is essentially *acid independent* over the pH range 7.8–12.1.[9]

To our knowledge, Macartney and McAuley's work[1] provides the only support for any significant dissociation of the aquo ligand in $(CN)_5Fe(H_2O)^{3-}$ over the pH range 6–13. Aside from the fact that their data stands apart from a large body of self-consistent work,[2,10] there are other considerations which indicate an incorrect assignment to reactions of monomeric species.

One would expect from well-known trends[11] in other aquo transition-metal systems that the iron(III) complex $(CN)_5Fe(H_2O)^{2-}$ would be substantially more acidic than the iron(II) complex $(CN)_5Fe(H_2O)^{3-}$, whereas Macartney and McAuley[1] conclude that the iron(II) complex is the more acidic.[12] Except for cases in which X is a good π acceptor, available evidence indicates that the $(CN)_5Fe^{II}$ center has a low affinity for σ-donor ligands like OH^- in the conjugate base $(CN)_5FeOH^{4-}$ (eq 1).[2] For this reason, we would expect that the latter would be more labile than its conjugate acid in eq 1, but Macartney and McAuley[1] report that the rate of substitution of X = thiourea on proposed monomeric aquopentacyanoferrate(II) centers *decreases* with increasing pH, which does not agree with experimental observations for other ligands and is not consistent with the above considerations.

We conclude that the spectral and kinetic data reported in ref 1 do not correspond to reactions of monomeric aquopentacyanoferrate(II) ions.

It may be that the spectral and kinetic measurements of ref 1 actually refer to iron(III)-containing species inadvertently produced in the synthesis of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ or in its subsequent isolation and treatment with methanol. We shall continue to follow the procedure of ref 2 for making up solutions of aquopentacyanoferrate(II) species from analyzed samples of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ under strictly anaerobic conditions.

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Registry No. $(CN)_5Fe(H_2O)^{3-}$, 18497-51-3.

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(9) Macartney and McAuley[2] report a sharp rate decrease in this pH range.

(10) For recent data, see, for example, H. E. Toma, J. M. Martins, and E. Giesbrecht, *J. Chem. Soc., Dalton Trans.*, 1610 (1978), and references therein.

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(12) The acid dissociation constant of $(CN)_5Fe(H_2O)^{2-}$(aq) is K_{AH1} = 4.0 × 10^{-9} M at 25 °C.[13]

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Photodissociation of the Iron Tricarbonyl Anion

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Unsaturated metal carbonyl compounds have been suggested as intermediates in the thermal and photochemical substitution reactions of transition-metal compounds,[1,2] but the corresponding neutral molecules have never been detected in solution or in the gas phase. While several papers have appeared predicting the geometry and d orbital energy levels of such molecules,[3,4] there are few experiments with which to compare these theories. These unsaturated molecules are unstable and cannot be isolated for study under conventional conditions, although they can be seen in low-temperature matrix experiments. Among those unsaturated species observed in this way,[5,6] $Fe(CO)_4$, $Fe(CO)_3$, and recently[7] $Fe(CO)_4^-$ have been formed by ultraviolet and vacuum ultraviolet irradiation of $Fe(CO)_5$. Visible irradiation of $Fe(CO)_4^-$ in a matrix leads to detachment of an electron[7] while in the gas phase dissociation occurs.[8]

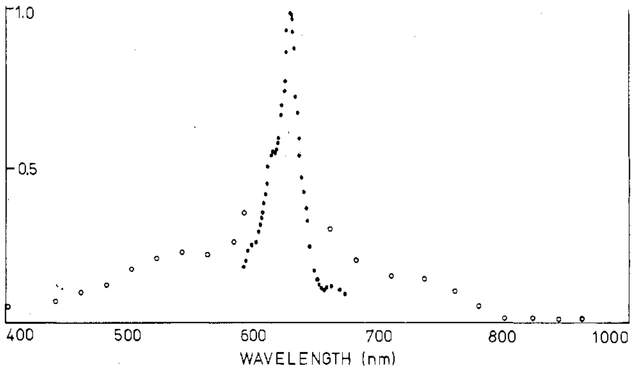

Figure 1. Relative photodissociation spectrum for photo increases of $Fe(CO)_2^-$ from $Fe(CO)_3^-$. The spectrum from 575 to 675 nm was taken at high resolution. The low-resolution spectrum has larger relative values due to the larger bandwidth of the monochromator.

