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SOLID-MATRIX LUMINESCENCE ANALYSIS

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Summary

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New interaction models were developed for the effects of moisture on the room-temperature fluorescence (RTF) and room-temperature phosphorescence (RTP) of compounds adsorbed on filter paper. The models described both dynamic and matrix quenching phenomena for the moisture quenching, and they also related the Young's modulus of filter paper to the quenching of a phosphor adsorbed on moist filter paper.

A detailed comparison was made between the photophysical parameters for lumiphors in solution and on solid matrices. Several important relationships and equations were derived. For example, the results showed that for some of the compounds investigated solid-matrix luminescence has greater analytical potential than solution luminescence. Also, the solid-matrix systems investigated to date fit into one of two categories depending on how the intersystem crossing rate constants change with temperature.

The first detailed investigation was carried out on the effects of heavy atoms on the photophysical parameters in solid-matrix luminescence. Several important conclusions were made. As an example, with some heavy atoms, the maximum solid-matrix phosphorescence quantum yield was obtained at room temperature, and there was no need to use low temperature to obtain a strong phosphorescence signal. Several other photophysical aspects were investigated. By studying the solid-matrix luminescence properties of phosphors adsorbed on sodium acetate and deuterated sodium acetate, a detailed interaction model was developed for the anion of p-aminobenzoic acid adsorbed on sodium acetate. In other experiments, it was shown that the energy-gap law was applicable to solid-matrix luminescence. Also, deuterated phenanthrene and undeuterated phenanthrene were used to study the nonradiative transition of the excited triplet state of the adsorbed phosphors.

The heat capacities of several solid matrices were obtained as a function of temperature and related to the vibrational coupling of the solid matrix with the phosphor. In addition, a detailed photophysical study was performed on the hydrolysis products of benzo(a)pyrene-DNA adducts. Also, an analytical method was developed for the characterization and determination of tetrols in human lung fractions.

In other experiments, work was initiated on the formation of room temperature glasses with glucose and trehalose. It is possible to obtain strong RTF and RTP signals from a variety of lumiphors dissolved in these glasses. Also, work has begun for the development of an oxygen sensor by measuring the RTP quenching of triphenylene on filter paper.

A. Introduction

In this report, the major results and conclusions of the research over the last two years and five months will be considered. The report discusses the physicochemical interactions discovered that are important for solid-matrix luminescence (SML), and the development of new interaction models which are very useful for the understanding the phenomena that are relevant for SML. In addition, some new analytical methodology and applications are discussed.

B. Models for Moisture Quenching of Solid-Matrix Luminescence on Filter Paper

In previous DOE reports, some consideration was given to the effects of moisture on the room-temperature fluorescence (RTF) and room-temperature phosphorescence (RTP) of compounds adsorbed on silica gel and filter paper. Under this DOE funding period, several important advances were made in understanding the effects of moisture on the SML of lumiphors adsorbed on filter paper. Because filter paper is the most widely used solid matrix in solid-matrix phosphorescence (SMP) research and applications, the recent advances in this work are important for the future implementation of SMP.

The SLM intensities and phosphorescence lifetimes of 4-phenylphenol and 2-phenylphenol adsorbed on filter paper without salt or with either NaCl, NaBr, or NaI were obtained over a wide range of relative humidities in a nitrogen atmosphere (1). The solid-matrix fluorescence intensities showed very little dependence on relative humidity, whereas the SMP intensities were highly dependent on the magnitude of the relative humidity. Surprisingly, the phosphorescence lifetimes were not affected much by relative humidity. The solid-matrix RTP results were interpreted with static and dynamic quenching models. These models showed that moisture did not diffuse readily to the phosphors, and the complex cellulose network protected the phosphors from moisture which helped to minimize dynamic quenching. The decreases in the phosphorescence intensities due to moisture adsorption were attributed to the changes in the Young's modulus of filter paper as the humidity increased. A new concept was developed from the results obtained from the quenching of the RTP signals. Because the solid matrix participated in the quenching process, due to the changes in the modulus of filter paper, the terminology "matrix quenching" should be used instead of static quenching. Static quenching is more properly reserved for solution quenching phenomena. Matrix quenching is the phenomenon whereby changes in the bonding characteristics of the three-dimensional solid matrix are altered, and the alterations in the bonding in the solid matrix cause a change in the RTP intensity.

