Structure and Electronic Properties of Ca-Doped CeO₂ and Implications on Catalytic Activity: An Experimental and Theoretical Study

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Doping CeO_2 with for example, Ca gives an enhanced reactivity toward reduction of SO₂ by CO, and total combustion of methane. Theoretical modeling using static minimizations and molecular dynamics (MD) simulations of the doped (110) face in combination with ab initio quantum chemical cluster models shows large effects on the Ce(IV)/Ce(III) balance due to the doping. Computed oxygen-to-cerium charge-transfer energies are strongly reduced as a result of the introduction of defects and oxygen vacancies, but not sufficiently to explain the observed reactivities. The structures resulting from the MD simulations for both the doped and undoped material are in good agreement with recent experimental pulsed neutron scattering results.

I. Introduction

One of the most important groups of materials for heterogeneous catalysis is that of the metal oxides. Understanding the mechanisms of catalyzed reactions over metal oxide surfaces and the influence of different material characteristics on the performance of the catalyst is therefore of central importance for future rational catalyst development. Cerium oxide (CeO₂) is commercially an important part of both oil-refining catalysts and automotive exhaust gas converters. It is also used as an oxidation catalyst for combustion of carbonaceous deposits in diesel exhaust gas particulate traps and as an oxygen and electron-transfer agent in catalysts for the ammoxidation of propylene in the production of acrylonitrile.¹ The ability of CeO₂ to store oxygen is utilized in the three-way car catalysts (TWC) for increasing the width of the lambda window, i.e., to increase the working range of redox conditions in which the catalyst is able to simultaneously convert NO_x, CO and unburned hydrocarbons to harmless products.² Its function in this application is, however, possibly more complicated than that of a simple oxygen storage component.¹

In principle, it should be possible to engineer, at the atomic level, active sites on a metal oxide surface to give a catalyst desired selectivity and activity for certain reactions; such an experimentally based molecular approach for enhancing the reactivity of cerium oxide by introduction of dopants has also recently been suggested.³ In this approach, cation dopants with oxidation states lower than +IV are incorporated in the lattice of CeO₂ leading to the formation of oxygen vacancies. The chemical and physical properties of these depend on the type of dopants introduced, where for example, the size of the vacancies can be expected to depend much on the size of the dopant; the concentration of oxygen vacancies depends on the oxidation state of the dopant, and the mobility of the oxygen

vacancy depends on the association energy between the vacancy and its surrounding. Furthermore, the local structures of the surface, as well as that of the bulk, of the doped samples are believed to depend on several properties of the dopant, such as its oxidation state, electronegativity, and size. The introduction of dopants in the CeO₂ lattice can thus be expected to affect both the oxygen-transfer and the electron-transfer characteristics of CeO₂.

For a more detailed understanding of the effects of dopants and the origin of the enhanced (or reduced) reactivity of these modified materials we believe that experiment need to be complemented by theoretical/computational studies. An atomic level description of the activity of a material as complex as doped CeO₂ requires consideration of the dopant effects on both the geometrical and electronic structures, especially for the surface layers. The particular approach taken in the present work is therefore to perform both static (energy minimization) and dynamical (including temperature effects) simulations of the crystal structure and then build quantum chemical embedded cluster models of different sites resulting from the simulations; the structures obtained from the molecular dynamics simulations are fed directly into the quantum chemical modeling program. Thus, the structural effects induced by the doping, such as the local geometry around vacancies and defects, are obtained from molecular dynamics (MD) simulations of a slab model exposing the desired crystal face, while the effects on the electronic structure of the material, mainly the availability of Ce(III) relative to Ce(IV), are investigated using fully quantum chemical methods. The structural results from the MD simulations on the bulk materials are supported by results from pulsed neutron scattering studies.

Due to its technological importance, CeO_2 has been the subject of a rather large number of earlier investigations where static simulation techniques have been applied.^{4–8} Since CeO_2 is a well-known oxygen storage material much of the interest

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has focused on determinations of oxygen transport and diffusion rates, but the charge-transfer properties and concomitant reduction of Ce(IV) to Ce(III) have also been of great interest. In two recent papers Balducci et al.^{7,8} discuss the properties of solid solutions of CeO₂ -ZrO₂ and find that the introduction of zirconia into the ceria lattice strongly lowers the reduction energy of Ce(IV); the resulting values are still positive, however.

The importance and usefulness of the experimental approach to use dopants for oxygen vacancy engineering has been verified experimentally for CeO₂ for three types of reactions. First, the oxygen storage capacity (OSC) was found to increase by 20– 40% by introducing dopants such as Ca, Nd, Pb, etc.⁹ Second, the light-off temperature for the reduction of SO₂ by CO to form elementary sulfur and CO₂ was lowered by 70 °C by doping CeO₂ with 10% Ca²⁺ as elaborately discussed in ref 10. Third, the activity for total oxidation of methane was also found to increase by doping with Ca, Mn, and Nd, whereas Pb-doping was found to decrease the activity of the material for this reaction.¹¹ Several other metal oxides are also expected to be useful candidates as host matrixes for oxygen vacancy engineering, e.g., oxides of Bi, Mo, Nb, Pr, Ti, V, W, and Zr to name a few.

The present paper aims at illuminating the effects on the structural and electronic properties of cerium oxide upon introduction of Ca²⁺ ions, and on the implications of these effects on the catalytic activity for redox reactions, in a combined theoretical and experimental study. The theoretical treatment is based on a molecular dynamics simulation of the ion positions in a slab model of the surface, followed by a calculation of the electronic properties for a small cluster model embedded in the remaining periodic MD slab. The main result is that, as a result of the modified structure and coordination around the Ce ions as obtained from the molecular dynamics simulations, we find a substantially reduced charge-transfer excitation energy in the doped CeO₂ lattice. In other words, we find a much lowered cost for reducing Ce(IV) to Ce(III) after doping with Ca. This is in agreement with what has been reported earlier,^{7,8} but the resulting values for the energy cost (endothermicity), computed using high-level ab initio quantum chemical techniques, are still rather high. Thus, additional energy-lowering contributions must be considered in order to completely understand the observed reactivities.

The layout of the paper is as follows. In the Methods part we describe in order the experiments, the static and dynamic atomistic simulations, and finally the quantum-chemical calculations. The same sequence is followed in the Results section. The results are tied together in the Discussion and Summary sections.

