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Slow photoelectron velocity-map imaging spectroscopy of the Fe$_3$O$^-$ and Co$_3$O$^-$ anions

Jongjin B. Kim, Marissa L. Weichman, and Daniel M. Neumark$^a$

Department of Chemistry, University of California, Berkeley, California 94720, USA and
Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

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We report high-resolution photoelectron spectra of the transition metal suboxide clusters Fe$_3$O$^-$ and Co$_3$O$^-$. The combination of slow electron velocity-map imaging and cryogenic cooling yields vibrationally well-resolved spectra, from which we obtain precise values of 1.4408(3) and 1.3951(4) eV for the electron affinities of Fe$_3$O and Co$_3$O. Several vibrational frequencies of the neutral ground state Fe$_3$O and Co$_3$O clusters are assigned for the first time, and a low-lying excited state of Fe$_3$O is observed. The experimental results are compared with density functional electronic structure calculations and Franck-Condon spectral simulations, enabling identification of the structural isomer and electronic states. As has been found in photoelectron spectra of other trimetal oxo species, Fe$_3$O$^{0^-}$ and Co$_3$O$^{0^-}$ are assigned to a $\mu_2$-oxo isomer with planar $C_2v$ symmetry. We identify the ground states of Fe$_3$O$^-$ and Co$_3$O$^-$ as $^{12}A_1$ and $^{13}B_2$ states, respectively. From these states we observe photodetachment to the $^{11}B_2$ ground and $^{13}A_1$ excited states of Fe$_3$O, as well as to the $^8A_1$ ground state of Co$_3$O.

I. INTRODUCTION

The properties of iron and cobalt oxides have been of interest for many years. Iron oxide-based materials are used for dehydrogenation catalysis, stimulating many bulk structural and reactivity studies in an effort to understand the underlying chemistry. While the primary industrial role of cobalt oxides is as pigments, these species have long been studied for potential uses in oxidation catalysis. Recent developments in artificial photosynthesis have also found that self-assembled cobalt-oxo-based materials can be a self-healing, oxygen-evolving catalyst. Understanding the fundamental properties of iron and cobalt oxides that govern their reactivity is a daunting task, made even more difficult by the fact that the reactivity of these inhomogeneous bulk materials will depend on the local geometry. These considerations have motivated gas-phase mass spectrometry studies on size-selected iron and cobalt oxide clusters, which have found dramatic effects in their chemistry as a function of size, charge, and stoichiometry. Interpreting these results requires spectroscopic experiments that can elucidate the energetics and structures of the clusters, a challenging task for clusters comprising multiple metal atoms that requires novel instrumentation. Here, we report vibrationally resolved photoelectron spectra of the trimetal clusters Fe$_3$O$^-$ and Co$_3$O$^-$ via slow-electron velocity-map imaging (SEVI) of cryogenically cooled anions and, with the aid of density-functional calculations, assign the vibrational structure and ground electronic states of the anionic and neutral clusters.

Spectroscopy of iron and cobalt oxides has been extensively carried out for the diatomic metal oxides with a variety of techniques. However, similar studies of the polymetal clusters have been historically limited; beyond the smallest species, a mix of cluster sizes is often produced, and thus mass-selection must almost always be coupled to a sensitive spectroscopic technique. The most successful methods for probing gas-phase metal oxide clusters have been based on IR photodissociation (IRPD) or anion photoelectron (PE) spectroscopy. In IRPD spectroscopy, anions or cations are mass-selected and fragmented with IR light resonant with vibrational modes; the photofragment yield is taken as a measure of the vibrational absorption spectrum. In anion PE spectroscopy, anions are mass-selected then photodetached; the measured kinetic energy distribution of the electrons gives information of the neutral vibronic structure. Conventional anion PE spectroscopy with an electrostatic or time-of-flight energy analyzer has been limited to a typical resolution of $\sim$100 cm$^{-1}$, often only providing partially resolved vibrational spectra of metal oxide clusters, but the development of slow electron velocity-map imaging (SEVI) has improved this to just a few wavenumbers, allowing for detailed vibrational information on previously poorly characterized metal oxides. The related technique of threshold photoionization spectroscopy has been useful in studying neutral and cation metal oxide clusters, either through mass-analyzed threshold ionization (MATI) or at sub-meV resolution by using zero-kinetic energy (ZEKE) spectroscopy.

For the Fe$_3$O$^{0^-}$ and Co$_3$O$^{0^-}$ clusters, the only spectroscopic studies reported have used anion PE spectroscopy, although magnetic deflection experiments of iron and iron-oxo clusters have also suggested that Fe$_3$O is a ferromagnetic species. No vibrational structure was observed in the
Fe$_3$O$^-$ and Co$_3$O$^-$ are identified as 12-motif with a bridging oxo (Fig. 1). The ground states of all charge states are found to have a triangular metal moieties assigned for the first time. Both trimetal oxo species are proven from prior studies, and various vibrational frequencies have been reported a structural isomer with a triangular metal moiety and inserted oxygen was found to be most stable form of neutral Co$_3$O$^-$ and of neutral Co$_3$O with PBE, another isomer with an in-plane oxo isomer was found to be the most stable form of Co$_3$O$^-$ clusters. The anions were mass-selected in a quadrupole target, and a burst of helium gas with trace oxygen from a pulsed valve was used to quench the plasma and create metal oxide clusters. The anions were mass-selected in a quadrupole mass filter that transmitted the $^{56}$Fe$_3^{16}$O$^{-}$ or $^{59}$Co$_3^{16}$O$^{-}$ clusters and were then transferred to an ion trap. There, the ions were cooled by a 1:4 mix of H$_2$/He buffer gas at 5 K for 40 ms.