To probe the phenomena responsible for RTP quenching additional work was performed to elucidate the effects of moisture on the RTP intensities and lifetimes of phosphors adsorbed on filter paper (2). The RTP properties of 4-phenylphenol, protonated benzo(f)quinoline, and two tetrol isomers (hydrolysis products of benzo[a]pyrene-DNA adducts) adsorbed on filter paper were determined as a function of adsorbed moisture content. As in previous work, the SMP intensity ratios behaved very differently than the phosphorescence lifetime ratios over a wide range of wt% adsorbed moisture. The changes in phosphorescence intensity ratios and lifetime ratios were related to regions before the monolayer coverage of water and beyond monolayer coverage of water on filter paper. An equation was developed that describes the changes in the phosphorescence intensity ratio as a function of phosphorescence lifetime ratio and an exponential expression that includes the wt% of adsorbed moisture. This equation is important because it considers both dynamic and solid-matrix quenching of phosphorescence by adsorbed moisture. The changes in RTP lifetimes were readily related to wt% adsorbed moisture with a simple dynamic quenching equation. The importance of this particular work is that it demonstrated more definitively that dynamic quenching was minimal, but matrix quenching was substantial after a certain amount of moisture was adsorbed by filter paper. In addition, the equations developed are very useful in predicting the trends of dynamic and matrix RTP quenching by moisture for phosphors adsorbed on filter paper.

The effects due to moisture quenching of solid-matrix RTP were explored even further by obtaining Young's modulus ratios of dry to wet paper as a function of adsorbed moisture content for filter paper samples with several different types of salt adsorbed on filter paper (3). In general, the Young's modulus of filter paper can be considered as a measure of the rigidity of filter paper. The Young's modulus ratios were correlated with the RTP intensities and lifetimes of several phosphors adsorbed on filter paper samples using a theory for the Young's modulus of paper and solid-matrix quenching concepts. In our work, filter paper was considered a hydrogen-bond-dominated solid. In other words, the hydrogen bonding network in filter paper determines the properties of filter paper and the adsorption of moisture alters the hydrogen bonding network of the paper. Thus, the modulus of the paper would be diminished with the adsorption of moisture. It was found that the RTP intensity ratios changed much more dramatically than the RTP lifetime ratios both with increasing moisture uptake on the filter paper and with decreasing modulus of the filter paper samples. Correlations were developed between the ratio of the RTP intensities to the RTP lifetimes and the ratio of the modulus of wet to the modulus of dry filter paper. One of the most important findings from this work was that the filter paper matrix participated in the quenching of the RTP signals. For example, water does not have to interact directly with the phosphor to cause major quenching of the RTP intensity. As a result of the alterations in the hydrogen bonding network in the amorphous regions of filter paper, due to moisture adsorption, the filter paper becomes less rigid. Thus, the vibrational activity in the amorphous regions of wet filter paper would be more active compared to the same amorphous region of dry filter paper. Recent experimental results from our work indicate that the spectral changes in the near-infrared spectra of moist filter paper can be correlated with the modulus data from moist paper. This indicates that it may not be necessary to acquire modulus data for moist filter paper in the future.

The results and conclusions from the modulus data form the basis of a unique SMP interaction model by using the effects of moisture on filter paper and the structural modifications of filter paper to describe RTP quenching. To date, we have obtained the most detailed information on the interactions related to SMP moisture quenching on filter paper. The model developed should have considerable application for the interpretation of solid-matrix RTP quenching data.

