UCRL-17808

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Part XI. ABSORPTION AND FLUORESCENCE SPECTRA OF MATRIX ISOLATED PHTHALOCYANINES

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March 1968

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Submitted to
Journal of Molecular Spectroscopy

UCRL-17808
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California
AEC Contract No. W-7405-eng-48

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Part XI.* ABSORPTION AND FLUORESCNECE SPECTRA OF MATRIX ISOLATED PHTHALOCYANINES†

Larry Bajema, Martin Gouterman, and Beat Meyer‡

Chemistry Department, University of Washington
Seattle, Washington

ABSTRACT

Absorption and fluorescence spectra of free base and zinc phthalocyanines (H_2Pc and ZnPc) were studied in matrices of Ar, Kr, Xe, CH_4, N_2, and SF_6 at liquid hydrogen temperature. ZnPc was also studied in CO. The spectra show considerable fine structure whose resolution decreases along the series Ar > CH_4 $\gtrsim$ Kr $\gtrsim$ Xe > N_2 $\gtrsim$ SF_6 > CO. Only part of the fine structure seen in absorption appears in emission. Provisionally we view the spectrum as made up of a broad band arising from phonon exchange with the lattice and no-phonon lines arising from distinct sets of molecules. However, the lack of apparent correspondence between the line structure of the two Q bands of H_2Pc remains unexplained.

* Paper X: M. Zerner and M. Gouterman, Theoret. Chim. Acta 8, 26 (1967).

† The liquid hydrogen work was carried out at the Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, Calif.

‡ Also affiliated with Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California.

A number of studies of absorption and emission spectra of porphyrins and phthalocyanines at liquid nitrogen temperature in linear hydrocarbon solvents such as octane, nonane, and decane have shown multiplet structure, the components of which have been referred to as "quasilines."[1-3] As in other such Shpol'skii spectra[4] the sharpness of the lines has been related to the length of the hydrocarbon chain. In an attempt to find the influence of a wider variety of solvent molecules on the multiplet structure, we have undertaken a study of phthalocyanines in various solvents using matrix isolation techniques. This paper constitutes a first report of our studies of phthalocyanines in solid matrices of Ar, Kr, Xe, CH_4, N_2, SF_6, and CO.

EXPERIMENTAL

Our apparatus was similar to one described previously.[5] A molecular beam of phthalocyanine was deposited by effusion from a quartz Knudsen double furnace. (In preliminary experiments we had found it difficult to control deposition rates with a single furnace temperature.) The solvent vapor entered through a separate orifice and both vapor beams were directed toward a sapphire window maintained at liquid hydrogen temperature. The front and back temperatures of the furnace were 520°C and 340°C, respectively for the free base phthalocyanine (H_2Pc); those used for Zn phthalocyanine (ZnPc) were 530°C and 350°C. These temperatures varied by ±15°C from experiment to experiment. Based on results obtained from vapor phase studies,[6] we estimate that the higher temperature corresponds very roughly to ~0.5 torr and the lower to ~10^{-4} torr. The phthalocyanine was outgassed at 200°C for at least an hour before deposition. During this period a

shutter shielded the target. The shutter was maintained in place for a few minutes on first reaching deposition temperature, as this initial period often seemed to show a transient burst of material from the furnace.

Solvent was deposited at a rate of about 1 ml STP per hour. Depositions were carried out over a period of 1.5 to 6 hours. During deposition the pressure was measured at about 6×10^{-6} torr falling to below 1×10^{-6} after deposition ceased. We estimate that in different experiments the matrices contained between 10^{-2} and 10^{-5} moles of phthalocyanine per mole of solvent.

The spectra were photographed on Kodak 103a-F and I-N plates using a Jarrell-Ash Czerny-Turner spectrograph equipped with a grating blazed for 5000Å giving a dispersion of 10Å/mm. Slit widths were characteristically 80μ for absorption and 200μ for emission. In absorption, a tungsten lamp served as a continuum source. For emission spectra, the 3600Å region of an AH-6 Hg high pressure lamp was used. The exciting light was isolated by a Farrand f/3 monochromator followed by a Corning glass filter No. C57-54. The emission was observed through a Corning glass filter No. C52-60 which was placed between the sample and the recording spectrometer.

In most experiments liquid hydrogen was used to cool the target. For annealing studies a Cryo-tip (Air Products and Chemical Co. Model No. AC2L) was used. During a typical annealing cycle, the temperature was raised from 20°K to the annealing temperature, which was maintained for about fifteen minutes. The absorption spectrum was then photographed, the temperature reduced to 20°K, and another photograph was taken. An annealing study consisted of a series of such cycles with the annealing temperature successively increased by about 5°C until the solvent vaporized.

