Reactions of fourth-period metal ions (Ca$^+$—Zn$^+$) with O$_2$: Metal-oxide ion bond energies

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Reactions of Ca$^+$, Zn$^+$ and all first-row atomic transition metal ions with O$_2$ are studied using guided ion beam techniques. While reactions of the ground states of Sc$^+$, Ti$^+$, and V$^+$ are exothermic, the remaining metal ions react with O$_2$ in endothermic processes. Analyses of these endothermic reactions provide new determinations of the M$^+$—O bond energies for these eight elements. Source conditions are varied such that the contributions of excited states of the metal ions can be explicitly considered for Mn$^+$, Co$^+$, Ni$^+$, and Cu$^+$. Results (in eV) at 0 K are $D^0$(Ca$^+$—O) = 3.57 ± 0.05, $D^0$(Cr$^+$—O) = 3.72 ± 0.12, $D^0$(Mn$^+$—O) = 2.95 ± 0.13, $D^0$(Fe$^+$—O) = 3.53 ± 0.06 (reported previously), $D^0$(Co$^+$—O) = 3.32 ± 0.06, $D^0$(Ni$^+$—O) = 2.74 ± 0.07, $D^0$(Cu$^+$—O) = 1.62 ± 0.15, and $D^0$(Zn$^+$—O) = 1.65 ± 0.12. These values along with literature data for neutral metal oxide bond energies and ionization energies are critically evaluated. Periodic trends in the ionic metal oxide bond energies are compared with those of the neutral metal oxides and those of other related molecules.

INTRODUCTION

The kinetics and thermodynamics of the oxidation reactions of transition metals are important to an understanding of corrosion processes and atmospheric chemistry. 1,2 One of the simplest transition metal ion-oxidant reactions is process (1):

$$\text{M}^+ + \text{O}_2 \rightarrow \text{MO}^+ + \text{O}.$$  \hspace{1cm} (1)

This reaction has been previously examined for several of the fourth row elements. Kappes and Staley (KS) have used ion cyclotron resonance (ICR) mass spectrometry to study reaction (1) for most of the first row transition metal ions (Ti$^+$—Zn$^+$), although only Ti$^+$ and V$^+$ exhibited any reactivity. 3 For several other metal ions, Cr$^+$—Zn$^+$, KS assigned upper and lower bounds to $D^0$(M$^+$—O) based on the observation that M$^+$ reacts with O$_2$ to form MO$^+$ at thermal energies and the failure to observe reaction of M$^+$ with N$_2$O. These limits, however, may not be accurate for two reasons. First, KS were not able to explicitly treat the possibility that excited states of their reactant ions were present. Second, beam studies by Armentrout, Hall, and Beauchamp (AHB) 4 have shown that there can be barriers in excess of the endothermicity for reaction of metal ions with N$_2$O, discrediting the upper limits set by KS.

The ion beam study by AHB also examined the kinetic energy dependence of reaction (1) for the endothermic reactions of M = Cr, Mn, Fe, Co, and Ni, and evaluated the data of Rutherford and Vroom 5 for M = Al. Employing empirical models, AHB concluded that the line-of-centers model provided a reasonable fit to the data for all six systems and yielded a threshold for reaction (1) with Al$^+$ in agreement with reasonably well-characterized literature thermochemistry. The LOC model was then used to determine reaction thresholds for process (1) for the five transition metal ions, and thus to derive M$^+$—O bond dissociation energies (BDEs) for M = Cr—Ni. Murad has performed a similar ion beam study of reaction (1) for M = Ca. 7

Two recent studies motivated us to return for a more detailed examination of reaction (1). First, Weber, Elkind, and Armentrout 8 (WEA) evaluated the translational energy dependence of reaction (1) with M = Al, using statistical as well as empirical models to analyze the data. Based on both methods of analysis, WEA determined a new threshold value for reaction (1) which indicated that Rutherford and Vroom probably had an inaccurate energy scale (~0.45 eV lower than WEA). In addition, WEA concluded that the LOC model could not adequately reproduce their experimental results. This, in turn, suggests that the other bond energies derived by AHB may be inaccurate due to the exclusive use of the LOC model.

The second study of interest is a thorough study of reaction (1) with M = Fe using four different ion sources. 9 It was found that both the $^6D$ ground state and $^4F$ first excited state react efficiently with O$_2$. Detailed analysis of the state-specific reactions of Fe$^+$ with O$_2$ and c-C$_2$H$_5$O yielded a value for $D^0$(Fe$^+$—O) which was much higher than the result of AHB.

In the present study, we measure the kinetic energy dependent cross sections for reaction (1) with M = Ca to Zn via guided ion beam techniques. For the endothermic reactions, the thresholds are determined and used to calculate
bond energies for the first-row transition metal oxides. We compare these $D_0^S(M^+\rightarrow oxygen)$ values to those available in the literature and discuss the nature of the bonding in the metal oxide ions. This study represents a continuation of our efforts to understand the reactivities of transition metal ions as well as periodic trends in gas-phase bond dissociation energies such as $M^+\rightarrow C$ single, double and triple bonds and various $M^+\rightarrow N$ bonds.\textsuperscript{10,11}

**EXPERIMENTAL SECTION**

**General**

The ion beam apparatus used in these experiments has been described in detail elsewhere.\textsuperscript{12} Metal ions are produced as described below. The ions are extracted from the source, accelerated, and focused into a magnetic sector momentum analyzer for mass analysis. The mass-selected ions are decelerated to a desired kinetic energy and focused into an octopole ion guide.\textsuperscript{13} The octopole passes through a reaction cell filled with the neutral reactant. Pressures of the neutral $O_2$ are maintained at sufficiently low levels (0.02 to 0.2 mTorr) such that multiple ion–molecule reactions are improbable. The octopole ion guide ensures efficient collection of all ionic products and transmitted reactant ions. After exiting the reaction cell, the ions are extracted from the octopole, focused into a quadrupole mass filter for mass analysis and detected using a scintillation ion detector and standard ion counting techniques. Raw ion intensities are then converted into absolute reaction cross sections as described in detail previously.\textsuperscript{12} Absolute cross sections are estimated to be accurate to $\pm 20\%$ while relative cross sections are accurate to $\pm 5\%$.

Laboratory ion energies are converted to energies in the center-of-mass frame (CM) by using the conversion $E_{CM} = E_{lab} M / (m + M)$, where $m$ is the ion mass and $M$ is the target molecule mass. The absolute energy scale and the corresponding full width at half maximum (FWHM) of the ion kinetic energy distribution are determined by using the octopole beam guide as a retarding potential analyzer.\textsuperscript{12} The uncertainty in the absolute energy scale is 0.05 eV lab ($\sim 0.02$ eV CM). The distributions of ion energies have an average FWHM of 0.7 eV for all the ions produced in the surface ionization source. The thermal motion of the gas in the reaction cell contributes an uncertainty of $\sim 0.42E_{CM}^{1/2}$ (eV) to the collision energy. Both effects are explicitly taken into account when analyzing the experimental results.\textsuperscript{12}

**Ion sources**

Surface ionization (SI) is used to produce all of the atomic metal ions except $Zn^+$. In the SI source, the vapor of an organometallic compound or a metal salt is exposed to a rhenium filament which is resistively heated to $\sim 2200$ K as measured by optical pyrometry. The metal complex decomposes on the filament and metal ions are produced by surface ionization of the resulting metal atoms. If we presume that the metal atoms reach equilibrium at the filament temperature before desorption, the electronic state distribution of the beam produced by SI should have a Maxwell–Boltzmann distribution. These distributions are shown in Table I. Previous studies\textsuperscript{14} in our laboratory on other systems indicate that this is a reasonable assumption. The compounds used in the SI source are $CaF_2$, $ScCl_3$, $TiCl_4$, $VCl_3$, $CrO_2Cl_2$, $MnCl_2\cdot 4H_2O$, $Fe(CO)_5$, $CoCl_3\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$, and $CuBr_2$.

Zinc has a sufficiently high ionization energy, $IE(Zn) = 9.39$ eV,\textsuperscript{15} that surface ionization does not produce adequate amounts of $Zn^+$. Instead, ground-state $Zn^+ (^S, 3d^{10} 4s^1)$ ions are produced by electron impact ionization (EI) of $Zn$ vapor escaping from an oven. This ionization source has been described and characterized previously.\textsuperscript{16} An electron impact source is also used to produce excited states of $Mn^+, Co^+, Ni^+$, and $Cu^+$. The compounds used are $Mn_2(CO)_10$, $Co_2(CO)_8$, $Ni(CO)_4$, and $Cu(CH_3CO)_2$, respectively. The ionization of these compounds by electron impact has been characterized previously.\textsuperscript{17,18}

**RESULTS**

**Calcium and zinc**

Results for the reaction of $Ca^+$ and $Zn^+$ with $O_2$ are shown in Fig. 1. These ions both have one valence electron in the 4$s$ orbital, but $Ca^+$ has an empty $3d$ shell whereas $Zn^+$ has completely filled $3d$ orbitals. The effect that the occupation of the $d$ orbitals has upon the reactivity and thermochemistry of these two metal ions is thus of interest and has been discussed elsewhere for reaction with $H_2$.\textsuperscript{19}
FIG. 1. Variation of the cross sections for reaction (1) with $M = \text{Ca}$ and Zn as a function of relative translational energy. The present data for $M = \text{Ca}$ (closed circles) are compared with literature results as reported by Murad (open circles). The arrow indicates the $O_2$ bond energy.