The ions were extracted from the trap and accelerated in a time-of-flight mass spectrometer. When the ion packets reached the interaction volume of the velocity-map imaging (VMI) electron spectrometer, they were photodetached with the output from a tunable pulsed dye laser. The VMI lens projected the resulting photoelectrons onto a planar position-sensitive detector; a single image results from the accumulation of photoelectrons from several thousand experimental cycles. As a unique axis is defined by the laser polarization axis, the projected image can be used to reconstruct the original electron velocity distribution, allowing us to obtain radial and angular information.

The radial photoelectron distribution is proportional to the speed; this distribution gives the electron kinetic energy (eKE) distribution at a given photon energy. As detailed previously, we obtain the highest resolution at lowest eKE, so the high-resolution, low-eKE portions of individual scans were spliced together and scaled to match the intensities from a lower resolution overview spectrum covering a broad range of eKE. For a more useful quantity, we report the energies as electron binding energies (eBE), defined as $eBE = h\nu - eKE$, which give the energy difference between the anion and neutral states.

We also measure photoelectron angular distributions (PADs), which for a one-photon detachment with linearly polarized light can be described by the formula,

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{tot}}{4\pi} \left( 1 + \beta \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \right).$$

The anisotropy of the PAD is defined by the parameter $\beta$, which varies from $-1$ to $2$, corresponding to the limits of a PAD aligned perpendicular to and parallel to the photon polarization. For a given transition, the value of $\beta$ depends on the photodetachment energy. However, its qualitative value can give insight to the nature and symmetry of the photodetachment transition. In this work, peaks with $0.1 < \beta < 2$ are labeled with a “+” PAD while those with $-1 < \beta < 0.1$ are labeled with a “−” PAD.
III. RESULTS

SEVI spectra of Fe$_3$O$^-$ and Co$_3$O$^-$ are shown in Figs. 2 and 3, respectively. Lower-resolution overview spectra are shown in top (blue), composed of an average of several scans taken near photon energies of 14 925 cm$^{-1}$ and 13 339 cm$^{-1}$. The high-resolution portions of SEVI spectra taken at various photon energies are spliced together below (black), highlighting the better-resolved vibrational structure at low eKE.

The overview spectra for Fe$_3$O$^-$ and Co$_3$O$^-$ are similar; both have a strong vibrational origin at peak A and a short progression comprising peaks A, B, and C, with a peak spacing of $\sim$210 cm$^{-1}$ and $\sim$190 cm$^{-1}$, respectively. There appears to be a minor recurrence of this progression starting at peak E, $\sim$660 cm$^{-1}$ higher in energy. Almost all features have a characteristic “−” PAD, but peaks H and K in the Fe$_3$O$^-$ spectrum have a “+” PAD, suggesting the onset of a new electronic band.

Higher-resolution spectra resolve the observed features in the Fe$_3$O$^-$ spectrum more clearly and show new features in the Co$_3$O$^-$ spectrum. The Fe$_3$O$^-$ spectra are still dominated by two main progressions comprising peaks A-D and E-G with a peak spacing of $\sim$210 cm$^{-1}$ and separated by $\sim$660 cm$^{-1}$. Peaks I and J are resolved between peaks H and K, but poor signal-to-noise prevents assignment of their PAD. The Fe$_3$O$^-$ spectra are congested above peak K, and high-resolution spectra at higher energies are not shown. In the Co$_3$O$^-$ spectra, the main features are still the A-D and E-G progressions. The peaks above the onsets A and E, however, are now resolved as doublets, with the weak peaks b, c, d, and f observed 13 cm$^{-1}$ above the corresponding stronger peaks B, C, D, and F. A weak but reproducible (and thus far unassigned) feature is also observed between peaks C and D and is labeled peak Z.

TABLE I. Peak positions (cm$^{-1}$), shifts from the origin (cm$^{-1}$), characteristic PADs, and assignments for the Fe$_3$O$^-$ SEVI spectra.