The photodissociation of negative ions in an ion cyclotron resonance spectrometer has enabled us to study the electronic structure of an unsaturated iron carbonyl compound in some detail. This note is concerned with the electronic structure of $Fe(CO)_3^-$.

The interaction of light with gas-phase negative ions often results in the detachment of an electron, since the energy required to remove an electron from an anion is usually less than the energy required to break a bond. Dissociation can occur,[8] however, and when it does, it appears to involve reactions from excited states.[9] Thus, measuring photodissociation as a function of wavelength gives information about the absorption spectrum which cannot be recorded otherwise. The quantum yield for dissociation is generally assumed to be unity and wavelength independent so that the photodissociation action spectrum is taken to be equivalent to the absorption spectrum.[9] This therefore is a convenient way to study electronic excited states in ions.

Iron pentacarbonyl undergoes dissociative electron capture upon impact with low-energy electrons,[8,10-13] producing mainly $Fe(CO)_4^-$ and CO. Some $Fe(CO)_3^-$ is also produced, but no $Fe(CO)_2^-$ is present. (Product ions may also be lost via reaction with $Fe(CO)_5$ producing $Fe_2(CO)_6^-$.) Above energies of 3.0 eV $Fe(CO)_2^-$ is also present.

Ions were produced, trapped, and detected by using a Varian V-5900 ion cyclotron resonance (ICR) spectrometer. In-

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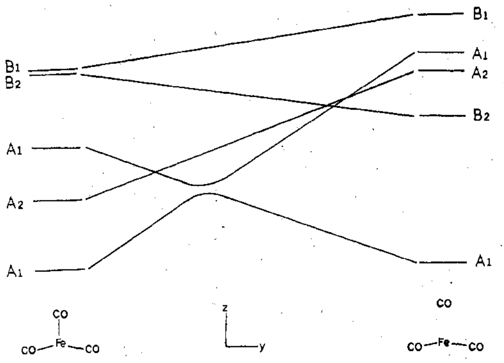

Figure 2. Correlation diagram, C_{2v}, for $Fe(CO)_3^- \rightarrow Fe(CO)_2^-$.

strument parameters and the method of data analysis have been described previously.[8] The low-resolution photodissociation spectra were taken with a 1000-W xenon arc lamp and a Schoeffel Instrument Corp. monochromator; 1.8- and 3.0-nm slits were employed, with 23.8- and 39.6-nm full width at half-maximums, respectively. Results agreed with previous work.[8,10-14] The high-resolution spectra were taken by using a Coherent Radiation Model 590 dye laser, pumped by all lines from an argon ion laser, Coherent Radiation Model CR-12. Rhodamine 6G and Rhodamine 640 were the dyes used to obtain the spectra. Two different electronic transitions and some vibrational structure can be seen in the high-resolution photodissociation spectrum of $Fe(CO)_3^-$ to $Fe(CO)_2^-$ which extends from 440 to 920 nm, with a strong peak at 627.8 nm having a width at half-maximum of 15 nm (Figure 1).