C. Comparison of Photophysical Parameters in Solution and on Solid Matrices

Because there was previously no major work done on comparing solution and SML parameters, we compared a large number of these parameters obtained under earlier DOE grants and new solid-matrix data obtained under the present DOE grant for several lumiphors adsorbed on a number of solid matrices (4). Comparisons were made for both room-temperature and low-temperature fluorescence and phosphorescence quantum yields, fluorescence and phosphorescence lifetimes, and a variety of photophysical rate constants. The comparisons revealed that SML can give greater fluorescence and phosphorescence quantum yields in many cases at room temperature, compared to the corresponding solution quantum yields at low temperature. The detailed comparisons of fluorescence and phosphorescence lifetimes and photophysical rate constants for the lumiphors adsorbed on solid matrices and in solutions revealed new insights into the differences between SML and solution luminescence. In most cases, the rate constants for fluorescence (k_f) and the rate constants for phosphorescence (k_p) were larger at room temperature with a solid matrix than with ethanol at 77 K. The previous results for the k_f and k_p values imply that SML has greater analytical potential than solution luminescence for the compounds investigated. However, for the triplet state transitions, in all but one case, the intersystem crossing rate constants for the triplet state to the ground state at room temperature on the solid matrices were larger than the respective rate constants obtained at 77 K with ethanol. This result showed that the nonradiative transition from the triplet state to ground state is more probable at room temperature with a solid matrix. Thus, if this nonradiative transition can be minimized in a solid matrix at room temperature, then room-temperature SMP quantum yield values have the potential of being greater than the low temperature solution quantum yield values. Several aspects of our research are directed to minimize the nonradiative transition from the triplet state to the ground state for a phosphor.

Additional work involved the comparison of the fluorescence-to-phosphorescence quantum yield ratios in SML as a function of temperature (5). An equation that relates the ratio of fluorescence to phosphorescence quantum yields as function of temperature to basic photophysical parameters was developed. The quantum yields were obtained for three compounds on three different solid matrices. Fluorescence quantum yields did not change much with temperature, while phosphorescence quantum yields changed more substantially with temperature. For some of the systems considered, it was possible to show that, as the temperature was lowered, the fluorescence to phosphorescence quantum yield ratio was only a function of the phosphorescence lifetime of the phosphor. However, with the other systems explored, the quantum yield ratio was dependent on both the rate constant of intersystem crossing from the singlet state to the triplet state and the phosphorescence lifetime. The equation developed is important in defining the fundamental parameters that cause the SML quantum yield ratios to change as temperature is lowered. For example, the equation below defines the fluorescence to phosphorescence quantum yield ratio (ϕ_f/ϕ_p) in terms of k_f, k_{is} (rate constant for intersystem crossing), k_p, and k_m (nonradiative rate constant from the triplet state to ground state).

$$\phi_f/\phi_p = [k_f/(k_{is} + k_p)][1/(k_p + k_m)]$$

It can be seen from the above equation that if k_f, k_{is}, and k_p are constant with temperature, then ϕ_f/ϕ_p only changes with k_m. Several SML systems fit into this category. For the situation where k_f and k_p are constant with temperature, then ϕ_f/ϕ_p is a function of k_{is} and k_m. The solid-matrix systems investigated to date fit into one of these two categories depending on how the rate constants change with temperature.

D. Changes in the Photophysical Properties with Heavy Atoms in Solid-Matrix Luminescence

The heavy-atom effect is extensively used in SMP work. However, essentially no work has been done in studying the effects of heavy atoms on the photophysical parameters in SMP. In this work, the fluorescence and phosphorescence quantum yields and fluorescence and phosphorescence lifetimes were obtained for 4-phenylphenol adsorbed on filter paper with either NaCl, NaBr, or NaI at 296 K and 93 K (6). From these data, several photophysical parameters were calculated and compared. Generally, the photophysical data showed that NaI gave the greatest heavy-atom effect. However, NaBr at 93 K showed both the heavy-atom effect and another effect which was particular to NaBr. For 4-phenylphenol with NaI, very little increase occurred for the phosphorescence quantum yield from 296 to 93 K, which showed that almost maximum phosphorescence quantum yield was achieved at room temperature. This is an important conclusion which is most likely applicable to several other phosphors in the presence of heavy atoms. In comparing k_p to k_m for 4-phenylphenol, it was found that k_m also increased in the presence of a heavy atom. Thus, even though the phosphorescence signals were increased significantly with a heavy atom, the nonradiative transition from the triplet state was also enhanced. This is another important conclusion because if means were developed to minimize the nonradiative transition with a heavy atom present, then the SMP signals would be even greater than the ones obtained in this work.

