Structures and vibrational spectroscopy of partially reduced gas-phase cerium oxide clusters†

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This work demonstrates that the most stable structures of even small gas-phase aggregates of cerium oxide with 2–5 cerium atoms show structural motifs reminiscent of the bulk ceria. This is different from main group and transition metal oxide clusters, which often display structural features that are distinctly different from the bulk structure. The structures of CeO2+ , Ce3O4+ , and (CeO2)4CeO+ clusters (m = 0–4) are unambiguously determined by a combination of global structure optimizations at the density functional theory level and infrared vibrational predissociation spectroscopy of the cluster–rare gas atom complexes. The structures of CeO2+ and CeO3+ exhibit a Ce–O–Ce–O four-membered ring with characteristic absorptions between 430 and 680 cm−1. Larger clusters have common structural features containing fused Ce–O–Ce–O four-membered rings which lead to intense absorption bands at around 500 and 650 cm−1. Clusters containing a terminal Ce=O bond show a characteristic absorption band between 800 and 840 cm−1. For some cluster sizes multiple isomers are observed. Their individual infrared signatures are identified by tuning their relative population through the choice of He, Ne or Ar messenger atoms. The present results allow us to benchmark different density functionals which yield different degrees of localization of unpaired electrons in Ce 4f states.

1 Introduction

Understanding how the structure and properties of a chemical compound change with its dimensionality, i.e., when passing from the three-dimensional bulk solid to two-dimensional thin films and to zero-dimensional nanosized clusters or small molecules, is of fundamental interest in physics and chemistry. Systems with reduced dimensionality can display unusual structural diversity even for metal oxides with inherently stable bulk structures. The prominent examples here are gas-phase aggregates of magnesium oxide. Similarly, aluminium oxide, Al2O3, as low-dimensional material in the form of thin films and clusters exhibits new structural features that are not found in any of its known solid polymorphs. It is therefore not surprising that also small aggregates of transition metal oxides show unusual structural features. For example, both charged and neutral vanadium oxide clusters form polyhedral cages unknown in bulk V2O5. A similar behavior was shown for bimetallic V–Ti oxide anion clusters and neutral (TiO2)n clusters. For the latter even clusters of sizes m = 9–15 show geometrical structures which do not correspond to any of the known TiO2 polymorphs. An overview on the vibrational spectroscopy of gas-phase metal oxide clusters and the assignment of structures compared with computational results is given by Asmis et al.

The surprising finding of the present study is that the most stable isomers of small cerium oxide clusters with 2–5 Ce atoms show structural elements typical of bulk CeO2. Global structure optimizations of the clusters with compositions CeO2+ , Ce3O4+ , and (CeO2)4CeO+ (m = 0–4) have been made employing density functional theory (DFT). Since DFT calculations are of limited accuracy the final structure assignment is achieved by comparing the infrared (IR) absorption spectra, calculated for the lowest energy isomers, with measured IR vibrational predissociation (IRVPD) spectra. Previously, this approach was applied to determine the structures of other metal oxide cluster cations, including vanadium, aluminium,
magnesium,\textsuperscript{1} and mixed V–Ce\textsuperscript{15} oxide clusters. Compared to previous work on cerium oxide clusters\textsuperscript{16–29} there are two novel aspects within our study. First, the structures are computationally predicted using \textit{ab initio} global structure optimizations. Second, vibrational spectra of mass-selected cluster cations are used to check the theoretical predictions and assign cluster structures on the basis of comparison of the experimental and simulated IR spectra.

So far IR matrix isolation\textsuperscript{16,17} and visible fluorescence\textsuperscript{18,19} spectroscopy have been used to characterize CeO and CeO\textsubscript{2}. Reactions of CeO\textsubscript{2}\textsuperscript{+} with unsaturated hydrocarbons have been studied using mass spectrometry and discussed in conjunction with the electronic structure of CeO\textsubscript{2}\textsuperscript{+} investigated by several \textit{ab initio} methods.\textsuperscript{20} Similarly, the reactivity of (CeO\textsubscript{2})\textsubscript{m}\textsuperscript{+} cerium oxide cations\textsuperscript{21} and cerium oxyhydroxide clusters\textsuperscript{22} has been investigated by mass spectrometry and interpreted based on DFT calculations. For neutral (CeO\textsubscript{2})\textsubscript{n} clusters different global minimum structures have been predicted computationally, depending on the exchange-correlation functional used.\textsuperscript{23,24} The properties of cerium oxide nanoparticles with octahedral shapes have been investigated using DFT and interionic potentials.\textsuperscript{25–27} These bulk-like structures are similar to those of ceria nanoparticles determined with X-ray diffraction and transmission electron microscopy.\textsuperscript{28,29}

