen bridges with the carbonyl oxygen are fluorescent, like 1,4-dihydroxyanthraquinone (44). Fluorescence spectra for AQ in neutral and basic solutions are shown in Figure 10. These are attributed to radical formation produced by intense radiation of the $\pi \rightarrow \pi^*$ absorption band in an inert atmosphere and in a solvent possessing an abstractable hydrogen atom. The alcohol solution of the semiquinone radical produced the most intense fluorescence. This is not evident from Figure 10 since the analyzer monochromator slit widths were 0.1 mm. for the alcohol solutions compared to 0.3 mm for the alkaline alcohol solution. The limit of detection of fluorescence for an alcohol solution of the semiquinone radical was found to be 5×10^{-7} M using slit widths of 0.3 mm. It should be noted that in the presence of air, the alcoholic solution of AQ was not fluorescent. This is attributed to the absence of the AQ radical due to trapping of the radicals by oxygen.

FIGURE 10

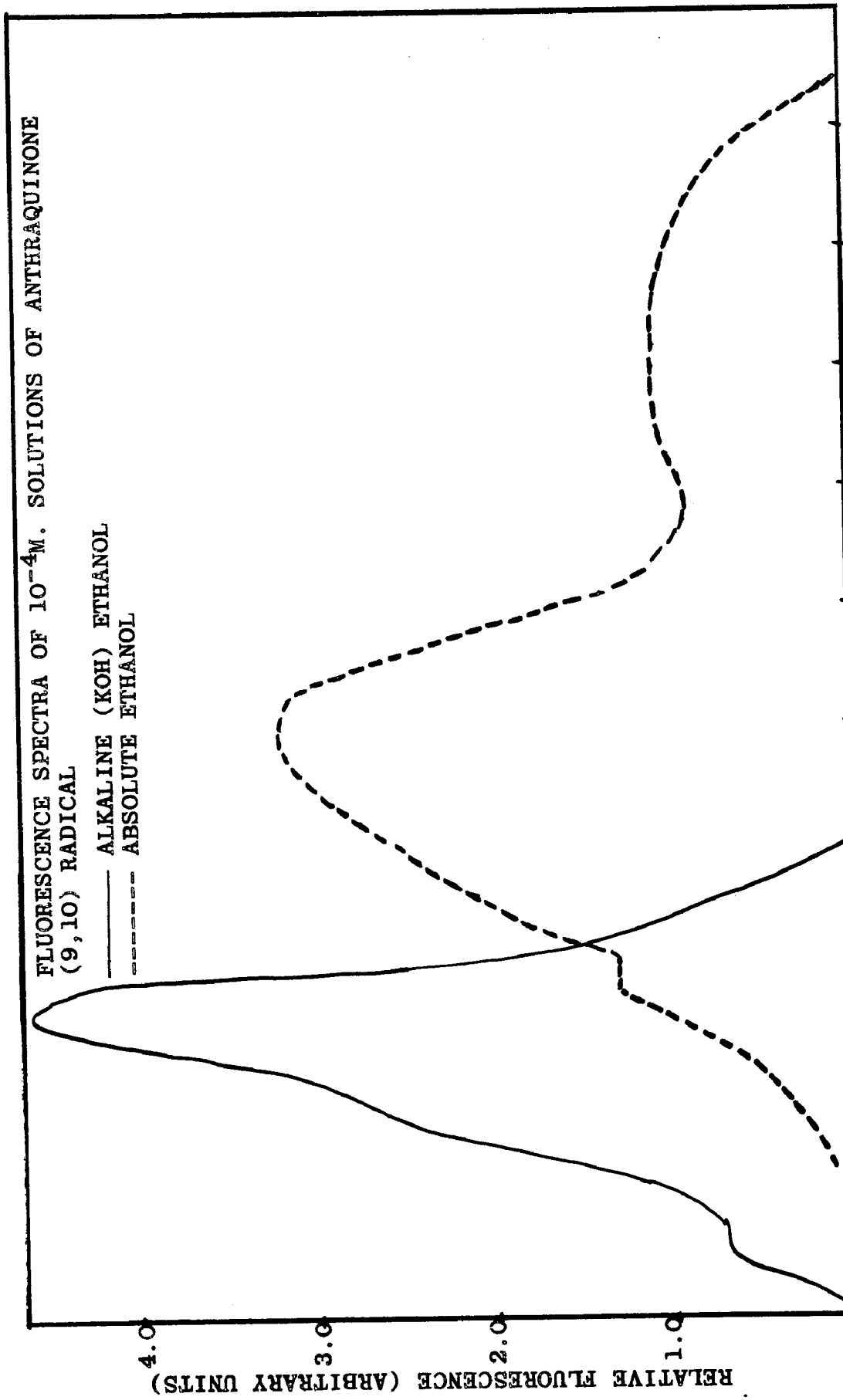

FLUORESCENCE SPECTRA OF 10^{-4}M. SOLUTIONS OF ANTHRAQUINONE (9,10) RADICAL
ALKALINE (KOH) ETHANOL
ABSOLUTE ETHANOL
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
0
1.0
2.0
3.0
4.0
16000
18000
20000
22000
24000
26000
FREQUENCY IN CM.-1

Figure 10 shows the similarities among the fluorescence spectra of the AQ solutions. The shift from 21,000 $cm.^{-1}$ to 18,600 $cm.^{-1}$ is caused by ionization of the semiquinone radical to a semiquinone radical ion. It is interesting to note that prolonged irradiation of a 5×10^{-6} M AQ solution in alcohol resulted in an intensity shift with the 24,250 $cm.^{-1}$ band becoming the most intense. This caused the band to show a peak at 25,000 $cm.^{-1}$ instead of being a broad band as shown in Figure 10. Apparently, decreased radical formation and increased formation of a fully reduced AQ or a dimer, caused this intensity change.

It should be noted that exposure to air, of an ethanol solution of AQ irradiated for 0.5 hour in a nitrogen atmosphere, produced practically the same absorption spectrum as a non-irradiated AQ solution. This is additional evidence for the yellow intermediate being a radical.

It is known that phenyl substitution for hydrogen in condensed ring hydrocarbons tends to increase the normal fluorescence intensity and to displace the absorption and fluorescence to longer wavelengths. This accounts for the differences in the absorption and fluorescence spectra of p-benzoquinone and 1,4 naphthoquinone when compared to AQ. Fluorescence bands were obtained in the presence of air for these two quinones as shown in Figures 11 and 12. Exclusion of air resulted in these same fluorescence bands becoming

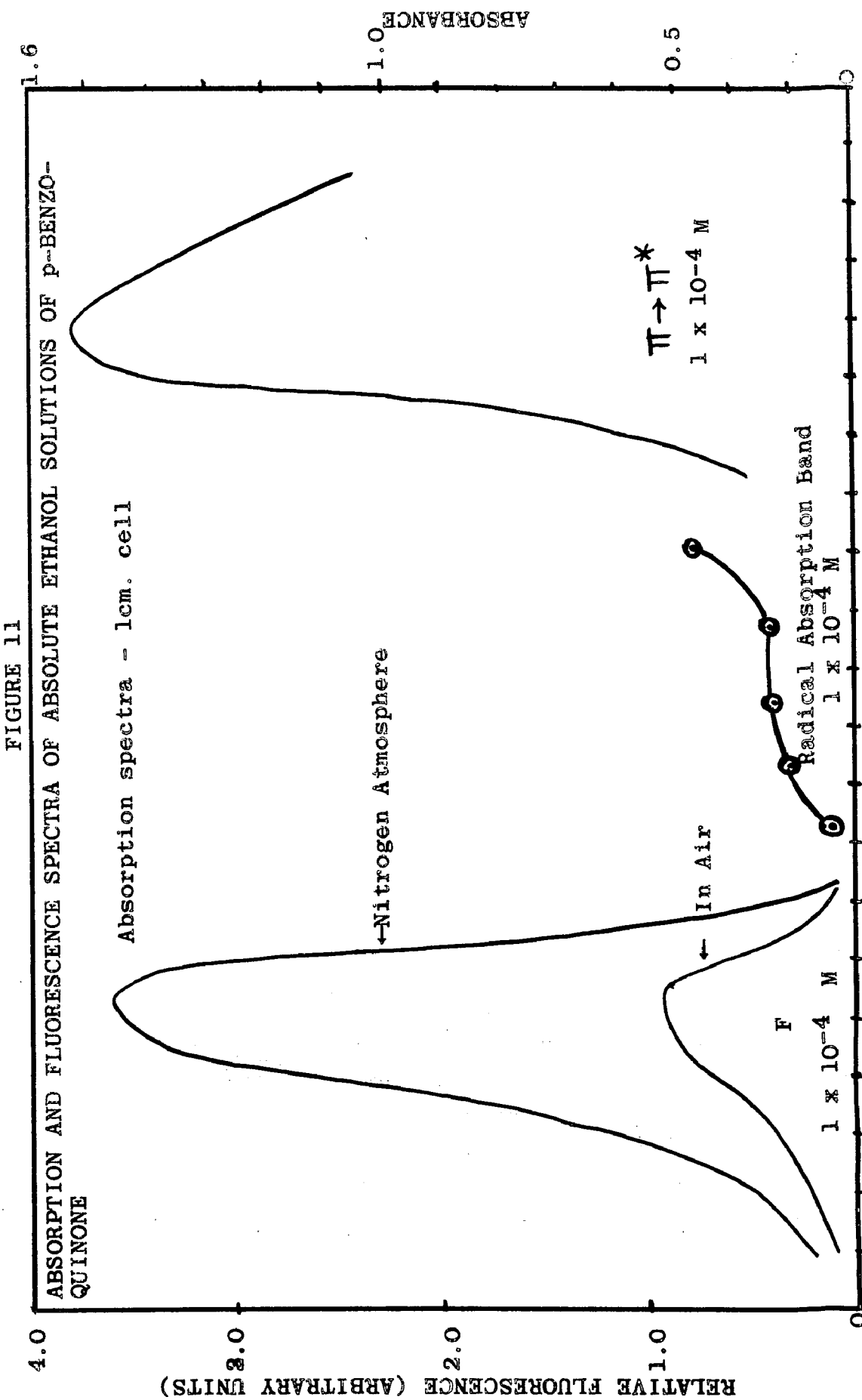
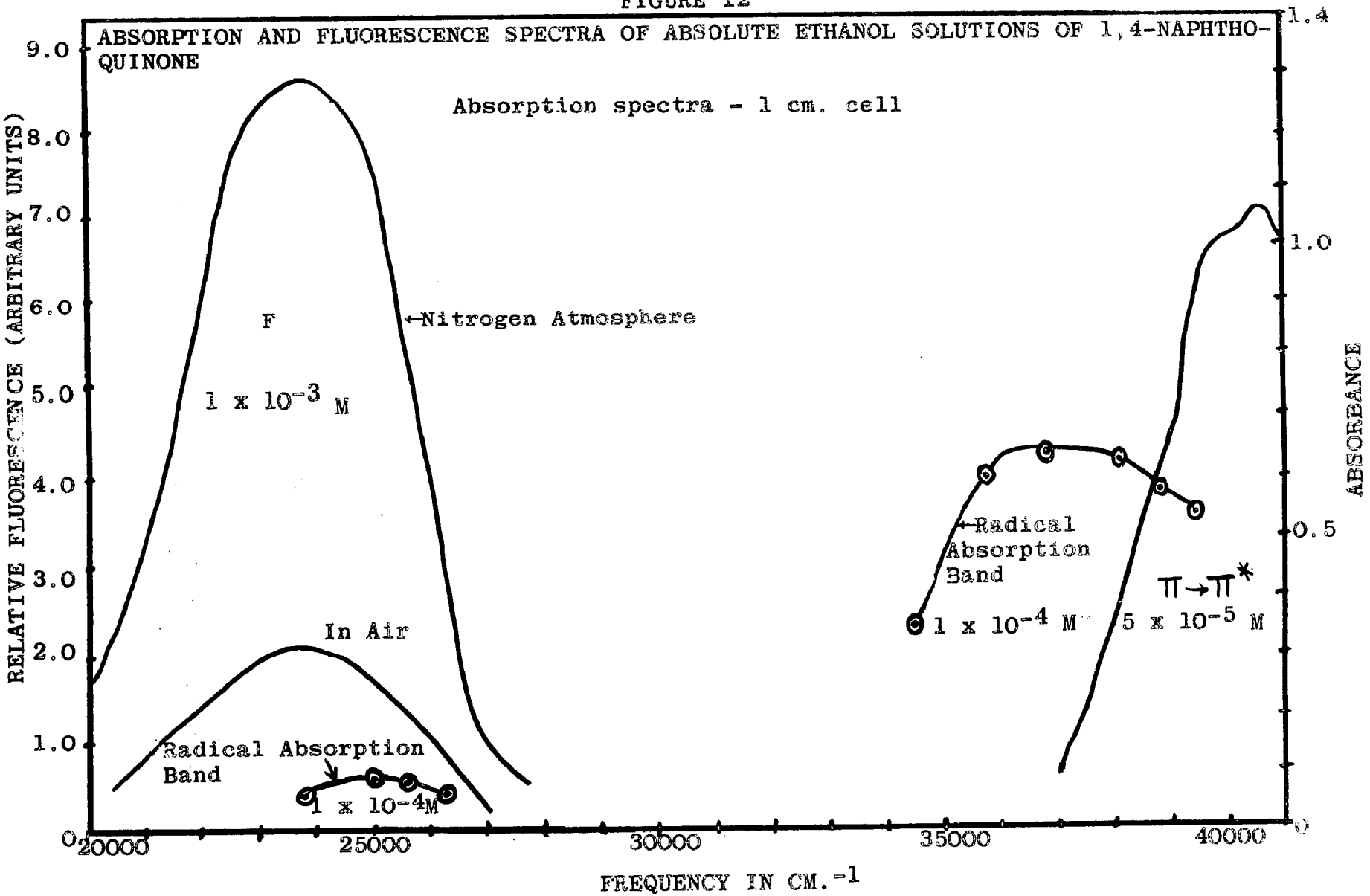

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF p-BENZO-QUINONE
Absorption spectra - 1cm. cell
←Nitrogen Atmosphere
← In Air
F
1 x 10⁻⁴ M
Radical Absorption Band
1 x 10⁻⁴ M
π→π*
1 x 10⁻⁴ M
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
ABSORBANCE
FREQUENCY IN CM.⁻¹
0
1.0
2.0
3.0
4.0
0.5
1.0
1.6
25000
30000
35000
40000

FIGURE 11

FIGURE 12


ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF 1,4-NAPHTHOQUINONE
Absorption spectra - 1 cm. cell
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
ABSORBANCE
FREQUENCY IN CM.-1
F
1 x 10-3 M
←Nitrogen Atmosphere
In Air
Radical Absorption Band
1 x 10-4M
←Radical Absorption Band
1 x 10-4 M
π→π*
5 x 10-5 M
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
20000
25000
30000
35000
40000
1.4
1.0
0.5
0

approximately four times more intense. In the presence of air there is a small amount of radicals present while in the absence of air the concentration of radicals is increased. It should be noted that the p-benzoquinone and 1,4 naphthoquinone solutions in ethanol were used within fifteen minutes after preparation. This was necessary since exposure of solutions to sunlight or even standing in the dark resulted in more intensely colored solutions.

Phenones

The absorption and fluorescence spectra for the phenones are presented in Figures 13 through 20. The only reference in the literature concerning the fluorescence of these compounds was reported for benzophenone (20). An isopropanol solution of benzophenone exhibited strong blue fluorescence when irradiated with 2537 Å radiation. However, this reference (20) failed to mention the wavelength of fluorescence.

Acetophenone and all of the substituted acetophenones produced fluorescence in an inert atmosphere under intense ultraviolet radiation. Only the 4-amino- and 4-bromoacetophenones exhibited fluorescence in the presence of air. The 4-hydroxy- and 4-methoxyacetophenone fluorescence spectra are not shown since the intensities of their broad bands were very weak. The peaks of these bands were at 3850 and 3600 Å, respectively. It is interesting to note

that aminoacetophenone produced the most intense fluorescence band of the acetophenones. This band at 27,300 $cm.^{-1}$ (3663 Å) is the normal $\pi \longrightarrow \pi^*$ fluorescence band. Atmospheric oxygen had no effect on the intensity of this band. In normal fluorescence, it is known that the presence of an amino group increases the fluorescence.

Nitro groups do not necessarily completely quench the fluorescence of compounds absorbing at longer wavelengths, especially if the molecule contains a substituent tending to intensify fluorescence. A concentrated sulfuric acid solution of acetophenone was found to have the same absorption bands (at longer wavelengths) as an irradiated ethanol solution of acetophenone in a nitrogen atmosphere. Matsen (45) described the interaction of the trivalent carbon atom (in carbonium ions, free radicals, and carbonions) with a vinyl or phenyl group in terms of the molecular orbital theory. He concluded that the molecular orbitals and their associated energy levels for one electron will be very similar for the carbonium ion, the free radical and the carbonion. Matsen (45) reported that the formation of an ion or radical conjugate to a benzene ring introduces a level into the center of the benzene level system which shifts the absorption to longer wavelengths. This is more evidence that the new band produced in the UV spectrum of an irradiated acetophenone solution in a nitrogen atmosphere is a free radical.

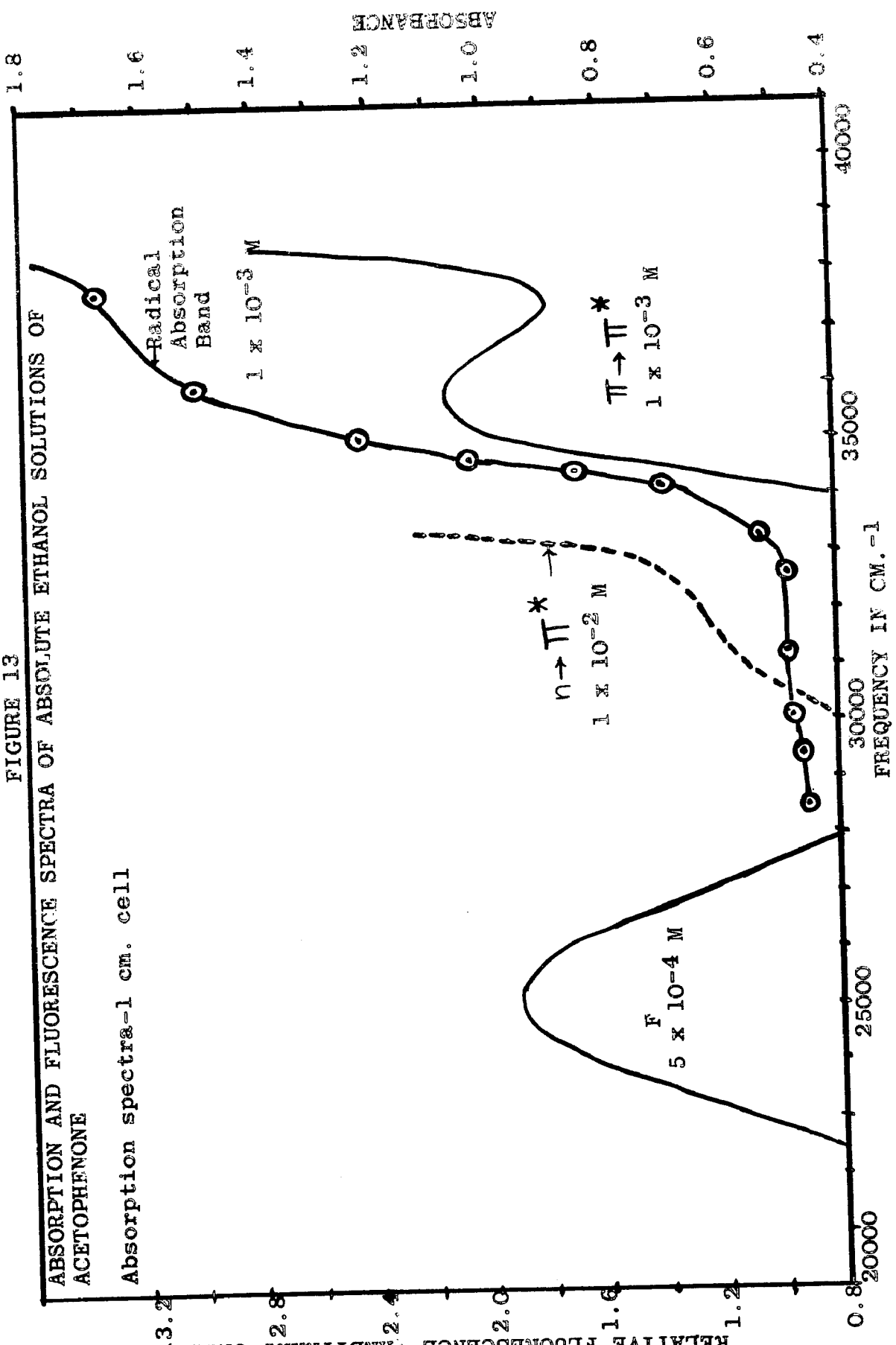

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF ACETOPHENONE
Absorption spectra-1 cm. cell
Radical Absorption Band
1 x 10⁻³ M
π→π*
1 x 10⁻³ M
n→π*
1 x 10⁻² M
F
5 x 10-4 M
ABSORBANCE
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
FREQUENCY IN CM.-1
20000
25000
30000
35000
40000

FIGURE 13

FIGURE 14

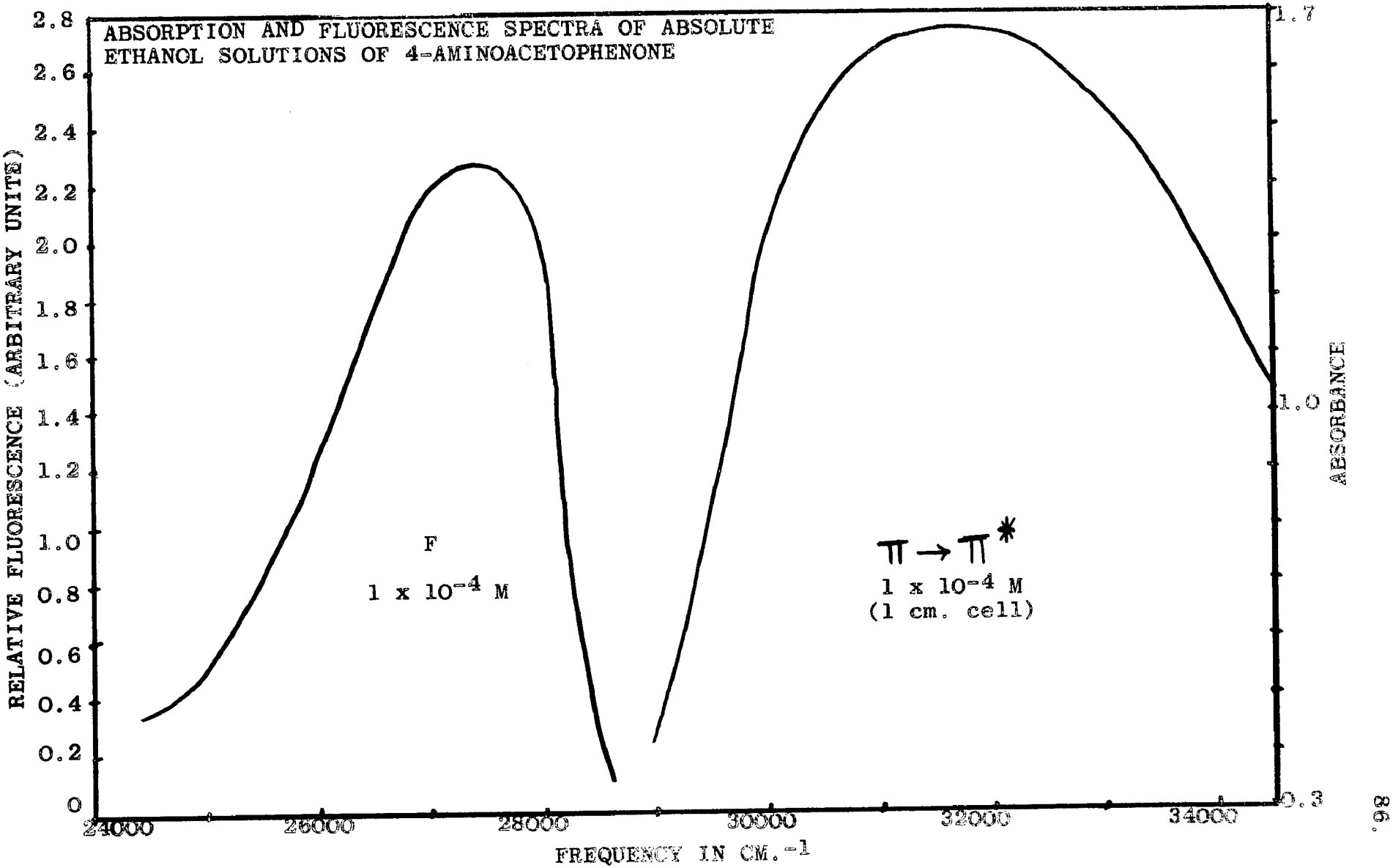

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF 4-AMINOACETOPHENONE
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
F
1 x 10-4 M
π → π*
1 x 10-4 M
(1 cm. cell)
1.7
1.0
0.3
ABSORBANCE
24000
26000
28000
30000
32000
34000
FREQUENCY IN CM.-1

