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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 ± 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 (1.26 ± 0.02) eV; for $Fe(CO)_2$, (1.22 ± 0.02) eV; for $Fe(CO)_3$, (1.8 ± 0.2) eV; for $Fe(CO)_4$, (2.4 ± 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[1] 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.[2] 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 $n = 0, 1, 2, 3$, or 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.[3] and Dunbar and Hutchinson.[4] 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.[3] by measuring the formation of the respective $Fe(CO)_{n-1}{}^-$ 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,[1] yield bond strengths of the neutrals. The appearance potentials of Compton and Stockdale provide the bond dissociation strengths of the anions in the process

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

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[5] 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 $Fe(CO)_n{}^-$ 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 intracavity beam of a 488-nm (2.540 eV) CW Ar ion laser, and electrons ejected into the acceptance angle of a hemispherical electrostatic monochromator are energy analyzed (resolution 60 meV fwhm). 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 III 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[5]

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

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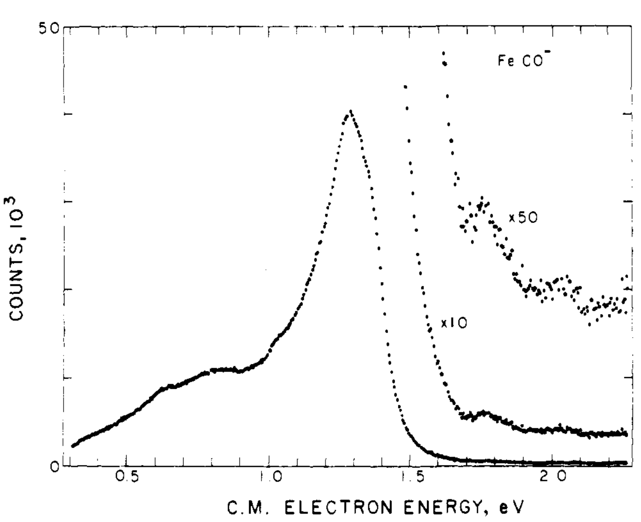

Figure 1. Photoelectron spectrum of $FeCO^-$ obtained with 2.54-eV (488 nm) photons. Spacing between data points is approximately 5 meV. The electron affinity corresponds to the peak at approximately 1.3 eV electron kinetic energy.

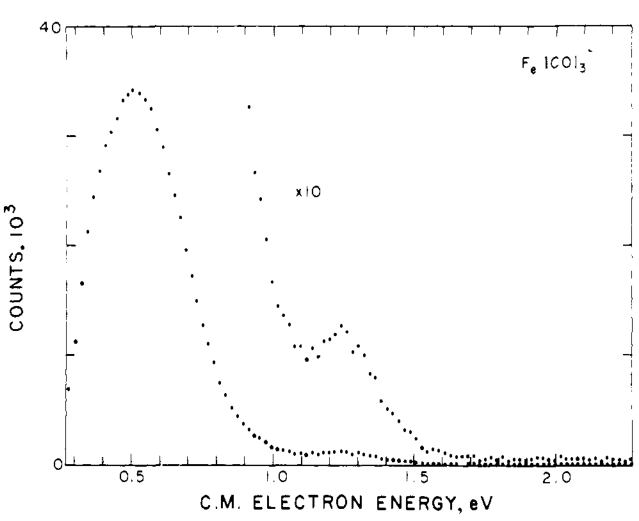

Figure 3. Photoelectron spectrum of $Fe(CO)_3^-$ ions obtained with 2.54-eV photons. Spacing between data points is approximately 20 meV. The breadth of the feature indicates a substantial geometry change between anion and the neutral. The falloff in electron counts near 0.4 eV is largely instrumental.

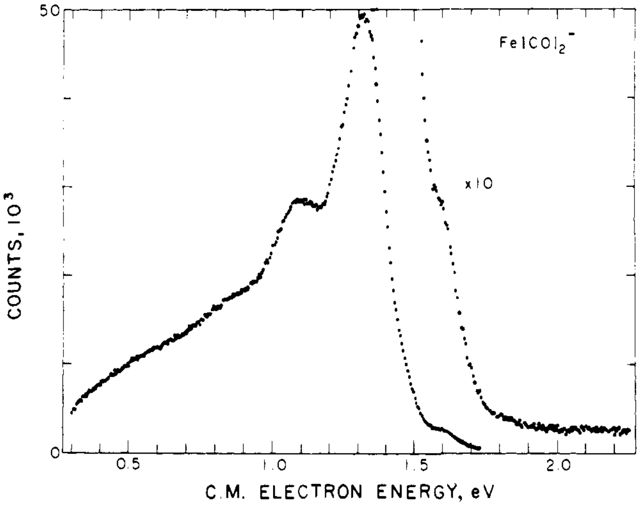

Figure 2. Photoelectron spectrum of $Fe(CO)_2^-$ ions obtained with 2.54-eV photons. Spacing between data points is 5 meV. See text for details.