The clusters studied in the present work are not fully oxidized, i.e., there are Ce atoms in the lower oxidation state than +IV. There is lively interest in partially reduced ceria\textsuperscript{30–35} which arises from a broad range of industrial applications\textsuperscript{36,37} including heterogeneous catalysis.\textsuperscript{30,38,39} Partially reduced ceria is formed when oxygen defects are created which leaves electrons in Ce 4f states. Experiments point to localized Ce 4f states\textsuperscript{31,35} but DFT results strongly depend on the chosen exchange-correlation functional. The local density approximation (LDA) and the generalized gradient approximation (GGA) lead to delocalized occupied Ce 4f states.\textsuperscript{40} In contrast, calculations using hybrid functionals\textsuperscript{41–44} or the DFT + U scheme\textsuperscript{45–47} lead to localized f states on single Ce sites. For extended systems such as nanoparticles and surfaces, calculations using more demanding functionals,\textit{ e.g.}, hybrid functionals are affordable only in exceptional cases.\textsuperscript{41–43} In contrast, cerium oxide clusters can be studied by a broad variety of functionals.\textsuperscript{20,21,23,24} Hence, the present joint computational-experimental study of clusters not only contributes to a better understanding of the properties and the electronic structure of partially reduced cerium oxide, but also serves as a benchmark for assessing the applicability of different computational methods to lanthanide oxide aggregates.

2 Computational details

DFT calculations are performed using the TURBOMOLE program package.\textsuperscript{48,49} For the global structure optimizations the hybrid \textit{ab initio} genetic algorithm\textsuperscript{50} is applied along with the TPSS exchange-correlation functional\textsuperscript{51} and triple-zeta valence plus polarization basis sets.\textsuperscript{52} The Stuttgart RSC Segmented basis set with polarization functions up to g functions\textsuperscript{53} [10s, 8p, 5d, 4f, 1g] and the relativistic small-core pseudopotential\textsuperscript{54} (28 electrons in the core) are adopted for cerium. In contrast to ref. 53 the cerium basis set contains only one polarization shell of g functions with exponent 0.35. Density fitting for the Coulomb term\textsuperscript{55,56} is applied to accelerate the self-consistent field (SCF) calculations. For all structures, final structure optimizations are performed using the B3LYP functional\textsuperscript{57,58} along with triple-zeta valence plus polarization basis sets\textsuperscript{59} on all atoms. The Ce basis set used for the global structure optimizations is augmented with two polarization shells of g functions with exponents 0.84 and 2.25. In addition, for the (CeO\textsubscript{2})\textsubscript{2}Ce\textsuperscript{3+} cation, the GGA functional of Becke and Perdew\textsuperscript{60,61} (BP-86) and the TPSSh meta-GGA hybrid functional\textsuperscript{62} are applied. Structures are optimized until the energy change is smaller than 1 \times 10\textsuperscript{−7} Hartree and the Cartesian gradients are smaller than 1 \times 10\textsuperscript{−4} Hartree per Bohr. The SCF convergence criteria are 1 \times 10\textsuperscript{−7} Hartree for the energy and 1 \times 10\textsuperscript{−7} a.u. for the root-mean-square of the density. Frequency calculations are performed within the harmonic approximation using analytical second derivatives.\textsuperscript{53,64} IR spectra are simulated using unscalled vibrational frequencies and intensities calculated in the harmonic approximation from analytical derivatives of the dipole moment. The latter are convoluted using a Gaussian shape function with a standard deviation of 4 cm\textsuperscript{−1}. For the optimized structure of the CeO\textsuperscript{3+}–He cation the rovibrational spectrum is simulated with the program PGRopher 7.0.\textsuperscript{65} The localization of occupied Ce f states is determined by spin density plots and, in addition, with a natural population analysis of the spin density.\textsuperscript{66}