The results of Fig. 1 are obtained by using the SI source to generate $\text{Ca}^+$ and an EI source to form $\text{Zn}^+$. The SI source yields essentially pure ground-state $\text{Ca}^+$ ($^2S$), 99.99% (Table I), since the first excited $^2D$ state is very high in energy, 1.7 eV. Likewise the first excited state of $\text{Zn}^+$ is very high in energy, 6.01 eV above the ground state. Although the excited state population of $\text{Zn}^+$ produced by EI cannot be determined precisely, previous studies have indicated that the populations of these states are less than 0.01%, even at an electron energy of 100 eV. In addition, there is no evidence for the presence of excited states in the present study, since reaction (1) should be exothermic for all excited states of $\text{Zn}^+$ and no indication of such cross section behavior is observed (Fig. 1).

The cross section for $\text{CaO}^+$ rises from an apparent threshold of $\sim 1.2$ eV and reaches a maximum at about 4 eV. The cross section then declines slightly, but reaches a plateau which lasts until about 9 eV. In contrast, the cross section for $\text{ZnO}^+$ rises slowly from a fairly high apparent threshold of $\sim 3.0$ eV, and peaks at $\sim 6$ eV. The maximum cross sections are 0.9 $\AA^2$ for $\text{Ca}^+$ and 0.55 $\AA^2$ for $\text{Zn}^+$, the smallest of all the ground-state metal ion species studied here.

The decline in the cross sections at high kinetic energies is due to the onset of reaction (2),

\[ M^+ + O_2 \rightarrow M^+ + O + O \]  (2)

which has a thermodynamic threshold equal to $D_{e}^\Sigma (O_2) = 5.12$ eV.\(^{28}\) As the kinetic energy increases, the excess energy available to the products can be distributed between product translation and internal motion of $\text{MO}^+$. If the internal energy of $\text{MO}^+$ exceeds its bond dissociation energy, process (2) can occur and the cross section for reaction (1) decreases. Ordinarily reaction cross sections for atom–diatom reactions peak close to the neutral diatom bond energy; see the examples below. This behavior indicates that the excess energy is distributed statistically. If the peak of the cross section occurs at higher energies than $D_{e}(O_2)$, this indicates that the reaction dynamics tend to preferentially place the excess energy in translation. The peak in the $\text{ZnO}^+$ cross section is quite close to the threshold for reaction (2), while the complex behavior of $\text{Ca}^+$ is not easily categorized. It is possible that the production of excited state $\text{CaO}^+$ which dissociates to an excited state asymptote is involved, but this cannot be determined with certainty here.

**Scandium, titanium, and vanadium**

Energy-dependent cross sections for reaction (1) with $M = \text{Sc}$, $\text{Ti}$, and $\text{V}$ are shown in Fig. 2. SI produces these ions primarily in their ground state [89% $^3\text{D}$, 63% $^4\text{F}$, and 81% $^5\text{D}$, respectively (Table I)]. The remaining fractions are in low-lying excited states. In the case of $\text{Ti}^+$, 36% is in the $b^4\text{F}$, only 0.10 eV above the $a^4\text{F}$ ground state (Table I).

The cross sections for reaction (1) with these transition metal ions increase with decreasing kinetic energy, demonstrating that they are exothermic reactions. This cross section behavior can be described by using the Langevin–Gioiumous–Stevenson (LGS) model equation (3):

\[ \sigma_{\text{LGS}} = \pi e(2\alpha/E)^{1/2}, \]  (3)

where $e$ is the electron charge, $\alpha$ is the polarizability of $O_2$ (1.57 $\AA^3$),\(^{22}\) and $E$ is the relative kinetic energy of the reactants. For $M = \text{Sc}$, $\text{Ti}$, and $\text{V}$, the reaction cross sections decrease as about 0.6, 0.7, and 0.5 $\sigma_{\text{LGS}}$, respectively, at the lowest energies ($<0.2$ eV), Fig. 2. This implies that the reaction of the ground states must be exothermic for all three metals since the magnitudes of the cross sections are too large to be accounted for exclusively by excited state ions.

At slightly higher kinetic energies, the cross sections for all three systems deviate from the $E^{-0.5}$ dependence and decline more steeply, as about $E^{-1}$. Both $\sigma(\text{ScO}^+)$ and $\sigma(\text{TiO}^+)$ diverge from $\sigma_{\text{LGS}}$ beginning at $\sim 0.5$ eV, where-

FIG. 2. Variation of the cross sections for reaction (1) with $M = \text{Sc}$, $\text{Ti}$, and $\text{V}$ as a function of relative translational energy.
as $\sigma(\text{VO}^{+})$ changes earlier, $\sim 0.25$ eV. These deviations are due to constraints in the reaction probability imposed by angular momentum conservation. We have previously outlined a simple model for this behavior that predicts where this deviation from LGS behavior will occur for exothermic reactions.\textsuperscript{23} Based on the thermochemistry discussed below, this model predicts that the cross sections will depart from $\sigma_{\text{LGS}}$ behavior beginning at $0.55 \pm 0.09$, $0.56 \pm 0.04$, and $0.24 \pm 0.03$ eV for Sc, Ti, and V, respectively, in remarkably good agreement with the data.

For Ti and V (and possibly Sc), the reaction cross sections begin to flatten out at $\sim 2.5$ and $\sim 1.5$ eV, respectively. One possible explanation for these features is production of MO$^+$ excited states, but no specific information regarding this possibility can be garnered here. At the highest energies, all three cross sections begin to decline due to reaction (2).

**Chromium and iron**

Cr$^+$ produced by SI is nearly pure 6S ground state (99.8%, Table I). Results for reaction (1) with Cr$^+$ produced by SI are shown in Fig. 3. The cross section rises from an apparent threshold of $\sim 1.3$ eV and peaks at approximately the neutral bond energy, consistent with process (2).

Detailed results for reaction (1) with $M^+ = \text{Fe}^+$ (6D) and Fe$^+$ (6F) have been published previously.\textsuperscript{29} Figure 4 shows the results for Fe$^+$ (SI) for comparison with the other systems studied here. The cross sections for both Fe$^+$ (6D) and Fe$^+$ (6F) have very similar shapes but magnitudes that are about 0.8 and 1.6 times as large, respectively. The ground-state cross section has an apparent threshold of $\sim 1.5$ eV, and peaks at an energy near the thermodynamic onset for reaction (2). The 6F cross section has a threshold which is lower by its excitation energy of 0.3 eV.

**Manganese**

Results for reaction (1) with Mn$^+$ produced by SI are shown in Fig. 5. The cross section rises from an apparent threshold of $\sim 2.0$ eV to a maximum near the thermodynamic threshold for reaction (2). The Mn$^+$ beam produced by SI is nearly pure 5S ground state (99.8%, Table I). Thus, the observed reactivity is likely to be due to ground-state ions;

![FIG. 3. Variation of the cross section for reaction (1) with \( M = \text{Cr} \) as a function of translational energy in the CM frame (lower scale) and lab frame (upper scale). Data are shown for \( \text{Cr}^+ \) ions formed by surface ionization (closed circles). AHB's data (Ref. 4), scaled by a factor of 1.5, are shown for comparison (open circles). The arrow indicates the \( \text{O}_2 \) bond energy.](image)

![FIG. 4. Variation of the cross section for reaction (1) with \( M = \text{Fe} \) as a function of translational energy in the CM frame (lower scale) and lab frame (upper scale). The results shown are for \( \text{Fe}^+ \) ions formed by SI and are taken from Ref. 9 (closed circles). AHB's data (Ref. 4) are also shown for comparison (open circles). The arrow indicates the \( \text{O}_2 \) bond energy.](image)

![FIG. 5. Variation of the cross section for reaction of Mn$^+$ with \( \text{O}_2 \) as a function of translational energy in the CM frame (lower scale) and lab frame (upper scale). Data are shown for Mn$^+$ ions formed by surface ionization (closed circles), and electron impact, \( E_e = 25 \) eV (open squares) and \( E_e = 60 \) eV (closed triangles). AHB's data (Ref. 4), scaled by a factor of 0.83, are shown for comparison (open circles). The arrow indicates the \( \text{O}_2 \) bond energy.](image)
however, previous studies with H₂ have observed the reactivity of the 0.2% excited states of Mn⁺ present in an SI generated beam. This is because the excited quintet states of Mn⁺ are much more reactive with these two molecules than the nearly inert septet ground state.

To see if this is true with O₂, reaction (1) was also studied using EI of Mn₃(CO)₁₀ to form the Mn⁺ ions. With the EI source, the ionization process is much more energetic and is known to lead to formation of substantial amounts of excited state Mn⁺. Figure 5 includes results for Mn⁺ produced by electron impact of Mn₃(CO)₁₀ at two different electron energies, Ee = 25 and 60 eV. Both of the electron energies are well above the appearance energy of Mn⁺, 20.4 ± 0.4 eV. In the 25 eV data, the reaction cross section has changed appreciably from the SI data, and there are now three distinct features. The dominant feature of the SI data is still present, but has decreased in magnitude and continues to decrease as the Ee is increased. One new feature in the EI reaction cross sections has an apparent threshold of ~0.7 eV, and another feature decreases with increasing energy, indicating an exothermic reaction. For the 60 eV data, the exothermic feature increases by a factor of about 6 from the 25 eV data, while the low-energy endothermic feature only increases by a factor of ~2.5. These two low-energy features must be due to excited states of Mn⁺, which are produced more efficiently as the electron energy is increased.

### Cobalt and nickel

Figures 6 and 7 show results for reactions of O₂ with Co⁺ and Ni⁺ produced by SI. These beams comprise mostly ground state ions, 84% Co⁺ (3F) with 16% Co⁺ (5F) first excited state also present, and 99% Ni⁺ (2D) (Table I). These cross sections rise from apparent thresholds of ~1.3 and ~2.0 eV, respectively, and rise to maxima near the thermodynamic threshold for process (2).