<table>
<thead>
<tr>
<th>Peak</th>
<th>eBE</th>
<th>Shift</th>
<th>PAD</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>A</td>
<td>11 620</td>
<td>0</td>
<td>0</td>
<td>$0^0$</td>
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<tr>
<td>B</td>
<td>11 828</td>
<td>207</td>
<td>0</td>
<td>$3^1_0$</td>
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<td>C</td>
<td>12 034</td>
<td>413</td>
<td>0</td>
<td>$3^2_0$</td>
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<tr>
<td>D</td>
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<td>E</td>
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<td>664</td>
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<tr>
<td>F</td>
<td>12 491</td>
<td>870</td>
<td>0</td>
<td>$1^3_0$</td>
</tr>
<tr>
<td>G</td>
<td>12 695</td>
<td>1075</td>
<td>0</td>
<td>$1^3_0$</td>
</tr>
<tr>
<td>H</td>
<td>12 987</td>
<td>1367</td>
<td>+</td>
<td>$\delta 0^0$</td>
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<tr>
<td>I</td>
<td>13 146</td>
<td>1525</td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>13 193</td>
<td>1572</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>13 265</td>
<td>1644</td>
<td>+</td>
<td>$\delta 2^0$</td>
</tr>
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</table>
IV. THEORETICAL RESULTS

A. Electronic structure theory

Previous calculations on Fe$_3$O$^{0/-}$ and Co$_3$O$^{0/-}$ have used the BPW91 functional with a 6-311+G* basis set, with reasonable agreement between the calculated and experimental EAs and assignment of a $\mu_2$-oxo isomer.\cite{38,39} Calculations with the PW91 functional found similar results for Fe$_3$O$^{0/-}$ \cite{44,45} Another study found a different ground state isomer for Co$_3$O.\cite{46} but used smaller double-zeta basis sets and the B3LYP hybrid functional, while a calculation with the PBE functional found the same $\mu_2$-oxo isomer for Co$_3$O.\cite{47} While BPW91 calculations reported use the same functional and basis set, they may differ in various parameters like the quadrature integration grid; a sufficiently fine grid is necessary for converged results at a given functional and basis set, especially for transition-metal systems and with some newer functionals.\cite{55,56}

For consistency, we performed an independent set of calculations of all species, also at the BPW91/6-311+G* level, with tight geometry optimization and an ultrafine integration grid as defined by Gaussian 09.\cite{57} The TPSS meta-GGA functional\cite{58} can have improved performance depending on the system and parameters studied,\cite{59} and a recent study of the difficult FeO$_2^+$ system found that of the functionals tested, only TPSS qualitatively agreed with high-level multireference \textit{ab initio} theory.\cite{60} Accordingly, geometry optimizations and frequency calculations were also performed at TPSS/6-311+G* level. Calculations were performed with and without symmetry, and wavefunction stability was enforced by the diagnostic in Gaussian. For interpreting the nature of the electronic states, a Natural Population Analysis was performed on selected states with the TPSS functional.\cite{61}

Fig. 4 shows the calculated energies of the three lowest-lying states of the $\mu_2$-oxo isomer for neutral and anionic Fe$_3$O and Co$_3$O. Numerical values and calculated $\langle S^2 \rangle$ values are given in Table S1 of the supplementary material.\cite{62} All states shown here have only minor deviations between $\langle S^2 \rangle$ and the ideal $S(S+1)$ value, suggesting there is only minor spin contamination and that DFT may provide a reasonable treatment for these systems. Moreover, the relative energies of all the states are similar between BPW91 and TPSS; these self-consistent results between different functionals suggest that the energies are reliable. Calculated geometries and harmonic vibrational frequencies from both functionals are reported in Table S2 in the supplementary material, while the results of the Natural Population Analysis are shown in Table S3 in the supplementary material.\cite{62}

All states converge to a planar $C_2v$ geometry except the sextet $^6A''$ Co$_3$O state, for which the oxygen atom is found to be out of the Co$_3$ plane by 46.5° by both BPW91 and TPSS. While the Fe$_3$O $^9A_1$ state and Co$_3$O $^9A_1$ state have imaginary frequencies using the TPSS and BPW91 functionals, respectively, the relaxation energy by breaking symmetry is only 14 cm$^{-1}$ and 1 cm$^{-1}$, well below the zero-point vibrational energy, and we consider them to be $C_2v$. The normal mode coordinates for all species are similar; those of an exemplar (Fe$_3$O, $^{11}B_2$ state) are displayed in Fig. 5.

![Image](https://example.com/image.png)

FIG. 4. Energy level diagram of the low-lying Fe$_3$O$^{0/-}$ and Co$_3$O$^{0/-}$ states calculated using the BPW91 and TPSS functionals. All energies are relative to the lowest-energy anion state.

We considered the possibility of alternative structural isomers and optimized for the various M$_3$O isomers considered in previous studies.\cite{39,46,47} However, regardless of metal and charge, all alternate isomers were found significantly higher in energy than the ground state, with the lowest-lying alternate isomer 0.33 eV higher in energy than the corresponding ground state, a neutral octet Co$_3$O isomer with a $\mu_1$-oxo pyramidal motif. Our calculations support the $\mu_2$-oxo isomer for these species.

