

Laser photoelectron spectrometry of FeO^- : Electron affinity, electronic state separations, and ground state vibrations of iron oxide, and a new ground state assignment*

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The photoelectron spectrum of FeO^- ions, obtained with 2.54 eV ArII irradiation, consists of a well resolved series of vibrational transitions from the ground electronic state of the negative ion to two low-lying electronic states of FeO . Analysis of this spectrum gives the electron affinity of FeO (1.492 ± 0.020 eV) and the vibrational frequency of the negative ion (740 ± 60 cm^{-1}). The vibrational frequency of the ground state of FeO is 970 ± 60 cm^{-1} ; the term energy T_0 of the first excited state of FeO is 3990 ± 100 cm^{-1} . The FeO vibrational frequency shows definitively that the accepted ordering of FeO states is incorrect, and that the previously assumed ground state must in fact be an excited state. Earlier spectroscopic studies of FeO are re-examined, and a new state ordering, consistent with all experimental data, is proposed.

I. INTRODUCTION

Very little is known about the low-lying electronic states of diatomic transition metal oxides and for most, including FeO , not even the ground state symmetry is known with certainty. Based upon partial spectroscopic analysis, Barrow and Senior¹ propose that the "X" state of FeO is a sigma state of high multiplicity. Low temperature Mössbauer studies² of FeO in inert gas matrices show that the iron nucleus experiences a magnetic field of about 400 kOe, indicative of a high spin multiplicity in the true FeO ground state.

Fairly elaborate calculations by Bagus and Preston³ and Walch and Goddard⁴ predict an FeO state ordering ${}^5\Delta$, ${}^5\Sigma^+$, ${}^5\Pi$, Neither group could obtain a ${}^5\Sigma$ state below the ${}^5\Delta$, and hence Bagus and Preston³ propose that the ground state of FeO is not ${}^5\Sigma^+$. Any of the three states studied would be consistent with the Mössbauer studies of the true ground state.

Most recently, West and Broida⁵ have utilized chemiluminescence and laser-excited fluorescence of FeO to attempt to clarify the state ordering and assignments. Additional spectroscopic constants were determined, but the state ordering is still not definitive. The best current FeO spectroscopic properties are summarized in Table I.

Based on the spectroscopic constants of the X state, 11 μm ir bands ascribable to FeO vibrations have been measured in $\text{Fe}(\text{CO})_5 + \text{O}_2$ shock tube experiments and line intensities were derived.⁶ However, these bands were accompanied by unidentified emissions in the 5.2- μm region, preventing a complete characterization of the shock wave. The source of these emissions has remained a mystery.

Accurate electron affinities of transition metals or their compounds are almost nonexistent.⁷ Our efforts to determine the electron affinity of iron⁸ led to the measurement of some iron compound electron affinities. Here we report the photoelectron spectrum of FeO^- , from which we determine E. A. (FeO), and are led to re-assess the spectroscopic states of iron oxide.

II. EXPERIMENTAL

The apparatus and techniques have been previously⁹ described in detail. Iron pentacarbonyl is burned with either N_2O or O_2 in a low pressure electrical discharge ion source to produce beams of FeO^- and O^- ions. The ions are extracted from the source, accelerated to 680 eV, and mass analyzed by a Wien filter. The 0.2–0.5 nA ion beam is crossed in a fieldfree interaction region by the intracavity beam of a 4880 Å (2.540 eV) cw ArII 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 components of a particular vibronic transition are smoothed into a nearly Gaussian peak ~90 meV in width.

The absolute detachment energies of peaks in the spectra are determined using simultaneously produced O^- as a calibration ion and the expression⁹

$$E_x = E. A. (\text{O}) + 1.0215 (\Omega_{\text{O}^-} - \Omega_{\text{X}^-}) + mW(1/M_{\text{O}} - 1/M_{\text{X}}); \quad (1)$$

$E. A. (\text{O}) = 1.465$ eV is the "effective"⁷ electron affinity of the oxygen atom, determined from the center of the O^- photodetachment peak, and $(\Omega_{\text{O}^-} - \Omega_{\text{X}^-})$ is the labora-

TABLE I. Spectroscopic constants of FeO (Ref. 13).