Also shown in Figs. 6 and 7 are the results for the reactions of these metal ions produced by using electron impact ionization with Ee = 50 eV on Co₂(CO)₈ and Ee = 23 and 50 eV on Ni(CO)₅. The appearance energy for Co⁺ from Co₂(CO)₈ is 16.9 ± 0.4 eV and that for Ni⁺ from Ni(CO)₅ is 13.8 ± 0.1 eV. It is obvious that the EI cross sections are significantly smaller than the SI cross sections, by 50% and 75%, respectively. These decreases are consistent with similar observations in our study of the reactions of Co⁺ and Ni⁺ with H₂, where the values were 50% and 80%. In addition, there are also low energy features in the EI data for both metal ions which are not present in the SI data, Figs. 6 and 7. These changes in the reaction cross sections indicate that the ground-state populations of these ions have been greatly reduced from SI conditions, and thus excited state ions must be present in significant quantities in the EI beam.

### Copper

Figure 8 shows results for the reaction (1) with Cu⁺ produced by both SI and EI. The Cu⁺ beam produced by SI comprises 100% 1S ground-state ions (Table I). The reaction cross section for reaction (1) with Cu⁺ shows markedly different behavior from that with Fe⁺, Co⁺, and Ni⁺. The apparent threshold for reaction in the SI reaction cross section occurs at a much higher energy of ~4 eV, and the maximum magnitude of the cross section is smaller by a factor of 3 from the NiO⁺ data. In addition, the cross section rises slowly from its threshold, and the peak of the reaction
in Murad's results. These differences can be attributed to inefficient product ion collection, a problem which is avoided in our apparatus by utilization of an octopole ion trap. Finally, the apparent threshold of Murad's data lies approximately 0.4 eV above ours. The reasons for this discrepancy are unclear but could be due to an error in Murad's energy scale. Murad measured the absolute zero of his energy scale by using retarding grids, a method which is notoriously difficult. In our case, the use of an octopole ion beam guide makes such measurements much more routine and accurate.

The cross sections for reaction (1) with \( M = \text{Cr--Ni} \) have been measured previously by AHB, and are shown for comparison with the present results in Figs. 3–7. At the lowest energies, the data of AHB show a nonzero baseline which makes accurate determination of the onset for reaction difficult. In the threshold regions, however, their data are qualitatively similar in shape to the results of the present study, although the absolute magnitudes of AHB's data are about half of those we measure for \( M = \text{Cr, Fe, Co, and Ni} \) (Figs. 3, 4, 6, and 7, respectively), and within 20% for \( M = \text{Mn} \) (Fig. 5). This is within the factor of 2 experimental error in AHB's absolute measurements. At higher kinetic energies (beginning about 4–5 eV), AHB's data decrease more rapidly than the present results, Figs. 3–7. As in the case of \( \text{Ca}^+ \), this difference is undoubtedly due to loss of product ions in an instrument which is not equipped with an octopole ion beam guide.

**THERMOCHEMISTRY**

**Thermochemical analysis**

In the cases where reaction (1) is exothermic, a lower limit for the metal–oxide ion bond dissociation energy (BDE) can immediately be derived, namely, \( D_{\text{BDE}}^0 (\text{MO}^+) > D_{\text{BDE}}^0 (\text{O}_2) = 5.12 \text{ eV}. \) More information is obtained by a detailed analysis of the threshold behavior of endothermic reactions. Cross sections for endothermic reactions of species having a known distribution of electronic states, denoted by \( i \), can be analyzed by using Eq. (4):

\[
\sigma(E) = \sum_i g_i \sigma_{i\alpha} (E - E_0 + E_i + E_{\text{rot}})^{\rho}/E^m
\]

which involves an explicit sum of the contributions of individual states weighted by their populations \( g_i \). Here, \( E_0 \) is the threshold for reaction of the lowest electronic level of the ion, \( E_i \) is the electronic excitation of each particular level, \( E_{\text{rot}} \) is the average rotational energy of the neutral \( \text{O}_2 \) (\( E_{\text{rot}} = 0.026 \text{ eV at } 300 \text{ K} \)), \( \sigma_{i\alpha} \) is an energy-independent scaling factor, and \( n \) and \( m \) are parameters which depend on the theoretical model being used.

In this study, Eq. (4) is evaluated by fixing \( m = 1 \) and allowing the parameters \( \rho, \sigma_{i\alpha}, \) and \( E_0 \) to vary freely to best fit the data as determined by nonlinear least squares analysis. This general form and its ability to reproduce our cross-section data have been discussed previously. A value of \( m = 1 \) is chosen because this form has been derived as a model for translationally driven reactions and has been found to be quite useful in describing the shapes of endothermic reaction cross sections and in deriving accurate thermochemistry for...
a wide range of systems. The Fe$^+$ + O$_2$ system, a value of \( m = 1 \) was found to accurately reproduce the cross-section data for both the $^5D$ and $^4F$ electronic states of Fe$^+$. For the Al$^+$ + O$_2$ system, several choices of \( m \) (including \( m = 1 \)) were tried and could be used to interpret the data.

To analyze the high-energy behavior of these cross sections, we use a model previously outlined which makes a simple statistical assumption within the constraints of angular momentum conservation.

**Derivation of bond energies**

The results of these analyses are summarized in Table II. For each metal system, between four and ten data sets are analyzed. The optimum \( E_D \) given in Table II is the average result for these data sets. The uncertainties are one standard deviation in this average. These threshold values can then be converted to bond dissociation energies for MO$^+$ at 0 K by using

\[
D_0^b(M^+ + O) = D_0^b(O_2) - E_D, \tag{5}
\]

where \( D_0^b(O_2) = 5.116 \pm 0.002 \text{ eV} \). Equation (5) implicitly assumes that there are no activation barriers in excess of the endothermicity. This assumption is generally true for ion–molecule reactions and has been explicitly tested a number of times. Table III summarizes the resulting bond energies and lists other directly measured values from the literature. Our results and a comparison with these literature values (which, in general, are not well characterized) are discussed in detail below for each metal. Based on these discussions, we recommend values and list these in Table IV.

### Table II. Optimum parameters for threshold fits.

<table>
<thead>
<tr>
<th>( M )</th>
<th>( n )</th>
<th>( E_D )</th>
<th>( \sigma_{m} )</th>
<th>( \rho )</th>
<th>( E_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>1.0 ± 0.1</td>
<td>1.55 ± 0.04</td>
<td>1.06 ± 0.05</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>Cr</td>
<td>1.5 ± 0.2</td>
<td>1.40 ± 0.12</td>
<td>0.72 ± 0.07</td>
<td>1</td>
<td>4.5</td>
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<tr>
<td>Mn</td>
<td>1.8 ± 0.2</td>
<td>2.11 ± 0.12</td>
<td>1.15 ± 0.22</td>
<td>1</td>
<td>5.1</td>
</tr>
<tr>
<td>Mn$^+$</td>
<td>1.8 ± 0.2</td>
<td>2.16 ± 0.13</td>
<td>1.25 ± 0.28</td>
<td>1</td>
<td>5.1</td>
</tr>
<tr>
<td>Fe$^+$</td>
<td>1.8 ± 0.1</td>
<td>1.54 ± 0.11</td>
<td>0.74 ± 0.15</td>
<td>1</td>
<td>5.2</td>
</tr>
<tr>
<td>Co$^+$</td>
<td>2.0 ± 0.1</td>
<td>1.81 ± 0.11</td>
<td>1.30 ± 0.18</td>
<td>1</td>
<td>4.9</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>1.9 ± 0.2</td>
<td>1.79 ± 0.03</td>
<td>1.52 ± 0.20</td>
<td>1</td>
<td>5.1</td>
</tr>
<tr>
<td>Ni</td>
<td>2.0 ± 0.2</td>
<td>2.38 ± 0.07</td>
<td>1.29 ± 0.23</td>
<td>2</td>
<td>6.5</td>
</tr>
<tr>
<td>Cu</td>
<td>3.1 ± 0.4</td>
<td>3.50 ± 0.15</td>
<td>0.10 ± 0.04</td>
<td>3</td>
<td>7.4</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>1.9 ± 0.1</td>
<td>0.54 ± 0.07</td>
<td>0.06 ± 0.01</td>
<td>1</td>
<td>1.9</td>
</tr>
<tr>
<td>Zn</td>
<td>1.7 ± 0.3</td>
<td>6.47 ± 0.2</td>
<td>1.97 ± 0.02</td>
<td>1</td>
<td>1.2</td>
</tr>
</tbody>
</table>

*Optimum values of parameters in Eq. (4) \((m = 1)\) for reaction (4).

*No values for \( p \) and \( E_D \) can be obtained for the calcium system due to its unusual high energy behavior.

*Parameters obtained by analyzing SI data assuming all states have equal reactivity.

*Parameters obtained by analyzing SI data assuming excited states are three times as reactive as the ground state, see text.

*Values from Ref. 9.

*Parameters obtained by analyzing SI data assuming excited states are half as reactive as the ground state, see text.

*Analysis of low-energy feature in EI data, see text. Value of \( E_D \) is uncorrected for excitation energy.

### Table III. Metal oxide ion bond dissociation energies at 0 K (eV).

<table>
<thead>
<tr>
<th>( M )</th>
<th>This study</th>
<th>Lit</th>
</tr>
</thead>
</table>
| Ca     | 3.57(0.05) | 3.30 ± 0.15$^a$
| Sc     | > 5.12     | 6.9 ± 0.3$^b$
| Ti     | > 5.12     | 6.93 ± 0.10$^b$
| V      | > 5.12     | 6.00 ± 0.10$^b$
| Cr     | 3.72(0.12) | 3.70 ± 0.10$^b$, 3.45 ± 0.10$^b$
| Mn     | 2.95(0.13) | 2.89 ± 0.10$^b$, 2.88 ± 0.12 eV$^c$, 2.48 ± 0.10$^b$
| Fe     | 3.53(0.06)$^d$ | 3.01 ± 0.10$^d$
| Co     | 3.32(0.06) | 3.26 ± 0.10$^b$, 2.76 ± 0.10$^d$
| Ni     | 2.74(0.07) | 2.82 ± 0.08$^b$, 1.95 ± 0.10$^d$
| Cu     | 1.62(0.15) | > 1.04$^b$, < 1.73$^b$
| Zn     | 1.65(0.12) | > 1.04$^b$, < 1.73$^b$

$^a$Reference 7.

