

Electronic Energy Transfer in Benzophenone Adlayer

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The extent to which energy transfer occurs in electronically excited organic adlayer films on dielectric surfaces is investigated. Migration and subsequent trapping of the energy in the film are observed by pumping the singlet state of an organic adlayer of benzophenone and by monitoring the phosphorescence and fluorescence lifetimes. To observe the effects of adsorption, benzophenone was chosen as the adlayer because the energies of its well characterized n, π^* carbonyl states are remarkably sensitive to solvent interactions. Upon excitation with a nitrogen laser, the perturbation on the electronic states of benzophenone by the substrate caused the emergence of the normally absent fluorescence from the adlayer traps at the interface between the surface of the dielectric substrate and the adlayer. Energy transfer to this interface was observed as a function of film thickness. On the surface of a single crystal of an organic crystal, naphthalene, energy transfer from the adlayer to the substrate was observed, whereas such transfer was not energetically possible with the other dielectric surfaces.

KEY WORDS: Energy transfer; adsorption; dielectric surfaces; benzophenone.

INTRODUCTION

Within the last decade, the photophysics of electronic energy transfer and subsequent trapping of the energy have been subjects of much research. The interest in electronic energy transfer from a spectrally sensitizing film on substrate is the result of the wide variety of its applications. For example, semiconductors upon which such sensitizers are adsorbed have been found to enhance their conductivity, thereby increasing the efficiency of the electrochemical reactions.^(1,2) Extensive studies have been done with adlayers on metal and metal oxide surfaces, whereas studies of electronic structure and surface geometries on dielectric surfaces have been limited. Examples of the latter include the surface photochemistry and fluorescence of organic molecules on

silica,⁽³⁾ the photochemistry of furans on alumina,⁽⁴⁾ and energy transfer of polymethine dyes adsorbed on inert and conductive surfaces.⁽⁵⁾ Work on these topics has been spurred by its importance in such applied areas as catalysis, chromatography, photochemistry of adsorbed molecules, lithography and dye sensitized liquid-junction solar cells.⁽⁶⁾

In these aforementioned studies, the focus has been primarily on the sensitization of the photochemistry. The process of energy transfer within the adlayer film is vitally important to the understanding of sensitized photochemistry. In this note, we report the extent to which energy migration occurs within the adlayer film and subsequent energy transfer to the substrate as a function of film thickness.

Benzophenone has well characterized excited electronic states.⁽⁷⁾ Intersystem crossing is known to be very efficient, with a quantum yield of almost unity. The effects of perturbation on the electronic energies can be observed through the depopulation rates from either the fluorescent or phosphorescent state. Energy migration

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and subsequent trapping within a thick adlayer film of benzophenone are observed on several dielectric surfaces, Al_2O_3 , borosilicate glass, and naphthalene, by fluorescence and phosphorescence lifetime measurements of the adlayer at 77 K. The simplicity in the well-defined electronic states of benzophenone in conjunction with a monochromatic excitation source which results in the sole excitation of the adlayer is the unique feature of this study.

Al_2O_3 and glass were chosen as substrates, since they have been reported to be electronically inert to organic adlayers.⁽⁸⁾ In addition to its inertness, naphthalene was chosen for a surface because the relative magnitude of its energy states to those of benzophenone allow for the possibility of energy transfer from the adlayer to the substrate.

The nitrogen laser used in the study was of sufficient energy to directly excite the benzophenone, but not the naphthalene. For example, the first excited singlet state of naphthalene is π, π^* and the transition from the ground state has a high absorption coefficient, but its energy is higher than that of the nitrogen laser. The lowest triplet state of naphthalene is T_{π, π^*} and the direct excitation is spin forbidden. However, the lowest triplet state of naphthalene is lower than that of benzophenone. Hence, using the nitrogen laser, the only mechanism by which naphthalene can be excited is by energy transfer from benzophenone. If energy transfer does in fact occur from the adlayer to the substrate, the characteristic emission from naphthalene will be distinct and readily identifiable. Finally, naphthalene was chosen as a substrate, because this study in the solid state might provide some additional insight into the photoreduction and quenching of benzophenone in solution, a much studied photochemical process.⁽⁹⁾

