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## Experimental and Theoretical Study of the Structure and Reactivity of $\text{Fe}_m\text{O}_n^+$ ( $m = 1, 2; n = 1-5$ ) with CO

Nelly M. Reilly,<sup>†</sup> J. Ulises Reveles,<sup>‡</sup> Grant E. Johnson,<sup>†</sup> Jorge M. del Campo,<sup>§</sup> Shiv N. Khanna,<sup>‡</sup> Andreas M. Köster,<sup>§</sup> and A. W. Castleman, Jr.,<sup>\*,†</sup>

Departments of Chemistry and Physics, Pennsylvania State University, University Park, Pennsylvania 16802, Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284-2000, and Departamento de Química, Cinvestav, Avenida Instituto Politécnico Nacional 2508, Apartado Postal 14-740, México D.F. 07000, México

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Studies involving small iron oxide cationic clusters,  $\text{Fe}_m\text{O}_n^+$  ( $m = 1, 2, n = 1-5$ ), and their reactivity in the presence of CO at near thermal energies were conducted by employing a guided ion beam mass spectrometer. Observed reaction channels included CO oxidation and oxygen replacement by CO which are shown to be dependent on cluster size and stoichiometry. First principles electronic structure studies within the density functional theory framework were carried out to address the structures and energetics of small cationic clusters and to probe the molecular level pathways for CO oxidation. The theoretical calculations, in conjunction with the experimental findings, are used to propose a coherent picture about the trends in the dissociation energies, which are largely dependent upon the metal to oxygen ratio, and the nature of the structure–reactivity relationships for the formation of the reaction products.

### Introduction

The oxidation of CO to  $\text{CO}_2$  is an important environmental reaction for the abatement of harmful carbon monoxide gas. The reaction involves breaking the O–O bond of the  $\text{O}_2$  molecule, and therefore, catalysts are generally employed to overcome this large energy barrier. Consequently, finding more efficient and selective catalyst materials with lower operating temperatures for this reaction would be beneficial. Transition metal oxides are known to provide good catalytic activity in oxidation reactions.<sup>1,2</sup> A potential advantage of using transition metal oxide clusters is that the oxygen atoms are bound atomically to the metal and there are no O–O bonds unless the oxygen to metal ratio is large. To this end, iron oxides may be an important alternative material for effecting the oxidation of CO at low temperature without the activation of strong O–O bonds. Iron oxides would be very practical in pollution abatement applications as they are abundant and inexpensive, in comparison to the precious metals based catalysts currently employed in CO oxidation.<sup>3</sup>

Previous studies involving iron oxide layers supported on gold have revealed the presence of both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  oxidation states, suggesting the participation of cationic iron in the oxidation of carbon monoxide.<sup>4</sup> PalDey and co-workers employed X-ray powder diffraction (XRD) to show that mixed catalysts containing  $\text{Fe}_2\text{O}_3$  had defect sites in the form of cationic vacancies.<sup>5</sup> These vacancies, which constitute regions of charge deficiency, may be important active sites for CO oxidation. It is particularly important, therefore, to understand the influence of charge state on the oxidation of CO in the presence of iron oxides. There is much debate over the role that charge transfer

plays in the active sites of supported condensed phase catalysts, and consequently, a better understanding of the mechanisms governing oxidation reactions may eventually lead to the design of more economical and efficient catalysts. Gas-phase cluster experiments and theoretical electronic structure calculations are suitable alternative methods for probing the effects of charge state on the reactivity of bulk catalytic materials. These studies allow for individual clusters and potential active sites to be investigated without the complications resulting from different catalyst preparation methods and support interactions.<sup>6</sup>

Schröder et al. have employed three gas-phase techniques, ion cyclotron resonance (ICR), guided ion beam (GIB), and selected ion flow tube (SIFT) mass spectrometry, to probe the reactivity of  $\text{FeO}^+$  toward the oxidation of hydrocarbons.<sup>2</sup> Their results provide evidence for the importance of gas-phase studies which showed similar reactivity among all three methods and uncovered the molecular level mechanisms involved in condensed phase oxidation reactions. Furthermore, Armentrout and co-workers have investigated the thermochemistry and bond energies of gas-phase iron cations with CO and  $\text{CO}_2$ .<sup>7,8</sup> and Schwarz et al. have also classified dissociation patterns of small iron oxide cations.<sup>9</sup> Therefore, gas-phase studies such as these are aiding in the elucidation of fundamental catalytic mechanisms.

Previous theoretical calculations have predicted the energetics of the reaction steps that occur over iron oxide catalysts. Findings by Yumura et al. for the oxidation of formaldehyde by  $\text{FeO}^+$  showed that complete oxidation to  $\text{CO}_2$  was exothermic and involved a carbon monoxide intermediate complex,  $\text{H}_2\text{O}-\text{Fe}^+-\text{CO}$ .<sup>10</sup> Other theoretical studies of the structure and reactivity of small iron oxide clusters have predicted weakly bound oxygen units to be the active sites effecting the oxidation of CO to  $\text{CO}_2$ .<sup>11,12</sup> A mechanism for the simultaneous oxidation of CO and reduction of NO utilizing iron oxide species with subsequent regeneration of active sites has been proposed.<sup>12,13</sup>

\* To whom correspondence should be addressed. Tel: (814) 865 7242. Fax: (814) 865 5235. E-mail: awc@psu.edu.

<sup>†</sup> Pennsylvania State University.

<sup>‡</sup> Virginia Commonwealth University. E-mail: snkhanna@vcu.edu (S.N.K.).

<sup>§</sup> CINVESTAV.

**TABLE 1: Comparison of Calculated Vertical Detachment Energies of  $\text{Fe}_m\text{O}_n^-$  Clusters with Respect to Experimental Values<sup>a</sup>**

cluster	state (M)	vertical detachment energies (eV)	
		this work	exptl <sup>33</sup>
$^4\text{FeO}^-$	3	2.18	2.36
	5	1.26	1.5
$^4\text{FeO}_2^-$	3	2.37	2.36
	5	2.37	
$^4\text{FeO}_3^-$	3	3.81	3.26
	5	4.46	
$^2\text{FeO}_4^-$	1	3.78	3.4
	3	4.72	
$^8\text{Fe}_2\text{O}^-$	7	1.27	1.63
	9	1.59	
$^2\text{Fe}_2\text{O}_2^-$	1	1.32	1.4
	3	2.13	2.36
$^2\text{Fe}_2\text{O}_3^-$	1	2.39	2.6
	3	2.86	3.06
$^2\text{Fe}_2\text{O}_4^-$	1	3.30	3.56
	3	3.57	
$^2\text{Fe}_2\text{O}_5^-$	1	3.99	3.9
	3	3.69	

<sup>a</sup> The superscripts indicate spin multiplicity, and M indicates the final molecular spin state of the neutral cluster.

**TABLE 2: Comparison of Calculated Dissociation Energies of  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{Fe}_m\text{O}_n^{0/+}$  Clusters with Respect to Experimental and Previous Theoretical Studies<sup>a</sup>**

reacn	dissociation energies (eV)	
	this work	exptl
$^3\text{O}_2 \rightarrow ^3\text{O} + ^3\text{O}$	6.20	5.115 <sup>35</sup>
$^1\text{CO}_2 \rightarrow ^1\text{CO} + ^3\text{O}$	6.34	5.543 <sup>36</sup>
$^5\text{FeO} \rightarrow ^5\text{Fe} + ^3\text{O}$	5.51	$4.7 \pm 0.2$ <sup>37</sup>
$^3\text{FeO}_2 \rightarrow ^5\text{Fe} + ^3\text{O} + ^3\text{O}$	10.56	$8.64 \pm 0.22$ <sup>32</sup>
$^3\text{FeO}_2 \rightarrow ^5\text{Fe} + ^3\text{O}_2$	4.36	$3.60 \pm 0.20$ <sup>38</sup>
$^6\text{FeO}^+ \rightarrow ^4\text{Fe}^+ + ^3\text{O}$	4.57	$3.53 \pm 0.06$ <sup>39</sup>
$^2\text{FeO}_2^+ \rightarrow ^6\text{Fe}^+ + ^3\text{O}_2$	1.98	$2.0 \pm 0.5$ <sup>40</sup>
$^4\text{FeCO}^+ \rightarrow ^4\text{Fe}^+ + ^1\text{CO}$	2.29	$1.36 \pm 0.08$ <sup>41</sup>
$^8\text{Fe}_2\text{O}^+ \rightarrow ^8\text{Fe}_2^+ + ^3\text{O}$	5.64	$5.15 \pm 0.05$ <sup>40</sup>
$^2\text{Fe}_2\text{O}_2^+ (\text{AF}) \rightarrow ^8\text{Fe}_2\text{O}^+ + ^3\text{O}$	5.47	$5.15 \pm 0.05$ <sup>40,42</sup>
$^7\text{Fe}_2\text{O} \rightarrow ^7\text{Fe}_2 + ^3\text{O}$	5.97	$>4.84 \pm 0.29$ , <sup>41</sup> $5.62$ <sup>34,b</sup>
$^7\text{Fe}_2\text{O} \rightarrow ^5\text{FeO} + ^5\text{Fe}$	2.96	$2.60$ <sup>34,b</sup>

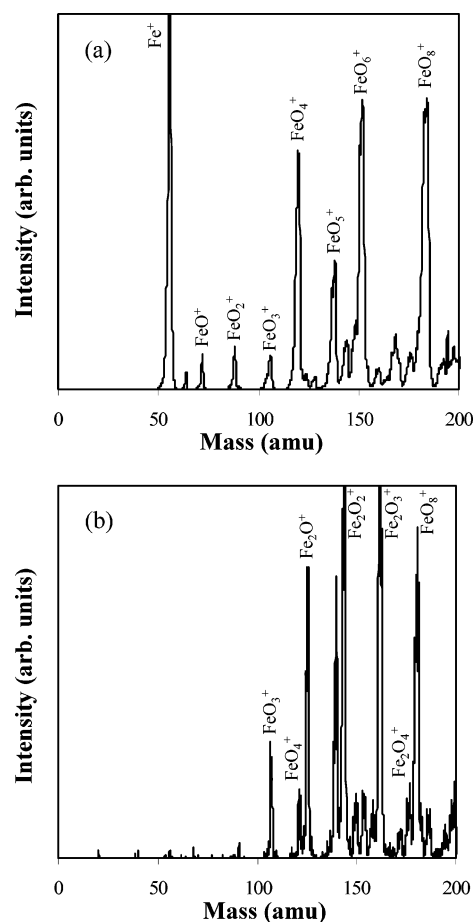
<sup>a</sup> The superscripts indicate spin multiplicity. <sup>b</sup> Theoretical.

