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# Low-Temperature Fluorescence of the Pentafluorophenol Radical Cation

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Absorption and laser-induced fluorescence spectra of the pentafluorophenol radical cation are reported and vibrationally analyzed. The fluorescence exhibits a lifetime of  $32 \pm 2$  ns, and its origin at  $22407 \text{ cm}^{-1}$  is in good agreement with the value derived from photoelectron spectra. The upper state vibrational structure shows a very strong similarity to the  $\text{C}_6\text{F}_6^+$  cation. Unlike  $\text{C}_6\text{F}_6^+$  or  $\text{C}_6\text{F}_5\text{CH}_3^+$  the ground-state vibrational levels do not show any evidence of perturbation due to the proximity of the low-lying  $\tilde{\text{A}}$  state.

## Introduction

Since the initial discovery that the hexafluorobenzene cation and several, related ions are highly fluorescent<sup>1</sup> their spectra have been extensively studied in a number of laboratories.<sup>2-4</sup> Particularly interesting among these compounds are hexafluorobenzene<sup>5</sup> and the symmetrically substituted  $D_{3h}$ ,  $\text{C}_6\text{H}_3\text{F}_3^+$  and  $\text{C}_6\text{H}_3\text{Cl}_3^+$  species.<sup>6-9</sup> These ions have a doubly degenerate ground electronic state and their emission spectra are very clear examples of the effects of Jahn-Teller distortion.<sup>10</sup> Extensive information about these species was obtained from low-temperature Ne matrix studies using techniques recently developed in our laboratory.<sup>11,12</sup> The excitation spectra of the Jahn-Teller molecules show a very regular vibrational structure for the nondegenerate excited state with prominent activity of the doubly degenerate Jahn-Teller modes. The resolved emission spectra of these ions, on the other hand, display a seemingly quite irregular structure for the ground electronic state. This perturbed nature of the spectra is the result of Jahn-Teller distortion and, when the theoretical models including mode mixing effects are used,<sup>13</sup> not only the vibrational intervals but also transition intensities can be predicted in detail.<sup>5,14</sup>

Quite recently we have observed that several substituents can be introduced into the fluorobenzene cations without quenching the fluorescence.<sup>15</sup> Thus several compounds containing  $\text{CH}_3$  and  $\text{CF}_3$  groups form strongly fluorescent cations. In the present manuscript we examine the introduction of a hydroxy group and report for the first time absorption and laser excited fluorescence spectra of the pentafluorophenol radical cation. While this manuscript was in preparation, this compound has also been the subject of a recent gas-phase photoelectron and emission study.<sup>16</sup>

## Experimental Section

Experimental techniques employed in this work were quite analogous to those used in our previous studies.<sup>11,12</sup> Dilute mixtures of the parent fluorobenzene were prepared (1:2000-1:20000) and deposited on a Pt mirror cooled to 4 K. The deposits were subsequently photolyzed by 1216-Å radiation for 5-30 s. Absorption spectra were obtained with a tungsten filament background source by use of a waveguide absorption technique.<sup>12</sup> Fluorescence was excited by a  $\text{N}_2$  laser pumped dye laser and resolved in a SPEX 14018 double monochromator.

A pentafluorophenol sample was obtained from Aldrich and, except for several freeze-pump-thaw cycles, used without purification. A deuterated sample was prepared by an exchange with excess of  $\text{D}_2\text{O}$ .