FIGURE 15

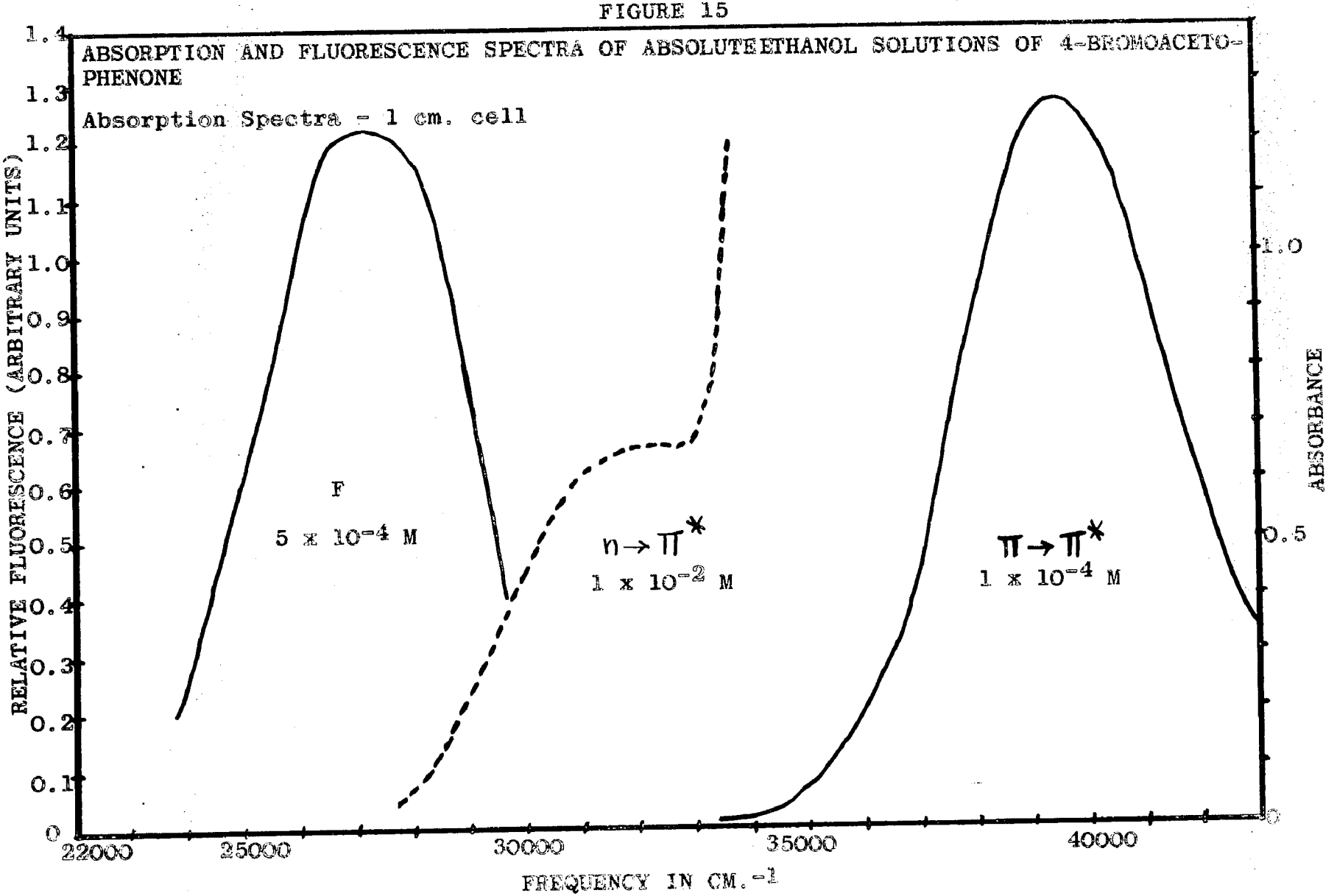
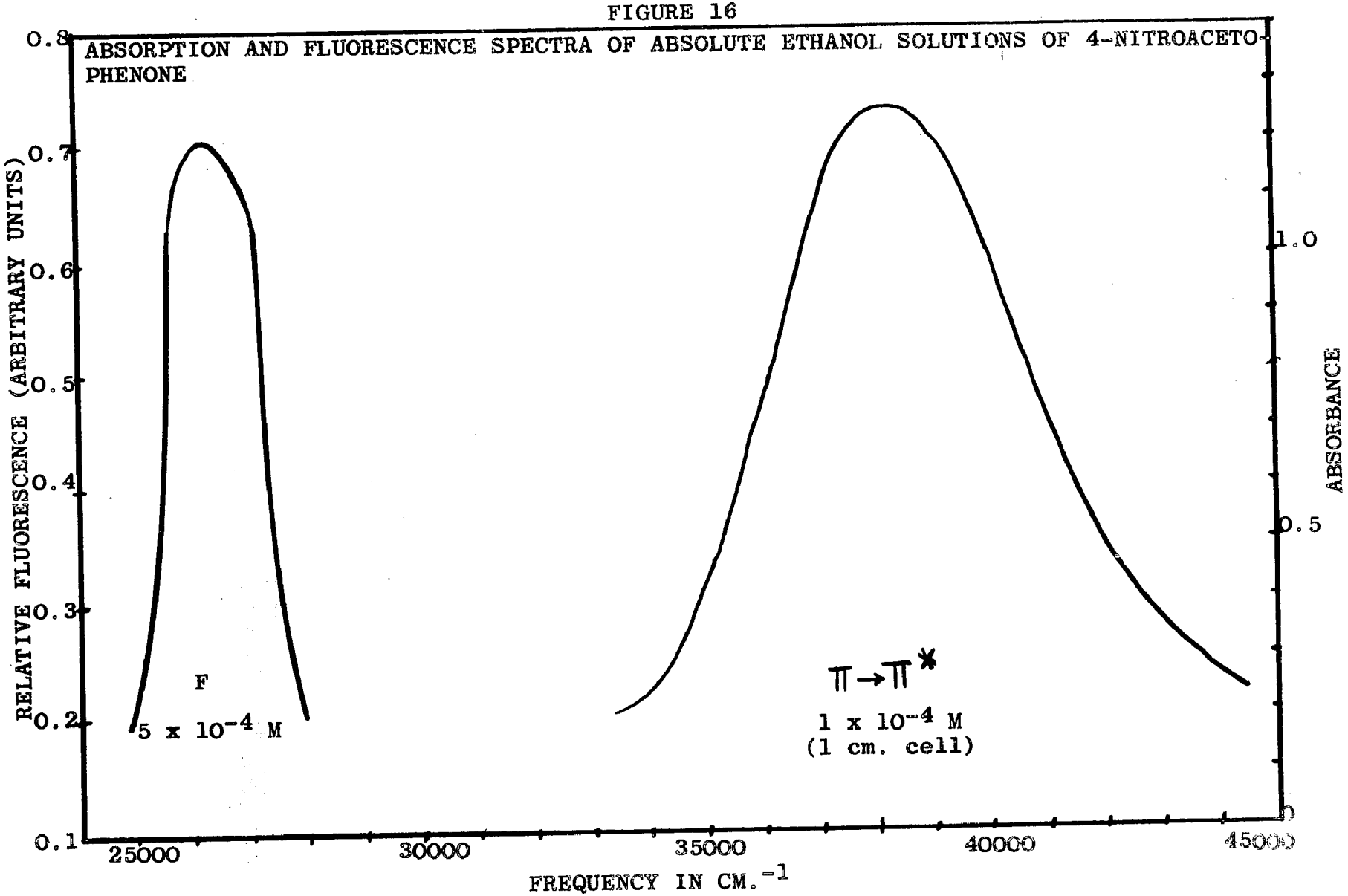

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF 4-BROMOACETOPHENONE
Absorption Spectra - 1 cm. cell
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
ABSORBANCE
FREQUENCY IN CM.-1
F
5 x 10-4 M
n → π*
1 x 10-2 M
π → π*
1 x 10-4 M
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
22000
25000
30000
35000
40000

FIGURE 16

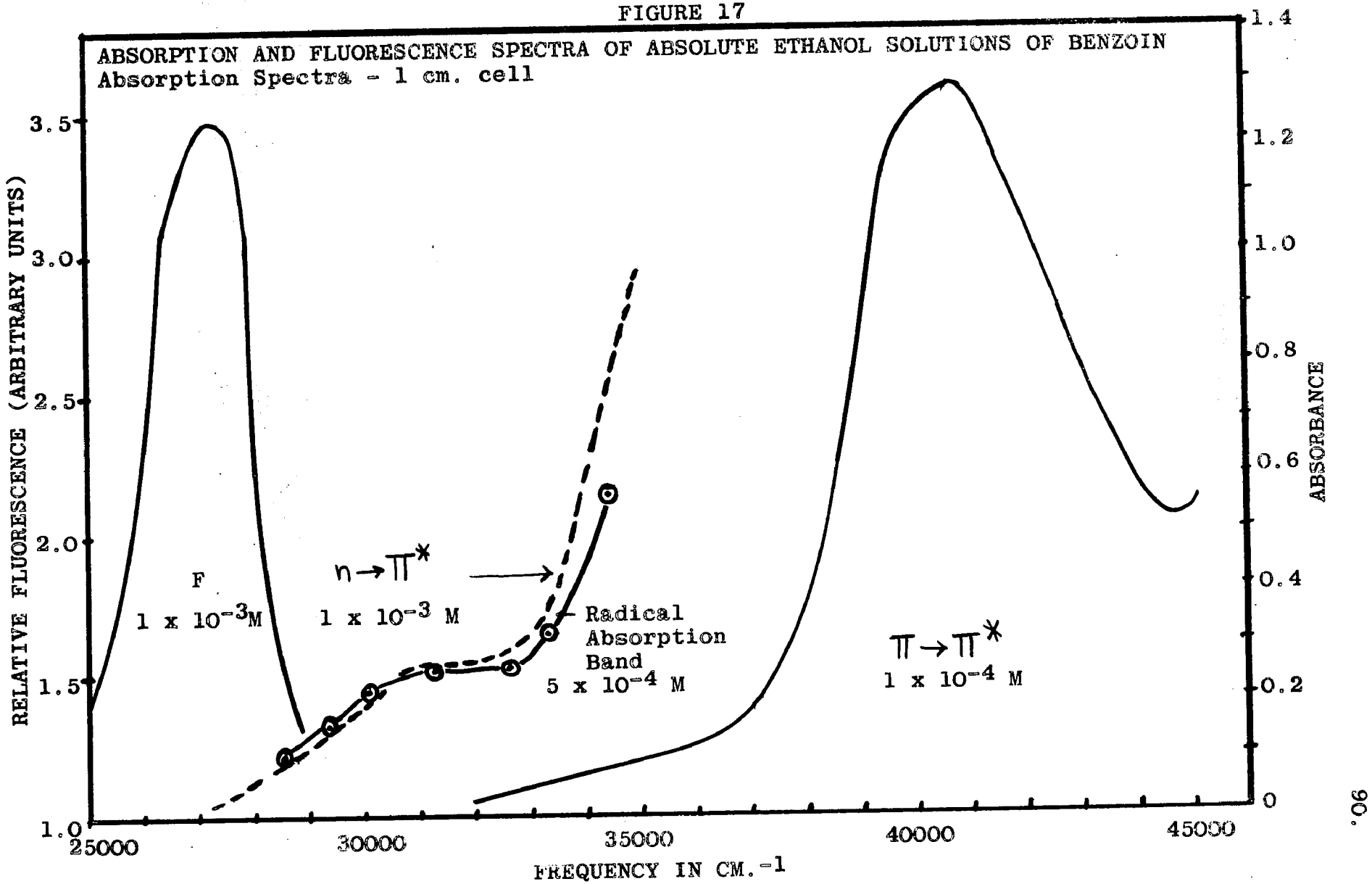

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF 4-NITROACETOPHENONE
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
F
5 x 10-4 M
π→π*
1 x 10-4 M
(1 cm. cell)
ABSORBANCE
1.0
0.5
0
25000
30000
35000
40000
45000
FREQUENCY IN CM.-1

In Figure 17 it is seen that benzoin has a strong fluorescence band at 27,000-27,400 cm.$^{-1}$ ($\approx$ 3680 Å). This band is completely quenched by air. The absorption spectrum of an irradiated benzoin solution in ethanol indicates the presence of a new band in the vicinity of the n $\longrightarrow \pi^*$ absorption band. Introduction of air into this irradiated sample resulted in the disappearance of this band. The presence of a benzoin free radical is probably the cause of this absorption band and the fluorescence band.

Benzophenone and the substituted benzophenones likewise exhibited fluorescence which have not been reported in the literature except for Pitts (20) mention of blue fluorescence for benzophenone. Figures 18 and 19 show the fluorescence bands for benzophenone and the 4-bromobenzophenone appear at exactly the same frequency, 26,800 cm.$^{-1}$ ($\approx$ 3730 Å). It is interesting to note that 4-bromobenzophenone exhibited a strong fluorescence, even though in normal fluorescence bromo-compounds are known to diminish fluorescence. The 4,4' dimethylbenzophenone solution in ethanol also produced fluorescence as shown in Figure 20.

Comparison of the fluorescence and absorption spectra of benzophenone, benzopinacol and benzhydrol clearly indicates what is happening in the photochemical reactions of these compounds. Benzophenone fluoresces at 26,800 cm.$^{-1}$

FIGURE 17


ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF BENZOIN
Absorption Spectra - 1 cm. cell
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
ABSORBANCE
FREQUENCY IN CM.-1
3.5
3.0
2.5
2.0
1.5
1.0
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
25000
30000
35000
40000
45000
F
1 x 10-3M
n→π*
1 x 10-3 M
Radical
Absorption
Band
5 x 10-4 M
π→π*
1 x 10-4 M

90.

FIGURE 18

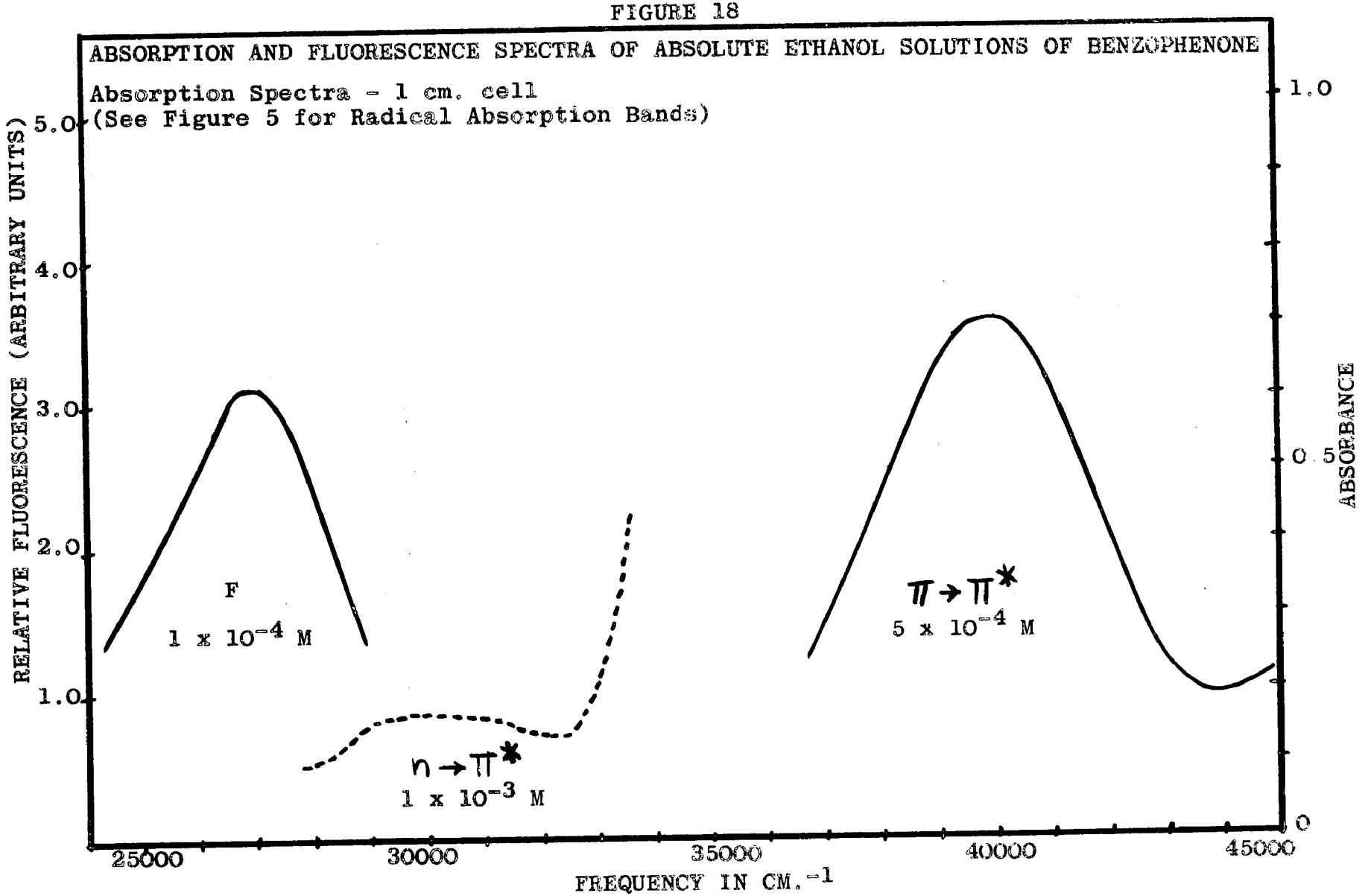

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF BENZOPHENONE
Absorption Spectra - 1 cm. cell
(See Figure 5 for Radical Absorption Bands)
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
5.0
4.0
3.0
2.0
1.0
F
1 x 10⁻⁴ M
n → π*
1 x 10⁻³ M
π → π*
5 x 10⁻⁴ M
1.0
0.5
0
ABSORBANCE
25000
30000
35000
40000
45000
FREQUENCY IN CM.⁻¹

FIGURE 19

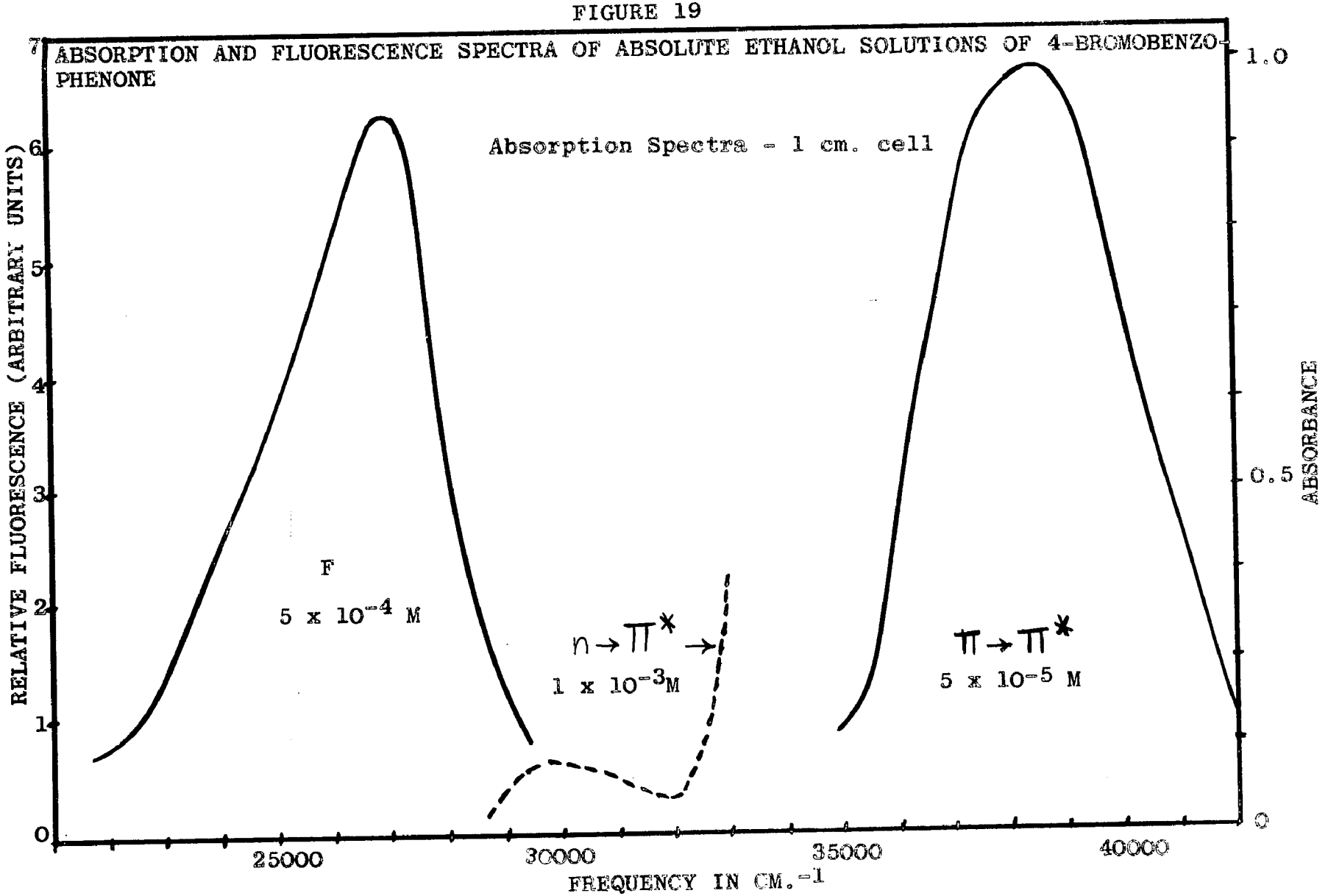
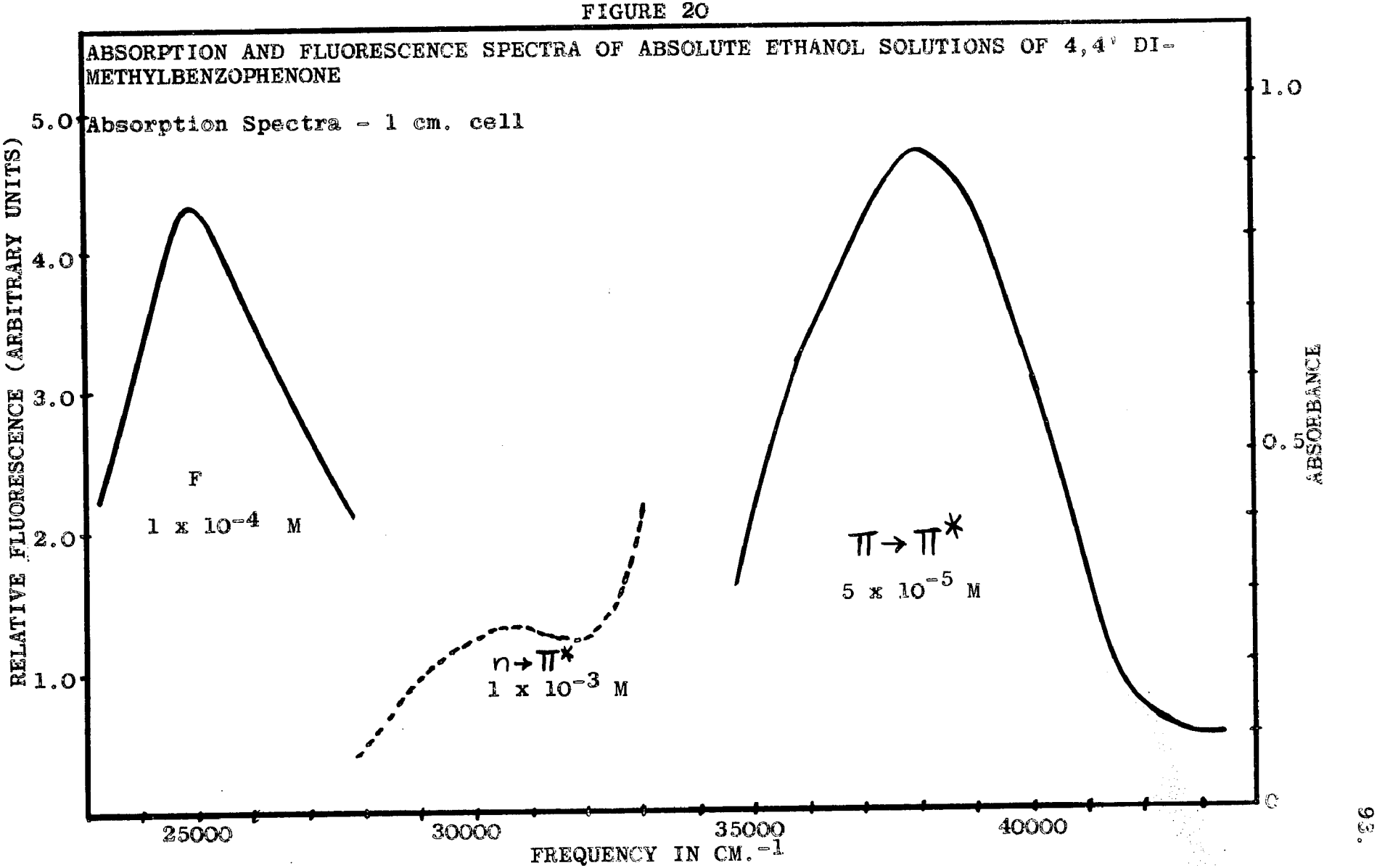