3 Experiment

IRVPD experiments are carried out using an ion trap/tandem mass spectrometer,\textsuperscript{67,68} temporarily installed at the Free Electron Laser for Infrared eXperiments (FELIX) facility\textsuperscript{69} at the FOM Institute Rijnhuizen (The Netherlands). Cerium oxide clusters are produced by laser ablation of a cerium target using a 10 Hz laser vaporization source.\textsuperscript{70} The plasma, containing the Ce atoms, is entrained in a pulse of 0.1% O\textsubscript{2} seeded in He carrier gas and expanded through a clustering channel. After passing through a 4 mm diameter skimmer the ions are collimated and translationally cooled in a buffer gas filled radio frequency (RF) decapole ion guide. Parent ions are mass-selected in a quadrupole mass filter, deflected by 90° in an electrostatic quadrupole deflector, and focused into a cryogenically cooled RF ring electrode ion trap. To allow for continuous ion loading, ion thermalization, and ion–rare gas atom (He, Ne, Ar) complex formation, the trap is continuously filled with a buffer gas of pure He, a mixture of 0.125% Ne, or 1% Ar in He at ion trap temperatures of 15 K, 24 K and 55 K, respectively. Rare gas tagged complexes are stabilized through three-body collisions.\textsuperscript{12} After filling the trap for 98 ms, all ions are extracted from the ion trap and focused both temporally and spatially into the center of the extraction region of an orthogonally mounted linear time-of-flight (TOF) mass spectrometer. Here, the ion packet can be irradiated with the IR laser pulse prior to the application of high voltage pulses on the acceleration electrodes and the subsequent measurement of the TOF mass spectrum. IR spectra are obtained in the difference mode of operation (laser on–laser off) and recorded by monitoring all ion intensities simultaneously as the laser wavelength is scanned (50–70 measurements per wavelength step). FELIX is operated at a repetition rate of 5 Hz in the
spectral range from 400–950 cm\(^{-1}\) with a bandwidth of 0.2% root mean square of the central wavelength and an average pulse energy of 10 mJ. The photodissociation cross section \(\sigma_{\text{IRVPD}}\) is determined from the relative abundances of the parent and photofragment ions, \(I_n\) and \(I(\nu)\), and the frequency dependent laser power \(P(\nu)\) using\(^{71}\)

\[
\sigma_{\text{IRVPD}} = -\ln[I(\nu)/I_0] / P(\nu).
\]  

4 Results

CeO\(^{+}\)

For the CeO\(^{+}\) cation, a bond distance of 1.76 Å and a stretching frequency of 911 cm\(^{-1}\) are calculated. The unchanged Ce\(=\)O bond distance in the CeO\(^{+}\)-He complex and the energy of only \(-4.9\) kJ mol\(^{-1}\) for its formation

\[
\text{He} + \text{CeO}^{+} \rightarrow \text{HeCeO}^{+}
\]  

demonstrate the very weak bonding between the He atom and CeO\(^{+}\). Structure 1-1 of CeO\(^{+}\)-He shown in Fig. 1 belongs to the symmetry point group \(C_{s}\). The single unpaired electron in different Ce \(f\) states leads to almost degenerate \(2\) \(s\) and \(2\) \(0\) electronic states. For both states, the calculated Ce\(=\)O stretch frequency is redshifted by 1 cm\(^{-1}\) compared to the bare CeO\(^{+}\) cation and slightly higher than the experimental value of 891 cm\(^{-1}\). The nonlinear structure of CeO\(^{+}\)-He is confirmed by the profile of the Ce\(=\)O stretch absorption band in the experimental IRVPD spectrum (Fig. 1), which shows three peaks that correspond to the P, Q, and R branches of an asymmetric rigid rotor.\(^{72}\) In contrast, the simulated IR spectrum of linear CeO\(^{+}\)-He lacks the Q branch and shows only two peaks.

