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Light-Assisted, Aqueous Redox Reactions at Chlorogallium Phthalocyanine Thin-Film Photoconductors: Dependence of the Photopotential on the Formal Potential of the Redox Couple and Evidence for Photoassisted Hydrogen Evolution

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Abstract: Our recent studies have shown that thin films of ordered chlorogallium phthalocyanine (GaPc-Cl) on metal substrates behave as efficient photoconductors in aqueous media, with photopotentials that are dictated by the relative chemical potentials of an electron in the substrate and in the solution redox couple. The magnitudes of the photopotentials are comparable to those seen for photoelectrodes consisting of thin films of a-SiH. When the surface of the phthalocyanine is modified by the addition of submonolayer quantities of platinum, photoassisted hydrogen evolution is observed at an underpotential of 450 mV. The power conversion efficiency of this process is low (less than 0.1%), compared to that seen on other semiconductor materials, but it encourages further development because of the polycrystalline, organic, and potentially more economic nature of the photoelectrodes employed.

Thin-film organic and inorganic materials sandwiched between chemically dissimilar phases are of interest as potential photovoltaic devices.[1-16] The criteria required for energy conversion in such systems have been outlined by Rose.[14,15] The photovoltage is controlled by the difference in the chemical potential of an electron in each phase contacting the thin-film photoconductor. The primary advantage in using thin-film organic photoconductors arises from the higher light absorption coefficients compared to many inorganic materials. Films of a thickness, $d \approx 1\ \mu$m, can be made with high optical densities that may permit cheaper polycrystalline materials to be used as long as the average crystallite size is of the same order as the film thickness and the penetation depth of the photon. Inefficiences due to intergrain-boundary recombination losses can be minimized. Photoelectrochemical effects at thin-film phthalocyanine (Pc) surfaces have been studied with a variety of metal substrates and redox couples. Most studies have indicated that Pc's are mainly hole conductors and that film structure, small crystallite size, and molecular disorder may be principally responsible for the low efficiency of light to electrical energy conversion in previous applications.[1-13] Doped, ordered Pc systems have proven to be quite good room-temperature dark conductors.[17-24]

We have recently demonstrated that film growth conditions affect the crystallite size and porosity of GaPc-Cl films deposited on a gold substrate.[1-3] Undoped nonporous GaPc-Cl thin films with crystallite sizes less than 300 nm on an edge (type A) appear to be efficient photoconductors. These films are fully insulating in the dark but under polychromatic illumination (100-150 mW/cm^2, 470-900 nm) show reversible behavior for the ferrocyanide/ferricyanide and hydroquinone/benzoquinone redox couples. However, small or nondetectable open-circuit photopotentials ($V_{\text{o.c.}}$) were observed. GaPc-Cl films with larger crystallites (0.700-1.0 μm) (type B) also show reversible photoelectrochemistry with the above redox couples and showed photopotentials up to 200 mV (vs. a Pt counterelectrode). The type B films were porous and showed photopotentials inversely dependent to the rate of heterogeneous electron transfer at the exposed metal substrate.

In this paper, we report on an optimized version (type C) of the GaPc-Cl/Au films which consists of crystallites greater than 1 μm on an edge, tightly packed together to form an electrochemically nonporous film. A linear relationship exists between the open circuit photopotential and the $E^{\circ\prime}$ of the redox couple contacting the Pc surface with both positive and negative photopotentials possible. A zero photopotential point near 0.0 V vs. Ag/AgCl was also observed. The photopotential is proportional to the difference in the chemical potential of an electron in the metal phase and that in the electrolyte. Hydrogen evolution is observed on a platinized GaPc-Cl/Au electrode at an underpotential of up to 500 mV and an efficiency between 0.05 and 0.10%.

Experimental Section

GaPc-Cl was synthesized in this laboratory, and its preparation is described elsewhere.[21] All solutions were prepared from deionized water

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doubly distilled from permanganate. Reagent grade chemicals were used as obtained except for hydroquinone (H_2Q), which was recrystallized from ethanol, and benzoquinone (BQ), which was purified by sublimation.

