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# A Simple Interpretation of the $Fe_2^-$ Photoelectron Spectrum

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# Abstract

The photoelectron spectrum of $Fe_2^-$ can be simply interpreted in terms of electron detachment from the mildly antibonding $4s\sigma_u^*$ orbital of a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ anion. This interpretation implies a $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ configuration for the ground state of $Fe_2$, correlating with one ground state ($4s^2 3d^6$) and one excited state ($4s^1 3d^7$) Fe atom. A comparison of the bond length and vibrational frequency of $Fe_2$ to values for transition metal dimers containing single $4s$-$4s$ bonds is suggestive of $3d$-$3d$ bonding in this molecule. The results of preliminary full-valence configuration interaction calculations provide strong support for the proposed $Fe_2$ and $Fe_2^-$ configurations.

## I. Introduction

A recent report of the photoelectron spectrum[1] of $Fe_2^-$ contrasted these results with *ab initio* predictions[2] of a 4*s*-4*s* singly bonded $Fe_2$ ground state arising from the interaction of two $4s^13d^7$ excited state atoms. The experimental data were shown to be incompatible with this picture, but an alternative model capable of satisfactorily explaining the spectrum remained elusive. Subsequently, photoelectron data[3,4] for $Cu_2^-$ and $Ni_2^-$, as well as careful theoretical investigations[5] of the electronic structure of $Cu_2^-$, have become available. In light of these results, we propose here a new qualitative model for the ground states of $Fe_2$ and $Fe_2^-$, one which affords a simple interpretation of the previously puzzling photoelectron spectrum.

## II. Review of Experimental Results

The photoelectron spectrum of $Fe_2^-$, reproduced in Fig. 1, shows just two vibronic band systems throughout the region probed by the 488 nm (2.540 eV) photodetachment laser. The bands at lower electron binding energy were assigned[1] to the transition between the electronic ground states of $Fe_2^-$ and $Fe_2$; this assignment is discussed further below. The data show that the ground state of $Fe_2^-$ has a vibrational frequency of $250 \pm 20\ cm^{-1}$, a bond length of $2.10 \pm 0.04$ Å, and a bond strength of $1.53 \pm 0.17$ eV (assuming values[2,6] of $2.02 \pm 0.02$ Å and $0.78 \pm 0.17$ eV for $Fe_2$). These results are indicative of a strong chemical bond in the anion. The second band system, $0.534 \pm 0.004$ eV higher in energy, was assigned to a transition from the ground state of the anion to an excited electronic state of $Fe_2$. Peak separations and relative intensities in both systems indicate the same vibrational frequency and bond length for the two observed $Fe_2$ states, within experimental error.

## III. Discussion

The photoelectron spectra of $Cu_2^-$, $Ni_2^-$ and of the first-row atomic transition metal anions[7] are all dominated by $4s$ rather than $3d$ electron detachment, strongly suggesting that the two band systems observed in the $Fe_2^-$ spectrum are also due to detachment from $4s$-like molecular orbitals. In view of the strongly bonding[8] $4s\sigma_g$ orbital in $Ni_2$ and $Cu_2$, and the similar vibrational frequencies and bond lengths of $Fe_2$,[6,9] $Ni_2$,[4,10] and $Cu_2$,[11,12] it is likely that the $4s\sigma_g$ orbital in $Fe_2$ is also strongly bonding. Therefore, the virtually identical bond lengths and vibrational frequencies in the two observed states of $Fe_2$ suggest that they both have the same $4s\sigma_g$ occupation.

This restriction leaves a limited number of possibilities. We first consider a $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{14}$ configuration for $Fe_2^-$, in analogy with the $Cu_2^-$ case.[3,5] The two $4s$-detachment processes of lowest energy would then produce the neutral molecule in $(4s\sigma_g)^2(3d)^{14}$ and $(4s\sigma_g)^1(4s\sigma_u^*)^1(3d)^{14}$ states, which differ in their $4s\sigma_g$ orbital occupancies. On the other hand, a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ configuration for $Fe_2^-$, correlating with ground state Fe $(4s^23d^6)$ and ground state $Fe^-$ $(4s^23d^7)$, would fulfill the necessary criterion. Detachment of either $4s\sigma_u^*$ electron would produce two $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ $Fe_2$ states with the $4s\sigma_u^*$ electron high- or low-spin coupled to the $(3d)^{13}$ "core". These states would undoubtedly display very similar vibrational frequencies and bond lengths, as is observed. The 0.53 eV separation between the two $Fe_2$ band systems is actually very similar to the 0.66 eV ($M_J$-averaged) splitting[13] between the $^3F$ and $^5F$ states of the Fe atom in its $3d^7(^4F)4s^1$ configuration.