II. Methods

A. Experimental. Nanophase cerium oxide solid solutions were prepared by coprecipitation of Ce and dopants in the form of oxalates followed by washing, drying, and calcination at 600 °C for 4.5 h in air. Details on the synthesis and characterization are given elsewhere.^{3,10} Chemical composition of the products was determined with an ARL 3520B inductively coupled plasma atomic emission spectrophotometer (ICP-AES). Experimental total neutron correlation functions T(r) were obtained through pulsed neutron scattering studies at the LAD instrument at the ISIS facility in the United Kingdom and details of these experiments and their interpretation are given elsewhere.¹² Catalytic activities were evaluated with a Micromeritics TPD/TPR 2900 Chemisorption Analyzer using a nearly stoichiometric reactant gas mixture containing 3.20% CO and 1.65% SO₂ in

He. The composition of outlet gas was analyzed with a Balzers mass spectrometer model QMG421C, and the CO and SO₂ gases were mixed just before the reactor inlet using two Brooks 5850E mass-flow controllers. The catalyst samples were pretreated in situ in a flow of air (600 °C, 30 min), after which they were cooled to room temperature before exposure to the reactant gas at a space velocity of 10 000 mL gas/h·g catalyst, and a temperature increase rate of 10 °C/min.

B. Atomistic Simulations. In this section we will describe the different aspects of the atomistic simulations of the bulk and surface models of CeO₂, both doped and undoped. Both static and dynamic simulations were performed on the basis of the same set of potential parameters that were taken from the literature. The pure CeO₂ bulk lattice has the well-known fluorite structure, in which each Ce⁴⁺ cation is surrounded by eight equivalent O²⁻ ions forming the corners of a cube, and with each O²⁻ coordinated to four Ce⁴⁺. The experimental lattice parameter is 5.41 Å leading to a Ce–O distance in the bulk of 2.343 Å.¹³ The (110) terminated CeO₂ surface-layer consists of 6-coordinated Ce⁴⁺ ions and 3-coordinated O²⁻ ions, and all planes parallel to the surface are charge neutral.

The programs used for the static simulations were GULP¹⁴ for the bulk structures while the MARVIN¹⁵ code was used for determining the relaxed surface structures. The MARVIN code was used to determine the relative stabilities of different faces of the CeO₂ crystal; the most interesting of these was then studied in the subsequent molecular dynamics simulations presented here. The MD simulations were performed using an in-house MD code.¹⁶

1. Interatomic Potentials. The interatomic potential parameters used in both the static energy minimizations and the MD simulations were those used by Sayle et al.⁵ in an earlier static modeling investigation of CeO₂. The $O^{2-}-O^{2-}$ and $Ca^{2+}-O^{2-}$ parameters in ref 5 were previously described by Lewis and Catlow,¹⁷ and the $Ce^{4+}-O^{2-}$ interaction in ref 5 is a modification of the potential by Butler et al.¹⁸ In the current paper the non-Coulombic cation-cation interactions were, as in the previous investigations, set to zero. The shell model¹⁹ was used to describe the polarization energy. In this model the polarizable ion is assigned two charges: one charge on the core (nucleus) and one charge on a displaceable shell which is linked to the core through a harmonic spring. In addition we have also, in the molecular dynamics simulations, assigned a fraction of the ion-mass to the shells of the ions, as first introduced by Mitchell and Fincham.²⁰

The Coulombic interaction was in all cases evaluated using the Ewald^{21–23} summation technique for 2-dimensional (slab models of surfaces) or 3-dimensional (bulk models) periodic systems, excluding the interaction between a core and its own shell.

The quality of the interaction potentials for the Ca-doped and undoped CeO₂ system was investigated by a comparison with experimental diffraction results. Thus, the crystallographic lattice parameter for the pure bulk crystal at 300 K obtained from the MD simulation was 5.42 Å, in very good agreement with the experimental value of 5.41 Å.¹³ Analysis of the pair distribution function, g(r), for the Ce–O distances from the 300 K MD simulation leads to an average r (Ce–O) of 2.33 Å to be compared to the 2.34 Å from the experimental structure.¹³ Upon 12.5% doping with Ca²⁺ ions the simulated cell expands by 2% in accordance with what has been found experimentally.¹²

A comparison between the pulsed neutron scattering data, T(r), and the MD results, G(r), (Figure 1), demonstrates a very good agreement, which will make a detailed analysis of the



Figure 1. Total neutron correlation functions for Ca-doped and undoped CeO₂. (a) Experimental T(r) curves from pulsed neutron scattering. (b) Molecular dynamics simulated total and partial pair distribution functions G(r).

structural peaks meaningful. In particular, the broadening of the peaks upon doping, the dopant-induced structures in the region 3-3.5 Å, and the shape of the peaks in the region from 3.5 to 4.5 Å are all well-reproduced by the simulation. Furthermore, the simulations allow a breakdown and detailed analysis of the individual ion contributions to the radial distribution functions which is invaluable for the analysis of the experimental data; the full, detailed analysis of the structure will be reported elsewhere.¹² We here conclude that the potential parameters and simulation procedures employed in this paper appear to give a realistic description of the bulk lattice structures for both the Ca-doped and undoped systems.

2. *MD Simulations*. Four oxide systems were investigated by MD simulations: two bulk systems (doped and undoped) and two slab systems (doped and undoped). The geometries of these systems will be discussed below. The MD simulations were performed with a constant-stress, constant-temperature molecular dynamics program for systems periodic in three and two dimensions, with dynamically variable lattice vectors (lengths and angle). The equations of motion for the box are handled by the Cleveland modification²⁴ of the Raman-Parrinello

scheme,^{25,26} ensuring a translationally invariant Hamiltonian. The Nosé-Hoover formalism^{27,28} was used for the constant temperature control. The Ewald summation technique for 2-dimensional periodic systems^{21–23,29} has been implemented for the slab simulations. Details about the MD program have been given elsewhere.¹⁶

All systems were equilibrated for 1.0 ps with temperature scaling invoked every tenth step, followed by production runs of 2 ps for the doped and undoped bulk and slab at 10 K, 8.5 ps for the undoped bulk and slab systems at 300 K and 24.5 ps for the doped bulk and slab systems at 300 K. All simulations used a time-step of 0.1875 fs. Such a short time-step was necessary to ensure the constancy of the Hamiltonian in these systems, where the ionic charges and interatomic forces are large; in particular the large charges in the shell model generate forces of a magnitude that make it necessary to use a small time step. The equilibration times of 1.0 ps appear to be sufficient for all our runs. For the 10 K runs, which essentially are energy minimizations, no changes were observed in thermodynamic, structural or dynamical parameters after the equilibration runs. The equilibrations at 300 K were started from previous simulations. Moreover, the cell volume and potential energy were monitored throughout the equilibrations and subsequent production runs, and were found to have stabilized well before the start of the production runs. Moreover, the positional order was monitored via a modification of Verlet's translational order parameter, which had stabilized already after half the equilibration time (0.5 ps). During the remaining equilibration time and during the subsequent production runs, all these quantities displayed appropriate fluctuations and no drifts. The resulting structures were then fed directly into the ab initio embedding program for the electronic structure calculations.