PROCEDURE

Benzophenone was subjected to multiple recrystallization from ethanol and zone refined for an equivalent of 300 passes. Benzophenone for the experiments was taken from the center portion of the tube in which the material was zone refined. The adlayer was prepared from a solution of benzophenone in methanol by a procedure similar to that used by Kemnitz *et al.*⁽¹⁰⁾ The methanol solution of the adlayer molecules were dropped on the surface of the substrates and the solvent allowed to evaporate. After the solvent was allowed to evaporate, the benzophenone was annealed on the surface of the substrate by heating the substrate very slowly until the adlayer became transparent and crystalline. The

coverage was determined from the concentration and volume of benzophenone placed on the surface.

The organic substrate, naphthalene, was recrystallized several times and zoned refined for an equivalent of 500 passes. The center section of the zoned refined material was then sealed in a pyrex ampoule under vacuum. Single crystal ingots were grown from the melt by slowly lowering (3 cm/day) the liquid through a temperature gradient in a Bridgeman furnace. Seeds for the single crystal were begun at the bottom of the crystal growing tube which had been made narrow and twisted. In the Bridgeman furnace, only a single seed crystal was allowed to pass through to the bulk of the melt to form a single crystal.

For very thick adlayers, crystals of benzophenone were grown from solution. The resulting thin crystals were placed on a freshly cleaved naphthalene crystal. Upon contact and slight frictional heating, the freezing point at the interface was sufficiently depressed to cause the two crystals to melt. When the resulting crystal was set aside, the melted layer froze. The coverage was estimated from the thickness of the benzophenone crystal.

The samples were then placed in a liquid nitrogen cryostat and a nitrogen laser was used to electronically excite the adlayer. The laser's output was at 337 nm with an average output of 0.55 mJ per 1.2 ns pulse. A scanning 1/4 m monochromator outfitted with 50 μ slits provided sufficient resolution for this work; time-resolved spectra were taken with a computer-interfaced stepper motor. The output of the photomultiplier mounted on the monochromator was monitored with a boxcar averager. The digitized data from the boxcar were analyzed using a spreadsheet program.

RESULTS AND DISCUSSION

In the benzophenone crystal, the lifetimes of lowest triplet state have been well documented. The lowest triplet state at 24,104 cm^{-1} which is an n, π^* state has a lifetime of 3–4 ms at 77 K.⁽⁷⁾ In these studies, the phosphorescent triplet state was pumped via the S^2_{π, π^*} state. The quantum yield for intersystem crossing ($S^2_{\pi, \pi^*} \rightarrow T^1_{n, \pi^*}$) into the triplet manifold is nearly unity, and fluorescence is not observed.

With the nitrogen laser as the excitation source, three possible routes exist for excitation and relaxation in benzophenone. First, optical pumping may directly excite the T^2_{π, π^*} . Second, direct excitation can occur to the T^1_{n, π^*} states. These two routes are spin forbidden. Furthermore attempts to directly excite the T^1_{n, π^*} using a nitrogen pumped turnable dye laser, did not result in

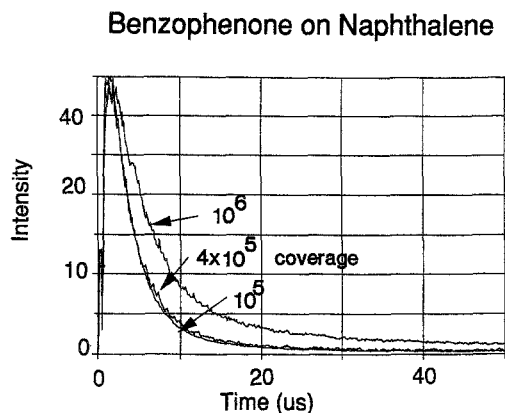


Fig. 1. Typical decays for three coverages of benzophenone on naphthalene.

