

Photoemission from ferrocene, decamethylferrocene, and decamethylferrocene-bis(7,7,8,8-tetracyano-*p*-quinodimethane)

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We present the first vacuum ultraviolet photoemission measurements of condensed ferrocene, decamethylferrocene, and the highly conductive charge transfer complex decamethylferrocene-7,7,8,8-tetracyano-*p*-quinodimethane, at photon energies from 7.7 to 21.2 eV. We compare the electronic spectra of these compounds and discuss substituent effects. The first ionization potentials are 6.1, 5.1, and 5.3 eV, respectively. The charge transfer complex is a semiconductor with its highest occupied states 0.8 eV below E_F . The electron scattering lengths in ferrocene and decamethylferrocene are ≈ 60 Å for electrons 0.5 eV above the vacuum level and decrease to ≈ 2.5 Å as the energy is increased to 16 eV. From this result we estimate the electron affinity of solid ferrocene and decamethylferrocene to be about 1 eV.

In recent years there has been considerable theoretical¹⁻⁴ and experimental⁵⁻⁷ effort aimed toward the elucidation of the bonding in the highly symmetrical organometallic sandwich compounds. For reasons of stability and historical interest, ferrocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ has been used as the model compound.

To further understand the physics of these organometallic compounds in the solid state, we have performed a series of ultraviolet photoemission experiments on ferrocene (Fc), decamethylferrocene $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}$ (DMFc), and decamethylferrocene-bis(7,7,8,8-tetracyano-*p*-quinodimethane), (DMFc)(TCNQ)₂. Our results show that the electronic structures of Fc and DMFc are largely unchanged when the molecules are condensed into a solid. Thus, an adequate theoretical description of the data can be obtained within the molecular orbital theory of ferrocene.

Commercially available ferrocene, decamethylferrocene, and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) were recrystallized before use. The 1:1 and 1:2 charge transfer salts of decamethylferrocene and TCNQ were prepared in >60% yield from the reaction of stoichiometric amounts of DMFc and TCNQ in acetonitrile. Recrystallization was effected from acetonitrile. Elemental analysis: calculated for $\text{Fe}[(\text{CCH}_3)_5]_2(\text{TCNQ})$: 72.45(C), 6.46(H), and 10.56(N); observed 72.17(C), 6.37(H), and 10.68(N). Calculated for $\text{Fe}[(\text{CCH}_3)_5]_2(\text{TCNQ})_2$: 71.93(C), 5.21(H), and 15.25(N); observed 71.83(C), 5.09(H), and 15.03(N). The conductivity of pressed pellets of the 1:1 and 1:2 salts were measured to be $>10^{-9}(\Omega\text{-cm})^{-1}$ and $0.1(\Omega\text{-cm})^{-1}$, respectively.

The experimental apparatus has been described previously.⁸⁻¹⁰ Samples were prepared by *in situ* sublimation onto freshly evaporated gold substrates at liquid nitrogen or dry ice temperatures. Low temperatures were used to prevent reevaporation of the thin films (<200 Å) necessary to prevent charging effects. Sample thickness was monitored by measuring the frequency change in a quartz crystal oscillating at 5 MHz which has a sensitivity of $1.77 \times 10^{-8} \text{ g cm}^{-2} \cdot \text{Hz}^{-1}$. Accurate depositions of submonolayer amounts of material are possible with this apparatus, and thus hot electron escape depths can be measured by studying the attenua-

tion of gold substrate emission as a function of coverage. All measurements were made at pressures of $<10^{-9}$ torr, the base pressure of the stainless steel vacuum system being about 3×10^{-11} torr before sample deposition.

It is generally acknowledged that few charge transfer salts involving TCNQ can be successfully prepared by thermal evaporation of bulk crystals. In fact, we first attempted to prepare (Fc)(TCNQ)₂ by this process but the bulk crystals decomposed on heating leaving behind a yellow residue similar to TCNQ. However, films of (DMFc)(TCNQ) and (DMFc)(TCNQ)₂ were successfully prepared by this method. This was verified by desolving the films in acetonitrile and measuring the electronic absorption spectra on a Cary 17D spectrophotometer.