E. A Variety of Photophysical Aspects Important to Solid-Matrix Luminescence

1. Sodium Acetate and Deuterated Sodium Acetate

The phosphorescence properties of the anion of p-aminobenzoic acid, p-hydroxybenzoic acid, and p-aminohippuric acid adsorbed on sodium acetate and deuterated sodium acetate were compared (7). However, emphasis was placed on the phosphorescence properties of p-aminobenzoic acid adsorbed on two different salts. Experiments were performed that showed no hydrogen deuterium exchange reactions occurred between the phosphors investigated and deuterated sodium acetate. The phosphorescence intensities and phosphorescence lifetimes as a function of temperature changed in a different fashion for a given model compound adsorbed on sodium acetate compared to deuterated sodium acetate. The phosphorescence results showed that a small structural difference in the solid matrix resulted in major changes in the phosphorescence properties. Comparison of the activation energy in terms of cm^{-1}, calculated from the phosphorescence lifetime data as a function of temperature, with infrared data showed that the CO_2 rocking motion in NaOAc was partly responsible for the nonradiative deactivation of the triplet state of the anion of p-aminobenzoic acid. The results from this work are significant because they deal with the detailed mechanistic aspects of the deactivation of the triplet state of a phosphor adsorbed on a solid matrix at room temperature.

2. Energy-Gap Law

Essentially the energy-gap law states that there is an inverse correlation between the rate constant of a nonradiative transition and the energy difference between the lowest excited state and the ground state of an organic molecule. Work was conducted to determine if the energy-gap law was applicable to lumiphors adsorbed on solid matrices (8). If it were applicable, then reasonable predictions could be made about which lumiphors would give strong signals on solid matrices. Eleven polycyclic aromatic hydrocarbons were investigated on 10% α-cyclodextrin/NaCl and 30% β-cyclodextrin/NaCl, and their respective fluorescence and phosphorescence lifetimes were obtained. Very good linear trends were obtained for log of the phosphorescence lifetimes versus the triplet energy levels for the polycyclic aromatic hydrocarbons adsorbed on the two solid matrices. In addition, very good linear trends were obtained for the log of the ratio of the phosphorescence lifetime to fluorescence lifetime versus the triplet energy levels. The results are very encouraging, and they essentially confirm that the energy-gap law is applicable to the systems investigated. The data acquired for this part of the research are still being interpreted.

3. Deuterated and Undeuterated Phenanthrene

It is documented in the literature that C-H vibrations in aromatic molecules can be involved in the nonradiative transition from the excited triplet state of a phosphor. To gain insights into the nonradiative transition from the excited triplet state, the effects of temperature on the phosphorescence intensities and phosphorescence lifetimes were acquired for deuterated and undeuterated phenanthrene on several solid matrices (9). These data are still being interpreted, but some important conclusions have been made. The solid matrices employed have a definite influence on the fluorescence and phosphorescence intensities of both the deuterated and undeuterated species. Also, the phosphorescence lifetime data revealed that there was a deactivation process from the triplet state of both the deuterated and undeuterated phenanthrene at room temperature that may be common to both deuterated and undeuterated phenanthrene.

4. Heat Capacities

Heat capacity data were obtained as function of temperature for several solid matrices from the research group of Dr. Julia Boerio-Goates of Brigham Young University. These data are being correlated with the phosphorescence lifetime data acquired from several phosphors adsorbed on solid matrices (10). The data are being interpreted with Einstein and Debye theories of heat capacity, and photophysical theories on the nonradiative transition from the excited triplet state to the ground state. To date, we have related the nonradiative rate constants of the triplet states to the bulk heat capacities of the solid matrices and to the one dimensional heat capacities of the solid matrices calculated from the Einstein and Debye theories. Strong evidence has been found that specific vibrational frequencies in the solid matrix couple with specific vibrational frequencies in the excited triplet state of the phosphor. This coupling mechanism is largely responsible for loss of nonradiative energy from the triplet state. The results from the heat capacity experiments are important because they focus on the fundamental interactions of the triplet state of a phosphor with a solid matrix. Based on the earlier results and the results from the heat capacity experiments, a new form of spectroscopy is being proposed in the DOE renewal proposal. Essentially this will involve exciting the vibrational modes of a phosphor adsorbed on a solid matrix with infrared radiation, and then recording phosphorescence spectrum of the phosphor. The same experiment would be done without excitation of the vibrational modes. More details are given in the renewal proposal.

