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Mechanism of Phosphorescence Quenching in Photomagnetic Molecules Determined By Positron Annihilation Spectroscopy

Jag J. Singh
A. Eftekhari
S.V.N.Naidu

NASA Langley Research Center
Hampton, VA.

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Photomagnetic Molecules Determined By
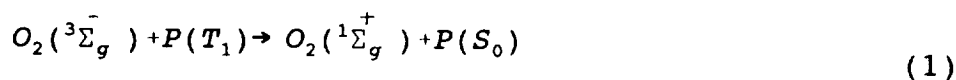# Positron Annihilation Spectroscopy

ABSTRACT

Platinum Octaethyl Porphyrin (Pt.OEP) is an efficient phosphor under ultraviolet excitation. The phosphorescent triplet state (T_1) is readily quenched by the oxygen (O_2) molecules. This phenomenon is being utilized as the basis for global air pressure measurements in aerodynamic facilities at various laboratories. The exact mechanism by which O_2 molecules quench the (T_1-S_0) transitions is still unknown. The diamagnetic S_n singlet states, which feed T_1 states via intersystem crossings, would presumably not be affected by O_2. It must be the magnetic T_1 states, which can interact with the paramagnetic O_2 molecules, that are affected. However, our positron lifetime and Doppler broadening studies suggest the formation of ($S_n.O_2$) complexes which can also eventually reduce the population of the T_1 states (i.e. quench phosphorescence). This is possible since higher triplet states in (Pt-OEP) are admixed with the S_n states via spin orbit interactions. The experimental procedures and the results of various measurements are discussed in this paper.

INTRODUCTION

The basic ring structure of a porphyrin molecule is characterized by a 4-fold symmetry, including 4-nitrogen atoms directed towards the center. When the 8-exohydrogens in it are replaced by CH_3CH_2 groups, the molecule becomes octaethyl porphyrin. If the 2-central hydrogens are also replaced by metal atoms, the molecule becomes a metalloporphyrin. These metal atoms can have significant effects on the

electronic and optical properties of parent molecules[1]. Amongst the most widely studied metalloporphyrins are Platinum-Octaethyl Porphyrin molecules. Figure -1(a) shows the chemical structure of Platinum-Octaethyl Porphyrin molecule. Figure -1(b) shows its schematic energy level diagram and decay scheme.

Under UV- irradiation, the Pt.OEP molecule is excited to a higher singlet state which decays very quickly to the lowest excited singlet state . From this singlet state, the molecule can decay to the ground state by a radiative/non-radiation transition or internally convert to the lowest excited triplet state. This triplet state can either be re-excited to the singlet state by thermal excitation or collision with another triplet state molecule or phosphoresce to the ground state with a lifetime of the order of 100 microseconds. It has been reported[2] that the presence of oxygen molecules near the photoexcited Pt.OEP molecules leads to the quenching of the phosphorescence in them. When an oxygen molecule comes in contact with a Pt.OEP molecule in its lowest excited triplet state[†] , P(T$_1$), it can lead to one of the following reactions:

$$O_2(^3\Sigma_g^-) + P(T_1) \rightarrow O_2(^1\Sigma_g^+) + P(S_0) \tag{1}$$

$$\rightarrow [O_2 \cdot P(T_1)] \tag{2}$$

$$\rightarrow O_2^- + P(S_0)^+ \tag{3}^{(*)}$$

(*) This reaction is possible only in
the condensed state of Pt.OEP formulation.

All these reactions result in the reduction of phosphorescence from the P(T$_1$) state. It is well recognized that the P(S$_n$)-states of the aromatic molecules are admixed with the higher triplet states. Thus the paramagnetic oxygen (O$_2$) molecule will not necessarily be repelled

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†We shall use P(S$_i$ or T$_i$) as the symbol for appropriate state of the
metalloporphyrin molecule in this paper.

molecule, it can form a transient $[O_2 . P(S_1)]^*$ complex. Such a complex is expected to be considerably higher in energy than $P(S_1)$ state. As seen in figure-2, $P(S_1)$ occurs at 5310 angstroms[3] above the ground state, $P(S_0)$. Because of the competing radiationless transitions from it, the formation of $[O_2 . P(S_1)]^*$ complex will also result in a net reduction in the phosphorescence from the $P(T_1)$ state. Currently, it is believed that the $[O_2 . P(T_1)]$ interaction alone is responsible for the reduction in the $P(T_1) \rightarrow P(S_0)$ radiative transitions.