Cyclic voltammetric measurements were made with a conventional three-electrode potentiostat (Eco 551). The potential scale was referenced to the saturated Ag/AgCl electrode. Most photoelectrochemical studies (hydroquinone/benzoquinone (H_2Q/BQ), $Fe(CN)_6{}^{3-,4-}$, and Fe(EDTA)$^{1-,2-}$) were conducted in a vacuum-deoxygenated potassium hydrogen phthalate pH 4 buffer, involving equimolar mixtures of the oxidized and reduced species at a GaPc-Cl modified, Au-MPOTE, rotating-disk electrode (RDE). When only one redox species was available (when oxygen sensitivity prevented preparation of a stable, equal molar mixture), stationary electrodes (SE) were used in a sandwich type spectroelectrochemical cell (methylviologen, MV; naphthoquinonesulfonic acid, NQ; anthraquinonesulfonic acid, AQ). Voltammetry in the light and dark on the GaPc-Cl films was compared with voltammetry on a bare gold RDE or a bare Au-MPOTE stationary electrode. The zero-current potential on bare gold was used as a measure of $E°'$ (±10 mV) (RDE), or for the SE studies, the median value of the anodic and cathodic voltammetric peak potentials $(E_{p,c} + E_{p,a})/2$ on the bare Au-MPOTE was used to estimate $E°'$.[3,4,6]

Open-circuit potential measurements (V_{oc}), approximating photovoltaic conditions, were made by measuring the potential of the electrode in question with respect to a large, coiled platinum wire electrode poised in the electrolyte solution. A PHM 84 research pH meter was used to measure the potentials. For stationary electrodes the open-circuit photopotential was taken as the difference between the light and dark open-circuit potentials. Ideally, the open-circuit photopotential should be simply the open-circuit voltage in the light. Thermal convection effects due to illumination caused considerable drift in the observed values. The difference between the light and dark open-circuit potentials was qualitatively consistent with the cyclic voltammograms. For RDE measurements, the dark open-circuit voltages were close to zero (±10 mV) as expected for a system at equilibrium, and for these electrodes the open-circuit voltage under illumination was taken as the open-circuit photopotential.

The radiation source consisted of the output of a 450-W xenon-arc lamp (Oriel) passed through a 4-in. water IR filter and a 470-nm long-pass filter (Oriel), creating a polychromatic (470–900 nm) radiation source of approximately 100–150 mW/cm^2. The GaPc-Cl films described in this paper have a very broadened absorbance spectra with optical densities exceeding 2.0 through most of the visible wavelength region. Solar efficiencies can then be taken directly from efficiencies measured by use of the xenon-arc lamp without significant error.

The scanning electron micrograph (SEM) was an ISI DS-130, operated at an electron gun voltage of 20 kV. The SEM samples were mounted on grounded, standard electron micrograph studs with double stick tape. The samples were sputter-coated with a 300-Å Au–Pd alloy film and a conductive connection to the stud was made with conductive carbon cement. Control micrographs were recorded to assure that the observed surface structure of the GaPc-Cl films was not due to the Au–Pd overcoat.

Electrode Preparation. Because of the morphology of the films, any direct optical measurement of film coverage of thickness failed to give accurate results. However, the quantity of dye was accurately obtained by dissolving the dye from the substrate with a measured volume of pyridine and the peak absorbance compared to prepared standards. Film thickness is defined in these studies as the number of equivalent closest packed monolayers (EQM). If each GaPc-Cl molecule is assumed to occupy a 150-Å^2 surface when lying flat, then one EQM corresponds to 1.11×10^{-10} mol/cm^2. The thickness of the films used in this study ranged from 1200 to 1600 EQM. Differences in the thickness of films in this range did not affect the electrochemical results except for small changes in magnitude of the photocurrent for a given type of film.

Stationary Electrodes (SE). Gold substrates were cut from Intrex films (Sierracin Corp.). They consisted of a vapor deposited, thin (300 Å), metal film on a transparent polyester sheet, forming a metallized plastic optically transparent electrode (Au-MPOTE).[22,23] The substrate electrodes were rinsed briefly in purified ethanol and then water and allowed to air dry. Deposition of the films occurred in a 3-in.-diameter glass cylinder with several milligrams of GaPc-Cl spread evenly across the bottom. The electrodes were suspended 1.75 in. above the bottom by an aluminum masking plate, held in place by indentations in the wall of the vessel. The vessel was placed in a 500-mL heating mantle (Glas-Col) and the glass wool packed around the vessel, filling the volume of the mantle. The temperature was measured by a thermometer inserted through the glass wool to as near the base of the vessel as possible. The vessel was evaluated to ca. 10^{-6} torr and the temperature increased, at typically 5 °C/min, until a steady state of about 275 °C was obtained. Some heat is transferred to the electrode substrates by this method. Sublimation took place over a period of 24 to 72 h, resulting in a sublimation rate of 0.3 to 0.5 EQM/min. The vessel was allowed to cool before opening, and the electrodes were stored covered in ambient atmosphere.