As noted above, the vibrational frequency, bond length and bond dissociation energy obtained from the photoelectron spectrum indicate that the $Fe_2^-$ anion has a strong chemical bond. This conclusion would at first appear to preclude a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ occupation, in which the four $4s$-derived electrons make no formal bonding contribution. However, a closer inspection of the $4s\sigma_u^*$ orbital in the anion indicates that the proposed configuration is in fact consistent with these data. Recent extensive *ab initio* calculations[5] of $Cu_2^-$ reproduce well the observed changes in bonding on electron attachment, and show that the $4s\sigma_u^*$ orbital is extensively polarized with little electron density in the internuclear region. Thus, although the $4s\sigma_g$ orbital is strongly bonding as expected, the antibonding character of the $4s\sigma_u^*$ orbital is greatly reduced by $4s\sigma$-$4p\sigma$ mixing. In the neutral metal dimers, on the other hand, this orbital is expected to be less diffuse and more antibonding. In the $Mn_2$ ground state, the analogous $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{10}$ configuration yields only a weak, van der Waals bond.[14]

These arguments support the view that $Fe_2^-$ has a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ ground state configuration, and thus that the two $Fe_2$ states observed in the photoelectron spectrum have $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ occupations. The 0-1 and 0-2 vibrational intervals of these $Fe_2$ states both agree with those reported[9] for the ground electronic state to within the uncertainty of the photoelectron experiment (15 $cm^{-1}$). This agreement indicates that the potential energy surfaces of both states are very similar to that of the ground state. In view of the strongly bonding character of the $4s\sigma_g$ orbital and the somewhat antibonding $4s\sigma_u^*$ orbital expected in the neutral molecule, such a close resemblance is highly unlikely for states with different $4s\sigma_g$ or $4s\sigma_u^*$ occupations. The 0-1 vibrational intervals of all of the first-row metal dimers investigated to date[1,3,4] decrease by ≈50 $cm^{-1}$ on addition of an electron to the $4s\sigma_u^*$ orbital, and the A <- X transition of $Cu_2$, which may be due to a $4s\sigma_u^* \leftarrow 3d$ excitation, is accompanied by a vibrational frequency decrease of 74 $cm^{-1}$.[15]

These considerations indicate that the <u>ground</u> state of $Fe_2$ also has a $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ configuration, presumably with the $4s\sigma_u^*$ electron high-spin coupled to maximize exchange interactions. This configuration clearly will give rise to a large number of electronic states with different couplings of electrons within the $(3d)^{13}$ "core", and it is likely that many of these states will exhibit similar vibrational frequencies. Consequently, it cannot be inferred from the vibrational data alone that the lowest energy $Fe_2$ state observed in the photoelectron spectrum is the ground state. In fact, the propensity for single electron photoelectron processes (i.e., detachment with no additional electron reorganization) would favor transitions to states with the same $3d$-shell configuration as in the ground state of $Fe_2^-$, which may well differ from that of $Fe_2$. However, previous experience in the photoelectron spectroscopy of negative ions, as well as neutral species, indicates that it is likely that the ground state transition would be detectable in a complex system such as $Fe_2$ due to electron correlation effects. These considerations strongly favor the assignment of the bands at lower electron binding energy to the ground state transition; however, this assignment is not critical to the central argument of this paper.