This study shows the importance of active iron oxide species in the abatement of harmful atmospheric pollutants.

In this work, a comprehensive joint experimental and theoretical study of the influence of charge state on the structure and reactivity of oxide cluster cations containing one and two iron atoms with CO was undertaken. Previously we have shown the dissociation patterns and reactivity of iron oxide anions toward  $\text{CO}^{14}$  and also the importance of charge state on the reaction pathways for both cationic and anionic  $\text{FeO}_3$ .<sup>15</sup> In this third paper, we focus on cationic clusters and the reactions that they undergo in the presence of CO. Interestingly, we show that iron oxide cations are active in the oxidation of CO at thermal energies and would, therefore, provide a very economical alternative to precious metals based catalysts. Most previous studies of iron oxides have focused specifically on FeO and  $\text{Fe}_2\text{O}_3$  as these are the most common bulk-phase stoichiometries. Herein we provide systematic information on clusters of different sizes and stoichiometries and present the reaction pathways and associated energetics.

## Experimental Methods

Gas-phase iron oxide cluster studies were carried out by employing a guided ion beam mass spectrometer coupled to a



**Figure 1.** Mass distribution of iron oxide cation clusters produced when employing (a) a 27 mm conical nozzle and (b) a 51 mm conical nozzle at the exit of the source.

laser vaporization source (LAVA), presented in detail in a previous publication.<sup>16</sup> Briefly, the second harmonic of a Nd:YAG laser was used to ablate a rotating and translating iron rod (PVD Materials Corp., 99.95% purity) ensuring a fresh surface was ablated with each laser pulse. At a predetermined time, oxygen seeded in helium ( $\sim 1\%$ ) was pulsed over the rod, forming a dense, hot plasma. A conical expansion nozzle was placed at the exit of the source to allow for more collisions and to aid in cluster formation. Two different nozzles were employed. The first nozzle was 27 mm long and composed of a 15 mm long channel with a 4 mm internal diameter and 12 mm long expansion cone with a  $30^\circ$  total internal angle. The second nozzle was 51 mm in total length possessing a 2 mm inner diameter channel and cone dimensions similar to those of the other nozzle. Once the clusters exited the nozzle, they were internally cooled by supersonic expansion and passed through a field-free region before being collimated through a 3 mm skimmer. The cooled clusters were focused by a set of electrostatic lenses and deflectors into the first mass-selecting quadrupole. Each cluster species was individually selected in the first quadrupole and then directed through a second set of electrostatic lenses into the octopole reaction cell. Carbon monoxide reactant gas was added to the reaction cell, and the pressure, ranging from 0 to 12 mTorr, was monitored by a MKS baratron capacitance manometer. The products were directed through a third set of lenses into a second mass-analyzing quadrupole and detected using a channel electron multiplier. Studies were also conducted by employing nitrogen gas in the octopole reaction cell under the same conditions of pressure and energy as carbon monoxide. These studies verified the

reaction products with carbon monoxide, since both CO and N<sub>2</sub> are of the same nominal mass and, therefore, products observed with inert N<sub>2</sub> are assumed to be collisional fragments. Also, energy-resolved collision-induced dissociation (CID) experiments were conducted to study the fragmentation patterns of the iron oxide clusters. In these experiments, inert xenon gas was introduced into the octopole reaction cell at single collision conditions of 0.09 mTorr while the kinetic energy in the collision cell was slowly increased from 0 to 40 eV laboratory-frame energy. Studies involving slightly higher pressures of 0.2 mTorr Xe were also carried out to find sequential fragmentation patterns at multiple collision conditions.

**Theoretical Methods.** Theoretical studies were carried out using a first principles electronic structure scheme implemented within a gradient-corrected density functional formalism.<sup>17</sup> The electronic structure was probed using a linear combination of atomic orbitals molecular orbital approach. Here, the wave function for the cluster was expressed as a linear combination of Gaussian type orbitals (LCGTO) situated at the atomic positions in the cluster. The actual calculations were carried out using the implementation in the code deMon2k.<sup>18</sup> The code uses a variational fitting of the Coulomb potential<sup>19</sup> to avoid the calculation of four-center electron repulsion integrals. The exchange and correlation effects were incorporated through the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof.<sup>20</sup> The exchange-correlation potential was calculated by a numerical integration on an adaptive grid.<sup>21</sup> The geometry optimization employed a quasi-Newton method in internal redundant coordinates.<sup>22</sup> For each cluster structure, the configuration space was sampled and optimized by starting from several initial configurations and spin multiplicities using the DZVP basis set<sup>23</sup> for C and O, the Wachters-F basis set<sup>24</sup> for Fe, the GEN-A2 auxiliary function set for C and O, and the GEN-A2\* function set for Fe. The transition state search was performed in two steps. First, the reactants and products were aligned to maximum coincidence and a reaction coordinate distance was defined. This distance was successively reduced, and the geometry was optimized subject to the constraint that the reaction coordinate distance remained fixed. At each step the lower energy end point was moved closer to the higher energy point. In this way the method “seesawed” up the approximate reaction path until the reaction coordinate distance was below a given threshold.<sup>25</sup> The obtained approximate transition state was then further refined by a local uphill walking algorithm employing the eigenvector following method in redundant coordinates.<sup>26,27</sup> In this second step, the initial second energy derivatives Hessian matrix was calculated numerically, and the Powell update<sup>27</sup> was employed. A vibrational analysis was performed to discriminate between minima and transition states. The second derivatives were calculated by numerical differentiation (two-point finite difference) of the analytic energy gradients.

To eliminate any uncertainty associated with the choice of basis set or the numerical procedure, we carried out supplementary calculations using the Naval Research Laboratory Molecular Orbital Library (NRLMOL) set of codes developed by Pederson and co-workers.<sup>28–30</sup> For these calculations a generalized gradient approximation<sup>20</sup> as in the deMon2k code was employed. A 5s, 4p, and 3d basis set for the C and O atoms, and a 7s, 5p, and 4d basis for the Fe atom was used.<sup>30</sup> In each case, the basis set was supplemented by a diffuse Gaussian. We found excellent agreement between the deMon2k and NRLMOL calculations. Both methods predicted the same ground-state multiplicities and geometries with differences in

**TABLE 3: Results of CID Studies Showing the Fragmentation Channels of Selected Fe<sub>m</sub>O<sub>n</sub><sup>+</sup> Clusters**

Fe <sub>m</sub> O <sub>n</sub> <sup>+</sup> ( <i>m</i> , <i>n</i> )	products with Xe <sup>a</sup> (Fe <sub>m</sub> O <sub>n</sub> <sup>+</sup> )	neutral(s) lost <sup>b</sup> (Fe <sub>n</sub> O <sub>m</sub> )	Fe <sub>m</sub> O <sub>n</sub> <sup>+</sup> ( <i>m</i> , <i>n</i> )	products with Xe <sup>a</sup> (Fe <sub>m</sub> O <sub>n</sub> <sup>+</sup> )	neutral(s) lost <sup>b</sup> (Fe <sub>n</sub> O <sub>m</sub> )
1, 1	1, 0	0, 1	2, 1	2, 0	0, 1
1, 2	1, 0 1, 1	0, 2 0, 1	2, 2	2, 1 2, 0 1, 2	0, 1 0, 2 1, 0 <sup>c</sup>
1, 3	1, 2 1, 1 1, 0	0, 1 0, 2 0, 3	2, 3	2, 2 2, 1 2, 0 1, 2	0, 1 <sup>d</sup> 0, 2 0, 3 <sup>c</sup> 1, 1 <sup>c</sup>
1, 4	1, 2 1, 3 1, 1 1, 0	0, 2 <sup>d</sup> 0, 1 0, 3 0, 4	2, 4	2, 2 2, 3 1, 4 1, 2	0, 2 0, 1 1, 0 1, 2
1, 5	1, 3 1, 4 1, 2 1, 1	0, 2 <sup>d</sup> 0, 1 0, 3 0, 4	2, 8	2, 6 2, 4 2, 2 2, 3	0, 2 <sup>d</sup> 0, 4 0, 6 0, 5
1, 6	1, 4 1, 2 1, 5 1, 1	0, 2 <sup>d</sup> 0, 4 0, 1 0, 5	2, 10	2, 8 2, 6 2, 4 2, 2	0, 2 <sup>d</sup> 0, 4 <sup>d</sup> 0, 6 0, 8
1, 7	1, 5 1, 3 1, 2 1, 1	0, 2 <sup>d</sup> 0, 4 0, 5 0, 6			
1, 8	1, 6 1, 4 1, 2 1, 7	0, 2 <sup>d</sup> 0, 4 <sup>d</sup> 0, 6 0, 1			
1, 9	1, 7 1, 5 1, 4 1, 3	0, 2 <sup>d</sup> 0, 4 <sup>d</sup> 0, 5 <sup>d</sup> 0, 6			
1, 10	1, 1 1, 8 1, 6 1, 4 1, 2 1, 9 1, 1	0, 8 0, 2 <sup>d</sup> 0, 4 <sup>d</sup> 0, 6 <sup>d</sup> 0, 8 0, 1 0, 9			

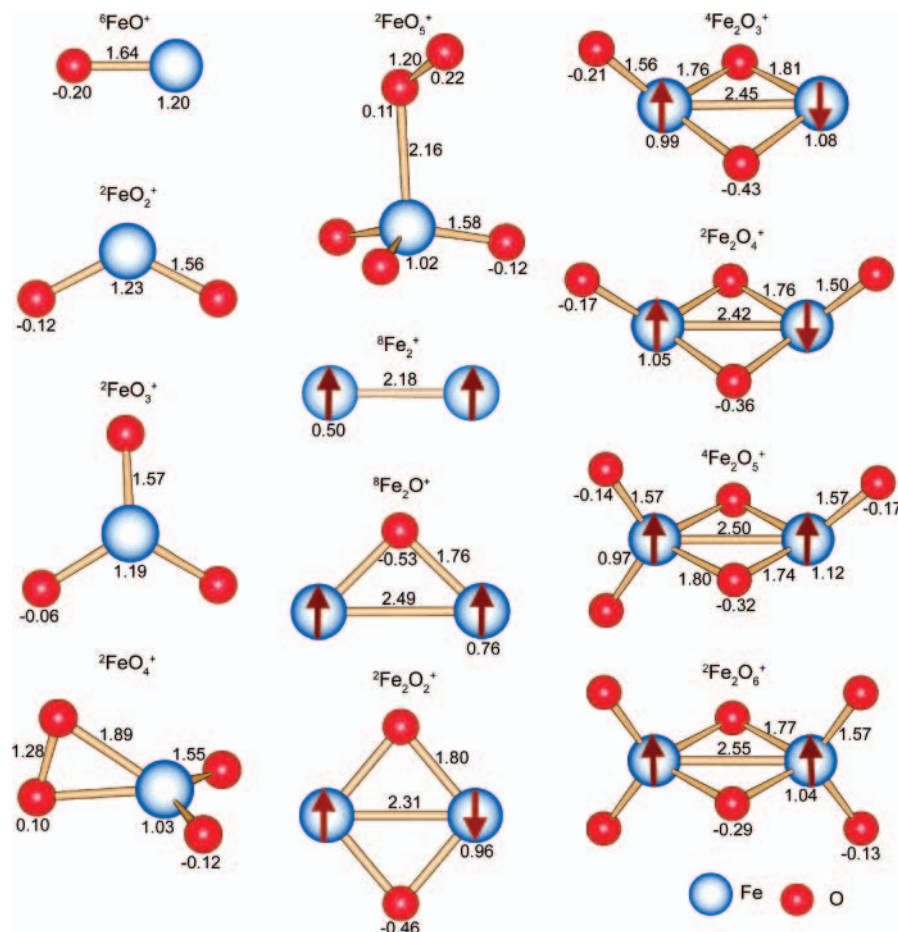
<sup>a</sup> Fragmentation channels are shown in order of observation with increasing collision energy. <sup>b</sup> The neutral loss is assigned on the basis of the difference between the selected cluster and fragment ion formed.