Using a windowless He discharge lamp as a source of 21.2 eV photons the energy distribution curves (EDCs) of Fig. 1 were obtained. The initial energy of the electrons is given with respect to the Fermi energy of the gold substrate. Ionization energies of electrons at any point on the EDC are obtained by subtracting their en-

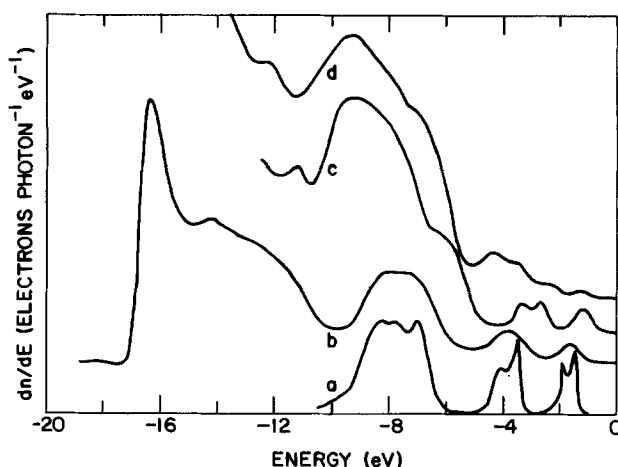


FIG. 1. Energy distribution curves with the energy axis given relative to the Au substrate Fermi level at a photon energy $h\nu = 21.2$ eV. (a) Ferrocene gas phase⁵ positioned to align the peaks with curve (b), (b) solid Fc, (c) solid DMFc, (d) solid (DMFc)(TCNQ)₂.

TABLE I. Ionization energies of highest occupied molecular orbitals.

| Orbital | Ionization energy (eV) | | |
|-----------|------------------------|----------|------------|
| | Fc gas ⁵ | Fc solid | DMFc solid |
| Threshold | | 5.4 | 4.7 |
| a_{1g} | 7.23 | 6.1 | 5.1 |
| e_{2g} | 6.86 | | |
| e_{1u} | 8.72 | 7.7 | 6.7 |
| e_{1g} | 9.38 | 8.2 | 7.3 |

ergy above the vacuum level cutoff (at -16.8 eV on this plot) from the photon energy (21.2 eV). In Table I we give the ionization energies for the first four peaks of Fc and DMFc together with the threshold ionization energies. Also given are the ionization energies of the corresponding gas phase peaks of Fc and their orbital assignments. The complete gas phase spectrum of Fc⁵, shifted so that the peaks coincide with the solid phase [curve (b)], is shown as Curve (a) in Fig. 1. Comparison of the gas and solid phase spectra shows that the two main effects of condensing ferrocene molecules into a solid are a reduction in the ionization energies and a broadening of the peaks. We find from Table I that the ionization energy reduction—the polarization energy—is constant at ≈ 1.0 eV for the orbitals compared.

The large width of spectral lines is a consequence of the photoemission process since our instrumental energy resolution is 0.15 eV. One possible source of broadening is due to the Franck-Condon effect which couples the electronic transition to vibrational modes of the molecules and the lattice. However, in these materials coupling to the lattice is very weak compared to intramolecular vibrational coupling and thus little additional broadening should be seen above that present in the gas phase spectra. Because the lifetime of the hole will be shorter in the solid than in the gas owing to increased overlap of molecular orbitals on adjacent molecules, as well as to the Coulomb attraction of nearby electrons by the charged hole, energy broadening will result. Although this effect is difficult to calculate, it will probably be small in molecular solids. Another likely source is the very short inelastic mean free path of the photoemitted electrons. We herein report that the inelastic mean free path may be only one or two molecular dimensions. Using the Heisenberg uncertainty relation $\Delta \times \Delta p > \frac{1}{2}\hbar$ this results in a momentum spread which is observed as energy broadening. A simple calculation shows that broadening of 0.5 eV is reasonable for this effect. This broadening considerably reduces the threshold for ionization below the measured peak values. Thus, the ionization thresholds are 5.4 eV for Fc, 4.7 eV for DMFc, and 4.7 eV for (DMFc)(TCNQ)₂.

Within the limitations imposed by solid state broadening we can study the substituent effects on the molecular orbital energy levels as shown in Fig. 1. Within about 0.1 eV the work functions are equal for the materials under study, hence the vacuum level cutoffs of curves (c) and (d) (not shown) are essentially the same as that

of curve (b), and relative ionization energies can be obtained directly from these EDCs. For the materials studied we expect the least bound molecular orbitals to be the same as those given for ferrocene¹¹ because addition of methyl groups to the cyclopentadienyl rings increases the electron density on the rings without significantly changing the strength of the π bonds to the iron, which are those low lying orbitals. Formation of the charge transfer salt (DMFc)(TCNQ)₂ removes the most weakly bound electron from DMFc. This charge transfer can account for most of the observed changes in orbital energies, however, an unambiguous description of these spectra may not be possible without a detailed calculation.