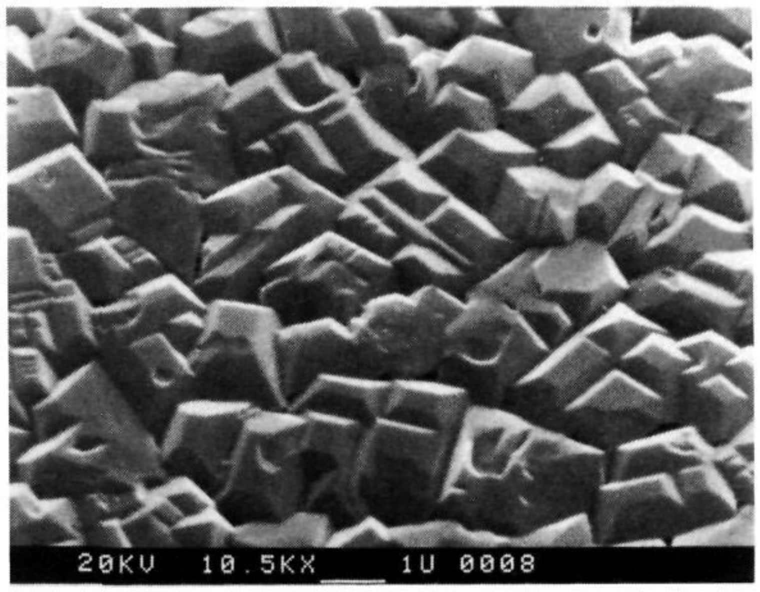

Figure 1. Scanning electron micrograph of type C, GaPc-Cl/Au, film at 10 500×. The horizontal line indicates 1-μm length.

Rotating Disk Electrodes (RDE). The GaPc-Cl/Au RDE consisted of a $^1/_4$-in.-diameter stainless steel demountable disk which screwed into a stainless steel shaft of the same diameter. The Teflon shroud screwed over the disk to provide a flat surface in the same plane as the electrode surface. Electrical contact was made through the stainless steel shaft.

A portion of the Au-MPOTE/GaPc-Cl stationary electrodes described above were epoxied onto the demountable disk and trimmed to the same diameter. Two small areas of conductive silver print extending between the electroactive area and the steel disk furnished electrical contact. The exposed silver print and the side of the disk were painted with an insulating layer of clear acrylic paint. In addition, a thin layer of Lubriseal grease between the disk and the Teflon shroud prevented solution creep into this space. A bare Au-MPOTE RDE without the GaPc-Cl was constructed and its behavior with ferri/ferrocyanide retained Levich behavior up to 4500 rpm. No silver electrochemistry could be observed from the silver paint contacts.

Results and Discussion

Figure 1 shows a scanning electron micrograph of the optimized version of sublimed thin films of chlorogallium phthalocyanine (GaPc-Cl)—one of a member of trivalent metal Pc's which exhibit extensive molecular aggregation.[1-3,14,25] This film (designated type C) shows a tightly packed, single layer of Pc crystallites that are, on average, 1 μm or greater in each dimension, including thickness. Such highly ordered arrays of GaPc-Cl are obtainable through the combination of metallized polymer substrates (Au-MPOTE[22,23]) sublimation rates approximating epitaxial growth conditions (less than one monolayer of Pc deposited per minute). We have previously reported on the photoelectrochemical activity of thinner (less than 200 nm), nonporous versions of this film (type A) or films of isolated Pc crystallites (ca. 1 μm × 1 μm × 1 μm) (type B),[2,3] which was significantly different than that reported here. Scanning electron micrographs of other phthalocyanines that we have explored under identical sublimation conditions show that many form long needles (CuPc, FCrPc) with linear dimensions on the order of microns or form crystallite sizes of no more than 20–50 nm (FePc, CoPc, H_2Pc).