State	T_e (cm^{-1})	ω_e (cm^{-1})	B_e (cm^{-1})	r_e (Å)
<i>f</i>	41 480
<i>e</i>	$x + 13\,042$	(670)
<i>d</i>	<i>x</i>	(955)
<i>c</i>	22 496	540
<i>b</i>	{ 17 918 and 18 014	{ 660 and 667	0.472	1.69
<i>a</i>	17 293	827	0.497 ^b	1.65 ^b
(<i>e</i>)	10 477	651 ^c		
X ^a	0 ^a	875.4 ^b	0.5127	1.626

^aThe work of this paper indicates this is not the ground state; hence, the T_e energy zero is in question.

^bWest and Broida (Ref. 5).

^cBass and Benedict (Ref. 15).

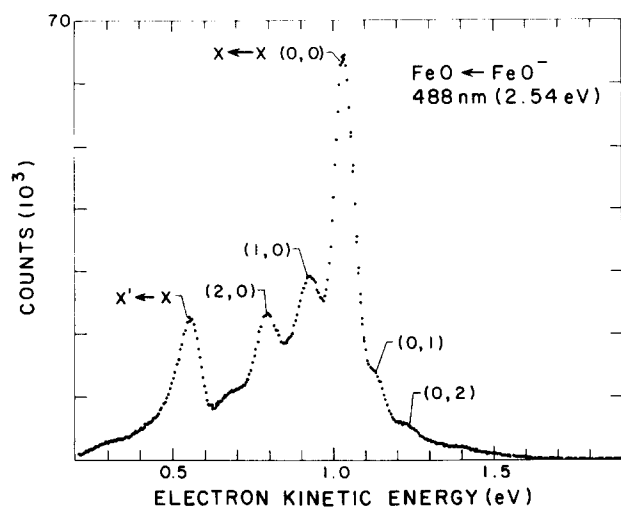


FIG. 1. FeO⁻ photoelectron spectrum of counts vs center-of-mass kinetic energy of the detached electrons. Peak markings show the vibrations (v' , v'') of the ground state (X) and the lower, ionic ground state, while the marking $X' \leftarrow X$ indicates the (0,0) detachment to the first electronic excited state of the neutral.

tory 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 by calibrating an NH⁻ photodetachment spectrum against the known values for the NH $^3\Sigma^- \rightarrow ^1\Delta$ splitting.¹⁰ The final term in Eq. (1) accounts for the fact that the electrons we detect must be backscattered (in the c. m. frame) into the energy analyzer and thus have a c. m. 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 to¹¹

$$I(\theta) = (\alpha/4\pi) [1 + \beta(E) P_2(\cos\theta)], \quad (2)$$

where σ is the average photodetachment cross section, β is the anisotropy parameter, and P_2 is the second Legendre polynomial. The spectrum shown in Fig. 1 was obtained with θ such that $P_2(\cos\theta)$ was zero, and thus reflects 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. RESULTS

Figure 1 shows the FeO⁻ photoelectron spectrum obtained with 2.54 eV photons. The main features are a (0,0) transition at 1.037 ± 0.008 eV electron energy, and a sequence of neutral vibrations at 0.917 ± 0.008 (1,0), 0.792 ± 0.008 (2,0), and 0.678 ± 0.02 eV (3,0); a new neutral electronic state appears at 0.549 ± 0.008 eV electron energy. At the high energy side of the (0,0) peak a weak hot-band system appears. No spin-orbit splittings are observed, but the resolution of the elec-

tron spectrometer is 60 meV FWHM. The observed peaks are broadened further by rotational transitions, and one does not expect to resolve any fine structure present.

The polarizations of all the lines indicate a large asymmetry with the electrons preferentially detached parallel to the electric vector of the light. The ratio I_{\parallel}/I_{\perp} decreases smoothly through the vibrational series and then abruptly changes as the new electronic state is reached (Fig. 2). No qualitative changes in the spectrum occur upon increasing the laser wavelength from 488 to 514.4 nm; this observation indicates that the observed intensities are characterized by Franck-Condon factors and a relatively constant electronic transition matrix element in this energy range.