There is no reason why $[O_2 . P(S_1)]^*$ complex formation, which can also reduce the population of the $P(T_1)$ state and hence the $P(T_1) \rightarrow P(S_0)$ radiative transition, can also not play a role. It is the purpose of this investigation to determine whether $[O_2 . P(S_1)]$ interaction plays a role in the O_2-induced quenching process of $P(T_1) \rightarrow P(S_0)$ phosphorescence in Pt.OEP molecules.

EXPERIMENTAL PROCEDURES AND RESULTS

Two types of metalloporphyrins were used in this study. (1) Platinum Octaethyl Porphyrin (Pt. OEP), which has a reported[3] phosphorescence quantum yield of approximately 90%. Figure-3 shows the emission spectrum of (Pt. OEP) molecule. Clearly, the phosphorescence peak at 6445Å dominates the spectrum. (2) Magnesium Octaethyl Porphyrin (Mg.OEP) whose phosphorescence quantum yield has been reported[1] to be less than 2%. Figure-4 shows the emission spectrum of (Mg. OEP) molecule. Clearly, the phosphorescence peak is very weak and the flourescence peak at 5835Å dominates the spectrum. The low phosphorescence yield of Mg.OEP may be due to the reduced population, or an even lower energy, of the $P(T_1)$ state in it. It may also be due to the lighter mass of the central substituent magnesium atom. However, Mg.OEP was selected for this study mainly on the assumption that the excited $S=0$ states in it are less admixed with the higher $S=1$ states.

The metalloporphyrin (M.OEP) targets were prepared by air-spraying a solution of

(M.OEP) molecules in trichloroethane ($C_2H_3Cl_3$) on thin aluminum substrates. The $C_2H_3Cl_3$ molecules evaporate quickly leaving the M.OEP molecules adhered to the aluminum substrates.

Positron lifetime and Doppler broadening measurements were made in M-OEP molecular films spray-coated on both sides of 0.010" thick aluminum substrates. The substrates were shaped into 2" high concentric cylinders of diameter 1.0" and 1.5", respectively. The aluminum cylinders were enclosed in a 3" high, 3" diameter glass cylinder, which could be pumped down to 10^{-4} Torr. A 50 μc Na^{22} positron source deposited on a steel needle tip was located at the center of the aluminum cylinders. The phosphor films were photoexcited with ultraviolet radiation from a Xenon short arc lamp located above the glass cylinder.

Positron lifetime measurements were made with a standard fast-fast coincidence system whose resolution time is of the order of 300 picoseconds. The Doppler broadening measurements were made with a high purity Germanium detector whose full width at half maximum (FWHM) resolution for Bi^{207} radiation is 1.28 kev. Both types of measurements were made <u>with</u> and <u>without</u> ultraviolet excitation of the phosphor molecules in vacuum , N_2, O_2, and air media at room temperature. Figure 5 shows the experimental set up for positron annihilation measurements.

The positron lifetime results in the Pt.OEP phosphor are summarized in tables I and II. The Doppler broadening results in Pt.OEP and Mg.0EP phosphors are summarized in Tables III and IV, respectively. Figure-6 illustrates the Doppler Broadening results. These results are discussed in the following section.

DISCUSSION

An examination of the data in Tables I and II shows that UV irradiation has little effect on the positron lifetime spectra in any one of the media surrounding the Pt.OEP-

coated aluminum cylinders. In particular, even pure oxygen environment does not seem to affect positron lifetimes. This may be due to the fact that the positronium atom (Ps) formed at the $[O_2 .P(S_1)]^*$ complex will be readily quenched by the paramagnetic O_2 molecule released in the process[5]. This fast positronium decay component will not be resolvable from the prompt component in the positron lifetime spectrum.

The Doppler broadening data in tables III and IV exhibit <u>two</u> interesting features (1) UV-irradiation does not affect the Doppler broadening parameter (S) in Mg.OEP molecules in any of the surroundings media, measurably; (2) The Doppler broadening parameter in Pt.OEP molecules under UV irradiation increases steadily as the partial pressure of oxygen in the surrounding medium increases. These data are consistent with a lower excitation energy for $P(S_1)$ state in Mg.OEP molecules[3] as seen in figure-7 and even lower probability for $[O_2 . P(S_1)]^*$ complex formation in them. Under these conditions Ps atoms are not formed at $P(S_1)$ sites in Mg.OEP molecules and therefore the Doppler parameter should not be affected as seen in figure-6(a). The excitation energy of the $P(S_1)$ state and the probability of $[O_2 . P(S_1)]^*$ complex formation in Pt.OEP, on the other hand, are quite adequate for the formation of Ps atoms at $P(S_1)$ sites. The formation of Ps atoms in Pt.OEP molecules should therefore lead to an increase in the Doppler parameter S with increasing concentration of oxygen under UV irradiation, as observed in figure-6(b).