The proposed $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ $Fe_2$ configuration corresponds to one ground state $(4s^23d^6)$ and one excited $(4s^13d^7)$ Fe atom at dissociation, and to an admixture of the $4s^23d^6$ and $4s^13d^7$ occupations for each Fe atom at finite separation. This molecular configuration is supported by a comparison of the ground state configurations of the first-row homonuclear metal dimers to their respective $4s^23d^m \rightarrow 4s^13d^{m+1}$ atomic promotion energies. At one extreme, the very large promotion energy of Mn (2.14 eV) results in a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{10}$ ground state configuration for $Mn_2$ correlating to the $4s^23d^5 + 4s^23d^5$ atomic limit.[14] In contrast, the $(4s\sigma_g)^2(3d)^{2m+2}$ ground state configuration is observed[8] for the dimers of V, Cr, Ni and Cu, which have $4s^13d^{m+1}$ atomic ground states or very small ($\leq$0.25 eV) promotion energies. The intermediate promotion energies[13] of Sc (1.43) and Ti (0.81 eV) favor the $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{2m+1}$ configuration, which correlates asymptotically to the mixed $4s^23d^m$ + $4s^13d^{m+1}$ atomic limit. This configuration has in fact been demonstrated for the $^5\Sigma_u^-$ ground state[16-20] of $Sc_2$ and has been calculated[17,20] to give rise to the ground state of $Ti_2$. In view of the similar $4s^23d^6$ -> $4s^13d^7$ atomic promotion energy of Fe (0.87 eV),[13] it appears quite reasonable that the ground state of $Fe_2$ should also derive from this mixed asymptote. Consistent with this view, the analogous $\sigma^2\sigma^{*1}d^6$ configuration of FeH produces an excited electronic state only 0.24 eV above the $\sigma^2d^7$ ground state.[21] The atomic promotion energy of Co (0.42 eV), and the similarities between the $Fe_2^-$ and $Co_2^-$ photoelectron spectra,[1] also suggest that the $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{15}$ configuration is a reasonable candidate for the ground state of $Co_2$.

The proposed $Fe_2$ configuration is also consistent with its lower ionization potential (6.30 ± 0.01 eV)[22] than that of $Cu_2$ (7.894 ± 0.015 eV)[23] or $Ni_2$ (7.1 ± 0.7 eV),[8,10] since in the latter two cases a $4s\sigma_g$ rather than a $4s\sigma_u^*$ electron must be detached. Furthermore, the photoionization spectrum of $Fe_2$ shows a sharp threshold to the 0-0 transition.[22] This result is difficult to reconcile with detachment of a strongly bonding $4s\sigma_g$ electron from the commonly assumed $(4s\sigma_g)^2(3d)^{14}$ ground state configuration, but is understandable in terms of the detachment of an only mildly antibonding $4s\sigma_u^*$ electron from a $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ molecule. The ground state configurations proposed here are also compatible with the surprising observation that the bond strength of $Fe_2^-$ (1.53 ± 0.17 eV)[1,3] is almost twice that of $Fe_2$ (0.78 ± 0.17 eV),[2] despite relatively modest changes in the vibrational frequency and bond length on electron attachment. To form $Fe_2$ in a $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ state one atom must be promoted to $4s^13d^7$, whereas a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ anion can be formed from the ground states of Fe and $Fe^-$. Thus, the anion bond energy would be expected to exceed that of the neutral molecule by approximately the atomic promotion energy (0.87 eV), even if the potential energy surface near equilibrium were to remain largely unchanged on electron attachment to the $4s\sigma_u^*$ orbital.

The important issue of the extent of 3*d*-3*d* bonding in $Fe_2$ can be addressed in light of these results. A $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ configuration would imply a formal bond order of only one-half for the 4*s*-4*s* bond in $Fe_2$. In contrast, both $Ni_2$ and $Cu_2$ are reported to have a $(4s\sigma_g)^2(3d)^{2m+2}$ ground state with a single 4*s*-4*s* bond and a nonbonding 3*d* core.[8,10] Nevertheless, the bond length of $Fe_2$ (2.02±0.02 Å)[6] is shorter than that of either $Ni_2$ (2.200±0.007 Å)[10] or $Cu_2$ (2.2197 Å).[11] In addition, the $Fe_2$ vibrational frequency (300 cm$^{-1}$)[9] is comparable to that recently observed[4] for $Ni_2$, and actually exceeds the $Cu_2$ value (266.43 cm$^{-1}$).[11] These comparisons corroborate the earlier conclusion[1] that the 3*d* electrons participate in the $Fe_2$ bond. A strengthened interaction between 3*d* orbitals over that predicted by previous *ab initio* calculations[2] would have the additional effect of reducing the density of electronic states in the spectral region probed in this experiment. The occurrence of 3*d*-3*d* bonding in $Fe_2$ (and, presumably, in $Fe_2^-$ as well) may account at least in part for the surprisingly sparse appearance of the photoelectron spectrum and for the absence of detectable transitions from electronically excited anions.

## IV. Calculations

To further assess the proposed assignment scheme, quantum mechanical calculations were performed. The electronic structure of the suggested states is obviously quite complicated. Walsh[24] has observed spontaneous symmetry breaking when $d^{13}$ occupations for $Fe_2$ are treated without imposing inversion symmetry, which indicates substantial correlation effects in the *d*-space. More recent studies by Bauschlicher[25] confirm that the inclusion of substantial dynamical correlation is required to describe the binding in these systems adequately. However, given that present calculations compare systems with the same *d* occupations (and, indeed, the same *d* spin and spatial coupling) at essentially the same bond lengths, it should still be possible to arrive at semi-quantitative results without accounting for these effects.

