A study of the low-lying electronic states of Fe$_2$ and Co$_2$ by negative ion photoelectron spectroscopy

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The anions Fe$_5^-$ and Co$_5^-$ were prepared and cooled to 300 K in a flowing afterglow ion source, and the low-lying electronic states of the neutral dimers were probed by negative ion photoelectron spectroscopy. Previous ab initio studies of Fe$_2$ and Co$_2$ have predicted single 4$s$-$4s$ bonds, and extremely high densities of low-lying states due to the small energy cost in transferring electrons among nonbonding 3$d$ orbitals. In contrast to the complex photoelectron spectra implied by these calculations, the observed spectra are remarkably simple. It is argued that this spectral simplicity implies a greater role for the 3$d$ electrons in the iron and cobalt dimer bonds. These data also provide values for the electron affinities of the neutral dimers (0.902 ± 0.008 eV Fe$_2$, 1.110 ± 0.008 eV Co$_2$), the bond elongation on electron attachment (0.08 ± 0.02 Å Fe$_2$, Co$_2$), and the vibrational frequencies of the anions (250 ± 20 cm$^{-1}$ Fe$_5^-$, 240 ± 15 cm$^{-1}$ Co$_5^-$).

Related studies of the atomic anions yield improved values for the electron affinities of Fe (0.151 ± 0.003 eV) and Co (0.662 ± 0.003 eV).

I. INTRODUCTION

The nature of bonding in transition metal dimers remains a largely unconquered problem toward which intense experimental and theoretical efforts are currently being directed. Spectroscopic and computational results have reached consonant descriptions for systems such as the singly $s$-$s$ bonded dimers of the $d^{10}$ coinage metals, and the quintuply $d$-$d$ bonded group VIA dimers. However, our understanding of the extent of $d$-electron participation in the metal-metal bonds of many systems falling between these two extremes is much less complete. For example, bond orders ranging from one to four have been predicted for Fe$_2$. The only ab initio configuration interaction (CI) studies of Fe$_4^4$ and Co$_4^6$ recently reported by Shim and Gingerich, find single $4s$-$4s$ bonds and essentially nonbonding $3d$ cores. This picture of the chemical bonding implies extremely high densities of low-lying electronic states due to weak interactions between $3d$ electrons localized around the two metal atoms: 112 Fe$_2$ states and 84 Co$_2$ states are predicted to lie within 0.5 eV of the ground states. Thus far, no spectroscopic data providing a test of these striking predictions have been reported.

In this paper, we report the first gas phase electronic spectra of Fe$_2$ and Co$_2$, obtained by photoelectron spectroscopy of the corresponding negative ions. In contrast to the extremely complex spectra that would be expected based upon the ab initio CI results described above, remarkably simple spectra are actually observed. Throughout the spectral regions spanned by the predicted dense electronic state manifolds, we observe photodetachment transitions to only two electronic states of each dimer; two additional Co$_2$ band systems appear at slightly higher energies. With due consideration of the propensity rules for photoelectron spectroscopy, we argue that the sparse spectra observed here provide strong evidence for $3d$-$3d$ bonding in Fe$_2$ and Co$_2$.

II. EXPERIMENTAL METHOD

The negative ion photoelectron technique has two important advantages for the electronic spectroscopy of transition metal molecules. Since the measured quantity is the kinetic energy of the photodetached electron (equal to the photon energy minus the ion-to-neutral transition energy), this experiment affords a continuous view of the low energy spectral region of the neutral molecule. For example, the present experiment accesses an energy range up to 1 eV above the ground states of Fe$_2$ and Co$_2$, covering the entire bound molecule region. In contrast, the relatively weak bond strengths and high state densities of such systems can yield exceedingly complex or unstructured spectra in the higher energy, optical region. A second advantage of this technique is that mass selection of the ion beam prior to photodetachment greatly expedites signal carrier identification.