The vibrational progression allows a determination of the vibrational frequency of the ground-state neutral—this is found to be 970 ± 60 cm⁻¹. The hot bands—not so well resolved—give an estimate of 740 ± 100 cm⁻¹ for vibrations in the negative ion. The band corresponding to the first neutral excited state does not show vibrations clearly but close inspection suggests vibrations are spaced (900 ± 100 cm⁻¹).

The smaller vibrational frequency in the ion relative to the neutral indicates a weakening of the bond and an increase in the bond length in the ion. A simple harmonic oscillator approximation for the vibrations in both the ion and the neutral ground states gives $[\gamma_e(\text{FeO}^-) - \gamma_e(\text{FeO})] = 0.06 \pm 0.02$ Å when adjusted to give Franck-Condon factors equal to the relative vibrational line intensities in the spectrum.¹² Unfortunately, neither the neutral nor the ion equilibrium distance is known, so only the difference is known.

Before an electron affinity can be established we must examine the rotational and vibrational effects that shift the observed peaks. Since little is known about the internuclear separations in the ion or in the neutral ground state, only a rough rotational correction will be attempted. We assume the bands are dominated by N -

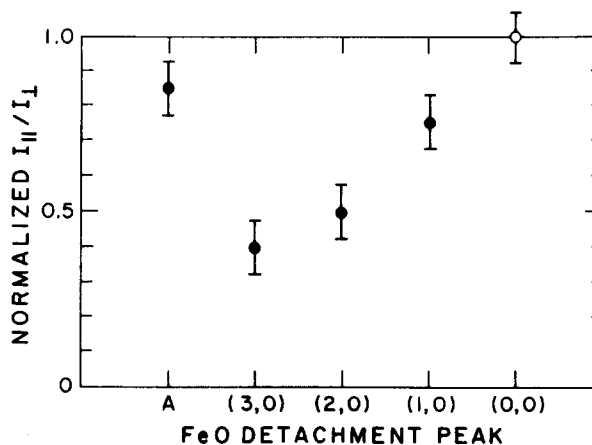


FIG. 2. FeO⁻ polarization dependence of relative peak intensities, with the (0,0) peak (open circle) normalized to one. The ratio I_{\parallel}/I_{\perp} represents the relative intensity of detached electrons parallel to the laser polarization vs that perpendicular to it.

TABLE II. FeO states observed in this experiment.

Electron affinity	T_0	ω_0	r_e	Probable assignment ^a
1.987 ± 0.020 eV	3990 ± 100 cm ⁻¹	$(900 \pm 100$ cm ⁻¹)?	$\approx r_e(\text{FeO}^-) + 0.02$ Å	$X'(X) \ ^5\Sigma^+$
1.492 ± 0.020 eV	0	970 ± 60 cm ⁻¹	$r_e(\text{FeO}^-) - 0.06 \pm 0.02$ Å	$X(d) \ ^5\Delta$, ground state

^aOld state designations in parentheses; symmetries assigned from calculations of Refs. 3 and 4.

conserving transitions from the maximally populated rotational level N_{\max} of the lower (ion) state, where

$$N_{\max} = \left(\frac{kT}{2B''} \right)^{1/2} - \frac{1}{2}.$$

The change in rotational energy $\Delta(F)$ upon detachment is

$$\begin{aligned} \Delta(F) &= F'(N_{\max}) - F''(N_{\max}) \\ &= (B' - B'')(kT/2B'' - 1/4). \end{aligned}$$

Taking $B' = 0.5127$ cm⁻¹ and $r_e'' = 1.63 \pm 0.10$ Å as a first estimate with a large uncertainty (see Table I) and with $T = 1000 \pm 500$ K, we obtain $N_{\max} \sim 28$, $B' - B'' = 0.038 \pm 0.02$ cm⁻¹, and $\Delta(F) = 30 \pm 20$ cm⁻¹. The reported electron affinity is so corrected.