RESULTS

A. Absorption Spectra

Figures 1 and 2 show reproductions of absorption and fluorescence spectra of H_2Pc and ZnPc in various solvents. Figures 3 and 4 display densitometer tracings. These figures show absorption bands with complex structure: well resolved absorptions with different linewidth and shape appear superimposed on an apparently continuous background. Individual features and their relative position vary among the different solvents and between the two molecules. The only generalization clear at first glance is that the main absorption regions correspond to those observed in H_2Pc in vapor[6] or in solution.[7] Therefore it seemed reasonable to tabulate the data with reference to the free molecule absorption.

The intense absorption of metal phthalocyanines in the 6000Å to 7000Å region is identified with transitions to doubly degenerate excited states called Q.[7] The 0-0 band of this transition is far more intense than transitions 0-1 to vibrationally excited states. In the free base the degeneracy of the Q states is lifted; two intense visible bands are seen due to the individual components Q_x and Q_y, whose transition dipoles are perpendicular and are determined by the H-H axis.[8] We shall refer to the lower energy component as Q_x. In general, our matrices were of such concentration and thickness that only the 0-0 bands were observed. However, in thicker films a number of other bands, identified as 0-1 transitions, appeared.

In Table I we have attempted to catalog the features observable in the various 0-0 bands. The limits of the band were chosen somewhat arbitrarily as may be seen on the traces. The "clear peaks" are determined

from the densitometer traces as points where the trace clearly shows a zero first derivative and negative second derivative. The "features" represent in addition to the "clear peaks" those peaks that do not clearly separate from the noise level on the traces but appear as recognizable features on the photograph or clear shoulders on the traces. We shall use the term line to refer to clear peaks whose half-width is considerably less than the width of the whole band. The lines in our traces show rather variable shapes and half-widths.

Although our spectral features are so blended that simple qualitative description is difficult, the following generalizations can be made: (a) The band width for the entire 0-0 absorption region for all bands in the table is between 210 cm^{-1} and 380 cm^{-1}. (b) The absorption region shifts among the solvents studied over a range of about 300 cm^{-1} with SF_6, N_2, Ar furthest blue, CH_4, Kr in the middle, and Xe furthest red. The vapor phase maxima[6] of the Q_x band of H_2Pc and the Q band of ZnPc comes roughly at the same wavelength as the absorption in CH_4 and Kr. However the vapor phase maximum of the H_2Pc Q_y band is some 180 cm^{-1} to the blue of the CH_4, Kr absorption. (c) The width of the absorption lines increases in the series $Ar < CH_4 \lesssim Kr \lesssim Xe < N_2 \lesssim SF_6$, which brings decreased resolution along this series. Except for the last two matrices, the Q_y band of H_2Pc shows less resolution than the Q_x.

B. Fluorescence Spectra

Fluorescence could be observed visually for all the cases listed in Table I except ZnPc in SF_6. All except this last were recorded photographically with exposure times between 30 seconds and 30 minutes. In

general the fluorescence of H_2Pc was weaker than that of ZnPc. Strangely enough, the strongest fluorescence of H_2Pc was recorded in SF_6.

Figures 1 and 2 show some fluorescence spectra paired with the corresponding absorption spectra. The fluorescence generally appears as a broad emission band somewhat red shifted from the absorption plus a number of superimposed lines that correspond with lines observed in absorption. However, almost all of the emission of H_2Pc in Ar comes out in the lines. The emission lines are often as sharp as the corresponding absorption lines. However, for H_2Pc in N_2 and Xe the emission features corresponding to absorption quasilines appear as broad peaks or shoulders on top of the general broad emission band.

There is a noticeable contrast between the emission spectra of H_2Pc and ZnPc. For H_2Pc, there is emission wherever intense absorption occurs although the emission may be broad. For ZnPc, several absorption lines are absent or very weak in emission.

C. Annealing

In order to test the extent to which the deposition conditions and target temperature influence the spectra, the effect of annealing was studied in three matrices. The means and methods of these studies are described above and have been applied to H_2Pc in Xe, Kr, and SF_6. The spectral features of H_2Pc in Xe at liquid hydrogen temperature were noticeably sharper after annealing at 60°K than on initial deposition. In SF_6 a similar phenomenon was observed with an annealing temperature of about ~65°K. In both cases spectra taken at the annealing temperature were broadened.

The most interesting annealing effects were shown by H_2Pc in Kr after annealing at ~48°K. As shown in Fig. 5, a line at the blue end of both Q_x and Q_y lost intensity, while a line at the red end of each band gained intensity and a new line appeared further to the red. Comparison shows that the absorption spectrum after annealing matches closely the emission spectrum taken in an unannealed matrix.