<sup>c</sup> Describes channels taking place under multiple collision conditions.

<sup>d</sup> Represents that dissociation occurs at near thermal energies.

the range 1–3 pm in the bond lengths. However, NRLMOL allowed us to investigate antiferromagnetic configurations for the clusters with two Fe atoms, and we found that for some cases these states were the ground states. For this reason we report the results from the NRLMOL calculations. The benchmarks on the accuracy of the theoretical calculations were established via calculations of ionization potentials (IP's), vertical detachment energies (VDE's), and dissociation energies (DE's) of Fe<sub>m</sub>O<sub>n</sub> clusters for which experimental data is available. The IP's of Fe, FeO, and FeO<sub>2</sub> were calculated to be 7.85, 8.8, and 10.23 eV, respectively, in excellent agreement with the experimental values of 7.87,<sup>31</sup> 8.8 ± 0.2,<sup>32</sup> and 9.5 ± 0.5<sup>32</sup> eV, respectively. The calculated VDE's of the Fe<sub>m</sub>O<sub>n</sub><sup>−</sup> (*m* = 1, 2, *n* = 1, 5) clusters were in good agreement with respect to the experimental VDE's reported by Wu et al.<sup>33</sup> as shown in Table 1. Additionally, the adiabatic electron affinity (AEA) of Fe<sub>2</sub>O was calculated to be 1.23 eV, while Gustev et al. reports 1.28 eV on the basis of DFT calculations.<sup>34</sup> Finally, in Table 2 we present the calculated dissociation energies of O<sub>2</sub>, CO<sub>2</sub>, and Fe<sub>m</sub>O<sub>n</sub><sup>0/+</sup> clusters and a comparison with experimental<sup>32,35–42</sup> and previous theoretical calculations.<sup>34</sup> Note that the theoretical





**Figure 2.** Ground-state geometries of  $\text{Fe}_m\text{O}_n^+$  clusters. The bond lengths are given in angstroms, and the superscripts indicate the spin multiplicity. The arrows indicate the spin polarization at the Fe atoms for the  $\text{Fe}_2\text{O}_n^+$  clusters. The Mulliken charges are marked below each atom.

calculations overestimate the experimental dissociation energies with a maximum deviation of 1 eV. As our results and discussion are based on relative differences in dissociation energies, we are confident about the conclusions based on the current approach.

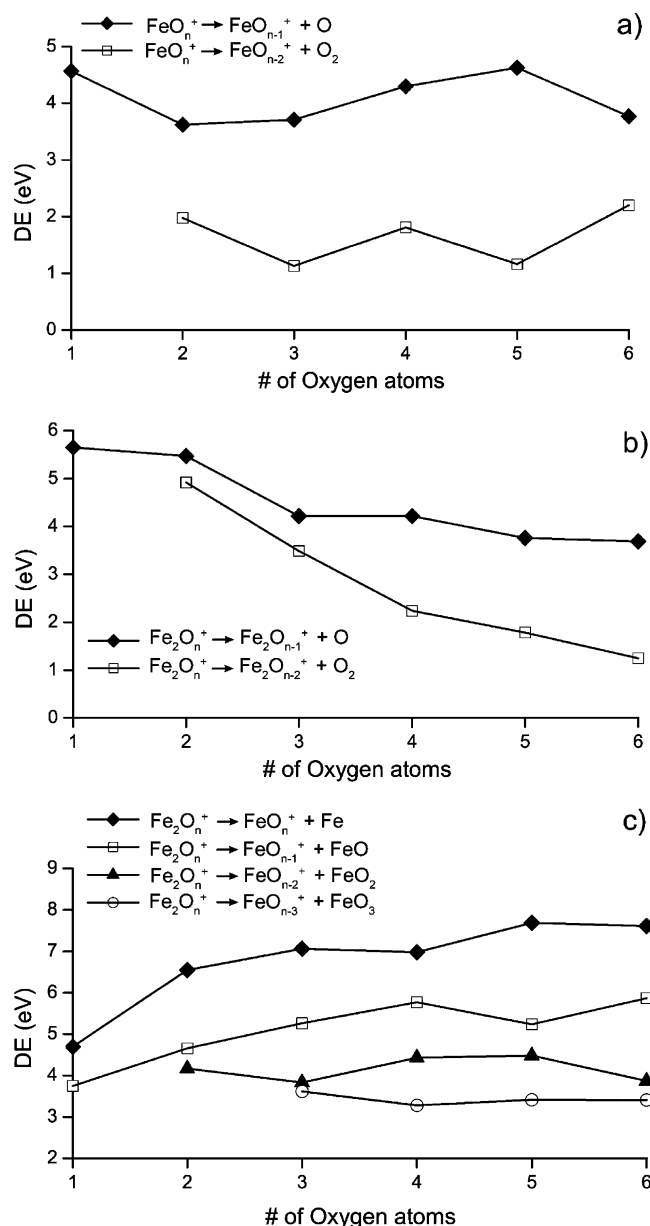
## Results and Discussion

Various cluster formation conditions were applied in the source region to optimize the mass distribution of iron oxide cations. Experiments conducted with no expansion nozzle produced only clusters containing one iron atom dominated by the  $\text{Fe}^+$  ion. Figure 1a shows a typical cationic iron oxide cluster distribution obtained with the 27 mm conical expansion nozzle in which clusters containing one iron atom were predominant. Figure 1b shows the distribution obtained with the 51 mm conical nozzle. The longer nozzle allowed for more three-body collisions which produced a higher intensity of iron oxide clusters with two iron atoms. Both nozzles were employed in these experiments depending on the cation cluster selected for study. Cationic  $\text{Fe}_m\text{O}_n^+$  clusters with a stoichiometry of  $m = n$  along with species that were oxygen rich with a ratio of  $m/n < 1$  were produced. The following studies were conducted on  $\text{FeO}_{1-10}^+$  and  $\text{Fe}_2\text{O}_{1-5,8,10}^+$  cationic species.

To understand the structure–reactivity relationships for these clusters, we performed CID experiments and theoretical calculations to aid in the structural characterization of cationic iron oxide clusters with one and two iron atoms. A discussion of the experimentally observed products with CO and the calculated energy profiles which serve to elucidate the reaction mechanisms follows.

**Structural Analysis.** A systematic energy-resolved CID study employing inert xenon gas was undertaken to investigate the fragmentation patterns of cationic iron oxides. Table 3 lists the fragmentation products of cationic iron oxide clusters in order of increasing kinetic energy for CID studies. The major product identified in the CID studies is loss of atomic oxygen for the oxygen-deficient species. Most clusters lost an oxygen atom at higher collision energies.  $\text{Fe}_2\text{O}_3^+$ , however, lost an O atom at near thermal energy.

The results of the theoretical calculation of the ground-state geometries and Mulliken population charges for  $\text{FeO}_n^+$  and  $\text{Fe}_2\text{O}_n^+$ , where  $n = 1-5$  and  $n = 0-6$ , respectively, are shown in Figure 2. Positive Mulliken charges indicate depletion of electronic charge. The structural calculations for cations show geometries similar to those reported previously for  $\text{Fe}_m\text{O}_n^-$  anion clusters.<sup>14</sup> For the  $\text{FeO}_{1-3}^+$  series, oxygen binds directly to the Fe atom with no molecular  $\text{O}_2$  units.  $\text{FeO}^+$  has a bond length of 1.64 Å, while  $\text{FeO}_2^+$  and  $\text{FeO}_3^+$  have reduced Fe–O bond lengths of 1.56 and 1.57 Å, respectively. The maximum coordination for a single Fe atom is four as shown in the  $\text{FeO}_4^+$  cluster. In this cluster two oxygen atoms bind atomically and the other two oxygen atoms form an  $\text{O}_2$  subunit.  $\text{FeO}_4^+$  exhibits two Fe–O bond lengths of 1.55 Å and two larger bond lengths of 1.89 Å corresponding to the two oxygen atoms forming the  $\text{O}_2$  unit. The spin multiplicity changes from sextet in  $\text{FeO}^+$  to doublet in  $\text{FeO}_{2-5}^+$  species. The Mulliken charges in the  $\text{FeO}_n^+$  series show that the positive molecular charge mainly resides on the Fe atom with atomic charges in the range 1.02–1.23 electrons.



**Figure 3.** Graphs of the dissociation energy (DE) associated with removing an O atom or O<sub>2</sub> subunit from (a) FeO<sub>n</sub><sup>+</sup> and (b) Fe<sub>2</sub>O<sub>n</sub><sup>+</sup> clusters. (c) Graph of the dissociation energy associated with removing Fe or FeO<sub>n</sub> from Fe<sub>2</sub>O<sub>n</sub><sup>+</sup> clusters.