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF 4-BROMOBENZOPHENONE
Absorption Spectra - 1 cm. cell
F
5 x 10⁻⁴ M
n → π*
1 x 10⁻³M
π → π*
5 x 10⁻⁵ M
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
ABSORBANCE
FREQUENCY IN CM.⁻¹
0
1
2
3
4
5
6
7
0
0.5
1.0
25000
30000
35000
40000

FIGURE 20


ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF 4,4' DI-METHYLBENZOPHENONE
Absorption Spectra - 1 cm. cell
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
5.0
4.0
3.0
2.0
1.0
F
1 x 10-4 M
n→π*
1 x 10-3 M
π→π*
5 x 10-5 M
1.0
0.5
0
ABSORBANCE
25000
30000
35000
40000
FREQUENCY IN CM.-1

due to formation of a benzophenone free radical, $\left[(C_6H_5)_2\dot{C}OH\right]$. Benzopinacol likewise shows this same fluorescence band in Figure 21. This is reasonable since the primary action of UV radiation on benzopinacol results in photodecomposition of benzopinacol to benzophenone and benzhydrol. The benzophenone in turn is converted to the radical, according to the reaction mechanism of Pitts et al (20), which then exhibits a fluorescence band at 26,800 $cm.^{-1}$. Benzhydrol shows a fluorescence band at approximately 27,000 $cm.^{-1}$ in Figure 22. The initial fluorescence spectrum of benzhydrol showed a very weak band at 27,000 $cm.^{-1}$. Prolonged radiation resulted in this band becoming more intense. This can be explained on the basis of benzhydrol being oxidized to benzophenone which in turn produces free radicals.

It should be noted that the absorption spectrum of benzophenone in concentrated sulfuric acid appeared similar to the spectrum of an irradiated, nitrogen-flushed, ethanol solution of benzophenone. The entire spectrum was shifted to longer wavelengths in acid. According to information given by Matsen (45), this is additional evidence for indicating the probable structure of the benzophenone radical to be $\left[(C_6H_5)_2\dot{C}OH\right]$.

Miscellaneous

In Figure 23, a fluorescence band at 26,800 to

FIGURE 21

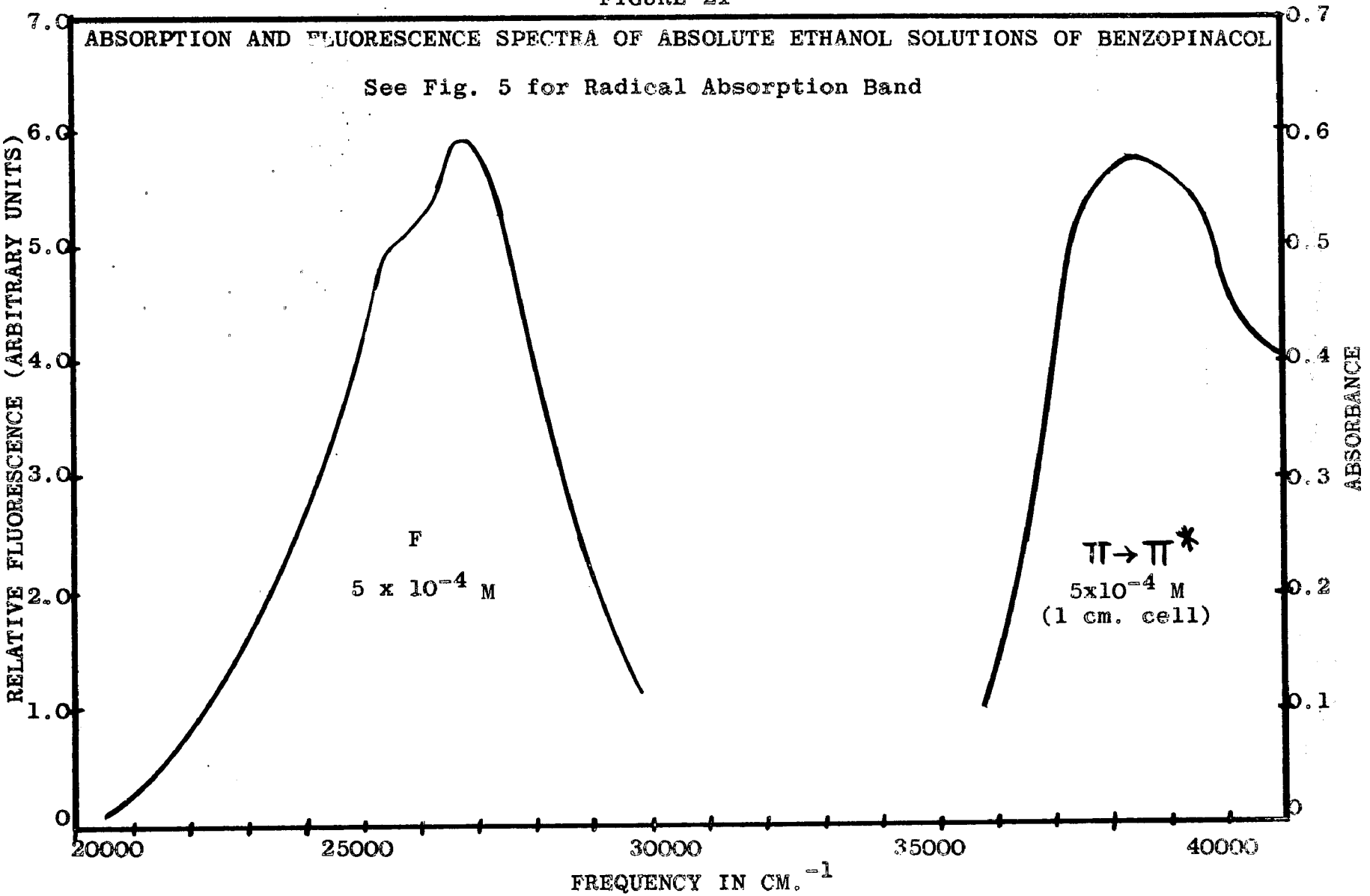

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF BENZOPINACOL
See Fig. 5 for Radical Absorption Band
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
ABSORBANCE
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
F
5 x 10-4 M
π→π*
5x10-4 M
(1 cm. cell)
20000
25000
30000
35000
40000
FREQUENCY IN CM.-1

FIGURE 22

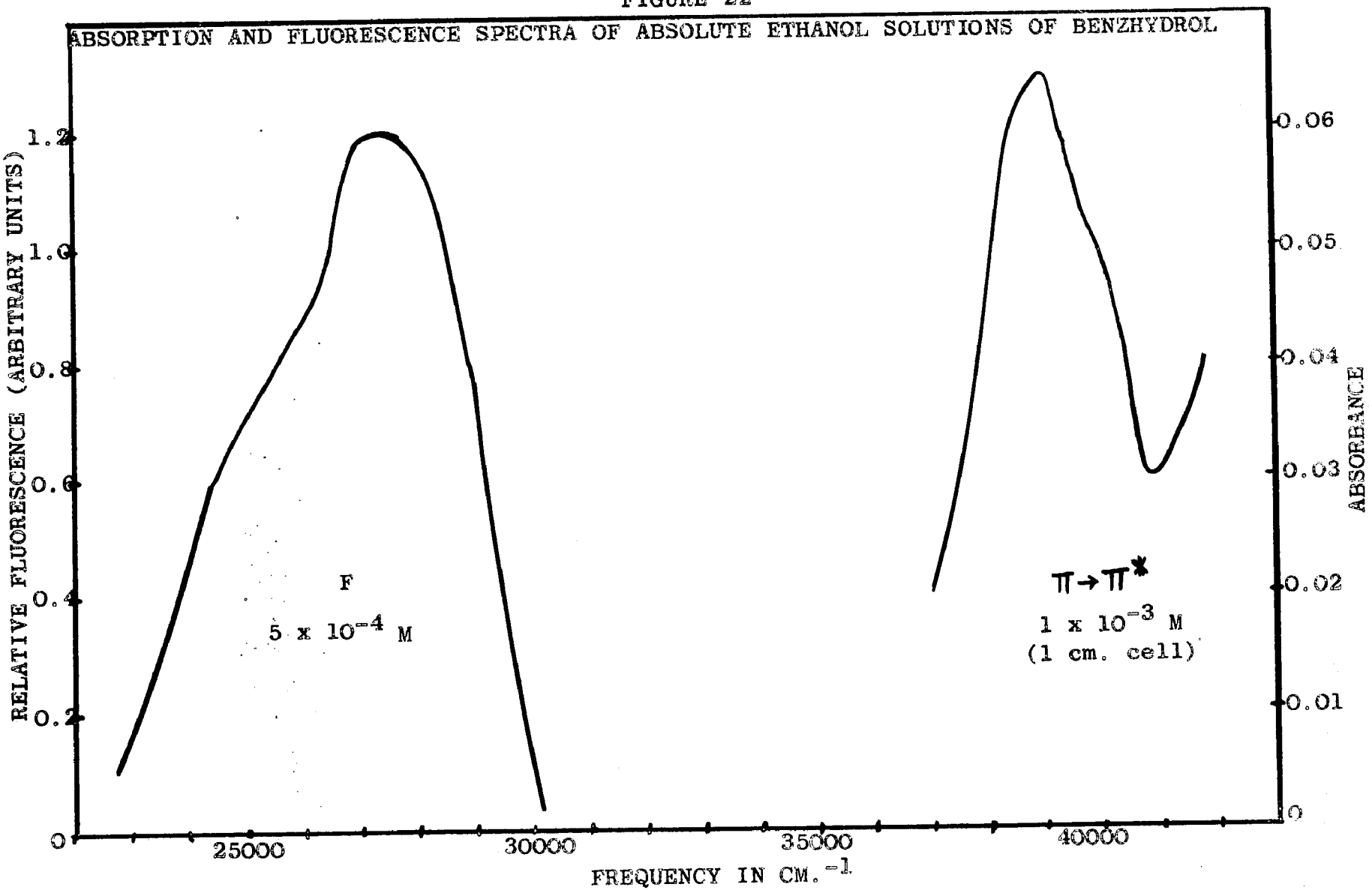
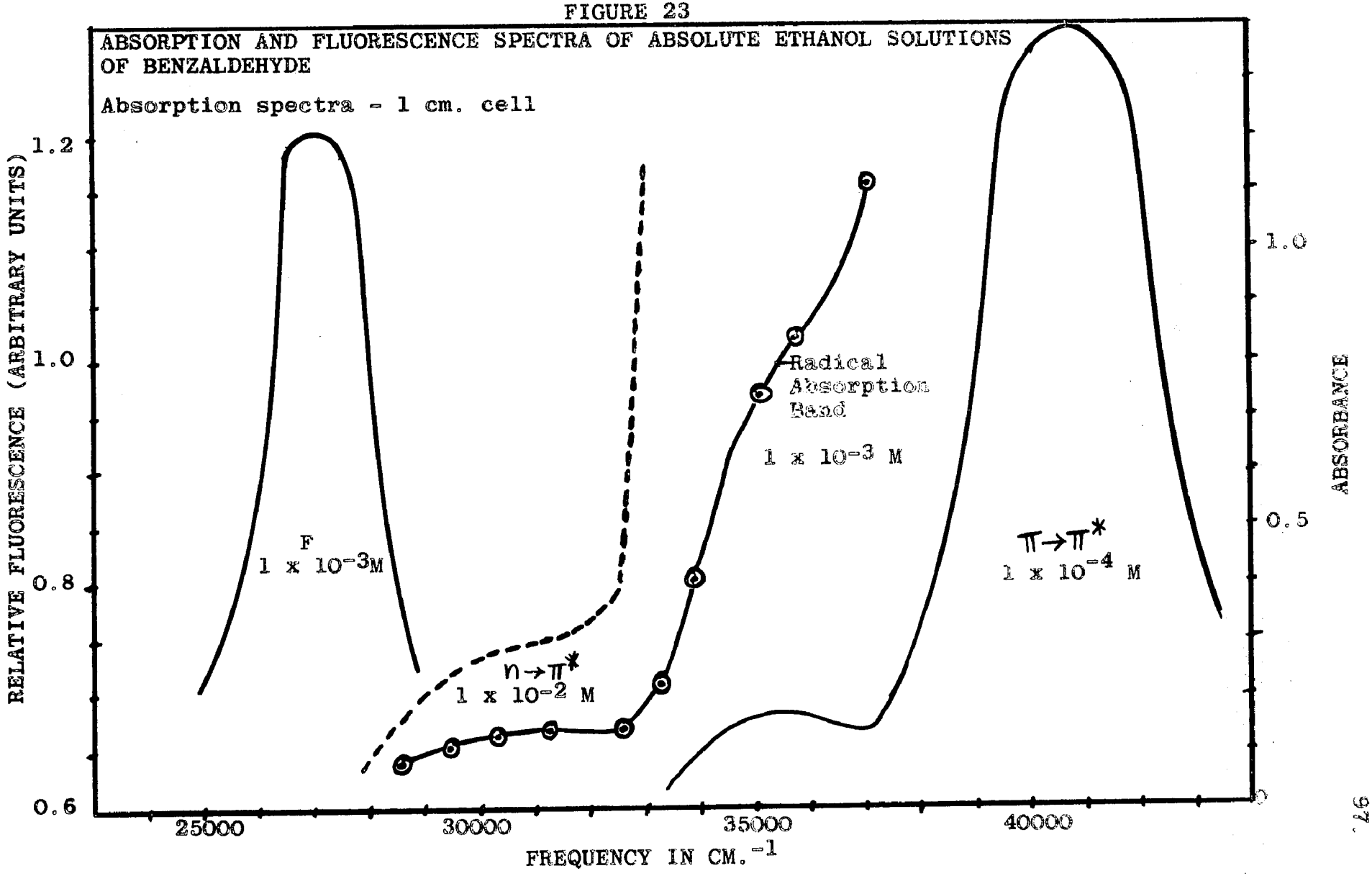

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF BENZHYDROL
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
1.2
1.0
0.8
0.6
0.4
0.2
0
F
5 x 10⁻⁴ M
π→π*
1 x 10⁻³ M
(1 cm. cell)
0.06
0.05
0.04
0.03
0.02
0.01
0
ABSORBANCE
25000
30000
35000
40000
FREQUENCY IN CM.⁻¹

FIGURE 23


ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF BENZALDEHYDE
Absorption spectra - 1 cm. cell
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
ABSORBANCE
1.2
1.0
0.8
0.6
0.5
0
F
1 x 10-3M
n→π*
1 x 10-2 M
Radical Absorption Band
1 x 10-3 M
π→π*
1 x 10-4 M
25000
30000
35000
40000
FREQUENCY IN CM.-1

27,400 cm.$^{-1}$ ($\approx$ 3730-3650 Å) is shown for benzaldehyde in absolute ethanol in a nitrogen atmosphere. Comparable fluorescence bands for some other compounds containing a ketone group are listed in Table XXI.

TABLE XXI

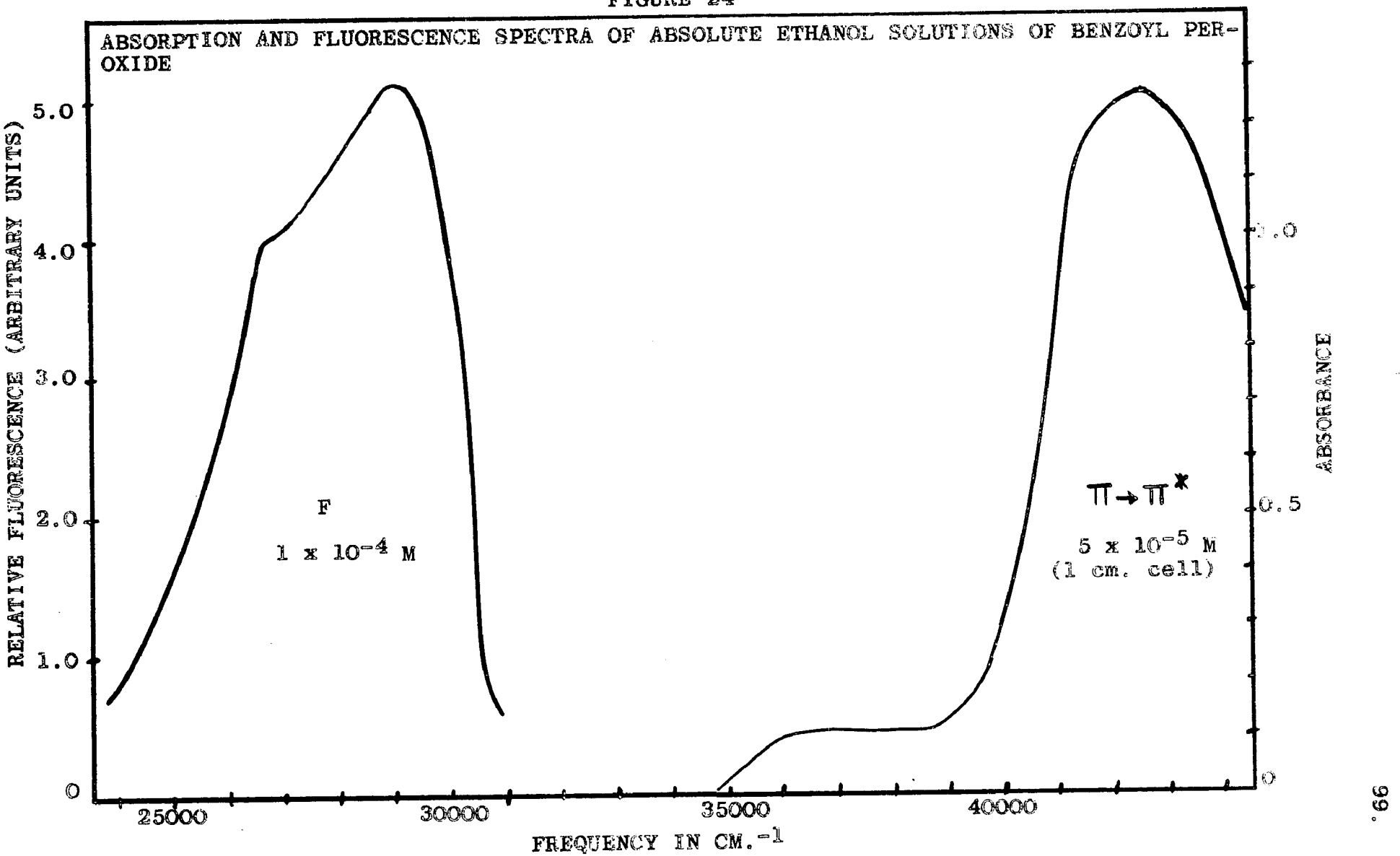
FLUORESCENCE BANDS FOR SOME COMPOUNDS CONTAINING A KETONE GROUP

Compound	Frequency in cm.$^{-1}$
Acetophenone	25,000
4-Bromoacetophenone	27,000
4-Nitroacetophenone	26,200
Benzoin	27,250
Benzophenone	26,800
4-Bromobenzophenone	26,800

Since benzaldehyde does not normally fluoresce, the fluorescence band is probably due to the benzaldehyde free radical $\left[C_6H_5\dot{C}OH \right]$.

An absolute ethanol solution of benzoyl peroxide in a nitrogen atmosphere exhibited the fluorescence spectrum shown in Figure 24. Benzoyl peroxide did not fluoresce in an atmosphere of air. Again, it is felt that the

FIGURE 24


ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF BENZOYL PEROXIDE
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
5.0
4.0
3.0
2.0
1.0
0
F
1 x 10⁻⁴ M
π→π*
5 x 10⁻⁵ M
(1 cm. cell)
1.0
0.5
0
ABSORBANCE
25000
30000
35000
40000
FREQUENCY IN CM.⁻¹

fluorescence is probably due to the benzoyloxy free radical, $\left[C_6H_5COO\cdot\right]$ resulting from the photodecomposition of benzoyl peroxide.

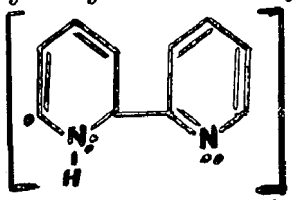
Figure 25 shows the fluorescence spectra of 2,2' Bipyridyl in alcohol in the presence and absence of air. Two new fluorescence bands appeared in the nitrogen-flushed sample. Normally, 2,2' Bipyridyl does not fluoresce. In view of the photopotential results due to presence of free radical, it can be concluded that the fluorescence is due to the bipyridyl radical, one of whose forms can be represented by  .

Figure 26 clearly indicates two well-defined peaks in the fluorescence spectra of Diphenylamine at 27,800 and 29,000 $cm.^{-1}$ (3597 and 3448 Å, respectively). Diphenylamine has been reported to exhibit a continuous fluorescence band at 3260-4150 Å in a Hexane solution (46). The diphenylamine radical $\left[(C_6H_5)_2\ddot{N}\cdot\right]$ is probably the cause of the fluorescence.