TABLE I:  $\text{C}_6\text{F}_5\text{OH}^+$  Excitation Spectrum in Solid Ne ( $\text{cm}^{-1}$ )

$\bar{\nu}$	$\Delta\bar{\nu}$	assignment	$\bar{\nu}$	$\Delta\bar{\nu}$	assignment
22 403		origin	23 533	1130	$2\nu_{17} + \nu_{21}$
22 671	268	$\nu_{21}$	23 555	1152	$\nu_{16} + \nu_a$
22 720	317	$\nu_{19}$	23 589	1186	$\nu_{10}$
22 833	430	$\nu_{17}$	23 638	1235	$\nu_{17} + 3\nu_{21}$
22 935	532	$2\nu_{21}$	23 647	1244	$\nu_{16} + \nu_{17} + \nu_{21}$
22 946	543	$\nu_{16}$	23 696	1293	$3\nu_{17}$
23 014	611	$\nu_a$	23 755	1352	$\nu_{16} + 3\nu_{21}$
23 043	640		23 782	1359	$2\nu_{16} + \nu_{21}$
23 099	696	$\nu_{17} + \nu_{21}$	23 800	1397	$2\nu_{17} + 2\nu_{21}$
23 202	799	$3\nu_{21}$	23 810	1407	$\nu_{16} + 2\nu_{17}$
23 215	812	$\nu_{16} + \nu_{21}$	23 905	1502	$\nu_{17} + 4\nu_{21}$
23 265	862	$2\nu_{17}$	23 914	1511	$\nu_{16} + \nu_{17} + 2\nu_{21}$
23 371	968	$\nu_{17} + 2\nu_{21}$	23 923	1520	$2\nu_{16} + \nu_{17}$
23 380	977	$\nu_{16} + \nu_{17}$	23 951	1548	$\nu_2$
23 474	1071	$4\nu_{21}$	24 076	1673	$\nu_{16} + 2\nu_{17} + \nu_{21}$
23 485	1082	$\nu_{16} + 2\nu_{21}$	24 214	1811	$\nu_2 + \nu_{21}$
23 492	1089	$2\nu_{16}$			

## Results

**Sample Photolysis and Identification of the Product.** Unphotolyzed samples of pentafluorophenol in a neon matrix exhibit no absorptions in the visible or near ultraviolet. Following photolysis at 1216-Å radiation, a very strong, structured absorption appears with origin at  $22407 \text{ cm}^{-1}$ . Photolysis duration of 10 s is sufficient to produce

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\* Summer student.

TABLE II: Vibrational Frequencies of Several Substituted Benzenes and Their Cations ( $\text{cm}^{-1}$ )

	$\text{C}_6\text{F}_6$			$\text{C}_6\text{F}_5\text{OH}$			$\text{C}_6\text{F}_5\text{CH}_3$			$\text{C}_6\text{F}_5\text{H}$		
	P <sup>a</sup>	X <sup>+</sup>	B <sup>+</sup>	P	X <sup>+</sup>	B <sup>+</sup>	P	X <sup>+</sup>	B <sup>+</sup>	P	X <sup>+</sup>	B <sup>+</sup>
$\nu_1$	1494		1520	1540	1489	$a_{1g}^b$	1525			1514	1533?	1459
$\nu_2$	559	554	540	560	558	543	552		527	578	595	566
						$e_{2g}^b$						
$\nu_{15}$	1659	(1650) <sup>c</sup>	1552	1660	1656	1548	1657		1546	1648	1595	1547
$\nu_{16}$	1159	(1150) <sup>c</sup>	1190	1151	1182	1186	1155			1075	902?	1335
$\nu_{17}$	445	(429) <sup>c</sup>	426	444	431	430	443		426	470	460	456
$\nu_{18}$	272	(260) <sup>c</sup>	265	268	266	268	268	266	268	272	278	268

<sup>a</sup> P stands for parent compound, X<sup>+</sup> for ground state of the cation, and B<sup>+</sup> for the  $\tilde{B}$  state of the cation. <sup>b</sup> Symmetry and mode designations are appropriate only for the  $\text{C}_6\text{F}_6$  species. Correspondence for  $\text{C}_6\text{F}_5\text{OH}$  numbering can be found in Table III. The correspondence for  $C_{2v}$  numbering for  $\text{C}_6\text{F}_5\text{CH}_3$  and  $\text{C}_6\text{F}_5\text{H}$  is  $C_{2v}:D_{6h} = 3:1, 8:2, 2:3, 6:10, 9:17, 11:18$ . <sup>c</sup> Deperturbed values.