$^b$Values as derived in Table IV.

$^c$298 K value from Ref. 43.

$^d$Reference 4.

$^e$Preliminary values from Ref. 54.

$^f$Reference 9.

$^g$Reference 62.

$^h$Reference 3.

In contrast to the ions, the neutral thermochemistry of the gaseous monoxides of the first row transition metals from calcium through zinc is fairly well characterized, as described in a recent review by Pedley and Marshall (PM). With few exceptions, we use the values provided by PM (also listed in Table IV) and the \( D_0^b(\text{MO}^+) \) values derived here to calculate ionization energies (IEs) for CaO and MnO–ZnO by using Eq. (6):

\[
\text{IE(}\text{MO}\text{)} = D_0^b(\text{MO}) + \text{IE(M)} - D_0^b(\text{MO}^+). \tag{6}
\]

The IEs derived here are compared to available literature values and the neutral metal oxide bond energies are also discussed below.

### Calcium

The SI source produces only ground-state Ca$^+$ ($^2S$) (> 99.99%), so Eq. (4) has only a single term for this system. Analysis of the cross section for reaction (1) with \( M = \text{Ca} \) (four data sets) yields a threshold (Table II), that leads to \( D_0^b(\text{CaO}^+) = 3.57 ± 0.05 \text{ eV} \) (823 ± 1.2 kcal/mol). The only directly measured value in the literature comes from the same reaction and type of experiment by Murad (Table III). The discrepancy between these numbers is discussed further below.

The recommended value for \( D_0^b(\text{CaO}) \) from PM (Table IV), is based mainly on two studies, a metathetical reaction with SO$^{2-}$ and a chemiluminescence study of the reaction of Ca + O$_2$. This latter study includes a detailed discussion of other literature values for \( D_0^b(\text{CaO}) \), including a much higher value of 4.76 ± 0.15 eV$^{39}$ which had been adopted by Huber and Herzberg. Based on this discussion, we accept the recommendation of PM. Use of our ion BDE and the neutral BDE of PM in Eq. (6) leads to IE(CaO) = 6.63 ± 0.20 eV, in agreement with the only direct measurement of this IE = 6.5 ± 1 eV$^{41}$.
### TABLE IV. Thermochemical data for gaseous metal monoxides at 0 K

<table>
<thead>
<tr>
<th>M</th>
<th>IE(M)$^a$</th>
<th>D$^o$(M–O)$^c$</th>
<th>D$^o$(MO)$^d$</th>
<th>IE(MO)$^e$</th>
<th>Δ$_H$(MO)$^f$</th>
<th>Δ$_H$(MO$^+$)$^g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>6.113</td>
<td>3.57(0.05)</td>
<td>4.12(0.17)</td>
<td>6.66</td>
<td>6(4)</td>
<td>160(1)</td>
</tr>
<tr>
<td>Sc</td>
<td>6.561</td>
<td>6.9 (0.3)$^i$</td>
<td>7.01(0.12)</td>
<td>6.6 (0.3)$^i$</td>
<td>-13(3)</td>
<td>141(7)</td>
</tr>
<tr>
<td>Ti</td>
<td>6.820</td>
<td>6.93(0.10)$^i$</td>
<td>6.92(0.10)</td>
<td>6.819(0.006)$^i$</td>
<td>11(2)$^i$</td>
<td>168(2)</td>
</tr>
<tr>
<td>V</td>
<td>6.740</td>
<td>6.00(0.10)$^i$</td>
<td>6.49(0.09)$^m$</td>
<td>7.230(0.005)$^m$</td>
<td>31(3)$^i$</td>
<td>199(3)</td>
</tr>
<tr>
<td>Cr</td>
<td>6.767</td>
<td>3.72(0.12)</td>
<td>4.41(0.30)</td>
<td>7.46</td>
<td>40(2)</td>
<td>223(3)</td>
</tr>
<tr>
<td>Mn</td>
<td>7.434</td>
<td>2.95(0.13)</td>
<td>3.82(0.08)$^j$</td>
<td>7.7</td>
<td>49(4)</td>
<td>229(3)</td>
</tr>
<tr>
<td>Fe</td>
<td>7.902</td>
<td>3.53(0.06)</td>
<td>4.21(0.09)$^j$</td>
<td>8.58</td>
<td>40(2)</td>
<td>258(1)</td>
</tr>
<tr>
<td>Co</td>
<td>7.86</td>
<td>3.29(0.06)$^j$</td>
<td>4.39(0.14)</td>
<td>8.51</td>
<td>69(3)</td>
<td>265(1)</td>
</tr>
<tr>
<td>Ni</td>
<td>7.638</td>
<td>2.78(0.07)$^j$</td>
<td>3.91(0.17)</td>
<td>8.77</td>
<td>71(4)</td>
<td>273(2)</td>
</tr>
<tr>
<td>Cu</td>
<td>7.726</td>
<td>1.62(0.15)</td>
<td>2.75(0.22)</td>
<td>8.86</td>
<td>76(5)</td>
<td>280(4)</td>
</tr>
<tr>
<td>Zn</td>
<td>9.394</td>
<td>1.65(0.12)</td>
<td>&lt;2.77(0.43)</td>
<td>&lt;10.51</td>
<td>&gt;26(10)</td>
<td>269(3)</td>
</tr>
</tbody>
</table>

$^a$Δ$_H$ values given in kcal/mol. IE and bond energies given in eV. Uncertainties in parentheses.
$^b$Values from Ref. 20. Uncertainties are <0.01 eV.
$^c$Recommended value from Table III, except where noted.
$^d$Except where noted, values are from Ref. 36.
$^e$Except where noted, values derived by using Eq. (6).
$^f$Values derived from neutral bond energies listed, Δ$_H$(M) and Δ$_H$(O) = 59 kcal/mol from Ref. 77.
$^g$Values derived from metal oxide ion bond energies, Δ$_H$(M$^+$) and Δ$_H$(O).

$^h$Reference 41.
$^i$Derived by using Eq. (6).
$^j$Reference 1.
$^k$Reference 29.
$^m$J. Harrington and J. C. Weisshaar (personal communication).
$^o$Reference 52.
$^p$Reference 48.
$^q$Average of the values from PM (Ref. 36), Ref. 44, and Ref. 46, see text.
$^r$Reference 57.
$^s$Value from average of Refs. 9, 57, 58, and 59, see text.
$^t$Reference 59.
$^u$Average of values derived from reactions with O$_2$ and C$_2$H$_2$O, see text.
$^v$Derived from Eq. (7), see text.
$^w$Reference 63.
$^x$Reference 65.

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**Scandium, titanium, and vanadium**

Reaction (1) is exothermic for $M = \text{Sc, Ti, and V}$, establishing that $D^o_0(\text{MO}^+) > 5.12 \text{ eV} = D^o_0(\text{O}_2)$ for these three metals. This limit is in agreement with previous determinations of the metal oxide ion bond energies for all three metals (Tables III and IV).

**Chromium**

The SI source produces only ground state Cr$^+$ (5$^2$S) (>99.8%), so Eq. (4) has only a single term for this ion. Analysis of this cross section with the parameters of Table II leads to $D^o_0(\text{CrO}^+) = 3.72 \pm 0.12 \text{ eV}$. For comparison with literature thermochemistry, we convert this to the 298 K value, $D^o_{298}(\text{CrO}^+) = 3.76 \pm 0.12 \text{ eV}$. This value is in good agreement with the upper and lower limits established by Kang and Beauchamp (KB). KB found that the reaction of Cr$^+$ (5$^2$S) with ethylene oxide to form CrO$^+$ is exothermic (a result that we have verified) giving a lower limit of $D^o_{298}(\text{Cr}^+ - \text{O}) > D^o(\text{C}_2\text{H}_4\text{O}) = 3.67 \pm 0.04 \text{ eV}$. In contrast, formation of CrO$^+$ from reaction of Cr$^+$ (5$^2$S) with propylene oxide is endothermic, implying that $D^o_{298}(\text{Cr}^+ - \text{O}) < D^o(\text{C}_3\text{H}_6\text{O}) = 3.77 \pm 0.01 \text{ eV}$. Since it is possible that reaction of Cr$^+$ with propylene oxide is near thermoneutral, we conservatively recommend the value $D^o_0(\text{CrO}^+) = 3.72 \pm 0.12 \text{ eV}$. The discrepancy with the results of the earlier ion beam study by AHB (Table III) is discussed below.

There appears to be considerable uncertainty in the correct value for the CrO neutral bond energy. PM recommends a 0 K value of $4.41 \pm 0.3$ based solely on the high-temperature mass spectrometry data of Grimley, Burns, and Ingham. Since this early study, two consistent values for
and lead to a threshold for reaction of ground state Mn$^+$ (5$^S$) of 2.11 ± 0.12 eV. Given this threshold, the thresholds for Mn$^+$ (5$^S$) and Mn$^+$ (5$^D$) should be ~0.9 and ~0.3 eV, respectively. Higher-lying states, 5$^G$ and above, should react in exothermic processes. The 25 eV EI data for Mn$^+$, Fig. 5, clearly show the presence of an exothermic reaction and also an endothermic reaction beginning about 0.5 eV. This latter feature is entirely consistent with reaction of a combination of the 5$^S$ and 5$^D$ states of Mn$^+$.