D. Other Porphyrins

In addition to H_2Pc and ZnPc, we studied the Cu and Zn salts of octaethylporphin (OEP). The Cu OEP was studied in Ar, Kr, Xe, N_2, and CH_4 using front and back furnace deposition temperatures of 380°C and 250°C. ZnOEP was studied in Ar and CH_4 using furnace deposition temperatures of 370°C and 270°C. For CuOEP in Ar a broad Soret band is observed at 3900Å with a broad weak satellite about 30Å to the red. For ZnOEP in Ar there is a broad Soret band at 4020Å plus a second somewhat weaker band of about half the width 100Å to the blue. No other absorptions are observed. A very weak fluorescence was visually observed for ZnOEP, but it was not photographed. No phosphorescence was observed for CuOEP.

DISCUSSION

Although the appearance of fine structure is a well known effect and is observed in electronic spectra of a wide variety of molecules and matrix trapped species, conclusive interpretation of fine structure is difficult because of the many possible causes. Among these are: (1) different solvent sites, (2) vibrational coupling between matrix and solute, (3) intrinsic structure arising from some type of degeneracy in the solute, and (4) solute-solute interaction. All of these effects might occur simultaneously

but with different relative importance in various solvent-solute systems. The isolation of the individual factors is a slow and tedious process.

One problem that confounds interpretation is the fact that, in addition to well-defined properties such as temperature and solvent to solute mole ratio (M/R), the method by which the sample is prepared can strongly influence the observed spectrum. This is in the nature of things, as the matrices are generally unstable thermodynamically at the temperatures studied. Recently[9] spectra of benzene in rare gas matrices simpler and sharper than those previously reported by Robinson[10] and by Schnepp[11] have been obtained in our laboratory by varying deposition conditions. Other benzene spectra more complex than those reported have also been obtained. It seems then that without extensive variation of deposition speed, geometry, and target temperature as well as annealing studies it is risky to assume that a particular spectrum is the simplest obtainable for a given M/R and T. Although the present phthalocyanine matrices were made under conditions similar to those used to obtain the simplest benzene spectra, it is possible that further simplification in the spectra could be obtained by varying conditions. In particular it may be that some solute-solute interaction is still present and that other deposition techniques will give simpler spectra. Hence any interpretation of present data is cautious and provisional.

Nonetheless our results do show some interesting relations:

(i) It is clear that a matching of the length of a solvent hydrocarbon chain with the size of the solute, such as has been found in the work of

Shpol'skii[4] is by no means the only factor that causes sharp line structure. Argon, the smallest of our solute molecules has provided the sharpest lines.

(ii) Our rare gas solvent shifts are similar to those found by Robinson for benzene.[10] However, although the H_2Pc Q_y band in vapor is to the blue of the band in Ar, the same relation Robinson found for benzene, the H_2Pc Q_x band and the ZnPc Q band in vapor are to the red of the band in Ar. This result may be understood by contrasting the fact that in benzene vapor individual vibronic components are resolved while in phthalocyanine vapor at elevated temperatures half widths are about 900 cm^{-1}.[6] It seems reasonable to ascribe these broad band widths to a superposition of v-v transitions from thermally populated levels. The center of gravity of the superposition of bands might well be shifted by a hundred cm^{-1} or so from the 0-0. Thus we need not attach too much significance to the phthalocyanine in vapor phase as they are subject to some type of thermal shift. It is, however, curious that the Q_x and Q_y bands seem to be differentially shifted.

(iii) Except for N_2 and SF_6, the matrices in which the line structure is the broadest, the Q_y band appears to show definitely broader lines than Q_x. We also photographed the absorption spectra in the 3000-4000Å region and found it completely diffuse in the low temperature matrices. It is possible that both effects are intrinsic to the molecule itself and might reflect some type of broadening due to vibronic coupling between the higher electronic states and the lower ones.

(iv) The similarity of the emission spectrum of H_2Pc in Kr with the absorption spectrum taken after annealing might have a most natural interpretation. Our excitation was carried out in the 3600Å region with

subsequent emission around 6900Å. The degradation of this much energy might well be accompanied by a certain amount of local heating. We could then imagine that the fluorescent site has been annealed by the energy degraded from the exciting photon. This hypothesis is subject to obvious experimental tests.