B. Franck-Condon simulations

To aid in the assignment of our spectra, Franck-Condon (FC) simulations of the possible photodetachment transitions were calculated with the ezSpectrum program.\cite{63} With this program, all modes are mixed with Duschinsky rotation and overlap integrals are calculated in the harmonic oscillator

![Image](https://example.com/image.png)

FIG. 5. Vibrational normal modes of the M$_3$O species.
approximation. Only photodetachment transitions with \( \Delta S = 1/2 \) are allowed and thus have their spectra simulated in this work. Calculated spectra are compared to experimental overview spectra in Figs. 6 and 7 for Fe\(_3\)O\(^-\) and Co\(_3\)O\(^-\), respectively. The stick spectra are displayed as well as spectra convolved with the instrumental resolution matching that of the overview spectrum, \( \Delta E / E = 3\% \).

However, the \( v_4 \) \( b_1 \) mode of the Co\(_2\)O\(^8\)A\(_1\) state is treated separately as an anharmonic oscillator and is left out of the ezSpectrum FC simulations. The frequency of this mode varies significantly with charge, state, and density functional. In particular, in the \( 8^A_1 \) state this mode has a small real frequency of 28 cm\(^{-1}\) with TPSS and a small imaginary harmonic frequency of 32i cm\(^{-1}\) using BPW91. This behavior is suggestive of a flat anharmonic potential along that mode. As a non-totally symmetric mode, \( \Delta v_4 \) = odd transitions are forbidden, but if the anharmonicity is sufficiently pronounced or the frequency changes a large degree between the initial and final states, \( \Delta v_4 = 2n \) excitation may have significant FC intensity. This treatment is discussed more thoroughly in Sec. V B.

V. DISCUSSION

A. Assignment of Fe\(_3\)O\(^-\) spectra

Peak A is assigned as the vibronic origin of the main photodetachment band; no features appear lower in energy, and as the ions were cooled in a cryogenic trap, the lowest-energy feature should correspond to the origin. All electronic structure calculations in this work and most previous theory support a \( \mu_\perp \)-oxo triangular metal isomer for the M\(_2\)O\(^{0\prime}\)- species here.\(^{38, 44, 45}\) Moreover, experimental studies of analogous trimetal oxo compounds using vibrationally resolved ZEKE and conventional anion PE spectroscopy studies have also been assigned to this structural isomer.\(^{37, 42, 43}\) Those spectra were similar in appearance to ours, with a strong vibrational origin and weak FC activity in just a few modes. These considerations suggest that Fe\(_3\)O\(^{0\prime}\) has the structural motif shown in Fig. 1, but comparison must be made between experimental and calculated spectra for an unambiguous determination.

We compare our results to calculated vibrational frequencies and Franck-Condon profiles. The FC-active modes of the \( \mu_\perp \)-oxo structure are the totally symmetric \( \nu_1 \), \( \nu_2 \), and \( \nu_3 \) modes (Fig. 5). Regardless of functional and spin state chosen, the calculated harmonic frequencies \( \omega_1 \), \( \omega_2 \), and \( \omega_3 \) for these modes lie within a narrow range: \( \omega_1 \approx 630–680 \) cm\(^{-1}\), \( \omega_2 \approx 320–340 \) cm\(^{-1}\), and \( \omega_3 \approx 200–230 \) cm\(^{-1}\) (Table S2 in the supplementary material).\(^{62}\) The experimental spectra show two progressions A-D and E-G, which are characteristic of Franck-Condon activity in two vibrational modes with frequencies \( \sim 210 \) cm\(^{-1}\) and \( 660 \) cm\(^{-1}\). By comparison with the calculated frequencies, there is a clear match for the \( \nu_1 \) and \( \nu_3 \) modes, supporting the validity of the calculated structure in Fig. 1, and allowing us to assign peaks A-D to the \( 3^R \) (\( n = 0–3 \)) progression, and peaks E-G to the \( 1^{3S}_{0} \) (\( n = 0–2 \)) progression.

Peaks H and K exhibit a different PAD than peaks A-G, suggesting a photodetachment transition with different electronic character. Assuming that ion trapping and cooling ensure that all the anions are in their ground electronic state, Peak H is assigned as the origin of a transition to an excited neutral state, lying 1300 cm\(^{-1}\) above the state responsible for the main band. Peak K is offset from peak H by 278 cm\(^{-1}\); by comparison with the calculated vibrational frequencies, this suggests a tentative \( 2_{0}^1 \) assignment in the excited state.

While assigning the vibrational structure is straightforward, a comparison of Franck-Condon activity is required for assignment of the electronic states. The calculations suggest that the ground states of anionic and neutral Fe\(_3\)O should be the \( 12^A_1 \) and \( 11^B_2 \) states, respectively. However, excited states are calculated to lie only a few tenths of an eV higher in energy. Nevertheless, we can use the Franck-Condon activity as a means to verify the reliability of calculations; if both the calculated energies and FC simulation are consistent with experiment, the electronic state assignment is likely to be correct.

