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Role of Atomic Electronics in f-Element Bond Formation: Bond Energies of Lanthanide and Actinide Oxide Molecules

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Metal oxide molecules are of particular interest from both a scientific and technological perspective in view of their elementary nature and role in such processes as high-temperature vaporization. A fundamental and important property is the bond energy between the metal center and the oxygen in neutral and ionic monoxide molecules, BDE[MO] and BDE[MO^+]. For the 4f-block lanthanide (Ln) and 5f-block actinide (An) inner transition metals, it has been demonstrated that many chemical properties can be rationalized from the electronic structures and energetics of the isolated metal atom or ion. In the present work, a relationship is developed to reliably predict known BDE[LnO], BDE[LnO^+], BDE[AnO], and BDE[AnO^+] energies from spectroscopically determined electronic properties; this relationship is employed to estimate unknown bond energies. A notable implication of the results is that effective bonding between the metal center and the oxygen atom in these species requires two unpaired valence d electrons.

Introduction

Solid crystalline oxides of electropositive metals, MO_n(cr), can usually be reasonably approximated as highly ionic compounds comprised of O^{2-} anions and $M^{(2n)+}$ cations.[1,2] For example, lanthanide sesquioxides, $LnO_{3/2}$(cr), can be represented as $Ln^{3+}O^{2-}{}_{3/2}$. The summed first three ionization energies of lanthanide atoms, $\Delta E[Ln \rightarrow Ln^{3+} + 3e^-]$, are in the range of 3.5−4 MJ.[1] The enthalpy for the association of an oxygen atom with two electrons, $\Delta H[O + 2e^- \rightarrow O^{2-}]$, is endothermic by 0.75 MJ.[2] Accordingly, the energy required for the gas-phase electron transfer, $Ln + 3/2O \rightarrow Ln^{3+} + 3/2O^{2-}$, is in excess of 4 MJ. Solid $LnO_{3/2}$(cr) can be approximated as fully ionic $Ln^{3+}O^{2-}{}_{3/2}$ only because of the large favorable lattice energy that results from the electrostatic interactions between the cations and multiple surrounding anions.[1,2]

In small gas-phase molecules such as LnO, the lattice energy is not available, and the interaction between the metal center and the oxygen is best represented as a polar (partially ionic) covalent bond: $Ln^{\delta+}{=}O^{\delta-}$. Accordingly, two outer valence electrons must be available at both the Ln atom and the oxygen atom to allow for formation of the partially ionic formally double bond. Two valence p electrons are available for participation in bonding for ground-state atomic oxygen with its $1s^22s^22p^4$ electron configuration.[2] Attempts to correlate/predict Ln-O and An-O bond dissociation energies then require knowledge of the energy to achieve an electronic configuration at the lanthanide or actinide metal center that has two suitable outer valence electrons for bonding with an oxygen atom. The goal of the present assessment is to provide an improved basis for correlating known lanthanide and actinide monoxide bond energies with measured electronic energetics of the free metal atoms and ions. This enables predictions of monoxide bond energies that are in question or unknown. In the presentation of the approach employed in this work, comparisons are made with related correlations previously reported in the literature.

Results and Discussion

The goal here is to develop a model to predict the bond energies of neutral and monopositive f-element monoxide molecules. The approach is to consider an elementary model that employs fundamental considerations of the variable electronic structures and energetics of the isolated metal atoms or ions. The basic assumption, which has been invoked elsewhere,[3,4] is that the energy necessary to achieve a suitable bonding configuration at the metal center for the free atom or ion can be used to predict the net bonding upon association with an oxygen atom. The details of this approach are developed for the lanthanides where abundant experimental information is available and then applied to the actinides where experimental results are substantially more sparse and uncertain. Ab initio calculations on the molecular structures of lanthanide and actinide oxide molecules have been carried out with significant success.[5−7] Such ab initio calculations must take into account the complex electronic structures of the heavy metals, including relativistic effects. The empirically based type of approach employed here depends on the availability of spectroscopically determined energetics for the metal center, which manifest effects that must be incorporated into effective ab initio methods.

Bond Dissociation Energies of Neutral Lanthanide Monoxides. For free lanthanide atoms the ground-state configurations are $4f^{n-3}5d6s^2$ for La, Ce, Gd, and Lu, and $4f^{n-2}6s^2$ for all other members of the series, where "n" represents the total number of electrons outside of the closed xenon core: $n = 3$ for La, $n = 4$ for Ce, etc.[8] It has been well-established that the 4f electrons of the lanthanides are localized and not chemically active in molecular bonding.[4,9] Accordingly, only the 5d/6s/6p outer valence electrons at the metal center can participate in covalent bonding in molecules such as lanthanide monoxides. As the spin-paired electrons in the filled $6s^2$ valence sub-shell are unavailable for bonding for a free atom or ion, excitation of

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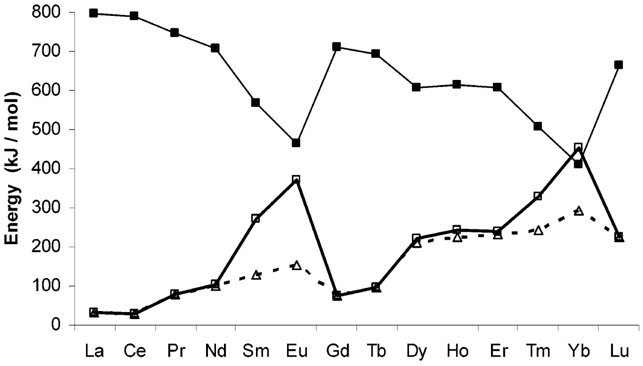

Figure 1. Lanthanide monoxide dissociation energies (BDE[LnO], solid squares)[13]; atomic promotion energies to the $4f^{n-3}5d^26s$ configuration ($\Delta E[5d^26s]$, open squares),[8] and atomic promotion energies to the $4f^{n-2}5d6s$ configuration (or $4f^{n-3}5d^26s$ configuration as specified in Table 1; $\Delta E[5d6s]$, open triangles).[8]

one of the two 6s electrons is required to achieve a prepared divalent configuration suitable for formation of the Ln═O bond. The expected inert character of the spin-paired $6s^2$ electrons in gas-phase chemistry has been clearly demonstrated by the reduced chemical reactivity of the Lu^+ ion,[4,10,11] which has a $5f^{14}6s^2$ ground state.[8]

For all of the lanthanide atoms, the two lowest-lying configurations for which one of the $6s^2$ electrons has been excited to an empty outer valence orbital are $4f^{n-2}5d6s$ and $4f^{n-3}5d^26s$.[8] For La, Ce, Gd, and Lu, the lowest-lying excited configuration is $4f^{n-3}5d^26s$ that results from promotion of a 6s electron to a 5d orbital. For Pr, Nd, Pm (estimate[12]), Tb, Dy, Ho, and Er, the $4f^{n-2}5d6s$ and $4f^{n-2}5d^2$ excited state configurations are within 20 kJ/mol of one another, indicating that the 5d and 6s orbital energies are essentially degenerate. For Sm, Eu, Tm, and Yb, the $4f^{n-3}5d^26s$ configuration lies between 86 kJ/mol (Tm) and 219 kJ/mol (Eu) higher in energy than the $4f^{n-2}5d6s$ configuration.[8] Because of the large discrepancy between the two relevant promotion energies for these latter four lanthanides, insights into the prepared divalent bonding configuration should be most evident there.