Figures 2a, 2b, and 2c are representative cyclic voltammograms for three of the six redox couples studied. Currents at or below our detection limits were observed to flow in the dark in the GaPc-Cl film for all redox couples, consistent with the nonporous nature of the film.[2,3] Under illumination at stationary GaPc-Cl electrodes, photocurrents were observed which were similar in size to those on bare gold but with sizeable shifts in the apparent $E°'$. Some enhancement of the SE current on the forward sweep vs. that seen on the reverse sweep was observed as was an enhancement of the peak current on illuminated GaPc-Cl over bare gold. These effects have been attributed to thermal convection of the solution near the Pc surface due to nonradiative energy decay pathways in the illuminated Pc film.[3] The potential dif-

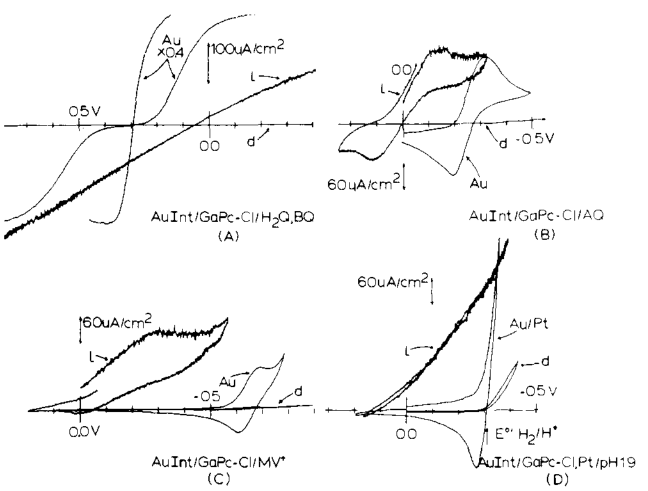

Figure 2. Voltammograms at a type C, GaPc-Cl/Au electrode in the dark (D) and under polychromatic illumination (L) and at a bare Au electrode: (a) 10^{-3} M H_2Q/BQ, pH 4 buffer solution; (b) 10^{-3} M AQ, pH 4 buffer solution; (c) a 10^{-3} M MV^+, pH 4 buffer solution; and (d) with platinum deposited on the surface and a pH 1.9 buffer solution. Potential measured vs. Ag/AgCl reference electrode.

ference ($E^{\circ\prime}_{(GaPc\text{-}Cl,light)} - E^{\circ\prime}_{(Au)}$) agrees qualitatively with the potentiometrically measured open-circuit photovoltage (V_{oc}) for the GaPc-Cl electrode (vs. a Pt or Au counter electrode). The open-circuit voltages drifted considerably on the stationary electrodes and were difficult to reproduce. This instability was also attributed to thermally induced concentration gradients. However, the magnitude of the difference between these two values, taken as V_{oc}, was consistent with the shift in the apparent $E^{\circ\prime}$ as measured in the cyclic voltammograms.

Figure 2a is illustrative of the RDE results. A very well-defined (±10 mV) shift of the zero-current potential between Au and GaPc-Cl/Au occurred. This value matched closely (±10 mV) the potentiometrically measured open-circuit photovoltage which was stable and reproducible. Illuminated RDE voltammograms show a linear i–V curve with a slope of 0.34 $\mu A/(mV\ cm^2)$ for 10^{-3} M concentrations of H_2Q/BQ, $Fe(CN)_6^{3-,4-}$, and $Fe(EDTA)^{1-,2-}$ between +800 and −600 mV. The slope of the curve was independent of rotation rate above 1000 rpm, and the nature of the redox couple which indicates charge conduction through the bulk of the film was determined by light intensity rather than slow heterogeneous kinetics at the dye–solution interface.

At a solid-gold RDE the H_2Q/BQ redox couple (Figure 2a) shows the two types of behavior depending on the electrochemical pretreatment of the electrode. The irreversible behavior is obtained on a clean electrode without further treatment before electrochemical testing. The reversible behavior was obtained by poising the electrode at +1.5 V vs. Ag/AgCl for 30–60 s and then scanning back to observe the H_2Q/BQ redox couple wave. The formation and reduction of gold oxide created a new surface that was kinetically more active than the as-prepared gold.

The intensity (I) dependence of the photocurrent (i_{ph}) was measured at a suitable potential for H_2Q/BQ (+350 mV), $Fe(CN)_6^{3-,4-}$ (+350 mV), and $Fe(EDTA)^{-1,2-}$ (+150 mV). The photocurrent (i_{ph}) was found to obey $i_{ph} \propto (I)^n$ where $n = 0.75$.