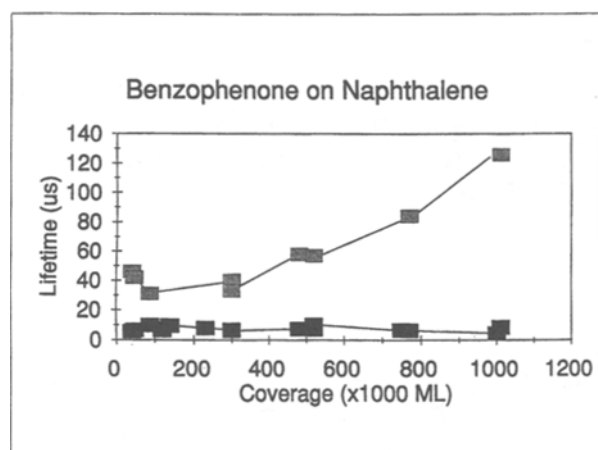


Fig. 2. Emissive lifetimes as a function of coverage for benzophenone on naphthalene single crystals. Upper trace is phosphorescence and the lower, fluorescence.

emission. Third, benzophenone may be optically pumped into the S^1_{n,π^*} state at $26,270\text{ cm}^{-1}$. From there, three routes exist for relaxation: (a) fluorescence may occur directly from the S^1_{n,π^*} state, (b) since a T^2_{π,π^*} state exists at $26,508\text{ cm}^{-1}$ which is nearly resonant with the S^1_{n,π^*} state, only a small solvent shift is sufficient to either raise or depress the energies of the S^1_{n,π^*} and T^2_{π,π^*} states, respectively, such that intersystem crossing to the T^2_{π,π^*} would become energetically allowed; once in the triplet state, internal conversion to the emitting T^1_{n,π^*} can occur, (c) intersystem crossing could occur directly to the emissive T^1_{n,π^*} state, although this route is symmetry forbidden.

If all routes which are forbidden by selection rules are excluded, then only the route last mentioned remains. For the neat single crystal of benzophenone, fluores-

cence is not observed when excited with a nitrogen laser. Since direct intersystem crossing to the emitting triplet is forbidden, phosphorescence from benzophenone is expected to be a result of the only remaining route (see (b) above), $S^1_{n,\pi^*} \rightarrow T^2_{\pi,\pi^*} \rightarrow T^1_{n,\pi^*}$. If, through external perturbation, this relaxation route becomes more or less allowed as reflected in the lifetimes and intensity of the emitting triplet, or the emergence of fluorescence from the S^1_{n,π^*} , then the presence of such an interaction may be assumed.

In all three adlayer-substrate systems, both fluorescence and phosphorescence from benzophenone is observed at all coverages. At low coverages, most of the total emission is fluorescence with a lifetime is $6.5 \pm 2\ \mu\text{s}$ and as mentioned, this emission persists at all coverages. The presence of this fluorescence which is absent in the single crystal of benzophenone indicates that electronic perturbation upon adsorption must cause intersystem crossing to not become the dominant pathway. This may be due to a selective interaction of the surface with the S^1_{n,π^*} or T^2_{π,π^*} , such that the T^2_{π,π^*} state is not able to serve as an intermediate in the intersystem crossing pathway. The observation that the intensity of fluorescence is independent of coverage would indicate that the interface created in the adlayer is the origin of the emission, and the concentration of the interfacial benzophenone molecules is nearly constant. The presence of both fluorescence and phosphorescence in the adlayer is an indication that the energy states of the S^1_{n,π^*} and T^2_{π,π^*} are such that the fluorescence pathway is favored for those molecules proximate to the surface.