CONCLUDING REMARKS

As indicated earlier, positron lifetime results by themselves do not appear to be sensitive indicators of the role of the $P(S_1)$ state in O_2-induced quenching of the $P(T_1) \rightarrow P(S_0)$ transition in the Pt.OEP molecular phosphor. However, concurrent Doppler broadening measurements clearly indicate a steady increase in the probability of positronium atom formation at $P(S_1)$ sites as partial pressure of oxygen in the surrounding medium increases. The formation of $[O_2.P(S_1)]^*$ complexes at $P(S_1)$ sites decreases the population of the

phosphorescing $P(T_1)$ states, thus effectively quenching the $P(T_1)$-$P(S_o)$ phosphorescence. It is therefore concluded that oxygen molecules quench the phosphorescence in the Pt.OEP phosphor molecules by interacting with both the lowest excited singlet states as well as the lowest excited triplet states. These conclusions are confirmed by positron annihilation measurements in non-phosphorescing Mg.OEP molecules.

REFERENCES

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5. C.I. Eom., S.V. Naidu, S.C. Sharma and J.M. Kowalski: Positronium Quenching via collisions with triplet states of photomagnetic molecules: Phys. Rev. A. Vol. 43(No.7), 3247, 1991.

Summary of Positron Lifetime Results
in (Pt.OEP)

Table- 1-   In the absence of UV- irradiation

Surrounding Medium	$\tau_1(ps)/I_1(\%)$	$\tau_2(ps)/I_2(\%)$	$\tau_3(ps)/I_3(\%)$
Vacuum	$246\pm2/87.0\pm0.6$	$781\pm32/8.7\pm0.4$	$3015\pm129/4.3\pm0.3$
Air	$251\pm1/89.8\pm0.4$	$870\pm44/6.1\pm0.4$	$2940\pm143/4.1\pm0.6$
Oxygen	$251\pm1/88.3\pm0.5$	$907\pm61/7.2\pm0.4$	$2977\pm96/4.4\pm0.3$

Table- 2-   In the presence of UV- irradiation

Surrounding Medium	$\tau_1(ps)/I_1(\%)$	$\tau_2(ps)/I_2(\%)$	$\tau_3(ps)/I_3(\%)$
Vacuum	$245\pm2/86.8\pm0.8$	$776\pm44/8.8\pm0.5$	$3029\pm180/4.3\pm0.5$
Air	$242\pm1/88.9\pm0.4$	$869\pm41/7.1\pm0.3$	$3023\pm147/4.0\pm0.4$
Oxygen	$249\pm1/88.4\pm0.5$	$927\pm62/7.4\pm0.4$	$3026\pm116/4.2\pm0.3$

Apparently, UV- irradiation does not affect the lifetime spectrum in any one of the media surrounding the porphyrin-coated aluminum cylinders.

Summary of the Doppler Broadening Data
in Metallized Porphyrins

$$S = Doppler \quad Parameter \quad = \left(\frac{Area \ of \ the \ Central \ Section \ of \ Peak}{Total \ Area \ of \ the \ Peak} \right)$$

$$R = \frac{S(\ With \ Light \ )}{S(\ NoLight \ )}$$

Table- III-   (Mg-OEP) Phosphor

Surrounding Medium	S (No Light)	S (With Light)	R
Vacuum	0.1086±0.0007	0.1078±0.0007	0.993±0.006
Nitrogen	0.1092±0.0004	0.1084±0.0004	0.993±0.004
Air	0.1077±0.0004	0.1086±0.0004	1.008±0.003
Oxygen	0.1075±0.0007	0.1081±0.0007	1.005±0.006
	Ave: (0.1083±0.0006)	(0.1084±0.0006)	(1.000±0.007)

Apparently, UV-irradiation does not affect Doppler parameter (S) in (Mg.OEP) phosphor.