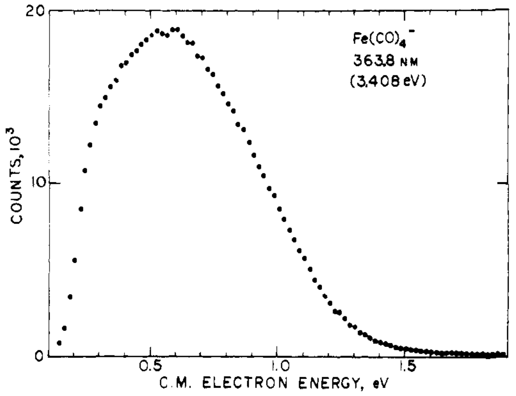

Figure 4. Photoelectron spectrum of $Fe(CO)_4^-$ ions obtained with 3.408-eV (363.8 nm) photons. The dominant photodestruction process in this case is photodissociation, rather than photodetachment. See text for discussion.

where $h\nu = 2.540$ or 3.048 eV depending upon the laser wavelength used to supply the energy for the detachment; EA(O) = 1.465 eV is the "effective"[6] electron affinity of the oxygen atom, determined from the center of O^- photodetachment peak; $(\Omega_{O^-} - \Omega_{X^-})$ is the laboratory energy difference between the O^- peak center and a particular X^- peak center. The factor 1.0215 is an energy scale compression factor described previously, determined by calibrating an NH^- photodetachment spectrum against the known values for the NH $^1\Delta$-$^3\Sigma$ splitting.[7] The final term in eq 1 accounts for the fact that the electrons we detect must be backscattered (in the center-of-mass frame) into the energy analyzer and thus have a center-of-mass component of energy perpendicular to the analyzer axis; W is the kinetic energy of the ion beam (680 eV), and m, M_O, and M_X are the masses of electron, oxygen atom, and molecule X, respectively.

The intensity of the photoelectrons at a given electron energy E depends upon the angle θ between the electric vector of the linearly polarized laser light and the electron collection direction according to[8]

$$I(\theta) = \sigma/4\pi)[1 + \beta(E)P_2(\cos\theta)] \qquad (2)$$

where σ is the average photodetachment cross section, β is the anisotropy parameter, and P_2 is the second Legendre polynomial. The spectra presented here were obtained with θ such that $P_2(\cos\theta)$ was zero, and thus reflect an average photodetachment cross section. A half-wave plate could be inserted to rotate the laser polarization, allowing measurement of the anisotropy of the detached electrons.

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 ^5D ground state or the ^5F and ^3F excited states. Since the spacing between these neutral states is well-known,[9] identification of the various peaks on the photoelectron spectra is straightforward. The electron affinity, the difference between the neutral $^5D_4$ level and the ionic $^4F_{9/2}$ level, is found to be (0.164 ± 0.035) eV. The details of this analysis are reported elsewhere.[10]

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

$$\Delta\omega e^{-\omega''/kT}$$

These can be estimated. If we assume the vibrational frequency of the ion to be $\omega'' = 600\ \mathrm{cm}^{-1}$, the change in frequency going to the neutral $\Delta\omega = \pm 0.1\omega''$, $\Delta B = \pm 0.1B''$, and $T = (1000 \pm 500)$ K, then there would be a vibrational correction of ±3 meV and a rotational correction of ±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 ±20 meV. Thus the reported electron affinity of FeCO is (1.256 ± 0.020) eV while that of $Fe(CO)_2$ is (1.221 ± 0.020) eV.

The $Fe(CO)_3^-$ species gives a broad spectrum for which it is difficult to assign the origin. The small structure appearing at 1.3 eV (EA ~ 1.25 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 ± 0.2) eV.

The $Fe(CO)_4^-$ 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 energies 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 ± 0.3) 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. Worse, the assumption that assigns to each molecule a single, dominant electron configuration may be itself suspect: published studies on NiCO indicate large configuration mixing,[11] 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 explanation 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 interpretation 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 $\pi^4\delta^3\sigma(^3\Delta)$ for the neutral and $\pi^4\delta^4\sigma(^2\Sigma)$ 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 rationale 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 successively 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 anharmonicity 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 configurations, 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 Stockdale[1] find a difference of about (2.0 ± 0.3) 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 Fe and FeCO, a simple thermodynamic cycle predicts a Fe–CO bond dissociation energy in the neutral of (0.9 ± 0.3) eV. This bond strength is close to the average bond energy in $Fe(CO)_5$ (1.25 eV).[12]

$Fe(CO)_2$. Similar to the FeCO molecule, the $Fe(CO)_2$ molecule should have an electronic configuration $\pi^4\delta^3\sigma(^3\Delta)$. Burdett[13] predicts a linear geometry for this molecule and its negative ion because the occupied π orbitals will destabilize on bending. Experimentally we find that the electron affinity of $Fe(CO)_2$ 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 vibration frequency of 1910 cm^{-1} suspected for $Fe(CO)_2$ 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 (observable in IR).