In the present assessment, the self-consistent set of BDE[LnO] values from Chandrasekharaiah and Gingerich are employed.[13] These are zero Kelvin bond energies, as are most appropriate for modeling based on the electronic considerations being employed; however, metal monoxide dissociation energies generally vary little between 0 and 298 K. For some of the actinides, higher-temperature experimental values are employed, but in these cases, the assigned uncertainties are much larger than any expected variation in the bond energies within this temperature range. In Figure 1, the BDE[LnO] are plotted along with the $\Delta E[\text{ground} \rightarrow 4f^{n-2}5d6s]$ and $\Delta E[\text{ground} \rightarrow 4f^{n-3}5d^26s]$ promotion energies. For all of the excited-state configurations, the lowest energy state in the manifold is employed as the relevant excitation energy. For those Ln for which the $4f^{n-3}5d^26s$ configuration is lower in energy than the $4f^{n-2}5d6s$ configuration, the promotion energy to a bonding configuration with one unpaired 6s and at least one 5d valence electron is considered to be $\Delta E[\text{ground} \rightarrow 4f^{n-3}5d^26s]$. Promethium is not included in Figure 1 as no experimentally measured BDE[PmO] is available. It is evident from this plot that there is a very good inverse correlation between the BDE[LnO] and $\Delta E[\text{ground} \rightarrow 4f^{n-3}5d^26s]$. The correlation between BDE[LnO] and $\Delta E[\text{ground} \rightarrow 4f^{n-2}5d6s]$ is reasonable, with the four obvious exceptions of Sm, Eu, Tm, and Yb, these being the elements for which there are substantial differences between the $\Delta E[\text{ground} \rightarrow 4f^{n-3}5d6s]$ and $\Delta E[\text{ground} \rightarrow 4f^{n-3}5d^26s]$ promotion energies. Figure 1 suggests that the energy for excitation to the $4f^{n-3}5d^26s$ configuration should be a more reliable indicator of the monoxide bond energy than is that for excitation to the $4f^{n-2}5d6s$ configuration.

To a first approximation, there is an intrinsic Ln−O bond energy that varies little across the lanthanide series.[4] The intrinsic bond energy, BDE*[LnO], is defined as the bonding interaction between an oxygen atom and a lanthanide atom, Ln*, that has an electronic configuration suitable for formation of the covalent formally double bond in the Ln═O molecule. The actual BDE[LnO] can then be expressed in terms of the intrinsic bond energy and the energy needed to excite the ground-state lanthanide atom to an electronic configuration suitable for bond formation, as shown in eq 1:

$$\text{BDE[LnO]} = \text{BDE*[LnO]} - \Delta E[\text{ground} \rightarrow \text{bonding configuration}] \quad (1)$$

This general approach was applied to the lanthanide monoxide ions, LnO^+, by Cornehl et al.,[4] where an additional term corresponding to the net loss of electron exchange energy at the Ln^+ metal center was included. In that assessment,[4] it was assumed that the prepared bonding configuration at the metal center was $4f^{n-2}5d6s$. The 5d/6s exchange energy was then presumed to be the relevant quantity. The loss of the 4f/6s and 4f/5d exchange energies were calculated based on a derived value and the assumption that this energy is linearly dependent on the number of unpaired 4f electrons. In the present treatment, the quantity referred to as the intrinsic bond energy, BDE*[LnO], includes any constant contribution to the loss of exchange energy. Such a nearly constant effect would likely be the case for the outer valence electrons involved in bonding, as was assumed by Cornehl et al.[4] Incorporation of a constant exchange energy term into eq 1 would result in a larger BDE*[LnO] but would not alter the calculated BDE[LnO]. In contrast to the previous treatment,[4] the possibility of an alternative prepared bonding configuration at the lanthanide metal center is considered in the present assessment. Also, no allowance is made here for the loss of 4f/6s and/or 4f/6d exchange energies because of the uncertainties associated with the estimate of this varying quantity; the omission of this potential contribution is further discussed and justified below in the context of the calculated $BDE[LnO^+]$. In the previous assessment of LnO^+ bond energies,[4] discrepancies between the experimental and calculated $BDE[LnO^+]$ were in excess of 100 kJ/mol for four of the eleven assessed LnO^+ (the calculations were normalized to $BDE[LaO^+]$ and $BDE[CeO^+]$).

The correlations seen in Figure 1 would suggest that it is actually the $4f^{n-3}5d^26s$ configuration rather than the $4f^{n-2}5d6s$ configuration that is relevant to bonding in the lanthanide monoxides. It should be noted that the $4f^{n-2}6s6p$ configuration lies lower in energy than the $4f^{n-2}5d6s$ configuration for several of lanthanide atoms but that the correlation between the promotion energies to the 6s6p prepared divalent state and the experimental bond dissociation energies is very poor. The BDE[LnO] were calculated according to eq 1 for both feasible bonding configurations, $4f^{n-2}5d6s$ and $4f^{n-3}5d^26s$. The intrinsic BDE*[LnO] is derived from the experimental BDE[LaO].[13] Because $\Delta E[\text{ground} \rightarrow 4f^{n-2}5d6s] = \Delta E[\text{ground} \rightarrow 4f^{n-3}5d^26s] = 32$ kJ/mol for La,[8] the derived BDE*[LnO] = {BDE[LnO] + 32 kJ/mol} = {795 kJ/mol + 32 kJ/mol} = 827 kJ/mol, is independent of which excited state is assumed to represent the relevant bonding configuration. In Table 1 are shown the relevant parameters and calculated BDEs assuming $4f^{n-2}5d6s$

TABLE 1: Lanthanide Atom Electronic Parameters and Bond Dissociation Energies[a]

	ground[b]	ΔE[5d6s][b]	ΔE[5d^{2}6s][b]	BDE[LnO][c]	BDE[5d6s][d]	BDE[5d^{2}6s][d]
La	$5d6s^2$	32 [d^2s]	32	795 ± 10	795 {0}	795 {0}
Ce	$4f5d6s^2$	28 [d^2s]	28	790 ± 17	799 {+9}	799 {+9}
Pr	$4f^36s^2$	80 [d^2s]	80	745 ± 10	747 {+2}	747 {+2}
Nd	$4f^46s^2$	101	105	706 ± 13	726 {+20}	722 {+16}
Pm	$4f^56s^2$	(115)	(129)	NA	(712)	(698)
Sm	$4f^66s^2$	129	272	569 ± 10	698 {+129}	555 {−14}
Eu	$4f^76s^2$	154	373	465 ± 15	673 {+208}	454 {−11}
Gd	$4f^75d6s^2$	76 [d^2s]	76	711 ± 13	751 {+40}	751 {+40}
Tb	$4f^96s^2$	98 [d^2s]	98	693 ± 21	729 {+36}	729 {+36}
Dy	$4f^{10}6s^2$	210	221	607 ± 21	617 {+10}	606 {−1}
Ho	$4f^{11}6s^2$	226	242	613 ± 10	601 {−12}	585 {−28}
Er	$4f^{12}6s^2$	231	241	607 ± 10	596 {−11}	586 {−21}
Tm	$4f^{13}6s^2$	244	330	508 ± 10	583 {+75}	497 {−11}
Yb	$4f^{14}6s^2$	293	447	401 ± 21	534 {+133}	380 {−21}
Lu	$4f^{14}5d6s^2$	225 [d^2s]	225	663 ± 10	602 {−61}	602 {−61}