Table- IV-   (Pt-OEP) Phosphor

Surrounding Medium	S (No Light)	S (With Light)	R
Vacuum	0.1086±0.0005	0.1103±0.0006	1.015±0.005
Nitrogen	0.1099±0.0004	0.1096±0.0004	0.997±0.004
Air	0.1093±0.0006	0.1153±0.0006	1.055±0.005
Oxygen	0.1093±0.0004	0.1171±0.0004	1.072±0.004

It appears that UV-irradiation increases the Doppler parameters (S) in (Pt.OEP) phosphor, ie.

$$S = (0. 110 \pm 0. 0006) + 0. 007 \ X \ (O_2)$$
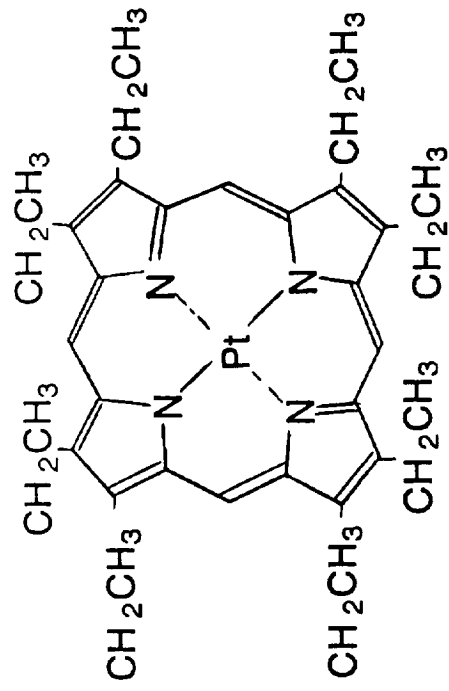
Figure -1 (a) Chemical Formula for Platinum-
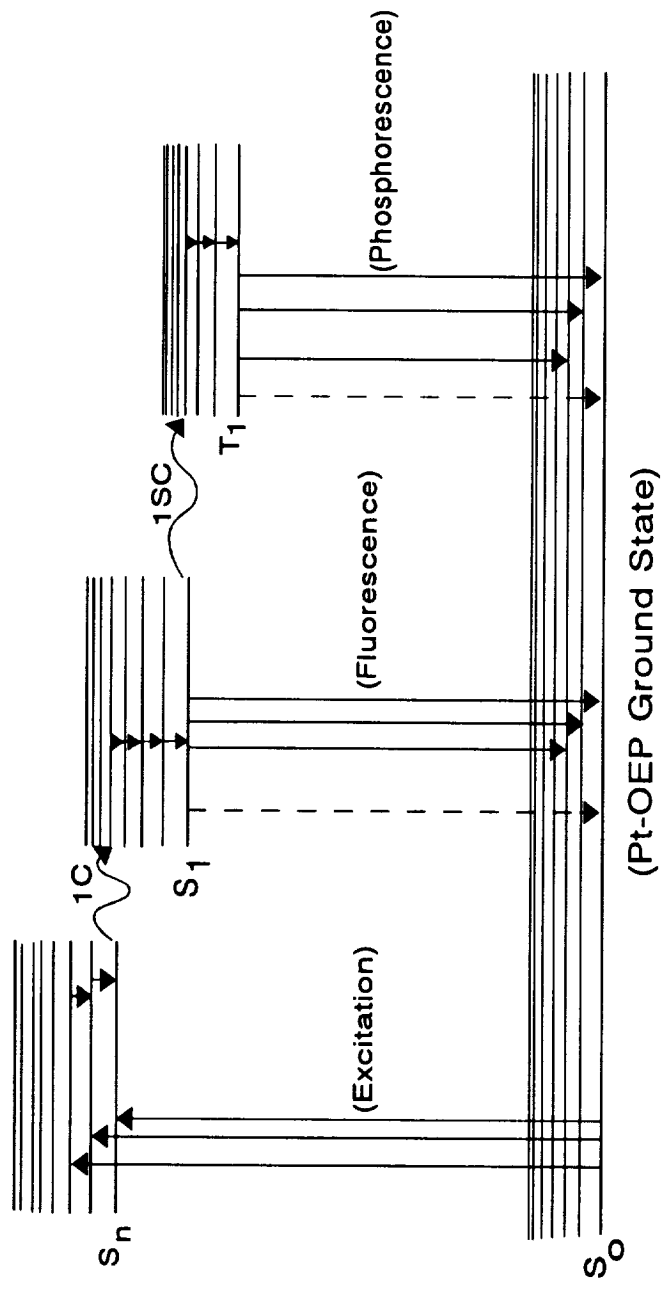Octaethylporphyrin (Pt-OEP)

