Laser Photoelectron Spectrometry of the Negative Ions of Iron and Iron Carbonyls. Electron Affinity Determination for the Series Fe(CO)$_n$, $n = 0, 1, 2, 3, 4$

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Abstract: With a fixed-frequency Ar ion laser, the photoelectron spectra of the negative ions Fe$^-$, FeCO$^-$, Fe(CO)$_2^-$, Fe(CO)$_3^-$, and Fe(CO)$_4^-$ have been obtained. The electron affinity of iron is found to be $(0.164 \pm 0.035)$ eV while the electron affinities for other members of this series increase roughly as the number of ligands. Thus for FeCO the EA is $(1.22 \pm 0.02)$ eV, for Fe(CO)$_2$, $(1.8 \pm 0.2)$ eV, for Fe(CO)$_3$, $(2.4 \pm 0.3)$ eV. In addition, the photoelectron spectra provide information on vibration frequencies, electronic states, and Fe–CO bond strengths in these compounds.

I. Introduction

Until recently there had been no experimental determination of the atomic electron affinity (EA) of iron, although efforts have been made to estimate this quantity for iron and also for a number of other atoms for which it remains unmeasured. We describe here a method for determining electron affinities directly and accurately by photoelectron spectrometry on beams of atomic or molecular anions. We apply this technique to determine the electron affinities of the carbonyl series Fe(CO)$_n^-$ with $n = 0, 1, 2, 3, 4$. These data afford a systematic study of successive ligand binding to a central metal atom.

Photodetachment of the negative ions of the iron carbonyls has been observed previously in ICR experiments of Richardson et al. and Dunbar and Hutchinson. Basically, the ions were trapped in an ion cyclotron resonance cell and their disappearance was monitored as a function of the intensity and wavelength of the irradiating light. There is some uncertainty about the nature of the photodisappearance, i.e., whether it is photodissociation by elimination of a CO group, or photodetachment by elimination of an electron. This question was partially answered by Richardson et al. by measuring the formation of the respective Fe(CO)$_n^-$ ion upon irradiation of the Fe(CO)$_n^+$ ion, indicating that photodissociation was occurring. However, it was uncertain whether the process of photodetachment was competing, and the thresholds for photodetachment were unknown. By establishing the electron affinities for these iron carbonyls with laser photoelectron spectrometry, this paper presents the determination of the energy threshold for photodetachment in these anions.

Additionally, the results of this work, combined with earlier mass spectrometric appearance potentials, yield bond strengths of the neutrals. The appearance potentials of Compton and Stockdale provide the bond dissociation strengths of the anions in the process

$$\text{Fe(CO)}_n^- \rightarrow \text{Fe(CO)}_{n-1}^- + \text{CO}$$

The bond dissociation energies for the corresponding neutrals may be obtained from a thermodynamic cycle once additional information, the energy needed to remove an electron from each of the anions, is known. This latter information is provided by the electron affinities measured here, and the resulting neutral bond strengths determined by combining the appearance potentials and the electron affinities will be given.

II. Experimental Section

The apparatus and techniques have been previously described in detail. Iron pentacarbonyl (Apache Chemicals) is dissociated in a low-pressure (1 Torr) electrical discharge ion source to produce beams of Fe$^+$ and Fe(CO)$_5^-$ ions. The ions are extracted from the source, accelerated to 680 eV, and mass analyzed by a Wien filter. The 0.5–10.0 nA ion beam is crossed in a field-free interaction region by the Ar electron laser, and electrons ejected into the acceptance angle of a spherical electrostatic monochromator are energy analyzed (resolution 60 meV full width at half maximum). At this resolution the many rotational components of a particular vibronic transition are smoothed into a nearly Gaussian peak 90 meV in width. For the high EA Fe(CO)$_4$ species, the 363.8-nm lines of an Ar ion laser was used.