One of the most interesting fluorescence spectra obtained in these studies is shown in Figure 27 for an absolute ethanol solution of Phenazine. In order to show the fluorescence intensity increase for the nitrogen-flushed solution, the relative fluorescence values are expressed in logarithms. It is seen that the 21,300 $cm.^{-1}$

FIGURE 25

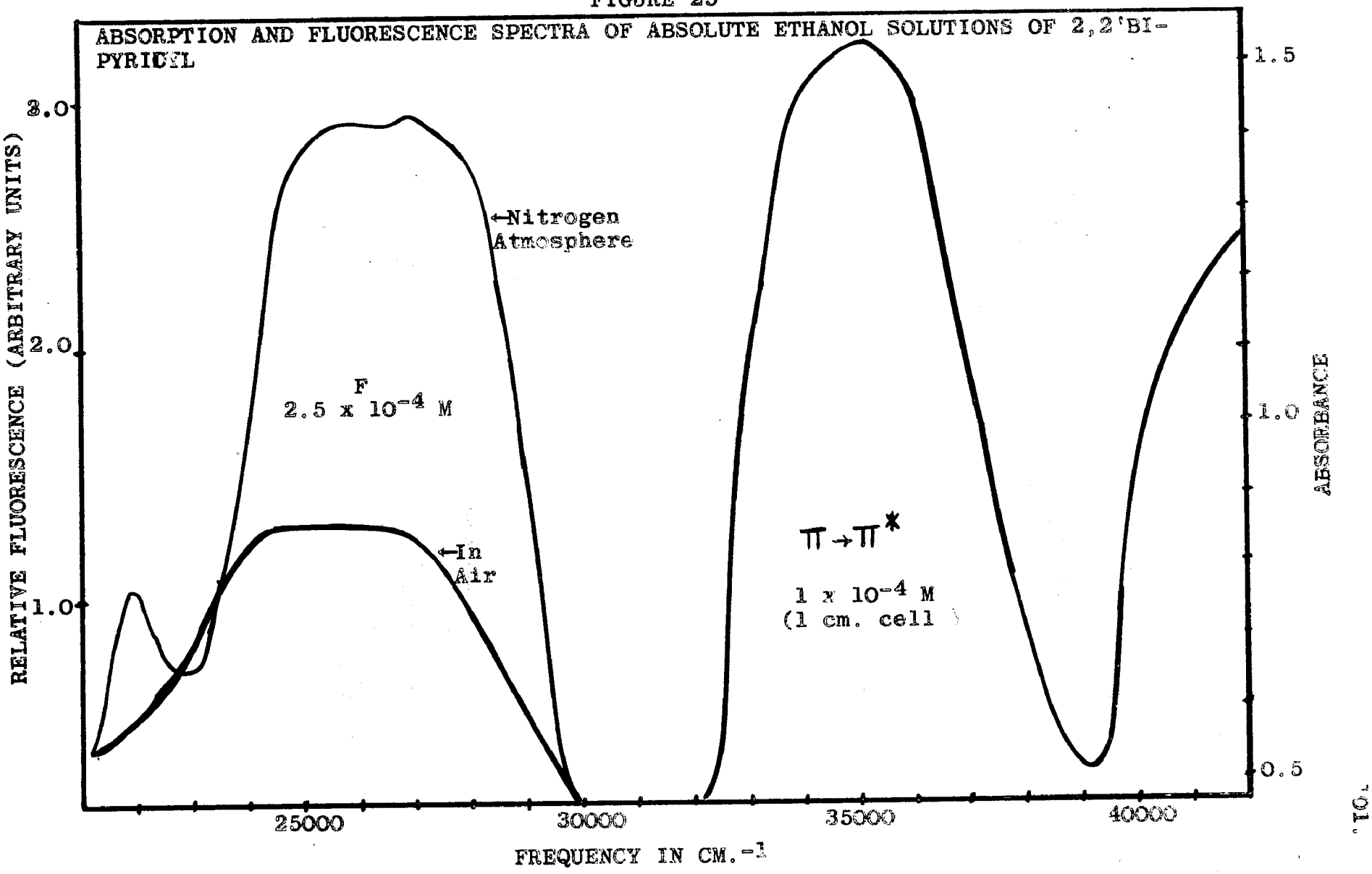

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF 2,2'BI-PYRIDYL
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
3.0
2.0
1.0
←Nitrogen Atmosphere
F
2.5 x 10⁻⁴ M
←In Air
π→π*
1 x 10⁻⁴ M
(1 cm. cell
1.5
1.0
0.5
ABSORBANCE
25000
30000
35000
40000
FREQUENCY IN CM.⁻¹

FIGURE 26

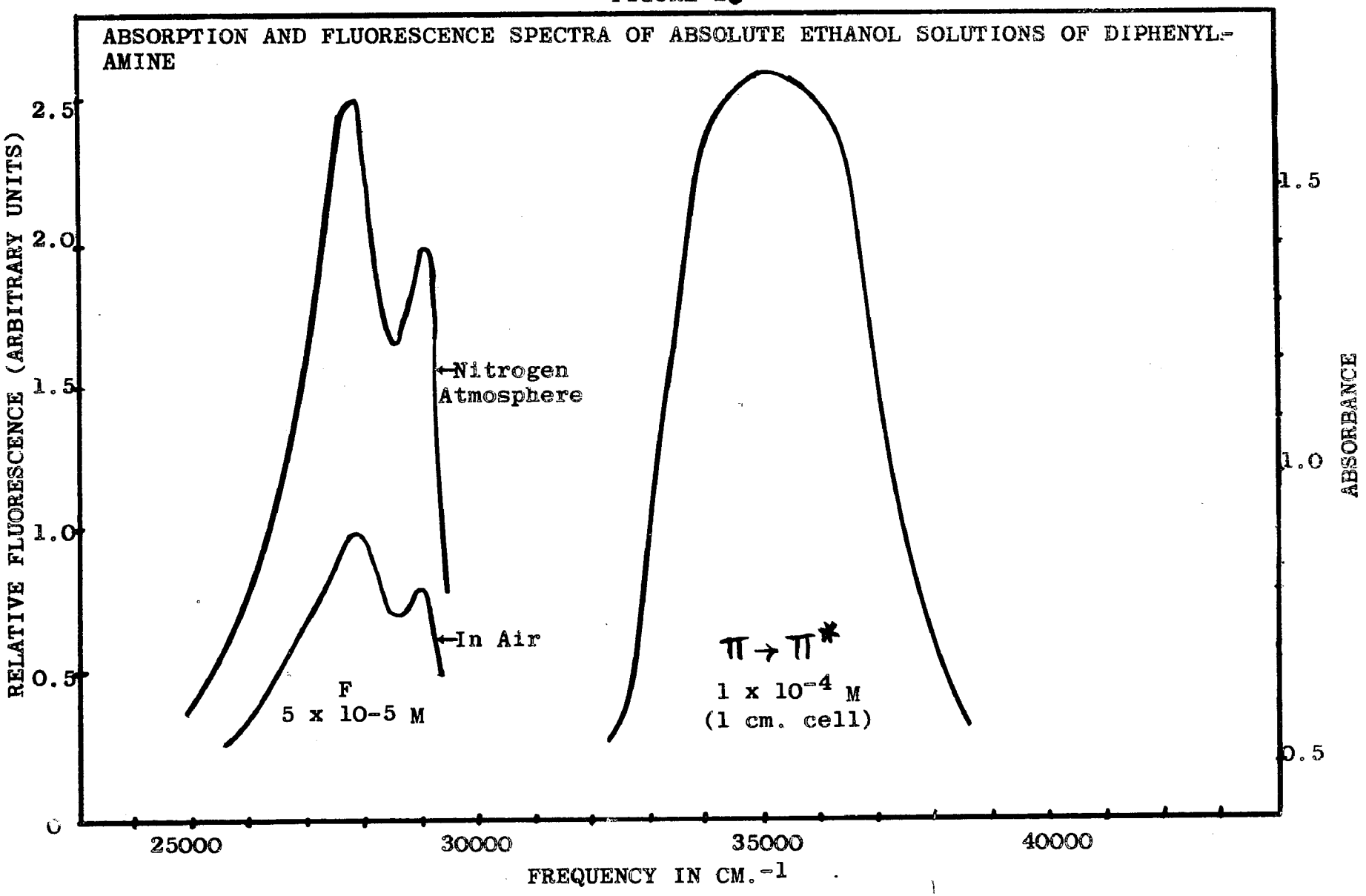
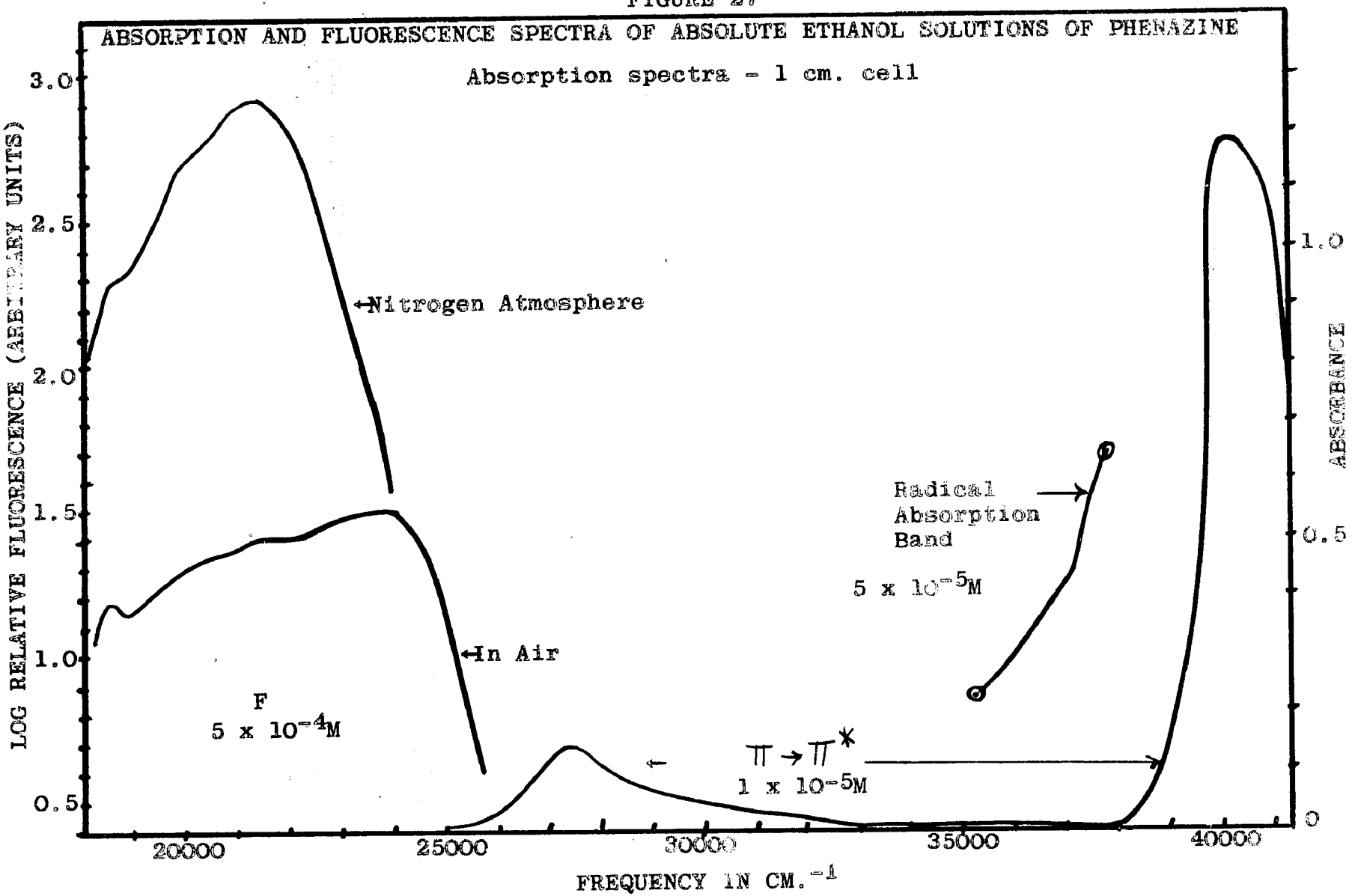
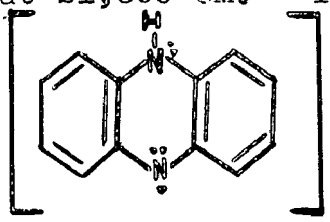

ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF DIPHENYL-AMINE
RELATIVE FLUORESCENCE (ARBITRARY UNITS)
2.5
2.0
1.5
1.0
0.5
0
←Nitrogen Atmosphere
←In Air
F
5 x 10-5 M
π → π*
1 x 10-4 M
(1 cm. cell)
1.5
1.0
0.5
ABSORBANCE
25000
30000
35000
40000
FREQUENCY IN CM.-1

FIGURE 27


ABSORPTION AND FLUORESCENCE SPECTRA OF ABSOLUTE ETHANOL SOLUTIONS OF PHENAZINE
Absorption spectra - 1 cm. cell
LOG RELATIVE FLUORESCENCE (ARBITRARY UNITS)
ABSORBANCE
3.0
2.5
2.0
1.5
1.0
0.5
1.0
0.5
0
←Nitrogen Atmosphere
←In Air
F
5 x 10⁻⁴M
Radical
Absorption
Band
5 x 10⁻⁵M
π → π*
1 x 10⁻⁵M
20000
25000
30000
35000
40000
FREQUENCY IN CM.⁻¹

(4695 Å) band is the most intense fluorescence band in the nitrogen-flushed solution. The 23,800 cm.$^{-1}$ (4202 Å) band which was the most intense fluorescence band in a solution containing air, appears to have disappeared or else has been completely smeared by the 21,300 cm.$^{-1}$ band. This intense band at 21,300 cm.$^{-1}$ is probably due to the phenazine radical,  . The intense green fluorescence cannot be attributed to contamination by phenazine-N-oxide or phenazine-di-N-oxide (47). The only other fluorescence bands reported for phenazine in the literature pertained to those bands produced by x-ray irradiation (48) of phenazine crystals.

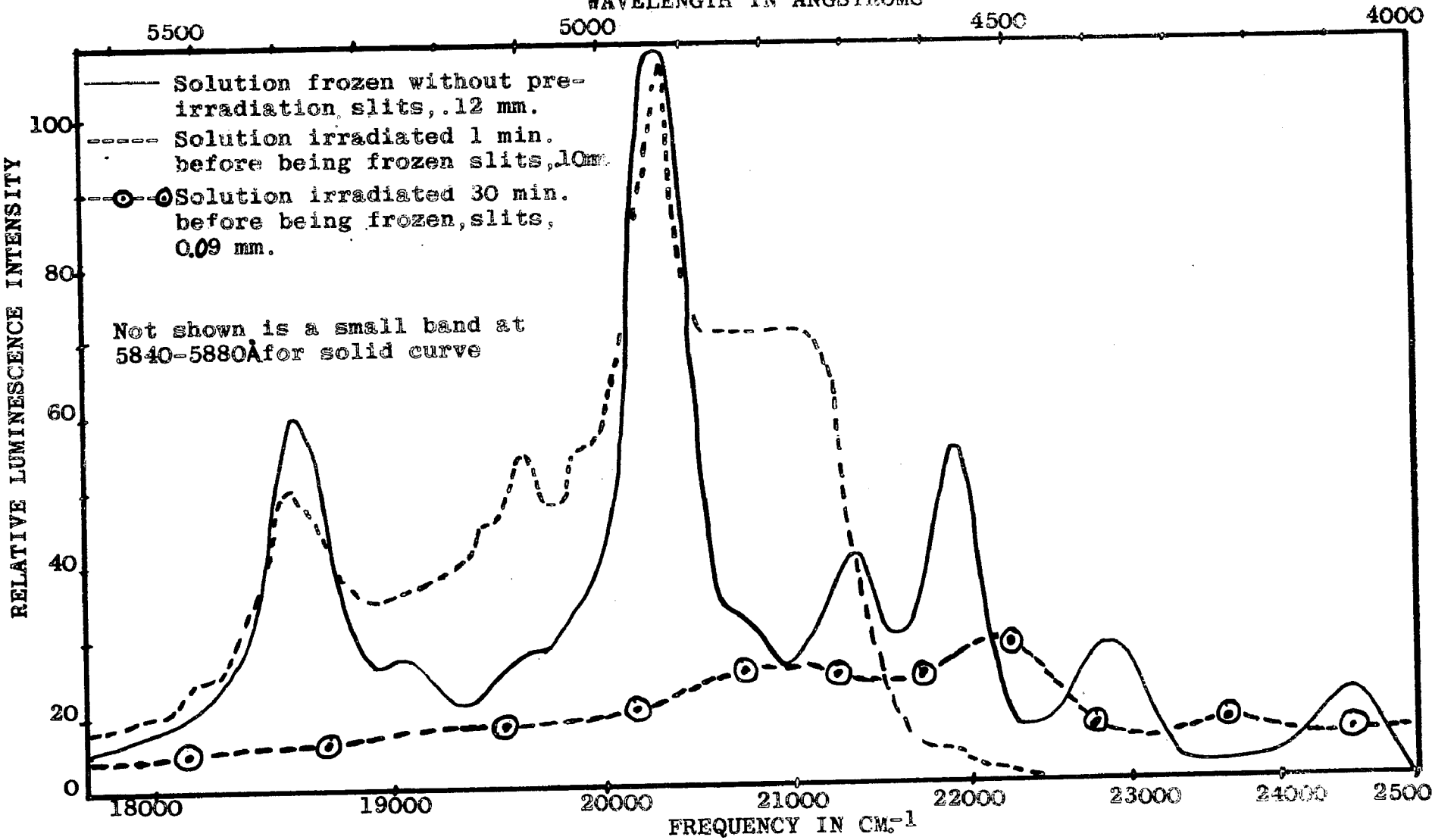
Luminescence Spectra at Liquid Nitrogen Temperature

Quinones

Figure 28 shows the luminescence spectra of AQ in EPA glasses at liquid-nitrogen temperature. These spectra are uncorrected for detector response. It is interesting to note that there is structure present in both spectra. As seen in Figure 10, the fluorescence spectra at room temperature shows broad bands. This agrees with the well-known fact that spectra are generally sharpened when frozen into glasses at low temperature, due to a decrease of thermal smearing. The solid curve represents the

FIGURE 28

LUMINESCENCE SPECTRA OF ANTHRAQUINONE (9,10) IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN



spectrum of an AQ solution in EPA which was frozen to a glass without any radiation treatment. This is the true phosphorescence spectrum for AQ since all of the bands in the spectrum agree with those reported by Lewis and Kasha (43). The dotted wave represents the luminescence spectrum of an AQ solution in EPA which was irradiated for approximately one minute before being frozen. It is seen that a new, intense, broad band appears in the 21,000-20,450 $cm.^{-1}$ region (4760-4890 Å) for the dotted curve. This band is due to the free radical which appears at approximately 21,000 $cm.^{-1}$ (4760 Å) in an ethanol solution at room temperature. In the EPA glass made from a non-irradiated solution, the solvent and solute molecules are rigidly fixed. Thus, interaction between the solvent and excited state solute molecules to form free radicals is greatly minimized. The EPA glass of AQ formed from an irradiated solution was melted and the solution was re-irradiated for thirty minutes. After re-freezing, a luminescence spectrum was run. This spectrum showed a band at 22,222 $cm.^{-1}$ (4500 Å) which was more intense than the 21,000 $cm.^{-1}$ (4760 Å) band mentioned above. The formation of a luminescent product accounts for this band and is additional proof for the 21,000 $cm.^{-1}$ band being caused by the formation of the yellow intermediate, the semiquinone radical of AQ. (Refer to page 79)

The luminescence spectra for EPA glasses of p-benzoquinone are shown in Figure 29. There is practically no difference between the spectra. Apparently, the radical detected at room temperature fluorescence decayed very rapidly after irradiation of the solution before freezing. The spectra are probably due to the phosphorescence of p-Benzoquinone. It should be noted that a blue phosphorescence which persisted for approximately 10 seconds was observed for the EPA glasses of p-Benzoquinone after removal from the exciting radiation.

Figure 30 shows the luminescence spectra for EPA glasses of 1,4 naphthoquinone. The curves shown probably represent the phosphorescence and radical spectra for 1,4-naphthoquinone. Irradiation of the solution before freezing produced the dotted curve. It can be seen that two new peaks appeared in the dotted curve. These must be attributed to the radical which produced a very intense fluorescence band at approximately 24,000 $cm.^{-1}$ (4167 Å) in ethanol at room temperature. It should be noted that the phosphorescence of 1,4-naphthoquinone and p-benzoquinone have not been reported in the literature prior to this work.

Phenones

The luminescence spectra of EPA glasses of acetophenone are shown in Figure 31. These spectra represent

FIGURE 29

LUMINESCENCE SPECTRA OF p-BENZOQUINONE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