$\approx 100\%$  absorption at the strongest, 0-0 band. This highly efficient formation is characteristic of photoionization processes in the matrix.<sup>9</sup> Photofragmentation is generally more hindered by the solid cage effects which result in low quantum efficiency. The position of the origin band is in reasonable agreement with the energy difference between the first and third bands in the photoelectron spectrum of the parent compound<sup>16</sup> of  $\approx 22\,130\text{ cm}^{-1}$  and remarkably close to the 0-0 band at  $22\,410\text{ cm}^{-1}$  in gas-phase emission.<sup>16</sup> We therefore assign the observed spectrum to the pentafluorophenol radical cation, and will show later that this is unambiguously confirmed by the vibrational structure.

Excitation of the sample with a laser tuned to one of the absorption bands produces a strong fluorescence easily observable by eye. The fluorescence exhibits a lifetime of  $32 \pm 2\text{ ns}$ . An excitation spectrum obtained by monitoring the intensity of the undispersed sample fluorescence and scanning the laser again shows an intense origin band at  $22\,407\text{ cm}^{-1}$  and in general mimics the absorption profile. This confirms that the fluorescing molecule is identical with the species responsible for the absorption spectrum.

**Vibrational Structure of the Excitation Spectrum and Comparison with  $\text{C}_6\text{F}_6^+$ .** The individual vibronic bands in absorption are relatively broad, with fwhm of  $\approx 20\text{ cm}^{-1}$ . This width is clearly due to inhomogeneous broadening. If only emission of a single "site" is selected from the broadened line width and the origin band fluorescence at  $22\,407\text{ cm}^{-1}$  is monitored with  $\approx 1\text{-cm}^{-1}$  bandpass, the excitation spectrum shown in Figure 1b is obtained. The transitions are now less than  $2\text{-}3\text{ cm}^{-1}$  wide, limited mainly by the instrumental resolution and the line width of the excitation source. The observed vibronic bands in the excitation spectrum are listed in Table I with their proposed assignments.

Even if one assumes a planar configuration for the OH group, the  $\text{C}_6\text{F}_5\text{OH}^+$  molecule has only a plane of symmetry and belong thus to the  $C_s$  group. In view of this, there will be  $10a''$  and  $23a'$  vibrational modes, with all of the latter being formally allowed in the electronic transition. In view of this low symmetry, many vibrational modes may be strongly mixed and one might expect a rather complex spectrum. If, on the other hand, the proton of the OH group is disregarded, an effective  $C_{2v}$  symmetry can be expected for an electronic transition involving mainly the phenyl ring. One may note further that the mass of OH group is similar to that of a fluorine atom and is bound to the ring by only a slightly weaker bond. One might therefore expect some similarity to  $\text{C}_6\text{F}_6^+$  in the vibrational structure of the spectra.

Indeed, except for an overall shift of  $\approx 850\text{ cm}^{-1}$  to higher energy, the excitation spectrum could at first sight be mistaken for that<sup>5</sup> of  $\text{C}_6\text{F}_6^+$  which we show for comparison in Figure 1a. Most of the bands in the spectrum fit into