The absolute, center-of-mass electron kinetic energies of peaks in the detachment spectra are determined using simultaneously produced O$^+$ as a calibration ion and the expression

$$E_X = h\nu - E_{A}(O) - 1.0215 (\Omega_{X^-} - \Omega_{X}) - mW (1/M_O - 1/M_X) \quad (1)$$

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Figure 1. Photoelectron spectrum of FeCO\(^{-}\) obtained with 2.54-eV (488 nm) photons. Spacing between data points is approximately 5 meV. The electron affinity corresponds to the peak at approximately 1.3 eV electron kinetic energy.

Figure 2. Photoelectron spectrum of Fe(CO)\(_{2}\)\(^{-}\) ions obtained with 2.54-eV photons. Spacing between data points is 5 meV. See text for details.

Figure 3. Photoelectron spectrum of Fe(CO)\(_{3}\)\(^{-}\) ions obtained with 2.54-eV photons. The breadth of the feature indicates a substantial geometry change between anion and the neutral. The falloff in electron counts near 0.4 eV is largely instrumental.

Figure 4. Photoelectron spectrum of Fe(CO)\(_{4}\)\(^{-}\) ions obtained with 3.408-eV (363.8 nm) photons. The dominant photodestruction process in this case is photodissociation, rather than photodetachment. See text for discussion.

III. Experimental Results

Determination of the electron affinity of atomic iron is relatively straightforward. Photodetachment of Fe\(^{-}\) with 488-nm radiation is energetically capable of producing Fe in the \(5\)D ground state or the \(5\)F and \(3\)F excited states. Since the spacing between these neutral states is well-known,\(^7\) identification of the various peaks on the photoelectron spectra is straightforward. The electron affinity, the difference between the neutral \(5\)D\(_{4}\) level and the ionic \(4\)F\(_{g,2}\) level, is found to be \((0.164 \pm 0.035)\) eV. The details of this analysis are reported elsewhere.\(^8\)

Determining the electron affinities of the iron carbonyls is more difficult because their spectra contain partially resolved vibrational and unresolved rotational structure, as shown in Figures 1–4. Both FeCO (Figure 1) and Fe(CO)\(_{2}\) (Figure 2) have rather sharp, presumably 0-0 peaks, which give electron affinities almost directly. Each peak center can be located to about 10 meV, but in addition to this uncertainty must be added the possible errors introduced by rotational pulling of the peak center and vibrational sequence bands underlying the origin. The magnitude of the possible errors due to rotational effects is on the order of \(\Delta B(kT/2B'' - 1/4)\)
and possible vibrational errors due to sequence bands are on
the order of

$$\Delta \omega e^{-\omega/4T}$$

These can be estimated. If we assume the vibrational frequency
of the ion to be $$\omega'' = 600 \text{ cm}^{-1}$$, the change in frequency going
to the neutral $$\Delta \omega = 0.1 \omega''$$, $$\Delta B = 0.1 B''$$, and $$T = (1000$$
$$\pm 500) \text{ K}$$, then there would be a vibrational correction of $$0.3$$
meV and a rotational correction of $$4 \pm 4$$ meV. Since changes in
bond lengths often accompany changes in molecular vibration
frequencies, these two corrections are correlated and should
be added. This increases the assignable error to almost $$\pm 20$$
meV. Thus the reported electron affinity of FeCO is $$(1.256 \pm$$
$$0.020) \text{ eV}$$ while that of Fe(CO)3 is $$(1.221 \pm 0.020) \text{ eV}$$.

The Fe(CO)4− species gives a broad spectrum for which it is
difficult to assign the origin. The small structure appearing
at $$1.3 \text{ eV}$$ (EA $$\approx 1.25 \text{ eV}$$), since it is quite far away from the
main peak, could represent an excited state of the negative ion.
This will have to be understood before the EA can be assigned
with certainty. Even so, the lack of any sharp, identifiable
features prevents an accurate location of the origin of the broad
system, and we assign the electron affinity to be $$(1.8 \pm 0.2)$$
eV.