A complete description of the negative ion photoelectron spectrometer has recently appeared. Briefly, anions are prepared in a flowing afterglow ion source, gently extracted into the low pressure regions of the apparatus, and mass selected. The beam of selected ions is then crossed by the intracavity beam of a cw argon ion laser tipped at the "magic" angle yielding photodetachment signal intensities proportional to average photodetachment cross sections. A small fraction of the photodetached electrons are energy analyzed at a resolution of 11 meV (90 cm$^{-1}$) by a hemispherical electrostatic monochromator with multichannel detection. The absolute photoelectron kinetic energy scale is calibrated with respect to the accurately known electron affinities of O$^-$ and S$^-$ and measured atomic fine structure splittings in the W$^-$ photoelectron spectrum.

In the experiments reported here, Fe$_5^-$ and Co$_5^-$ were prepared from the stable metal carbonyl precursors Fe$_2$(CO)$_{10}$, Fe$_3$(CO)$_{12}$, and Co$_3$(CO)$_{18}$. Vapors from the gently heated solid samples were injected into the flowing...
afterglow negative ion source downstream of a 2.45 GHz microwave cavity discharge in 0.7 Torr of helium. Sample ion currents of ~5 pA were obtained following mass selection. Rapid rotational equilibration of the ions to 300 K was provided by collisions with the He buffer gas; hot band intensities in the photoelectron spectra indicate that vibrational equilibration of the Fe$_2^-$ and Co$_2^-$ anions was also reached. Experiments carried out at 457.9, 488.0, and 514.5 nm verified the independence of relative peak intensities on photoexcitation energy, demonstrating that the unexpected simplicities of the observed spectra are not due simply to accidental resonances. Scans to higher electron kinetic energy of the spectral regions displayed below revealed no additional photodetachment signal.

III. RESULTS

Figure 1 shows the Fe$_2^+$ + e$^-$ $\rightarrow$ Fe$_2^-$ photoelectron spectrum. Unambiguous identification of the signal carrier as Fe$_2^-$ rather than Fe(CO)$_3^-$ (also 112 amu) is provided by the very different spectrum observed$^{14}$ for the latter species. The vibronic band system at high electron kinetic energy is assigned to the transition between the Fe$_2^-$ and Fe$_2^+$ electronic ground states. This assignment is supported by the excellent agreement of the 300 $\pm$ 15 cm$^{-1}$ neutral molecule vibrational frequency observed here with that obtained$^{15}$ in low-temperature matrix resonance Raman studies. Consistent with this agreement, gas-to-matrix shifts for the first row transition metal diatomics (with the exception of the weakly bound Mn$_2^+$ molecule) have in general been found to not exceed a few wave numbers.$^{16}$ The origin band position implies a Fe$_2^+$ electron affinity of 0.902 $\pm$ 0.008 eV, and the hot band observed to its right indicates an anion frequency of 250 $\pm$ 20 cm$^{-1}$. A harmonic Franck-Condon analysis of the vibronic band intensity profile yields a bond length change of 0.08 $\pm$ 0.02 Å on electron attachment. Use of the Fe$_2^+$ value of 2.02 $\pm$ 0.02 Å, obtained by EXAFS of Fe$_2$ in solid neon$^{17}$ then implies a bond length of 2.10 $\pm$ 0.04 Å for Fe$_2^-$.

Only one excited electronic state of Fe$_2^+$ is observed in the photoelectron spectrum. Its relatively large separation from the ground state of 0.534 $\pm$ 0.004 eV (4310 $\pm$ 30 cm$^{-1}$) precludes its assignment to a spin-orbit component of the Fe$_2^+$ ground state. Peak separations and relative intensities in both band systems indicate the same vibrational frequency and bond length for the ground and excited Fe$_2^+$ states, within our experimental error.