Loss of molecular oxygen from oxygen-rich clusters, Fe<sub>m</sub>O<sub>n</sub><sup>+</sup> having a stoichiometry of  $n \geq m + 2$ , was another major fragmentation channel that was observed. This is reasonable in the cases of FeO<sub>5</sub><sup>+</sup> and FeO<sub>6</sub><sup>+</sup>. In FeO<sub>5</sub><sup>+</sup> the fifth oxygen atom is attached to one of the atomically bound oxygen atoms forming a molecular O<sub>2</sub> unit with an elongated Fe–O<sub>2</sub> bond of 2.16 Å (Figure 2). FeO<sub>6</sub><sup>+</sup> (not shown in Figure 2) optimized in a quartet spin state to the FeO<sub>4</sub><sup>+</sup> geometry with an O<sub>2</sub> unit attached to one atomically bound oxygen at a distance of 3.35 Å. Molecular O<sub>2</sub> loss from clusters with no O–O bonds in the ground state structure is also possible given the vibrational energy gained by the cluster through raising the kinetic energy of the collision in the octopole. This causes rapid vibrational bond rearrangement and fragmentation facilitated by the large gain in energy by forming O<sub>2</sub>. For example, for the doublet spin state FeO<sub>2</sub><sup>+</sup> cluster we found an isomer 0.24 eV higher in energy with a sextet spin state, where the oxygen atoms bind to form an O<sub>2</sub> unit. This higher energy isomer is reached from the FeO<sub>2</sub><sup>+</sup>

**TABLE 4: Products of the Reaction between Selected Iron Oxide Cluster Cations and Carbon Monoxide<sup>a</sup>**

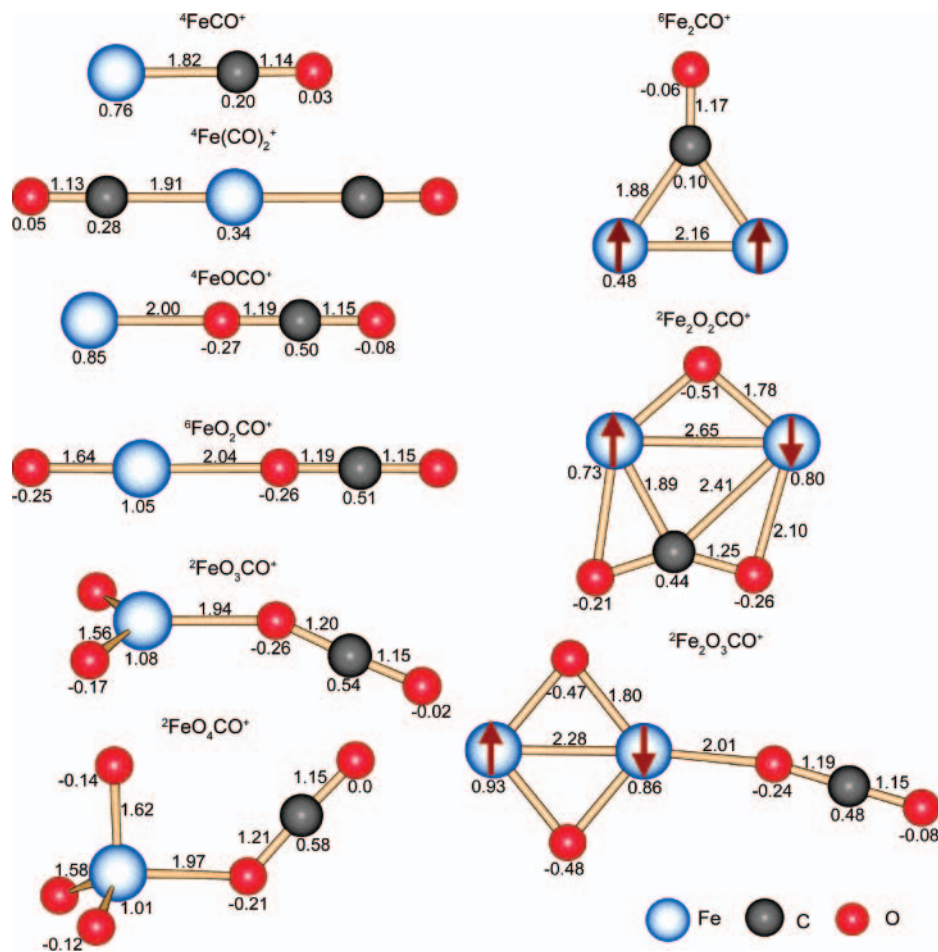
Fe <sub>m</sub> O <sub>n</sub> <sup>+</sup> ( <i>m</i> , <i>n</i> )	products with CO	DE (eV)	products with N <sub>2</sub>
1, 1	Fe <sup>+</sup>	1.78	no products
1, 2	FeO <sup>+</sup>	2.72	no products
	FeCO <sup>+</sup>	0.31	
1, 3	FeO <sup>+</sup>	5.36	FeO <sup>+</sup>
	FeOCO <sup>+</sup>	1.66	
	Fe <sup>+</sup>	0.65	
	FeO <sub>2</sub> <sup>+</sup>	2.64	
1, 4	FeO <sub>2</sub> CO <sup>+</sup>	2.17	FeO <sub>2</sub> <sup>+</sup>
	Fe(CO) <sub>2</sub> <sup>+</sup>	6.90	Fe <sup>+</sup>
	FeO <sup>+</sup>	0.92	
1, 5	FeO <sub>3</sub> <sup>+</sup>	-1.16	FeO <sub>3</sub> <sup>+</sup>
	FeO <sub>3</sub> CO <sup>+</sup>	3.06	
2, 1	Fe <sub>2</sub> <sup>+</sup>	0.69	no products
2, 2	Fe <sub>2</sub> O <sup>+</sup>	0.87	Fe <sub>2</sub> O <sup>+</sup>
	Fe <sub>2</sub> <sup>+</sup>	1.56	
	Fe <sub>2</sub> CO <sup>+</sup>	3.07	
2, 3	Fe <sub>2</sub> O <sub>2</sub> <sup>+</sup>	2.12	Fe <sub>2</sub> O <sub>2</sub> <sup>+</sup>
2, 4	Fe <sub>2</sub> O <sub>2</sub> CO <sup>+</sup>	6.17	Fe <sub>2</sub> O <sub>2</sub> <sup>+</sup>
	Fe <sub>2</sub> O <sub>2</sub> <sup>+</sup>	4.25	Fe <sub>2</sub> <sup>+</sup>
	Fe <sub>2</sub> O <sub>3</sub> <sup>+b</sup>	2.12	
2, 5	Fe <sub>2</sub> O <sub>3</sub> <sup>+</sup>	4.7	Fe <sub>2</sub> O <sub>3</sub> <sup>+</sup>
	Fe <sub>2</sub> O <sub>2</sub> <sup>+</sup>	6.83	
	Fe <sub>2</sub> O <sub>3</sub> CO <sup>+</sup>	9.62	
	Fe <sub>2</sub> O <sup>+</sup> <sup>+b</sup>	7.70	
	Fe <sub>2</sub> O <sub>2</sub> CO <sup>+b</sup>	8.75	

<sup>a</sup> Positive values in DE indicate exothermic reactions. <sup>b</sup> Denotes a minor product channel whose relative intensity is less than 1% and not shown in the branching ratios for clarity.

ground state through a transition state 2.05 eV higher in energy, and the vibrational energy input into the cluster from the collision overcomes this barrier. The observation that the reaction of FeO<sub>2</sub><sup>+</sup> with N<sub>2</sub> does not produce O<sub>2</sub> fragmentation at thermal energies can be explained by considering that the collisional energy of N<sub>2</sub> is not large enough to overcome the energy barrier to form the O<sub>2</sub> unit from atomic O in FeO<sub>2</sub><sup>+</sup>. For FeO<sub>3</sub><sup>+</sup>, in contrast, the distance between the O atoms bonded to the Fe center is much shorter. This results in a smaller energy barrier to O<sub>2</sub> formation. Indeed, O<sub>2</sub> loss is observed from FeO<sub>3</sub><sup>+</sup> in N<sub>2</sub> studies at thermal energy.

Extremely oxygen-rich clusters, for example FeO<sub>10</sub><sup>+</sup> and FeO<sub>9</sub><sup>+</sup>, lost successive O<sub>2</sub> molecules at near thermal energy uncovering a FeO<sup>+</sup> core structure. During mass selection of these clusters it was observed that an oxygen molecule would dissociate without any gas addition. This suggests that these clusters contained metastable O<sub>2</sub> subunits which are very weakly associated as in the case of FeO<sub>6</sub><sup>+</sup>.

The common products observed for iron oxide cations containing two iron atoms were atomic oxygen loss and molecular O<sub>2</sub> loss for the more oxygen-rich species, as presented in Table 3. Starting with clusters containing two iron atoms, fragmentation of a Fe–Fe bond with increasing kinetic energy in Fe<sub>2</sub>O<sub>2–4</sub><sup>+</sup> clusters revealed a basic core structure of FeO<sub>2</sub><sup>+</sup>. Structural calculations of the iron dimer cation show a Fe–Fe bond length of 2.18 Å and a spin multiplicity of octet (Figure 2). In the Fe<sub>2</sub>O<sub>n</sub><sup>+</sup> clusters, a basic ring structure composed of Fe<sub>2</sub>O<sub>2</sub><sup>+</sup> with oxygen bridging each Fe atom is formed. For Fe<sub>2</sub>O<sub>n</sub><sup>+</sup> with  $n \geq 3$ , oxygen atoms are bound to iron outside of the ring. The Fe–Fe bond length increases from 2.31 Å for Fe<sub>2</sub>O<sub>2</sub><sup>+</sup> to a maximum of 2.55 Å for Fe<sub>2</sub>O<sub>6</sub><sup>+</sup>. The Fe–O bond length ranges from 1.74 to 1.81 Å within the ring and from 1.50 to 1.57 Å outside the ring. The spin multiplicity is octet for Fe<sub>2</sub>O<sup>+</sup> and changes to doublet and quartet states for even and odd numbers of oxygen atoms, respectively. An antiferro-

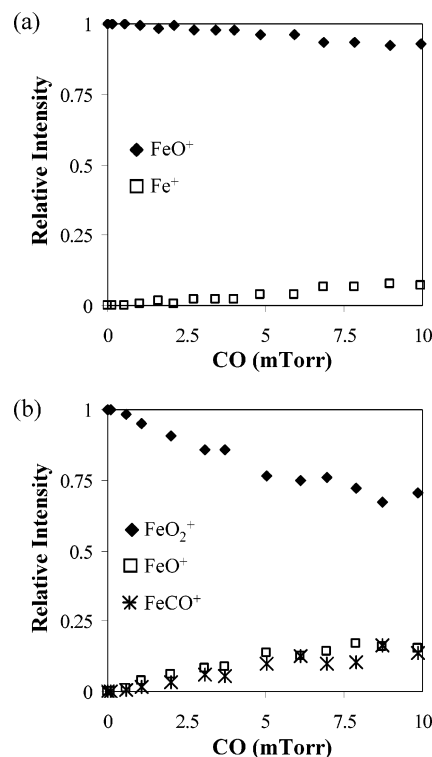


**Figure 4.** Ground-state geometries of  $\text{Fe}(\text{CO})_{1,2}^+$  and  $\text{Fe}_m\text{O}_n\text{CO}^+$  clusters. The bond lengths are given in angstroms, and the superscripts indicate the spin multiplicity. The arrows indicate the spin polarization at the Fe atoms for the  $\text{Fe}_2\text{O}_n\text{CO}^+$  clusters. The Mulliken charges are marked below each atom.

magnetic spin coupling was found for  $\text{Fe}_2\text{O}_2^+$ ,  $\text{Fe}_2\text{O}_3^+$ , and  $\text{Fe}_2\text{O}_4^+$  cluster species, while the Fe sites in  $\text{Fe}_2\text{O}_5^+$  and  $\text{Fe}_2\text{O}_6^+$  were found to be coupled ferromagnetically. The Mulliken charges in the  $\text{Fe}_2\text{O}_n^+$  series again show that the positive molecular charge resides mainly on the Fe atoms with atomic charges of 0.76 for  $\text{Fe}_2\text{O}^+$  and approximately 1 electron for the  $\text{Fe}_2\text{O}_{2-6}^+$  series.