The Fe(CO)6− ion gives only a weak photoelectron signal
at only the very lowest electron energies when using 488-nm
radiation. With the laser operating in the UV at photon ener-
gies of 3.408 eV, a successful spectrum was obtained (Figure
4). Structure is not resolved and again locating the origin for
this system is difficult. The electron affinity is assigned to be
$$(2.4 \pm 0.3) \text{ eV}$$. Even with the UV laser, the photodetachment
cross section was qualitatively smaller than for any of the other
species in this study, indicating either that ion absorption is weak
or that another process, photodissociation, is the major
photodestruction process.

IV. Discussion

Any discussion of bonding for these molecules will be at best
tentative and incomplete. For example, the concept of an
electron configuration is almost essential to understanding
bonding; yet present evidence for a particular configuration
for any of the molecules studied here is indirect and incomplete.
Uncertainty as to which configuration assignments to each molecule a single,
dominant electron configuration may be itself suspect; published
studies on NiCO indicate large configuration mixing, and
the analogous situation may complicate the bonding in iron
carbonyls. Recognizing that the true situation undoubtedly will be
complex, we yet have attempted a simple economy in the
following discussion, permitting only the minimal theory that
might explain our results, and allowing only the least expla-
nation sufficient to make the details consistent. The data
available do not justify a more sophisticated treatment at
present.

FeCO. The increase in electron affinity from Fe (0.164 eV)
to FeCO (1.26 eV) is difficult to ascribe to a unique cause.
Chemically, the CO ligand is a "π acid" and may be thought
to stabilize an electron entering a π-type orbital on the iron.
However, a molecular orbital picture reveals that this inter-
pretation is probably too simplistic to explain the increase in
electron affinity brought on by the CO ligand. In forming the
iron anion, the extra electron enters an open 3d orbital. In iron
monocarbonyl, these orbitals are split: interaction with the CO
π* orbitals will stabilize d orbitals of π symmetry, while the
nonbonding σ orbitals on the CO will destabilize the d orbital
having σ symmetry. Therefore, the most probable high-spin,
d-electron configuration is $$(\pi^* 3d)^{(2)}$$ for the neutral and
$$(\pi^* 3d)^{(2)}$$ for the negative ion. This means that the electron
goes into a nonbonding δ orbital (not a π orbital) and it is at
first difficult to see how the electron affinity of this δ orbital
would increase by CO bonding, since it is not directly stabilized
by the ligand.

The formation of a bond increases the electron affinity in
a more indirect way. In forming a bond with CO, the electron
density increases in the region between Fe and C nuclei, and
decreases away from this bonding region. The δ electrons reside
in a plane perpendicular to the axis at the Fe nucleus; therefore,
forming a bond reduces the amount of shielding between these
electrons and the iron nucleus. The net result is an increase in
the bonding of an electron to the iron in these orbitals, a ra-
tionale for the increased electron affinity of FeCO with respect to
Fe.

The FeCO spectrum shows vibrational features to the left
of the central peak, the closest and strongest spaced 1815 cm−1
away, followed by progressively weaker peaks spaced success-
ively 1735 and 1695 (±100) cm−1. This series could be a
strongly anharmonic vibrational progression of the C−O
stretch. This frequency is about what one would expect if there
is a Fe−C bond with considerable π back-bonding. The an-
harmonicity could indicate that this π back-bonding increases
with excitation of the CO stretch. A progression of about 1980
(±100) cm−1 appears to the right of the central peak. This
almost certainly is the C−O stretch in FeCO−. Because this is
a higher frequency in the negative ion, one is tempted to say
that less back-bonding is occurring in the anion than in the
neutral. However, this is not evident from the electron con-
figurations, which have equal electron populations in the π
back-bonding orbitals.

In addition to these progressions in the C−O stretching
mode, a shoulder 740 cm−1 to the right of the assigned origin
likely represents excitation of the Fe−C stretch in the negative
ion. This frequency of this mode is probably even lower in the
neutral, and therefore is not resolved on the other side of the
origin peak.

