

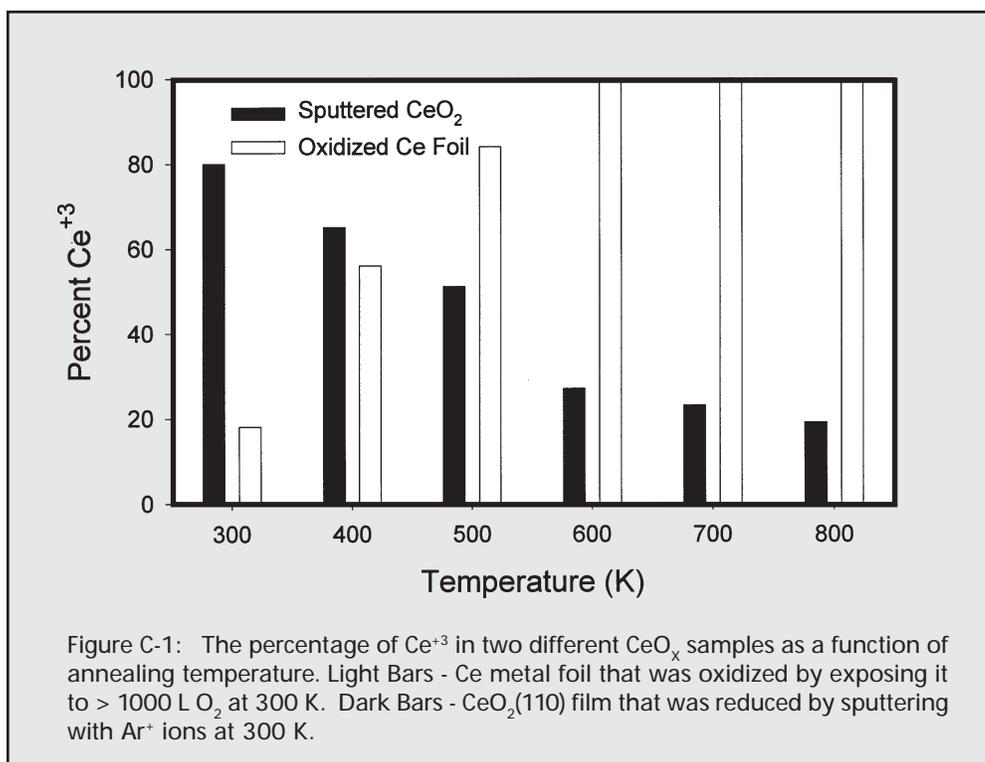
Analysis of Model Automotive Exhaust Catalysts: The Oxidation and Reduction of CeO_2

D. R. Mullins, D. R. Huntley and S. H. Overbury (Oak Ridge National Laboratory), G. N. Glavee (Lawrence University)

Modern automotive exhaust catalysts aid in the removal of toxic emissions by converting the harmful gases into more benign substances. In particular CO is oxidized into CO_2 and NO_x is reduced to N_2 and O_2 .^[1] Current automotive fuel systems are designed to maintain the air to fuel ratio in the proper stoichiometric proportions so that CO and NO_x are almost fully oxidized and reduced, respectively. However, during acceleration and deceleration the air to fuel ratio can move away from the optimal mixture so that the toxic emissions are not fully converted. Various materials have been added to the catalyst formulation in order to widen the air to fuel ratio

window in which the catalyst efficiently operates. One important component is CeO_2 .^[2] Cerium has the ability to readily convert between the +3 and +4 oxidation states, thereby releasing and storing oxygen. In doing so, it is able to assist in the reduction of NO_x under oxidizing conditions.

In order to understand the behavior of CeO_2 , the Surface Science and Catalysis Group at Oak Ridge National Lab has been studying the oxidation and reduction of Ce metal foil and single crystal CeO_2 films under UHV conditions and small $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ particles at atmospheric pressure.