At higher coverages, the phosphorescence intensity becomes comparable, and even exceeds that of fluorescence, especially at the higher coverages. That the emission from the nitrogen laser pumped benzophenone does in fact originate from both the S^1_{n,π^*} and the T^1_{n,π^*} states was determined from the time-correlated spectra. The coverage at which a short-lived component in the total phosphorescence is observed differs for the three substrates. The lifetime of this component is coverage dependent, being short at the lower coverages and increasing at the higher coverages. The short-lived phosphorescence most likely is an indication of the presence of external spin-orbit interaction which enhances the coupling between the singlet and the emitting triplet states for the intersystem crossing to occur via the intervening T^2_{π,π^*} state.

Shown in Fig. 1 are typical decays for benzophenone on naphthalene. These decays were analyzed by least-squares regression on a spreadsheet program. Figure 2 shows the lifetimes of the fluorescence and phosphorescence as a function of coverage. The relative

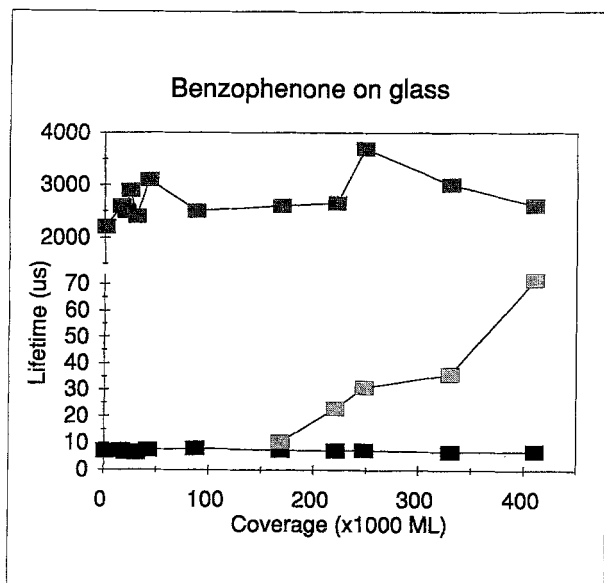


Fig. 3. Lifetimes as a function of coverage for benzophenone on Al₂O₃. Upper traces are for phosphorescence and the lower trace is for fluorescence.

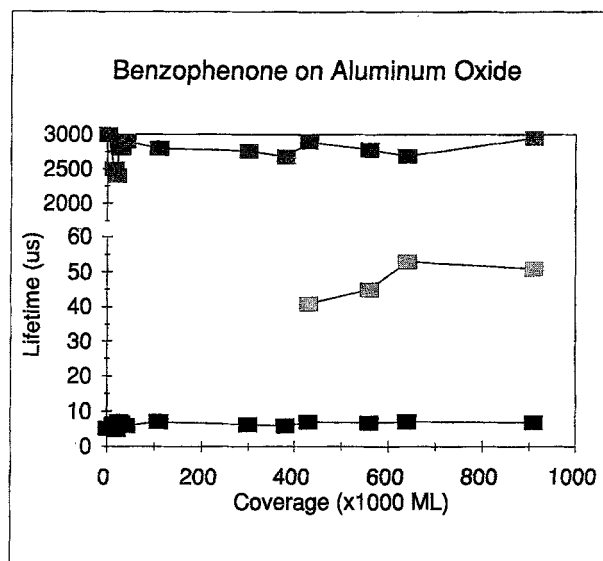


Fig. 4. Lifetimes as a function of coverage for benzophenone on glass. Upper traces are for phosphorescence and the lower trace is for fluorescence.

intensity and lifetime of the phosphorescence are coverage dependent. At coverages greater than approximately 400,000 layers, the lifetimes begin to increase. The single crystal lifetime of 3–4 ms for a single crystal is not observed at coverage up to 1 million. Since the

single crystal limit in the lifetime is not observed, energy migration and transfer can be concluded to be very efficient. The shortened phosphorescence lifetimes which originate from the lowest T^1_{n,π^*} state may be due to energy migration and transfer to naphthalene as evidenced by the presence of phosphorescence from naphthalene. As mentioned above, the two reasons why this emission from naphthalene is due to energy transfer and not from the direct excitation of naphthalene by the nitrogen laser, are first, the nitrogen laser is not energetic enough to pump the lowest singlet state of naphthalene. Second, since the dipole moment matrix element coupling the ground to the lowest triplet is sufficiently small, direct excitation would not be expected. This was verified experimentally.