The Fe–CO bond in the $Fe(CO)_2^-$ ion is weaker than the same bond in $FeCO^-$. Compton and Stockdale[1] observe about (1.0 ± 0.3) 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.

$Fe(CO)_3^-$. The tricarbonyl, rather than being D_{3h}, is expected to have lower symmetry.[13,15] The netural 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[13] 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.[14]

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 bicarbonyl 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_{2v}).

A controversy still surrounds the Fe-CO bond strength in $Fe(CO)_3^-$. At variance are the appearance potential measurements,[1] which give a bond strength of 2.0 eV, and the ICR photodissociation measurements,[3] which give a threshold for the disappearance of $Fe(CO)_3^-$ and appearance of $Fe(CO)_2^-$ of about 1.4 eV. The apparent threshold for the disappearance at 1.4 eV can possibly be attributed to "hot bands" arising from vibrational or electronic excitation of the negative ion; this interpretation is supported by noticing a similar "hot band" in our photoelectron spectrum. However, a strong process of photodisappearance of $Fe(CO)_3^-$ begins at about 2 eV in the ICR experiments, and is associated with a peak in the photoappearance of $Fe(CO)_2^-$, indicating almost incontestably that the dissociation occurs at an energy less than this. If (2.0 ± 0.2) eV is taken as the dissociation energy in the ion, the dissociation energy of the neutral becomes (1.4 ± 0.3) eV.

$Fe(CO)_4$. Because the predicted[13] geometry changes from D_{2d} in the anion to C_{2v} in the neutral (C_{2v} is observed in matrices),[16] the $Fe(CO)_4^-$ photoelectron spectrum should contain long vibrational progressions, consistent with the broad feature we observe (Figure 4). The appearance potential work[1] 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 $Fe(CO)_4^-$ 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,[16] 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.[1] Thus the assignment of an EA of (2.4 ± 0.3) eV is consistent with this body of data, and implies $D[Fe(CO)_3\text{-}CO] = 0.2$ (+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[3,4] the cross section for photodisappearance of $Fe(CO)_4^-$ measured as a function of excitation energy shows a sharp increase at 2.5 eV. The photoproduction of $Fe(CO)_3^-$ also shows a sharp increase at this energy,[4] 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.[17] 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 $Fe(CO)_4$-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[1] and our EAs. Furthermore, Compton and Stockdale note[1] that the process

$$e^- + Fe(CO)_5 \rightarrow Fe(CO)_4^- + CO$$

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-

Table I. Iron Carbonyl Properties

species	EA, eV	Fe–C bond strength, eV
FeCO	1.26 ± 0.02	1.0 ± 0.3
$Fe(CO)_2$	1.22 ± 0.02	1.0 ± 0.3
$Fe(CO)_3$	1.8 ± 0.2	1.4 ± 0.3
$Fe(CO)_4$	2.4 ± 0.3	0.2 ± 0.4
$Fe(CO)_5$	?	2.4 ± 0.5

brations are excited by nuclear geometry changes occurring upon electron detachment.

These data can be used to determine the Fe–C bond strengths in the neutral carbonyls. These determinations are made by combining our EA values with the measurements of Compton and Stockdale[1] of the appearance potentials of various $Fe(CO)_n^-$ species. These bond strengths, shown in Table I, have direct applicability to an understanding of the chemistry of these iron carbonyls.

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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 $3s \leftarrow n$ 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 Å^3, respectively. These values for formaldehyde are 0.33 D and 70 Å^3, 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 $3s \leftarrow n$ 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 $B_2 \leftarrow A_1$, $3sa_1 \leftarrow nb_2$ 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 ($a = \mu_g - \mu_{ex}$) of 2.66 D suggested that the dipole moment of this excited state in formaldehyde is very nearly zero, 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 ($b = 60$ Å^3), together with other evidence,[3,4] favor an extravalent assignment for this absorption.

The original electric field spectrometer[6] has been modified permitting the acquisition of both electrochromism and electric linear dichroism spectral data. Electrochromism 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 dc 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.[6-10] 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

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