[a] All energies are in kJ/mol. [b] The electronic configurations and excitation energies are from ref 8, except for the estimates for Pm.[12] The ΔE[5d6s] are the same as ΔE[5d^{2}6s] where indicated. Calculated values based on other models are available, including for PmO (see text). [c] Experimental bond dissociation energies from ref 13; no experimental value is available (NA) for PmO. [d] The BDE[5d6s] and BDE[5d^{2}6s] were calculated using eq 1 as described in the text. The numbers in brackets are the deviations of the calculated from the experimental values.

and $4f^{n-3}5d^26s$ as the prepared bonding configurations. The BDE[5d6s] and BDE[5d^{2}6s] in Table 1 correspond to employing eq 1, BDE*[LnO] = 827 kJ/mol, and the excitation energies to the $4f^{n-2}5d6s$ configuration (ΔE[5d6s]) and $4f^{n-3}5d^26s$ configuration (ΔE[5d^{2}6s]), respectively. For La, Ce, Pr, Gd, Tb, and Lu, the $4f^{n-3}5d^26s$ configuration lies lower in energy than the $4f^{n-2}5d6s$ configuration and is therefore employed as the lowest-energy configuration with at least one unpaired 6s electron; that is, ΔE[5d6s] = ΔE[5d^{2}6s] for these particular lanthanide atoms, as noted in Table 1.

The results in Table 1 indicate that the BDE[5d^{2}6s] are generally closer to the experimental BDE[LnO] than are the BDE[5d6s]. For each calculated BDE, the deviation from the experimental value is indicated in brackets. The perfect agreement for BDE[LaO] is an artifact of employing LaO as the prototype to derive the intrinsic BDE*[LnO]. An experimental value is not available for comparison in the case of PmO. For the other 13 LnO, the average deviation between BDE[LnO] and BDE[5d6s] (absolute values) is 57 kJ/mol, whereas that between BDE[LnO] and BDE[5d^{2}6s] is 21 kJ/mol. It is for the eight LnO where the $4f^{n-2}5d6s$ configuration lies below the $5d^26s$ configuration that the calculated values differ, and comparison for those LnO thus provides the best indicator of the comparative reliabilities of the two approaches. The corresponding average deviations are 75 kJ/mol for BDE[5d6s] and only 15 kJ/mol for BDE[5d^{2}6s] for these eight LnO. The greatest deviation between BDE[LnO] and BDE[5d^{2}6s] is 61 kJ/mol in the case of LuO; all other BDE[5d^{2}6s] are within 40 kJ/mol of the experimental values. Atomic Lu is unique in having a $4f^{14}5d6s^2$ ground-state configuration that comprises a filled 4f subshell. Jensen[14] has summarized arguments that Lu is a d-block transition metal and not a true lanthanide. From this perspective,[14] it would be expected that a model for predicting lanthanide monoxide bond energies would not be applicable to LuO.

The good agreement of the BDE[5d^{2}6s] with the experimental values suggests that the bonding configuration of the Ln metal center in the LnO is $4f^{n-3}5d^26s$ rather than $4f^{n-2}5d6s$. One rationale for this observation is that particular $5d^26s$ hybrid orbitals possess appropriate symmetry for bonding with an oxygen atom. However, the results below for the LnO$^+$ ions suggest that it is the $5d^2$ electrons alone that are key to providing a suitable bonding configuration. Sievers et al.[15] assessed bond energies of several second row d-block transition metal oxides (and carbides) using the model of Carter and Goddard.[3] There,[15] the bond energies were rationalized in the context of promotion to a $4d^{n-1}5s$ configuration, with the assumption that an unpaired 5s electron is necessary for effective M−O bonding. A theoretical treatment of d-block transition metal oxide bond energies by Siegbahn[16] indicated that the very large variations in bond strengths for the second row transition metal monoxides are due to the decrease in the interaction between the oxygen lone pair electrons and the metal 4d orbitals as these 4d orbitals are increasingly occupied upon proceeding across the series. Such a variation would not be expected for the lanthanides, where the 5d orbital occupancy is constant for the presumed bonding configurations, and electron contribution from the oxygen ligand to several vacant 5d orbitals can occur across the series. One implication of the potential for back-bonding from oxygen to the metal center is that the M−O bonds may have some triple-bond character.[16] The triple bond character of early transition metal monoxides has been discussed by Armentrout and co-workers.[17,18]

Because of the uncertainty in deriving accurate 4f/6s and 4f/5d exchange energies and the indeterminate variation in the total 4f-related exchange energy as a function of f-orbital population, this factor was not included in the results shown in Table 1. The loss of 4f-exchange energy should be greatest in the case of Gd where the proposed bonding configuration is high-spin $4f^75d6s^2$. The BDE[5d^{2}6s] (and identical BDE[5d6s]) for GdO exhibits the largest positive deviation from the experimental value, and this discrepancy would be reduced by inclusion of the f-electron exchange energy terms and loss of this energy upon bond formation. Similarly, the $4f^{14}5d6s^2$ configuration of Lu has a filled 4f shell and there should be no loss of f-electron exchange energy; BDE[5d^{2}6s] coincidentally exhibits the largest negative deviation from the experimental value for LuO. Although it would appear that there may be some nontrivial contribution from loss of 4f/6s and/or 4f/5d exchange energies, it would appear impractical to empirically quantify this effect as a function of 4f-orbital occupancy, particularly in view of the uncertainties in the experimental bond dissociation energies. Qualitative adjustments to calculated bond dissociation energies to account for this exchange energy may be appropriate but it is currently difficult to quantify, as elaborated on below in the context of the LnO$^+$ ions.

Several years ago, Ames et al.[19] noted a correlation between the lanthanide 4f-to-5d promotion energies and the BDE[LnO]. Those authors presented a plot showing predicted BDE[LnO] along with the experimental values but did not tabulate the predicted values. From their plot (Figure 2 in ref 19), discrepancies of up to ~1 eV (1 eV = 96 kJ/mol) appear between the predicted and experimental values. Furthermore, it was assumed[19] that it is the $4f^{n-3}5d6s^2$ lanthanide configuration that is pertinent to bond formation, despite that the $6s^2$ electrons are spin-paired and unavailable for bonding. Murad and Hildenbrand[20] refined the treatment of Ames et al.[19] by assuming covalent bonding in the LnO molecules (as was done here) and employing free atomic, rather than solvated ion, excitation energies. The experimental data were generally well reproduced in a parametrization that assumed a monotonic decrease in the intrinsic Ln-O bond energy across the series, from 795 kJ/mol for LaO to 665 kJ/mol for LuO, and a correlation with the $4f^{n-2}6s^2 \rightarrow 4f^{n-3}5d6s^2$ atomic Ln promotion energies.[20] (This approach was subsequently applied to the actinides by Haire[21,22] to estimate BDE[AnO] for which experimental bond energies are unavailable.) However, it is not obvious why such a significant decrease in bond energies should be expected between La and Lu. In comparison, for example, BDE[MO] are essentially the same, to within 20 kJ/mol, for KO, RbO, and CsO.[23] The 4f → 6d promotion energies are related to the $\Delta E[5d^26s]$ in Table 1 in such a manner that inclusion of a decrease in the intrinsic bond energy across the series using a model that employs four experimental BDE[LnO] as parameters would be expected to give agreement comparable to that achieved using the more fundamental model of Carter and Goddard,[3] first applied to the LnO^+ by Cornehl et al.[4] and further developed in the present work. It is concluded here that the intrinsic lanthanide and actinide monoxide bond energies vary little across the series and that two valence d electrons, i.e., a $5d^2$ configuration for the Ln, are required for effective Ln-O bonding. As discussed below, the same conclusion is arrived at for bond formation in the $Ln^+{-}O$ ions.