Vibrational sequence bands also shift the apparent electron affinity towards too high a value. At 1000 K, the $V=1$ level will have about a quarter of the population. This will shift the unresolved bands by

$$\frac{1}{4} \times (970 - 740) \text{ cm}^{-1} = 55 \text{ cm}^{-1},$$

with the error on this about ± 30 cm⁻¹. Combining the rotational and vibrational corrections yields a total correction of 85 ± 50 cm⁻¹ to the electron affinity, giving E. A. (FeO) = 1.492 ± 0.020 eV. No spin-orbit corrections have been made since they are unknown. Consequently, the reported E. A. corresponds essentially to the energy difference between term centers of gravity.

Similar corrections made for the electron affinity of the FeO excited state using vibrations of 875 cm⁻¹ and $r_e = 1.63$ Å give E. A. (X') = 1.987 ± 0.020 eV. The difference between this and the ground state E. A. gives a separation of 3990 ± 100 cm⁻¹ for these two excited states.

A summary of the results of the photoelectron experiments is shown in Table II. There are no other measurements or calculations of the electron affinity of FeO. The present literature (Table I) on FeO shows neither the 970 ± 60 cm⁻¹ vibration in the ground state, nor any nearby state. This leads to a new table of FeO spectroscopic states, Table III. The reasons for these assignments are discussed in the following section.

IV. DISCUSSION

The most striking result contained in the data is the 970 ± 60 cm⁻¹ vibrational frequency of the FeO ground state, not at all in agreement with the 875 cm⁻¹ value derived^{5,13} for the old (Table I) spectroscopic X state. This implies that the state designated X cannot be the ground state, compelling a re-examination of the FeO spectroscopic assignments.

Evidence for another FeO ground state has already accumulated. First, an ir transition¹⁴ designated $e-d$ seems to have an adjoining, lower energy transition that has vibrational constants indicative of an $e-X$ transition.¹⁵ This assignment would place state d below state X , and was discarded until recently revived by West and Broida (who discarded the $e-d$ transition).⁵ Our review of their published data, however, supports the $e-d$ assignments with only a small shift in the origin (Table IV).¹⁶ Thus, unless one postulates two separate upper states for these two transitions, one is forced to place d below X by 3896 cm⁻¹ (West and Broida's wavenumbers,⁵ our assignment). Secondly, calculations^{3,4} indicate that the lowest state of FeO is $^5\Delta$, not $^5\Sigma$, the "high multiplicity sigma" Barrow¹ associated with state X . Very interestingly, Bagus and Preston³ obtained the $^5\Sigma - ^5\Delta$ splitting of about 3000 cm⁻¹, and Walch and Goddard⁴ calculate the same state ordering with an energy difference of ~ 7000 cm⁻¹.

The spectroscopic evidence is in favor of assigning d to the ground state (calling it now X and priming the original X because of its historical significance). The reasons are twofold: (1) two transitions, assignable to $e-X'$ and $e-X(d)$ are observed spectroscopically with a splitting that very nearly corresponds to the splitting of the two lowest states in the photoelectron spectrum, and (2) the state $X(d)$ is the only observed state with the correct vibrational frequencies. It is improbable for all the transitions to the ground state to be unobserved

TABLE III. New FeO assignments and molecular constants.^a

State ^c	T_e (cm ⁻¹)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	r_e (Å)
f	45 415			
c	26 431	540		
(c')	23 556	535) ^b		
b	21 949	667	0.471	1.69
	21 853	660		
a	21 228	827	0.497) ^b	1.65) ^b
$e(^5\Pi)^c$	14 412	651) ^b		
$X' \ ^5\Sigma^+$	4 035	875.4	0.51271	1.626
$X \ ^5\Delta$ (formerly d)	0) ^{d,e}	970 ± 60) ^e (955)		1.57 ± 0.03) ^e

^aData from Ref. 13 unless otherwise noted.

^bWest and Broida (Ref. 5).

^cSymmetries are from the calculations of Bagus and Preston (Ref. 3) and Walch and Goddard (Ref. 4).