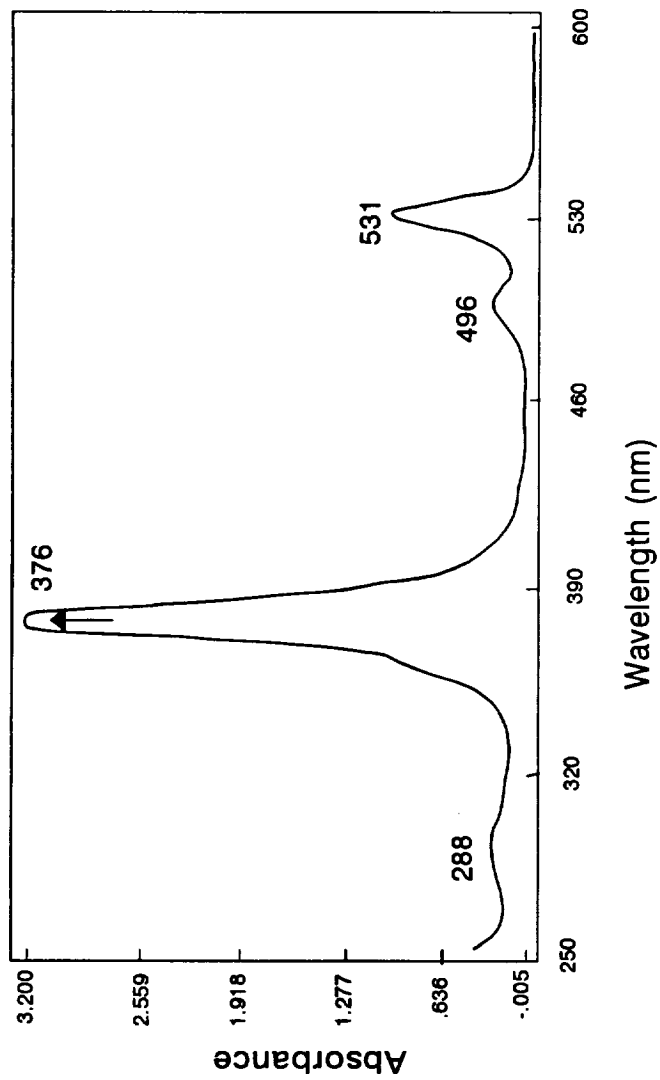Figure -1(b). Typical level Scheme for a
metalloporphyrin molecule.

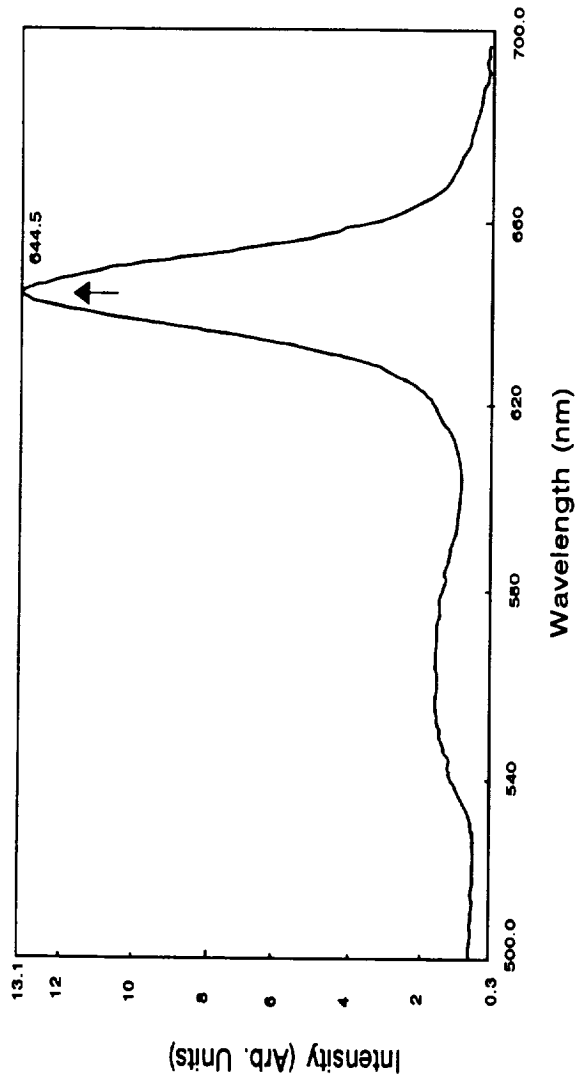Figure-2. Absorption Spectrum of Pt.OEP molecules dissolved in CH$_2$Cl$_2$.