These assignments can be verified by comparison of the relative cross section magnitudes with the estimated populations derived previously from a study of Mn$^+$ with H$_2$.

The relative cross section magnitudes for the SI, and 25 and 60 eV EI data in Fig. 5 have ratios of 1:0.8:0.5 in the region of 5–9 eV. This is consistent with the data in the H$_2$ experiment, which indicate that the population ratio for the 5$^S$ ground state is 1:0.9:0.5 for SI, 25, and 50 eV EI data. Between 0.5 and 2 eV, the cross sections of Fig. 5 are in the ratio 1:18:48 for the SI, 25 and 60 eV EI data. Again, this is in reasonable agreement with the H$_2$ study where the ratio of quintet states is 1:21:74 for the SI, 25 and 50 eV EI data. Quantitative differences in these ratios between the O$_2$ and H$_2$ studies could be due to different filament temperatures and electron energies (especially for the low Ee where production of excited states is most sensitive to the exact Ee values). At the lowest kinetic energies, the relative cross-section magnitudes of the exothermic features in Fig. 5 are in the ratio 1:6 for the 25 and 60 eV EI data. In the H$_2$ study, no evidence for reaction of higher excited states of Mn$^+$ was found. A similar result has been observed for Fe$^+$, namely, that high-lying excited states of Fe$^+$ that react with O$_2$ are not observed to react with H$_2$.

A final check on the possibility that a reaction barrier exists for formation of MnO$^+$ is to analyze the Ee = 25 eV EI data. After subtracting contributions for the ground-state reaction and for the small exothermic cross section, the remaining cross section should only contain contributions from the two quintet excited states. This was then fit with contributions from both the 5$^S$ and the 5$^D$ excited states (in proportions established in Ref. 17). For consistency, this excited state cross section was analyzed by holding n to 1.8, the value used in fitting the SI data and one similar to that of other metals. This results in a value of $E_o$ of 2.08 eV, in excellent agreement with the value obtained from analysis of the SI data. We conclude that there is no evidence for barriers in excess of the endothermicity for reaction of ground state Mn$^+$ (5$^S$).

We can also check the assumption that the various states have equal reactivity. Since the absolute population of the quintet states is known fairly accurately for ions generated by SI (0.23%) and the ratio of this cross section to that for the 25 eV EI data is known, the absolute cross section for the quintet states can be roughly determined. Analysis of this cross section as described above yields a scaling parameter of $\sigma_{5S} \approx 3.2$, approximately a factor of 2.7 larger than the $\sigma_e$ value for the septet state (Table II). This result is comparable to that observed for iron, where the excited states were about twice as reactive as the ground state. If the SI data are now reinterpreted by assuming that the quintet states are
three times more reactive than the ground state, the $E_0$ value shifts up by 0.05 eV. We consider this to be our most accurate determination of the true threshold value, but include the uncertainty associated with the different excited state interpretations.

We obtain a bond energy of $D_0^0$ (MnO$^+$) = 2.95 ± 0.13 eV (681 ± 3.0 kcal/mol). This value is in good agreement with preliminary values derived from the reaction of Mn$^+$ with NO and NO$_2$, 2.89 ± 0.30 and 2.88 ± 0.12 eV, respectively. Until this latter work is completed, we choose the present determination as the best available value, 2.95 ± 0.13 eV.

The MnO neutral bond energy recommended by PM, 4.13 ± 0.43 eV, is “the average of two doubtful measurements.” More recent measurements obtain a lower value for this bond energy. In our laboratory, we examined the reaction of Mn$^+$ with ethylene oxide$^{52}$ and obtained a value of 3.71 ± 0.26 eV, in good agreement with a value determined by Burns, 3.70 ± 0.17 eV$^{35}$ and one from previous ion beam studies, 3.8 ± 0.2 eV.$^{56}$ Smoes and Drowart have obtained 3.82 ± 0.08 eV from a recent high-temperature mass spectrometry study.$^{57}$ We choose this latter value as the best since it is the most precise and is entirely consistent with the other three recently determined values. Combined with our ion BDE, this leads to IE(MnO) = 8.30 ± 0.15 eV, somewhat higher than the imprecise value obtained directly by Smoes and Drowart (Table IV).$^{57}$

Iron

An extensive discussion of the Fe$^+$ –O bond energy is given in Ref. 9. Briefly, analysis of both the Fe$^+$ ([D] and Fe$^+$ ([F]) data for reaction (1) gave consistent results, with the thresholds for reaction differing by the expected difference in excitation energies. These results were found to be in excellent agreement with the thermochemistry derived from reaction of Fe$^+$ with ethylene oxide to form the metal oxide ion.

For the neutral, values for $D_0^0$ (FeO) from Balducci et al. (4.21 ± 0.13 eV)$^{58}$ Hildenbrand (4.20 ± 0.13 eV)$^{59}$ Smoes and Drowart (4.16 ± 0.08 eV)$^{57}$ and Loh et al. (4.27 ± 0.10 eV)$^{58}$ are all in good agreement and lead to an average value of 4.21 ± 0.09 eV. Hildenbrand has also determined the most precise value for IE(FeO), 8.71 ± 0.10 eV, although this is slightly higher than the value derived from Eq. (6), 8.58 ± 0.11 eV. As in the case of CrO, it seems possible that the adiabatic IE is not correctly identified due to a slow ionization onset. Nevertheless, it can be seen that the ion and neutral thermochemistry are in good overall agreement.

Cobalt

In the Co$^+$ system, both the $^1F$ ground state and the $^3F$ first excited state were included in the data analysis using Eq. (4) with the individual $J$ levels resolved.$^{60}$ The data could not be adequately reproduced unless contributions from both states were included in the analysis. Using the parameters of Table II in Eq. (4) (with the assumption of equal reactivity) leads to $D_0^0$ (CoO$^+$) = 3.34 ± 0.11 eV.

A more detailed consideration of the contributions of Co$^+$ excited states is more difficult than in the Mn system since the excited state cross-section features in the EI data are not very distinct (Fig. 6). In the Fe and Mn systems, we observed that excited states having electron configurations of $3d^m$ were about twice as reactive as ground states having $4s3d^{n-1}$ configurations. Here, a comparable result means that the Co$^+$ ($^2F, 3d^7$) excited state is about half as reactive as the Co$^+$ ($^3F, 3d^8$) ground state. If we assume this relative reactivity, interpretation of the SI data yields a slightly lower threshold value that provides a more consistent interpretation of the four available data sets and a lower uncertainty in the derived bond energy, $D_0^0$ (CoO$^+$) = 3.32 ± 0.06 eV. As in the case of Mn, we consider this to be the best analysis of the data, but include the uncertainty associated with the different excited state interpretations. This yields $D_0^0$ (CoO$^+$) = 3.37 ± 0.06 eV, in excellent agreement with the value derived in our recent study of the reaction of Co$^+$ with c-C$_2$H$_4$O, 3.26 ± 0.07 eV.$^{62}$ Our best value is the average of these two values, 3.32 ± 0.06 eV (75.9 ± 1.4 kcal/mol). This is significantly higher than that determined by AHB from reaction (1), $D_0^0$ (CoO$^+$) = 2.76 ± 0.15 eV.

The value for $D_0^0$ (CoO) recommended by PM, Table IV, is based on three Knudsen cell mass spectrometry studies. Using Eq. (6) and our ion BDE, this provides an IE that is in rough agreement with a direct but imprecise measurement from high temperature mass spectrometric studies (Table IV).$^{63}$ These values are also consistent with preliminary results from the reaction, Co$_2^+$ + O$_2$ → CoO$^+$ + CoO.$^{64}$ Here, the production of CoO$^+$ + CoO is endothermic by 0.4 ± 0.15 eV. We assume the reaction conditions are characteristic of a 298 K temperature such that the following relationship holds:

$$D_0^0(\text{CoO}) + D_0^0(\text{CoO}^+) = D_0^0(\text{Co}_2^+) + D_0^0(\text{O}_2) - 0.4 \text{ eV.}$$

(7)

Use of $D_0^0$ (O$_2$) = 5.16 eV, $D_0^0$ (Co$^+$) = 2.75 ± 0.10 eV,$^{64}$ and our value of $D_0^0$ (Co$^+$) = 3.34 ± 0.06 eV$^{62}$ in Eq. (7) gives $D_0^0$ (CoO) = 4.17 ± 0.19 eV, which is equivalent to a 0 K value of 4.13 ± 0.19 eV.$^{42}$ This determination of $D_0^0$ (CoO) also allows an independent determination of IE(CoO) = 8.69 ± 0.20 eV.

Nickel

For the Ni$^+$ system, contributions from the individual $J$ levels of the $^2D$ ground state were included in the data analysis with Eq. (4).$^{66}$ It was found that the data reproduction was equivalent whether it was assumed that the $^2F$ excited state (which contributes less than 1.5% to the SI beam, Table I) was completely unreactive or equally reactive to the $^2D$ state. This leads to a bond energy, $D_0^0$ (NiO$^+$) = 2.74 ± 0.07 eV, which compares favorably with the value derived from the reaction of Ni$^+$ with ethylene oxide, 2.82 ± 0.08 eV.$^{62}$ We recommend the average of these two values, 2.78 ± 0.07 eV (64.1 ± 1.6 kcal/mol), and note that it is much higher than that derived by AHB, 1.95 ± 0.10 eV.
We can also analyze the EI data for Ni$^+$ in a manner similar to the Mn system. A crude analysis of the low-energy feature in the 23 eV EI data yields a threshold of ~1.3 eV. This is about 1.1 eV below the ground-state threshold, comparable to the excitation energy of the $^4F$ first excited state, 1.16 eV. The scaling parameter for this analysis suggests that this state is less reactive than the doublet ground state by a factor of <3, in agreement with the reactivity limits assumed above. The 23 eV EI data also contain evidence for a small amount of reactivity due to the $^2F$ second excited state, 1.76 eV above the ground state. The 50 eV EI data clearly show exothermic reactivity which must be due to states above the $^2F$.