The Co$_2^+$ + e$^-$ $\rightarrow$ Co$_2^-$ spectrum is displayed in Fig. 2. The intense group of peaks at high electron kinetic energy is comprised of two vibronic progressions whose origin bands, indicated by the arrows, are separated by 600 $\pm$ 20 cm$^{-1}$. In the lower electron kinetic energy region, at least two weaker transitions to Co$_2$ states ~5000 cm$^{-1}$ higher in energy are observed. As for the Fe$_2^+$ dimer, the two strong Co$_2^+$ band systems each show the same vibrational intervals and intensity profiles. The 280 $\pm$ 20 cm$^{-1}$ Co$_2^+$ frequency observed here is consistent with the reported matrix value$^{18}$ of 290 cm$^{-1}$. Hot bands from the $v = 1$ and 2 vibrational levels of the anion determine the Co$_2^-$ frequency to be 240 $\pm$ 15 cm$^{-1}$. The observed vibronic band intensity profiles, and the bond weakening suggested by the frequency decrease in the anion, indicate that the Co$_2^-$ internuclear separation exceeds the (unknown) value in Co$_2^+$ by 0.08 $\pm$ 0.02 Å.

Although the relatively small separation of 600 $\pm$ 20 cm$^{-1}$ between the two intense band systems does not itself preclude their assignment to different fine-structure levels of the Co$_2^+$ or Co$_2^-$ ground states, other considerations argue against this assignment. This portion of the Co$_2^-$ spectrum is remarkably similar to the corresponding region of the Re$_2^-$ spectrum,$^{19}$ despite the very different spin-orbit couplings expected for the first and third row dimers. In addition, the nearly equal intensities of these two band systems are unexpected. It may also be noted that the calculated$^1$ bond

![Graph 1](image1.png)

**FIG. 1.** Fe$_2^+$ + e$^-$ $\rightarrow$ Fe$_2^-$ photoelectron spectrum at 488 nm (2.540 eV). Arrows mark origins of the two observed vibronic band systems. The weak, broad band between these is due to a small amount of Fe(CO)$_3^-$ impurity in the 112 amu ion beam.

![Graph 2](image2.png)

**FIG. 2.** Co$_2^+$ + e$^-$ $\rightarrow$ Co$_2^-$ photoelectron spectrum at 488 nm (2.540 eV). Origins of the two overlapping vibronic band systems observed in the high electron kinetic energy region are indicated by arrows. The congested appearance of the relatively weak bands at lower electron kinetic energy suggests the activities of at least two electronic transitions in this region; the indicated feature is separated from the ground state origin band by 5060 $\pm$ 50 cm$^{-1}$.

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characteristic of transitions between different spin-orbit components observed in the photoelectron spectra of related systems, such as the corresponding atomic and metal monoxide anions. An alternative assignment of these bands to transitions from different \( \text{CO}_2^- \) states to the \( \text{CO}_2 \) ground state is also improbable in view of the relatively weak intensity expected for a 600 cm\(^{-1} \) excited anion state at the 300 K ion source temperature. Thus, the most likely assignment for these band systems, as for the two band systems observed in the spectrum of \( \text{Fe}_2^- \), is to transitions from the anion ground state to the ground state and an excited electronic state of the neutral molecule. The origin of the band system at higher electron kinetic energy then yields an electron affinity of 1.110 \( \pm \) 0.008 eV for \( \text{CO}_2^- \).

We have also recorded spectra of the \( \text{Fe}^- \) and \( \text{CO}^- \) atomic anions, at a resolution improved by a factor of six over that obtained in the original \(^{21(b),21(c)} \) studies. The resulting atomic electron affinities, which are consistent with the previous results but considerably more precise, are 0.151 \( \pm \) 0.003 eV for Fe and 0.662 \( \pm \) 0.003 eV for Co.

IV. DISCUSSION

The photoelectron data for \( \text{Fe}_2 \) and \( \text{CO}_2 \) show several close similarities. In both cases, a relatively small bond elongation of 0.08 Å (\( \sim \) 4% of the \( \text{Fe}_2 \) bond length) and a vibrational frequency reduction of \( \sim \) 20% occurs on electron attachment to the neutral molecule ground state. The first excited states observed in these spectra also display vibrational frequencies and bond lengths equal to those of the \( \text{Fe}_2 \) and \( \text{CO}_2 \) ground states, within our experimental error. In addition, similar signal intensities are observed for both of these systems in each spectrum. Based upon past experience with transition metal atomic anions, \(^{21} \) we infer from these intensity similarities that both band systems in each spectrum arise from electron detachment from an orbital of the same type (4s or 3d) of atomic parentage. Thus, we conclude that the four prominent band systems observed in the \( \text{Fe}_2^- \) and \( \text{CO}_2^- \) photoelectron spectra are all associated with detachments out of orbitals of mainly either 4s or 3d parentage.