(v) In the matrices Ar, Kr, CH_4 that showed better resolution, there are obviously more lines observed in the ZnPc Q band than in the H_2Pc Q_x band. Moreover, there are noticeable lines in absorption for which no emission or a weak emission occurs. This strongly suggests that there has been some lifting of the ZnPc electronic degeneracy and perhaps that there is thermal relaxation between the two resultant states. However, attempts to clearly identify pairs of lines as due to such a split degeneracy have so far not been successful.

There are two principal explanations for line structure: (i) the lines can represent distinct transitions in one set of molecules or (ii) the lines can represent a single transition somehow shifted among distinct sets of molecules. (And of course both phenomenon can be occurring at once in a particular experiment.) Recently Rebane and Khiznyakov[12] have given a theory for line structure based on vibrational coupling that is essentially of the first type. They predict that the spectrum of a solute in a rigid matrix should consist of a broad band due to exchange of phonons with the lattice plus certain lines due to no-phonon transitions and to transitions that excite local vibrations. According to their theory the lines might not show internal structure. More recently Svishchyov[13] has studied the fluorescence excitation spectra of distinct fluorescence lines of coronene, pyrene, and 3-4 benzopyrene in normal alkane matrices.

The results of this study are most simply understood by attributing the doublet structure of coronene and pyrene to two distinct sets of molecules and the quartet structure of 3-4 benzopyrene to four distinct sets.

Which of these explanations -- distinct transitions or distinct molecules -- best fit our results? Our results agree qualitatively with the theory of Rebane and Khiznyakov in that they can be viewed as containing both a broad absorption and "quasilines." Moreover, as they suggest, our lines often show peculiar shpaes that might reflect unresolved internal structure. The width of the broad absorption is relatively independent of solvent as might be expected if the amount of energy exchange with the lattice phonons depends largely on the solute shape change on excitation. However, there are two points of divergence. Although Rebane and Khiznyakov are not clear on this point, their paper seems to suggest that the no-phonon line should be pre-eminent. Our spectra show no such pre-eminent peak. Also they give no reason to expect that emission should not occur from a thermally relaxed excited state. Our experiments are performed with $kT/hc \sim 14\ cm^{-1}$. Thus there is no way to understand the appearance in emission of absorption lines that are separated by several tens of cm^{-1} if these lines are due to excitation of local vibrations.

A model that attributes the distinct lines to distinct sets of molecules allows ready explanation for the appearance of the same lines in absorption and emission. The absence of certain strong absorption lines from the emission of ZnPc could then be explained as due to a lifting of the ZnPc orbital degeneracy -- perhaps due to anisotropy in the local environment -- with thermal equilibrium established between the two levels.

However, two objections can be raised to this interpretation. We would

expect a one-to-one correspondence between the line structure of the Q_x and Q_y bands of H_2Pc, which is not at all apparent in the data. A less serious objection arises when we notice the appearance of a similar triplet structure in the Q_y band of H_2Pc in several distinct solvents. This forces us to suppose that the solute often determines the line structure. Since the most likely explanation for distinct sets of solute molecules is distinct lattice sites, it is hard to see why such similar multiplet structure should arise among rather different solvents.

ACKNOWLEDGEMENTS

This research was supported in part by the Public Health Services Research Grant BM-14292 (MG, LB), and by the National Science Foundation (LB, BM). The liquid hydrogen experiments were performed under ths sponsorship of the United States Atomic Energy Commission. The authors wish to thank Professor Leo Brewer, head of Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California for his generous help. The H_2Pc and ZnPc were supplied by the Du Pont Company and purified by Mr. Lawrence Edwards; the OEP samples were the gift of Dr. David Dolphin of Harvard University. Drs. Jerry Smith and De Lyle Eastwood often provided help and advice in the laboratory.

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TABLE I

Molecule	Band	Matrix	Absorption Region	Clear Peaks	Features	Fluorescence Region	Clear Peaks	Features
H_2Pc $T \sim 20^oK$	$Q_x(0-0)$	Ar	6710-6860	2	14	6740-6865	4	4
		Kr	6770-6890	3	13	6770-6960	2	6
		Xe	6845-6960	3	4	6845-7025	1	5
		N_2	6710-6870	1	4	6735-6890	1	4
		CH_4	6775-6920	3	9	6775-6960	5	9
		SF_6	6710-6850	1	5	6680-7005	2	3
H_2Pc $T \sim 20^oK$	$Q_y(0-0)$	Ar	6325-6475	3	6			
		Kr	6370-6505	3	5			
		Xe	6425-6580	3	5			
		N_2	6315-6480	4	6			
		CH_4	6350-6505	3	5			
		SF_6	6315-6430	2	3			
ZnPc $T \sim 20^oK$	Q(0-0)	Ar	6500-6680	10	14	6520-6910	5	10
		Kr	6550-6700	6	9	6560-6825	4	6
		Xe	6620-6740	3	12	6620-6870	2	3
		N_2	6450-6670	3	6	6510-7165	4	12
		CH_4	6550-6700	7	7	6550-6860	4	8
		SF_6	6490-6595	1	7			
		CO	6540-6690	1	3	6545-6810	0	4
H_2Pc[a] $T \sim 77^oK$ (ref.4)	$Q_x(0-0)$	C_8H_{18}	6893-6938	5	5	6893-6938	5	5
		$C_{10}H_{22}$	6882-6956	4	6	6882-6956	6	6
	$Q_y(0-0)$	C_8H_{18}	6517-6552	4	4			
		$C_{10}H_{22}$	6501-6537	4	5			

