1. A. TECHNICAL PROGRESS REPORT

MASTER

While the overall aims of the project remain unaltered from what was stated in the original research proposal, the specific experiments we have been able to complete during the last twelve months differ from the ones suggested in the last year's progress report. I would like to briefly describe the completed research problems before relating them to the overall goals of the research project.

Luminescence of Pyridines:

The emission properties of pyridine have attracted much attention. No phosphorescence or fluorescence has been observed in spite of repeated attempts in many laboratories. The presence/absence of pyridine emission is a crucial test for some of our current concepts of nonradiative transitions. These concepts are discussed below with the aid of the energy level diagram in Fig.1.

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Figure 1

Excitation into S_2 or S_1 would lead to the "immediate" population of the S_1 state. $S_1 \rightarrow S_0$ should have a long life-time (due to the fact that $S_0 \rightarrow S_1$ is weak) and can not

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compete with $S_1 \rightarrow S_0$. Thus the absence of fluorescence may be rationalized. $S_1 \rightarrow T_2$ should be slow¹ because there is no spin-orbit interaction between two triplet (n, π^*) states.² Thus we do not expect phosphorescence.

The fact that no emission of pyridine has been observed is not a proof for the above ideas, because the inability to experimentally observe an emission can be due to a multitude of reasons including the lack of skill on the part of the experimenter. What is needed is a positive test. Two such tests are:

((i) Emission of pyridine in acidic solvents: In acidic solvent the order of the $S_1(n, \pi^*)$ and $S_2(\pi, \pi^*)$ levels should change. One should then expect a strong fluorescence from the lowest (π, π^*) level.

((ii) Ultraviolet absorption of 2-chloropyridine and 2-fluoropyridine³ indicates that in these two molecules the lowest singlet is a (π, π^*) state. Therefore it should be possible to detect phosphorescence and fluorescence in these molecules.

Experimental observations: We did find the phosphorescence of 2-chloropyridine. The 0,0 band is located at 3665Å and the maximum of emission at 4325Å. Preliminary photoselection data indicates that the phosphorescence is polarized perpendicular to the absorption - which may lead to a (π, π^*) assignment for the lowest triplet.

The experiments on pyridine in acidic solutions have been inconclusive.

Polarization of the Phosphorescence of Nitroaromatic Molecules:

Very little information is available on the singlet-triplet transitions of nitroaromatic molecules, in spite of the persistent speculation regarding the nature of their lowest triplet state in photochemical investigations. Although it is known that many of these molecules phosphoresce but do not fluoresce, the assignment of the lowest triplet state in these molecules has remained doubtful⁴ and somewhat controversial.⁵

We have succeeded in investigating the phosphorescence of these molecules through photoselection techniques. The direction of the moment of the lowest singlet-triplet transition is determined in four nitroaromatic molecules from the relative polarization of their phosphorescence. The results indicate that the lowest triplet is an ($\underline{n}, \underline{n}^*$) in nitroanisole and a (π, π^*) state in 1-nitronaphthalene, 1-nitro-4-methoxynaphthalene and N,N-dimethyl-p-nitroaniline. The more interesting molecule, nitrobenzene, phosphoresces too weakly to be investigated by this method. It is safe to assume, from these results, that the lowest triplet is an ($\underline{n}, \underline{n}^*$) state in nitrobenzene and nonconjugatively substituted nitrobenzenes and that it may be a (π, π^*) state in nitroaniline and nitronaphthalenes.

These results will be communicated for publication soon.

A. New Method for Measuring Phosphorescence:

Conventional techniques for measuring phosphorescence of glassy samples usually make use of a Becquerel-type phosphoroscope or a rotating hollow cylinder phosphoroscope. When these devices are employed, the arrangement is such that the direction of the excitation is either at right angles to the direction of observation or at 0° . In the latter case the transparent sample is excited on one face and the emission is observed from the opposite face. There are two important disadvantages for these modes of excitation: (i) The measurement of emission from opaque samples is very difficult and in many cases impossible. (ii) Polarized light tends to become depolarized when it traverses the whole thickness of the sample.

The method described here avoids these disadvantages since it relies on front surface emission without sacrificing the advantages of a phosphoroscope. The excitation light is reflected from a rotating sector which is mirrored on the sample side. (See Fig. 2). Excitation light scattered in the direction of the detector can not enter the detector during the course of excitation because of the obstruction due to the mirror. Half a cycle later a slot in the sector is positioned between the detector and the sample. At this time the undeflected excitation light goes through the slot perpendicular to the axis of observation. Thus the excitation and phosphorescent beams are 180° out of phase with each other and there is minimal overlap between the two beams.

The sector used in our experiments was prepared and mirrored in the Optics Science department of this university. We used a PAR HR-8 Lock-in Amplifier to detect the emission at the reference

frequency of the rotating sector.

We are in the process of writing these results for publication.

S: Sample

D: Detector

R: Rotating sector

E: Excitation beam

P: Phosphorescent beam

Figure 2

Footnotes

1. S. K. Lower and M. A. El-Sayed, Chem. Rev., 66, 199 (1966).
2. L. Goodman and V. G. Krishna, Rev. Mod. Phys., 35, 541 (1963).
3. H. P. Stephenson, J. Chem. Phys., 22, 1077 (1954).
4. S. P. McGlynn, T. Azumi and M. Kinoshita, Molecular Spectroscopy of the Triplet State (Prentice-Hall, 1969).
5. J. N. Murrell, The Theory of Electronic Spectra of Organic Molecules (Wiley and Sons, 1963) p293