3. System Geometries. Within the MARVIN code the static simulation cell is repeated infinitely in two dimensions, x and y, with the free surface perpendicular to the z direction. The atoms in the "surface region" are allowed to relax while those in the "bulk region" are kept fixed. Here we studied the relative stabilities of the undoped (111), (110), (211), and (310) surfaces, and for reasons discussed in the Results section, we have chosen to concentrate on the (110) surface in the present study.

The MARVIN code was also used to investigate the interaction between dopant and vacancy for the (110) plane. The experimental investigation was done at 10% doping which was simulated by introducing one dopant—vacancy pair per two crystallographic unit cells, resulting in a doping level of 12.5%. Two different combinations of dopants and vacancies are then possible within this expanded cell; first, with the created oxygen vacancy next to the dopant and second, with the vacancy as far as possible from the dopant. The first situation can be seen as a neutral bound pair, while the second as an unbound pair.

MD simulations of the undoped CeO₂ (110) slab were performed at different temperatures. Since the (111) face shows the highest stability and furthermore has been shown to be inefficient for oxygen exchange,³⁰ we here selected to study only the (110) surface; the (211) and (310) faces could in principle also be of interest, but were excluded in the present work in order to perform a more complete simulation study of the (110) face. The pure CeO₂ (110) surface system in the MD simulations was described as a slab, 12 atomic layers thick and periodic in two dimensions (*x* and *y*), with faces perpendicular to *z* and -z. The *x*, *y*, and *z* directions are equivalent to the (0 0 1), (1–1 0) and (1 1 0) directions in the CeO₂ bulk crystal.



Figure 2. Definition of different embedded cluster surface models of doped CeO_2 in the full surface environment; atoms contained in the model cluster are highlighted. Cluster models 5A (right), 5B (center), and 5C (left) have five-coordinated central cerium ions, while clusters 6B (right), 6A (center), and 6C (left) represent fully coordinated surface cerium ions.

The MD box volume was $16 \times 15 \times 23$ Å³ and contained altogether 432 ions. All ions were allowed to move in the MD simulations.

The doped slab system in the MD simulations was doped with $1/8 \text{ Ca}^{2+}$ ions, as in the static simulations, and was then charge-balanced with oxygen vacancies. The initial configuration was taken from the ordered dopant-vacancy distribution found to give the lowest surface energy in the static calculations (namely "the bound pair"; note, however, that the "unbound pair" gave a slightly lower bulk energy). The dopants and the corresponding oxygen vacancies were introduced in such a way as to preserve the zero net dipole moment across the surface region; otherwise the total energy increases with increasing thickness of the slab and the surface energy is not defined.

MD simulations for the 3-dimensional CeO₂ bulk crystal (pure and doped) were performed to provide a reference for comparison with the undoped and doped slab systems. The MDbox for the undoped bulk system consisted of 324 ions and its volume was approximately $16 \times 16 \times 16$ Å³. The doped bulk system was doped with 1/9 Ca²⁺ ions, and was then chargebalanced with oxygen vacancies.

C. Ab Initio Cluster Calculations. In the present work, we have calculated the energies and several electronic properties of cerium ions in pure and calcium-doped cerium oxide crystals based on the structures obtained either from the pair-potential minimizations or from the MD simulations. It has been shown³¹ that relatively small and also nonstoichiometric clusters, if properly embedded, can provide a good model of the crystal. In the description of strongly ionic systems, an embedding of the cluster into a lattice of point-charges will lead to an artificial polarization of the anions in the cluster.³¹⁻³⁴ This may be avoided by a proper embedding scheme using effective core potentials (ECP) based on the frozen ionic charge distribution^{35–37} to describe the neighbors nearest to the cluster. In the present work we have used the AIMP embedding^{35,36} together with a representation of the crystal potential of the different lattices based on structures obtained either from the static or MD simulations. The crystal potential was included through evaluation of all integrals over the explicit Ewald²¹⁻²³ sums over the infinite crystal based on the simulation cell, always using the nominal ionic charge for the ions. The embedding scheme is based on total-ion model potentials which include an approximate description of all quantum mechanical and electrostatic interactions with the surrounding crystal. Thus, the short-range Coulomb (incomplete screening), exchange, and orthogonality interactions, together with the major relativistic effects (Darwin and Mass-velocity potentials) are included in the description.

In the different embedded cluster calculations, ions out to a certain distance from any cluster ion are represented by totalion model potentials; this distance was always larger than 13 Å to ensure a large enough buffering region between the cluster ions and the unscreened point-charges. To represent the bulk and (110) surface of undoped ceria, we have chosen embedded $(CeO_8)^{12-}$ and $(CeO_6)^{8-}$ clusters, respectively; here, e.g., $(CeO_8)^{12-}$ denotes a cluster model with one cerium and eight oxygens. For the Ca-doped ceria crystal, we have chosen $(CeO_6)^{8-}$ and $(CeO_5)^{6-}$ clusters for the (110) surface (see Figure 2 for the definition of the different embedded cluster models), while $(CeO_8)^{12-}$ and $(CeO_7)^{10-}$ were constructed for the bulk situation. It should be noted that each model is charge neutral when both the central cluster and the embedding are considered together. The details about the basis sets used in the calculation of the electronic structure of the clusters and of the potentials used to represent the lattices are given in the appendix.

The ECPAIMP program³⁸ has been used to evaluate the AIMP (core and embedding) potential integrals and to generate the one-electron integrals over the Madelung potential. The implementation is such that the unit cell from, for example, the MD simulations can be read directly into the program and the potential from the fully 2-D periodic structure used for the calculations. The one-electron integrals can then be replaced in a number of different programs, and two of these programs, the ones used here, are the direct-SCF code DISCO³⁹ and the Stockholm program package.⁴⁰

The relative stability of Ce(III) and Ce(IV) in the different lattice positions in the undoped and doped structures was investigated by explicitly performing the required oxygen-cerium charge-transfer excitation within the embedded cluster models. For this purpose we have performed SCF and Modified Coupled Pair Functional (MCPF)⁴¹ calculations on the different clusters mentioned above. Some additional calculations to investigate the electron affinity of cerium ions in different positions were furthermore performed.