a. Since the data was presented rather differently in ref. 4 from our own tabulation, the criterion for these numbers is not the same as for our own data.

FIGURE CAPTIONS

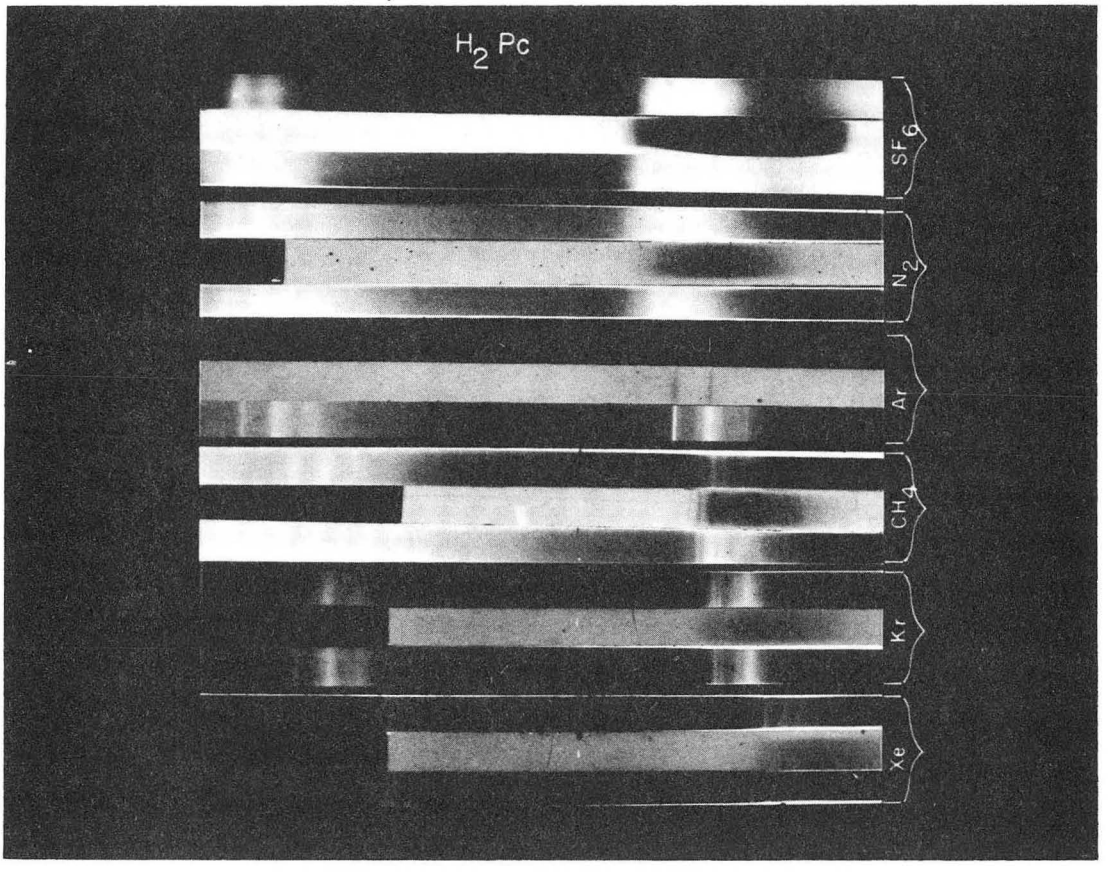
Fig. 1 Absorption and fluorescence of H_2Pc in various solvents.

Fig. 2 Absorption and fluorescence of ZnPc in various solvents.

Fig. 3 Traces of absorption and fluorescence plates of H_2Pc. Circles indicate fluorescence curves, and the bar indicates the Hg 2×3341.5Å line.