Compton and Stockdale1 find a difference of about $$(2.0 \pm$$
$$0.3) \text{ eV}$$ between the appearance potentials of FeCO− and Fe−
in an electron bombardment, mass spectrometry experiment,
indicating a Fe−C bond strength of this magnitude for the
negative ion. When this bond strength of the negative ion is
taken with the EAs of FeCO and Fe(CO)3, a simple thermodynamic
cycle predicts a Fe−CO bond dissociation energy in the neutral
of $$(0.9 \pm 0.3) \text{ eV}$$. This bond strength is close to the average
bond energy in Fe(CO)3 (1.25 eV).12

Fe(CO)3. Similar to the FeCO molecule, the Fe(CO)3 mole-
cule should have an electronic configuration $$(\pi^* 3d)^{(1)}$$.
Burden2 predicts a linear geometry for this molecule and its
negative ion because the occupied π orbitals will destabilize
on bonding. Experimentally we find that the electron affinity of
Fe(CO)3 is very close to that of FeCO. The electron adds
to the same nonbonding δ orbital as in the monocarbonyl ion:
therefore, there is no expectation of a markedly different
electron affinity.

Our photoelectron spectrum shows a feature 1950 ± 100
cm−1 to the left of the strong central peak. This probably is the
C−O symmetric stretch. It is very close to the asymmetric vi-
bration frequency of 1910 cm−1 suspected for Fe(CO)3 in a
matrix.14 In a similar manner, our spectrum shows a feature
2250 ± 100 cm−1 to the right of the central peak, which can
be assigned to the C−O stretch in the negative ion. However,
this frequency is greater than that of the free C−O frequency
(2170 cm−1). This is inconsistent with π back-bonding, which
would be expected to lower the CO stretch frequency. It is not
understood why this frequency would be this high, although
it should be realized that this symmetric mode frequency
should be higher than the asymmetric mode frequency (ob-
serveable in IR).

The Fe−CO bond in the Fe(CO)3− ion is weaker than the
same bond in FeCO−. Compton and Stockdale1 observe about
$$(1.0 \pm 0.3) \text{ eV}$$ difference in the appearance potentials of these
two species, making the Fe–CO bond only that strong in the anion. Using our data, we can deduce that the (FeCO–CO) bond dissociation energy is also (1.0 ± 0.3) eV.

$\text{Fe(CO)}_5^-$, The tricarbonyl, rather than being $D_{3h}$, is expected to have lower symmetry. The neutral is expected to assume either $C_{2v}$ (low spin) or $C_{3v}$ (high spin) symmetry, while the iron would be $C_{2v}$. Our spectra provide evidence for a different geometry in the ion from that of the neutral. In the negative ion ($C_{2v}$) one in-plane ligand–metal–ligand bond angle is predicted to be 150°, making the other two 105°. In the $C_{3v}$, neutral these bond angles are symmetrical but the CO groups are out of plane by 17° each. Thus a considerable geometry change would occur in photodetachment. This $C_{3v}$ geometry is consistent with the broad spectrum we observe, which could be caused by a long bending progression accompanying geometry change. Matrix isolation studies of Fe(CO)$_3$ also support this $C_{3v}$ assignment for the neutral.

The electron affinity increases going from Fe(CO)$_2$ to Fe(CO)$_3$ and these simple bonding pictures again are adequate to rationalize the result. In the mono- and dicarbonyl anion, the additional electron enters an essentially nonbonding orbital. In Fe(CO)$_3^-$, significant π back-bonding would be able to stabilize this orbital and increase its electron affinity. This orbital would be further stabilized by the molecular distortion in changing the molecular geometry from the neutral ($C_{3v}$) to the ion ($C_{3v}$).