Bond Dissociation Energies of Lanthanide Monoxide Monopositive Ions. The bond dissociation energies of the lanthanide monoxide monopositive ions, $BDE[LnO^+]$, have also been derived from experimental measurements and again the self-consistent values given by Chandrasekharaiah and Gingerich[13] are employed in this assessment. In analogy with the neutral monoxides, formation of a formally double bond in $\{Ln{=}O\}^+$ requires two outer valence electrons available for bonding at both the lanthanide metal center and the oxygen; as discussed above, additional bonding may result from dative-type bonding with vacant 5d orbitals.[16] Because $BDE[LnO^+]$ is defined as the energy for dissociation to Ln^+ and an oxygen atom, the issue in predicting the $BDE[LnO^+]$ is the electronic configuration at the lanthanide metal ion center that is suitable for formation of the $Ln^+{=}O$ bond. As with neutral LnO molecules, it is assumed that the localized quasivalence 4f electrons do not participate in covalent bonding with an oxygen atom. For the Ln^+, the $4f^{n-3}5d^26s$ excited-state configurations, where "*n*" is now the total number of electrons outside of the xenon core for the Ln^+ ions, $n = 2$ for La^+, $n = 3$ for Ce^+, etc., are too high in energy relative to the ground-state configuration to be viable as the prepared state for double bond formation. This contrasts with the neutral lanthanide monoxides, where it was concluded that $4f^{n-3}5d^26s$ was the bonding configuration.

For the Ln^+ ions, the two low-lying configurations with two non-4f electrons in half-filled valence orbitals are $4f^{n-2}5d6s$ and $4f^{n-2}5d^2$. The promotion energies to these configurations are shown along with the $Ln^+{-}O$ bond dissociation energies ($BDE[LnO^+]$) in Figure 2. In contrast to Figure 1, it may not be as immediately obvious from Figure 2 which excited-state Ln^+ configurations best represent the bonding configurations at the metal center in LnO^+. In direct analogy with eq 1 for the neutral LnO, it is proposed that the bond dissociation energies of the LnO^+ can be estimated according to eq 2:

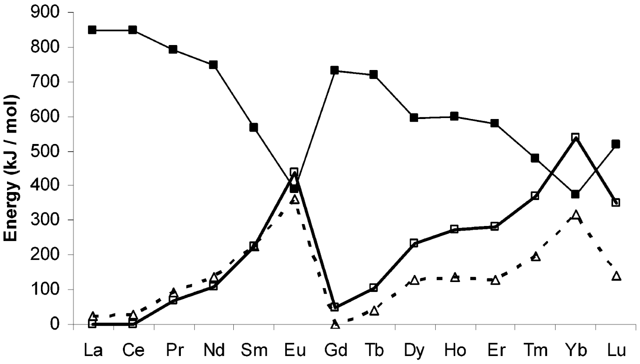

Figure 2. Lanthanide monoxide ion dissociation energies (BDE[LnO], solid squares);[13] atomic promotion energies to the $4f^{n-2}5d^2$ configuration ($\Delta E[5d^2]$, open squares);[8] and atomic promotion energies to the $4f^{n-2}5d6s$ configuration (ΔE[5d6s], open triangles).[8]

$$BDE[LnO^+] = BDE^*[LnO^+] - \Delta E[\text{ground} \rightarrow \text{bonding configuration}] \quad (2)$$

On the right-hand side of eq 2, $BDE^*[LnO^+]$ corresponds to the intrinsic bond energy between the Ln^+ with a configuration suitable for formation of a double bond with an oxygen atom, and the second term represents the energy needed to achieve that configuration. Assuming that the loss of 5d/6s and/or 5d/5d exchange energies upon bond formation is constant across the series, these exchange energy effects are incorporated into $BDE^*[LnO^+]$ (as would also be any energy that may be needed to excite the ground state oxygen atom to its bonding configuration). As with the neutral LnO species, no provision is initially made for loss of 4f/5d or 4f/6s exchange energy because of the impracticality of accurately estimating this effect, particularly as a function of f-orbital occupancy; the issue of f-electron exchange energy is further discussed below.

The $4f^{n-2}5d6s$ and $4f^{n-2}5d^2$ are the two lowest-lying divalent configurations for all of the Ln^+, except for Lu^+ where the $4f^{14}6s6p$ configuration is 25 kJ/mol lower in energy than the $4f^{14}5d^2$ configuration. As with the neutrals, the valence 6p electrons do not appear to play a significant role in bonding in the monoxide ions. Close examination of Figure 2, particularly for the second half of the series, would seem to suggest that the inverse correlation between bond energies and promotion energies may be better for the $4f^{n-2}5d^2$ configurations, as is borne out by the following calculations.

The $BDE[LnO^+]$ were calculated using eq 2 for both the $4f^{n-2}5d6s$ and $4f^{n-2}5d^2$ configurations, and the results are given in Table 2. As with the neutral LnO, LaO^+ has been employed as the prototype to establish the intrinsic bond energy, $BDE^*[LnO^+]$ using the experimental $BDE[LaO^+]$ of 847 kJ/mol. Because ΔE[ground → 5d6s] (ΔE[5d6s]) is 24 kJ/mol and $\Delta E[\text{ground} \rightarrow 5d^2]$ ($\Delta E[5d^2]$) is zero for La^+, the derived $BDE^*[LnO^+]$ are 871 kJ/mol (i.e., {847 + 24} kJ/mol) for ΔE[5d6s] and 847 kJ/mol for $\Delta E[5d^2]$.

For each of the calculated BDE[5d6s] and $BDE[5d^2]$, the deviation from the corresponding experimental $BDE[LnO^+]$ is included in brackets in Table 2. The agreement is exact for both calculated values for LaO^+ only because the $BDE^*[LnO^+]$ were defined using LaO^+ as the prototype. For the other 13 LnO^+ for which comparisons can be made (no experimental $BDE[PmO^+]$ is available), the average deviation between the