Figures 3 and 4 show the lifetimes of the benzophenone on Al₂O₃ and glass, respectively, as a function of coverage. On the Al₂O₃ and glass surfaces, benzophenone exhibits single crystal phosphorescence lifetime at all coverages in addition to (a) fluorescence, and (b) a short phosphorescence component which becomes increasingly more prominent at higher coverages. Since this single crystal lifetime for benzophenone is observed for even the lowest coverage on Al₂O₃ and glass, but not on naphthalene, the cause must be the absence of energy transfer from the adlayer to the substrate, a process which effectively competes with radiative relaxation. Previous studies of aromatic ketones adlayers on powdered alumina show definite effects on the electronic state upon adsorption.⁽¹¹⁾ In fact, the optically detected magnetic resonance line width for benzophenone, upon adsorption, has been reported to broaden from 1.3 MHz to nearly 1000 MHz.⁽¹¹⁾ In a study of another aromatic ketone, 4-benzoylpyridine, adsorption on powdered alumina had the effect of lowering the energy of the triplet state by about 250 cm⁻¹.⁽¹²⁾ Hence, it would be reasonable to assume that the adsorption on dielectric surfaces will perturb the electronic states sufficiently to generate adlayer traps from which the relaxation may occur. The degree of perturbation would depend upon the proximity of these molecules to the surface.

For benzophenone on Al₂O₃, the observed shortest-lived emission is fluorescence, as verified by time-resolved spectra. As the adlayer coverage is increased, a short-lived phosphorescence from the T^1_{n,π^*} is observed at approximately 400,000 layers. At these coverages, the emission is predominantly phosphorescence, and its intensity relative to fluorescence increases with coverage. For benzophenone on glass, the onset of the fast phosphorescence occurs at coverages of about 200,000. The increase in the lifetime of the short-lived phosphorescence is more gradual on glass, which may be due to

lack of order on the surface as compared to Al_2O_3 . As is the case of benzophenone on naphthalene, even at the highest coverage, the lifetime of the fast phosphorescence does not reach that of the single crystal. This would again be an indication of the large excitation migration path length, prior to the trapping at the interfacial benzophenone molecules. Considering the lifetime of the phosphorescent state and assuming an average size for the benzophenone molecule, an estimate of the incoherent excitation hopping rate is about 10^{-4} s^{-1} .

In summary, for benzophenone on the three substrates, the effect on the emission lifetimes occurs at about 200,000–400,000 layers. When benzophenone is adsorbed on a dielectric surface, traps are created by benzophenone molecules which are proximate to the surface and when favorable energies exist, energy transfer can occur through the interface. Such information might be useful in determining the optimum thickness for spectral sensitizing films on semiconductors and solar cells.

At first sight, the efficiency of the energy transfer in the adlayer is rather unexpected. In order to substantiate this result, further work along the following lines are being conducted. (a) Energy transfer studies in chemically mixed crystal of naphthalene in benzophenone are being done. Preliminary results indicate a dramatic decrease in the lifetime of benzophenone at roughly 5 mole/mole % concentration of naphthalene in benzophenone. Theoretical models of energy transfer in two and three dimensions are currently being considered. (b) By depositing a thin film of durene, which has energy states higher than either benzophenone or naphthalene, at the interface between the adlayer and substrate, tunneling across a energy barrier is being studied. Preliminary results indicate that tunneling occurs with durene thickness of 10–20 layers, which would confirm the efficiency of the energy transfer process.

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