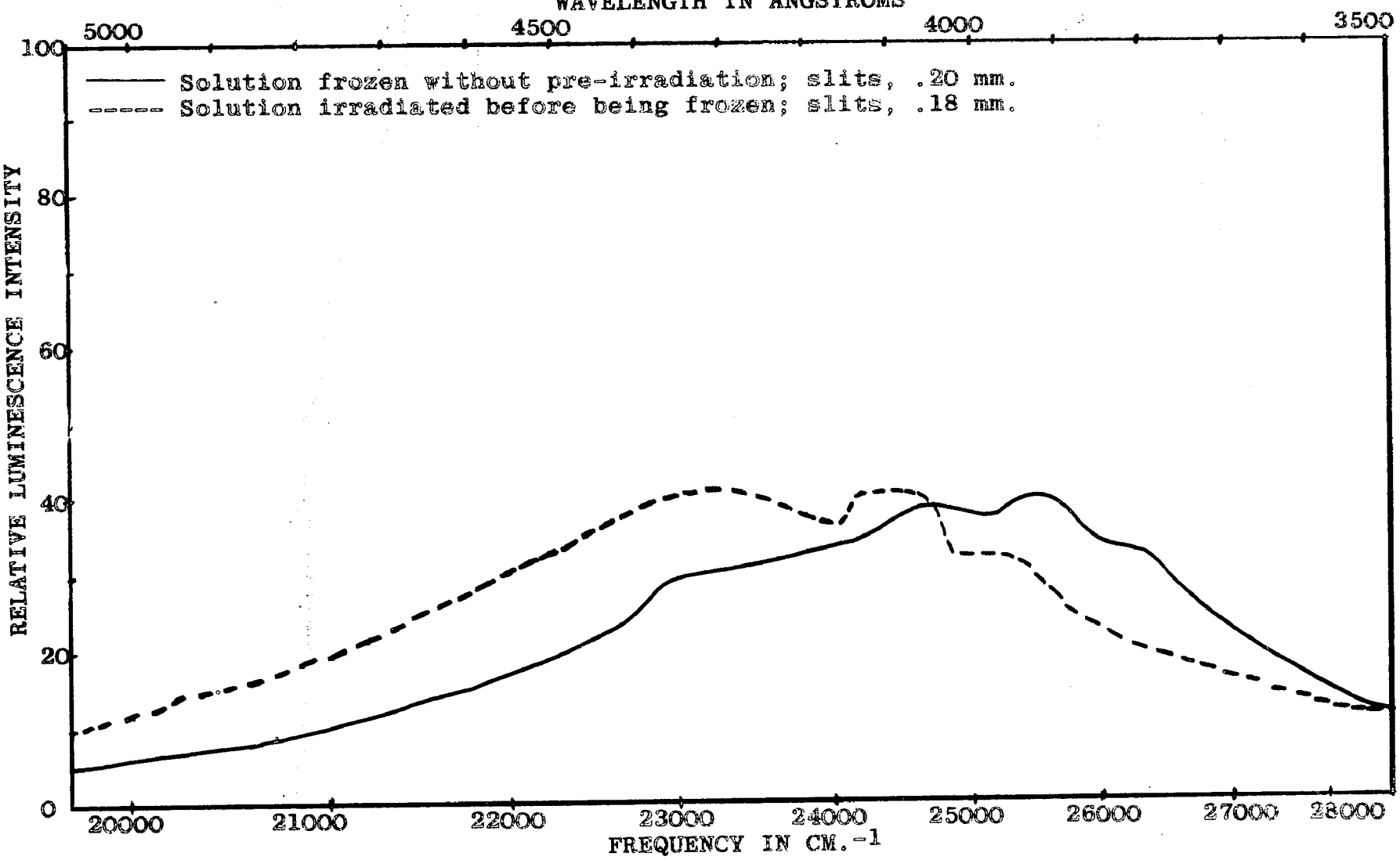
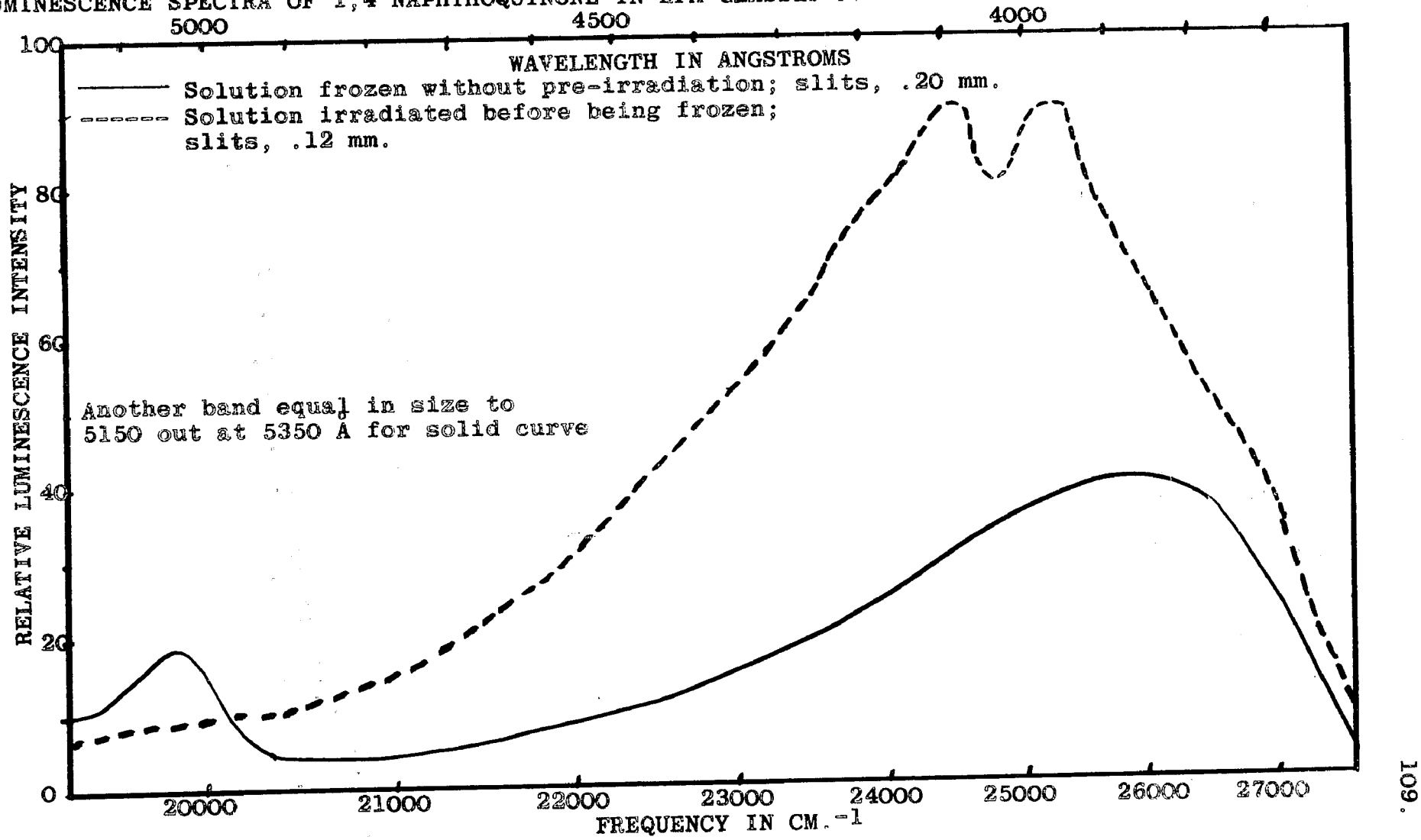


FIGURE 30

LUMINESCENCE SPECTRA OF 1,4 NAPHTHOQUINONE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN



the phosphorescence of acetophenone. Lewis and Kasha (43) found a phosphorescence spectrum of acetophenone in the same wavelength region in EPA at low temperatures, but did not describe the details of the spectrum. A more recent investigation by Vanselow and Duncan (49) described the details of the spectrum of acetophenone in EPA at liquid-nitrogen temperature. Both curves in Figure 31 are practically identical and are in complete agreement with the spectrum reported in Reference 49.

Figure 32 shows the luminescence spectra of 4-amino-acetophenone to be the same for both EPA glasses. These spectra are due to phosphorescence and fluorescence of 4-aminoacetophenone. A visual observation regarding the color and duration of phosphorescence after removal of the EPA glass from the exciting radiation revealed a blue color which lasted approximately four seconds. This is due to the broad band which appeared at 4300-4900 Å. The bands at approximately 3580 and 3680 Å (28,000 $cm.^{-1}$ and 27,174 $cm.^{-1}$) are due to fluorescence of 4-aminoaceto-phenone.

The luminescence spectra of 4-bromoacetophenone in EPA at liquid-nitrogen temperatures are shown in Figure 33. It can be seen that radiation of the solution before freezing resulted in an increase in luminescence intensity in the 27,000 $cm.^{-1}$ region which might be due to presence

FIGURE 31

LUMINESCENCE SPECTRA OF ACETOPHENONE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

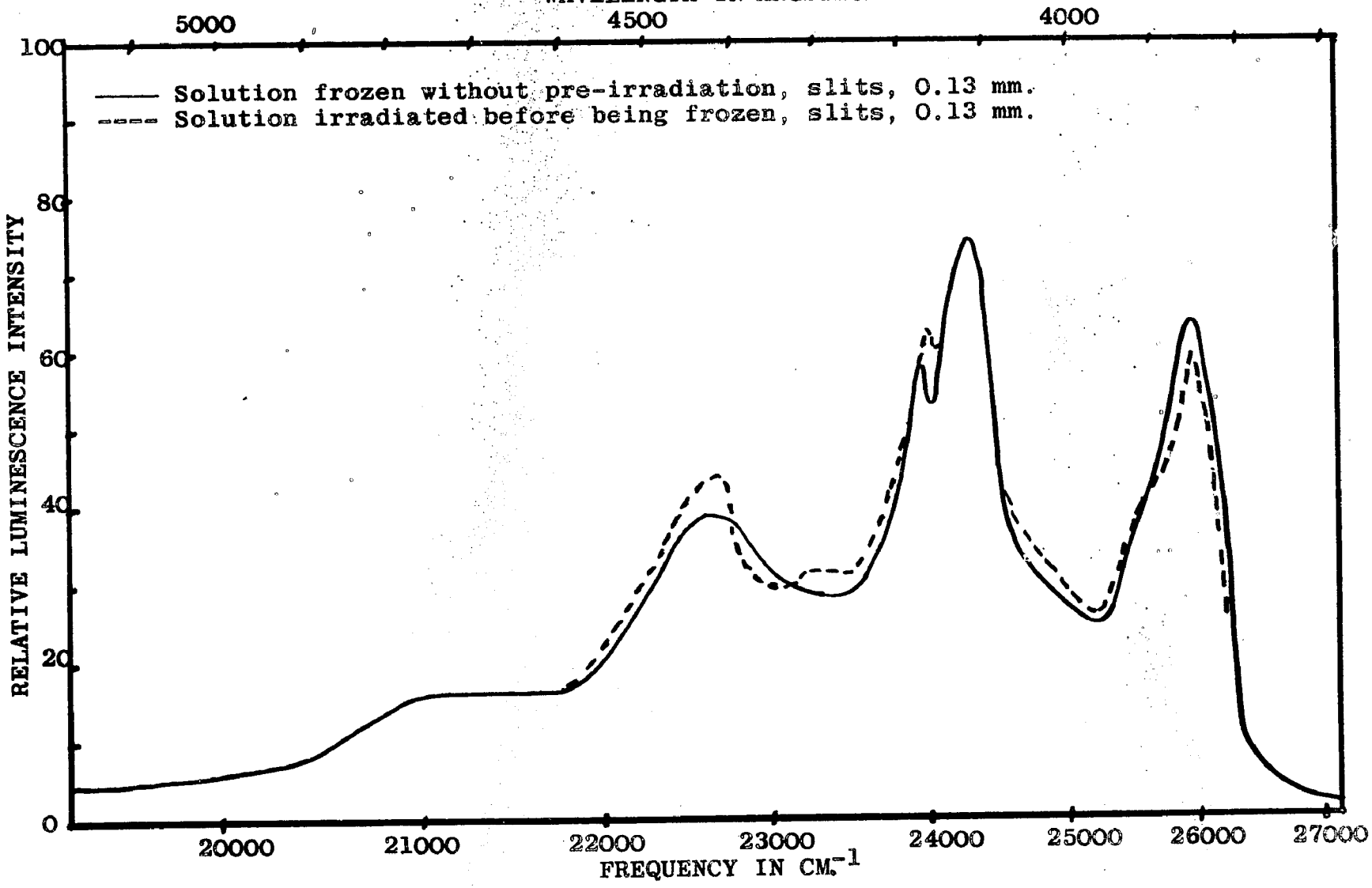


FIGURE 32

LUMINESCENCE SPECTRA OF 4-AMINOACETOPHENONE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

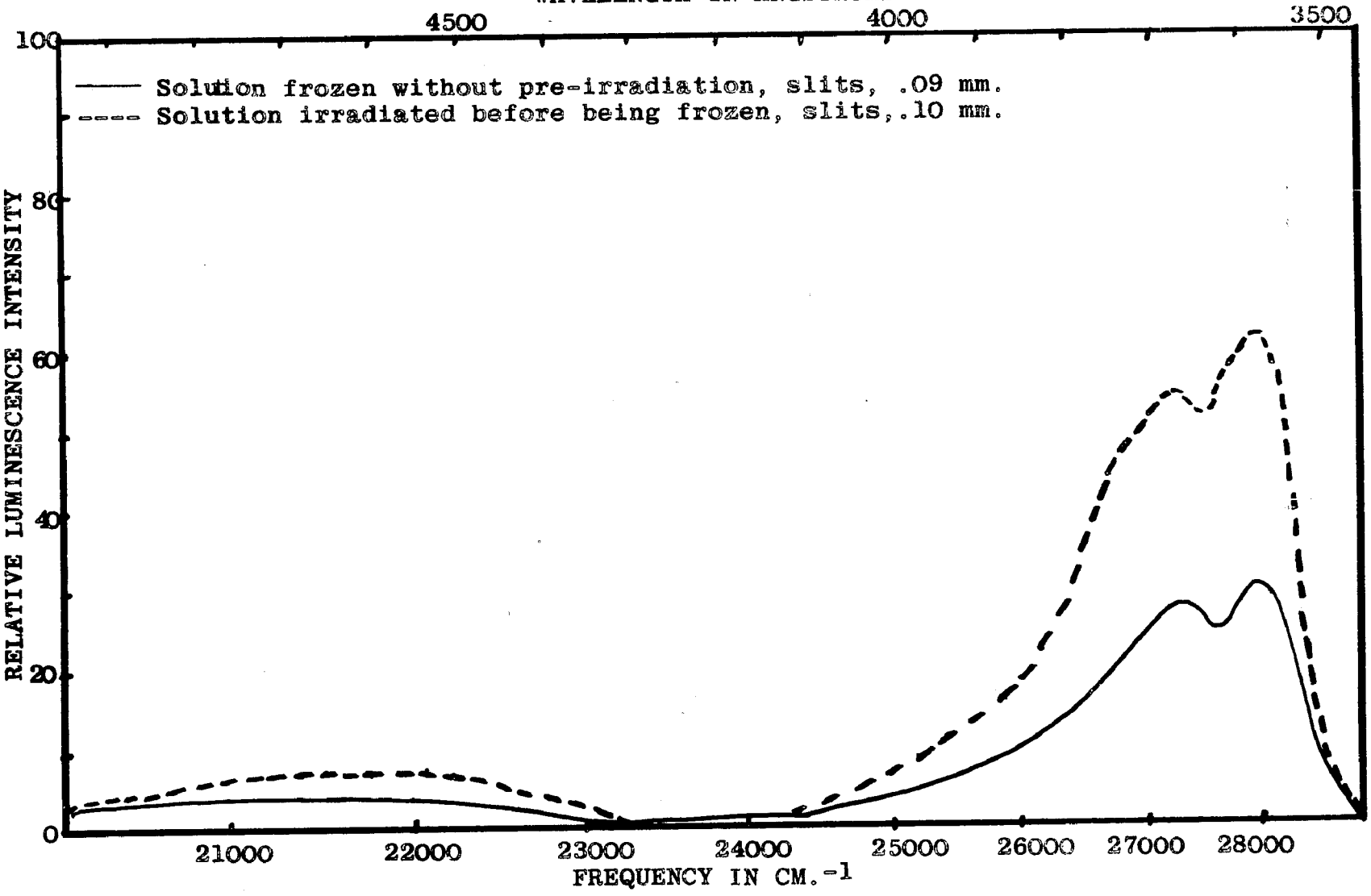
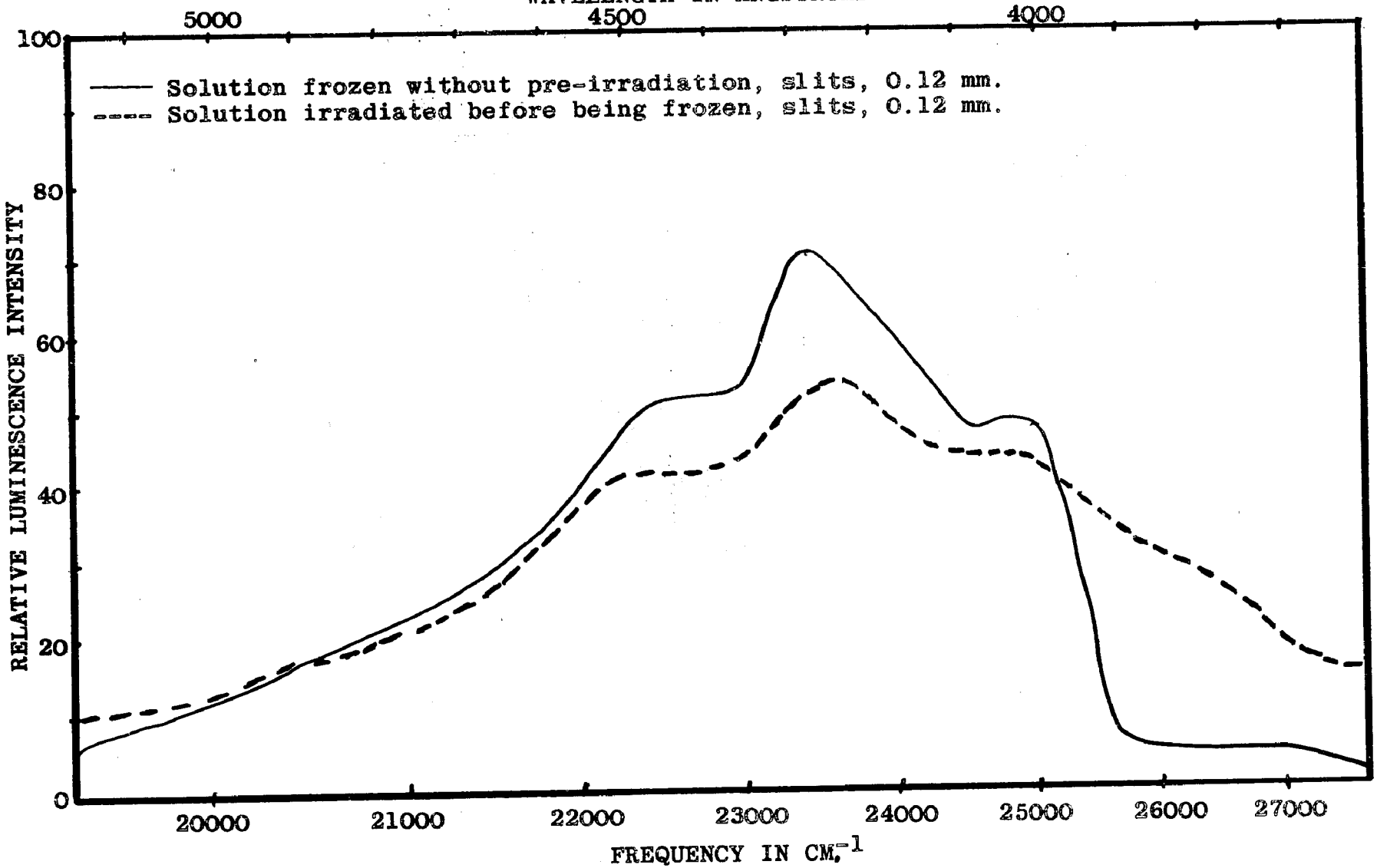


FIGURE 33

LUMINESCENCE SPECTRA OF 4-BROMOACETOPHENONE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN



of a radical. Table XX indicates 4-bromoacetophenone exhibited a blue phosphorescence for approximately two seconds. Therefore, the bands having a frequency of less than 24,000 cm.$^{-1}$ probably represent the true phosphorescence for this compound.

The luminescence spectra of the EPA glasses of 4-hydroxy- and 4-methoxyacetophenones are shown in Figures 34 and 35, respectively. These probably represent the phosphorescence of both compounds since both exhibited blue phosphorescence for approximately 4 seconds as indicated in Table .

Examination of Figure 36 shows that irradiation of a benzoin solution in EPA prior to freezing results in a decrease in the intensity of the 3900 Å (25,641 cm.$^{-1}$) band and the appearance of new bands in the 27,000 cm.$^{-1}$ region. The benzoin radical was found to fluoresce at approximately 27,000 cm.$^{-1}$ in ethanol at room temperature as shown in Figure 17. The new bands in the EPA glass around 27,000 cm.$^{-1}$ must be attributed to the radical. The remainder of the EPA spectra probably represents the phosphorescence of benzoin which exhibited a violet color for approximately four seconds as indicated in Table XX .

Lewis and Kasha (43) reported the detailed phosphorescence spectrum for benzophenone in EPA at liquid-nitrogen temperatures. Figure 37 is in complete agreement with their