The longer bond lengths and lower vibrational frequencies observed for the anionic dimers, as compared with the corresponding neutral molecules, suggest that the orbitals from which the electrons are detached are of antibonding character. However, since these changes are relatively small, and since the shielding effects of the additional electron will certainly alter both the relative energies and radii of the 4s and 3d-type orbitals in the negative ions, it appears most prudent to conclude that the observed detachment transitions are associated with either weakly antibonding or essentially nonbonding orbitals.

An additional factor common to both the \( \text{Fe}_2^- \) and the \( \text{CO}_2^- \) photoelectron spectra is that the peak widths in their prominent vibronic band systems are instrumentally (90 cm\(^{-1} \)) limited, and show no evidence of thermal broadening due to appreciable population of more than one electronic state of the negative ion at 300 K. Thus, the high density of excited states predicted \(^{4,8} \) for the neutral dimers in the vicinity of their ground states apparently does not occur for the anionic dimers. We can further conclude from the observed band widths and arguments presented in the previous section that either each band system involves significant contributions from only one spin-orbit transition, or the splittings between multiple spin-orbit transitions are small (\( \leq 30 \) cm\(^{-1} \)) compared to our instrumental resolution.

Before discussing the probable spectral signatures of the predicted neutral molecule electronic state densities, it is useful to outline several of the major determinants of observable states in this experiment: (1) Photoelectron selection rules \(^{21(b),21(c)} \) depend upon the angular momentum carried off by the detached electron. For example, for atomic orbitals \( \Delta L = 0, |\Delta S| = 1/2 \) transitions are allowed for s-electron detachments and \( |\Delta L| < 2, |\Delta S| = 1/2 \) transitions are allowed for d-electron detachments. (2) For most systems, single electron processes (i.e., detachment with no additional electron reorganization) are expected to give rise to the strongest photoelectron transitions. \(^{21} \) However, this propensity is likely to become less important for transition metal dimer anions, due to the profound effects of configuration interaction in these systems. (3) Franck–Condon considerations can render invisible those electronic states of the neutral molecule whose associated internuclear separations differ substantially from that of the anion.

We next inquire whether the observed spectra are consistent with the \( \text{ab initio} \) CI predictions of Shim and Gingerich \(^{4,8} \) for the neutral dimers. According to this model, the \( \text{Fe}_2 \) and \( \text{CO}_2 \) bonds are due primarily to filled 4s\( \sigma \)\( \tau \) orbitals, and the 3d\(^7 \)Fe and 3d\(^8 \)Co cores are essentially nonbonding and localized on the metal atoms. We consider two possibilities for the negative ion dimers based upon these predictions: either the extra electron attaches to an antibonding 4s\( \sigma \)\( \tau \) orbital, or to a nonbonding 3d orbital. In the first case, the two prominent band systems observed in each spectrum, which we have noted above are most likely due to detachments from orbitals of the same type of atomic parentage, must be assigned to 4s\( \sigma \)\( \tau \) and 4s\( \sigma \)\( \tau \) detachments. These processes would produce the neutral molecule in its (4s\( \sigma \)\( \tau \))^2 ground state, and in a (4s\( \sigma \)\( \tau \))(4s\( \sigma \)\( \tau \)) excited state, respectively. The critical bonding role attributed to the 4s\( \sigma \)\( \tau \) orbital would then imply very different bond lengths and vibrational frequencies in these two electronic states. This, however, is not consistent with our results. The second possibility is that the extra electron is associated with a nonbonding 3d orbital and the observed spectra are due to d-electron detachments. In that case, many transitions would be expected to occur in the spectral region probed here in view of the low energies predicted by Shim and Gingerich for the neutral molecule excited states, and the considerations discussed in the preceding paragraph. This situation would give rise to a far more complex photoelectron spectrum than is actually observed. Therefore, we conclude that the photoelectron data are not consistent with the proposed model for the chemical bonding in these dimers.