^d X zero is set 4035 ± 100 cm⁻¹ below X' based on photoelectron data; the spectral assignments ($e-X$) of this work and ($e-X'$) of Ref. 5 place this 3944 cm⁻¹ below X' .

^eFrom present photoelectron data.

TABLE IV. Partial Deslandres table, FeO $e-X$ system.^a

$v'' \backslash v'$	0	1	2	3	4	5
0	<u>14 245</u> (676) (960)	<u>14 921</u> (700)	<u>15 621</u> (603) (973)	<u>16 224</u> (663) (996)	<u>16 887</u> (609)	<u>17 496</u> (944)
1	<u>13 285</u> (943)	...	<u>14 648</u> (580)	<u>15 228</u> (983)	nr	<u>16 552</u> (931)
2	<u>12 342</u> (667) (949)	<u>13 009</u> (957)	...	<u>[14 245]</u> ^b (960)	<u>[14 921]</u>	<u>[15 621]</u>
3	<u>11 393</u> (659) (979)	<u>12 052</u> (611) (1 018)	<u>12 663</u> (622) (984)	<u>[13 285]</u> (1 003)
4	<u>10 414</u> (620) (1027)	<u>11 034</u> (645) (966)	<u>11 679</u> (603) (941)	<u>12 282</u> (609) (941)	<u>12 891</u> (573) (961)	<u>13 464</u>
5	<u>9 387</u> (681) (895)	<u>10 068</u> (670) (986)	<u>10 738</u> (603) (997)	<u>11 341</u> (589) (931)	<u>11 930</u> (920)	...
6	<u>8 432</u> (650) (951)	<u>9 082</u> (659) (918)	<u>9 741</u> (673) (960)	<u>[10 414]</u> (596) (941)	<u>11 010</u> (942)	...
7	<u>7 481</u> (683)	<u>8 164</u> (617)	<u>8 781</u> (692)	<u>9 473</u> (595)	<u>[10 068]</u> (613)	<u>10 681</u>

^aFormerly designated $e-d$. Transitions shown as wavenumbers (underlined) are from Ref. 5, the others in the lower left hand corner are from Ref. 15. Differences are in parentheses. See Ref. 16.

^bA transition in brackets is duplicated; probably this transition obscures another. This could be especially true since $3\omega' = 2\omega''$ and the (3, 2) sequences bands should pile up.

and our search for the ground state should begin with the known spectroscopic states. Thus, the assignment of the former state d as the ground state is made in Table III. The next point that should be made explicit is the assignment of the state X' to lie (3990 ± 100) cm^{-1} above the ground state. This is a low-lying state very close to the ground state as evidenced by its confusion with it. Both our spectrum, and the difference in the spectroscopic transitions $e-X(d)$ and $e-X'$, give its separation from the ground state and allow its assignment to the old X state.

The symmetries of these states may now be assigned from theory. Extensive calculations, including CI, have been completed^{3,4} for both the ${}^5\Delta$ and ${}^5\Sigma$ states. Additionally, spectroscopic evidence indicates ${}^5\Sigma$ for the X' state. Thus, we advance the assignment of ${}^5\Delta$ for the ground state and ${}^5\Sigma$ for the first excited state. Furthermore, ${}^5\Pi$ is assigned to the state e , partially based on these same calculations and partially based on the observed (and hence allowed) transitions to both the $X' {}^5\Sigma$ and $X {}^5\Delta$. These assignments are summarized in Table III. Lastly, knowledge of r_e of the FeO state $X' {}^5\Sigma^+$ now can be converted into an r_e for the ion. Since no significant vibrational sequence occurs on peak $X' - X$ in the photoelectron spectrum, $r_e(X' {}^5\Sigma^+ \text{FeO}) \approx r_e(\text{FeO}^-) \pm 0.02$ Å. Additionally, Franck-Condon analysis gives $r_e(X {}^5\Delta \text{FeO}) = r_e(\text{FeO}^-) - 0.06 \pm 0.02$ Å. These two expressions imply $r_e(X') - r_e(X) = 0.06 \pm 0.03$ Å for FeO, and from the known value for X' the value 1.57 ± 0.03 Å for the ground state is derived.