To determine IE(NiO), we use the value recommended by PM for $D_0^\infty$(NiO), which comes from a metathetical reaction with CoO, and gas-phase equilibrium data. We obtain a value which is somewhat lower than the imprecise literature value determined by high temperature mass spectrometry (Table IV).

**Copper**

The optimum parameters used in Eq. (4) to analyze the cross section for M = Cu(SI) are very different than those used for any of the other metal ions (Table II). This implies that the reaction mechanism for this process is unique, a conclusion which is discussed further below. The threshold of 3.50 ± 0.15 eV leads to $D_0^\infty$(CuO$^+$) = 1.62 ± 0.15 eV (37.4 ± 3.5 kcal/mol) (Table III). This is consistent with the value from KS's bracketing experiments, the only other determination of the CuO$^+$ bond energy in the literature. KS observed reaction of Cu$^+$ with O$_3$, suggesting that $D_0^\infty$(CuO$^+$/O$_3$ + Cu) < 1.04 eV, but they failed to observe reaction with N$_2$O which they took to imply an upper limit of 1.73 eV.

Further confirmation of this bond energy comes from analysis of the EI data. The optimum parameters for fitting the low energy feature are listed in Table II. Note that the $n$ and $p$ parameters are very similar to the parameters used to fit the other metal systems, unlike the ground-state parameters, and the $\sigma_{lo}$ values indicate comparable reactivity for ground and excited states. The threshold and dissociation energies [obtained using a single state in Eq. (4)] given in Table II are both about 3 eV below the threshold for the ground-state reaction (Fig. 8). This is roughly consistent with the excitation energies of the $^3D$ first excited state (2.81 eV) and the $^1D$ second excited state (3.26 eV). If this cross section is attributed to reaction of the $^3D$ state alone, this gives a bond energy of 1.77 ± 0.07 eV; if attributed to the $^1D$ state alone, a BDE of 1.32 ± 0.07 eV is obtained. A mixture of 90% Cu$^+$ ($^3D$) and 10% Cu$^+$ ($^1D$) yields a bond energy nearly identical to that derived from the SI data. Because the relative contributions of the $^3D$ and $^1D$ states to the EI data cannot be unequivocally determined, we take the value derived from the SI data to be our best determination.

There has only been one determination of the neutral bond energy for CuO, which is dependent on a metathetical reaction with NiO. This is the value recommended by PM and employed by us to determine IE(CuO) (Table IV).

**Zinc**

Since the EI source used to produce Zn$^+$ produces nearly 100% ground-state ions and we do not observe any evidence of excited state reactivity (which should be exothermic), the ZnO$^+$ cross section is analyzed with only a single term in Eq. (4). The threshold for reaction (1) with $M = Zn$ is nearly as high as that for $M = Cu$ (Table II) but the value for $n$ in Eq. (4) is similar to the other transition metals. Use of the parameters in Table II results in $D_0^\infty$(ZnO$^+$) = 1.65 ± 0.12 eV (38.1 ± 2.8 kcal/mol).

This is consistent with the large range in ZnO$^+$ BDEs determined in KS's bracketing experiments. Like Cu$^+$, Zn$^+$ ions react exothermically with O$_3$ but not with N$_2$O to produce ZnO$^+$. In direct contrast to these results, Bartmess and Kester observed the formation of ZnO$^+$ from the reaction of Zn$^+$ with N$_2$O. The authors note, however, that this result was not very reproducible and was most likely due to the reaction of excited state Zn$^+$ ions. Overall, these experiments are in agreement with the thermochemistry derived here.

There has only been one determination of the neutral zinc oxide bond energy (Table IV) which comes from a mass spectrometric measurement by Anthrop and Searcy. Use of our ZnO$^+$ bond energy and Eq. (6) leads to the IE(ZnO) value given in Table IV. There are no independent measurements of the ionization energy of ZnO.

**Comparison to previous ion-beam results**

Our results can be compared with the past ion-beam results for reaction (1) with $M = Ca$ and Cr–Ni. In the case of Ca, the shape and threshold of our results and those of Murad differ appreciably (Fig. 1). The discrepancy in the threshold values is partly due to differences in the interpretation of the data. Murad measured the reaction threshold by a linear extrapolation of his data to zero. This gave a threshold which was then approximately corrected for the ion energy distribution to yield a threshold energy of 1.82 ± 0.15 eV. We find that a linear cross section cannot be used to reproduce our data, showing that this type of interpretation is less accurate than the method used here. Also, as mentioned above, there is the possibility that the energy scales of the two experiments differ (by about 0.6 eV in the laboratory). Thus, we recommend the 0 K BDE determined here.

As noted above, the cross sections obtained here and by AHB are similar in shape in the threshold regions, Figs. 3–7, although there is a nonzero baseline in the AHB data. Because the determination of threshold energies depends only on the shape of the cross sections and not their magnitude, the discrepancies between the BDEs derived by AHB and those derived here do not arise primarily from differences in the data, but rather from differences in the interpretation. One difference is that AHB did not explicitly consider excited states in their interpretation, but the dominant difference is the parameters used in Eq. (4) to model the reaction cross sections. As stated in the Introduction, the thermochemistry cited by AHB was determined by exclusive use of the line-of
centers (LOC) model \((n = m = 1)\) to analyze their data. This model rises rapidly from threshold, resulting in an \(E_0\) value that is high compared to models which rise more slowly \([e.g., \text{the } n = 1.5 - 2, m = 1\text{ parameters used here (Table II)}]\). The LOC model thus leads to BDEs which are systematically too low by amounts that are much larger than the stated error limits of AHB (which actually define the precision of the measurement given the LOC model). In both the aluminum\(^8\) and iron\(^7\) systems, it was found that the LOC model could not adequately reproduce our experimental results. This is also true for the \(M = \text{Cr, Mn, Co, and Ni}\) systems. In contrast, the threshold regions of AHB’s data for all five metals are nicely reproduced by using the \(n\) and \(E_0\) parameters of Table II. These conclusions are well illustrated in Fig. 9 for the particular case of Mn.

**DISCUSSION**

**General behavior**

The reactivity of the first row transition metal ions with \(O_2\) does not differ greatly as the metal ion is changed. This is shown by the comparable shapes of the reaction cross sections and the similarities in the parameters \(n, p,\) and \(E_D\) given in Table II. The most conspicuous exceptions to this are calcium and copper (although the excited state of copper is not exceptional). The Ni system also shows some differences in that it has a cross section maximum which occurs at a higher energy than the threshold for reaction (2), but the general cross section shape and value of \(n\) for \(NiO^+\) formation are similar to the other reaction systems.

One indication of the uniqueness of the Ca\(^+\) and Cu\(^+\) reactions is the value of \(n\) required to reproduce the data. As mentioned above, \(m = 1\) was selected to reproduce the experimental results because this is predicted as a model for translationally driven (direct) reactions. Chesnavich and Bowers\(^9\) derived this model using transition state theory with modifications\(^9\) such that the translational energy dependence is explicitly displayed. For atom–diatom reaction, this model predicts that \(n = \frac{1}{4}, \frac{1}{2}, \frac{3}{2} \text{ or } 2\) depending on the nature of the transition state. Most of the metal oxide systems, including Al \((n = 1.5 \pm 0.15\) for the \(Al^+ + O_2\) system\(^8\) employ \(n\) values which fall in the predicted range (Table II). The only exception is Cu.

The large value of \(n\) required to reproduce the CuO\(^+\) cross section reflects the observation that the CuO\(^+\) reaction cross section rises from threshold much more slowly than those of the other transition metal oxides. In addition, this cross section reaches a maximum at a much higher energy, as shown by the value of \(E_D\) in Table II. This general type of behavior has been observed previously for the reactions of \(H_2\) with \(Mn^+ (S^1), Fe^+ (D^1),\) Zn\(^+ (S^1),\) and other nonmetallic atomic ions with \(H_2^1\). In these cases, the reactions are believed to occur via a fairly repulsive potential energy surfaces such that the reactions are inefficient at threshold and impulsive at higher kinetic energies.\(^17\) In the limit of a “pairwise” impulsive process (where the interactions are exclusively between pairs of atoms acting as hard spheres), the reaction cross section should be shifted by a simple mass factor.\(^17\) For the \(Cu^+ + O_2\) system, the mass factor is 1.66, which predicts that dissociation to \(Cu^+ + 2O\) can begin at 8.5 eV, in reasonable agreement with the peak in the experimental cross section (Fig. 8). This agreement suggests that the \(Cu^+ + O_2\) reaction occurs on a relatively repulsive potential energy surface which seems consistent with the closed shell character of the \(Cu^+ (S^1, 3d^{10})\) electron configuration.

Such impulsive behavior may also provide an explanation for the unusual behavior observed at high kinetic energies in the cross section for formation of CaO\(^+\) (Fig. 1). If such an impulsive process were occurring in this system, dissociation to Ca\(^+ + 2O\) should begin at 8.0 eV (based on a mass factor of 1.56), which is comparable to the energy at which the CaO\(^+\) cross section begins to decline more rapidly. The speculative implication is that Ca\(^+\) reacts with \(O_2\) via two mechanisms: one which rises rapidly from the thermo-dynamic threshold and one which is impulsive. Indeed, the CaO\(^+\) cross section of Fig. 1 can easily be reproduced with two such components. It is also possible that such a mechanism might explain why the cross sections for ScO\(^+\), TiO\(^+\), and VO\(^+\) flatten out at elevated energies.