F. Work with the Hydrolysis Products of Benzo[a]pyrene-DNA Adducts

The hydrolysis products of benzo[a]pyrene-DNA adducts are called tetrols, and these compounds are very important in cancer research. Research with the tetrols was developed via a funded EPA project. However, essentially all of the work discussed about tetrols in this report, was done under DOE funding. One important aspect of this work is that it demonstrates how SML can be applied to a very important problem in cancer research. The luminescence properties and analytical figures of merit were acquired for the tetrols adsorbed in α-, β- and γ-cyclodextrin/NaCl mixtures (11). It was found that 10% α-cyclodextrin/NaCl was a very effective solid matrix for obtaining the luminescence properties of the tetrols. Limits of detection for the tetrols were in the femtomole range. To elucidate the physicochemical interactions of the tetrols with 10% α-cyclodextrin/NaCl, a detailed investigation of the photophysical parameters of the tetrols was carried out (12). The fluorescence and phosphorescence lifetimes and quantum yields were obtained for the tetrols both at room temperature and at low temperature with 10% α-cyclodextrin/NaCl and in solutions. Relatively large changes in the solution fluorescence lifetimes of the tetrols were obtained from room temperature to 77 K. However, very small changes were observed for the fluorescence and phosphorescence lifetimes of the tetrols on 10% α-cyclodextrin/NaCl from room temperature to 93 K. Several photophysical rate constants for various photophysical processes were calculated. Comparisons were made between the room-temperature and low-temperature photophysical parameters. In addition, several approaches were considered for characterizing and identifying the tetrols by their SML properties and solution fluorescence properties. The results of this work form the basis of development of analytical methods for the tetrols adsorbed on solid matrices.

A comprehensive study was undertaken on the effects of heavy-atom salts on the luminescence properties of one of the tetrols adsorbed on several α-cyclodextrin/NaCl mixtures (13). It was shown that $TlNO_3$ and TlF proved to be very useful for enhancing the RTP intensities of the tetrol. Also the composition of the α-CD/salt mixture was important in obtaining the maximum enhancement of the RTP signals. The limit of detection for tetrol adsorbed on α-cyclodextrin:$TlNO_3$:$NaNO_3$ (1:1:8) was 0.38 femtomole/mg. The limit of detection could be lowered even further by additional purification of the solid matrix to decrease the background signal of the solid matrix. To show the use of SMP to an important cancer research problem, SMP was employed to identify and quantitate tetrols derived from the acid hydrolysis of benzo(a)pyrene-DNA adducts from human lung fractions by using the α-cyclodextrin:$TlNO_3$:$NaNO_3$ solid matrix. (14). The samples were provided by Dr. Ainsley Weston of the Environmental Health Sciences Center, Mount Sinai Medical Center in New York. The tetrols were identified by their RTP excitation and emission spectra and RTP lifetimes, and they were determined to be at the femtomole level.

G. New Solid Matrices

With work under an EPA funded project, it was discovered that a phase separation paper (1PS), sold by Whatman, Inc., was very effective in obtaining both RTF and RTP signals from adsorbed lumiphors. In recent work under the DOE project, we have shown that the 1PS paper can be used to directly extract organic compounds from water and the adsorbed compounds can be characterized by SML. More details on this novel approach are given in the renewal proposal.

A new direction for our research is the formation of glasses at room temperature in which the lumiphor is dissolved in either glucose or trehalose. The experimental technique has been almost fully developed under the present DOE project and more details on this new way of obtaining SML are given in the renewal proposal.

H. Oxygen Sensor

Preliminary results have been obtained for the development of an oxygen sensor. Encouraging results have been obtained by measuring the SMP quenching of triphenylene adsorbed on filter paper in the presence of oxygen. One of the main advantages in the approached being used is the simplicity of the methodology. Additional details are given in the renewal proposal.

I. Manuscripts and Presentations

The manuscripts published, in press, in review, or to be submitted in the near future are listed at the end of this report. Several other manuscripts are in preparation. A total of fourteen presentations of the work under this project were given at various meetings by the principal investigator, postdoctoral associate, and graduate students.

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