Our results suggest that the d electrons of the two metal atoms are more delocalized than is predicted by these careful, state-of-the-art \( \text{ab initio} \) CI calculations. A strengthened interaction between d orbitals would reduce the number of accessible states in the 0–1 eV spectral range probed in this.
length for Fe₂ exceeds the matrix EXAFS result\(^{17}\) by 0.4 Å, and the calculated Fe₂ and Co₂ vibrational frequencies\(^{28}\) of 204 and 162 cm\(^{-1}\) are considerably lower than the experimental values. These discrepancies are in the directions that would be expected were \(d-d\) bonding underestimated in these calculations, although they clearly do not necessarily imply that this is the case. Below we discuss two alternative models for Fe₂ and Co₂ which differ with respect to the relative \(s-s\) and \(d-d\) contributions to the chemical bonding, and we attempt to assess their compatibility with the present data.

An interpretation of the photoelectron spectra consistent with the strongly bonding character attributed to the 4s\(\sigma\)ₐ orbitals in these theoretical studies would involve their assignments to nonbonding or weakly antibonding \(d\)-orbital detachments. An illustration of one such assignment scheme is provided by results of the electronic structure calculations for Fe₂ reported by Harris and Jones using density functional methods.\(^{6}\) These authors obtain a formally triply bonded \(\Delta\)ₐₐ lower energy state (in agreement with recent SCF-Xα studies\(^{2,3}\)) involving one \(s-s\) and two \(d-d\) bonds, with only weakly bonding and antibonding \(\delta\)ₐ and \(\delta\)ₐ orbitals. The lowest excited state, \(\pi\) \(\Delta\)ₐ state presumably due to a \(\cdots(\delta\)ₐ)\(^2\)(δ\(\pi\)\)\(^{-1}\) \(\delta\)ₐ \(\delta\)ₐ \(\delta\)ₐ \(\cdots\) \(\pi\) promotion, is predicted to occur at \(\sim 0.5\) eV and to have an internuclear separation similar to that of the ground state. Accordingly, a \(\cdots(\delta\)ₐ)\(^3\)(δ\(\pi\)\)\(^{-1}\) \(\delta\)ₐ \(\delta\)ₐ \(\delta\)ₐ \(\delta\)ₐ \(\cdots\) \(\pi\) anion configuration could conceivably account for the two band systems observed in the Fe₂ spectrum, and for the lack of intervening bands.\(^{23}\) This example is meant to be illustrative rather than unique; Harris and Jones are careful to caution against too literal an interpretation of their calculated excited state ordering. In addition, since they do not report all of the calculated low-lying excited states and configurations, the consistency of this model with the lack of observed photoelectron transitions to higher excited states cannot be tested.

An alternative assignment for the most intense band systems in the Fe₂ and Co₂ spectra to detachments out of orbitals of \(4s\) parentage is suggested by the strong dominance of such processes in the photoelectron spectra of the atomic transition metal negative ions.\(^{21}\) Detachments of 4s\(\sigma\)ₐ and 4s\(\sigma\)ₐ electrons from a \(\cdots(4s\sigma\)ₐ\)\(^{-2}\)(4s\(\pi\)\)ₐ\) anion, producing low spin (4s\(\sigma\)ₐ\)\(^{-2}\) and high spin (4s\(\sigma\)ₐ\)\(^{-2}\)(4s\(\pi\)ₐ\)\(^{-1}\)) neutral molecule configurations, could then account for the two intense band systems observed in each spectrum. The relatively weak intensities of the bands in the low electron kinetic energy region of the Co₂ spectrum would then suggest that they arise from \(d\) electron detachments.\(^{21}\) In view of the slight bond elongations and frequency reductions on electron attachment associated with the intense band systems, this assignment would imply that both the 4s\(\sigma\)ₐ and 4s\(\sigma\)ₐ orbitals are weakly antibonding (or essentially nonbonding), and thus that the Fe₂ and Co₂ molecules are primarily \(d-d\) bonded.