The immediate implications of this result to the ir vibrational bands of FeO are two: First, any 880 cm^{-1} bands are not vibrations of the ground state, and second, there should be intense 970 cm^{-1} bands correspond-

ing to vibrations in the ground state. However, 10.4 μm transitions in CO_2 would obscure this region, and CO_2 would result from preparation of FeO by oxidation of iron carbonyl. This, combined with a lack of previous motive for a critical examination of this region, accounts for the 970 cm^{-1} vibrations being unnoticed. In lieu of measurements, the band contours of the 880 cm^{-1} band (mistakenly believed to be that of the ground state) had to be calculated¹⁷ instead of being simply measured. In shock tube experiments with $\text{Fe}(\text{CO})_5$, von Rosenberg and Wray⁶ intended to measure the FeO transition strength at 880 cm^{-1} . In fact, at low temperature a significant portion (about 95% at 1700 K) of the FeO should be in the ground state if thermal equilibrium is assumed, and radiation at the fundamental 970 rather than 880 cm^{-1} should be the dominant FeO emission. Since 970 cm^{-1} is also marginally passed by their filter at 11 μm , which was intended for a 880 cm^{-1} transition, the value measured by von Rosenberg and Wray for the integrated band intensity cannot be assigned strictly to one or the other state. This brings the use of this measurement to assign a transition strength into question. These authors admitted to such a possibility, especially after noting unaccountably high emission in the 5.2 μm region (1940 cm^{-1}), indicating another radiating species (or state) present which they were unable to identify. This could be the first overtone of the 970 cm^{-1} vibration in the FeO ground state.

V. CONCLUSIONS

The photoelectron spectrum of FeO^- yields information on both the ion and the neutral, most of which is summarized in Table II. The vibrational frequency in the negative ion is 740 ± 60 cm^{-1} and 970 ± 60 cm^{-1} in the

neutral ground state. The vibrations of the ground state neutral preclude the identification of this state with the spectroscopic X state which probably lies $3990 \pm 100 \text{ cm}^{-1}$ (T_0) above it. Only one known¹³ spectroscopic state d has the correct vibrational frequency and we identify this as the FeO ground state, label it X , and correct the spectroscopic assignments as shown in Table III. After having identified the states involved, and knowing changes in r_e obtained from a Franck-Condon analysis of the photodetachment data, the FeO ground state $r_e(X^5\Delta) = 1.57 \pm 0.03 \text{ \AA}$ has been determined, and entered in Table III. Thus, the photoelectron spectrum of FeO^- not only provides an electron affinity [$E. A. (\text{FeO}) = 1.492 \pm 20 \text{ eV}$] but also aids and corrects the interpretation of the spectrum of FeO .

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¹⁶Of the 25 transitions in the region $13500\text{--}10000 \text{ cm}^{-1}$ that West and Broida and Bass and Benedict concurrently designate, there is a systematic shift of 15 cm^{-1} to higher wavenumbers in West and Broida's data, while about this there is an rms deviation of 35 cm^{-1} . If this is taken as the inherent variability of the assignments, and if $\pm 50 \text{ cm}^{-1}$ is allowed for spin-orbit splittings, $\omega_e x_e$ effects, and the sensitivity of the bandheads to changes in the rotational constants with vibrational levels, $\pm 60 \text{ cm}^{-1}$ variability in the differences between Deslandres table entries can be tolerated within the data. The actual $e-X$ ($e-d$) Deslandres table (Table IV) gives a fit of $\bar{\omega}' = 632 \pm 38 \text{ cm}^{-1}$, while $\bar{\omega}'' = 965 \pm 26 \text{ cm}^{-1}$. The somewhat larger standard deviation on the $\bar{\omega}'$ reflects a nonnegligible $\omega_e x_e$ dependence of vibrational spacing on vibrational quantum number. In fact, fitting the data this way gives $\bar{\omega}'_e \approx 650 \text{ cm}^{-1}$ with $\omega'_e x'_e \approx 5 \text{ cm}^{-1}$.

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