DMFc has more negative charge on the cyclopentadienyl rings than does Fc. This reduces the binding energy of the filled π orbitals. Thus, the first peak containing the nonbonding $a_{1g}(d_{z^2})$ and $e_{2g}(d_{x^2-y^2}, d_{xy})$ orbitals shifts up in energy by 0.7 eV in DMFc compared with Fc. Furthermore, the energy difference between these orbitals is larger for DMFc than for Fc since we cannot resolve these two orbitals in Fc, but a definite shoulder appears 0.4 eV above the first peak in DMFc, Fig. 2. This weak shoulder indicates that the least bound electrons in DMFc reside in the a_{1g} orbital since the occupancy of a_{1g} is half that of e_{2g} . However,

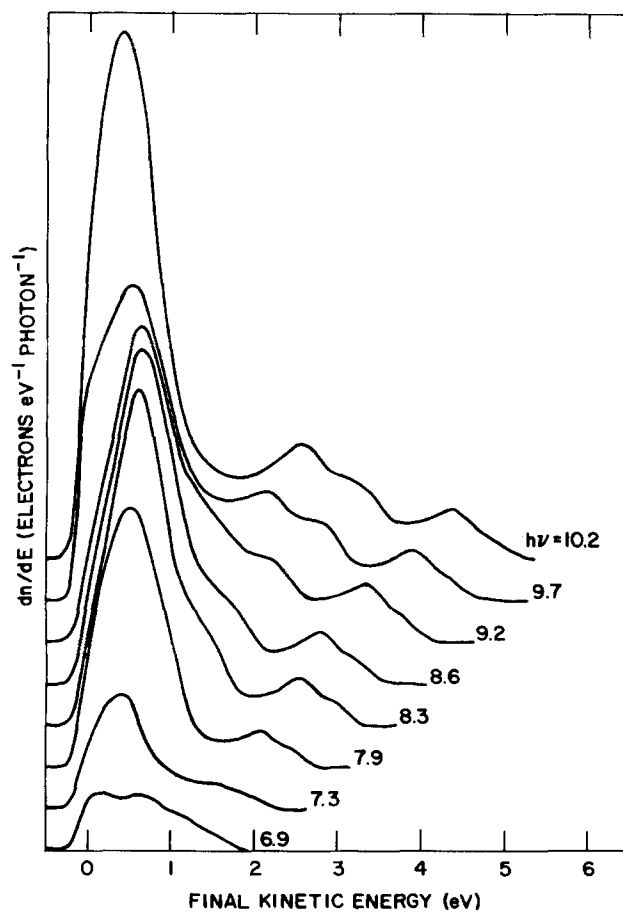


FIG. 2. DMFc energy distribution curves for various photon energies ($h\nu$). The curves are normalized to constant photon flux.

TABLE II. Hot electron escape depth vs kinetic energy above vacuum level.

| Energy (eV) | Escape depth | |
|----------------|--------------|---------|
| | (Hz) | (Å)(Fc) |
| 0.4 | 50 | 60 |
| 1.5 | 19 | 23 |
| 5.6 | 6 | 7.2 |
| 14.6 | 2.5 | 3.0 |
| 16.2 | 2 | 2.4 |

gas phase measurements on ferrocene indicate the least bound state to be of e_{2g} symmetry.⁵⁻⁷ A relative reduction in the ionization energy of the a_{1g} orbital with respect to the e_{2g} orbitals in DMFc might be expected since the a_{1g} highest occupied orbital points into the cyclopentadienyl rings whereas the e_{2g} orbitals are parallel to the rings and should be less repelled by increased ring charge. However, this a_{1g} , e_{2g} order reversal on methyl substitution could not have been anticipated by previous measurements on dimethylferrocene.⁶ The lowest ionization energy belongs to the e_{2g} orbitals (splitting due to lower molecular symmetry is not resolved) and although (as in our measurements) the ionization energy is reduced by methyl substitution, the gap between e_{2g} and a_{1g} is constant. Similarly, the $e_{1u}(p_x, p_y)$ orbitals in DMFc shift to lower ionization energies than observed in Fc and the energy difference between these levels increases enough for our measurements to clearly distinguish two peaks. This increased splitting may be due to the fact that e_{1u} orbitals are parallel to the cyclopentadienyl rings, whereas $e_{1g}(d_{xz}, d_{yz})$ orbitals point towards the rings and should become relatively less tightly bound when ring charge increases. However, the small increased splitting may also be due to different intramolecular relaxation effects in Fc and DMFc. In addition, the more deeply bound a_{2u} and a_{1g} orbitals which we identify with the broad peak in ferrocene at -7.5 eV in Fig. 1 are seen to shift toward lower ionization energy by about 1 eV in DMFc and new structure due to the methyl groups appears below -7 eV.