We have performed full-valence configuration interaction calculations for $4s\sigma_u^*$ electron detachment from a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ $Fe_2^-$ anion. At each bond length studied, a CASSCF calculation was performed on $Fe_2^-$, including four electrons in the two 4*s*-derived MOs and all possible distributions of 13 electrons in the ten 3*d*-derived MOs. Several different $(3d)^{13}$ occupancies, each with maximum spin $S = 7/2$, were considered. Full valence CI calculations were then performed on states with one electron removed from the $4s\sigma_u^*$ orbital, selecting those CI roots whose $(3d)^{13}$ occupancy matched that of the ion calculation. For example, to model detachment from the $^8\Phi_g$ $Fe_2^-$ state, the appropriate $^9\Phi_u$ and $^7\Phi_u$ states of $Fe_2$ were used. This procedure is analogous to the use of Koopmans' theorem for single determinant wavefunctions, but it allows for relaxation effects and recouplings in the 3*d* shell. Bond lengths and harmonic frequencies were obtained from quadratic fits in 1/r to energies calculated at three bond lengths. All calculations were performed using the MOLECULE-SWEDEN[26] codes on the CRAY X-MP/48 at NASA-Ames.

The basis set used in these calculations was derived from Wachters (14*s* 9*p* 5*d*) primitive set,[27] with the outermost two *s*-type primitives replaced with four (exponents 0.26, 0.08, 0.03, 0.012). The set was further augmented with three *p*-type primitives (exponents 0.20237, 0.06276, 0.025) and two *d*-type primitives (exponents 0.1133 and 0.044). With the resulting (16*s* 12*p* 7*d*) uncontracted set a CI calculation on $Fe^-$ was performed, including all single and double excitations from a single reference configuration and correlating the valence electrons only. The basis was then contracted to [6*s* 5*p* 3*d*] using the most strongly occupied natural orbitals from the CI calculation as basis functions.[28] The resulting basis is effectively of triple zeta quality in the valence.

For all of the cases examined [$(3d)^{13}$ core configurations $^8\Phi_g$, $^8\Delta_g$, and $^8\Sigma_g^-$] the high- and low-spin states of the neutral molecule were found to be split by about 0.32 eV, 0.13 eV lower than the calculated atomic $^5F$-$^3F$ splitting of 0.45 eV. The experimentally observed molecular splitting (0.53 eV) is also 0.13 eV lower than the known 0.66 eV ($M_J$-averaged) splitting for the Fe atom in the $3d^7 4s^1$ configuration. The calculated bond lengths (2.16 Å) and vibrational frequencies (323-327 cm$^{-1}$) of these states are virtually identical (experimental: 2.02 Å, 300 cm$^{-1}$). The calculated vibrational frequency, as well as the frequency reduction (35-40 cm$^{-1}$) and bond elongation (0.04 Å) on addition of the second $4s\sigma_u^*$ electron, are also in agreement with the experimental results ($\Delta\nu = 50 \pm 20$ cm$^{-1}$, $\Delta r = 0.08 \pm 0.02$ Å). Thus, these calculations provide strong support for the proposed ground state configurations of $Fe_2$ and $Fe_2^-$.

## V. Conclusion

We have proposed a simple interpretation of the $Fe_2^-$ photoelectron spectrum based on detachment of $4s\sigma_u^*$ electrons from a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ anion. This interpretation implies a $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ ground state configuration for $Fe_2$, rather than the $(4s\sigma_g)^2(3d)^{14}$ configuration that has generally been assumed. The former configuration correlates to an admixture of the $4s^2 3d^6$ and $4s^1 3d^7$ occupations for each atom at finite separation, an admixture that is also important in describing the bonding in FeH and related metal hydrides.[29] The proposed $Fe_2$ configuration gives a formal 4*s*-4*s* bond order of only one-half. A comparison of its bond length and vibrational frequency to those of related metal dimers containing single 4*s*-4*s* bonds then indicates some additional 3*d* contribution to the bonding in $Fe_2$. The results of preliminary valence CI calculations provide strong support for the proposed $Fe_2$ and $Fe_2^-$ configurations. The arguments presented here suggest that states arising from the mixed $4s^2 3d^m + 4s^1 3d^{m+1}$ atomic asymptote be more carefully considered in future theoretical investigations of $Fe_2$ and $Co_2$.