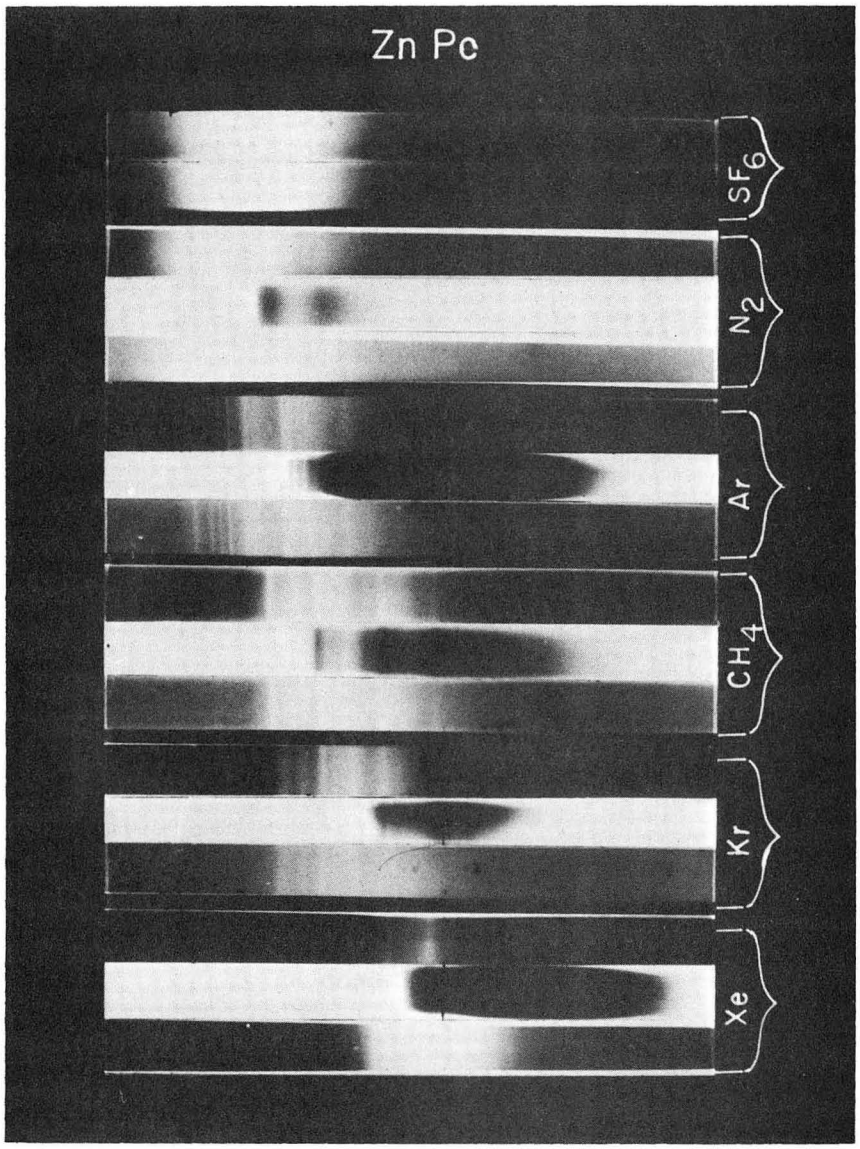
Fig. 4 Traces of absorption and fluorescence plates of ZnPc. Circles indicate fluorescence curves, and the bar indicates the Hg 2×3341.5Å line.

Fig. 5 Effect of annealing at 48°K of H_2Pc in Kr.



