

Thus, the nature of a supported platinum-tin system is dependent on the particular support used and on the conditions employed in the preparation of the material. The metallic entities in the Pt-Sn/SiO₂ sample consist primarily of bimetallic clusters or alloy crystallites containing substantial amounts of both platinum and tin. This is not true for the Pt-Sn/Al₂O₃ catalyst, which consists essentially of platinum clusters in a very highly dispersed state, the dispersion presumably being enhanced by an interaction with Sn²⁺ at the surface of the alumina.

As indicated in the Introduction, the Pt-Sn/Al₂O₃ catalyst of this investigation is representative of one type of catalyst that is used in the reforming of petroleum fractions. For reforming, alumina is preferred over silica as a support because of its acidic properties and because it gives higher platinum dispersion. High metal dispersion is a desirable feature in a reforming catalyst.¹

The observation that platinum is more highly dispersed on alumina when tin is present is clearly of interest in this regard.

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Effect of Adsorption on Thin Silver Films on the Phosphorescent Triplet State of 4-Benzoylpyridine

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The effect of adsorption on the phosphorescent triplet state in an aromatic ketone, 4-benzoylpyridine, is observed. The silver surface was prepared by thin-film deposition techniques on optically flat sapphire substrates. The effect of such an adsorption was observed as a function of the Ag film thickness by a method in which the coupling of the magnetic spin sublevels in the phosphorescent triplet state was optically detected.

Introduction

In the past several years, considerable interest has been directed to the study of electronic energy transfer from luminescent molecules adsorbed on metal surfaces. The initial experimental work on the effects of distance to the metal surface upon the luminescence behavior of organic dyes was done by Kuhn and Drexhage,¹ who used the Langmuir-Blodgett² technique in which fatty acid layers separated the emitting molecules from the metal surface. The theoretical interpretation of these results was given by the elegant works of Chance, Prock, and Silbey³ and others.^{4,5}

Experimental Details

The metal surfaces were generated by thin-film deposition onto an optically flat piece of sapphire, and the thickness of the film was controlled with a shutter and monitored with a thickness gauge. 4-Benzoylpyridine, 4-BZP, was then vacuum deposited onto a cold thin-film surface. A constant amount of 4-BZP was used for the vacuum deposition, and the adlayer thickness was estimated to be between 30 and 50 monolayers.

The sapphire substrate was clipped onto the end of a stainless steel coaxial cable in such a way that the metal film could also be used as a conductor of the microwave energy necessary to couple the zero-field sublevels of the emitting triplet state. The entire assembly was then immersed in a liquid helium bath, and the adsorbed molecules were optically pumped with a well-filtered but broad-banded light source. The surface emission was observed with a monochromator equipped with a photomultiplier. Simultaneous to the optical pumping of the triplet state, microwave energy sufficient to couple the zero-field sublevels was impinged upon the molecules via the conductive silver thin-film surface. The zero-field energies were observed by adiabatic rapid passage

through the zero-field transitions.⁶ In some cases, the detection was accomplished by slowly sweeping the microwave frequency through the transition while the power was amplitude-modulated at a frequency appropriate to cause the molecular luminescence to return to steady state during the off-time of the perturbing microwave power. Simultaneously, the phosphorescence emission intensity was detected by a lock-in amplifier. Total phosphorescence rate constants and relative radiative rates were determined by the adiabatic rapid passage technique.⁶

Results and Discussion

The electron spin Hamiltonian in the absence of an external magnetic field can be expressed as

$$H = D(S_z^2 - \frac{1}{3}S^2) + E(S_x^2 - S_y^2)$$

in terms of the principal axes that diagonalize the zero-field tensor. The variation in the D and E values as a function of the Ag film thickness is shown in Table I.