FIGURE 34

LUMINESCENCE SPECTRA OF 4-HYDROXYACETOPHENONE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

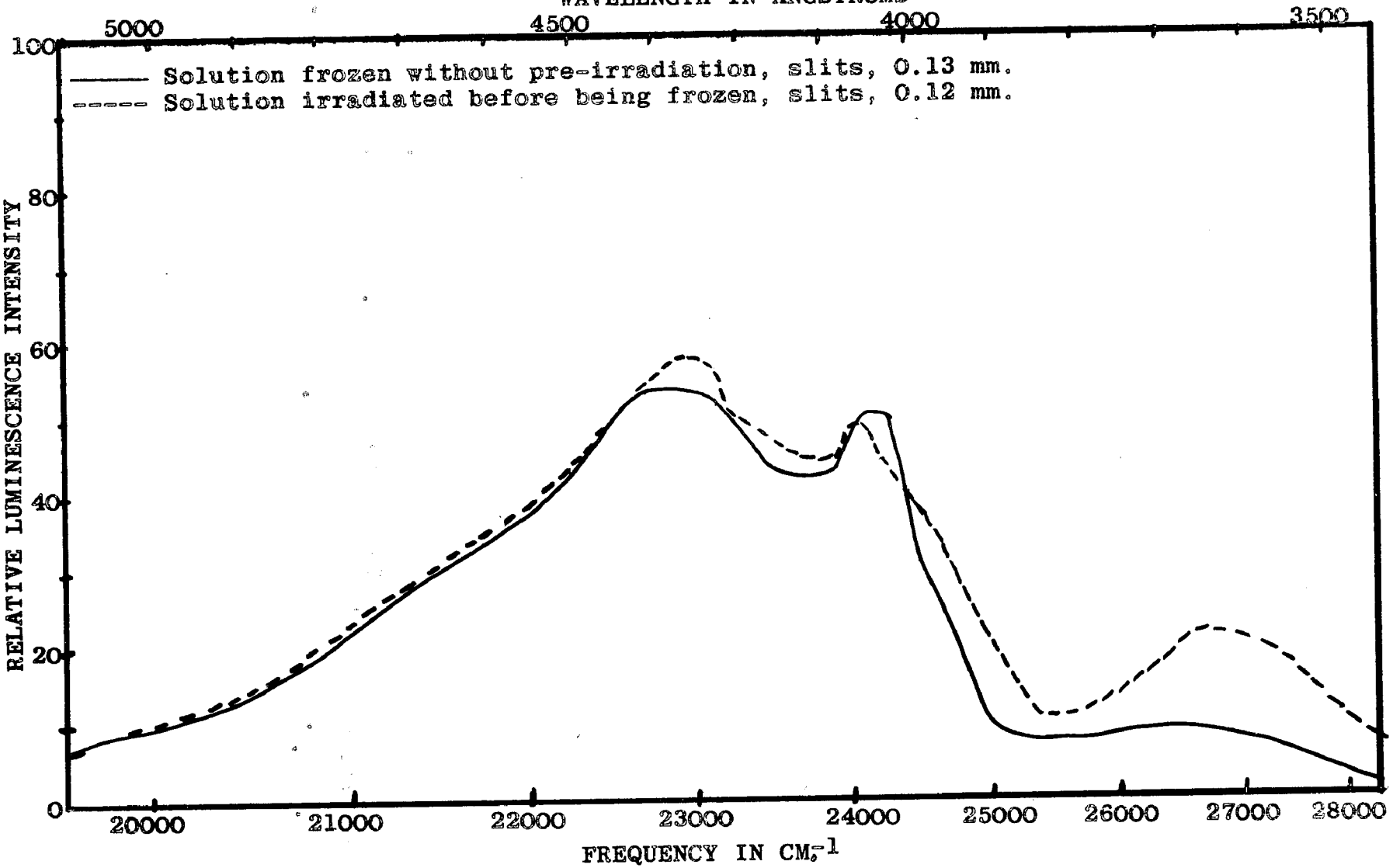


FIGURE 35

LUMINESCENCE SPECTRA OF 4-METHOXYACETOPHENONE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

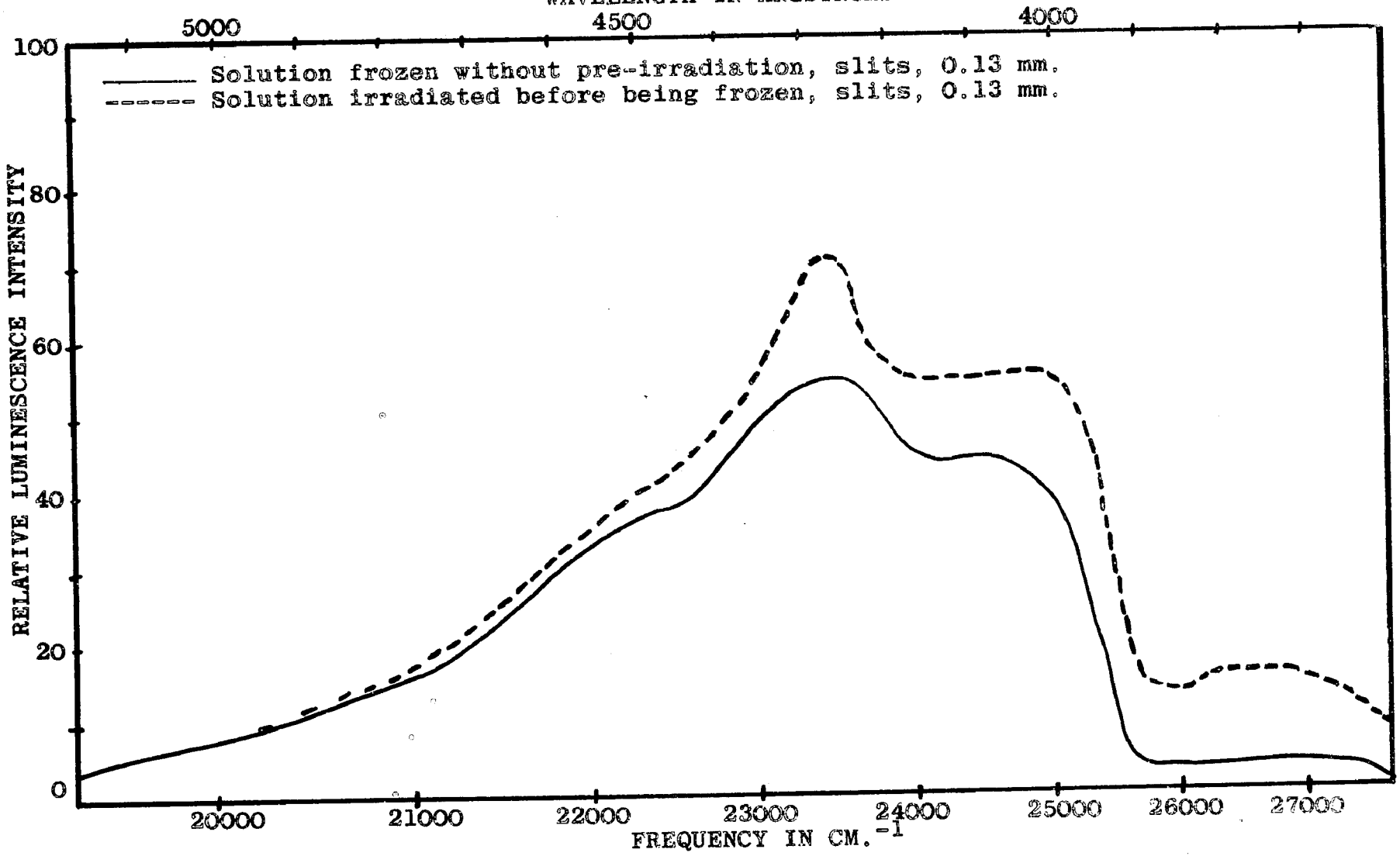
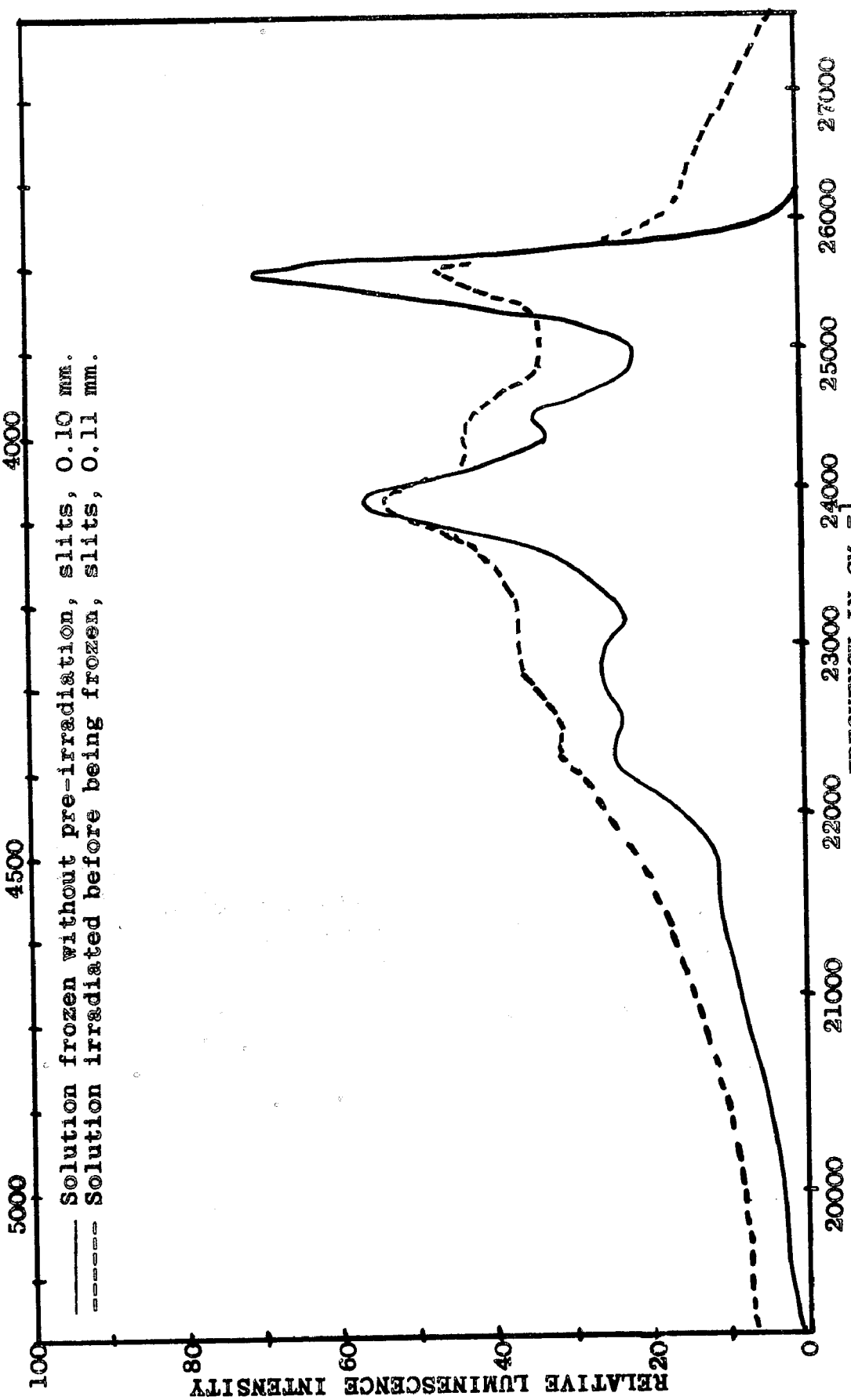


FIGURE 36

LUMINESCENCE SPECTRA OF BENZOIN IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN



work. The spectrum of an EPA glass made from the irradiated benzophenone solution shows a broad band in the 25,000-27,000 cm.$^{-1}$ region which is probably due to the benzophenone free radical. Fluorescence spectrum of a benzophenone solution in ethanol has a band around 26,800 cm.$^{-1}$ which is attributed to the free radical.

Figure 38 shows the luminescence spectra of 4-bromobenzophenone which probably represents the phosphorescence spectra. In addition to changes in intensity, there appears to be something underlining the dotted curve which could be due to radical phosphorescence or product phosphorescence.

Radiation of a 4,4'-dimethylbenzophenone solution in EPA just prior to freezing results in significant intensity changes and the appearance of two new bands in the luminescence spectrum as shown in Figure 39. These are probably due to the presence of radicals which were produced in the solution before freezing.

Figure 40 shows the luminescence spectrum of an EPA glass of benzopinacol. This spectrum is identical with the spectrum shown in Figure 37 for an EPA glass of benzophenone whose solution was irradiated before being frozen. This is reasonable since benzopinacol is photodecomposed into benzophenone and benzhydrol. Life-time measurements with low intensity radiation are necessary to identify the fluorescence and phosphorescence bands in this luminescence spectrum.

FIGURE 37

LUMINESCENCE SPECTRA OF BENZOPHENONE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

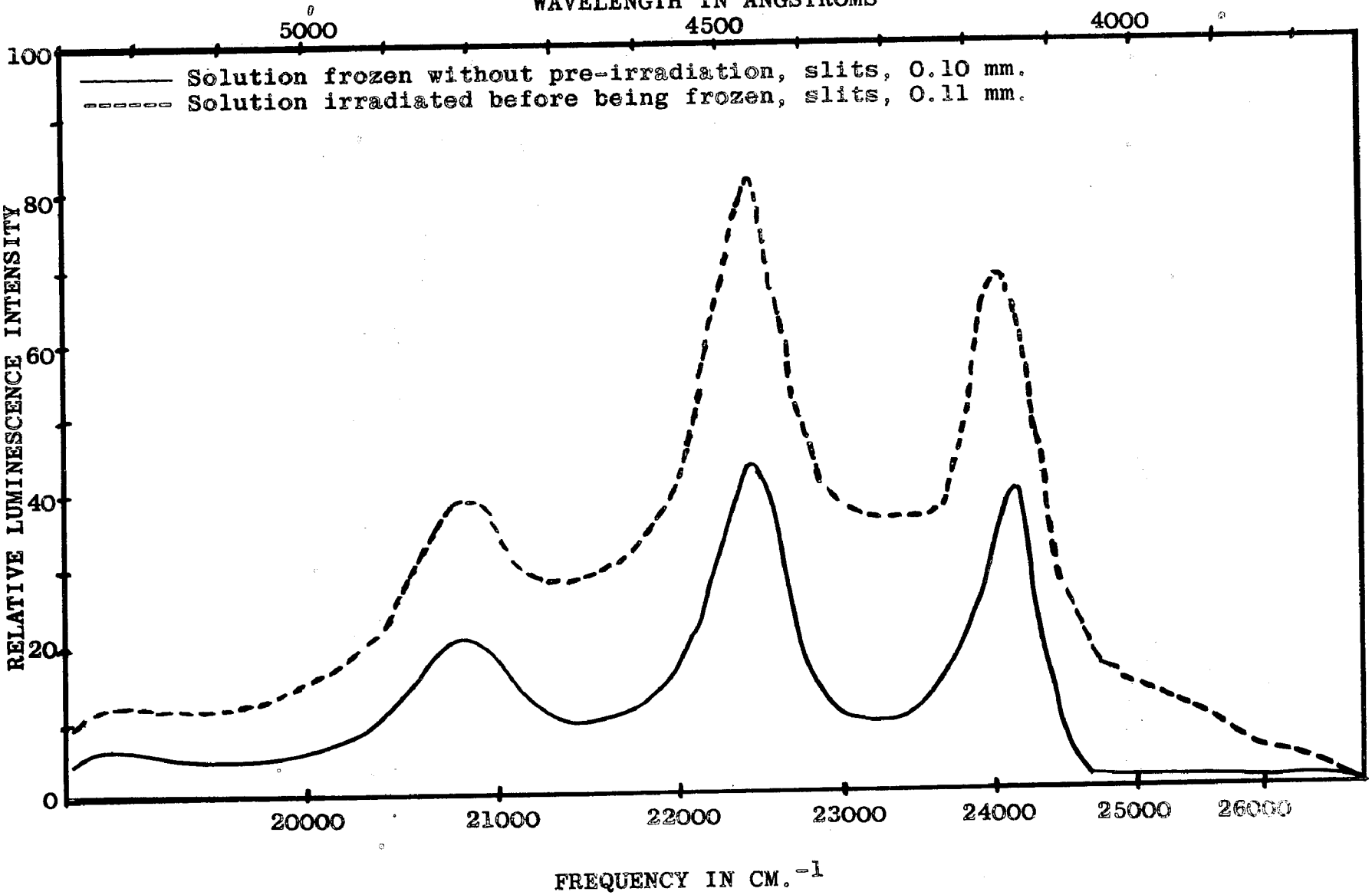


FIGURE 38

LUMINESCENCE SPECTRA OF 4-BROMOBENZOPHENONE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

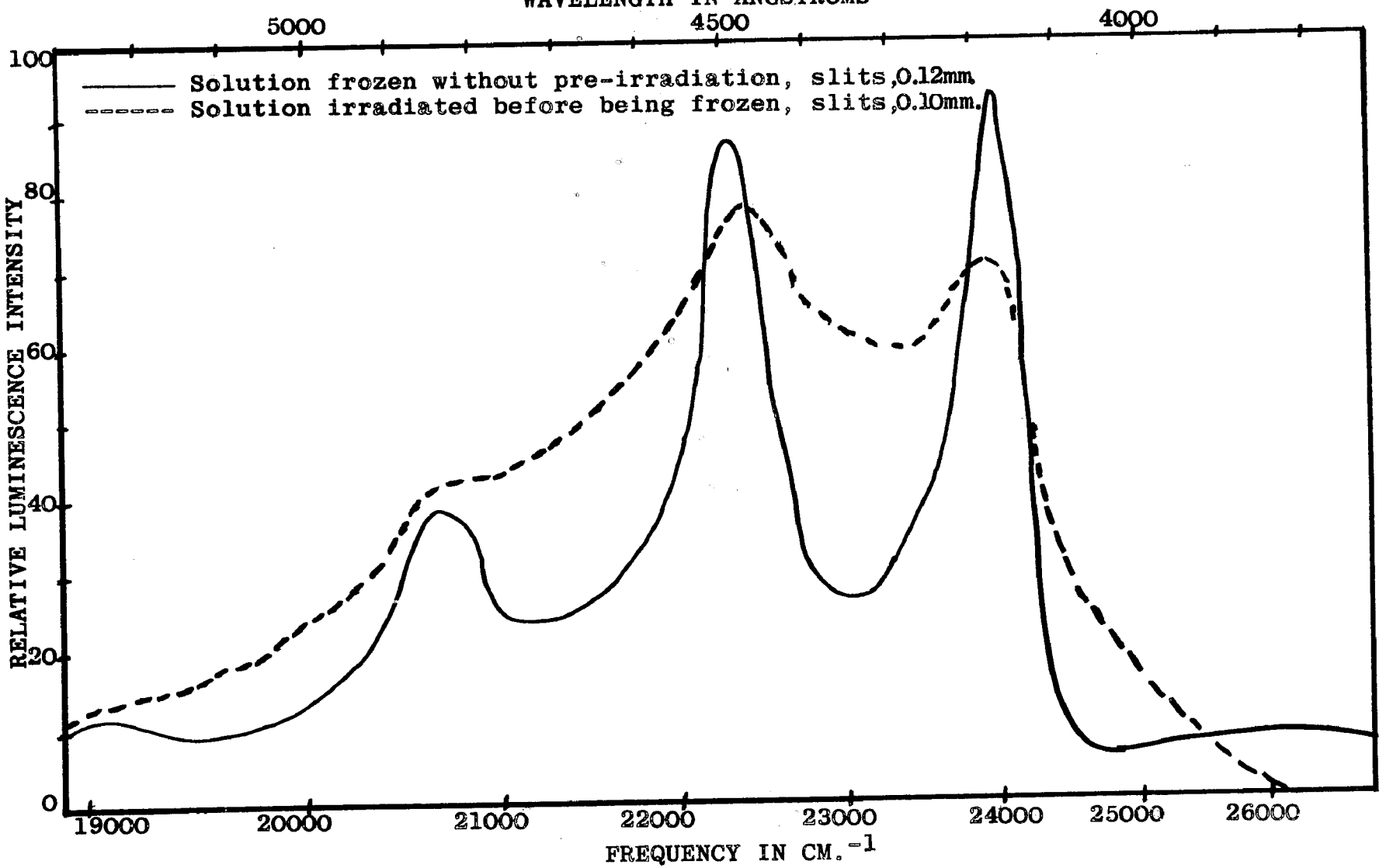


FIGURE 39

LUMINESCENCE SPECTRA OF 4,4'DIMETHYLBENZOPHENONONE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

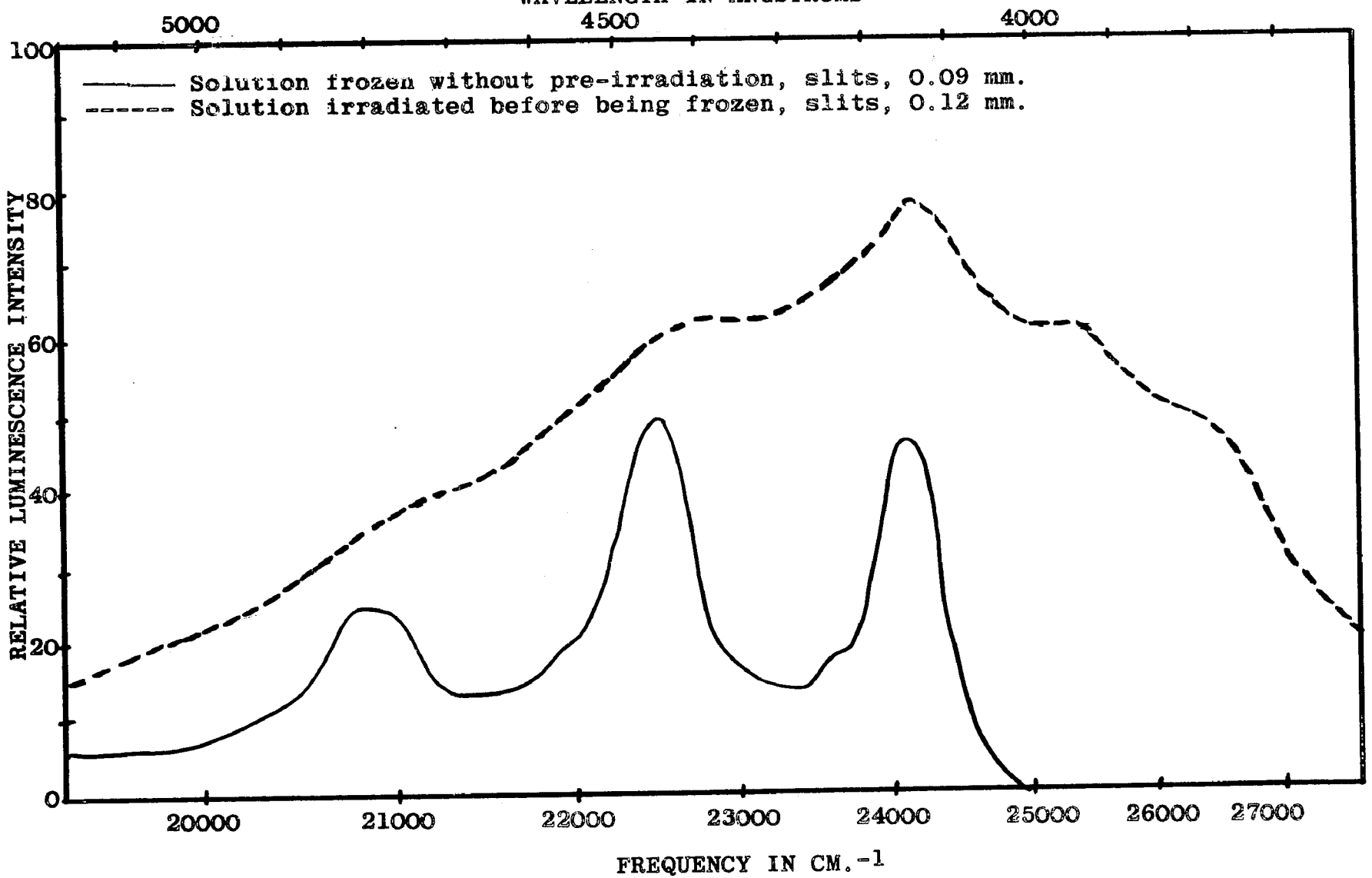
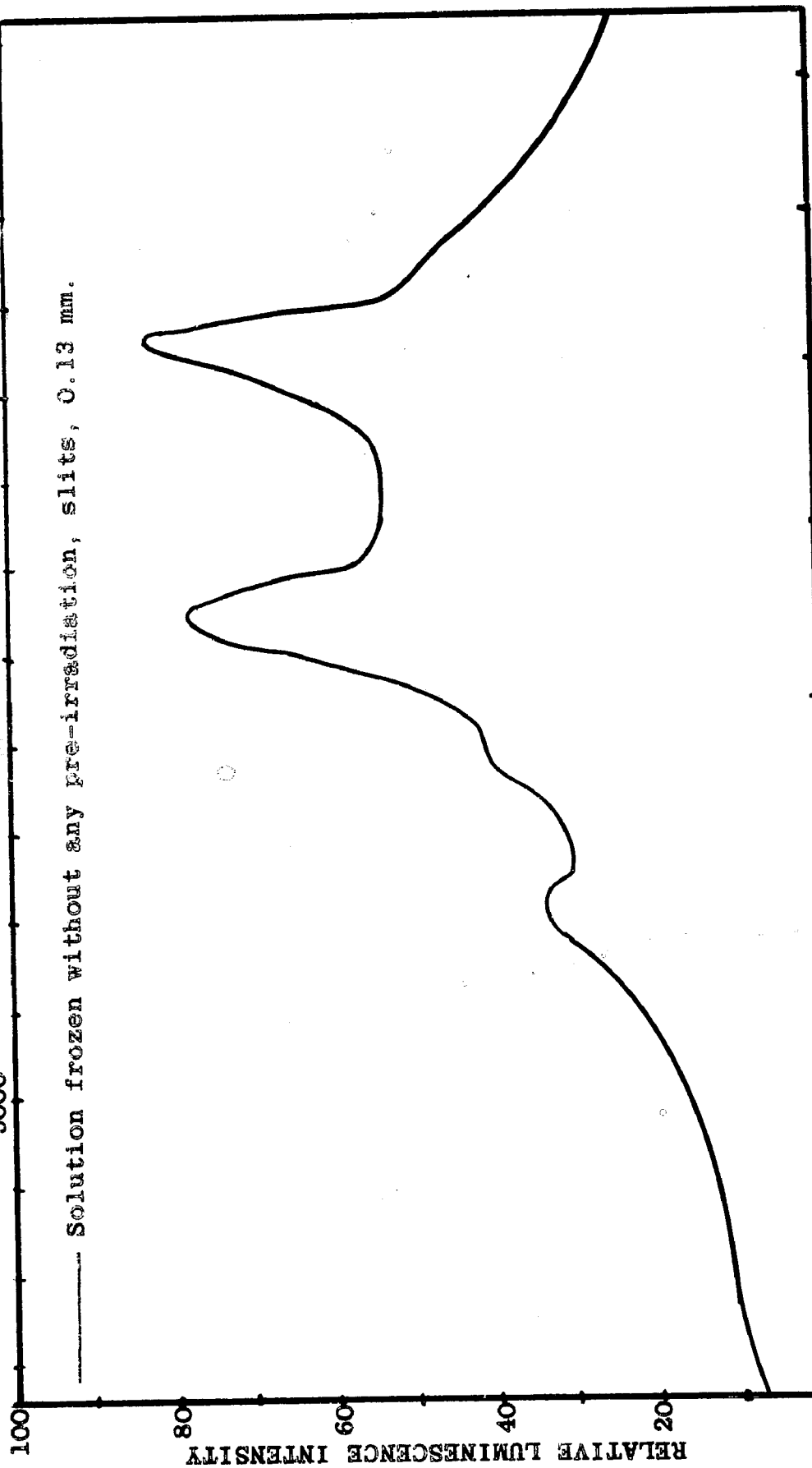


FIGURE 40

LUMINESCENCE SPECTRUM OF BENZOPINACOL IN AN EPA GLASS AT THE TEMPERATURE OF LIQUID NITROGEN



Miscellaneous

Figure 41 is in complete agreement with the phosphorescence spectrum reported for benzaldehyde (43). Radiation of a solution of benzaldehyde before freezing results in an intensity change and smearing of the 27,000 $cm.^{-1}$ band. Apparently the benzaldehyde free radical is very short-lived and disappears in the time required to transfer the radiated solution to a liquid-nitrogen bath.

The luminescence spectrum of an EPA glass made from an irradiated benzoyl peroxide solution is shown in Figure 42. This glass exhibited a blue phosphorescence for approximately 6 seconds as indicated in Table XX . An EPA glass made from a non-irradiated benzoyl peroxide solution did not exhibit any luminescence in the 3000-7050 Å region. The cause of this luminescence is probably the benzoyloxy radical. This is based on the lack of similarity between the phosphorescence spectra of benzoic acid, which is a known product, and the benzoyloxy radical. Additional work pertaining to the identification of the fluorescence and phosphorescence bands would help to account for the luminescence spectrum.