FC simulations of Fe\(_3\)O\(^-\) photodetachment are shown in Fig. 6, with all possible one-electron detachment transitions between the states in Fig. 4 considered. To a first approximation, all the simulations are reasonable matches; the vibrational origin is the first or second most intense peak, consistent with the expectations provided from previous photoelectron studies of similar systems.\(^{37, 42}\) However, the simulated \( 11^B_2 \leftrightarrow 12^A_1 \) transition is clearly a better match to the experiment than the other transitions. The intensities of the \( 3^R \) and \( 1^{3S}_{0} \) progressions are well-reproduced, and there is negligible excitation in the \( \nu_2 \) mode, consistent with the experimental spectra. Those two states are also calculated to be the lowest energy states of the neutral and anion Fe\(_3\)O, respectively, and the calculated EA is around 1.33 eV (Table S1 in the supplementary material).\(^{62}\) In reasonable agreement with the eBE of peak A at 1.4408 eV. The good match of calculated energies, FC activity, and experimental spectra leads us to assign the anion and neutral ground states as the \( X^12^A_1 \) and \( X^11^B_2 \) states, respectively, and the main photodetachment band to the transition between these two states.

The assignment of the excited state beginning at peak H is more tentative. As the anion is now established as a \( 12^A_1 \) state, we need only consider undetetct and tridetet states of neutral Fe\(_3\)O. As we have not performed excited-state calculations, we cannot rule out the presence of an excited undetetct state. However, the lowest-lying tridetet state, a \( 13^A_1 \) state, is calculated to lie only 0.51 or 0.35 eV above the ground state, depending on the functional used. Peak H is offset from the ground state origin by 0.1694 eV, a smaller value than the calculated term energy, but within reasonable error of DFT.

Unfortunately, the experimental FC activity is not as well-resolved for this band, as the spectra are congested above peak K. Nevertheless, it is sufficient to determine that peak H and K have roughly comparable intensities, and peak K is tentatively assigned as a \( 2_{0}^1 \) transition. It is possible that one of peaks I and J correspond to a \( 3_{1}^R \) transition, but peak positions compared to calculated frequencies are ambiguous; regardless, \( \nu_3 \) activity is at most minor relative to \( \nu_2 \) activity. The \( 13^A_1 \leftrightarrow X^12^A_1 \) FC simulation is a reasonable match to these
observations, with weak $\nu_3$ activity, stronger $\nu_2$ activity, and a roughly comparable intensity between the $0_0^0$ and $2_1^0$ transitions. We tentatively assign peaks H and K to the Fe$_3$O $\tilde{a}^1A_1$ state.

Photoelectron anisotropies and threshold intensities are consistent with the assignments of both bands. Qualitative predictions of the PAD can be made using the Wigner Threshold Law: at low $eKE$, the photodetachment cross-section for negative ions goes as $\sigma \propto eKE^{l+1/2}$, where $l$ is the orbital angular momentum of the detached electron.\textsuperscript{64} Hence, only the lowest-order partial waves contribute significantly to photodetachment near threshold. Considering only the $l = 0$ and $l = 1$ waves, we can use a model developed by Sanov and co-workers to predict the sign of the PAD for polyatomic species.\textsuperscript{53,65} For $C_{2v}$ systems like the M$_3$O species considered in this work, only detachment from an $a_1$ orbital would exhibit a “+” PAD, and while detachment from an $a_2$, $b_1$, or $b_2$ orbital would have a “−” PAD. Moreover, as the $A_1$ irreducible representation does not contain any $x$, $y$, or $z$ components, detachment from an $a_2$ orbital would proceed by $l = 1$ in the lowest order and thus would drop off in intensity at very low $eKE$.\textsuperscript{51,66} All peaks maintained reasonable intensity close to threshold, consistent with s-wave ($l = 0$) detachment and ruling out detachment from an $a_2$ orbital. The $\tilde{X}^{11}B_2 \leftarrow \tilde{X}^{12}A_1$ transition has a “−” PAD consistent with detachment from a $b_2$ orbital, while the $\tilde{a}^{13}A_1 \leftarrow \tilde{X}^{12}A_1$ transition has a “+” PAD consistent with detachment from an $a_1$ orbital.

The assigned states, state energies, and vibrational frequencies are summarized in Table III. We report only the vibrational fundamentals for Fe$_3$O.

### B. Assignment of Co$_3$O$^-$ spectra

As in the Fe$_3$O$^-$ spectra, peak A is the lowest-eBE and most intense feature, so it is assigned to the vibrational origin of the main photodetachment band. The overall vibrational structure is similar, also suggesting the same $\mu_2$-oxo structural isomer. However, the finer vibrational structure is characteristic of FC activity in three modes, not just two. The main progressions A-D and E-G once again suggest vibrational