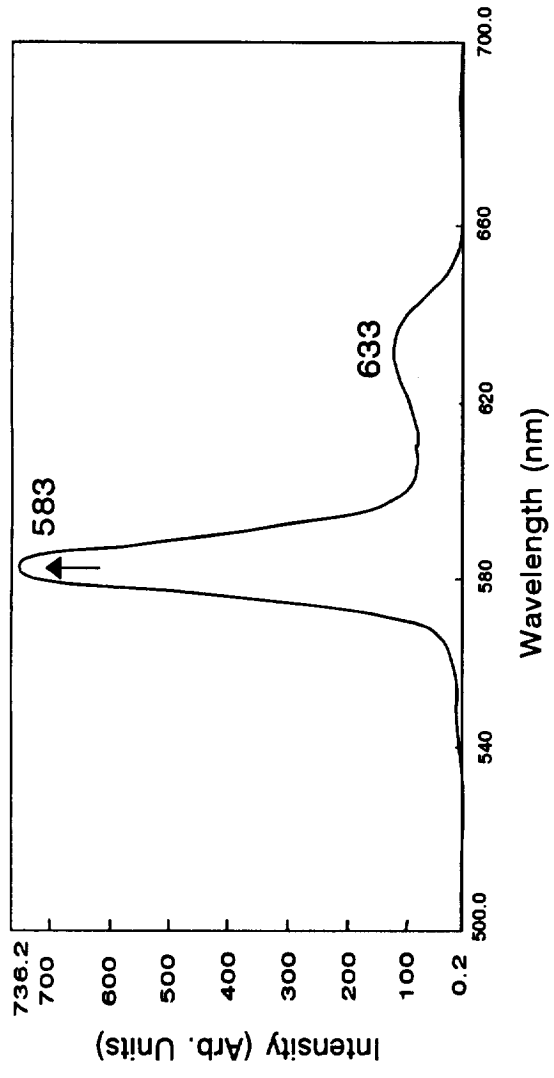Figure-3. Emission Spectrum from Pt.OEP molecules dissolved in CH_2Cl_2, excited at 3760 Å.

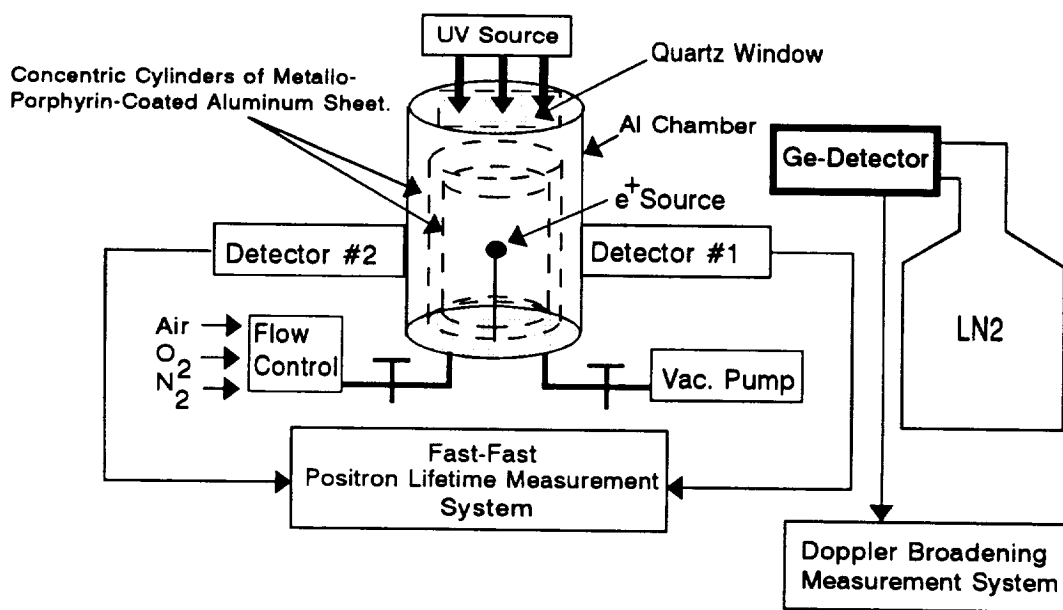Figure-4. Emission Spectrum from Mg.OEP molecules dissolved in CH$_2$Cl$_2$,excited at 4010 Å.