An odd power of the intensity dependence lying between 0.5 and 1.0 can be accounted for where holes are the majority carriers,[14] filled recombination centers are assumed to be absent at zero light intensity, and hole traps have an exponential density distribution starting at the Fermi level and increasing toward the valence band.[14,15] As the light intensity increases and the hole steady-state Fermi level shifts toward the valence band, hole traps are converted into recombination centers. This increase in recombination centers competes with the increased carrier photogeneration rate such that the photocurrent will be less than directly proportional to the light intensity.

Figure 3 shows V_{oc} vs. the measured $E^{\circ\prime}$ of each redox couple. A linear relationship exists and both *positive* and *negative photopotentials* are possible, with an X-axis intercept near 0.0 V vs. Ag/AgCl. When −4.6 eV is assumed as the potential of an electron vs. vacuum in the normal hydrogen electrode (NHE),[26] the X-axis intercept is ca. −4.8 eV vs. vacuum. This must correspond to the Fermi level of gold (vs. an electron in vacuum) in films prepared in this manner because the photopotential developed is proportional to the differences in the chemical potential of an electron in the isolated electrolyte containing a redox couple and in the isolated gold substrate. Figure 4 illustrates this more clearly for three cases. The top portion of the figure shows an example of the relative electron energy levels of three phases before equilibration of these levels, while the bottom portion of the figure shows the energy levels and band bending at equilibrium. Equilibration and band bending will occur at each interface in accordance with the preequlibrium difference between energy levels at that interface. The net result will be a potential drop in the Pc film equivalent to the difference in the chemical potential of the isolated metal and the isolated redox couple. In case A, a negative photopotential is expected as obtained with H_2Q/BQ, $Fe(CN)^{3-,4-}$, and NQ redox couples. In case B no photopotential should occur, while in case C a positive photopotential is expected as obtained with $Fe(EDTA)^{1-,2-}$, AQ, and MV^+. The slope of the V_{oc} vs. $E^{\circ\prime}$ relationship is not 1.0 but 0.78, since some fraction of the potential drop may occur in the Helmholtz double layer in solution rather than in the Pc film. Only that proportion of

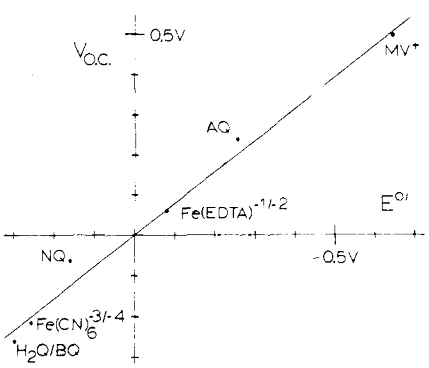

Figure 3. Open-circuit photopotential ($V_{oc} = E^{\circ\prime}_{(GaPc\text{-}Cl/Au)} - E^{\circ\prime}_{(Au)}$ vs. the formation potential $E^{\circ\prime}$, at pH 4, of the redox couple in contact with the GaPc-Cl/Au electrode. Potential measured vs. Ag/AgCl reference electrode.

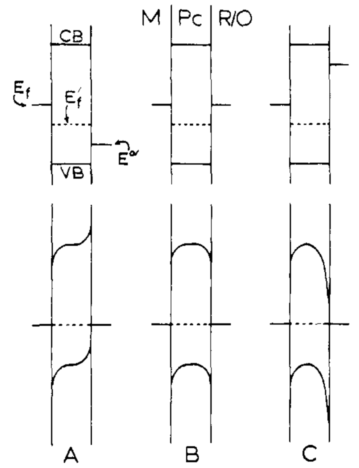

Figure 4. Hypothesized relative electron energy levels and band structure in the gold (E_f), the Pc thin film (E'_f), and the electrolyte with a redox couple ($E^{\circ\prime}$) before electron equilibration (top) and after electron equilibration (bottom) for these cases: (a) $E_f > E^{\circ\prime}$ with a negative photopotential, (b) $E_f = E^{\circ\prime}$ with no photopotential, and (c) $E_f < E^{\circ\prime}$ with a positive photopotential.