TABLE 1: Experimental Characterization of Different Cerium Oxide Samples Studied: Oxygen Deficiency (δ) Measured at Room Temperature, Unit Cell Parameter (*a* in Å), BET Area (*S* in m²/g), and Light-Off Temperatures Corresponding to 50% Conversion of CO ($T_{50,CO}$) and SO₂ (T_{50,SO_2}), Respectively (in °C)



Figure 3. Experimentally measured SO₂, CO, and CO₂ flow rates in reactor outlet as a function of catalyst temperature over undoped and Ca-doped CeO₂. Circles (\bigcirc) and crosses (x) indicate the results for the undoped and doped samples, respectively.

III Results

A. Experimental. Chemical compositions of the experimentally studied samples are given in Table 1. XRD patterns collected on a conventional X-ray diffractometer of the samples revealed that the Ca-doped sample retains the fluorite structure with a slightly increased unit cell parameter as compared to the undoped CeO₂. The use of the very intense pulsed neutron beam showed, however, the presence of a small fraction of CaCO₃ in that sample in agreement with X-ray photoelectron spectroscopy (XPS) results.^{12,42} The oxygen deficiency values, δ , in Ce_{1-x}Ca_xO_{2- δ}, agree well with the expected values considering the oxidation state of the dopant.

Figure 3 shows the ability of the materials to catalyze the reduction of SO_2 by CO described in reaction 1 below:

$$SO_2 + 2CO \rightarrow S^0 + 2CO_2 \tag{1}$$

In this reaction, elementary sulfur and CO_2 are formed. The sulfur was condensed in a cooling trap, whereas the concentrations of SO₂, CO, and CO₂ were quantified by mass spectrometer. In Figure 3 the flow rates of the gases in the reactor outlet are presented as a function of catalyst temperature. It is clear that both the on-set and the light-off temperatures were much lower for the Ca-doped sample compared to those of the undoped CeO₂ sample. The light-off temperatures corresponding to 50% conversion, T_{50} , are given in Table 1, and both samples showed lower values of $T_{50,CO}$ than of T_{50,SO_2} , which indicates that the first step in the mechanism of reaction 1 is the oxidation of CO by oxygen from the catalyst surface. Then, as the surface becomes sufficiently reduced, at a slightly higher temperature, it reduces the SO₂, thus completing the catalytic cycle.

B. Atomistic Simulations. *1. Low-Temperature Surface Systems (0 and 10 K).* The impact of doping on the catalyst reactions and the reason and mechanism for the increased OSC

TABLE 2: Surface Energies, E (in J/m²), of Pure CeO₂

surface	E before relaxation	E after relaxation
(111)	1.72	1.22
(110)	3.60	1.65
(211)	6.85	1.84
(310)	11.59	2.54

can only be understood when reasonable models for both the doped and undoped surface structures exist. From pure static energy minimizations we found, in agreement with other groups,^{4–6} that the most stable surface is (111), followed by (110), (211), and (310), see Table 2. Most stable often means least reactive, and it has been shown³⁰ that the (111) surface does not release oxygen easily. Thus, in the following we focus our interest on the (110) surface, which has a sufficiently low surface energy that it can be expected to be exposed on the small CeO₂ particles.

The resulting surface energy for the relaxed (110) surface computed with the MARVIN program is 1.65 J/m^2 . This is about half of the surface energy of the unrelaxed surface, which indicates the importance of including these effects in the modeling; it can be expected that, in a theoretical study, the unrelaxed surface should exhibit an artificially increased reactivity over that of the fully relaxed surface.⁴³

Since the Ca(+II) dopant has a lower valency than the Ce(+IV) of the original material, each dopant has to be charge compensated through the creation of an oxygen vacancy. For a given level of doping this introduces questions about how the dopants and vacancies should be distributed initially in the simulation cell; for gases and liquids, final distributions can be expected to be reasonably independent of the initial guess, but this may not be the case for a high-melting-point oxidic material such as the present. Using the MARVIN code the interaction between dopant and vacancy was first investigated: the calculated surface energy of the Ca-doped (111) CeO2 is 0.56 J/m^2 for the bound pair system and 0.67 J/m^2 for the unbound, but this is due to a somewhat greater bulk stability of the unbound pair system. The energy difference, 0.02 eV/unit cell, between the two situations is very small, indicating only a very slight interaction energy between dopant and vacancy. However, to draw conclusions on the mobility of oxygens one would also need an estimate of the barrier to migration.

Doping of the material could cause a segregation of the dopant ions resulting in different concentrations at the surface and in the bulk. This was investigated by obtaining the surface energies for the (110) crystal with the dopants and vacancies introduced only in one layer and varying the distance from the surface of this layer. The thus obtained surface energy as a function of the distance of the introduced defect layer from the surface of CeO₂ showed it to be energetically more favorable for the dopant layer to be at the surface. However, not surprisingly, the MD simulations show no tendency for Ca²⁺ migration for any feasible simulation time. The surface energy is also dependent on the concentration of defects at the surface, with a rapidly increasing surface energy (for the model with dopants and vacancies in one layer only) as the concentration increases; values of 28.4, 8.2, 4.5, and 1.6 J/m² (note that in this case much higher surface formation energies are obtained due to the inhomogeneity in the dopant concentrations) were found for concentrations of 50, 12.5, 5.5, and 0%, respectively. Thus, as the dopant concentration is increased, it is likely to prevent further segregation and no significant segregation will be expected.

Figure 4 shows the relaxed slab structure of the Ca^{2+} -doped slab after 1.9 ps of simulation at 10 K. The figure is a projection



Figure 4. The 12.5% Ca^{2+} -doped CeO_2 (110) slab after relaxation for 1.9 ps at 10 K. The figure is a projection of all ions onto the plane of the paper, which is the *xz* plane. The slab surfaces are normal to the *z* direction.

of all ions onto the plane of the paper, which is the *xz*-plane. It can be seen that the relaxation introduces a rather large overall distortion from the ideal CeO_2 structure, but, more importantly, the distortion is larger at the surface than in the middle of the slab.