<table>
<thead>
<tr>
<th>Anion</th>
<th>Fe$_3$O</th>
<th>Co$_3$O</th>
</tr>
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<tbody>
<tr>
<td>$12A_1$</td>
<td>$9B_2$</td>
<td>$8A_1$</td>
</tr>
<tr>
<td>$11B_1$</td>
<td>$10B_2$</td>
<td>$9B_2$</td>
</tr>
<tr>
<td>EA (eV)</td>
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<td>1.3951(4)</td>
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<td>$\nu_1$ (cm$^{-1}$)</td>
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<td>660(3)</td>
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<td>185(2)</td>
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<td>$2\nu_4$ (cm$^{-1}$)</td>
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<tr>
<td>$\tilde{a}$</td>
<td>$13A_1$</td>
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<tr>
<td>$T_0$ (eV)</td>
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<td>$\nu_2$ (cm$^{-1}$)</td>
<td>278(3)</td>
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</table>
activity in two modes with frequencies \( \sim 190 \text{ cm}^{-1} \) and \( \sim 660 \text{ cm}^{-1} \). The spread of calculated frequencies is larger than in Fe\(_3\)O, with the various harmonic frequencies of neutral Co\(_3\)O spanning 617–665 cm\(^{-1}\), 286–322 cm\(^{-1}\), and 184–244 cm\(^{-1}\) for \( \omega_1 \), \( \omega_2 \), and \( \omega_3 \), respectively. Nevertheless, we can once again match peak spacings to progressions in the \( \nu_1 \) and \( \nu_3 \) modes. We assign peaks A–D to the 3 \( \nu_1 \) modes and peaks E–G to the 1\( \nu_1 \) (n = 0–2) progression, with that expected for detachment from a planar to non-planar structure, and the 10 \( \nu_1 \) simulation is also very extended. The other three transitions, however, have the expected strong origin and moderate FC activity. In more detail, the \( ^8A_1 \leftarrow ^7B_2 \) transition has negligible calculated FC intensity in the area shown, due to the large change in geometry from a planar to non-planar structure, and the 10 \( B_2 \leftarrow ^{11}B_1 \) simulation is also very extended. The other three transitions, however, have the expected strong origin and moderate FC activity. In more detail, the \( ^8A_1 \leftarrow ^7B_2 \) simulation exhibits notably less FC activity than the experimental spectrum, but the \( ^8A_1 \leftarrow ^9B_2 \) and 10 \( B_2 \leftarrow ^{11}B_2 \) transitions qualitatively match the experimental overview spectrum. Neither is as good a match as the Fe\(_3\)O \( ^{11}B_2 \leftarrow ^{12}A_1 \) simulation, however. The \( ^8A_1 \leftarrow ^9B_2 \) simulation is dominated by a progression in the \( \nu_1 \) mode but the calculated frequency of 244 cm\(^{-1}\) is larger than our experimental value of 185 cm\(^{-1}\). The 10 \( B_2 \leftarrow ^9B_2 \) simulation has insignificant \( \nu_1 \) activity, but both \( \nu_2 \) and \( \nu_3 \) modes are active, in disagreement with the experiment showing no activity in the \( \nu_2 \) mode.

Differentiating between the likeliest \( ^8A_1 \leftarrow ^9B_2 \) or 10 \( B_2 \leftarrow ^9B_2 \) transitions requires consideration of angular information. The PADs of all listed peaks are qualitatively similar, consistent with a common electronic transition for these peaks. All features have a characteristic “+” PAD, consistent with that expected for detachment from a \( b_2 \) orbital and thus supports assignment to the \( ^8A_1 \leftarrow ^9B_2 \) transition. The 10 \( B_2 \leftarrow ^9B_2 \) transition, however, occurs by detachment from an \( a_1 \) orbital and would be expected to have a “−” PAD.

Assignment of the \( ^8A_1 \leftarrow ^9B_2 \) transition by the PAD also allows for an explanation of the doublet structure in the spectra from even quanta excitation of the \( \nu_4 \) mode. The weak peaks b, c, d, and f neighboring the main progressions suggest weak excitation in another mode with a frequency close to the \( \nu_3 \) mode, \( \sim 200 \text{ cm}^{-1} \). However, this frequency is not compatible with calculated frequencies for the last totally symmetric mode, \( \nu_2 \). The doublet structure may thus originate from \( \Delta v = 2 \) excitation of a non-totally symmetric mode. As mentioned in Sec. IV B, the \( \nu_4 \) mode of the Co\(_3\)O \( ^8A_1 \) state is a good candidate for this behavior. In contrast, the 10 \( B_2 \) state is a poor candidate; the non-totally symmetric modes are consistently above 137 cm\(^{-1}\), consistent with harmonic behavior, and two-quanta excitation of any of these would be significantly larger than \( \sim 200 \text{ cm}^{-1} \).

The FC activity of the \( \nu_4 \) mode of the Co\(_3\)O \( ^8A_1 \) state is assessed by treating it as an anharmonic oscillator.
As seen in Fig. 8, the flat potential near the ground state. The assigned states, electron affinity, and vibrational frequencies are summarized in Table III. Due to the expected anharmonicity of the υ4 mode, we report the 2υ4 energy.