Since the luminescence spectra of the EPA glasses of 2,2'-bipyridyl are practically the same as shown in Figure 43, no conclusion can be made regarding the contribution of the radical to luminescence. Table XX indicates

FIGURE 41

LUMINESCENCE SPECTRA OF BENZALDEHYDE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

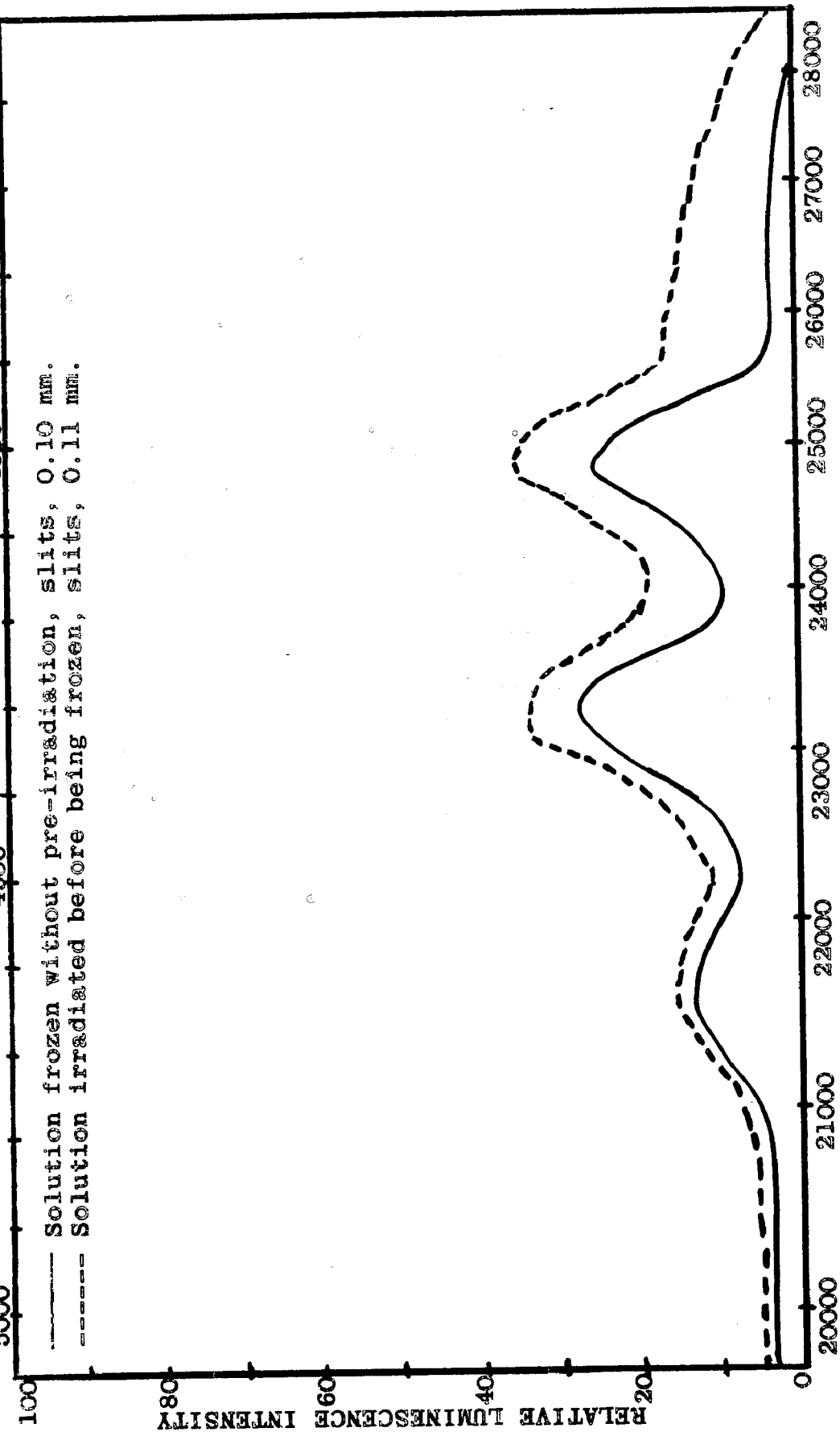
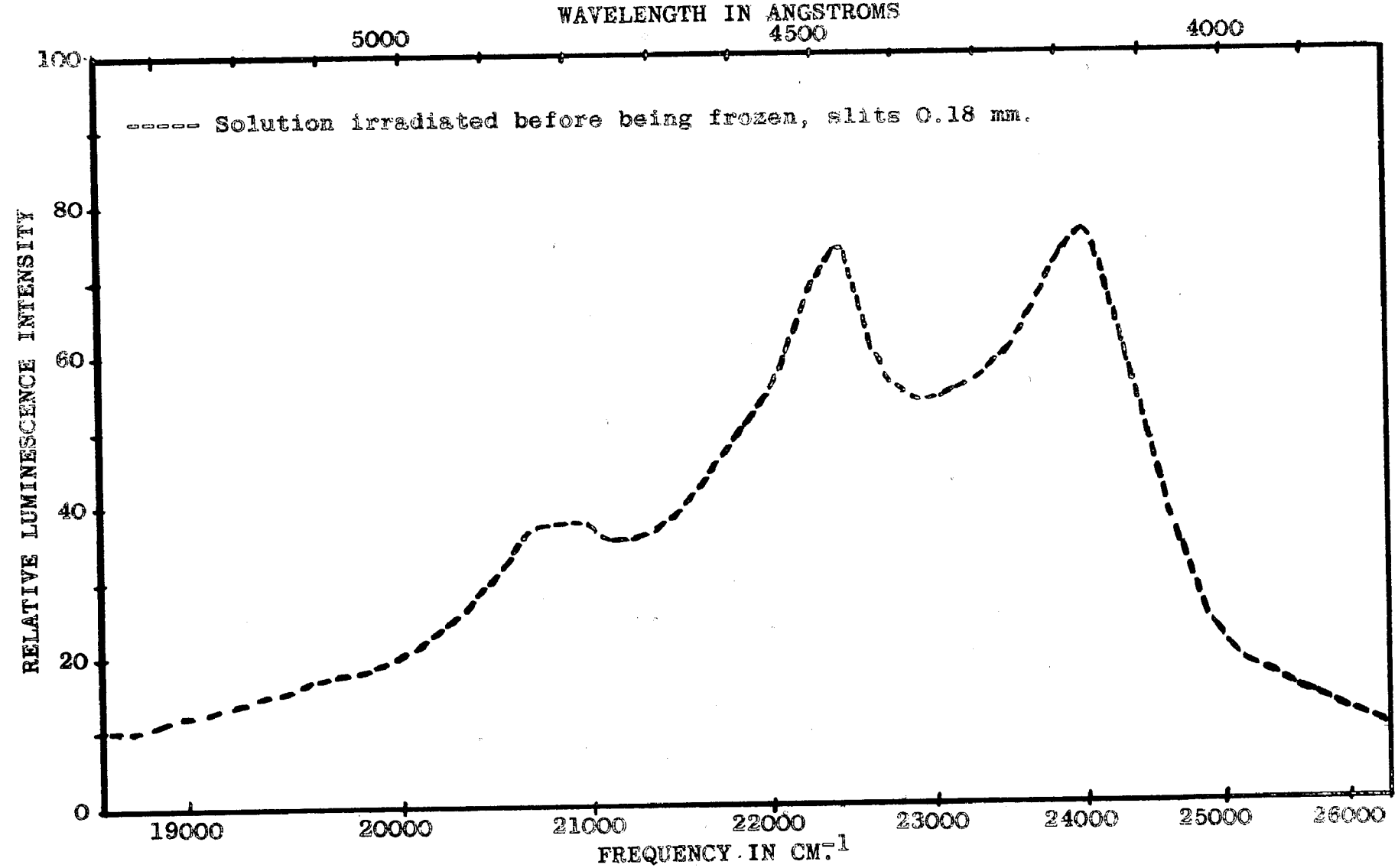


FIGURE 42

LUMINESCENCE SPECTRUM OF BENZOYL PEROXIDE IN AN EPA GLASS AT THE TEMPERATURE OF LIQUID NITROGEN



that 2,2'-bipyridyl exhibited a sky blue phosphorescence. This indicates that Figure 43 probably represents the phosphorescence spectrum of 2,2'-bipyridyl.

Figure 44 shows the luminescence spectra of the EPA glasses of diphenylamine. The solid wave represents the phosphorescence spectrum for diphenylamine. Lewis and Kasha (43) reported the detailed phosphorescence spectrum for diphenylamine. They reported bands at exactly the same frequencies shown for the solid curve in Figure 44. Radiation of an EPA solution of diphenylamine before freezing resulted in production of 3 new bands. These bands, probably due to the diphenylamine radical, exhibit a red shift when compared to the fluorescence bands in Figure 26. Diphenylamine exhibited a brilliant blue phosphorescence for approximately ten seconds as noted in Table XX.

According to Lewis and Kasha (43) the normal phosphorescence of phenazine occurs in the infra-red region. An EPA glass made from a non-irradiated phenazine solution exhibited no luminescence in the 3000-7050 Å region. However, when an EPA solution of phenazine was irradiated for approximately one minute, just prior to freezing, luminescence was detected as shown in Figure 45. This is probably due to radical formation. The luminescence spectrum closely follows the fluorescence spectrum of phenazine in ethanol at room temperature as shown in

FIGURE 43

LUMINESCENCE SPECTRA OF 2,2'BIPYRIDYL IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

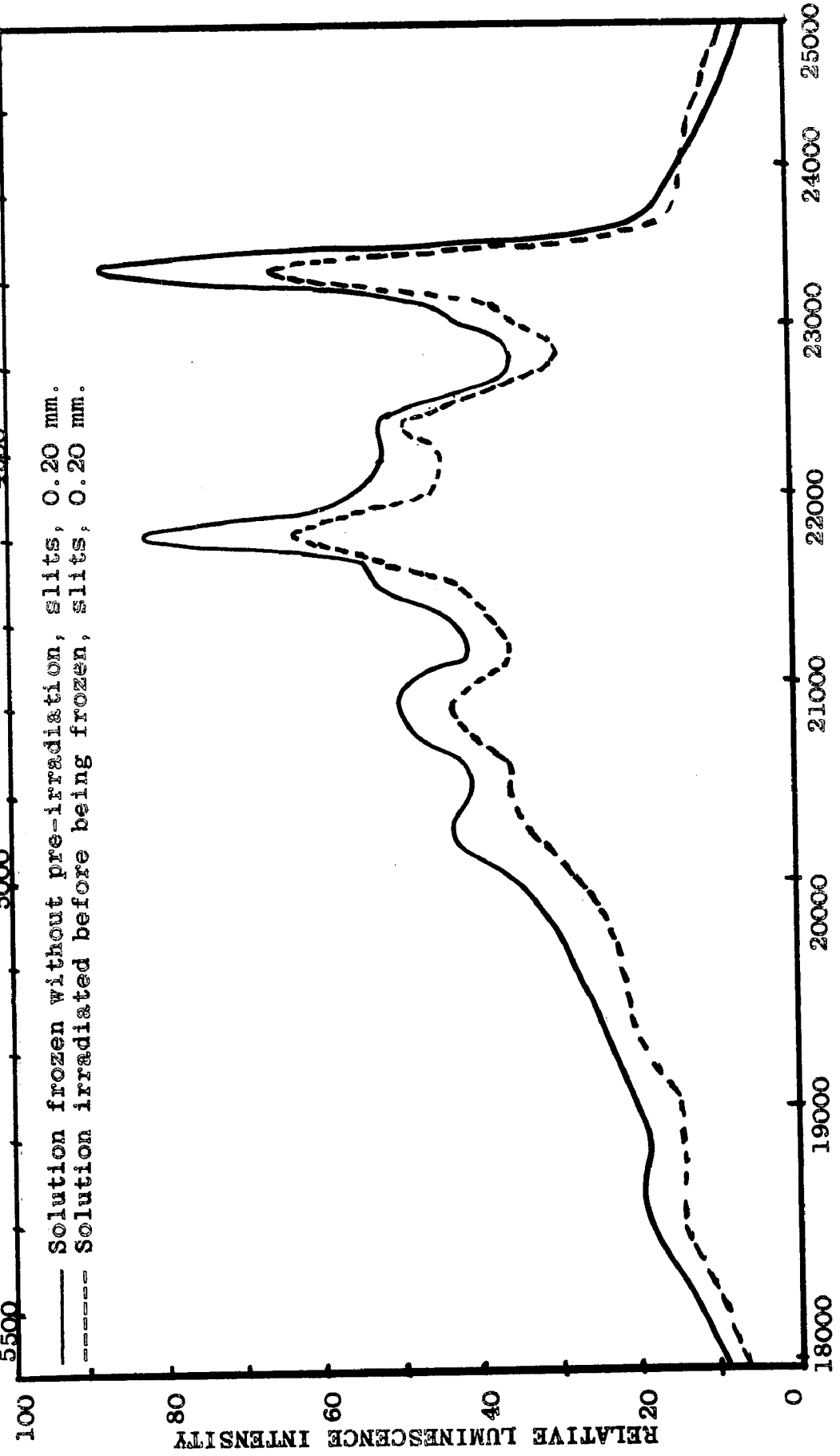


FIGURE 44

LUMINESCENCE SPECTRA OF DIPHENYLAMINE IN EPA GLASSES AT THE TEMPERATURE OF LIQUID NITROGEN

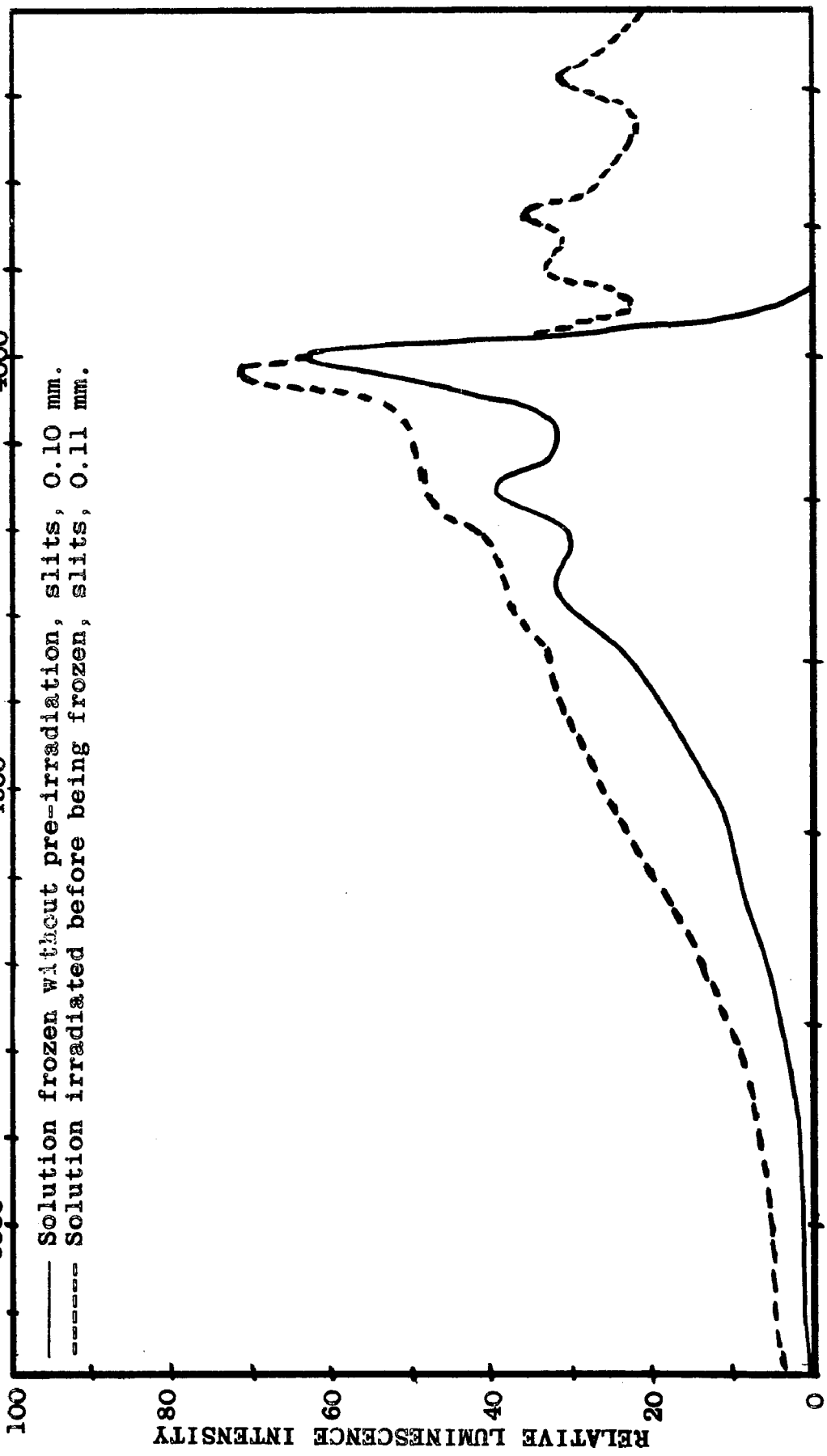
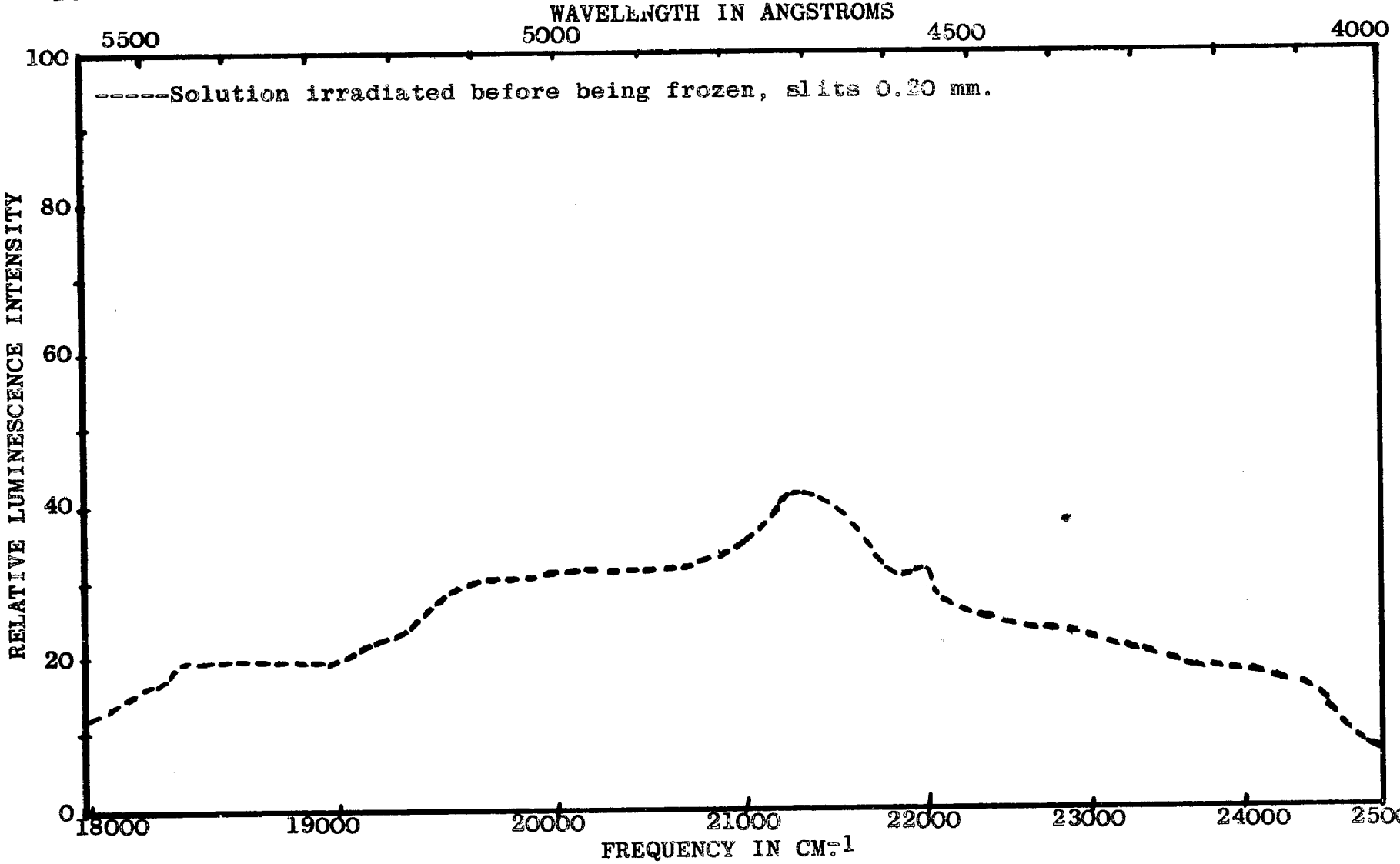


Figure 27. It should be noted that this EPA glass of phenazine exhibited a green phosphorescence for approximately five seconds after removal from the exciting radiation.

FIGURE 45

LUMINESCENCE SPECTRUM OF PHENAZINE IN AN EPA GLASS AT THE TEMPERATURE OF LIQUID NITROGEN



CONCLUSIONS

This investigation of photo-induced luminescence can be summarized by the following conclusions:

1. The semiquinone radical and radical ion of anthraquinone (9,10) have been shown to fluoresce. The limit of detection for the former was found to be 5×10^{-7} M.

2. Detailed fluorescence spectra are shown for seventeen compounds. Except for benzophenone and diphenylamine, these compounds have never before been reported as being fluorescent. The fluorescence spectra are attributed to radical formation produced by intense ultraviolet radiation of the $\pi \rightarrow \pi^*$ absorption band in an inert atmosphere and in a solvent possessing an abstractable hydrogen atom.

3. Detailed luminescence spectra for various compounds at liquid-nitrogen temperature are shown. In most cases, these represent the true phosphorescence spectra previously reported in the literature. However, irradiation of the EPA solution before freezing, produced changes in the luminescence spectra which can probably be attributed to radical formation in most cases.

APPENDIX A

INSTRUMENTATION AND PROCEDURES

Photopotentials

Instrumentation

A "T" shaped cell made by joining together three 24/40 standard tapered Vycor ground-glass joints so as to have a maximum capacity of 30 ml. was used to determine photopotentials. (See Figure 46). One short arm of the cell contained a 24/40 ℧ Pyrex ground glass stopper. The other short arm of the cell contained a platinum electrode, 0.5 mm. in diameter sealed in a standard tapered Pyrex joint leaving a small exposed length of approximately 2.0 mm. This electrode was supported in the cell against the irradiated side. A silver-silver Chloride electrode was used as the dark electrode in most cases. This electrode was made by anodizing a 1 mm. dia. silver wire in a 2 M HCl solution for 5 minutes using a constant current of 5 milliamperes. In cases where the solutions were strongly alkaline, a platinum foil 1 x 1 cm. x .035 cm. thick was used as the dark electrode. The dark or reference electrode was placed in the long arm of the cell in a position where light could not strike it. The long arm of the cell had a specially designed cap with four inlets. One inlet was for the reference electrode; the second, an inlet for bubbling nitrogen into the solution; the third, an inlet for maintaining a nitrogen atmosphere above the solution, and the fourth inlet was used as an opening to the atmosphere.