The MD simulations at 10 K show that, without dopantvacancy (DV) pairs in the slab the relaxation consists of a rather small rumpling in the four outermost layers, while the rest of the slab remains rather bulklike. The rumpling mainly involves the oscillatory interplanar relaxation of Ce^{4+} ions by -10%, +9.4%, -2.6%, and +2.6% in the first, second, third, and fourth layers, respectively, while the oxygen ions relax less than 1%, and in the opposite direction compared with the cerium ions (see Figure 5). In a parallel investigation on a large number of low-index cuts of CeO₂, Vyas et al.⁴⁴ find a rather large dependence on the potential for the relaxations of the outermost layers as obtained from static energy minimizations (corresponding to our 10 K simulations). For the most stable, (111), plane the largest relaxation effects were found for the oxygen ions, while the cerium ions were found to relax to a much smaller extent leading to the opposite rumpling compared to our present investigation of the (110) plane. Results for the relaxation of the (110) plane were not reported in ref 44 making a detailed comparison difficult. However, for the higher-index planes, e.g., the (331) surface, larger distortions and oscillations for both types of ions are reported, showing that the details of the relaxation effects at the surface depend both on the specific potential and on the specific plane chosen for study.

In the presence of DV pairs the relaxation effects are much more pronounced, especially in the close vicinity of the DV

Both in the bulk and in the slab system the relaxation effects in the close vicinity of the DV pairs involve the displacement of ions, mainly oxygen ions, from their crystallographic equilibrium positions by as much as 0.7 Å. In the slab system some oxygen ions also migrate to other crystallographic sites or, for the outermost layer, to new sites off the crystallographically determined positions. The mechanism of these ionic relaxations/migrations depends on the ion's distance from the surface. For oxygen ions located deeper than the outermost layer, the migration only occurs along the x-direction (crystallographic (001) or (001) directions) from an occupied oxygen site to an oxygen vacancy (Type I). For oxygen ions in the outermost layer of the slab, the migrations also occur in the x-direction, but the ions stay between two equivalent crystallographic sites, somewhat displaced in the z-direction (Type II) due to the higher degree of translational freedom that the ion possesses near the surface. Moreover, at the surface we can also observe migrations in the yz-direction (Type III) (crystallographic (010) or $(0\overline{10})$ direction), or more specifically, if the dopant is located in the outermost layer the associated oxygen vacancy maintains its position in the outermost layer, but if the dopant resides in the second layer the associated oxygen vacancy migrates out to the topmost layer, keeping the Ca²⁺ dopant in the second layer fully coordinated. This indicates that oxygen vacancies are more stable at the surface than in the bulk, in agreement with an earlier investigation of isolated defect formation energies when doping with Rh³⁺, Pd²⁺, and Pt^{2+ 45} and the recent investigation of doping with zirconia by Balducci et al.8 In the present investigation we find that this turns out to be true even at higher defect concentrations and in the close vicinity of a Ca²⁺ dopant, both when the dopant is located in the uppermost layer and when located in the second layer.

2. Temperature Effects on the CeO_2 (110) Surface. The structure of the oxide substrate at different temperatures, both at an atomic scale and at a time-resolved level, is of great interest. In particular, a closer analysis of the dynamics at the surface of the slab in terms of mean-square and instantaneous displacements of the ions could answer questions such as whether reactive sites could become available, i.e. the surface activated, through large-amplitude motions and jumps of the ions at the surface, and whether it would be possible to have a reduction of barrier heights for specific reactions as an effect of surface ion mobility.

Increasing the temperature up to 300 K does not alter the oscillatory interplanar distance behavior for the relaxation, described above, in the pure and doped CeO₂ slab. The number of migration events, on the other hand, appears to increase with temperature. During 24.4 ps of simulation time at 300 K, two migrations of Type I were observed in the doped bulk system, and five events of Type II in the doped slab system. The Ca²⁺ doping of bulk CeO₂ results in higher atomic mean-square displacements (msd's). The msd's for Ce⁴⁺ increase from approximately 0.0022 Å² (average of *x*, *y* and *z* directions) in the undoped ceria to 0.0026 Å² when doped, and the msd's for O²⁻ increase from 0.0039 Å² in the undoped bulk to 0.0047 Å² for doped ceria. The dopant has an msd of 0.0043 Å².



Figure 5. Average distances between adjacent planes in the x, y, and z directions in the slab (definitions in the text). For comparison, the corresponding interplanar distances in the bulk are given, where "Bulk 110" corresponds to the value for the y and z directions (equivalent distances) and "Bulk 001" corresponds to the value for the x direction.

When the above msd's are studied as a function of depth in the undoped slab system at 300 K (Figure 6) one can observe msd's higher than the bulk values down to about 6 Å from the surface, while the msd's in a 4 Å thick region in the middle of the slab are essentially the same as in the bulk. A very similar situation appears for the doped systems. The increase is largest in the x and z directions, and for z follows the oscillatory interplanar distance behavior observed in the relaxation (see above). Upon doping, the effects of increased atomic msd's are suppressed for the cerium ions and enhanced for the oxygen ions. In the outermost layer, some oxygen ions have a higher msd than the average in the same layer, which can be explained by oxygen ions that have migrated, according to a Type II mechanism, to a new, less strongly bound site.

C. Ab Initio Calculations. Ca-doped CeO₂ has experimentally been found to have greatly increased oxygen ion conductivity compared to undoped CeO₂.⁴⁶ This may be connected with the higher catalytic activity for reaction 1 found for the Cadoped sample. The concentration of oxygen vacancies is higher for Ca-doped CeO₂, which should contribute to a higher oxygen ion mobility and a higher concentration of active sites for, e.g., SO₂ reduction. In addition to the oxygen transfer processes, involved in the reduction of SO₂ by CO, there must however be elementary steps involving charge-transfer processes. Hence, the electronic properties, e.g., electron affinities or availability of charge-transfer (C-T) excitations, of the materials are likely of importance for the catalytic activity of these materials.

1. Ce(IV) to Ce(III) Excitations (C-T). As a consequence of the obtained structural model for the doping, the cerium ions are not all fully coordinated; this might be expected to lead to more easily reduced species. We have computed the energy required to transfer an electron from O^{2-} to Ce^{4+} for each of the three different five- and six-coordinated cerium ions in the doped (110) surface and have compared those with the corresponding values for the bulk and the undoped surface.