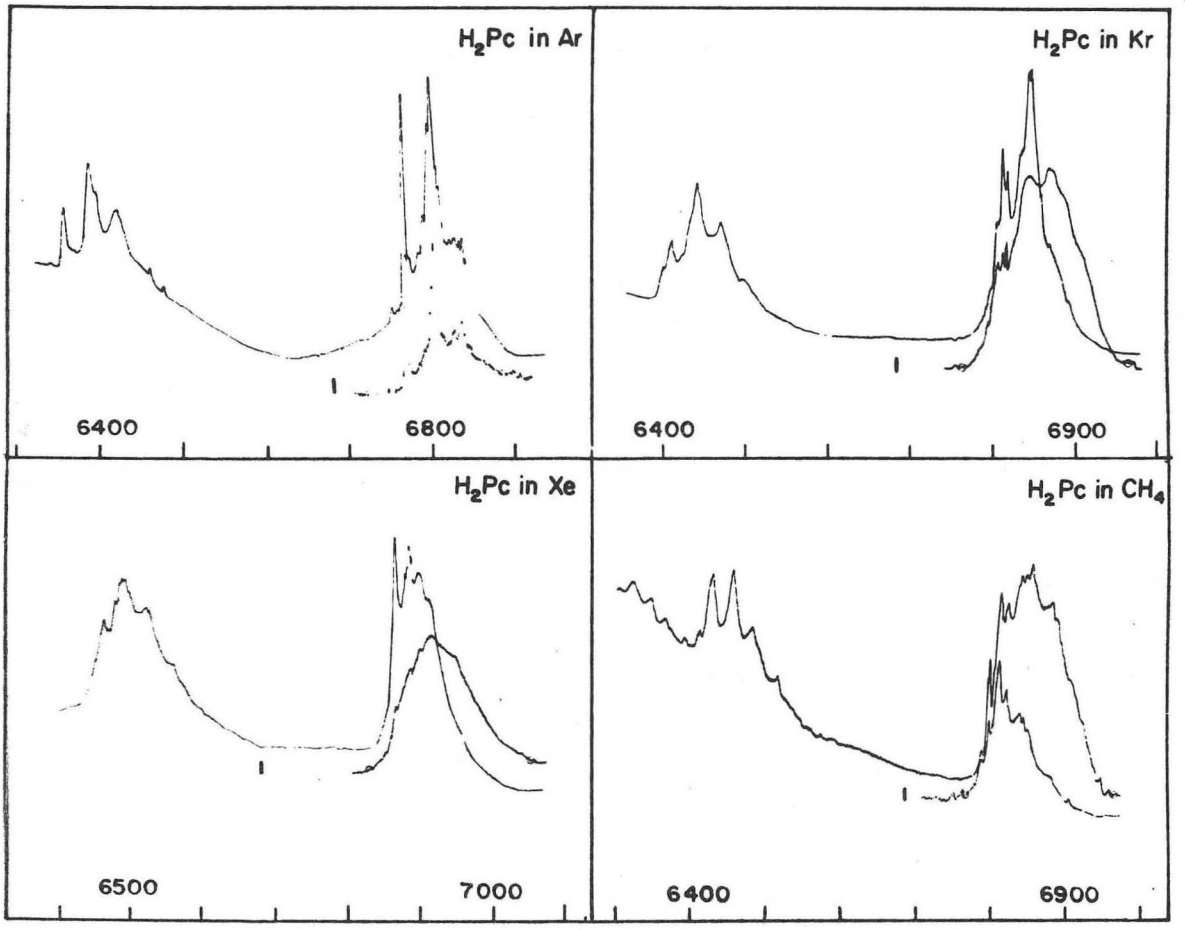
XBB 682-711

Fig. 1



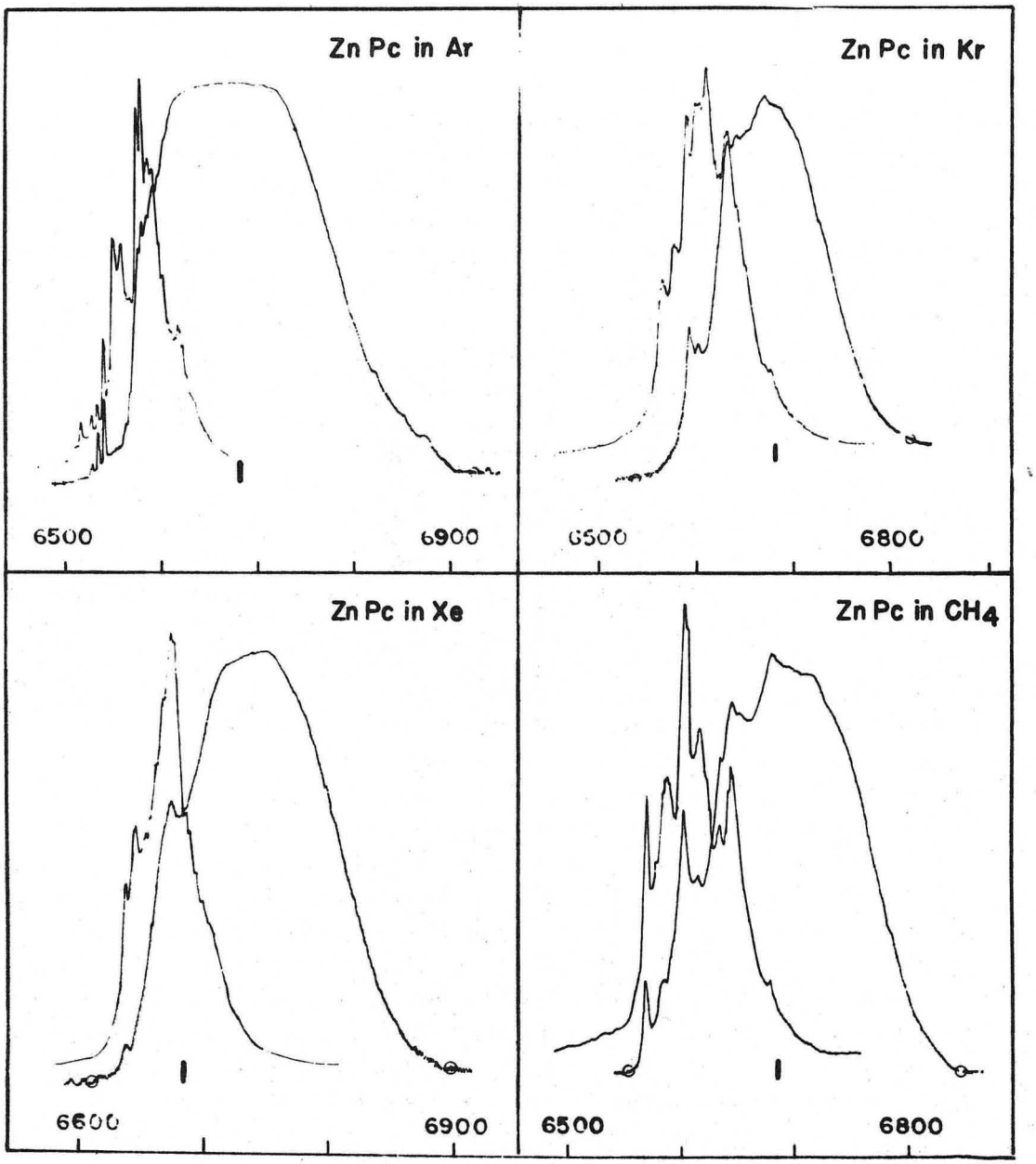
XBB 682-712

Fig. 2