Ce\(_2\)O\(_2\)\(^{+}\)

The lowest energy structure 2-2 of the Ce\(_2\)O\(_2\)\(^{+}\) cluster is a \(D_{2h}\)-symmetric four-membered ring (Fig. 2). Three unpaired electrons in the Ce \(f\) states form a quadruplet spin state with both Ce atoms formally in the oxidation state +2.5. Two unpaired electrons occupy the virtually degenerate \(b_{1u}\) and \(b_{3u}\) orbitals delocalized over both Ce atoms and composed of \(f\) functions. The third unpaired electron occupies the fully symmetric \(a_{1g}\) orbital lying 250 kJ mol\(^{-1}\) higher in energy.

![Fig. 2 Simulated IR absorption spectrum of structure 2-2 and experimental IRVPD spectrum of Ce\(_2\)O\(_2\)\(^{+}\)-Ne. In the simulated spectrum, the absorption bands are labeled with the irreducible representations belonging to the vibrational normal modes.](image)

Ce\(_2\)O\(_2\)CeO\(^{+}\)

Fig. 3 shows the two most stable structures of the Ce\(_2\)O\(_2\)+ cation, 2-3a and 2-3b. The trigonal bi-pyramid with a \(C_{3v}\) symmetry, 2-3b, is 7 kJ mol\(^{-1}\) higher in energy than the \(C_{1v}\)-symmetric structure 2-3a consisting of a four-membered ring with the additional terminal O atom linked to one cerium atom. In the \(2\) \(A^\prime\) electronic state of 2-3a one unpaired electron occupies an \(f\) orbital on the twofold coordinated Ce atom. Structures 2-3a and 2-3b yield two different IR spectra (Fig. 4). While structure 2-3b is clearly not observed, the simulated spectrum of 2-3a agrees well with the experimental IRVPD spectrum of Ce\(_2\)O\(_2\)+-CeO\(^{+}\)-Ne. In this spectrum, the three intense transitions in the range from 527 to 674 cm\(^{-1}\) are assigned to three in-plane modes of the ring (Fig. 5) and the signal at 840 cm\(^{-1}\) to the terminal Ce\(=\)O stretching mode. A weak absorption (1.4% intensity with respect to the peak at 684 cm\(^{-1}\)) is calculated for the fourth IR active in-plane mode at 254 cm\(^{-1}\). In addition, the experimental IRVPD spectrum shows several bands of small intensity at 506, 655, 690, 703, and 790 cm\(^{-1}\), which are enhanced by exchanging the Ne with a He messenger atom (see ESI).

Ce\(_3\)O\(_4\)\(^{+}\)

The most stable isomer 3-4a shown in Fig. 3 contains three four-membered rings forming three faces of a rhombohedral
a terminal O atom to one Ce site. 3-5b forms a distorted trigonal bi-pyramid with $C_3v$ symmetry. In each isomer, there is one unpaired electron in the f states localized at one Ce atom forming a doublet spin state. (CeO$_2$)$_2$CeO$^+$ shows different IRVPD spectra depending on the messenger atom used (Ne and Ar, Fig. 4). The IRVPD spectrum of the Ne-tagged cluster exhibits a Ce=O stretching band at 817 cm$^{-1}$ which is not present in the spectrum of the Ar-tagged cluster. This indicates that the Ne atom preferentially binds to a structure containing a Ce=O moiety whereas the Ar atom stabilizes a structure without it. Comparison of the experimental to the simulated IR spectra (Fig. 4) confirms that two isomers, 3-5a and 3-5b, are probed experimentally. The contribution of each isomer can be identified by changing the messenger atom which effectively tunes the relative isomer population.