For the oxygen-rich clusters,  $\text{Fe}_2\text{O}_8^+$  and  $\text{Fe}_2\text{O}_{10}^+$ , a stable core structure of  $\text{Fe}_2\text{O}_2^+$  was revealed after collisional loss of oxygen molecules. There was no Fe–Fe fragmentation in these clusters, and therefore, the building blocks of small iron oxide cations were identified as  $\text{FeO}^+$ ,  $\text{FeO}_2^+$ , and  $\text{Fe}_2\text{O}_2^+$ .

General trends can be established between the calculated dissociation energies and the order of the observed CID products with increasing collision energy. Figure 3 shows graphs of the DE associated with removing an O atom or  $\text{O}_2$  subunit from  $\text{Fe}_m\text{O}_n^+$  clusters and the DE required for removing Fe or  $\text{FeO}_n$  from  $\text{Fe}_2\text{O}_n^+$  clusters. Numerical values for the graphs are shown in Table S1 (Supporting Information). For a single Fe atom, the  $\text{FeO}_n^+$  clusters contain bound  $\text{O}_2$  molecules for  $n \geq 4$ . In these cases, the energy to remove  $\text{O}_2$  is less than to dissociate an O atom and consequently  $\text{O}_2$  fragmentation is the favored channel. For  $\text{Fe}_2\text{O}_n^+$ , the energy to remove an  $\text{O}_2$  progressively decreases and becomes significantly less than the energy to remove an O atom at  $\text{Fe}_2\text{O}_4^+$ . However, for  $\text{Fe}_2\text{O}_2^+$  and  $\text{Fe}_2\text{O}_3^+$ , shown in Figure 3b, the energy needed to fragment an oxygen atom is close to the energy required to fragment  $\text{O}_2$  (<1 eV difference).



**Figure 5.** Ion intensity changes of (a)  $\text{FeO}^+$  and (b)  $\text{FeO}_2^+$  and their respective observed products with CO as a function of increasing CO pressure.



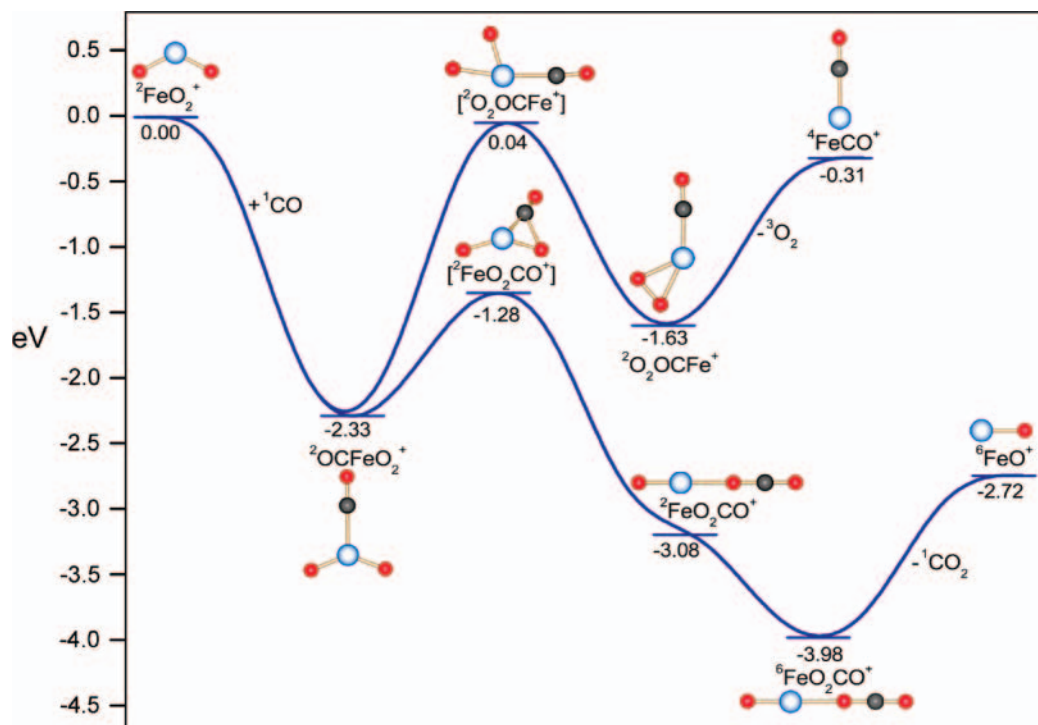


Figure 6. Change in energy ( $\Delta E$ ) for each step of the reaction pathway of  $\text{FeO}_2^+$  with CO. The superscripts indicate spin multiplicity.

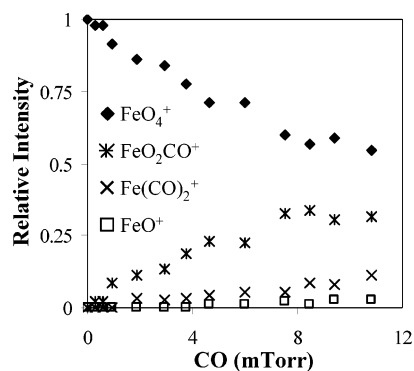


Figure 7. Ion intensity changes of  $\text{FeO}_4^+$  and its observed products with CO as a function of increasing CO pressure. Note that two CO molecules became attached to bare iron.

It can be seen in Figure 3c that the energy needed to produce a neutral Fe atom increases as the clusters become more oxygen rich, while  $\text{FeO}_3$  is the lowest energy dissociation channel for oxygen-rich  $\text{Fe}_2\text{O}_{3+}$  species. It is interesting to note that Schwarz and co-workers showed that neutral O, FeO, and  $\text{FeO}_2$  loss was dependent on the iron to oxygen ratio of the parent cluster.<sup>9</sup> In oxygen-rich  $\text{Fe}_m\text{O}_n^+$  clusters with a metal to oxygen ratio of  $1 > m/n > 2/3$ , neutral loss of  $\text{FeO}_2$  and  $\text{O}_2$  became more dominant. The trends in bond energy discussed above are used to justify the CO oxidation and oxygen replacement by CO reaction pathways that were observed for  $\text{Fe}_m\text{O}_n^+$  clusters.

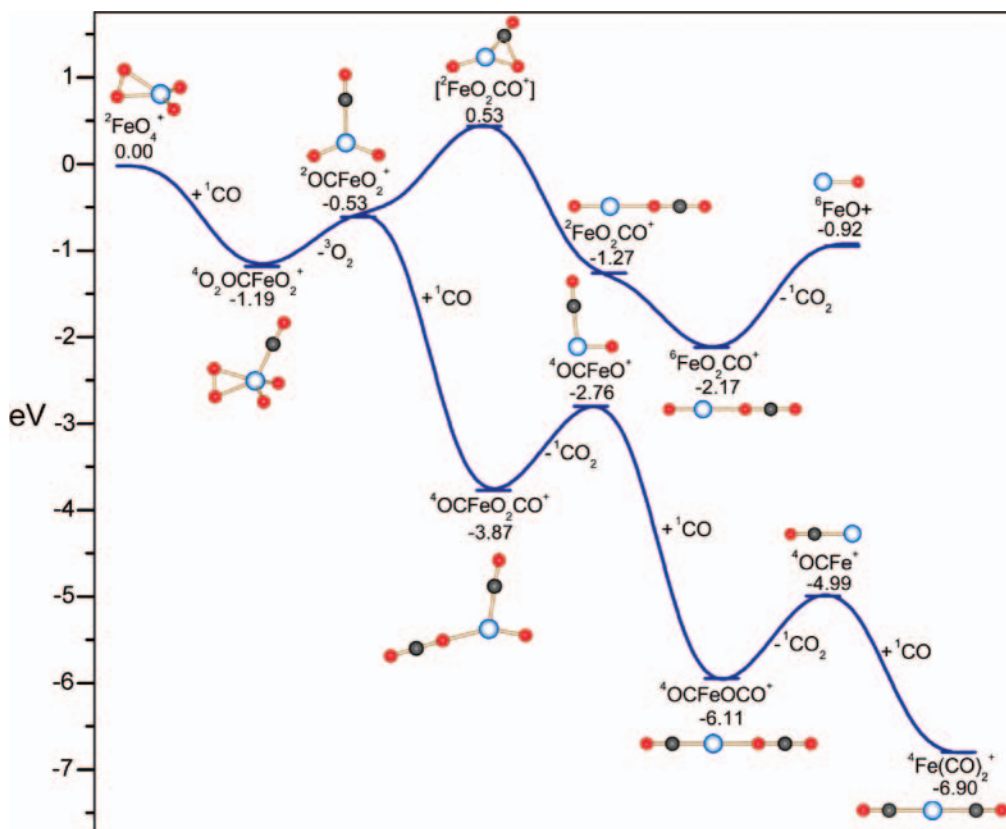
**Reactivity Studies.** The observed reaction products for  $\text{FeO}_{1-5}^+$  and  $\text{Fe}_2\text{O}_{1-5}^+$  cluster species with either carbon monoxide or nitrogen are shown in Table 4. Notice the attachment of a CO molecule to several Fe cationic clusters. To understand these reaction products, the ground-state geometries and the Mulliken population charges for the experimentally observed iron oxide clusters with CO molecules associated were calculated. The structures of  $\text{Fe}(\text{CO})_x^+$  with  $x = 1$  and 2,  $\text{FeO}_n\text{CO}^+$  with  $n = 1-4$ , and  $\text{Fe}_2\text{O}_n\text{CO}^+$  with  $n = 0, 2$ , and 3 are presented in Figure 4.