The CaO\(^+\) cross section is also unusual since it rises more rapidly than the other cross sections (as evidenced by the low value of \(n\), Table II) and it reaches a maximum below the dissociation onset for reaction (2). The underlying explanations for this behavior are not presently understood.

**Reaction efficiencies**

Several reports on the reactions of first-row transition metal ions with \(H_2, D_2,\) and HD have indicated that the
efficiencies of these reactions depend strongly (factors of 10–100) on the electronic state of the metal ion. These differences have been explained in terms of molecular orbital and spin-conservation ideas which are extremely useful for understanding the $\text{M}^+ + \text{H}_2$ system as well as larger alkane systems. The results of the present study for $\text{M}^+$, $\text{Co}^+$, $\text{Ni}^+$, and $\text{Cu}^+$ and the state-specific results obtained previously for $\text{Fe}^+$ indicate that similar large differences in the reactivity of different electronic states are not observed for reactions of these same species with $\text{O}_2$. Although states which react efficiently with $\text{H}_2$ are still more reactive in the $\text{O}_2$ systems, the relative reactivities of the different states are substantially reduced.

The most obvious consideration in understanding the differences in reactivity of the first-row transition metal ions with $\text{H}_2$ versus $\text{O}_2$ is the spin state of the reactant. We have pointed out that reaction of $\text{H}_2$ with all low-lying states of the transition metal ions is spin-allowed, but low-spin states are observed to react more efficiently. One of the reasons for this is that the ground states of the $\text{MH}_3$ intermediates are also low spin, such that formation of this intermediate is spin-allowed for reaction of low-spin metal ion states with the singlet $\text{H}_2$ molecule but not for the high-spin metal ion states. $\text{MO}_2$ intermediates are also likely to be low spin and to be strongly bound. Unlike the $\text{H}_2$ system, however, access to these intermediates is now spin-allowed from both high- and low-spin states of the metal ion because the $\text{O}_2$ molecule has a triplet ground state. A more detailed discussion of the possible potential energy surfaces which might evolve in such systems is included in our paper on the $\text{Fe}^+ + \text{O}_2$ system.

Another difference between the $\text{H}_2$ and $\text{O}_2$ systems is seen when the reactivities of $\text{Ca}^+$ and $\text{Zn}^+$ are compared in order to ascertain the effect of the 3$d$ orbital occupation on reactivity. In the $\text{H}_2$ system, the accessibility of empty 3$d$ orbitals on $\text{Ca}^+$ allowed this reaction to proceed at the thermodynamic threshold. In $\text{Zn}^+$, however, the reaction proceeds largely via an impulsive mechanism, indicating that the potential energy surface is repulsive, a consequence of the fully occupied 3$d$ orbitals. In the $\text{O}_2$ system, the most obvious difference between the reactivity of $\text{Ca}^+$ and $\text{Zn}^+$ is the energetics, discussed further below. $\text{Zn}^+$ does not exhibit impulsive behavior, but reacts with $\text{O}_2$ much as the other metal ions do. Large differences in reactivity between $\text{Ca}^+$ and $\text{Zn}^+$ are no longer apparent. This is again presumably due to the diradical character of the $\text{O}_2$ reactant.

**Periodic trends in thermochemistry**

A detailed understanding of the variations in the first-row transition metal oxide ion BDEs is hindered by the lack of spectroscopic and theoretical information. Few of the transition metal oxide ions ($\text{TiO}^+$, $\text{VO}^+$, $\text{CrO}^+$) have been studied theoretically, and photoelectron spectroscopy is the primary source of spectroscopic information for these species (again limited to $\text{TiO}^+$, $\text{VO}^+$, and $\text{CrO}^+$). In order to make some progress in understanding these periodic trends, we will compare the $\text{M}^+ - \text{CH}_2$ thermochemistry with that previously discussed for $\text{M}^+ - \text{CH}_2$ species and with the better understood neutral metal oxides.

**Comparison to isoelectronic ligands.** As shown in Fig. 10, the $\text{MO}^+$ BDEs exhibit the "double-humped" shape characteristic of many periodic properties of the transition metals. In order to understand these bond energies in a systematic way, Fig. 10 compares the $\text{MO}^+$ BDEs to those for the isoelectronic species $\text{MCH}_2^+$. We have recently discussed the periodic trends in the $\text{MCH}_2^+$ BDEs for $\text{M} = \text{Sc-Cu}$ and found that they could be explained by using promotion energy arguments. We find a good correlation between the $\text{MCH}_2^+$ BDEs and the energy necessary to promote the $\text{M}^+$ ground state to a 4$s^2$3$d^{n-1}$ electron configuration where two electrons are spin-decoupled from the non-bonding 3$d$ electrons. The picture that emerges is that of a largely covalent double bond formed between $\text{M}^+$ and $\text{CH}_2$.

Figure 9 shows that the $\text{MCH}_2^+$ BDEs also exhibit the "double-hump" shape, and that the $\text{MO}^+$ and $\text{MCH}_2^+$ BDEs are similar for the late transition metals. In contrast, the early transition metals have much higher $\text{MO}^+$ BDEs than $\text{MCH}_2^+$ BDEs. Clearly, the promotion energy arguments used to understand the periodic trends in the $\text{MCH}_2^+$ BDEs and also $\text{MH}^+$, $\text{MCH}_2^+$, $\text{MCH}_4^+$, and $\text{M(CH}_3)_2^+$ BDEs are inadequate to understand the $\text{MO}^+$ values. However, the agreement between the values for $\text{Mn, Fe,}$ and $\text{Co}$ strongly suggests that the $\text{MO}^+$ and $\text{MCH}_2^+$ bonding have similar characteristics for these three elements.

The deviations between the BDEs of $\text{ScO}^+$, $\text{TiO}^+$, $\text{VO}^+$, and $\text{CrO}^+$ and their $\text{MCH}_2^+$ counterparts are quite large, 1.5–3 eV. This could be because these metal oxide bonds are actually more like triple bonds than double bonds, which suggests a comparison with the $\text{M}^+ - \text{CH}$ BDEs for

![FIG. 10. Bond strengths of various metal–ligand species for the first row transition metal oxides: $D^0(\text{M}^-\text{O})$ (closed circles) taken from Table IV; $D^0(\text{M}^-\text{O})$ (open circles) taken from Table IV; $D^0(\text{M}^-\text{CH}_2)$ (open squares) taken from Ref. 79; $D^0(\text{M}^-\text{CH}) + 0.74\text{eV}$ (see text) (open triangles) taken from Refs. 80 and 83.](image-url)
Ti, V, and Cr. To make this comparison properly, we note that formation of a triple bond with CH requires promotion of the CH from its 3Σ ground state to the 5Σ excited state, 0.74 eV higher. When this correction is included in the MCH + BDEs (Fig. 10) the agreement between the MO + and MCH + BDEs is satisfactory.

One interesting aspect of this comparison concerns CrO +. While the absolute CrO + BDE is comparable to those of Mn, Fe, and Co, and is much smaller than the VO + BDE, the analysis suggests that the bond is more like a triple bond than a double bond. The large decline in BDE compared with ScO +, TiO +, and VO + is due mainly to the increased number of 3d electrons. This increases the number of d-d exchange terms lost when the MO + bond is formed, and results in a corresponding decrease in the bond energy. This also can explain why the VO + BDE is somewhat smaller than the TiO + BDE.

The observation that metals on the left-hand side of the Periodic Table have much higher MO + BDEs than those on the right-hand side is the result of the contribution of oxygen lone pair electrons to the bonding (dative bonding). This preferentially occurs when there is an empty 3d orbital on the metal atom for an electron pair to donate into. Clearly, Ca +, Sc +, Ti +, and V + have such empty orbitals. This can explain why the CaO + BDE is comparable to the double-bonded MO + BDEs even though Ca + has only a single valence electron. In contrast, Zn + (which also has a single valence electron) has a much weaker bond since the fully occupied d orbitals on Zn prevent such lone pair electron donation. It also explains why the ScO + bond can be a triple bond even though Sc + (with two valence electrons) cannot form a strong triple bond with CH, which has no lone pair electrons. This type of dative bonding by a ligand has also been observed for the bonding between NH and NH2 with Sc +, Ti +, and V +.10,11

Another potential reason for the very weak MO + BDEs of Cu and Zn is that these bonds are fairly ionic and therefore cannot be described in the same terms as the more covalently bonded MO + species on the left-hand side of the Periodic Table. This is discussed further in the next section.

Comparison to the neutral metal oxides. Unlike the ionic metal oxides, neutral transition metal oxides have been the subject of numerous spectroscopic and theoretical studies.64,85,86,87 The experimentally determined dipole moments85 and theoretical calculations86 of MO show that 0.5–0.7 electrons are transferred from the metal to oxygen in the neutral transition metal oxides. Thus, the bonding has both ionic and covalent contributions, although we will emphasize the latter means of approximating the bonding, as per Merer.85 The ground states and leading valence electron configurations of the neutral metal oxides [excluding the O(2s) electrons] are listed in Table V.

Consider first the ScO molecule. The electron configuration has three fully occupied strongly bonding orbitals, the 8σ which is a bonding combination of M(4s) and O(2p), and the two 3π's which are O(2p) + M(4p). These orbitals are dominated by the oxygen atom contributions. The 9σ orbital is largely M(4s) in character and is only slightly bonding. Calcium oxide presumably has a weaker BDE than ScO because there is much less covalent bonding character in the 8σ and 3π orbitals (because the d orbitals are higher in energy than for Sc). As we go from ScO to TiO to VO, the additional electrons are placed in the nonbonding 6 orbitals (Table V) such that the neutral bond strengths do not change appreciably. The decrease that is observed for D3′(VO) is probably due to an increase in the d-d exchange energy lost when the MO bond is formed.