TABLE 2: Lanthanide Ion Electronic Parameters and Bond Dissociation Energies[a]

	ground[b]	ΔE[5d6s][b]	ΔE[5d^2][b]	BDE[LnO$^+$][c]	BDE[5d6s][d]	BDE[5d^2][d]
La	5d^2	24	0	847 ± 15	847 {0}	847 {0}
Ce	4f5d^2	28	0	849 ± 15	843 {−6}	847 {−2}
Pr	4f^{3}6s	94	70	792 ± 15	777 {−15}	777 {−15}
Nd	4f^{4}6s	135	110	749 ± 15	736 {−13}	737 {−12}
Pm	4f^{5}6s	(131)	(114)	NA	(740)	(733)
Sm	4f^{6}6s	227	227	565 ± 15	644 {+79}	620 {+55}
Eu	4f^{7}6s	361	438	389 ± 15	510 {+121}	409 {+20}
Gd	4f^{7}5d6s	0	48	732 ± 15	871 {+139}	799 {+67}
Tb	4f^{9}6s	39	106	718 ± 15	832 {+114}	741 {+23}
Dy	4f^{10}6s	127	234	593 ± 15	744 {+151}	613 {+20}
Ho	4f^{11}6s	137	275	598 ± 15	734 {+136}	572 {−26}
Er	4f^{12}6s	128	283	579 ± 15	743 {+164}	564 {−15}
Tm	4f^{13}6s	198	368	478 ± 15	673 {+195}	479 {+1}
Yb	4f^{14}6s	319	538	372 ± 15	552 {+180}	309 {−63}
Lu	4f^{14}6s^2	141	351	520 ± 15	730 {+210}	496 {−24}

[a] All energies are in kJ/mol. [b] The electronic configurations and excitation energies are from ref 8, except for the estimates for Pm.[24] [c] Experimental bond dissociation energies from ref 13; no experimental value is available (NA) for PmO. [d] The BDE[5d6s] and BDE[5d^2] were calculated using eq 2 as described in the text. The numbers in brackets are the deviations of the calculated from the experimental values. Calculated values based on other models are available, including for PmO$^+$, as discussed in the text.

experimental and calculated values is 117 kJ/mol for BDE[5d6s] and 26 kJ/mol for BDE[5d^2]. The values calculated using the two excitation energies are in good agreement for the early lanthanides, through SmO$^+$, as would be expected from the near coincidence of the excitation energy curves for the early lanthanides in Figure 2. For the lanthanides beyond Sm, each of the calculated BDE[5d6s] differs from the experimental values by more than 100 kJ/mol.

Among the calculated BDE[5d^2] for the LnO$^+$, the greatest discrepancy from the experimental values is for GdO$^+$. This may be related to the distinctive ground state 4f^{7}5d6s configuration of Gd$^+$ which has a half-filled 4f^7 subshell with seven unpaired f electrons. Because inclusion of 4f/5d exchange energy terms would decrease the predicted bond energies to the greatest extent for those Ln$^+$ with the most unpaired 4f electrons, the positive deviations of BDE[6d^2] from the experimental values for SmO$^+$, EuO$^+$, GdO$^+$, TbO$^+$, and DyO$^+$ may be related to the neglect of the 4f exchange energy loss. If it is assumed that the 4f/5d exchange energy for the 4f^{n-2}5d^2 configuration, ΔE[4f^{n-2}/5d^2], is a linear function of the number of unpaired 4f electrons, N_f, then the +67 kJ/mol discrepancy for BDE[5d^2] in the case of GdO$^+$ can be used to obtain ΔE[4f^{n-2}/5d^2] = {1/7 × 67 kJ/mol} ≈ 10 kJ/mol per 4f electron. Cornehl et al.[4] inferred a much larger value for the {4f/5d + 4f/6s} exchange energy of 29 kJ/mol per 4f electron by using the difference between of the calculated and experimental BDE[CeO$^+$]. Using the exchange energy per 4f electron derived here, the BDE[5d^2] in Table 2 can be recalculated incorporating the 4f/5d exchange energy term in eq 3:

$$\mathrm{BDE[LnO^+]} = \mathrm{BDE^*[LnO^+]} - \Delta E[5d^2] - (N_f)(10\ \mathrm{kJ/mol}) \tag{3}$$

The BDE[LnO$^+$] obtained according to eq 3 are all smaller than the experimental values, with the exceptions of perfect agreement for BDE[LnO$^+$] and BDE[GdO$^+$], which were employed to obtain the BDE*[LnO$^+$] (847 kJ/mol) and ΔE[4f^{n-2}/5d^2] (10 kJ/mol) used in eq 3. The average deviation from the experimental BDE[LnO$^+$] increases from 26 kJ/mol using the BDE[5d^2] and eq 2, to 31 kJ/mol using eq 3, and to 33 kJ/mol if BDE[GdO$^+$] is excluded as it was used in the parametrization of eq 3. The conclusion is that although the loss of 4f/5d exchange energy may play a role in decreasing the bond energies for certain LnO$^+$ and LnO, it does not appear practical at this point to reliably quantify this effect across the series.

The BDE[LnO$^+$] derived by Cornehl et al.[4] using ΔE[5d6s] and terms for the 5d/6s, 4f/5d, and 4f/6s exchange energies exhibit substantially greater deviations from the experimental values than do the calculated BDE[5d^2] values in Table 2. Because no experimental BDE[PmO] or BDE[PmO$^+$] are given here, it should be noted that the experimental BDE[PmO$^+$] cited in ref 4 is not actually a measured valued but was obtained from an interpolation by Kordis and Gingerich.[25] This estimate[4] for BDE[PmO$^+$] of 674 ± 67 kJ/mol is 59 kJ/mol lower than the BDE[5d^2] for PmO$^+$ of 733(±60) kJ/mol derived from the present analysis. Koyanagi and Bohme[26] studied the reaction of lanthanide ions with N$_2$O and identified a correlation of the reaction rates with the promotion energies to the presumed 4f^{n-2}5d6s bonding configuration at the metal center in the LnO$^+$ products. However, quantification of this correlation required the assumption that the efficiencies of electronic excitation for the early and late lanthanides are entirely disparate, purportedly because of the differing 4f-electron populations.[26] This correlation[26] is intriguing but does not appear to provide evidence that the 4f^{n-2}5d6s configuration is indeed the bonding configuration at the lanthanide center in the LnO$^+$.

The calculated BDE[5d^2] for YbO$^+$ (Table 2) is only 309 kJ/mol, 63 kJ/mol less than the experimental bond energy. This calculated value is less than would be expected for a single metal−oxygen bond (e.g., BDE[BaO$^+$] = 389 kJ/mol[23]). In those cases where the metal ion promotion energy to a divalent bonding state is so large that the resulting bond energy is less than that for a single bond, promotion would not be expected, and only a single bond should be formed using the single unpaired valence electron at the metal center. In support of this, the experimental BDE[YbO$^+$] of 372 ± 15 kJ/mol is only 17 kJ/mol lower than BDE[BaO$^+$]. Evidently a ground-state Yb$^+$ ion combines with an oxygen atom to produce a single Yb$^+$−O bond using the unpaired 6s electron at the metal center. The calculated BDE[5d^2] for EuO$^+$ is 409, whereas the experimental BDE[EuO$^+$] is 389 ± 15 kJ/mol, identical to BDE[BaO$^+$]; the europium ion−oxygen bond may also be of single character. When the calculated bond energy is significantly less than 450 kJ/mol, the model employed in the present assessment is likely inapplicable. When the calculated bond energy for YbO$^+$ of 309 kJ/mol is excluded from consideration, the average deviation between the calculated and experimental values for the remaining LnO$^+$ (excluding LaO$^+$ and PmO$^+$) decreases to 23 kJ/mol. The predicted BDE[YbO$^+$] employing Δ[5d6s], rather