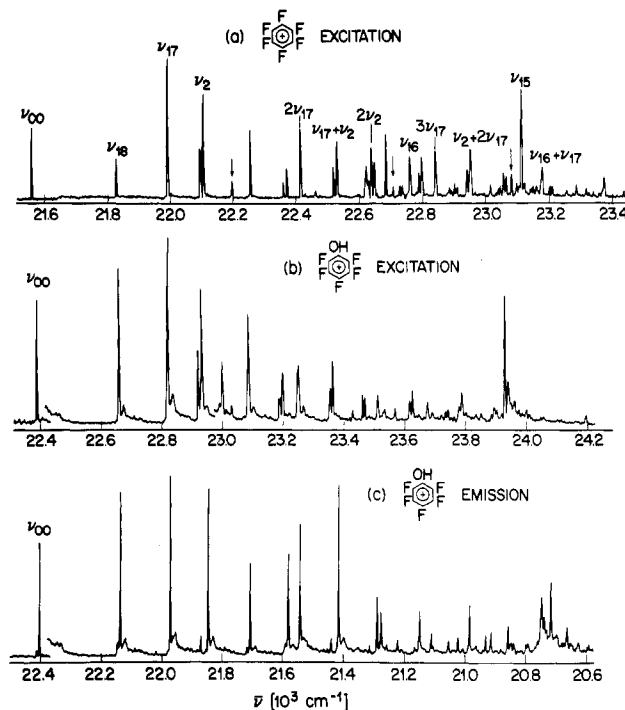


Figure 1. (a) Laser excitation spectrum of the hexafluorobenzene radical cation. The spectrum was not corrected for variation of laser power. (b) Laser excitation spectrum of the pentafluorophenol radical cation. This is a composite of scans over the range of several laser dyes. The 0-0 fluorescence intensity at  $22\,400\text{ cm}^{-1}$  was monitored. (c) Resolved emission spectrum of the pentafluorophenol cation. The 0-0 band was recorded in a separate scan with excitation of the  $21_0^1$  band at  $22\,671\text{ cm}^{-1}$ .

a remarkably regular and harmonic pattern involving the ring C-C stretching vibration at  $1548\text{ cm}^{-1}$  and three low-frequency vibrations of  $268, 430$  and  $543\text{ cm}^{-1}$ . These numbers can be compared with the corresponding hexafluorobenzene intervals of  $1552, 265, 426$ , and  $540\text{ cm}^{-1}$ . Furthermore, even the intensity distribution in the spectrum and the relative activity of the individual modes are quite similar. The  $540\text{-cm}^{-1}$  vibration of  $\text{C}_6\text{F}_6^+$  was assigned to the totally symmetric  $\nu_2'$  ring "breathing" vibration of  $a_g$  symmetry. The remaining intervals were assigned to nontotally symmetric  $e_{2g}$  vibrations,  $\nu_{15}$ , the C=C stretch, and two low-frequency in-plane deformation vibrations,  $\nu_{17}$  and  $\nu_{18}$ . We give a partial listing of the observed absorption-excitation bands and their assignments in Table I. For ease in comparison we use the  $C_s$  mode numbering which was used in interpreting the vibrational spectra of the parent compound. In Table II we summarize the  $a_g$  and  $e_{2g}$  vibrational fundamentals of the  $\text{C}_6\text{F}_6^+$  species and compare them with the corresponding

TABLE III:  $C_6F_5OH^+$  Emission in Solid Ne ( $cm^{-1}$ )

$\bar{\nu}$	$\Delta\bar{\nu}$	assignment <sup>a</sup>	$\bar{\nu}$	$\Delta\bar{\nu}$	assignment
22 403		origin	21 110	1293	$3\nu_{17}$
22 137	266	$\nu_{21}$ (18)	21 053	1350	$\nu_7$
22 020	383	$\nu_{19}$	21 022	1381	$2\nu_{16} + \nu_{21}$
21 972	431	$\nu_{17}$ (17)	20 984	1419	$\nu_{16} + 2\nu_{17}$
21 870	533	$2\nu_{21}$	20 931	1472	$\nu_6$
21 845	558	$\nu_{16}$ (2)	20 914	1489	$\nu_5$ (1)
21 705	698	$\nu_{17} + \nu_{21}$	20 858	1545	$2\nu_{16} + \nu_{17}$
21 579	824	$\nu_{16} + \nu_{21}$	20 792	1611	$\nu_{10} + \nu_{17}$
21 540	863	$2\nu_{17}$	20 747	1656	$\nu_3$ (15)
21 439	964	$\nu_{17} + 2\nu_{21}$	20 715	1688	$\nu_{21}, \nu_{16} + 2\nu_{17} + \nu_{21}$
21 414	989	$\nu_{16} + \nu_{17}$	20 663	1740	
21 312	1091	$\nu_{16} + 2\nu_{21}$	20 481	1922	$\nu_3 + \nu_{21}$
21 288	1115	$2\nu_{16}$	20 448	1955	$\nu_2 + \nu_{21}$
21 275	1128	$2\nu_{17} + \nu_{21}$	20 318	2085	$\nu_3 + \nu_{17}$
21 256	1147	$\nu_{11}$	20 285	2118	
21 221	1182	$\nu_{10}$ (16)	20 236	2167	
21 148	1255	$\nu_{16} + \nu_{17} + \nu_{21}$	20 158	2245	$\nu_2 + \nu_{16}$