As we move across the periodic table to CrO, the neutral BDE drops precipitously (Fig. 10). Now, there is significantly more d-d exchange energy lost when the MO bond is formed and the additional electron is placed in an antibonding 4σ orbital (Table V). Addition of another electron again decreases the bond energy (Fig. 10) consistent with addition of a second antibonding 4σ electron. For FeO, CoO, and

### Table V. Metal oxide electron configurations.

<table>
<thead>
<tr>
<th>M</th>
<th>Neutral state</th>
<th>Atom config</th>
<th>Molecular config</th>
<th>Ion config</th>
<th>Ion state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>3Σ +</td>
<td>4s^2</td>
<td>8s^2 3p^6</td>
<td>4s</td>
<td>3Π (− 3σ)</td>
</tr>
<tr>
<td>Sc</td>
<td>5Σ +</td>
<td>4s3d^2</td>
<td>8s^2 3p^6 9s^1</td>
<td>3d^2</td>
<td>5Σ + (− 9σ)</td>
</tr>
<tr>
<td>Ti</td>
<td>3Δ</td>
<td>4s3d^3</td>
<td>8s^2 3p^6 9s^1 16d^1</td>
<td>3d^3</td>
<td>3Δ (− 9σ)</td>
</tr>
<tr>
<td>V</td>
<td>4Σ −</td>
<td>4s3d^4</td>
<td>8s^2 3p^6 9s^1 16d^2</td>
<td>3d^4</td>
<td>4Σ (− 9σ)</td>
</tr>
<tr>
<td>Cr</td>
<td>3Π, 4s3d^5</td>
<td>8s^2 3p^6 9s^1 16d^2 4π^1</td>
<td>3d^5</td>
<td>3Π (− 9σ)</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>5Σ +</td>
<td>4s3d^6</td>
<td>8s^2 3p^6 9s^1 16d^2 4π^2</td>
<td>3d^6</td>
<td>5Σ + (− 9σ)</td>
</tr>
<tr>
<td>Fe</td>
<td>5Δ</td>
<td>4s3d^7</td>
<td>8s^2 3p^6 9s^1 16d^2 4π^2</td>
<td>3d^7</td>
<td>5Δ (− 9σ)</td>
</tr>
<tr>
<td>Co</td>
<td>6Δ</td>
<td>4s3d^7</td>
<td>8s^2 3p^6 9s^1 16d^2 4π^2</td>
<td>3d^8</td>
<td>6Δ (− 9σ)</td>
</tr>
<tr>
<td>Ni</td>
<td>7Σ −</td>
<td>4s3d^8</td>
<td>8s^2 3p^6 9s^1 16d^2 4π^2</td>
<td>3d^8</td>
<td>7Σ (− 9σ)</td>
</tr>
<tr>
<td>Cu</td>
<td>2Π</td>
<td>4s3d^10</td>
<td>8s^2 3p^6 9s^1 16d^2 4π^2</td>
<td>3d^10</td>
<td>2Π (− 9σ)</td>
</tr>
<tr>
<td>Zn</td>
<td>2Σ +</td>
<td>4s3d^10</td>
<td>8s^2 3p^6 9s^1 16d^2 4π^2</td>
<td>4s3d^10</td>
<td>2Σ (− 4σ)</td>
</tr>
</tbody>
</table>
NiO, the successive electrons are now placed in the non-bonding 1\(\delta\) and 9\(\sigma\) orbitals (Table V) and the bond energies change only slightly. In this region of the Periodic Table, the nuclear charge increases to the point where the character of the molecular orbitals changes somewhat due to d orbital contraction. By NiO, the 8\(\sigma\) has changed to being largely M(\(4d\)) while the 9\(\sigma\) orbital is a bonding orbital between M(4s) and O(2p). The 3\(\pi\) and 4\(\pi\) are still bonding and anti-bonding combinations of the M(\(4d\)) and O(2p) but the 3\(\pi\) is now weighted more heavily toward the metal. These changes mean that the ionic character of these species is more apparent and contributions from the covalent d bonding interactions discussed above are smaller. Thus, the BDEs for CuO and ZnO are considerably less than those for earlier transition metal oxides since the bonding is primarily ionic. The main difference between NiO and CuO is that there is much less d-\(\delta\)-p bonding.  

If we now examine the ionic BDEs, we find that the periodic trends in the ion BDEs follow those of the neutrals fairly closely (Fig. 10). We conclude that the explanations for the changes in the ion BDEs are probably similar to those discussed above for the neutral BDEs. The obvious distinction between the ionic and neutral BDEs is that the ionic BDEs get increasingly weaker than the neutral BDEs as one moves from left to right.

To understand this, we first examine the types of states and electron configurations which might be expected for the ions (Table V). The entries in this table anticipate that there is a preference for removing a metal 4s electron (the 9\(\sigma\) molecular orbital) upon ionization since this is the electron lost in ionizing the metal atoms. This is the calculated result for TiO and VO. The situation is less clear for CrO (Table V) since removal of the 9\(\sigma\) electron has nearly the same energetics as removing the 4\(\pi\) electron, as discussed above. This ambiguity persists through most of the remaining entries until reaching CuO\(^{+}\) and ZnO\(^{+}\) where the preference for Cu\(^{+}\) (3d\(^{10}\)) and Zn\(^{+}\) (4d\(^{10}\)) configurations on the metals are probably pronounced.

If we now examine Sc and Ti, we find that the ionic and neutral BDEs are nearly identical, consistent with removing a 9\(\sigma\) electron which is only slightly bonding (Table V). This suggests that the ionic and neutral BDEs might not vary for metals further to the right either, in contrast with observation. Proposing that a 4\(\pi\) electron is lost is no better, since this orbital is antibonding, which means that the ion BDE should be higher than the neutral BDE. One way around this dichotomy is to recognize that the 9\(\sigma\) orbital is bonding for the late transition metal oxide neutrals. Removal of an electron from such an orbital is clearly consistent with the decrease in ion BDE compared to the neutral.

Since the transition between a nonbonding 9\(\sigma\)(4s) orbital and a bonding 9\(\sigma\)(4s + 2p\(\delta\)) orbital occurs because of contraction of the d orbitals, this transition should occur earlier in the periodic table for the ions. Based on the data in Fig. 10, this transition must occur around V or Cr. Note that this is consistent with the promotion energy arguments used in the past to explain the periodic trends in the MH\(^{+}\), MCH\(_3\)^{+}, MCH\(_2\)^{+} species. These arguments suggest that a dominant metal atom configuration in these species is the 4s\(^{3}3d\(^{n-1}\). Another way of thinking of this change is that the bonds of the ions are weaker than those of the neutrals for metals to the right in the Periodic Table because the 4d orbitals have contracted in the ionized species and this reduces their ability to form covalent bonds (as discussed above for neutral CuO and ZnO). Further, the ionic contribution to the bonding is altered since it should now be energetically more costly for M\(^{+}\) to donate electrons to the O atom.

ACKNOWLEDGMENT

This research was supported by the National Science Foundation, Grant CHE-8917980.

6 The I\(\delta\)-O\(\delta\) model is given by Eq. (4), with \(\nu = m = 1\). R. D. Levine and R. B. Bernstein, Molecular Reaction Dynamics and Chemical Reactivity (Oxford University, New York, 1987), p. 61.
27 Indeed, we can mimic the cross section obtained by Murad by reducing the energy at which the ions are passed through the analysis quadrupole mass filter. This discriminates against ions with large transverse energies.
30 This expression implicitly assumes that the same product states can be produced by all reactant ion states.
30 To convert $D^0_0(MO^-)$ to a 298 K value, we require the 0 and 298 K enthalpies for $M^+$, O and MO$^-$. The first two are well known, but that for MO$^-$ is generally not. However, the change in enthalpies is known for most MO species, so that $D^0(MO)$ can be calculated at 0 and 298 K. We assume here that the change in $D^0(MO)$ from 0 to 298 K is nearly the same as that of $D^0(MO)\approx 0.04$ eV for most of the metals. Any deviation from this value is accounted for by including an uncertainty of $\pm 0.02$ eV.
35 D. E. Clemmer and P. B. Armentrout (work in progress).
43 This value is listed as a private communication in C. J. Cetham and R. B. Barrow, Adv. High Temp. Chem. 1, 7 (1967).
48 Energies for the individual J states are taken from Ref. 20. Populations are based on a Maxwell–Boltzmann distribution at 2250 ± 100 K.
49 This relative reactivity is consistent with an analysis of the low-energy feature in the El cross section (similar to that described in detail for Mn$^+$. This analysis suggests that the $b^2 F(4s2d^7)$ excited state is less reactive than the $a^2 F(3d^7)$ ground state by a factor of $<3$.
64 In the cases where thermochemical information is available (Cr and Fe). Cr$^{2+}$ the MO$^-$ intermediates are bound by 1–2 eV compared to the reactants.
70 P. B. Armentrout, ACS Symposium Series (in press).
75 V. Srdanov, Ph.D. thesis, University of California, Santa Barbara; D. Harris (personal communication).
76 The promotion energy for a single covalent bond is best defined as the energy necessary to take a metal atom in its ground state to an electron configuration where there is one electron in the valence $s$ orbital which is spin-decoupled from the remaining metal $d$ electrons. For multiple covalent bonds, additional metal $d$ electrons need to be spin-decoupled from the remaining $d$ electrons.
77 The calculations of Harrison on CrO$^+$ indicate that the number of electrons transferred from the metal to the oxygen is about the same as in the neutral CrO$^+$. Since this electron transfer must require more energy in the ion, this suggests that the CrO$^+$ BDE should be weaker than the CrO BDE, as observed experimentally.