TABLE 3: Actinide Atom Electronic Parameters and Bond Dissociation Energies[a]

	ground[b]	$\Delta E[6d^x7s]$[b]	$\Delta E[6d^27s^y]$[b]	BDE[AnO]	$BDE[6d^x7s]$[c]	$BDE[6d^27s^y]$[c]
Ac	$6d7s^2$	110 {2}	110	(794)[d]	720	720
Th	$6d^27s^2$	66 {3}	0	877[e]	764 {−113}	830 {−47}
Pa	$5f^26d7s^2$	84 {2}	24	788[f]	746 {−42}	806 {+18}
U	$5f^36d7s^2$	75 {2}	75	755[e]	755 {0}	755 {0}
Np	$5f^46d7s^2$	85 {2}	85	731[g]	745 {+16}	745 {+16}
Pu	$5f^67s^2$	162 {1}	178	661[h]	661 {0}	652 {−9}
Am	$5f^77s^2$	173 {1}	245	553[i]	657 {+104}	585 {+32}
Cm	$5f^76d7s^2$	121 {2}	121	728[j]	709 {−19}	709 {−19}
Bk	$5f^97s^2$	205 {1}	257	(598)[d]	625	573
Cf	$5f^{10}7s^2$	240 {1}	377	(498)[d]	590	453
Es	$5f^{11}7s^2$	275 {1}	430	(460)[d]	555	400
Fm	$5f^{12}7s^2$	311 {1}	466	(443)[d]	519	364
Md	$5f^{13}7s^2$	(335) {1}	(610)	(418)[d]	(495)	(220)
No	$5f^{14}7s^2$	(359) {1}	(729)	(268)[d]	(471)	(101)
Lr	$5f^{14}7s^27p$	(329) {dsp}	(406)	(665)[d]	(501)	(424)

[a] All energies are in kJ/mol. [b] The electronic configurations and excitation energies are from ref 27. The value of x for $\Delta E[6d^x7s]$ is given in brackets. The value of y for $\Delta E[6d^27s^y]$ is 2 for Th and Pa, and 1 for all other An. [c] The $BDE[6d^x7s]$ and $BDE[6d^27s^y]$ were calculated using a relationship analogous to eq 1 in the text. The numbers in brackets are the deviations from the experimental values. The calculated values for MdO, NoO, and LrO, in parentheses, are extrapolations outside of the range of the model. [d] Estimate from ref 21. [e] Reference 23. [f] Reference 28. [g] Reference 29. [h] The preferred BDE[PuO] is from the evaluation of Hildenbrand et al.[30] rather than from a recent measurement,[31] based on mass spectrometric studies of plutonium oxide thermochemistry.[32,33] [i] Reference 33. [j] Reference 34.

than $\Delta[5d^2]$, is 552 kJ/mol which is 180 kJ/mol larger than the experimental value. This suggests that the $4f^{n-2}5d6s$ configuration is not suitable for double bond formation with oxygen, and instead a single bond is formed in YbO^+.

In view of the conclusion that promotion to the prepared divalent configuration at the metal center is a valid model only when the predicted bond energy exceeds the single bond energy, the results for the neutral monoxides deserve comment in this regard. The BDE[CsO] of 282 kJ/mol[23] is significantly smaller than BDE[BaO^+] and can be considered as a typical single bond energy for heavy metal neutral monoxides. The calculated BDE[YbO] of 380 kJ/mol is greater than this single-bond energy, suggesting that the Yb−O bond is of a double character. The possibility of single-bond formation for the neutrals can furthermore be excluded based on electronic considerations. The ground state of Yb, $4f^{14}6s^2$, has its two outer valence electrons in a closed $6s^2$ subshell, so that excitation to a prepared divalent state must occur for formation of even a single bond; accordingly, a more energetically favorable double bond can be presumed. It is only when the ground-state configuration at the metal center comprises a spin-unpaired outer valence electron that bond formation may occur without electronic excitation. This condition is not fulfilled for most of the neutral Ln, which have a $4f^{n-2}6s^2$ ground-state configuration (see Table 1).

Bond Dissociation Energies of Neutral Actinide Monoxides. For the actinides, experimental knowledge of monoxide bond dissociation energies, BDE[AnO], is very limited, and a plot analogous to that in Figure 1 cannot be created. It is desirable to estimate the unknown actinide monoxide bond dissociation energies, and we propose that the model used for the 4f-lanthanide monoxides should also be applicable to the 5f-actinide monoxides. The validity of the model that most reliably predicted the BDE[LnO] can be assessed based on the few known BDE[AnO]; these experimental values are included in Table 3. Spectroscopic energies of actinide atomic energy levels are known for the actinides through Fm[27] and have been estimated for Md, No, and Lr.[12] For the neutral lanthanide atoms, the $4f^{n-3}5d^26s$ configurations were the lowest-lying states with two valence 5d electrons. In analogy, the $5f^{n-3}6d^27s$ configurations are the lowest-lying states with two valence 6d electrons for most of the actinide atoms, where "n" for the actinides represents the total number of electrons outside of the closed radon core, $n = 3$ for Ac, $n = 4$ for Th, etc. Two exceptions to the generalization regarding the lowest-lying relevant configurations are Th and Pa, for which the $6d^27s^2$ and $5f6d^27s^2$, respectively, are the lowest lying configurations that have two 6d electrons available for bonding. The results for the LnO^+ indicated that it is the two $5d^2$ electrons, and not the unpaired 7s electron, that participate in formation of the $Ln^+{=}O$ formally double bond. Accordingly, for Th and Pa, the energies of the $6d^27s^2$ and $5f6d^27s^2$ configurations are considered in the assessment, and the relevant promotion energy in Table 3 is $\Delta E[6d^27s^y]$ where $y = 2$ for Th and Pa and $y = 1$ for all other An. For the lanthanide atoms, the lowest lying configurations with one valence 6s electron and at least one valence 5d electron are either $4f^{n-2}5d6s$ or $4f^{n-3}5d^26s$; the latter cases are noted in Table 1. For the actinide atoms, the lowest-lying configuration with one valence 7s electron and at least one valence 6d electron is either $5f^{n-2}6d7s$ or $5f^{n-3}6d^27s$ (except for Th which has a lower-lying $6d^37s$ configuration and Lr which has a lower-lying $5f^56d7s7p$ configuration[12]). The $\Delta E[6d^x7s]$ given in Table 3 are for $x = 1$, 2, or 3 (Th), with the value of x indicated in brackets, with the distinctive exception of Lr for which "$\Delta E[6d^x7s]$" is actually $\Delta E[6d7s7p]$. Having defined $\Delta E[6d^x7s]$ and $\Delta E[6d^27s^y]$ for the actinides, these energies are given in Table 3. The BDE[AnO] are calculated employing a modified eq 1 in which "Ln" is replaced by "An."