<sup>a</sup> Numbers in parentheses refer to corresponding  $a_{1g}$  or  $e_{2g}$  mode designation in  $D_{6h}$  symmetry.

modes of  $C_6F_5OH^+$ , as well as with those of  $C_6F_5CH_3^+$  and  $C_6F_5H^+$ .<sup>19</sup>

The appearance of these nontotally symmetric  $e_{2g}$  vibrations in the  $C_6F_6^+$  excitation spectrum was attributed to the distortion of the doubly degenerate ground state due to Jahn–Teller effect. The close resemblance of the present excitation spectrum to that of hexafluorobenzene suggests very similar geometries for the two ions. In other words, the geometry of the Jahn–Teller distorted  $\tilde{X}^2E_{1g}$  ground state of  $C_6F_6^+$  must be very similar to the ground state of  $C_6F_5OH^+$ , and vice versa.

The similarity between the two spectra goes beyond the strongest bands. In the  $C_6F_6^+$  spectrum a weaker band 631  $cm^{-1}$  above the origin was observed, which could be attributed neither to an  $a_g$  nor to an  $e_{2g}$  mode. We have denoted it  $\nu_a$  and suggested that an overtone of some out-of-plane vibration might be involved. The analogues  $C_6F_5OH^+$  vibration occurs at 611  $cm^{-1}$ , again with comparable relative intensity. Also the  $\nu_{16}$  ( $e_{2g}$ ) mode which appeared weakly in the spectrum of  $C_6F_6^+$  at 1190  $cm^{-1}$  is present in the  $C_6F_5OH^+$  spectra at 1186  $cm^{-1}$ .

Several additional, extremely weak bands appear in the spectrum of  $C_6F_5OH^+$ , which have no counterpart in the hexafluoro compound. These can be readily attributed to other in-plane fundamentals, which appear weakly due to the lowering of the symmetry caused by introduction of the OH group.

**Resolved Fluorescence Spectra.** In our study of  $C_6F_6^+$  we have observed that the ground-state vibrational structure appears to be quite different from that of the excited state, with the vibrational spacings very irregular. The intensity distribution in the emission spectrum is also quite different from that of the absorption. We have further demonstrated that these effects are due to the Jahn–Teller interactions. Using a theoretical model including mode-mixing effects, we were able to reproduce very satisfactorily both the vibrational structure and the intensity distribution observed in the spectrum.<sup>5</sup>

The situation is quite different in the  $C_6F_5OH^+$  compound, where the emission spectrum is very regular, and represents to a good approximation a “mirror image” of the excitation spectrum. This can be seen quite clearly by comparing the  $C_6F_5OH^+$  excitation and emission spectra

shown in parts b and c of Figure 1, respectively. In  $C_6F_5OH^+$  the electronic degeneracy of the ground state is lifted owing to the lowered symmetry, and the splitting of individual vibrational levels due to Jahn–Teller interactions does not take place. The emission spectrum of  $C_6F_5OH$  is thus to a good approximation like a “Jahn–Teller deperturbed” spectrum of  $C_6F_6^+$ .