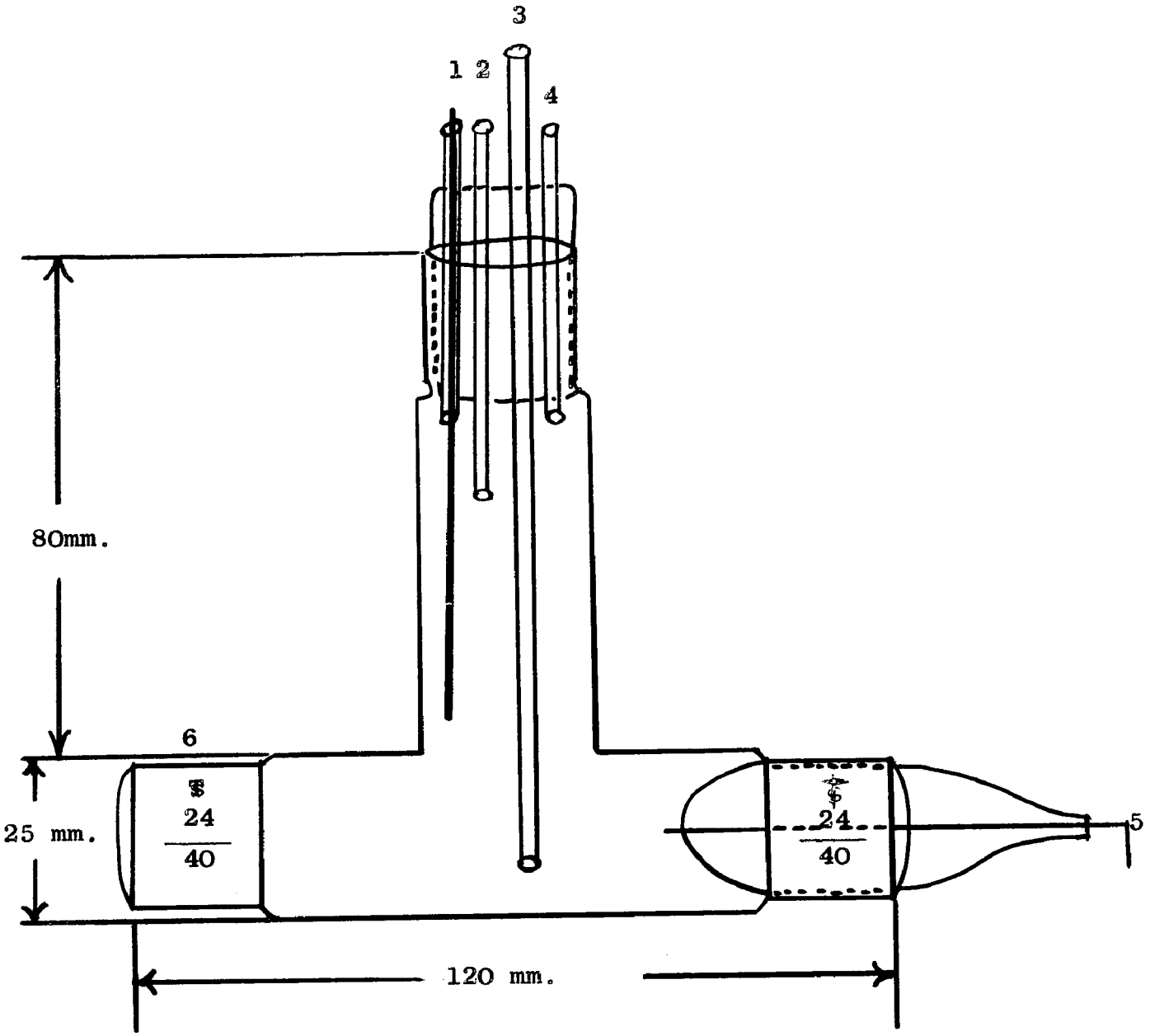


FIGURE 46: VYCOR CELL DIAGRAM

1. Ag-AgCl electrode
2. Inlet for maintaining nitrogen atmosphere above solution
3. Inlet for bubbling nitrogen into solution
4. Opening to atmosphere
5. Platinum point electrode
6. Glass stopper, ⅋ 24/40

The entire cell was covered with black "Scotch" electrical tape No. 33 except at the irradiation point where an area of approximately 1.5 square centimeters was left uncovered.

The irradiation system consisted of a Hanovia high pressure D.C. Xenon Compact Arc lamp (900 watts), air cooled, housed in a hood. A double convex quartz lens, one inch in diameter and having a focal length of 14 cm. was used in the incident light beam. A Corning No. 7-54 filter Corex Glass No. 9863, 3.05 mm thick (2400-4200 $\mathring{A}$ light transmission) was placed between the lens and iris diaphragm.

The detection system consisted of a D.C. electrometer (17) having an impedance of 10^{12} ohms and a high speed, low impedance Brown recorder having a one second response time for a full scale deflection. By means of a switching panel, the output of the electrometer was connected to the recorder in such a manner so as to give photopotentials in positive or negative millivolts. The recorder was further modified with two, 1000 ohm, 10 turn Beckman Helipots to enable one to change the starting position and sensitivity.

Operating Procedure

To obtain a photopotential-time curve the following was adopted as standard operating procedure:

1. The cell was mounted on a heavy ring stand placed on a 23" x 23" x 1/2" thick piece of iron which was further

cushioned with foam rubber to minimize vibration. The distance between light source and cell was 56 cm. Since the laboratory was air conditioned and the lamp was properly cooled, no further precautions were necessary to maintain the cell at constant temperature.

2. 25 ml. of sample solution were added to the Vycor cell and were then flushed with oxygen free nitrogen for ten minutes.

3. An atmosphere of Nitrogen was maintained above the sample solution in the cell after the initial flushing.

4. After allowing the solution to come to equilibrium in approximately five minutes, the recorder was started, then UV radiation was made incident on the cell by means of a cable control on the iris diaphragm and the photopotential-time curve was recorded.

5. After completion of several runs on one solution, the cell and irradiated electrode were cleaned before making a run with a new solution.

Cleaning Procedures

1. The cell was cleaned with water containing some Alconox wetting agent, rinsed with distilled water and thoroughly dried before re-use.

2. The platinum electrode, used as the irradiated electrode, was immersed in hot (110°C) Chromic acid cleaning solution for three minutes, rinsed with distilled water, cathodized in a 1 M H_2SO_4 solution for ten minutes using a constant current of five milliamperes and rinsed with absolute ethanol before re-insertion into the cell. This electrode was always cleaned just prior to use in the cell in order to remove oxide films on the platinum surface and also to minimize the contamination of the clean surface with atmospheric oxygen.

3. The reference electrode, silver-silver chloride, was always rinsed with absolute ethanol and wiped before re-use in the cell. When needed, the silver-silver chloride was cleaned by immersion in concentrated Ammonium Hydroxide for ten minutes, followed by polishing with an Emory cloth before anodization in a 2 M HCl solution.

Calibrations

In order to obtain a correlation of photopotentials and radiation absorption as a function of wavelength for various compounds in absolute ethanol, the relative intensities for the Xenon lamp had to be determined. The apparatus used in these investigations was composed of: a source of radiation, a monochromator to analyze the emitted radiation, a detector to produce a signal proportional to the light emittance and a milliammeter to indicate the amplified output

of the photomultiplier detector. Each of the components is described in detail below.

Source of Radiation: Exciting radiation was obtained from a low pressure Hydrogen lamp in the first part of the calibration procedure. A high pressure Xenon Compact Arc lamp D.C. operated and rated at 900 watts was used in the second part.

Monochromator: A Bausch and Lomb, Ebert mount, grating monochromator was used as the analyzer monochromator. The grating contained 1200 grooves/mm and the efficiency was 65% at 3000 Å. The spectral range of the monochromator extended from 2000 to 7000 Å and the focal length was 500 mm. The monochromator possessed a high degree of spectral purity, 0.03% straylight at 3000 Å and had a linear dispersion of 16.5 Å/mm. Further information concerning the efficiency of the monochromator at various wavelengths and the calibration of the wavelength drive of the monochromator is given in Reference 18.

Detector: The detector used in this investigation was an R.C.A. 1P28 photomultiplier tube. This phototube was used throughout the spectral region 2500 to 4200 Å.

The output of the photomultiplier was amplified and introduced into a Milliammeter.

Calibration Procedure Part I

All equipment was turned on one half hour before use to insure maximum stability. The analyzing wavelength was then set on the Bausch and Lomb monochromator. With the entrance and exit slits closed, the slit widths were set at 1.5 mm each. After setting the photomultiplier sensitivity, the slits on the monochromator were opened for one minute and the reading on the Milliammeter was recorded. The slits were then closed and the analyzing wavelength was changed. This procedure was repeated every 50 Å for the spectral range of 2500 to 4200 Å. These readings were corrected by using an energy output as a function of wavelength value supplied by the United States Bureau of Standards for a hydrogen lamp. These readings and relative intensities based on the 3350 Å output being 100% are listed in Table XXII.

Calibration Procedure Part II

Part I was repeated using the Xenon lamp as the radiation source and monochromator slit widths of 0.18 mm each. These readings were corrected by using the relative intensities for the hydrogen lamp at each wavelength. These readings and corrected relative intensity values for the Xenon lamp are listed in Table XXIII. These relative intensity values were then used in preparation of a response curve for the 1P28 photomultiplier tube as a function of wavelength as shown in Figure 47.

Calibration Procedure Part III

Photopotentials for various compounds in absolute ethanol were obtained at different wavelengths as follows:

1. The wavelength was set on the monochromator. Slit widths were set at 10 mm each.

2. The cell with 25 ml of nitrogen flushed sample was mounted two inches away from the monochromator exit.

3. With the recorder running, the entrance slit to the monochromator was opened first followed by immediate opening of the exit slit to allow the radiation to strike the cell and the photopotential-time rise curve was recorded.

4. To obtain the decay curve, the exit slit was closed first followed quickly by closing the entrance slit in the monochromator.

5. Steps 2-4 were repeated for different wavelengths.

The photopotential as a function of wavelength results are listed in Tables XVI through XVIII.

TABLE XXII

RELATIVE INTENSITY CALIBRATION FOR THE HYDROGEN LAMP

Wavelength in Å	(A) Milliamps $X10^{-5}$	(B) Energy Output U.S.B.S. Lamp watt per cm^2	A/B $X10^{-5}$	% Relative Intensity Based on 3350 Output
2500	9.60	0.200	48.0	64.2
2550	9.35	0.190	49.2	65.6
2600	9.05	0.171	52.9	70.6
2650	8.70	0.161	54.0	72.1
2700	8.40	0.151	55.6	74.3
2750	8.15	0.139	58.6	78.3
2800	7.90	0.131	60.3	80.5
2850	7.70	0.123	62.6	83.6
2900	7.55	0.117	64.6	86.2
2950	7.45	0.113	65.8	87.9
3000	7.40	0.105	70.5	94.2
3050	7.25	0.107	67.8	90.5
3100	7.15	0.105	68.1	91.0
3150	7.05	0.102	68.8	92.0
3200	7.05	0.101	69.9	93.4
3250	7.00	0.098	71.0	94.8
3300	7.10	0.097	73.2	97.8
3350	7.15	0.0955	74.9	100.0
3400	7.00	0.095	73.8	98.7
3450	6.60	0.094	70.3	93.9
3500	6.15	0.093	66.2	88.5
3550	5.70	0.092	62.0	82.8
3600	5.50	0.091	60.5	80.7
3650	5.50	0.090	61.2	81.7
3700	5.60	0.089	62.9	84.0
3750	5.30	0.088	60.3	80.5
3800	5.30	0.087	60.9	81.4
3850	4.75	0.086	55.2	73.7
3900	4.15	0.085	48.9	65.4
3950	3.90	0.084	46.4	62.0
4000	4.00	0.083	48.2	64.3
4050	3.95	0.082	48.2	64.3
4100	3.30	0.081	40.7	54.4
4150	3.10	0.080	38.7	51.7
4200	3.40	0.079	43.0	57.5

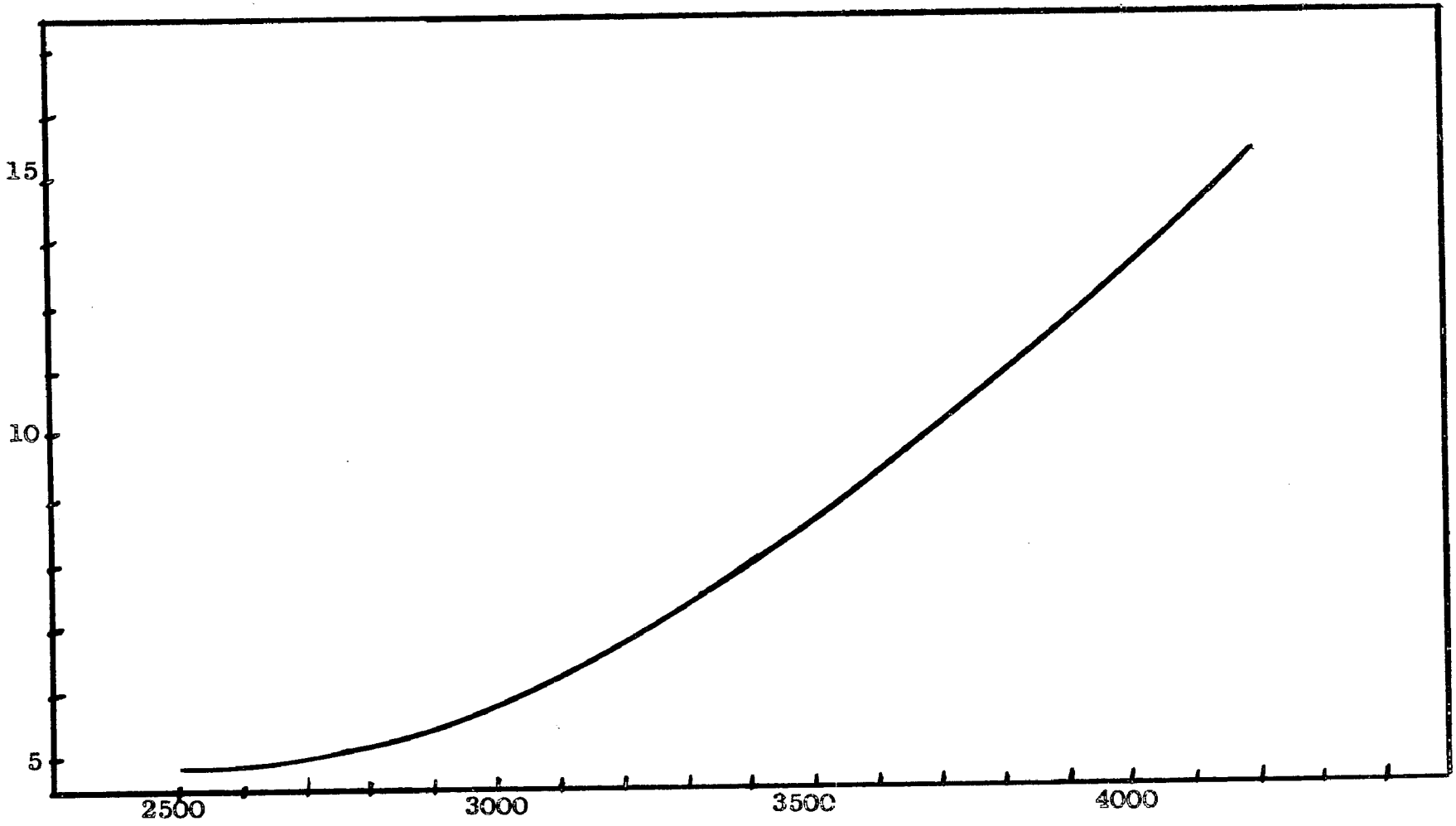
TABLE XXIII

RELATIVE INTENSITY CALIBRATION FOR THE XENON LAMP

Wavelength in Å	(C) Microamps	(D) % Relative Intensity for Hydrogen Lamp Based on 3350 Å. Output	% Relative Intensity for Xenon Lamp C/D X10
2500	25.0	64.2	3.90
2550	117.0	65.6	17.85
2600	36.5	70.6	5.16
2650	33.0	72.1	4.57
2700	31.5	74.3	4.24
2750	32.0	78.3	4.08
2800	33.0	80.5	4.11
2850	35.0	83.6	4.18
2900	42.0	86.2	4.87
2950	39.0	87.9	4.44
3000	43.0	94.2	4.57
3050	45.0	90.5	4.98
3100	47.0	91.0	5.14
3150	53.0	92.0	5.76
3200	54.0	93.4	5.79
3250	57.0	94.8	6.00
3300	61.0	97.8	6.24
3350	71.0	100.0	7.10
3400	70.0	98.7	7.10
3450	70.0	93.9	7.46
3500	68.0	88.5	7.68
3550	67.5	82.8	8.15
3600	68.0	80.7	8.40
3650	77.0	81.7	9.42
3700	78.0	84.0	9.30
3750	79.5	80.5	9.77
3800	78.0	81.4	9.58
3850	72.0	73.7	9.76
3900	70.0	65.4	10.70
3950	73.0	62.0	11.75
4000	72.0	64.3	11.20
4050	66.5	64.3	10.34
4100	67.5	54.4	12.38
4150	64.0	51.7	12.38
4200	73.0	57.5	12.70

FIGURE 47

RESPONSE CURVE FOR 1P28 PHOTOMULTIPLIER TUBE USING A XENON LAMP AS SOURCE OF IRRADIATION AND A BAUSCH AND LOMB MONOCHROMATOR AS EMITTANCE ANALYZER. (REFER TO TABLE XXIII)



REFERENCES

1. E. Becquerel, Compt. rendu., 9, 144, 561 (1839).
2. A. W. Copeland, O. T. Black and A. B. Garrett, Chem. Rev., 31, 177 (1942).
3. A. L. Hughes and L. A. DuBridge, Photoelectric Phenomena, Ch. IX, McGraw-Hill, New York, 1932.
4. I. Levin and C. E. White, J. Chem. Phys. 18, 417 (1950).
5. ibid. 19, 1079 (1951).
6. I. Levin, J. R. Wiebush, M. B. Bush and C. E. White, J. Chem. Phys., 21, 1654 (1953).
7. V. I. Veselovskii, J. Phys. Chem. (U.S.S.R.) 15, 145-55 (1941).
8. ibid 20, 269-96 (1946).
9. ibid 23, 1095-1105 (1949).
10. V. I. Ginzburg and V. I. Veselovskii, J. Phys. Chem. (U.S.S.R.) 24, 366-78 (1950).
11. W. H. Brattain and C. G. B. Garrett, Bell System Tech. J. 34, 129 (1955).
12. H. Gobrecht, R. Kuhnkies, and A. Tausend, Z. Elektrochem. 63, 541 (1959).
13. J. E. Baer and M. Carmack, J. Am. Chem. Soc. 71, 1214 (1949).
14. R. Williams, J. Chem. Phys. 32, 1505 (1960).
15. L. Meites, Polarographic Techniques, Interscience, New York, 1955, p. 34.

16. I. Heilbron, Dictionary of Organic Compounds, Oxford University Press, New York, 1953.

17. R. R. H. Miron, Ph. D. Thesis, Lehigh University, 1959.

18. R. E. Rehwoldt, M. S. Thesis, Lehigh University, 1959.

19. J. L. Bolland and H. R. Cooper, Proc. Roy. Soc. 225A, 405 (1954).

20. J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, J. Am. Soc., 81, 1068 (1959).

21. J. H. Merz and W. A. Waters, J. Chem. Soc., 5 (1949).

22. A. Y. Drummond and W. A. Waters, J. Chem. Soc., 3119 (1953).

23. N. K. Bridge and G. Porter, Proc. Roy. Soc., 244A, 259 (1958).

24. V. F. Tsepalov and V. IA. Shliapintokh, DAN USSR, 116, 641-644, (1957) (See Sov. Phys. Doklady, 635-638, 1957).

25. V. F. Tsepalov and V. IA. Shliapintokh, IAN USSR, OKhN, 4, 637-643, (1959).

26. N. N. Bubnov, L. A. Kibalko, V. F. Tsepalov, and V. IA. Shliapintokh, OPTIKA I SPEKTROSKOPIIA, Vol. VII, No. 1, 71, (1959).

27. A. Hantzsch, Ber. 49, 511 (1916).

28. R. E. Kagarise and L. A. Weinberger, Infrared Spectra of Plastics and Resins, PB 111438, NRL Report 4369, Office of Technical Services, United States Department of Commerce, (May 26, 1954).

29. R. Pummerer and H. Kehlen, Ber., 66, 1107 (1933).

30. B. R. Chinmayanandam and H. W. Melville, Trans. Faraday Soc., 50, 73 (1954).

31. R. M. Joyce (to E. I. duPont de Nemours & Co.) U. S. 2,647,080, July 28, 1953.

32. C. M. McCloskey and J. Bond, Ind. Eng. Chem., 47, 2125 (1955).

33. S. G. Cohen, B. E. Ostberg, D. B. Sparrow, and E. R. Blout, J. Polymer Sci., 3, 264 (1948).

34. G. M. Burnett and H. W. Melville, Proc. Roy. Soc., 189A, 456 (1947).

35. G. A. Schröter, Kunststoffe, 41, 291 (1951).

36. M. Adams, M. S. Blois, Jr. and R. H. Sands, J. Chem. Phys., 28, 774 (1958).

37. D. E. G. Austen, P. H. Given, D. J. E. Ingram, and M. E. Peover, Nature, 182, 1784 (1958).

38. P. D. Bartlett and K. Nozaki, J. Am. Chem. Soc., 69, 2299 (1947).

39. G. N. Lewis and D. Lipkin, J. Am. Chem. Soc., 64, 2801 (1942).

40. C. A. Parker and C. G. Hatchard, J. Phys. Chem., 63, 22 (1959).

41. S. Wawzonek, R. Berkey, E. W. Blaha, and M. E. Runner, Jour. Electrochem. Soc., 103, No. 8, 456 (1956).

42. R. L. Edsberg, D. Eichlin, and J. J. Garis, Anal. Chem. 25, No. 5, 798 (1953).

43. G. N. Lewis and M. Kasha, J. Am. Chem. Soc., 66, 2100 (1944).

44. W. West, Technique of Organic Chemistry, Vol. IX, Chapt. 6, Interscience, New York, 1956.

45. F. A. Matsen, Technique of Organic Chemistry, Vol. IX, Chapt. 5, Part 2, Interscience, New York, 1956.

46. P. Pringsheim, Fluorescence and Phosphorescence, Interscience, New York, 1949.

47. R. W. Harrell, Ph. D. Thesis, Florida State University, 1959.

48. G. A. Swan, and D. G. I. Felton, The Chemistry of Heterocyclic Compounds, Phenazines, Interscience, New York, 1957.

49. R. D. Vanselow and A. B. F. Duncan, J. Am. Chem. Soc., 75, 829 (1953).

VITA

John J. Surash, son of Mrs. Sarah Havrilchick and the late Ignatius Surash, was born on February 10, 1926 in Pringle, Pennsylvania. With the exception of four years of grammar school in St. Hedwig's Parochial School, Kingston, Pennsylvania, he attended the public school of Luzerne Pennsylvania, graduating from Luzerne High School with the Class of 1944.

He reported for active duty with the Army of the United States on August 14, 1944. After completing basic training at Camp Wheeler, Georgia, he was sent to Europe in January, 1945, and was assigned to the 69th Infantry Division. He served as a first scout with that division in Europe and was wounded in action outside Kassel, Germany on April 6, 1945. He was honorably discharged from the Army on August 8, 1946.

In February 1947 he entered Wilkes College, Wilkes-Barre, Pennsylvania, and was graduated from that institution with a Bachelor of Science degree in Chemistry in June 1950. He then entered Lehigh University, Bethlehem, Pennsylvania in September of 1950 as a graduate teaching assistant in Chemistry. The degree of Master of Science was awarded in February, 1952.

After receiving his M. S. in Chemistry he was employed by the Duplan Corporation, Kingston, Pennsylvania as

assistant chief chemist. In December, 1952 he was promoted to the Technical Department and made Head of the Research and Development Laboratory. In October, 1953 he was promoted to Assistant to the Director of Research and Development and was transferred to Charlotte, North Carolina. In November, 1953 he married Miss Marlyn A. Goham of Pittston, Pennsylvania. In October, 1954 his marriage was blessed with the birth of a son, John. He resigned his position with the Duplan Corporation and joined Celanese Corporation of America, Cumberland, Maryland in September, 1955 as a Textile Engineer-Chemist. In May 1956, a daughter, Carol Ann was born. In December 1956, he was promoted to the position of Group Leader in the Textile Technical Department. In September, 1957 he was granted a three years leave of absence by Celanese in order to accept a position as Instructor of Chemistry with Lehigh University for the purpose of becoming a candidate for the degree of Doctor of Philosophy. During this period he became the father of another son, Robert Gerard, and another daughter, Rosemary. He was employed as an Analytical Chemist in the summer of 1958 at Celanese's Research Laboratory, Summit, New Jersey. In the summer of 1959 he was awarded a National Science Foundation Summer Fellowship. As of September, he will join Eastman Kodak Corporation in Rochester, New York.