Because no accurate experimental value for BDE[AcO] is available, the intrinsic BDE*[AnO] cannot be derived in analogy with the derivation of BDE*[LnO] from the known BDE[LaO]. Reliable BDE[AnO] are available for An = Th and U.[23] It would appear more appropriate to employ the experimental BDE[UO], rather than BDE[ThO], to derive an intrinsic BDE*[AnO]. The primary basis for this preference is that the distinctive electronic structure and energetics of the Th atom, as discussed above, suggest that Th may not be a characteristic actinide. The general character of thorium as a d block, rather than an f block, transition element has been discussed elsewhere.[35] The BDE*[AnO] derived using BDE[ThO] and the actinide equivalent of eq 1 are 943 kJ/mol using $\Delta E[6d^x7s]$, and 877 kJ/mol using $\Delta E[6d^27s^y]$. The BDE*[AnO] of {755 kJ/mol + 75 kJ/mol} = 830 kJ/mol obtained using $\Delta E[6d^x7s] = \Delta E[6d^27s^y]$ in the case of uranium is nearly identical to the BDE*[LnO] = 827 kJ/mol derived above. Such similar BDE*[LnO] and BDE*[AnO] might be expected based on the corresponding comparison between LaO and YO. Using BDE[YO] = 714 kJ/mol from

Sievers et al.[15] and ΔE[$4d5s^2$ (ground) $\rightarrow$ $4d^25s$] = 131 kJ/mol for the neutral Y atom from Moore,[36] an intrinsic BDE*[YO] of {714 + 131} = 845 kJ/mol is obtained. This BDE*[YO] is only 18 kJ/mol greater than the BDE*[LaO] = 827 kJ/mol derived above, and a similar correspondence between BDE*[LnO] and BDE*[AnO] would seen reasonable as Ac is the heavier homologue of La. In further support of using BDE[UO] to derive BDE*[AnO], it is noted that the deviations from the few known BDE[AnO] (except for ThO) are all greater if ThO is employed as a prototype. As for the lanthanides, the loss of d/s and/or d/d exchange energy upon bond formation is implicitly included in the derived BDE*[AnO]. Because the uranium atom, unlike actinium, has three 5f electrons in both the $5f^36d7s^2$ ground state and the $5f^36d^27s$ excited state, the derived BDE*[AnO] may also incorporate some loss of 5f/6d and/or 5f/7s exchange energy. However, any variation in this quantity with 5f-orbital occupancy is not included in the assessment because of the uncertainties in accurately estimating this variable energy loss. Although significant bonding participation of the quasivalence 5f electrons is not expected for small actinide molecular species, some 5f participation for the light actinides may be feasible and neglect of this possibility in the present treatment should be noted.

In accord with the lanthanide results, the comparisons between the calculated and experimental BDE[AnO] in Table 3 suggest that excitation to a $6d^2$ configuration with two valence d electrons available for formation of the An−O bond better predicts the actinide monoxide bond energies. With the exception of PuO, where both calculations exhibit very good agreement with the experimental value, the deviation from experiment is smaller, or necessarily identical where ΔE[$6d^x7s$] = ΔE[$6d^27s^y$], when the $6d^2$ configuration energy is employed. The greatest deviation is for BDE[ThO] which may be related to the electronic considerations discussed above. The much better agreement in the case of BDE[AmO] particularly supports the use of the $6d^2$ configuration as the bonding configuration. The good agreement between the experimental and predicted BDE[PaO] suggests that the 7s electrons do not play a significant role in the bonding because the $6d^2$ configuration in the case of Pa is $6d^27s^2$, in which the two 7s electrons are paired. The simplistic picture of two electrons remaining in a filled inert $7s^2$ orbital at the metal center in PaO may be unrealistic; instead, it may be that the 7s orbitals of Pa hybridize with empty 6d orbitals to enable effective bonding.

For AcO and all of the transcurium AnO, experimental BDEs are not available. The lanthanide results indicated that the BDEs could be accurately predicted by assuming excitation to a $5d^2$ rather than a 5d6s configuration, even when the $5d^2$ promotion energy was greater than the 5d6s promotion energy by as much as 219 kJ/mol, as in the case of Eu. In cases where the promotion energy difference exceeds this value, it cannot be confidently assumed that the model will remain valid. Instead, it is feasible that the additional promotion energy is not offset by the evidently more efficient bonding of a metal center with a $6d^2$ configuration. For Ac, Bk, Cf, Es, and Fm, the $6d^2$ bonding configuration is <200 kJ/mol higher in energy than the 5d6s configuration, and the calculated BDE[AnO] for these five actinides in the final column of Table 3 are considered accurate to within ±50 kJ/mol. For Md, No, and Lr, the promotion energies are only estimates. For Md and No, the estimated $6d^2$ promotion energies exceed the 6d7s promotion energies by >250 kJ/mol, and for Lr, the ground and excited state energetics are unique among the f elements, as is evident from Table 3. For these reasons, the parenthetical BDE[AnO] given in Table 3 for the three heaviest actinides are not considered reliable, though these results are intriguing. It would be particularly interesting to obtain experimental BDE[AnO] for CfO, EsO, and FmO in view of the large discrepancies between the values predicted based on promotion to the 5d6s and $5d^2$ divalent configurations. The BDE[$6d^27s^y$] estimates from the model employed here are in accord with the experimental observations reported by Haire.[21,22] In that work, the An^+/AnO^+ ion intensity ratios were obtained by electron impact ionization mass spectrometry of the high-temperature vapor species in equilibrium with solid Am_2O_3, Cm_2O_3, Bk_2O_3, Cf_2O_3, and Es_2O_3. The qualitative nature of those experimental results precludes any quantitative comparisons with the present bond energy estimates. Haire also estimated unknown BDE[AnO][21,22] using the parametrized approach developed by Murad and Hildenbrand;[20] these estimates are included in Table 3.

TABLE 4: Actinide Ion Electronic Parameters and Bond Dissociation Energies[a]

	ground[b]	ΔE[6d7s][b]	ΔE[$6d^2$][b]	BDE[AnO^+]	BDE[6d7s][c]	BDE[$6d^2$][c]
Ac	$7s^2$	57	158	NA	753	704
Th	$6d^27s$	0 [$6d^27s$]	0 [$6d^27s$]	875[d]	810	862
Pa	$5f^27s^2$	10	57	NA	800	805
U	$5f^37s^2$	3	55	807[d]	807	807
Np	$5f^46d7s$	0	84 ± 36	773 ± 43[d]	810	778 ± 36
Pu	$5f^67s$	104	207	683 ± 55[e]	706	655
Am	$5f^77s$	245	347 ± 24	560 ± 30[f]	565	515 ± 24
Cm	$5f^77s^2$	48	177	NA	762	685
Bk	$5f^97s$	148	263 ± 36	NA	662	599 ± 36
Cf	$5f^{10}7s$	(289)	406 ± 48	NA	(521)	456 ± 48

[a] All energies are in kJ/mol. “NA” indicates that an experimental BDE is not available. [b] The electronic configurations and excitation energies are from ref. 27. For Th^+, both ΔE[6d7s] and ΔE[$6d^2$] are taken as zero because the ground state is $6d^27s$. [c] The BDE[6d7s] and BDE[$6d^2$] were calculated using a relationship analogous to eq 2, as described in the text. The specified uncertainties for some of the BDE[$6d^2$] reflect only the additional uncertainty introduced from the ΔE[$6d^2$], not the inherent uncertainty. [d] Reference 23. [e] Reference 30. [f] Reference 33.