The individual vibronic bands observed in emission and their proposed assignments are listed in Table III. The vibrational structure shows close similarity both to the excited electronic state and, like most of the other halobenzene cations studied, also to the parent compound. An overview of the observed fundamental vibrations in the ground state of  $C_6F_5OH^+$  with the  $\tilde{B}$  state, with the ground state of the parent compound, and finally with the corresponding modes of several related compounds is given in Table II. The prominent 558- $cm^{-1}$  ring-breathing vibration is almost identical with the 559- $cm^{-1}$  parent value, and also the two low-frequency in-plane deformation vibrations at 266 and 431  $cm^{-1}$  agree well with the parent (268 and 444  $cm^{-1}$ , respectively). The ring C–C stretching vibration which is at 1660  $cm^{-1}$  in the parent is almost unchanged at 1656  $cm^{-1}$  in the ion and decreases somewhat in the  $\tilde{B}$  state to 1548  $cm^{-1}$ . This decrease in the excited electronic state appears to be a common feature in all the studied halobenzene cations.

Over the entire range of energies studied (up to  $\approx 2500$   $cm^{-1}$ ), the vibrational structure of the  $\tilde{X}^2A'$  state of  $C_6F_5OH^+$  is quite regular and harmonic and shows no trace of the severe perturbations which are so apparent in  $C_6F_6^+$ . It is very interesting to compare the observation for  $C_6F_5OH^+$  with those for the several other fluorobenzene radical cations also listed in Table II. The cations  $C_6F_6^+$ ,  $C_6F_5CH_3^+$ , and  $C_6F_5OH^+$  are in some ways most alike. The “sixth” ring substituent, F,  $CH_3$ , and OH all have approximately the same mass, hence all three compounds have roughly the same “vibrational” symmetry. On the other hand,  $C_6F_6$  has  $D_{6h}$  electronic symmetry so the ion has a doubly degenerate  $^2E_{1g}$  ground electronic state whose degeneracy is broken by the Jahn–Teller effect. Formally  $C_6F_5CH_3^+$  and  $C_6F_5OH^+$  can have no higher than  $C_{2v}$  symmetry (treating OH and  $CH_3$  as single points) and the  $^2E_{1g}$  state is broken into two nondegenerate electronic states. Photoelectron and gas-phase emission spectra indicate that in all three cases the  $\tilde{A}-\tilde{X}$  separation is  $\approx 0.2-0.3$  eV, but there is considerably uncertainty in these values.<sup>16,18,20</sup>

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Based upon our observations the lowering of the electronic symmetry is apparently "clean" in the case of  $C_6F_5OH^+$ , yielding, as we have noted above, a simple (and comparable) vibrational structure in both the ground and excited electronic states. Because of the almost identical vibrational symmetry, the excitation spectra of  $C_6F_6^+$  and  $C_6F_5OH^+$  are nearly identical (save for a shift in origin) and the observed emission spectrum characterizing the ground state of  $C_6F_5OH^+$  yields vibrational frequencies almost identical with the deperturbed frequencies revealed for  $C_6F_6^+$  by the Jahn-Teller analysis.<sup>5</sup>

For  $C_6F_5CH_3^+$  the lifting of the degeneracy of the  $\tilde{X}^2E_{1g}$  state is probably not so "clean". Indeed, it would appear based on the very irregular and perturbed emission spectrum reported<sup>15</sup> for  $C_6F_5CH_3^+$  that the separation between the vibrationless levels on the  $\tilde{A}$  and  $\tilde{X}$  states is comparable to the vibrational intervals in the ground state. One would then have to conclude that electronically  $CH_3$  more nearly mimics F than does OH.

On the other hand, the Jahn-Teller effect is clearly only indirectly affected by a change in vibrational symmetry.