A controversy still surrounds the Fe–CO bond strength in Fe(CO)$_5^-$ at variance with the proposed geometry changes from $D_{3d}$ in the anion to $C_{2v}$ in the neutral ($C_{2v}$ is observed in matrices). The Fe(CO)$_5^-$ photoelectron spectrum should contain long vibrational progressions, consistent with the broad feature we observe (Figure 4). The appearance potential work indicates that dissociation of the anion would be expected for vibrational excitation greater than 0.6 eV, placing an upper bound on the vibrational energy content of Fe(CO)$_5^-$ ions from our source. If this value is taken as the upper limit for the extent of hot band structure, the electron affinity can be no greater than 2.6 eV. However, assuming an electron affinity even this high leads to a predicted instability of Fe(CO)$_4$ [D(Fe(CO)$_3$–CO) ≈ 0 eV]. The observation of this compound in a matrix, indicating that it is stable, leads to the expectation that the EA is less than 2.6 eV. The formation of Fe(CO)$_4^-$ by collision of potassium atoms with iron pentacarbonyl also suggests an electron affinity in this neighborhood. Thus the assignment of an EA of (2.4 ± 0.3) eV is consistent with this body of data, and implies $D(\text{Fe(CO)}_3\text{–CO}) = 0.2 (+0.3$ or $-0.2$) eV.

Although our experiments do not measure photodissociation directly, the qualitatively weak photoelectron signals from Fe(CO)$_4^-$, in contrast to the other compounds studied here, are consistent with a strong, competing process. In ICR experiments, the cross section for photodisappearance of Fe(CO)$_3^-$ measured as a function of excitation energy shows a sharp increase at 2.5 eV. The photoproduction of Fe(CO)$_4^-$ also shows a sharp increase at this energy, indicating that photodissociation is a mechanism of destruction of Fe(CO)$_4^-$.

Our experiments show, however, that photodetachment also becomes allowed at this energy, and hence the two processes must be competing for photon energies above about 2.5 eV. For photon energies less than this, the only photodestruction mechanism available is photodissociation.

The very low dissociation energy obtained for Fe(CO)$_4$ has implications in light of some interesting recent work. Davies et al. have reported isotopically selective isomerizations of Fe(CO)$_4$ at 20 K in a matrix when irradiated at 10 μ with a CO$_2$ laser. In interpreting these results, the authors invoked a "non-Berry" pseudorotation of the ligands attached to the iron core. They ruled out a dissociation–recombination mechanism because they felt that the energy available, 0.23 eV in a C–O stretch mode, would be too low to dissociate the molecule. However, dissociation would be permitted if the bond strength is 0.2 eV. Therefore, dissociation of Fe(CO)$_4$ followed by recombination is a possible mechanism, and the photoisomerization results should be examined with this possibility in mind. Specifically, if one invokes dissociation as the first step in the mechanism, it becomes almost imperative to assume that the dissociation is mode selective in order to explain the isotopic isomerizations. Thus, Fe(CO)$_4$ may provide the first case of mode-selective photodissociation with IR radiation.

Fe(CO)$_5$ Although our experiments do not directly measure properties of this species, we can add to the body of information on this molecule by establishing the Fe(CO)$_5$–CO bond dissociation energy. This bond dissociation energy must be (2.4 ± 0.5) eV, based on the difference between the thermochemical value for the dissociation of Fe(CO)$_5$ to Fe + 5CO and the value for dissociating Fe(CO)$_4$ to Fe + 4CO that is obtained here from appearance potentials and our EAs. Furthermore, Compton and Stockdale note that the process

$$e^- + \text{Fe(CO)}_5^- \rightarrow \text{Fe(CO)}_5^- + \text{CO}$$

is approximately thermoneutral. Since the EA of Fe(CO)$_4$ is (2.4 ± 0.3) eV, the energy required to break a Fe–C bond in Fe(CO)$_5$ must be approximately this, in agreement with the above determination. This result implies that bonding of carbonyl ligands to iron is "synergistic"; the addition of the last CO in Fe(CO)$_5$ is aided by the bonding of the previous four.