At short distances, such as those encountered here, in which the emitting chromophore is estimated to be approximately 6 Å from the surface, spin-orbit interaction with the surface is expected to be large. That the zero-field energies do vary with the film thickness indicates that the interaction is over many layers of Ag atoms. It should be noted that the D and E values for 4,4'-di-

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TABLE I: Triplet-State Zero-Field Parameters ($\pm 0.0005 \text{ cm}^{-1}$), Total Phosphorescence Rate Constants from the Individual Sublevels ($\pm 5\%$), Relative Radiative Rates ($\pm 10\%$), and the State Energies ($\pm 5\%$) for 4-Benzoylpyridine Adsorbed on Varying Thickness of the Silver Thin Film Measured at 1.4 K^a

film thickness, Å	zero-field splittings, cm^{-1}		decay rate constants, s^{-1}			rel radiative rates			state energy, cm^{-1}
	<i>D</i>	<i>E</i>	k_z	k_y	k_x	k_z^r	k_y^r	k_x^r	
0	-0.134	0.0155	650	76	39	60	1	1.5	23 710
30	-0.132	0.0148	675	410	24	5	1	2	23 640
60	-0.130	0.0146	760	490	57	8	1	2	23 630
120	-0.128	0.0139	790	570	70	15	1	2	23 600
270	-0.120	0.0080	810	650	80	17	1	1.7	23 600
2000	-0.120	0.0080	1100	880	80	18	1	1	23 580
4000	-0.119	0.0080	1400	930	80	20	1	0.75	23 450

^aThe data shown for 0 film thickness are for the neat single crystal. The signs of the zero-field splittings were extrapolated from those for benzophenone.

iodobenzophenone are -0.0888 and -0.0079 cm^{-1} , respectively. The same values for 4,4'-dichlorobenzophenone are -0.1449 and $+0.0246$, and -0.1581 and 0.0211 for benzophenone.⁷

The total phosphorescence rate constants for each of the magnetic sublevels are given also as a function of the silver film thickness in Table I. Also shown are the relative radiative rates. Two possible causes may be postulated for the observed enhancement in the rates as a function of the increase in the thin metal film. The first is that the radiative rate is increased due to the proximity of the surface to the emitter, causing an efficient spin-orbit coupling of the molecules of the adlayer with the silver atoms in the first few layers of the film. This cause is supported by the observed increase in the relative radiative rate along the C=O, or the *z*, direction as a function of the film thickness. Note that the relative radiative rates for the *z* spin sublevel parallel the total rate constants along the same spin axis. A secondary contribution to the enhancements in the rate constant as a function of the film thickness might be attributed to nonradiative processes. Since the transfer from an emitting dipole to a thin film or to modes localized at the surface occurs at a smaller inverse power dependence than for bulk metal surfaces,³ the contribution of the varying power dependence terms may be the cause of the observed enhancement. The surface plasmon resonance for silver surfaces has been reported to be near $28\,570 \text{ cm}^{-1}$, which is reasonably close to the 0,0 energy of the emitting 4-BZP moiety. Enhancements in the nonradiative energy transfer would be predicted as the molecular electronic energy is relatively close to the surface plasmon energy.³

Also shown in Table I is the variation in the triplet-state energy as calculated from the 0,0 vibronic origin in the phosphorescence

spectra taken with a high-resolution spectrometer. The lowering of the triplet-state energy with increasing film thickness is anomalous, since both spin-orbit coupling and surface plasmon resonance should cause only small changes in the energy levels. What might seem reasonable is that the molecular distortion of the triplet state is enhanced by the thicker metal film, perhaps due to the larger numbers of interactive spheres of Ag atoms in the thicker films.

Conclusion

Our preliminary results indicate that important information can be obtained by the method of optical detection of the magnetic spin states in molecules adsorbed on thin-film surfaces. Further work along the lines of using either the Langmuir-Blodgett fatty acid monolayer assembly technique or the deposition of inert gas spacers to vary the distance of the molecule to the surface is currently underway. In addition, the observed increase in the relative radiative rate constants along the *z* spin sublevel, which is parallel to the C=O axis, might be an indication of the strength of the interaction of the oxygen and the silver atoms on the surface. Such an interaction might cause an alignment of the adlayer molecules that could be observed by photoselection.

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