We found that the C atom of the CO molecule attached to the Fe atom in the  $\text{Fe}(\text{CO})_x^+$  clusters and that the complex had a quartet spin multiplicity state. The Fe–C bond length was optimized to 1.82 and 1.91 Å for  $x = 1$  and 2, respectively. The CO bond length was approximately 1.13 Å, very close to the bond length of 1.14 Å in the isolated CO molecule. In accordance with the Mulliken charges in  $\text{FeCO}^+$ , the positive charge mainly resides on the Fe atom with an atomic charge of 0.76 electrons, while in the case of  $\text{Fe}(\text{CO})_2^+$  the positive charge in the Fe sites reduces to 0.34 electrons. This charge transfer underlies the strong binding of Fe and C. A detailed analysis of the reaction pathways for  $\text{FeO}_n^+$  clusters with CO, discussed below, shows Fe–C attachment as the initial step of the reaction. However, the structures in Figure 4 were fully optimized with CO bound to an oxygen atom, which is the lowest energy configuration found along the reaction pathway. The  $\text{FeO}_n\text{CO}^+$  clusters optimized to structures of the type  $\text{FeO}_{n-1}\text{CO}_2^+$  with a  $\text{CO}_2$  unit attached at a bond length in the range of 1.94–2.04 Å.

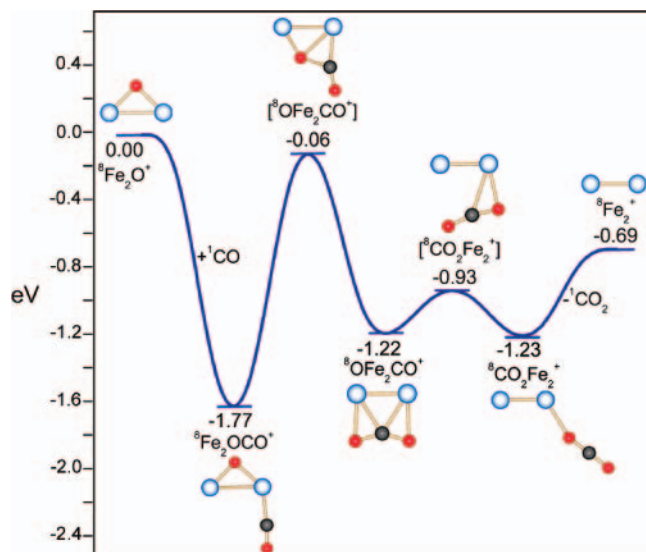
The spin multiplicity was quartet for  $\text{FeOCO}^+$ , sextet for  $\text{FeO}_2\text{CO}^+$ , and doublet for  $\text{FeO}_n\text{CO}^+$ ,  $n = 3$  and 4. The  $\text{CO}_2$  unit contained two different oxygen bond lengths, a bond length of 1.15 Å and a larger bond length around 1.20 Å for the O atom that was shared with the  $\text{FeO}_{n-1}^+$  cluster. The Fe atomic Mulliken charges ranged from 0.85 electrons for  $\text{FeOCO}^+$  to around 1 electron for the  $\text{FeO}_{2-4}\text{CO}^+$  series.

In clusters of  $\text{Fe}_2\text{O}_n^+$  with CO we found two types of structures. The first type represents a strong bonding with CO as shown in  $\text{Fe}_2\text{CO}^+$  and  $\text{Fe}_2\text{O}_2\text{CO}^+$  clusters, while the second type, exhibited in  $\text{Fe}_2\text{O}_3\text{CO}^+$ , was optimized to a  $\text{Fe}_2\text{O}_2\text{CO}_2^+$  structure. In  $\text{Fe}_2\text{CO}^+$ , the carbon atom of the CO unit bonded to both Fe atoms in a bridging configuration at a distance of 1.88 Å in a sextet spin state. The Fe–Fe bond length was 2.16 Å, consistent with other cationic structures. It was revealed in  $\text{Fe}_2\text{CO}^+$  that most of the positive molecular charge resides in the Fe atoms according to the atomic Mulliken charges.  $\text{Fe}_2\text{O}_2\text{CO}^+$  presented a ring structure in an antiferromagnetic doublet spin state. The CO was inserted with the carbon atom attached to both Fe atoms possessing bond lengths of 1.89 and





**Figure 8.** Change in energy ( $\Delta E$ ) for each step of the reaction pathway of  $\text{FeO}_4^+$  with CO. The superscripts indicate spin multiplicity.



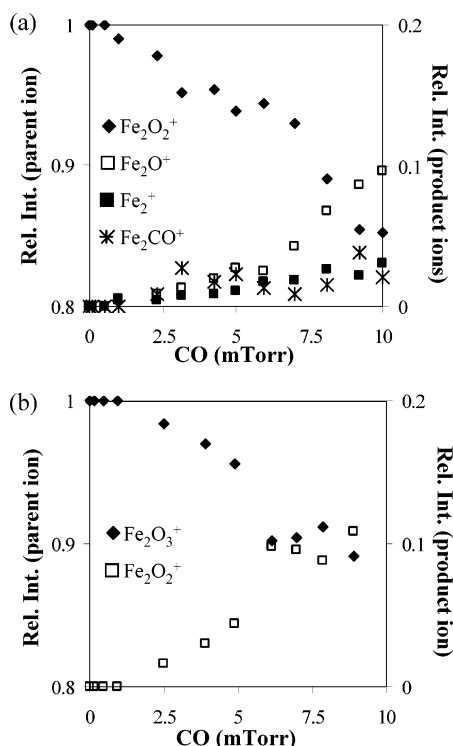
**Figure 9.** Change in energy ( $\Delta E$ ) for each step of the reaction pathway of  $\text{Fe}_2\text{O}^+$  with CO. The superscripts indicate spin multiplicity.

2.41 Å, respectively. The Fe–Fe bond length was optimized to 2.65 Å. Finally,  $\text{Fe}_2\text{O}_3\text{CO}^+$  was optimized to an antiferromagnetic doublet spin state with bond lengths very close to  $\text{Fe}_2\text{O}_2^+$  and with the  $\text{CO}_2$  unit attached at 2.01 Å. These findings show that, in contrast to the other clusters, the CO unit did not bind directly to the Fe atom in  $\text{Fe}_2\text{O}_3^+$ . This is due to the very stable  $\text{CO}_2$  unit that is formed from CO attachment onto the weakly bound oxygen atom. It is interesting to note that, in  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3^-$ , the C atom of the CO binds to the Fe atom to form  $\text{OCFe}_2\text{O}_3$  and  $\text{OCFe}_2\text{O}_3^-$ , respectively, as shown in previous papers.<sup>12,14</sup> The atomic Mulliken charges in  $\text{Fe}_2\text{O}_2^-$

$\text{CO}^+$  and  $\text{Fe}_2\text{O}_3\text{CO}^+$  show that the positive molecular charge is mainly located at the Fe atomic sites which act as charge donors.

Now a discussion of specific clusters and their reaction pathways is presented to differentiate whether the observed CO attachment to the metal cluster is an intermediate species to CO oxidation or whether it is a separate product. The intensity of  $\text{FeO}_{1,2}^+$  clusters and their products with CO as a function of increasing CO pressure are presented in Figure 5. The dissociation energy (DE) values associated with the CO product channels are listed in Table 4. For these clusters oxygen atom transfer is the dominant reaction channel in the presence of CO. This reaction was confirmed by nitrogen studies which showed no collisional loss of an oxygen atom under the same experimental pressures as the CO reactant gas.

The reaction profile for  $\text{FeO}_2^+$  with CO was calculated to explain the energetics of the two products generated with CO,  $\text{FeO}^+$ , and  $\text{FeCO}^+$ . Figure 6 shows the change in energy along the reaction pathway of  $\text{FeO}_2^+$  with CO (numerical values given in Table S2). In the initial step, attachment of the C atom of CO to the Fe atom forms an intermediate  $\text{OCFeO}_2^+$  species with an energy gain of 2.33 eV. The formation of the Fe–C bond is consistent with the electron-donating behavior of CO and the partial positive charge present on the Fe site as revealed by the Mulliken population calculation. From this  $\text{OCFeO}_2^+$  intermediate complex there are two possible channels. The first involves the formation of an  $\text{O}_2$  unit with subsequent fragmentation. This pathway contains a transition state that is 2.37 eV higher in energy and results in an energetically equivalent reaction. From the transition state there is a gain of 1.66 eV of energy for the formation of the  $\text{O}_2\text{OCFe}^+$  cluster with a molecular  $\text{O}_2$  unit. Subsequent release of  $\text{O}_2$  requires 1.32 eV of energy to produce  $\text{FeCO}^+$  in an overall exothermic process. The second possibility from the  $\text{OCFeO}_2^+$  intermediate is the



**Figure 10.** Ion intensity changes of (a)  $\text{Fe}_2\text{O}_2^+$  and (b)  $\text{Fe}_2\text{O}_3^+$  and their respective observed products with CO as a function of increasing CO pressure.

displacement of CO onto an adjacent O atom through a transition state 1.06 eV higher in energy. This generates a doublet  $\text{FeO}_2\text{-CO}^+$  complex, with an energy gain of 1.80 eV. The  $\text{FeO}_2\text{CO}^+$  ground state is then produced after a spin multiplicity change from doublet to sextet with an extra energy gain of 0.9 eV. The final step in the reaction pathway is the emanation of  $\text{CO}_2$  from  $\text{FeO}_2\text{CO}^+$ , which generates the oxygen atom transfer product  $\text{FeO}^+$  observed in the experiments.

It can be seen in Figure 6 that the generation of  $\text{FeCO}^+$  proceeds through a reaction path that involves a high-energy transition state. This is consistent with the experimental results in Figure 5 which show that the intensity of  $\text{FeO}^+$  is greater than that of  $\text{FeCO}^+$  due to this higher energy pathway. We believe that this transition state argument accounts for  $\text{FeO}^+$  being observed before  $\text{FeCO}^+$  as seen in Table 4 and that the existence of energy barriers may account for the order of the observed products with CO in the  $\text{Fe}_m\text{O}_n^+$  series, as discussed later.