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the potential drop which occurs in the film will contribute to the photopotential. As expected, thinner, type A, GaPc-Cl films have shown much diminished photopotentials (typically less than 20 mV) for the same redox couples as in Figure 3.[3]

At illuminated GaPc-Cl/Au films, hydrogen evolution was possible at under-potentials of up to 500 mV on the as-prepared GaPc-Cl films but at very low power efficiencies (<0.001%). The shape of the SE voltammogram suggested that the photocurrents were limited by H_2-evolution kinetics rather than photon-limited, bulk conduction. Significant improvements were made when platinum catalytic sites were electrochemically deposited (less than 1 equiv of monolayer), as per the method of Heller for InP.[27] Figure 2d shows the SE voltammogram for a Pt treated GaPc-Cl electrode in a pH 1.9 buffer, compared to a Au-MPOTE electrode platinized to the same surface coverage. Hydrogen evolution occurred at 450 mV underpotential, and the slope of the *i*–*V* was very close to that of the RDE studies of other redox couples. The power conversion efficiency was estimated from the *i*/*V* curves to be between 0.05 and 0.1% and is chiefly limited by the internal resistance of the Pc film. Continuous operation at an applied potential of −200 mV vs. Ag/AgCl showed a decrease of current density of 60% over 7 h. This decrease in stability could be attributed however to the loss of Pt activity—replatinizing of the electrode returned the photocurrent to the initial value. These currents were not due to trace oxygen in solution, as indicated by the lack of current observed at potentials positive of −0.40 V on the platinized-gold electrodes.

Conclusion

It is clear from these studies that the photoelectrochemical results observed with the GaPc–Cl/Au electrodes are quite encouraging for further development of organic thin films. This success and further developments hinge on the ability to grow continuous films of large, blocklike crystals of about 1 μm thickness. Previous Pc thin-film photoelectrochemical redox processes have been observed with significantly lower efficiencies which we attribute to porous films, submicrometer sized crystallites, or randomly oriented needle or platelet crystals having poor contact with the conducting substrate.[1-13] The thickness and ordering of the type C Pc films are producible at a level where the minimum defect density is ca. $10^{18}/\mathrm{cm}^{-3}$, estimated from the Pc concentration on the edge and lattice termination sites in Figure 1 (assuming these to be the active recombination sites and ignoring possible bulk recombination sites). That defect density is within an order of magnitude of that required in the model of Rose for energy conversion using thin-film photoconductors sandwiched between two dissimilar phases.[14,15] In contrast to most single crystal materials, a higher defect density of the Pc films can be tolerated because of the smaller migration distances required of the charge carriers while still maintaining a high optical density. The efficiencies for the photoelectrochemical reactions are still considerably lower than for the single-crystal semiconductor materials.[27-30] The promise of decreasing the defect density of the ordered Pc film further and/or increasing the photoconductivity through the addition of dopants is being explored with encouraging preliminary results. The thermodynamic driving force for the photoelectrochemical processes is limited by the difference in chemical potential of an electron in the redox couple and the metal, which points to the use of metal substrates with larger work functions and aqueous couples with more extreme emf's to maximize the photovoltage of a thin-film Pc device.

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Registry No. GaPc-Cl, 19717-79-4; H_2, 1333-74-0; Pt, 7440-06-4.

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IR Laser Induced Isomerization of $Fe(CO)_4$: A Unique Example of the Jahn–Teller Effect

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Abstract: We present the first explanation of the non-Berry pseudorotation of $Fe(CO)_4$ (Davies, B.; McNeish, A.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 7573–79). A topological model, the *distortion octahedron*, is developed to represent possible distortions of a T_d four-coordinate molecule and the lowest energy isomerization pathways between equivalent C_{2v} distorted geometries. The model provides a simple rationalization of why intramolecular ligand exchange in $Fe(CO)_4$ differs from that in SF_4, which has a similar C_{2v} geometry. Our qualitative arguments are fully supported by a rigorous application of the Jahn–Teller theorem, the results of which are briefly summarized here. The precise information provided by the IR laser induced isomerization allows the distortions of $Fe(CO)_4$ to be analyzed in more detail than is usually possible with thermally induced processes.

$Fe(CO)_4$ is a coordinatively unsaturated molecule, which plays a central role in the photochemistry of $Fe(CO)_5$ and $Fe(CO)_4$-(olefin) species.[2,3] In low-temperature matrices, $Fe(CO)_4$ has been shown[4] to have a C_{2v} structure with bond angles $\sim$145° and $\sim$120°. The symmetry is the same as that of SF_4, but the bond angles are significantly different[5] (SF_4, 183° and 104°). $Fe(CO)_4$ has never been directly observed in solution, but recently-obtained time-resolved IR spectra show that $Fe(CO)_4$ almost certainly has

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