Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information. Structures and Vibrational Spectroscopy of Partially Reduced Gas-Phase Cerium Oxide Clusters

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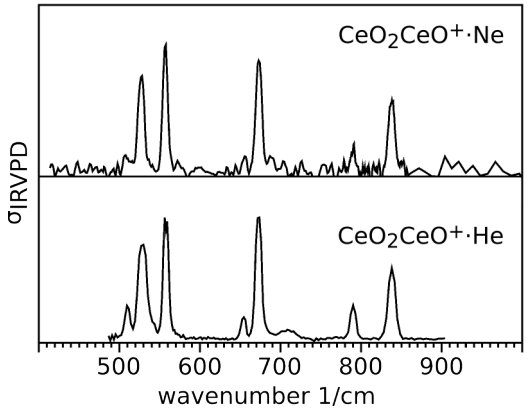
1 Experimental IRVPD spectra of CeO_2CeO^+·Ne and CeO_2CeO^+·He

The simulated IR absorption spectrum of the structure **2-3a** agrees well with the experimental IRVPD spectrum of CeO_2CeO^+·Ne (cf. Figure 4 of the publication). In this spectrum, the three intense transitions in the range from 527 to 674 cm^{-1} and the peak at 840 cm^{-1} are attributed to **2-3a**. In addition, the experimental IRVPD spectrum shows several bands of small intensity at 506, 655, 690, 703, and 790 cm^{-1}, which are enhanced exchanging the Ne with a He messenger atom. The experimental IRVPD spectra of both complexes, CeO_2CeO^+·Ne and CeO_2CeO^+·He, are given in Figure S.1.

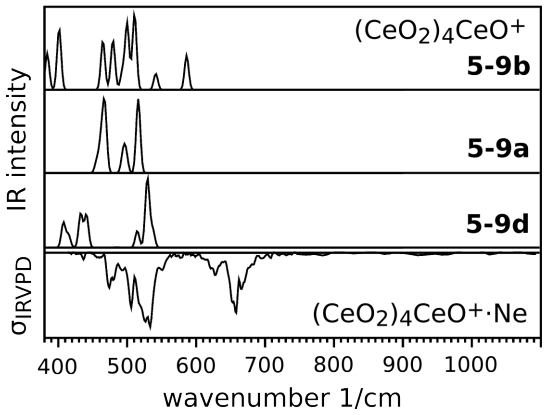
Fig. S.1: Experimental IRVPD spectra of the complexes CeO_2CeO^+·Ne and CeO_2CeO^+·He.



2 Simulated IR absorption spectra of $(CeO_2)_4CeO^+$ (BP-86 functional)

For the $(CeO_2)_4CeO^+$ cluster, the simulated IR absorption spectra of the structure **5-9d** obtained with the B3LYP and TPSSh exchange-correlation functionals are in good agreement with the experimental IRVPD spectrum of the complex $(CeO_2)_4CeO^+$·Ne. This is not the case for the simulated IR absorption spectrum obtained with the BP-86 functional (Figure S.2).

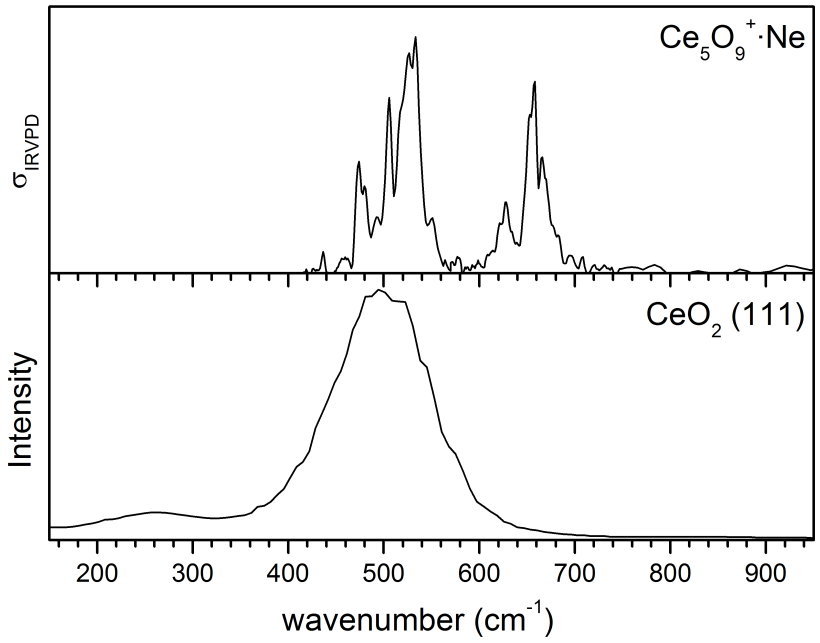
Fig. S.2: Simulated IR absorption spectra of the structures **5-9a**, **5-9b**, and **5-9d** using the BP-86 functional and the experimental IRVPD spectrum of the cluster-rare gas atom complex $(CeO_2)_4CeO^+$·Ne.



3 IR spectra of the oxygen-terminated (111) ceria surface

Stubenrauch *et al.* measured the high resolution electron energy loss (HREEL) spectrum of the oxygen-terminated (111) surface ceria (see reference 74 in our publication). This spectrum is displayed in Figure S.3 and compared with the experimental IRVPD spectrum of $(CeO_2)_4CeO^+ \cdot Ne$. In these spectra, the regions between 400 and 600 cm^{-1} show similar absorption bands for the two systems. The absorptions of the cluster-rare gas atom complex around 650 cm^{-1} are not observed in the spectrum of the surface.

Fig. S.3: Experimental IRVPD spectrum of the cluster-rare gas atom complex $(CeO_2)_4CeO^+ \cdot Ne$ and experimental HREEL spectrum of the oxygen-terminated (111) surface ceria.



4 Atomic distances and coordination numbers

The following Table S.1 shows Ce–O distances (Å) and coordination numbers for B3LYP optimized structures shown in the Figures 1, 2, and 3 of the publication. Distances are presented separately for different types of Ce and O atoms: The column O_{term}–Ce–O_μ shows distances Ce–O_{term}/Ce–O_μ of terminal O atoms (O_{term}) and bridging O atoms (O_μ) to their shared Ce atom which is always Ce(+IV). Distances of O_μ atoms to Ce(+IV) and Ce(+III) atoms without terminal oxygen are presented in the column Ce–O_μ. If there is more than one distance of the same type in a single cluster then the average is taken. Coordination numbers are determined by the interatomic distances.

Tab. S.1: Ce–O distances (Å) and coordination numbers for B3LYP optimized structures.

	O_{term}–Ce–O_μ	Ce–O_μ		Ce coordination	
isomer	Ce(+IV)	Ce(+IV)	Ce(+III)	Ce(+IV)	Ce(+III)
1-1	1.76/$\cdots$				1
2-2			2.08[a]		2×2[a]
2-3a	1.77/2.19		2.02	3	2
3-4a			2.17		3×3
3-4b			2.13		2+2×3
3-5a	1.78/2.35	2.01	2.18	3+4	3
3-5b		2.14	2.28	2×4	4
4-7a	1.79/2.31	2.14	2.17	3×4	3
5-9a		2.15	2.18	3×4+5	3[b]
5-9b		2.12	2.27	3+2×4+5	4
5-9c		2.12	2.28	3+2×4+5	4
5-9d		2.23	2.36	4×5	5

[a] Both Ce atoms are in oxidation state +2.5.

[b] In the B3LYP optimized structure the central O atom is not coordinated to Ce(+III) since the distance is 3.12 Å.