V. Conclusions

The photoelectron spectra of a number of iron carbonyl negative ions have been obtained by photodetachment of mass-selected beams of carbonyl anions of the type Fe(CO)$_n^-$. By interpreting these spectra we can obtain the electron affinities for the neutral iron carbonyls. Iron itself is found to have an EA of (0.164 ± 0.035) eV while FeCO and Fe(CO)$_2$ are found to have EAs of (1.26 ± 0.02) and (1.22 ± 0.02) eV, respectively. It is more difficult to assign an electron affinity to a unique feature in the spectra of Fe(CO)$_3^-$ and Fe(CO)$_4^-$, and the larger uncertainties associated with the EAs of these two species reflect this: (1.8 ± 0.2) and (2.4 ± 0.3) eV are the EAs of Fe(CO)$_3$ and Fe(CO)$_4$, respectively.

The photoelectron spectra also contain information on the vibrations that can occur in either the ions or neutrals. Thus it is found that FeCO and Fe(CO)$_2$ neutrals have C–O stretch frequencies of (1815 ± 100) and (1950 ± 100) cm$^{-1}$, while their negative ions have slightly higher C–O stretch frequencies, (1980 ± 100) and (2250 ± 100) cm$^{-1}$, respectively. The two other species studied, Fe(CO)$_3^-$ and Fe(CO)$_4^-$, have only broad spectra to which no distinct vibrations are assignable. However, molecular vibrations contribute to the spectra; the breadth of the spectra of these anions is caused by long progressions in low-frequency bending modes. These bending vi...
Electric Dichroism Spectroscopy in the Vacuum Ultraviolet.

2. Formaldehyde, Acetaldehyde, and Acetone

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Abstract: Electric field studies, including electric linear dichroism and electrochromism spectroscopy, have been completed for the second excited singlet of formaldehyde, acetaldehyde, and acetone in the gas phase. Transition-moment directions, excited-state dipole moments, and excited-state mean polarizabilities are determined. The data support the 3s ← n assignment for these bands. The excited-state dipole moment and mean polarizability determined for acetone are 0.19 D, electron density away from the oxygen. and 450 Å³, respectively. These values for formaldehyde are 0.33 D and 70 Å³, respectively. Excited-state parameters of this magnitude give additional support for the extravalent assignment. Acetaldehyde excited state properties cannot be determined quantitatively, but analysis of the spectrum gives some evidence that the transition moment of the absorption in question is in the molecular plane as would be expected for the 3s ← n Rydberg transition. Finally, strong perturbation of the transition-moment lengths suggests the presence of an underlying transition of the same symmetry as the second excited singlet.

Introduction

The second singlet excitation in the electronic absorption spectra of aldehydes and ketones has received a variety of assignments. Recently, a study of this absorption in formaldehyde gave tentative support to the B2 ← A1, 3sα1 ← nβ2 assignment for this transition.1 In this earlier work, the unpolarized light electrochromism spectrum of the 174.9-nm band was reported. A large positive dipole moment change (e = μg − μc) of 2.66 D suggested that the dipole moment of this excited state in formaldehyde is very nearly, since the ground-state dipole moment is reported to be 2.33 D.2 This change in dipole moment and the corresponding change in the mean polarizability (b = 60 Å³), together with other evidence, favor an extravalent assignment for this absorption.

The original electric field spectrometer3 has been modified permitting the acquisition of both electrochromism and electric linear dichroism spectral data. Electric dichroism is a differential absorption resulting from molecular orientation in a modulated electric field, where the incident radiation may be either unpolarized or at a fixed polarization angle with respect to the orienting field. Electric linear dichroism results when the polarization angle of photons incident to a oriented molecule in a static electric field is modulated between 0° and 90° to that field. The origin of all three types of spectra and the theoretical expressions and dependencies have been given in the literature.6-11 Only certain aspects of the experiment are discussed here.

The theoretical description of the electric field effect gives rise to this general expression for the intensity of transmitted