The calculations have been performed at the Hartree–Fock level with an estimate of effects of correlation from MCPF

calculations on the embedded ions. The lowest charge transfer state found was from the 2p level of one of the oxygens in the cluster model (localized excitation) to Ce(4f), which results in an increased screening of the Ce valence and outer core orbitals making the Ce(III) ion about 5% larger than the Ce(IV) ion. The values computed are expected to provide an upper bound to the energy required to change the charge states since several energy-lowering effects are not included. In particular, polarization effects in the lattice, which will be present for the C-T state but not for the ground state, could be expected to lower the energy by at least 1 eV.⁴⁷ This will however be canceled by the correlation energy contribution which is about 2 eV larger for the $Ce^{4+}O^{2-}$ pair than for the $Ce^{3+}O^{-}$ combination. However, since the size of the cerium ion increases, some geometrical effects may be expected, where the structure around the larger Ce(III) ion expands to accommodate it; this can only reduce the CT excitation energy. In an effort to estimate the magnitude of this effect a limited geometry optimization was performed of the oxygen positions in the embedded cluster. Since the optimization now is done at a different level of theory compared to what was used to generate the embedding potential it is essential to first establish the optimum geometry of the quantum mechanically described embedded cluster. The geometry of the oxygens around the embedded cerium(IV) ion was thus optimized giving very small differences from the geometry determined from the simulations; this is a gratifying result showing the stability of the chosen combination of techniques. Changing the electronic structure of the cerium to Ce(III) by considering the triplet state of the cluster and redoing the optimization again resulted in only minor modifications with only a small resulting effect on the CT energy, less than 0.1 eV.

The results from this study are reported in Table 3. The doping and the modified coordination around the ceria is seen to lead to a substantial reduction (by over 2 eV) of the CT excitation energy. The electron affinity computed for the Ce ions in the different clusters (last column of the same table)



Figure 6. Mean-square displacements (msd's) as a function of depth in the *x*, *y*, and *z* directions for Ce⁴⁺ and O²⁻ in the undoped CeO₂ (110) slab at 300 K. The bulk msd's in the corresponding directions are given for comparison. Each point on the slab curves is the average of 9 values, each computed as the average msd during a 0.94 ps long time interval (the total simulation time was 8.46 ps). Each error bar is the standard deviation of these 9 values; no drift was observed. The outermost point corresponds to a depth z = 0.5 Å, i.e., it contains all atoms between z = 0 and z = 0.5 Å.

TABLE 3. Computed Charge-Transfer Energies and Electron Affinities (eV), for Different Ce Sites in the Top Layer of Ca-Doped (110) CeO_2^a

cluster type	<i>n</i> -fold Ce	СТ	EA
5A-(110)	5	2.09	-0.41
5B-(110)	5	3.34	0.70
5C-(110)	5	2.27	-0.05
6A-(110)	6	2.40	-2.10
6B-(110)	6	2.63	-0.58
6C-(110)	6	2.55	-1.37
7-bulk	7		-2.54

^{*a*} The 6-fold coordinated Ce in pure (110) has a computed C–T energy of 4.18 eV and E A = -1.14 eV. The different clusters are denominated according to Figure 2.

shows a rather similar picture. In the undoped (110) CeO_2 surface, the 6-coordinated cerium has a calculated electron affinity of -1.14 eV, i.e., it prefers to remain as Ce(IV), while doping results in a less negative electron affinity for all the 5-coordinated and for one of the 6-coordinated ceriums. This would imply that, at least the 5-coordinated ceriums should be more easily reduced from +IV to +III and this could be one contributing factor in explaining the higher catalytic activity of the doped compared to the undoped sample.

IV. Discussion

The reactivity of metal oxides in general is largely dependent on the amount and character of coordinatively unsaturated exposed ions at the surface and especially the presence of oxygen vacancies efficiently exposes highly unsaturated cations.^{48,49} Characteristic of cerium oxide is that the cerium ion may have two oxidation states, whereby these ions can participate in reactions that involve changes in the oxidation state of the cation. By substituting part of the Ce^{4+} in the CeO_2 structure by other cations, the properties of the material are affected, e.g., the concentration and mobility of oxygen vacancies are increased, and several electronic properties are greatly altered. It is hence not certain which of these contribute the most to an increase in the catalytic activity of the material.

The static and the MD simulations of the calcium-doped ceria show that the created oxygen vacancies prefer to be located away from the top layer for the (111) surface, while for the (110) surface the vacancies were more stable at the surface. These exposed oxygen vacancies could of course be of importance and a reason for the increased OSC. In addition, they may well have a central role in the catalytic efficiency of the material. For example, a first step in reaction 1 can be assumed to be the adsorption of a CO molecule on the surface, followed by the reaction with an oxygen atom by this CO forming CO₂; this would leave behind an oxygen vacancy and two electrons, i.e., a reduced surface. The electrons can be assumed to be localized to two adjacent Ce ions reducing them to the Ce³⁺ state or be associated with the vacancy as an F_s^+ center and one Ce(III).⁵⁰ In a following step, an SO₂ molecule adsorbs on the oxygen vacant site and the two electrons are utilized for the first step of the reduction of SO₂, which then dissociates into O²⁻ and SO. The SO can then in a similar fashion be further reduced by two more electrons from an additional oxygen vacancy forming elementary sulfur and an oxidized surface. The efficiency of a catalyst following this scheme would be favored by the availability of low-lying CT excitations for the transfer of charge from the oxygens to the cerium in order to facilitate the oxidation of the CO. In the second step, however, the Ce^{3+} ions, or Ce^{3+} plus F_s^+ center, should have a low affinity for this electron in order to facilitate the reduction of the SO₂ molecule. There should hence be an optimum electron affinity of the Ce ions for which redox reactions such as the one in reaction 1 occur at the highest rate, assuming all other conditions being constant.

Speculating in a possible explanation and a mechanism for the increased OSC could thus be that the reduction and the oxidation balance of cerium, Ce(+III)/Ce(+IV), has become more accessible, and knowing that this balance is essential for the OSC, this could be the key. The proposed mechanism is thus: two Ce(+IV) are reduced to two Ce(+III) or the two electrons are distributed over one cerium and the F_s^+ center, through the reaction of a surface oxygen with e.g. the CO molecule in the SO₂ desulfurization reaction, creating an oxygen vacancy and a reduced surface. Then, as the surface has been reduced, it has the ability to pick up oxygen (from various oxygen-containing molecules). The way this can be achieved is by the donation of electrons from the Ce³⁺ to the oxygencontaining molecule, which is looking to be reduced and releases an O²⁻ to the surface.