Three vibrational bands can be distinguished within the narrow peak, with maxima at 598, 614, and 627.8 nm. Their spacing corresponds to vibrations of 435 and 359 cm^{-1}, presumably a metal carbonyl stretch. While M–C stretches and M–C–O bends are expected to occur around 650–350 cm^{-1} in metal carbonyls, as observed[15] for $Co(CO)_4$, an exact prediction cannot be made for these ions.[16]

The photodissociation of $Fe(CO)_4^-$ and that of other metal carbonyl anions has been attributed to the metal to ligand charge-transfer transitions that occur at high energies,[13] although the lowest energy bands in $Fe(CO)_5$ itself have been identified as ligand field transitions.[17] Tricoordinate molecules such as $Fe(CO)_3^-$ are predicted to have C_{2v} symmetry while the product ion $Fe(CO)_2^-$ is expected to be linear.[3,4] The lowest optical transition in $Fe(CO)_3^-$, $A_1 \rightarrow A_2$, is forbidden. (See Figure 2.) The lowest *allowed* transition occurs to a level whose energy dependence upon bond angle is quite different from that in the ground state. This $A_1 \rightarrow A_1$ transition therefore has large nondiagonal Franck–Condon factors, causing the transition to be very broad. This is consistent with the photodissociation extending from 440 to 920 nm. The absorption corresponding to the peak at 627.5 nm is the second allowed transition $A_1 \rightarrow B_1, B_2$. It occurs to a level which has an energy–geometry dependence similar to that of the ground state. This band is therefore narrow and higher in intensity.

The A_1 excited state produced by the transition corresponding to the broad absorption connects with the ground state of the products through an avoided crossing, as shown in Figure 2. The B_1, B_2 states do not correlate directly with the ground state of the linear product $Fe(CO)_2^-$ which has A_1 symmetry. These excited states must thus also undergo a radiationless transition before dissociation can take place. The radiationless transitions must be fairly fast, however, since the vibrational bands appear to be broadened. Calculations of the line broadening due to Zeeman splitting and to rotational broadening indicate that the first effect is very small, with the magnitude of the magnetic fields used. The rotational broadening based on C_{2v} geometry, is estimated at 4.4 cm^{-1}, much smaller than that observed.[18]

In an ICR spectrometer it is often possible to observe the direction of the transition moment relative to the direction of dissociation.[19] Thus, a decrease in product signal size change may be observed for different orientations of plane polarized light. The signal for $Fe(CO)_3^-$ *production* has a dependence upon the orientation of polarized light, requiring a nontetrahedral geometry[8] of $Fe(CO)_4^-$. However, the production of $Fe(CO)_2^-$ from $Fe(CO)_3^-$ does not show any additional dependence.

The $A_1 \rightarrow A_1$ transition is allowed for light polarized along the C_2 axis (the *z* direction). For this transition, a greater loss in ion product signal is expected for light polarized perpendicular to the trapping plates. This is not observed, possibly because in this spectral region the reaction occurs with very little excess translational energy.

The $A_1 \rightarrow B_2$ transition in $Fe(CO)_3^-$ is allowed for *y* polarized light, while the $A_1 \rightarrow B_1$ occurs with *x* polarized light. Thus for any orientation of the ion in the cell, dissociation should be isotropic and no polarization dependence would be expected for these transitions, as is observed. This is consistent with the expected C_{2v} geometry of the molecule. The transitions occurring in a C_{3v} molecule would be expected to show a dependence on polarization.

In summary, the photodissociation spectrum for $Fe(CO)_3^- \rightarrow Fe(CO)_2^-$ has been studied at high resolution. A resonance at about 630 nm appears to have vibronic structure and is suggested to be an $A_1 \rightarrow B_1, B_2$ transition embedded in a broad $A_1 \rightarrow A_1$ transition. Assignment of these transitions could be made consistent with expected geometry changes and energy levels on the basis of theoretical predictions. This constitutes one of few direct spectral observations of a highly unsaturated transition-metal complex.

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Preparation and Mössbauer Spectra of Neptunium(III)-Alkali Metal-Chloro Compounds[1]

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Drozdzynski has recently reported[2] the preparation and some properties of uranium(III)–chloro compounds of the

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