The nonbonding or weakly antibonding 4s\(\sigma\) orbitals implied by this assignment is reasonable if the optimal bonding radius of these orbitals significantly exceeds the equilibrium internuclear separation. According to a growing body of theoretical\(^{24}\) and experimental\(^{25}\) work, this situation does occur in the multiply \(d-d\) bonded group VIA dimers, Cr₂ and Mo₂. The gas phase spectra of these molecules also display electronic transitions involving only small bond length changes,\(^{25}\) which have been assigned\(^{24,c}\) to promotions out of nonbonding \(\sigma\)ₐ orbitals. For Ni₂\(^{26}\) and Cu₂\(^{27}\) on the other hand, the chemical bonding appears to be due essentially entirely to the 4s\(\sigma\)ₐ orbital. Therefore, this interpretation of the photoelectron spectra of Fe₂ and Co₂ would suggest that for atoms with at least half-filled \(d\) shells in the first transition series (excluding the exceptionally stable \(5d^1\) Mn atom), the chemical bonding in the homonuclear diatomics changes from 3d–3d to 4s–4s between Co₂ and Ni₂.

V. CONCLUSIONS

Negative ion photoelectron spectroscopy of Fe₂ and Co₂ has been employed to probe the electronic states of the neutral metal dimers up to 1 eV above their ground states. These data provide measurements of the electron affinities of Fe₂ and Co₂, the gas phase vibrational frequencies of these molecules and their negative ions, and the differences in bond lengths between the neutral and anionic dimers. Related studies have also provided more precise values for the corresponding atomic electron affinities. The qualitative result to be emphasized concerning the metal dimer spectra is that they are remarkably simple. This observation, combined with previously reported \(ab\) \(initio\) CI calculations for the low-lying states of singly 4s–4s bonded neutral dimers with nonbonding 3d cores, indicates that the 3d electrons in Fe₂ and Co₂ are delocalized and participate in the bonding of these molecules. Two alternative interpretations of the observed spectra have been discussed, which imply quite different pictures of the relative contributions of \(s-s\) and \(d-d\) bonding in these systems. While the picture of \(d-d\) bonding is more appealing in light of its intuitive consistency with the simplicity of the observed spectra, the available data do not at present permit a definitive preference to be expressed. It is hoped that theoretical calculations of energy separations between the possible neutral molecule states accessed in these experiments, as well as negative ion photoelectron angular distribution studies of these and related systems such as Cr₂ and Ni₁², will soon yield a unique interpretation.

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\(^{1}\)For recent reviews, see (a) W. Weltner, Jr. and R. J. Van Zee, Annu. Rev. Phys. Chem. 35, 291 (1984); (b) V. E. Bondybayev, Science 227, 125 (1985); (c) Faraday Symp. 14, 7–250 (1980).


We note that the lack of observed spin-orbit splittings is not necessarily inconsistent with this assignment. If such splittings are relatively large in the anion, only the lowest spin-orbit component may have appreciable thermal population. Transitions from a $^3P_{1/2}$ anion to the $^3D_2$ lowest spin-orbit components of the neutral molecule states could (based upon our atomic results) exhibit substantially greater intensities than transitions to the higher energy $\Omega = 4$ components, yielding only one spin-orbit transition with appreciable intensity in each band system. On the other hand, if spin-orbit splittings are relatively small in both the anion and the neutral, multiple spin-orbit transitions could be present but not detectable at our 90 cm$^{-1}$ resolution. We thank a referee for suggesting that we clarify this point.


27. See Ref. 1(a) for a review of the extensive literature on Cu$_2$. 

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