From the computed CT energies and electron affinities it is clear that the Ce(IV)/Ce(III) balance has been affected. However, we still find the Ce³⁺O⁻ species to be higher in energy for all structures considered in the present work, even though the energy difference has become substantially reduced. Furthermore, we have not been able to find any site with a hydrogen affinity large enough to even approach the requirements for hydrogen abstraction from methane, which is another reaction proceeding more easily over the doped CeO₂. It is clear that

the internal charge distribution in the crystal is determined by the Madelung potential; if this becomes weaker through an expansion of the lattice or a distortion of the lattice structure the CT energy should go down. Thus, the present work suggests that additional distortions could be important in order to explain the observed reactivities. One such possibility could be through larger-amplitude thermal motions at the surface where, e.g., an anion moves out of the stabilizing crystal potential and thus becomes more reactive. The combination of the MD simulations with quantum chemistry allows for a direct calculation of the electronic structure of representative, or particularly interesting, instantaneous geometrical structures and, indeed, preliminary studies of particular such structures do indicate an even lower CT energy in some such cases and, as a result, a significant reactivity toward, e.g., hydrogen abstraction and abstraction of lattice oxygen using CO as in the desulfurization reaction.⁵⁰ It is clear that the combination of experimental and different theoretical approaches involving both temperature and electronic structure determinations is a prerequisite for the development of a reliable and realistic picture of the complicated surface processes going on in the complex oxide materials studied in the present paper.

V. Summary and Conclusions

The present work combines molecular dynamics simulations of both doped and undoped CeO_2 with quantum chemical studies of the electronic structure of embedded cluster models built from the MD structures. The two theoretical techniques are applied in an effort to understand the enhanced reactivity for e.g. SO_2 decomposition and total combustion of methane that is found experimentally upon doping of CeO_2 . Several interesting aspects are studied which may bear upon the origin of this reactivity: in particular, the finding of coordinatively unsaturated cerium ions at all depths in the doped crystal leads to interesting possibilities for CT reactions where the Ce(IV) may accept an electron from a neighboring oxygen anion or some other electron donor to become Ce(III).

The techniques involved are shown to give consistent results, where in particular the agreement between the experimental radial distribution functions from pulsed neutron scattering and those obtained from the molecular dynamics simulations is very striking. Furthermore, the experimentally observed bulk expansion upon doping is also reproduced by the simulations. Thus, the present theoretical description seems to give a very reliable picture of the structural effects on the CeO₂ lattice upon doping.

The structures generated through the molecular dynamics simulations are directly fed into the quantum chemical modeling calculations. Here the effects on the electronic structure from the doping are studied using embedded cluster models based on the MD results. The average, low-temperature geometries obtained from the MD simulations are found to be close to optimal also for the quantum chemical calculations, lending further support to the chosen combination of techniques. The computed CT energies leading to a Ce(III) species are found to be significantly reduced, but still insufficient to by themselves explain the observed reactivity of the material; the energy cost is still of the order of 2-3 eV which is too high to lead to exothermic or thermoneutral reactions. It is suggested that additional temperature-controlled distortions could be important for a complete understanding of chemical reactions involving the doped and undoped CeO₂.

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Appendix: Cluster Basis Set

In all the cluster calculations, the basis set for the oxygen atoms is a (9s 5p) primitive basis taken from ref 51, augmented with one s and one p function (these extra functions have been taken from ref 32 and two d polarization functions (exponents $\alpha_1 = 0.5657$, $\alpha_2 = 0.2828$), so that the final contraction is [5s4p2d]. For the study of charge-transfer excitations only one d function ($\alpha = 0.5657$) was used.

For the cerium atom, an ab initio core model potential $(AIMP)^{52}$ representation developed for the present work has been used. These are based on a [Kr]-core AIMP (CG-quasirelativistic^{55,56}) and a (13s10p6d6f) valence basis set optimized for the ³*H* state of the cerium neutral atom, corresponding to the electronic configuration ([Xe]4f² 5d⁰ 6s²), the SCF ground state. This valence basis set, that is used to describe the 4d 4f 5s 5p 6s valence of the cerium atoms, has been finally contracted to [5s4p4d2f].

A. Embedding Potentials and Computational Techniques. The AIMP embedding approach^{35,36} is based on a division of the wave function for the crystal into a local part describing the cluster and the external wave function. External ionic wave functions, suitable to generate the embedding model potentials, were obtained from self-consistent embedded ion (SCEI) calculations.^{35,36} Briefly, SCF wave functions appropriate for the embedded Ce⁴⁺ and O²⁻ ions are found and then used to generate the corresponding total-ion model potentials. These give an approximate description of the short-range Coulomb (incomplete screening), exchange, and orthogonality interactions, together with the major relativistic effects (Darwin and mass– velocity potentials), obtained within the Cowan–Griffin approximation.⁵⁷

The SCEI calculations have been performed using the perfect crystal structures taken from ref 13. The basis set used for the Ce embedded ion calculations has been developed for this work: a (11s10p6d) valence basis set together with a [Kr]-core CG-AIMP, optimized for the ¹S state of Ce⁴⁺, totally uncontracted; the basis set for the O²⁻ ion is the O(53/5) basis set from the compilation of Huzinaga and co-workers,⁵⁸ augmented with a p function describing the anion⁵⁹ and totally uncontracted.

References and Notes

(1) Kilbourn, B. T. *Cerium: A guide to its role in chemical technology*; Molycorp, Inc.: Fairfield, NJ, 1992.

(2) Kreuzer, T.; Lox, E. S.; Lindner, D.; Leyrer, J. Catal. Today 1996, 29, 17.

(3) Persson, A. E.; Zhang, Y.; Muhammed, M. *Catalyst materials for high-temperature processes, ceramic transactions 73*. American Ceramic Society, Westerville, OH, 1997; p 85.

(4) Sayle, T. X. T.; Parker, S. C.; Catlow, C. R. A. J. Chem. Soc., Chem. Commun. 1992, 977.

(5) Sayle, T. X. T.; Parker, S. C.; Catlow, C. R. A. Surf. Sci. 1994, 316, 329.

(6) Conesa, J. C. Surf. Sci. 1995, 339, 337.

(7) Balducci, G.; Kašpar, J.; Fornasiero, P.; Graziani, M.; Saiful Islam,M. J. Phys. Chem. B 1997, 101, 1750.

(8) Balducci, G.; Kašpar, J.; Fornasiero, P.; Graziani, M.; Saiful Islam,
 M. J. Phys. Chem. B 1998, 102, 557.

(9) Zhang, Y.; Andersson, S.; Muhammed, M. Appl. Catal., B: 1995, 6, 325.

(10) Palmqvist, A. E. C.; Zwinkels, M. F. M.; Zhang, Y.; Järås, S. G.; Muhammed, M. Nanostruct. Mater. 1997, 8, 801.