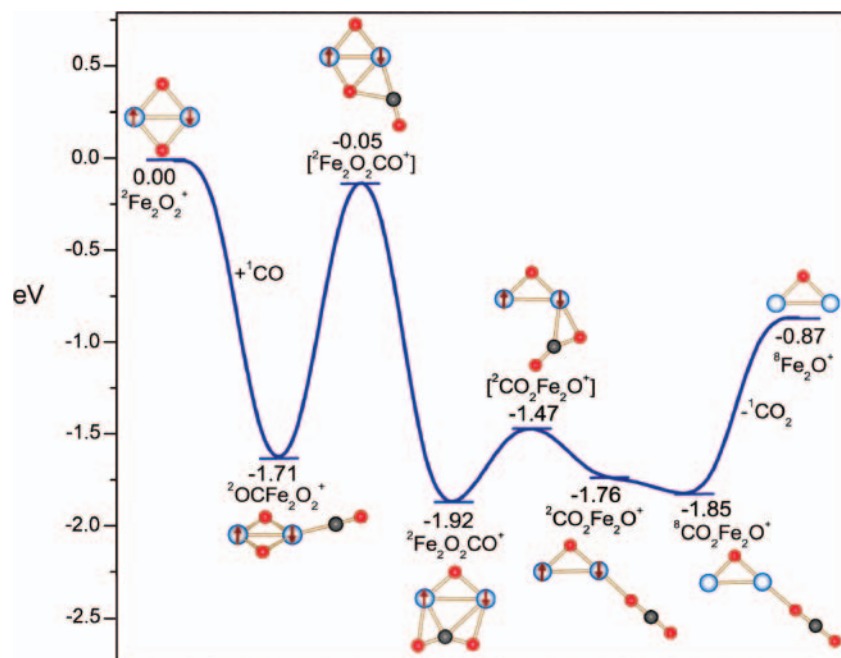
The reaction of  $\text{FeO}_3^+$  with CO generates four products through an exothermic process,  $\text{FeO}^+$ ,  $\text{FeOCO}^+$ ,  $\text{Fe}^+$ , and  $\text{FeO}_2^+$ .  $\text{FeO}_3^+$  was presented in a previous paper which focused on the influence of charge state differences on the O atom transfer reaction pathway.<sup>14</sup> However, to compare all the reaction products of  $\text{FeO}_3^+$  with  $\text{FeO}_2^+$ ,  $\text{FeO}_4^+$ , and  $\text{FeO}_5^+$ , we discuss the changes in energy and show in Figure S1 and Table S3 (Supporting Information) the reaction pathway of  $\text{FeO}_3^+$  with CO. The initial step is similar to  $\text{FeO}_2^+$ , where the C atom of CO attaches to the Fe atom. The formation of  $\text{OCFeO}_3^+$  species occurs with an energy gain of 1.86 eV. From this complex, the pathway generating an  $\text{O}_2$  unit requires surmounting a transition state 1.68 eV higher in energy. Therefore this channel proceeds in an exothermic way. The transition state generates the stable  $\text{O}_2\text{OCFeO}^+$  structure in a doublet spin state and later the quartet ground state after energy gains of 1.41 and 0.42 eV, respectively. The release of an  $\text{O}_2$  molecule requires 1.29 eV and generates the  $\text{OCFeO}^+$  cluster species. This cluster transforms into the

$\text{FeOCO}^+$  ground state through a transition state 0.47 eV higher in energy with an energy gain of 1.42 eV.  $\text{FeOCO}^+$  is then able to release  $\text{CO}_2$  with an energy requirement of 1.01 eV producing  $\text{Fe}^+$ . The second possible pathway from the CO-associated complex,  $\text{OCFeO}_3^+$ , is the displacement of CO onto an adjacent O atom through a transition state that is only 0.30 eV higher in energy. This forms the  $\text{FeO}_3\text{CO}^+$  ground state after an energy gain of 2.66 eV.  $\text{FeO}_3\text{CO}^+$  then releases  $\text{CO}_2$  and produces  $\text{FeO}_2^+$  with an energy requirement of 1.58 eV. Finally, the formation of  $\text{FeO}^+$  is attributed to two possible paths, the reaction of  $\text{FeO}_2^+$  with CO as described in Figure 6 and the release of  $\text{O}_2$  from  $\text{FeO}_3^+$  by collisional energy transfer similar to the reaction observed with  $\text{N}_2$ .

The major product for  $\text{FeO}_4^+$  with CO was  $\text{O}_2$  replacement by CO. Figure 7 shows the intensity of  $\text{FeO}_4^+$  and its products with CO as a function of increasing CO pressure. In Figure 8 we present the energy profile for the reaction of  $\text{FeO}_4^+$  with CO. The corresponding energies are provided in Table S4. The initial step is analogous to  $\text{FeO}_2^+$  and  $\text{FeO}_3^+$  with the attachment of the C atom of CO to the Fe atom. The formation of the  $\text{OCFeO}_4^+$  species occurs with an energy gain of 1.19 eV.  $\text{OCFeO}_4^+$  then releases  $\text{O}_2$  to form  $\text{OCFeO}_2^+$  requiring a change in spin multiplicity from quartet to doublet state and 0.66 eV of energy. The profile of the  $\text{OCFeO}_2^+$  intensity observed in Figure 7 suggests that this species is probably an unstable intermediate which can further undergo reactions at higher pressures. From  $\text{OCFeO}_2^+$  we found two possibilities, the first involves the displacement of CO onto an oxygen atom to form a  $\text{CO}_2$  unit through a transition state 1.06 eV higher in energy. The  $\text{CO}_2$  molecule is then released, and the  $\text{FeO}^+$  cluster is generated as described in Figure 6. However, in this case, the 1.06 eV of energy required to surmount the transition state is not supplied by the association energy of CO with  $\text{FeO}_4^+$ . This then implies an endothermic step of 0.53 eV. We believe that this explains the low intensity of  $\text{FeO}^+$ , which is produced only at higher CO pressures after multiple energizing collisions. The second possibility from  $\text{OCFeO}_2^+$  is the successive attachment of another two CO molecules and the release of two  $\text{CO}_2$  molecules. The  $\text{Fe}(\text{CO})_2^+$  species is produced as a final product after CO attachment to  $\text{FeCO}^+$  in an overall exothermic process.  $\text{FeO}_4^+$  was the only species observed to have two CO molecules attached to the metal center. It is interesting to note that Armentrout and co-workers studied the bond energies of gas-phase iron carbonyls and found the strongest bond dissociation energy (BDE) to be for the second CO ligand<sup>7,8</sup> supporting the high stability of Fe–C bonds.

The major reaction product for  $\text{FeO}_5^+$  was  $\text{O}_2$  release after CO collision. Figure S2 and Table S5 show the change in energy along the reaction pathway of  $\text{FeO}_5^+$  with CO. The initial step in this case begins with the release of  $\text{O}_2$  to form  $\text{FeO}_3^+$ , which requires 1.16 eV. This channel is also found in the reaction between  $\text{FeO}_5^+$  with  $\text{N}_2$  which is evidence that the energy needed to break the  $\text{O}_2$  bond with the Fe atom is supplied through multiple collisions. The second reaction product observed follows a path for the simultaneous attachment of CO and release of  $\text{O}_2$ . This generates the  $\text{OCFeO}_3^+$  cluster with an energy gain of 0.7 eV.  $\text{OCFeO}_3^+$  then proceeds into the  $\text{FeO}_3\text{-CO}^+$  ground state through a transition state 0.30 eV higher in energy and an energy gain of 2.66 eV.

The reaction pathways of the iron oxide clusters containing two iron atoms were also calculated, and the DE's corresponding to the experimentally observed products are presented in Table 4. There was only one product detected for the  $\text{Fe}_2\text{O}^+$  cluster. This species, therefore, was selective toward oxygen atom



**Figure 11.** Change in energy ( $\Delta E$ ) for each step of the reaction pathway of  $\text{Fe}_2\text{O}_2^+$  with CO. The superscripts indicate spin multiplicity.

transfer to CO, as confirmed with  $\text{N}_2$  studies which showed no collisional products. Figure 9 and Table S6 show the change in energy for the reaction pathway of  $\text{Fe}_2\text{O}^+$  with CO. The initial step begins with attachment of the C atom of CO to the Fe atom with an energy gain of 1.77 eV to form  $\text{Fe}_2\text{OCO}^+$ . This species converts into the  $\text{OFe}_2\text{CO}^+$  and  $\text{CO}_2\text{Fe}_2^+$  intermediates through two transition states 1.71 and 0.29 eV higher in energy with gains in energy of 1.16 and 0.30 eV, respectively. Finally, after  $\text{CO}_2$  emanation and an energy requirement of 0.54 eV, the  $\text{Fe}_2^+$  cluster is formed in an overall exothermic reaction.

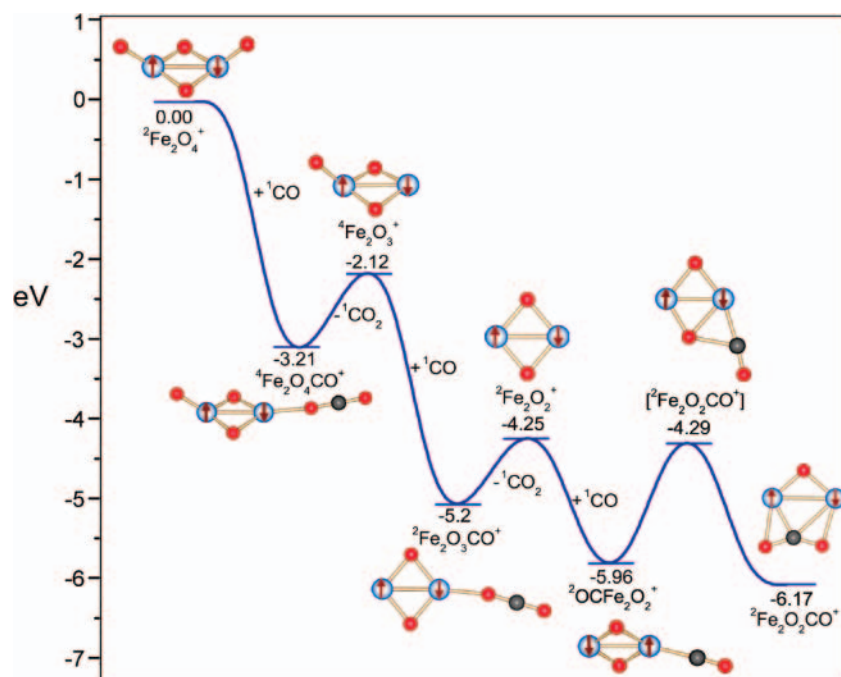
Figure 10a shows the intensity of  $\text{Fe}_2\text{O}_2^+$  and its products with CO as a function of increasing CO pressure. In this case, the major product species  $\text{Fe}_2\text{O}^+$  was generated from reactions with CO gas as well as with  $\text{N}_2$  gas. However, in the studies involving nitrogen, the observed oxygen atom loss product was observed under pressure conditions typically considered to be multicollisional. Figure 11 and Table S7 show the change in energy for the reaction pathway of  $\text{Fe}_2\text{O}_2^+$  with CO. As in the case of  $\text{Fe}_2\text{O}^+$ , the initial step is the C atom attachment to Fe to form  $\text{OCFe}_2\text{O}_2^+$  with an energy gain of 1.71 eV. Then,  $\text{OCFe}_2\text{O}_2^+$  transforms into the  $\text{Fe}_2\text{O}_2\text{CO}^+$  ground state through a transition state 1.66 eV higher in energy with an energy gain of 1.88 eV. The  $\text{CO}_2\text{Fe}_2\text{O}^+$  intermediate is then formed through a transition state 0.45 eV higher with energy gains of 0.28 and 0.09 eV and a spin multiplicity change from doublet to octet. Finally,  $\text{CO}_2\text{Fe}_2\text{O}^+$  emanates  $\text{CO}_2$ , generating  $\text{Fe}_2\text{O}^+$  and requiring 0.98 eV in an overall exothermic reaction. From  $\text{Fe}_2\text{O}^+$ , another CO molecule is oxidized producing  $\text{Fe}_2^+$  and neutral  $\text{CO}_2$  as described in Figure 9. It is not surprising that bare iron clusters were detected as products from  $\text{FeO}^+$ ,  $\text{FeO}_3^+$ ,  $\text{Fe}_2\text{O}^+$ , and  $\text{Fe}_2\text{O}_2^+$  species, since iron is easily reduced. No iron carbides were observed, which suggests that all the carbon present was oxidized.<sup>43</sup> However, for the bare  $\text{Fe}_2^+$  cluster a strong positive charge on the Fe atom favors the association of CO to produce  $\text{Fe}_2\text{CO}^+$  with a change of multiplicity from octet to sextet and with an energy gain of 1.51 eV.