Bond Dissociation Energies of Actinide Monoxide Monopositive Ions. It is also reasonable to use the model developed above to predict bond energies for actinide monoxide monopositive ions, BDE[AnO^+]. These bond energies can be measured by various mass spectrometric techniques but the existing data on BDE[AnO^+] is quite limited, with only BDE[ThO^+] = 875 ± 16 kJ/mol and BDE[UO^+] = 807 ± 22 kJ/mol[23] known with reasonably good accuracy. Other reported experimental values for BDE[AnO^+] are given with their associated uncertainties in Table 4. As with the neutrals, it is considered appropriate to employ UO^+ as a prototypical AnO^+ in the absence of an experimental BDE[AcO^+]. The analogous relationship to eq 2 for the lanthanides is applied to the AnO^+, where the two relevant promotion energies are to the $5f^{n-2}6d7s$ ($6d^27s$ for Th^+) and $5f^{n-2}6d^2$ ($6d^27s$ for Th^+) configurations, ΔE[6d7s] and ΔE[$6d^2$]. The spectroscopically determined configuration energies are also less well established for most of the transuranium actinide ions, An^+, compared with the neutrals.[27] In those cases where these uncertainties are greater than ~10 kJ/mol, they are included with the excitation energies, ΔE values, given in Table 4. From the experimental BDE[UO^+], two intrinsic bond dissociation energies are obtained: BDE*[AnO^+] = 810 kJ/mol for the $5f^{n-2}6d7s$ configuration and BDE*[AnO^+] = 862 kJ/mol for the $5f^{n-2}6d^2$ configuration. The latter value is close to the corresponding BDE*[LnO^+] (i.e., 862 vs 847 kJ/mol), whereas the former is not (i.e., 810 vs 871 kJ/mol), supporting the hypothesis that it is the $5d^2$ configuration that is relevant to $An^+{=}O$ bond formation.

The results are summarized in Table 4 where the indicated error limits on selected BDE[6d^2] represent only the additional uncertainty introduced from the spectroscopic ΔE[6d^2], not the base uncertainty inherent to the approach. In view of the large uncertainties in the promotion energies for the heavy An$^+$, the calculated results are given only through Cf. Because of the relatively large uncertainties in some of the experimental BDE[AnO$^+$] and/or the calculated BDE[6d^2], it is impractical to effectively evaluate whether the calculated BDE[6d7s] or BDE[6d^2] better reflect the actual bond energies. For ThO$^+$, the 6d^2 value is significantly closer to the experimental value than is the 6d7s value, but thorium is not considered a particularly representative actinide. For NpO$^+$, PuO$^+$, and AmO$^+$, the error limits are too large compared with the differences between BDE[6d7s] and BDE[6d^2] to establish that the latter are more reliable; the greater reliability BDE[6d^2] in Table 4 can only be presumed based on the lanthanide and neutral actinide oxide results. Accordingly, the values in the final column of Table 4 are considered the best available estimates for the AnO$^+$ bond energies. It is emphasized that, in addition to the indicated uncertainties, there is an inherent additional uncertainty for all of the calculated values in Table 4 which is estimated as up to ±60 kJ/mol based on the evaluations for lanthanide and neutral actinide monoxides.

Summary and Conclusions

A model for covalent bond formation by lanthanide and actinide atoms and ions has been refined and employed to predict unknown monoxide bond energies. The general approach is in accord with observations by Scott and Richards[37] regarding bonding in transition metal hydrides. The correlation between metal−ligand bonding and the electronic structures and energetics of metal ions was further elaborated by Armentrout et al.[38] Subsequently, Carter and Goddard[3] related d-block transition metal organometallic bond energies, BDE[M$^+$−C], to the electronic structures and energetics of the free metal ion, M$^+$. This model was applied to the lanthanide monoxide ions, LnO$^+$, by Cornehl et al.[4] The analysis presented here for the neutral LnO molecules and their monopositive ions, LnO$^+$, has led to the conclusion that the Ln−O and Ln$^+$−O bonds are evidently formed using two 5d electrons, rather than one 5d and one 6s electron.[4] This implications of this conclusion are intriguing and cast some doubt on the assumption that it is necessarily the 4f^{n-2}5d6s lanthanide metal ion configuration that is required for gas-phase bond activation.[4,11]

The bond energies calculated according to the model described here are generally close to the experimental values. As there is no experimental value for BDE[PmO] that given in the final column of Table 1 is of special interest. Using the model described here, an estimate of BDE[PmO] = 698 ± 40 kJ/mol is obtained. For comparison, Kordis and Gingerich[25] estimated BDE[PmO] ≈ 644 kJ/mol, this being the average of their experimental values for BDE[NdO] and BDE[SmO]. Haire[21,22] has estimated BDE[PmO] ≈ 711 kJ/mol.

In the present analysis, the intrinsic lanthanide monoxide bond energy, BDE*[Ln−O] was taken as 827 kJ/mol, the sum of the experimental BDE[La−O] = 795 kJ/mol and ΔE[5d^{2}6s] = 32 kJ/mol for La (Table 1). A general intrinsic BDE*[Ln−O] can be obtained by summing the experimental BDE[Ln−O] and ΔE[5d^{2}6s] for each of the lanthanides and determining the average. Using the values given in Table 1 for the 13 Ln excluding Pm and Lu (for the reasons discussed in the text), a BDE*[LnO] = 827 ± 21 kJ/mol is obtained, the same value as was derived using LaO alone. The analogous exercise using the experimental BDE[LnO$^+$] and ΔE[5d^2] from Table 2 for the 12 Ln excluding Pm, Yb, and Lu (see text) yields an average intrinsic BDE*[LnO$^+$] = 837 ± 29 kJ/mol, a value 10 kJ/mol smaller than the value derived using BDE[LaO$^+$] = 847 kJ/mol and ΔE[5d^2] = 0.

The model successfully demonstrated here for the lanthanides was applied to the actinides, where experimental information is sparse and/or less well-established because of experimental constraints. Employing UO and UO$^+$ as prototypes, bond energies were estimated for other AnO and AnO$^+$, with the values given in the final columns of Tables 3 and 4. As indicated in Table 3, it is not reasonable to confidently extrapolate to cases such as NoO, where the predicted bond energy of only 101 kJ/mol is outside of the demonstrated range of applicability.

The relationship between ionization energies (IEs) and bond energies in eq 4 indicates that the difference between IE[MO] and IE[M] is related directly to that between BDE[MO] and BDE[MO$^+$]:

$$\mathrm{IE[MO]} - \mathrm{IE[M]} = \mathrm{BDE[MO]} - \mathrm{BDE[MO^+]} \qquad (4)$$

If IE[M] is known, then IE[MO] can be calculated using the two monoxide bond energies. With the typical exceptions of the distinctive lanthanides, Gd and Lu, the inference is that the IE[Ln] and IE[LnO] are within ~0.5 eV of one another.[13] Similar agreement within 0.5 eV is found for IE[An] and IE[AnO] using both the experimental BDEs and those calculated in the present work, providing an additional indication that the nature of the bonding in the lanthanide and actinide monoxides is similar and that the same model should be applicable to both series. Based on the inferred bonding configuration of f^{n-3}d^{2}s for the MO and f^{n-2}d^2 for the MO$^+$, the similarity between the atomic and monoxide ionization energies may be attributed to the removal of a nonbonding valence 6s electron from the LnO and a 7s electron from the AnO to achieve ionization. Murad and Hildenbrand[20] similarly concluded primarily 5d-electron bonding in lanthanide monoxides, and ionization by removal of a nonbonding 6s electron, based on their assessment of the relevant electronic considerations. From the present work, it is concluded that the intrinsic lanthanide and actinide monoxide bond energies vary little across the series and that two valence d electrons, 5d^2 for the Ln and 6d^2 for the An, are required for effective f-element bonding in both M−O and M$^+$−O.

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