(11) Palmqvist, A. E. C.; Johansson, E. M.; Järås, S. G.; Muhammed, M. Catal. Lett. 1998, 56, 69.

(12) Palmqvist, A. E. C.; Berastegui, P.; Eriksson, S.; Hannon, A. C.; Furenlid, L. R.; Baudin, M.; Wójcik, M.; Hermansson, K. To be published.

- (13) Wyckoff, R. W. G. Crystal Structures; Wiley: New York, 1963.
 (14) General Utility Lattice Program (GULP); developed by J. D. Gale, Royal Institution of Great Britain/Imperial College, 1992–1995.
- (15) Gay, D. H.; Rohl, A. L. J. Chem. Soc., Faraday Trans. 1995, 91, 925.
- (16) Baudin, M.; Wójcik, M.; Hermansson, K. Surf. Sci. 1997, 375, 374.
- (17) Lewis, G. V.; Catlow, C. R. A. J. Phys. C.: Solid State Phys. 1985, 18, 1149.
- (18) Butler, V.; Catlow, C. R. A.; Fender, B. E. F.; Harding, J. H. Solid State Ionics **1983**, *8*, 109.
- (19) Dick, B. G.; Overhauser, A. W. Phys. Rev. 1958, 112, 90.
- (20) Mitchell, P. J.; Fincham, D. J. Phys.: Condens. Matter 1993, 5, 1031.
 - (21) Ewald, P. P. Ann. Phys. 1921, 64, 253.
 - (22) Parry, D. E. Surf. Sci. 1921, 49, 433.
 - (23) Parry, D. E. Surf. Sci. 1976, 54, 195
 - (24) Cleveland, C. L. J. Chem. Phys. 1988, 89, 4987.
 - (25) Parinello, M.; Raman, A. Phys. Rev. Lett. 1980, 45, 1196.
 - (26) Parinello, M.; Raman, A. J. Appl. Phys. 1981, 52, 7182.
 - (27) Nosé, S. J. Chem. Phys. 1984, 81, 511.
 - (28) Hoover, W. G. Phys. Rev. A 1985, 31, 1695.
- (29) Heyes, D. M.; Barber, M.; Clarke, J. H. R. J. Chem. Soc., Faraday Trans. 2 1977, 10, 1485.
- (30) Cordatos, H.; Bunluesin, T.; Vohs, J. M.; Gorte, R. J. J. Phys. Chem. 1996, 100, 785.
- (31) Pascual, J. L.; Pettersson, L. G. M. Chem. Phys. Lett. 1997, 270, 351.
- (32) Nygren, M. A.; Pettersson, L. G. M.; Barandiarán, Z.; Seijo, L. J. Chem. Phys. **1994**, 100, 2010.
 - (33) M. Pöhlchen; Staemmler, V. J. Chem. Phys. 1993, 97, 2583.
 - (34) A. M. Ferrari; G. Pacchioni. Int. J. Quantum Chem. 1994, 58, 241.
 - (35) Barandiarán, Z.; Seijo, L. J. Chem. Phys. 1988, 89, 5739.
- (36) Barandiarán, Z.; Seijo, L. In *Studies in Physical and Theoretical Chemistry: Vol.* 77(B), *Computational Chemistry: Structure, Interactions and Reactivity*; Fraga, S. Ed.; Elsevier: Amsterdam, 1992; p 435.

(37) J. A. Mejias; J. Fernández Sanz. J. Chem. Phys. 1995, 102, 327.
(38) ECPAIMP is an integral program for ECP and AIMP calculations written by L. G. M. Pettersson, L. Seijo, and M. A. Nygren.

- (39) Almlöf, J.; Faegri, K., Jr.; Feyereisen, M.; Korsell, K. DISCO, a direct SCF and MP2 code.
- (40) STOCKHOLM is a general purpose quantum chemical set of programs written by P. E. M. Siegbahn, M. R. A. Blomberg, L. G. M. Pettersson, B. O. Roos, and J. Almlöf.
 - (41) Chong, D. P.; Langhoff, S. R. J. Chem. Phys. **1986**, 84, 5606.
- (42) Palmqvist, A. E. C.; Wirde, M.; Gelius, U.; Muhammed, M. To be published.
- (43) Nygren, M. A.; Pettersson, L. G. M.; Freitag, A.; Staemmler, V.; Gay, D. H.; Rohl, A. L. J. Phys. Chem. **1996**, 100, 294.
- (44) Vyas, S.; Grimes, R. W.; Gay, D. H.; Rohl, A. L. J. Chem. Soc., Faraday Trans. 1998, 94, 427.
- (45) Sayle, T. X. T.; Parker, S. C.; Catlow, C. R. A. J. Phys. Chem. 1994, 98, 13625.
- (46) Yashiro, H.; Ohuchi, T.; Eguchi, K.; Arai, H. J. Mater. Sci. 1988, 23, 1036.
- (47) Janssen, G. J. M.; Nieuwpoort, W. C. *Phys. Rev. B* 1988, *38*, 3449.
 (48) Wise, H.; Oudar, J. *Materials Concepts in Surface Reactivity and Catalysis*; Academic Press: San Diego, 1990.
- (49) van Santen, R. A.; Niemantsverdriet, J. W. Chemical Kinetics and Catalysis; Plenum Press: New York, 1995.
- (50) Triguero, L.; de Carolis, S.; Nygren, M. A.; Pettersson, L. G. M. To be published.
- (51) Dunning, T. H., Jr. J. Chem. Phys. 1970, 53, 2823.
- (52) Huzinaga, S.; Barandiarán, Z.; Seijo, L.; Klobukowsky, M. J. Chem. Phys. 1987, 86, 2132.
- (53) Seijo, L.; Barandiarán, Z.; Huzinaga, S. J. Chem. Phys. 1989, 91, 7011.
- (54) Barandiarán, Z.; Seijo, L.; Huzinaga, S. J. Chem. Phys. 1991, 94, 3762.
- (55) Barandiarán, Z.; Seijo, L. Can. J. Chem. 1992, 70, 409.
- (56) Barandiarán, Z.; Seijo, L.; Huzinaga, S. J. Chem. Phys. 1990, 93, 5843.
- (57) Cowan, R. D.; Griffin, D. C. J. Opt. Soc. Am. 1976, 66, 1010.
- (58) Andzelm, J.; Klobukowsky, M.; Radzio-Andzelm, E.; Sakai, Y.;
- Tatewaki, H. Gaussian basis sets for molecular calculations; Elsevier: Amsterdam, 1984.
- (59) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaeffer, H. F., III, Ed.; Plenum: New York.