The reaction of  $\text{Fe}_2\text{O}_3^+$  with CO produced an oxygen atom transfer product as shown in Figure 10b. The mechanism is

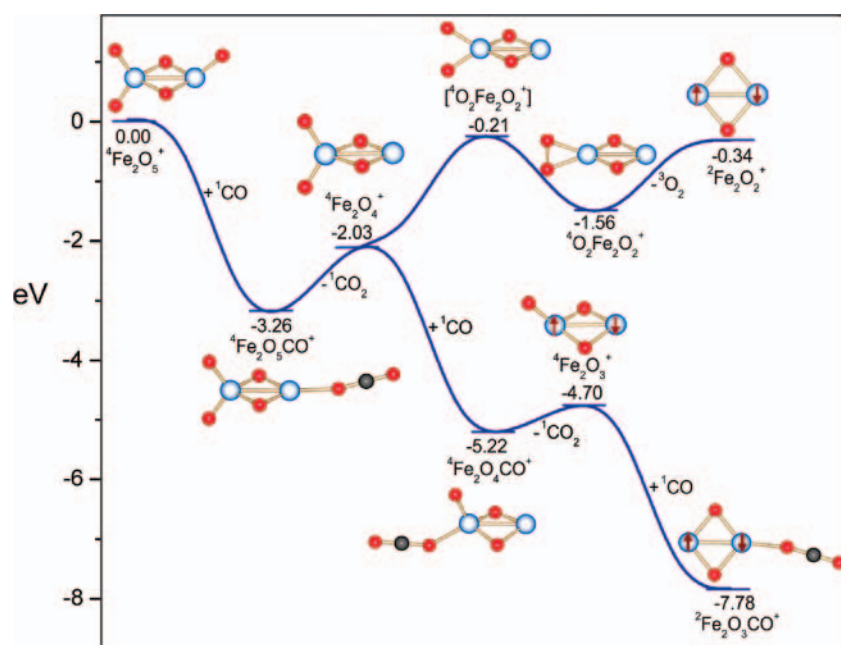
overall exothermic by 2.12 eV and involves CO binding to a weakly bound oxygen atom with subsequent  $\text{CO}_2$  loss. Our experiments show that  $\text{Fe}_2\text{O}_3^+$  promotes CO oxidation similar to studies involving neutral  $\text{Fe}_2\text{O}_3$  nanoparticles which demonstrate iron to work both as a catalyst in the presence of oxygen and a direct oxidant which loses lattice oxygen in the absence of oxygen.<sup>43</sup> The relatively weakly bound oxygen atom on the outer  $\text{Fe}_2\text{O}_2^+$  ring of  $\text{Fe}_2\text{O}_3^+$  shows increased activity for O atom transfer to CO. Cationic iron centers bind oxygen atoms more weakly than the previously studied anionic iron oxides.<sup>14</sup> Indeed, CID studies employing inert Xe gas revealed a minor atomic oxygen loss product without the addition of any kinetic energy to the cluster. An analysis of the velocity distribution of the  $\text{Fe}_2\text{O}_3^+$  ions in our instrument discovered that a small portion of the ions had kinetic laboratory frame energies up to 3.6 eV, which translates to up to 1.6 eV in the center of mass frame. Combined with the fact that the calculated binding energies are systematically larger than the experimental values, as shown in Table 2, we suggest that O atom loss from this species may be due to the clusters in the high-energy tail of the  $\text{Fe}_2\text{O}_3^+$  velocity distribution. Nitrogen experiments also showed O atom loss at multiple collision conditions, consistent with the weakly bound nature of the oxygen atom.

The major reaction products for  $\text{Fe}_2\text{O}_4^+$  were  $\text{Fe}_2\text{O}_2\text{CO}^+$  and  $\text{Fe}_2\text{O}^+$ . A very minor reaction pathway observed for  $\text{Fe}_2\text{O}_4^+$  was oxygen atom transfer producing  $\text{Fe}_2\text{O}_3^+$ . This oxidation product, however, is minimal considering the higher selectivity of the other two products which are energetically more stable. Figure 12 and Table S8 show the change in energy along the reaction pathway of  $\text{Fe}_2\text{O}_4^+$  with CO. The successive attachment of two CO molecules to an oxygen atom and the release of two  $\text{CO}_2$  molecules generates the  $\text{Fe}_2\text{O}_2^+$  species. The exothermic nature of this pathway does not allow for the intermediate species,  $\text{Fe}_2\text{O}_3^+$ , to be observed in any appreciable amount in the experiments. The reaction of  $\text{Fe}_2\text{O}_2^+$  with another CO molecule forms the  $\text{Fe}_2\text{O}_2\text{CO}^+$  ground state as described in Figure 11 due to CO attraction to the strong positive iron center.





**Figure 12.** Change in energy ( $\Delta E$ ) for each step of the reaction pathway of  $\text{Fe}_2\text{O}_4^+$  with CO. The superscripts indicate spin multiplicity.



**Figure 13.** Change in energy ( $\Delta E$ ) for each step of the reaction pathway of  $\text{Fe}_2\text{O}_5^+$  with CO. The superscripts indicate spin multiplicity.

This path implies spin changes from doublet to quartet and from quartet to doublet.

$\text{Fe}_2\text{O}_5^+$  reacts with CO to produce the major product,  $\text{Fe}_2\text{O}_3^+$ . The detection of several product cluster species such as  $\text{Fe}_2\text{O}_2^+$  and  $\text{Fe}_2\text{O}_3\text{CO}^+$  reveals a sequential oxidation process. To explore this possibility, the reaction pathway of  $\text{Fe}_2\text{O}_5^+$  with CO was calculated as shown in Figure 13 and Table S9. In the initial reaction step a CO molecule attaches to the O atom bonded to Fe with the lowest coordination. From this intermediate,  $\text{CO}_2$  emanation requires 1.23 eV of energy and generates the  $\text{Fe}_2\text{O}_4^+$  cluster in a high-energy state where the two external O atoms are binding to one Fe atom. From this species, there are two possible reaction channels. The first pathway releases  $\text{O}_2$  and proceeds through a transition state 1.82 eV higher in energy, with an energy gain of 1.35 eV to generate the  $\text{Fe}_2\text{O}_2^+$

cluster. The second possibility from the  $\text{Fe}_2\text{O}_4^+$  cluster is the CO attachment to an O atom generating the  $\text{Fe}_2\text{O}_3^+$  species after  $\text{CO}_2$  release. Finally, the association of CO with  $\text{Fe}_2\text{O}_3^+$  generates  $\text{Fe}_2\text{O}_3\text{CO}^+$ . This species releases  $\text{CO}_2$  and forms  $\text{Fe}_2\text{O}_2^+$  through a second possible channel. The final products observed,  $\text{Fe}_2\text{O}^+$  and  $\text{Fe}_2\text{O}_2\text{CO}^+$ , result from CO reactions with  $\text{Fe}_2\text{O}_2^+$  as described in Figure 11. The low intensity of  $\text{Fe}_2\text{O}^+$  and  $\text{Fe}_2\text{O}_2\text{CO}^+$  species is due to the fact that these clusters are generated from an unstable intermediate,  $\text{Fe}_2\text{O}_2^+$ . Further reaction of  $\text{Fe}_2\text{O}_2^+$  with CO generates products that are less exothermic than reacting CO with  $\text{Fe}_2\text{O}_5^+$ .

In general we found that only  $\text{Fe}_m\text{O}_n^+$  clusters with a  $n \leq m + 1$  stoichiometry ( $\text{FeO}^+$  and  $\text{Fe}_2\text{O}^+$ ), and  $\text{Fe}_2\text{O}_3^+$  showed oxygen atom transfer to CO producing neutral  $\text{CO}_2$  as the major reaction pathway. Higher oxides,  $\text{Fe}_2\text{O}_n^+$  ( $n > 3$ ), were not



found to be selective toward oxygen atom transfer to CO. Therefore, iron oxides with a stoichiometry of three oxygen atoms or less are proposed to be the most important reactive centers in clusters containing one and two iron atoms.

## Conclusion

Interpretation of structural calculations and dissociation energies of iron oxide cluster cations allowed trends to be established that correlate well with the order of fragmentation products in experimental CID studies. The reaction pathways found in the presence of CO were fully accounted for by the bond energies and the gain in energy from binding CO to the metal cluster. It is shown for certain stoichiometries that CO oxidation is selective and energetically feasible. However, for oxygen-rich iron oxide clusters,  $\text{Fe}_m\text{O}_n^+$  where  $n \geq 3$ , intermediate species with associated CO molecules were also observed and furthermore decreased the selectivity for oxygen transfer from the parent ion. These studies provide a foundation for further research in transition metal oxide clusters as catalytic systems. They show that iron oxides directly participate in the oxidation of CO. It would, therefore, be interesting to study iron oxide reactivity in the presence of oxygen and CO and in the presence of other metals.

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**Supporting Information Available:** A table with the dissociation energies corresponding to Figure 3, reaction profiles for  $\text{FeO}_3^+$  and  $\text{FeO}_5^+$  (Figures S1 and S2, respectively), and tables containing numerical values for reaction pathways in Figures 6, 8, 9, 11–13, S1, and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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