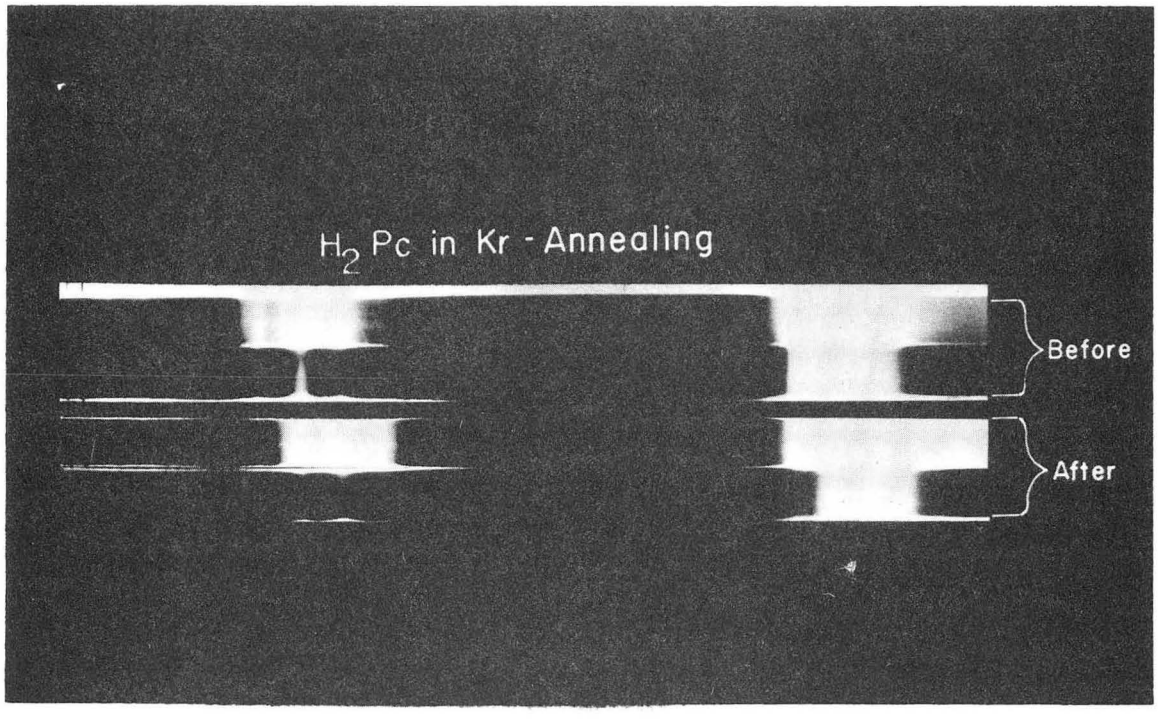
XBL 682-162

Fig. 3



XBL 682-161

Fig. 4



XBB 682-713

Fig. 5

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