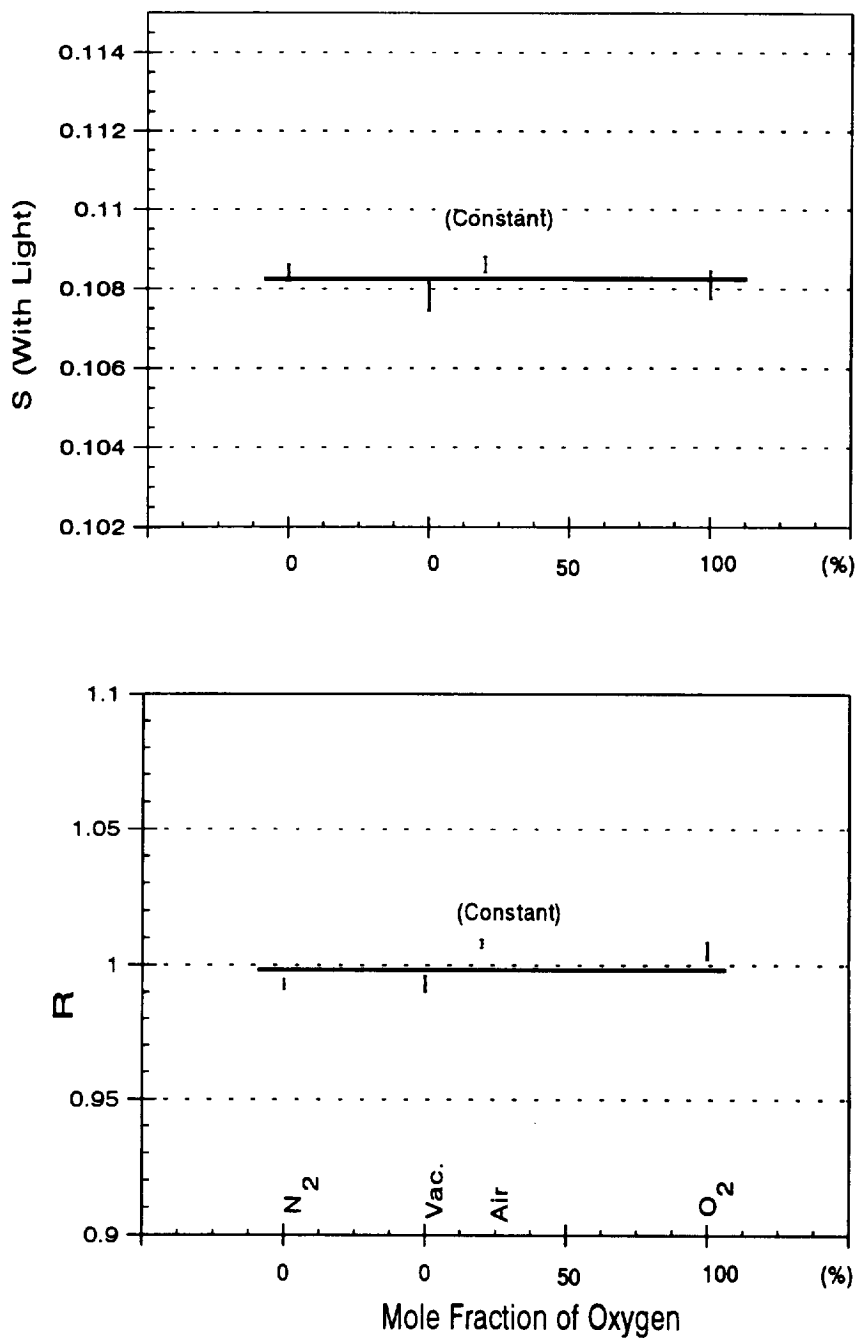Figure 5. Schematic Diagram for Positron Annihilation Studies in Metallo-Porphyrins.