**C. Electronic states**

The M3O clusters bind the excess anion electron in a largely metal 4s orbital. Detachment from the alpha HOMO of Fe3O− and Co3O− anions forms the corresponding ground state neutral species. This orbital looks very similar for the two different species (Fig. 9). It is largely centered on the metal atoms and is dominated by two in-plane lobes of opposite phase; the simple structure with one dominant node suggests that the orbital corresponds largely to a Fe or Co 4s weakly antibonding orbital, with electron density mostly on the oxo-bridged metal atoms. The orbitals do not have density centered directly over the metal atoms, suggesting polarization by the 4p orbitals. Natural Population Analysis seems to corroborate this assignment (Table S3 in the supplementary material).62 The Fe 3d occupation is almost identical between the ground state anion and neutral species. However, the metal 4p and, even more so, the 4s occupation decreases upon electron detachment. Natural Population Analysis is not a reliable method for determining the precise metal 4p contribution in first-row transition metals, but qualitative trends should hold.68, 69

Attachment of the excess electron in the metal valence s orbitals is consistent with other work. Upon electron attachment, all transition metal atoms with an unfilled valence s shell add the excess electron in that shell.70 For the first row transition metal dimers, the most consistent assignments for the Fe2−, Ni2−, and Cu2− photoelectron spectra have the excess electron largely in a 4s σ∗ orbital.71–74 Previous calculations for larger Fe2O clusters found the anion alpha HOMO to have significant 4s character.38 Analysis of the experimental photodetachment cross-sections of V2O−, Nb2O−, and Ta2O− suggest that the excess electron is held in an orbital primarily of metal valence s character.42 In general, metal and metal suboxide clusters seem to bind excess electrons in the s shell.

The electronic character of the detachment transitions is also consistent with both the geometry changes and the FC activity. Both the Fe3O− and Co3O− alpha HOMOs have some antibonding character between the oxo-bridged metals. As a result, the most significant calculated geometry change upon detachment is that the R2 bond length decreases by 0.05–0.07 Å. Similarly, the most FC-active mode should have significant symmetric stretching motion between the two oxo-bridged metal atoms; as shown in Fig. 5, this would be the υ4 mode, which is in fact the most active mode in both transitions. The excited 13A1 state of Fe3O is accessed by detachment from the beta HOMO, a weakly bonding orbital with electron density on all three metal centers (Fig. 9 and Table S3 in the supplementary material).62 Consequently, the major geometry change upon detachment is a metal trimer ring expansion; R2 and R3 are calculated to increase ~0.07 Å, and
the most active mode is the \( v_2 \) ring-breathing mode (Fig. 6), consistent with our assignments.

The overall spin states assigned are consistent with a picture of ferromagnetically coupled small iron and cobalt clusters. Stern-Gerlach magnetic deflection studies of size-selected iron and cobalt clusters have determined that almost all of these clusters are ferromagnetic, including neutral iron-oxo clusters.\(^{41,75-81}\) Although there is considerable disagreement on the details, the overall consensus is that there is a typical spin magnetic contribution of \( \sim 3 \) electrons per iron atom and \( \sim 2 \) electrons per cobalt atom. The qualitative model used to explain this trend is based on band theory.\(^78\) Low-coordination regions like surfaces and defects form a large portion of small clusters, resulting in narrower bands than that for the bulk material. Upon promotion of a 4s electron to the 3d orbital, the larger 4s orbitals delocalize, forming a broad s-band and the majority of the metal bonding. The smaller 3d orbitals interact weakly and do not delocalize as much as the bulk 3d band or the low-coordinate 4s band. As a result, the observed magnetic moment is due to the spin excess in the 3d band as given by Hund’s rules for the atoms.

Models based on band theory would not be expected to hold exactly for Fe\(_2\)O and Co\(_2\)O; a trimer is a small cluster and the oxygen will perturb the electronic structure. Nonetheless, if the species can be considered ferromagnetic, these values should roughly hold true. Starting with atomic configurations of \([\text{Ar}]4s^{1}3d^{7}\) and \([\text{Ar}]4s^{1}3d^{8}\) for the three iron and cobalt atoms with 4s \( \rightarrow \) 3d promotion, the 3d band would have a spin excess of 9 and 6 electrons, respectively. The 4s band would have a doubly occupied bonding orbital and a singly occupied antibonding orbital, resulting in a final 2\(S + 1\) value of 11 and 8 for Fe\(_2\)O and Co\(_2\)O. Remarkably, the neutral Fe\(_2\)O and Co\(_2\)O states are assigned exactly those spin multiplicities. The Natural Population Analysis also gives 3d occupations close to 7 and 8 for each iron and cobalt atom. The success of this simple model suggests that the single oxygen does not perturb the ferromagnetic behavior significantly. Previous low-resolution PE studies of various Fe\(_2\)O\(^{-}\) and Co\(_2\)O\(^{-}\) clusters also noted that the electron affinities were very similar to the corresponding pure metal clusters.\(^{38,40,82}\)

### D. Comparison with prior work

The only prior experimental studies on the M\(_3\)O\(^{3-}\) (M = Fe, Co) clusters used conventional anion PE spectroscopy.\(^{38-40}\) Due to lower resolution, around 30 meV, and likely higher ion temperatures, vibrational structure was not resolved. However, as the vibrational origin is strong, the onset of the ground state photodetachment band was clear in those experiments, yielding EAs of 1.44(2) eV for Fe\(_2\)O and 1.38(8) eV for Co\(_2\)O. The earliest report on cobalt oxo clusters did not list a value for the EA of Co\(_2\)O, but the onset in the spectrum appears to be \( \sim 1.3 \) eV.\(^30\) These values are consistent with our more precise values of 1.4408(3) eV and 1.3951(4) eV, respectively. The vibrational assignments made in this work are the first reported experimentally for Fe\(_3\)O and Co\(_3\)O.