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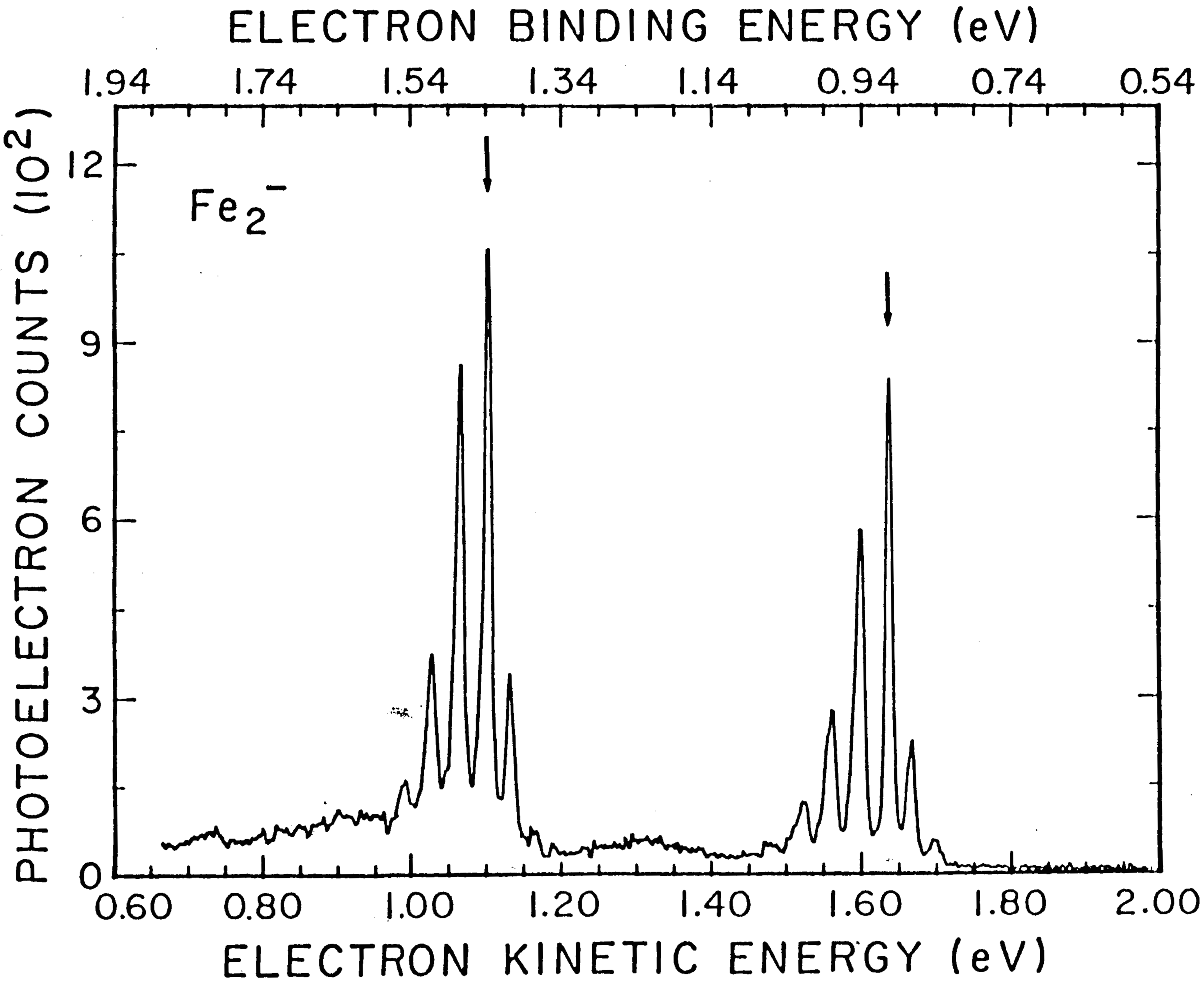
Figure Caption

Fig. 1 $Fe_2^-$ --> $Fe_2$ + $e^-$ 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 $Fe(CO)_2^-$ impurity in the 112 amu ion beam. Reprinted from Ref. 1.


ELECTRON BINDING ENERGY (eV)
1.94
1.74
1.54
1.34
1.14
0.94
0.74
0.54
PHOTOELECTRON COUNTS (10$^2$)
12
9
6
3
0
$Fe_2^-$
0.60
0.80
1.00
1.20
1.40
1.60
1.80
2.00
ELECTRON KINETIC ENERGY (eV)