In our recent studies of  $sym-C_6H_3F_3^+$  we have noted that partial deuteration even though it lowers substantially the "vibrational" symmetry and causes appreciable changes in the vibrational frequencies, seems to leave the Jahn-Teller splitting unaffected. Both the linear and the quadratic Jahn-Teller constants appear to be in the lower symmetry  $D_2H$  and  $DH_2$  species of the same magnitude as in the symmetric  $D_{3h}$  isotopic varieties. Apparently, even though considerable mass asymmetry occurs in these species, the electronic wave functions retain the higher symmetry, maintaining the electronic degeneracy of the ground-state ions. In a similar way we note that  $C_6F_5H^+$  lowers both the electronic and vibrational symmetry of  $C_6F_6^+$ . We have previously reported<sup>19</sup> simple regular vibrational structure in both the ground and excited electronic states. The former observation is clearly consistent only with the "clean" breaking of the  $\tilde{A}$  and  $\tilde{X}$  state degeneracy. The vibrational frequencies of  $C_6F_5H^+$  given in Table III show small but significant shifts from the other ions due to the different "vibrational" symmetry in  $C_6F_5H^+$ .

## Photovoltage and Stability of an n-Type Silicon Semiconductor Coated with Metal or Metal-Free Phthalocyanine Thin Films in Aqueous Redox Solutions

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An n-type silicon (n-Si) semiconductor coated with an evaporated thin film of metal phthalocyanine (MPc) or metal-free phthalocyanine (H<sub>2</sub>Pc) worked as a fairly stable photoanode in aqueous redox solutions. The photovoltage observed for a photocell, (n-Si)[CuPc]/Fe<sup>3+</sup>/Fe<sup>2+</sup> aqueous solution (pH 4.2) |Pt, was 0.50 V, only slightly less than that for a p-n junction Si photocell (~0.6 V). The action spectrum was similar to that of a bare n-Si electrode, except for a depression caused by photoabsorption by the CuPc film in the red region. The above wet photocell had current-voltage characteristics better than those for a solid photocell, (n-Si)[CuPc]/Pd.

### Introduction

The photovoltaic effect at a semiconductor-solution interface has been attracting considerable attention in view of solar energy conversion. The main difficulties in utilizing such systems arise from the fact that most available semiconductors having small bandgaps, 1.0-2.0 eV, are subject to corrosion when operated in electrolyte solutions.

We reported previously<sup>1</sup> that n-type silicon (n-Si) or gallium phosphide (n-GaP) can be stabilized by coating the surface with a thin noble metal film. Unfortunately, the photovoltage observed was relatively small (e.g., 0.1 ± 0.1 V for n-Si), and the metal film attenuated the light in a wide wavelength region. Morisaki and Yazawa,<sup>2</sup> Tomkiewicz and Woodall,<sup>3</sup> and Bard et al.<sup>4</sup> reported the

effect of coating n-Si or n-GaAs with stable metal oxide films such as TiO<sub>2</sub>, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc. Such systems responded mostly to light of energy higher than the bandgaps of the oxides. Recently, Wrighton et al.<sup>5</sup> reported the stabilization of n-Si by binding ferrocenyl compounds to the surface with a silane coupling reagent.

In the present paper we will report on the effect of coating n-Si with evaporated phthalocyanine thin films.

### Experimental Section

Single crystals of n-Si in the form of wafers were obtained from Shin-etsu Semiconductor Co., Ltd. They were doped with phosphor, having a resistivity of ca. 0.4 Ω cm, and cut perpendicular to the <111> axis. The ohmic contact was made by evaporating indium metal.

The n-Si electrode was polished with 0.3-μm alumina powder and then etched with CPD-2 (an etching solution containing hydrofluoric acid, nitric acid, and a small amount of bromine) for several seconds. After washing and drying, the phthalocyanine was evaporated under 2 × 10<sup>-5</sup>

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