Similar vibrational structure has been seen in vibrationally resolved photoelectron spectra of related metal oxide clusters, as mentioned in Section V A. High-resolution (sub-meV) photoionization spectra of neutral Zr\(_2\)O and Nb\(_2\)O were acquired by ZEKE.\(^{37,43}\) and photoelectron spectra of M\(_3\)O\(^{-}\) anions (M = V, Nb, Ta) were measured at 5–7 meV resolution.\(^42\) Though the energy resolution in the anion PE study was not high as in the ZEKE and SEVI spectra, it was sufficient for assigning the observed vibrational structure.

All these studies observed a prominent origin and a short progression in the \( v_1 \) mode, with minor to negligible FC activity in the other totally symmetric modes. This overall FC profile is similar to that observed here for the Fe\(_3\)O\(^{-}\) and Co\(_3\)O\(^{-}\) SEVI spectra. The \( v_1 \) frequencies ranged from 215 to 355 cm\(^{-1}\). The photodetachment spectra also showed minor FC activity in the \( v_1 \) mode, with frequencies 710–770 cm\(^{-1}\). These frequencies are similar to but larger than our \( v_1 \) frequencies for Fe\(_3\)O and Co\(_3\)O (Table III). This systematic difference is probably due to the weaker bonding in the clusters comprising the later transition-metal elements iron and cobalt compared to the earlier Group 4 and 5 metals. With a \( d\)-shell more than half full, there is more occupation in the metal antibonding orbitals, and the bond strength and force constants are diminished, as has been observed in the pure transition metal trimers.\(^83\)

The experimental results are consistent with previous studies, but the electronic structure calculations are not. Although the same electronic structure program suite (Gaussian) and theory (BPW91/6-311+G*) were used, we have obtained different results than Gutsev et al.\(^{38}\) and Li et al.\(^{39}\) for the Fe\(_3\)O\(^{3-}\) and Co\(_3\)O\(^{3-}\) species. We obtain the same spin states corresponding to the ground state anion and neutral Fe\(_2\)O with Gutsev et al. However, the relative energies of some states also differ by up to 0.2 eV. The geometries for the Fe\(_2\)O\(^{3-}\) decet and dodecet states are also noticeably different; we find a planar decet state while Gutsev et al. found a nonplanar state, and our calculated R2 bond lengths are shorter by 0.26 and 0.29 Å, respectively. These differences are significant, since our FC simulations show that the experimental \( v_3 \) vibrational structure is consistent with a \( \sim 0.06 \) Å change in R2 upon photodetachment (Sec. V C), while Gutsev et al. predict a change of 0.25 Å, which would result in much more FC activity than that observed.

Our calculations for Co\(_3\)O\(^{3-}\) are also in qualitative agreement with those of Li et al.,\(^{39}\) but there are again notable differences. As with Fe\(_2\)O, both reports found the same spin state and overall structure for the anion and neutral Co\(_2\)O. However, Co-Co bond lengths differ by \( \sim 0.04 \) Å for both the anion and neutral species, the previous study obtained \( C_3 \) symmetric solutions while our ground states have \( C_{2v} \) symmetry for both anion and neutral, and we could not reproduce the relative energies of the low-lying isomers. Li et al. located alternate structural isomers within 0.2 eV of the ground states for both the anion and neutral species, but we found those higher in energy by 0.54 and 0.33 eV, respectively. FC spectra for our lowest-energy alternate isomers of Co\(_3\)O\(^{3-}\) are shown in Fig. S1 in the supplementary material.\(^62\) Both are poorer matches to the experiment than the assigned isomer and transition.
VI. CONCLUSIONS

We report high-resolution anion photoelectron spectra of Fe$_3$O$^-$ and Co$_3$O$^-$. The combination of ion trapping and cooling with the SEVI electron spectrometer allows for the acquisition of vibrationally well-resolved spectra of these systems for the first time, providing improved electron affinities and several new experimental vibrational frequencies for the neutral species. The electronic states of the anion and neutral species have been determined by comparison of calculated energies, FC simulations, and expected photoelectron anisotropies with the experimental spectra. Consistent with previous reports, on the basis of calculated energies and Franck-Condon intensities, the electronic state of anion and neutral metal oxide species is assigned to a triangular metal moiety with a μ$_3$-oxo ligand.

Cold anion PE spectroscopy using SEVI can yield vibrationally well-resolved spectra of polymetal species. Assigning the important features, however, requires comparison with results from electronic structure calculations. In turn, it is difficult to obtain reliable results from calculations of polymetal species, but confidence in the results can be bolstered if spectroscopic and theoretical results are mutually self-consistent. SEVI can provide a rich set of experimental results, with photoelectron anisotropies, vibrational frequencies, detachment energies, and Franck-Condon profiles, all of which can be compared to theoretical expectations for different states, allowing us to assign electronic states and vibrational frequencies of anion and neutral metal oxide clusters.

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