Figure-6 (a) Variation of Doppler Broadening parameter in (Mg.OEP) Molecules as a function of Mole Fraction of Oxygen.
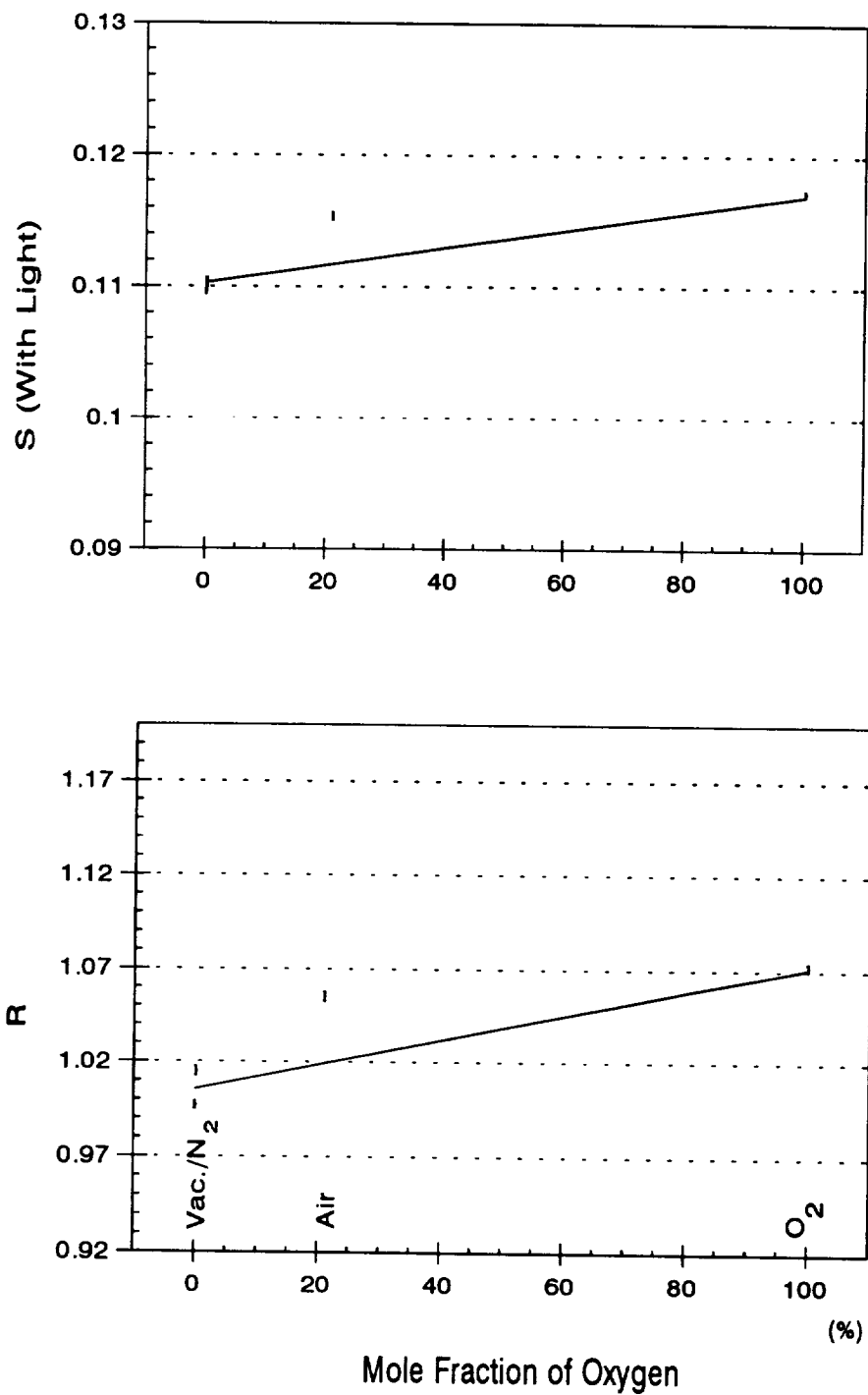
Figure-6 (b). Variation of Doppler Broadening Parameters in (Pt.OEP) Molecules as a Function of Mole Fraction of Oxygen.
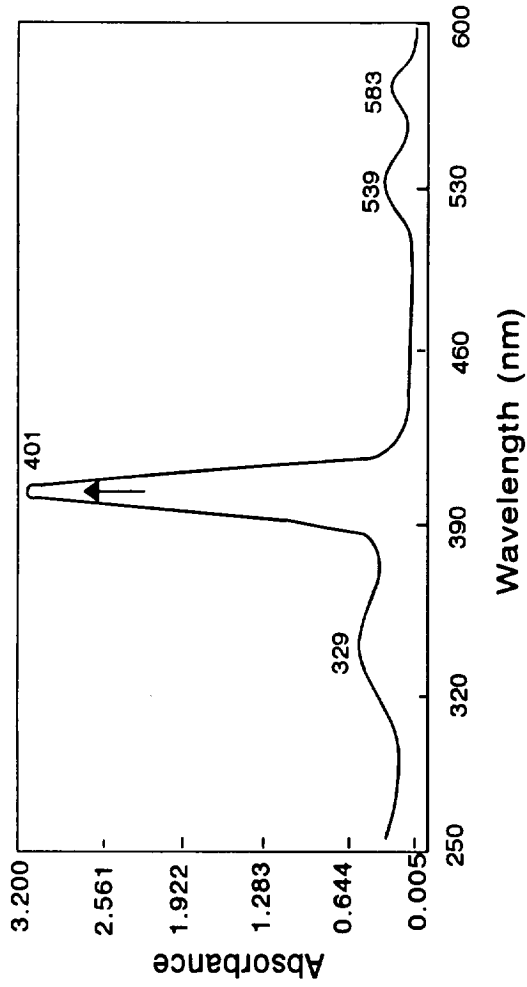
Figure-7. Absorption Spectrum of Mg-OEP molecules dissolved in CH_2Cl_2.