Fig. 3 shows the four most stable structures found for (CeO$_2$)$_3$CeO$^+$. The isomers 4-7b to 4-7d are located $+7$, $+19$, and $+19$ kJ mol$^{-1}$, respectively, above the global minimum structure 4-7a. Structure 4-7a consists of three pyramidal units fused such that six twofold and one fourfold coordinated O atoms are formed whereas all Ce atoms are fourfold coordinated. The topology of 4-7a can be derived from 4-7b by disconnecting one twofold coordinated O atom from one Ce atom. In this way, a terminal Ce=O bond and a threefold coordinated Ce atom are formed in the relaxed $C_s$-symmetric structure 4-7a. 4-7c is composed of two pyramidal units which share one edge yielding two fourfold and two twofold coordinated Ce atoms. One twofold coordinated Ce atom is connected to the terminal O atom. 4-7d is formed by two bi-pyramidal units sharing one face. The most stable electronic state of all (CeO$_2$)$_3$CeO$^+$ isomers is a doublet state with a single unpaired electron in a Ce f orbital. In all structures the Ce(III) site coincides with the Ce atom of lowest coordination. The simulated IR absorption spectrum of structure 4-7a agrees with the experimental IRVPD spectrum of (CeO$_2$)$_3$CeO$^+$.Ne (Fig. 4) except for the transition at 507 cm$^{-1}$. For this transition, calculations yield a very small intensity while the experimental spectrum shows an intense peak. However, the best agreement between the experimental and the simulated spectra is found for 4-7a confirming the structure assignment.

Fig. 3 shows the three most stable structures of (CeO$_2$)$_2$CeO$^+$. The energies of 3-5a and 3-5b are within 1 kJ mol$^{-1}$ whereas the energy of 3-5c is 6 kJ mol$^{-1}$ higher. Structures 3-5a and 3-5c can be derived from 3-4a and 3-4b, respectively, by adding

\[(\text{CeO}_2)_2\text{CeO}^+\]
features with 3-4b and 4-7a, i.e., the six-membered ring and the two pyramidal units sharing one face.

All structures have one unpaired electron in the Ce f states. The degree of localization of the occupied f state depends on the exchange–correlation functional used. Structure 5-9d is used to demonstrate this behavior for the functionals BP-86, B3LYP, and TPSSh. The localization of the occupied f state is quantified by natural population analysis of the spin density. With BP-86, this f state contributes 0.27 a.u. to the spin density on four Ce atoms and 0.05 a.u. on the fifth Ce atom. For B3LYP and TPSSh the spin density resides almost completely on one Ce atom making it formally Ce(III). For TPSSh the spin density on Ce(IV) sites is 0.007 a.u. and one magnitude larger than for B3LYP (−0.0009 a.u.). Different spin localizations for the same structure type lead to different stable minima, e.g., 5-9b and 5-9c (Fig. 3).

Using the BP-86 functional, it was found that structure 5-9d is lowest in energy followed by 5-9a and 5-9b with 1 and 25 kJ mol⁻¹, respectively. For B3LYP, the most stable structure is 5-9a while 5-9b, 5-9c, and 5-9d are higher by 18, 23, and 24 kJ mol⁻¹, respectively. Employing the TPSSh functional, structure 5-9d is obtained as the global minimum while 5-9a is 40 kJ mol⁻¹ higher in energy. The “Ce(III) isomers” 5-9b and 5-9c are 61 and 68 kJ mol⁻¹ higher in energy, respectively.

Only the IR absorption spectra of 5-9d obtained with the B3LYP and TPSSh functionals are in good agreement with the IRVPD spectrum of the (CeO₂)₄CeO⁺·Ne complex (Fig. 4). Hence, structure 5-9d is attributed to the experimental spectrum. The simulated spectra using the functional BP-86 do not show such an agreement for any of the structures (see ESI†).

Fig. 4 Simulated IR absorption spectra (B3LYP level, for (CeO₂)₄CeO⁺ additionally TPSSh) of the clusters shown in Fig. 3 and experimental IRVPD spectra of the cluster–rare gas atom complexes.
V2O2 IR active in-plane deformation modes of the ring (Fig. 5). The structural motif of 3-4a is also found in the oxygen-terminated (111) surface with the highlighted pyramidal CeO4 unit.