The spectra for (DMFc)(TCNQ)₂ are more difficult to interpret. This material was first synthesized in an attempt to understand the physical properties associated with the highly conducting one-dimensional (Fc)(TCNQ)₂.¹² The fact that the conductivity of (DMFc)(TCNQ)₂ is quite high [$\sim 0.1(\Omega\text{-cm})^{-1}$ in a pressed pellet] suggests a structure containing segregated stacks of TCNQ moieties forming a one-dimensional chain. In principle, photoemission experiments should be able to distinguish between metals and insulators by giving the density of occupied states at the Fermi energy (which is coincident with the substrate Fermi energy); however, previous studies of organic metals based on TCNQ¹⁰ have shown no clear distinction between metals and semiconductors. Nevertheless, the ionization threshold for (DMFc)(TCNQ)₂ is 0.8 eV below the Fermi energy as seen in Fig. 1, suggesting that (DMFc)(TCNQ)₂ is a semiconductor. The first peak with an ionization energy of 5.3 eV is most likely due to the highest oc-

cupied state in TCNQ⁻ and is similar in structure to that observed¹⁰ in Na⁺TCNQ⁻. The next three peaks with ionization energies of 6.3, 7.3, and 8.3 eV are similar to the highest occupied levels of DMFc shifted to greater binding energy due to a removal of one electron in creating DMFc⁺. The 6.3 eV structure is likely the unresolved a_{1g} and e_{2g} orbitals which are nearly degenerate in the ferricinium ion.¹³ The next two orbitals e_{1u} at 7.3 eV and e_{1g} at 8.3 eV show increased splitting in (DMFc)(TCNQ)₂ over that in DMFc, possibly due to stronger attraction of e_{1g} to the hole in DMFc⁺.

Further measurements on Fc, DMFc, and (DMFc)(TCNQ)₂ included energy distribution curves obtained as a function of incident light energy. These are shown in Fig. 2 for DMFc. Similar results were obtained for the other materials. The light source consisted of a hydrogen discharge lamp and a vacuum uv monochromator. These measurements confirmed and refined the 21.2 eV studies. With the exception of the large peak below 1 eV final state kinetic energy, no new structure was observed. This indicates that there is little structure in the density of states above the vacuum level and no appreciable energy dependence of optical absorption matrix elements. The amplitude of the low kinetic energy peak increases with increasing photon energy indicating that it depends on the number of high energy electrons which can be inelastically scattered to lower energy. This peak is primarily due to the longer mean free path of low energy electrons.

The escape depths of hot electrons were measured by depositing submonolayer amounts of the material under study onto a gold substrate and then measuring energy distribution curves of the gold emission as a function of coverage. This technique has been used to show that photoemission from tetrathiofulvalene-7,7,8,8-tetracyano-*p*-quinodimethane, (TTF)(TCNQ), samples only the first monolayer of surface molecules.¹⁴ The escape depth was taken to be the sample thickness at which emission from the gold substrate decreased to $1/e$ of the clean substrate value. For kinetic energies below 2 eV where the gold emission is weak the escape depth was obtained by noting the sample thickness beyond which no change in relative EDC peak heights occurred. The results given in Table II were essentially the same for both Fc and DMFc. Results could not be obtained for (DMFc)(TCNQ)₂ since at low coverage the sample consisted of aggregates and did not uniformly cover the substrate. Thickness has been given in terms of frequency change of the thickness monitor. We do not know the density of DMFc or (DMFc)(TCNQ)₂, but for Fc with a density of 1.516 g/cm³¹⁵ our calibration is 1.2 Å/Hz, assuming thin films to have bulk density. Except at very low kinetic energies the present results agree with previous studies on TTF and TCNQ¹³ which found the mean free path for inelastic scattering to be only one or two molecular dimensions. As previously mentioned, this very short mean free path is a prime contributor to solid state broadening of measured photoemission lines and is the reason for the extreme surface sensitivity of the technique.

The long mean free path at low kinetic energy is eas-

ily understood as the result of a transition from a state of strong electron-electron scattering to a state of much weaker electron-vibration scattering, as the electron kinetic energy is decreased.¹⁶ The smallest energy that an electron moving among Fc molecules can lose by electron-electron collisions is that required to produce an exciton. The onset of the first absorption band in Fc is at ~ 2.5 eV and the peak is at 2.8 eV.² In order for an electron in the solid to lose the exciton energy its energy after the collision must still be sufficient to place it among the empty molecular orbitals. Consequently, the minimum electron energy in the crystal (relative to the highest occupied orbital) before the collision must be $E_{\text{min}} = 2.5 + I_c - A_c$, where I_c and A_c are the crystal ionization energy and crystal electron affinity. We observe a rapid increase in escape depth at 1.5 eV electron kinetic energy outside the sample, or $1.5 + I_c$ energy inside. Setting $1.5 + I_c = E_{\text{min}} = 2.5 + I_c - A_c$, we measure the electron affinity of Fc and DMFc to be about 1 eV in the solid.

We conclude that photoemission studies of solid ferrocene, DMFc, and (DMFc)(TCNQ)₂ contain information about their molecular orbitals with little consequences of the solid state interactions. We have interpreted peaks in our measured energy distribution curves in terms of a simple extension of the molecular orbital theory of ferrocene.^{2,11} Orbital ionization potentials, electron affinity, and hot electron escape depths have been determined.

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