5 Discussion

The cerium oxide clusters investigated in the present work reveal structural features closely related to bulk ceria. The most stable structures of Ce2O2+ and Ce2O3+ contain a Ce-O-Ce-O four-membered ring which is also part of the bulk structure (cf. Fig. 6). This ring structure is similar to the V2O2+ and V2O3+ divanadium clusters which have been investigated before.13 The calculated spectral signature of the D2h-symmetric four-membered Ce2O2+ ring consists of two absorption bands at 457 and 528 cm⁻¹ (Fig. 2) assigned to the IR active in-plane deformation modes of the ring (Fig. 5). The V2O2+ cation shows an additional IR active in-plane vibration due to a lower symmetry (C1, or C2v). The four-membered ring of 2-3a shows four IR active in-plane modes (Fig. 3). Three of them are assigned to the three absorption bands from 527 to 674 cm⁻¹ in the IRVPD spectrum (Fig. 4). This pattern is also observed for the V2O3+ cation in the region from 650 to 1050 cm⁻¹. Similarly, the work on zirconium oxide clusters73 gave experimental evidence for four-membered rings as a structural motif of small metal oxide clusters. The clusters with more than two Ce atoms, e.g., 3-4a are composed of pyramidal units leading to strong IR signals at around 500 and 650 cm⁻¹. The structural motif of 3-4a is also found in the oxygen-terminated (111) ceria surface (Fig. 6). The high resolution electron energy loss spectrum of this surface measured by Stubenrauch et al.24 shows only a single broad (~100 cm⁻¹) band at 500 cm⁻¹ (see also ESI†). This suggests that the absorption features at around 650 cm⁻¹ mentioned above should be further redshifted in larger cerium oxide clusters.

The computational results show that in all clusters with a terminal O atom, this is always connected to a Ce atom of the oxidation state +IV. This Ce atom and the terminal O atom form the shortest bond in the clusters (1.76–1.79 Å, see ESI†) with stretching frequencies between 800 and 840 cm⁻¹ in the IRVPD spectra of 2-3a, 3-5a, 4-7a. The Ce(+III) atoms in the clusters have larger Ce-O distances (2.02–2.36 Å) than Ce(+IV) atoms which do not have bonds to the terminal O atoms (2.01–2.23 Å).

The electronic structure of partially reduced cerium oxide clusters obtained with the B3LYP and TPSSh hybrid functionals displays Ce atoms in oxidation states +III and +IV. The Ce(+III) atoms are formed by occupation of the 4f states. At the B3LYP level these f states are localized on single Ce atoms except for the clusters 2-2, 3-4a, and 3-4b. In structure 2-2 this leads to two Ce(+2.5) atoms. In the (CO2)2+CeO2+ cluster, the occupied Ce 4f states delocalize if the electronic structure is calculated with the BP-86 functional. Similar results are obtained for reduced ceria surfaces.7

A previous DFT + U study predicted the structures for neutral cerium oxide clusters.22 Some of them have the same composition as the ones investigated in the present work, i.e., (CO2)mCeO+ (m = 1–3). The predicted structures of these neutral clusters are similar to the cationic structures presented in Fig. 3 but the most stable structures of the neutral clusters are different from the global minimum structures of the cations.

Chen et al.24 performed a global minimum search for (CO2)2K using the fast inertial relaxation engine75 combined with simulated annealing on the PW91 potential energy surface. The (CO2)2K structure found is similar to the structure one would obtain if an additional O atom were inserted between two fourfold coordinated Ce atoms in isomer 5-9a of (CO2)3CeO+.

6 Summary and conclusions

The structures of the partially reduced gas-phase cerium oxide clusters with compositions Ce2O2+, Ce2O3+, and (CO2)mCeO+ (m = 0–4) are identified. Given the different predictions of different density functionals, we conclude that both theory and experiment are required for determining the lowest energy isomers of these clusters. The dicerium clusters form Ce-O-Ce-O four-membered rings typical for small transition metal oxide clusters.
The clusters containing more than two Ce atoms are composed of “pyramidal” structural subunits leading to intense IR signals at around 500 and 650 cm⁻¹. Absorption signals in the range from 800 to 840 cm⁻¹ are fingerprints for terminal Ce=O in all clusters. Whereas smaller gas-phase metal oxide clusters often have quite different structural features and properties compared to the corresponding bulk metal oxides, we find the cerium oxide gas phase clusters to represent “slightly modified” cerium oxide clusters of bulk ceria. This key finding supports the use of gas-phase cerium oxide clusters in mass spectrometric reactions, e.g., ref. 21 as models for catalytic processes on ceria surfaces.

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