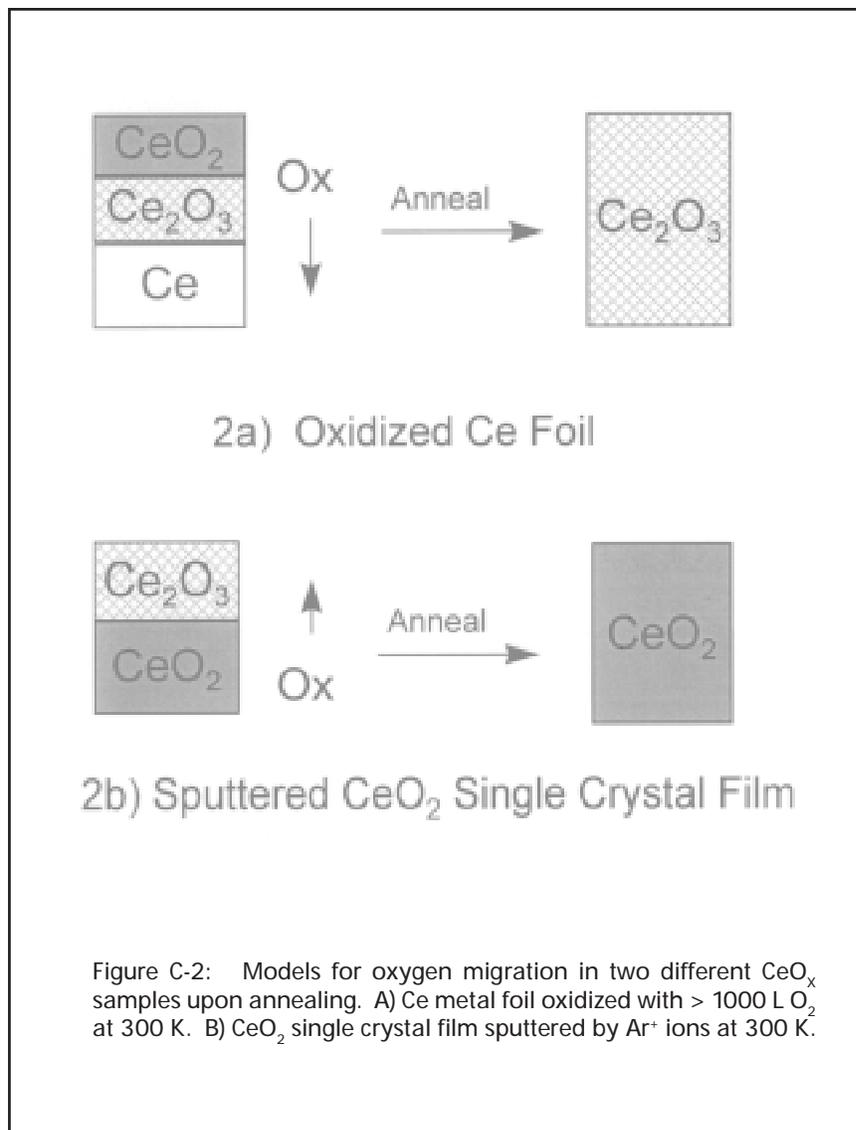


Ce Metal Foil and Single Crystal CeO₂ Films

Ce metal oxidizes readily and must be stored in an inert gas environment in order to prevent total oxidation to CeO₂. A oxygen free surface can be prepared in UHV and then the degree of oxidation can be varied by controlling the oxygen exposure. Various techniques can be used to monitor the Ce oxidation state. These methods include Ce 4d and valence band photoemission (XPS) and x-ray absorption spectroscopy (XAS) at the O 1s absorption edge.^[3] These experiments have been performed on beamline X1B.

At room temperature low exposures of O₂ (< 10 L) produce Ce(III) oxide. This layer is fairly stable and inhibits the uptake of additional oxygen. Large exposures of O₂ (~ 1000 L) are needed to produce Ce(IV) oxide. **Figure C-1** (light bars) shows the relative amount of Ce⁺³ and Ce⁺⁴ as a function of temperature. The Ce foil is the most oxidized at 300 K. The Ce(IV) oxide layer is themally unstable due to oxygen diffusion and oxidation of the underlying Ce⁰. The results indicate that oxygen transport through the Ce substrate is the limiting factor in the oxidation of the Ce bulk. The process is shown schematically in **Figure C-2a**.

The reducibility of fully oxidized CeO₂ was studied by examining single crystal CeO₂ films. These films were very difficult to reduce showing little evidence of Ce⁺³ even after exposure to > 1000 L of H₂ or CO at temperatures up to 800 K. These films could only be reduced in UHV by sputtering with inert gas ions. As shown by the dark bars in **Figure C-1**, the sputtered surfaces re-oxidized as the sample was annealed above room temperature. These surfaces were also thermally unstable due to oxygen diffusion from the bulk. This process is shown schematically in **Figure C-2b**.



Ce_xZr_{1-x}O₂ and Rh/Ce_xZr_{1-x}O₂

The oxidation and reduction of small ceria particles at atmospheric pressures were studied by x-ray absorption spectroscopy (XAS) at the Ce L_{III} edge on beamline X19A.^[4] Particles with surface areas ~ 100 m²/g were synthesized using sol-gel techniques and hypercritical drying. In addition to pure CeO₂, mixed oxides were prepared with Zr forming Ce_xZr_{1-x}O₂ particles. Some of these oxide were impregnated with 0.5 - 2% Rh, by weight. The oxides were reduced in 4% H₂/He and were oxidized in zero gas air.

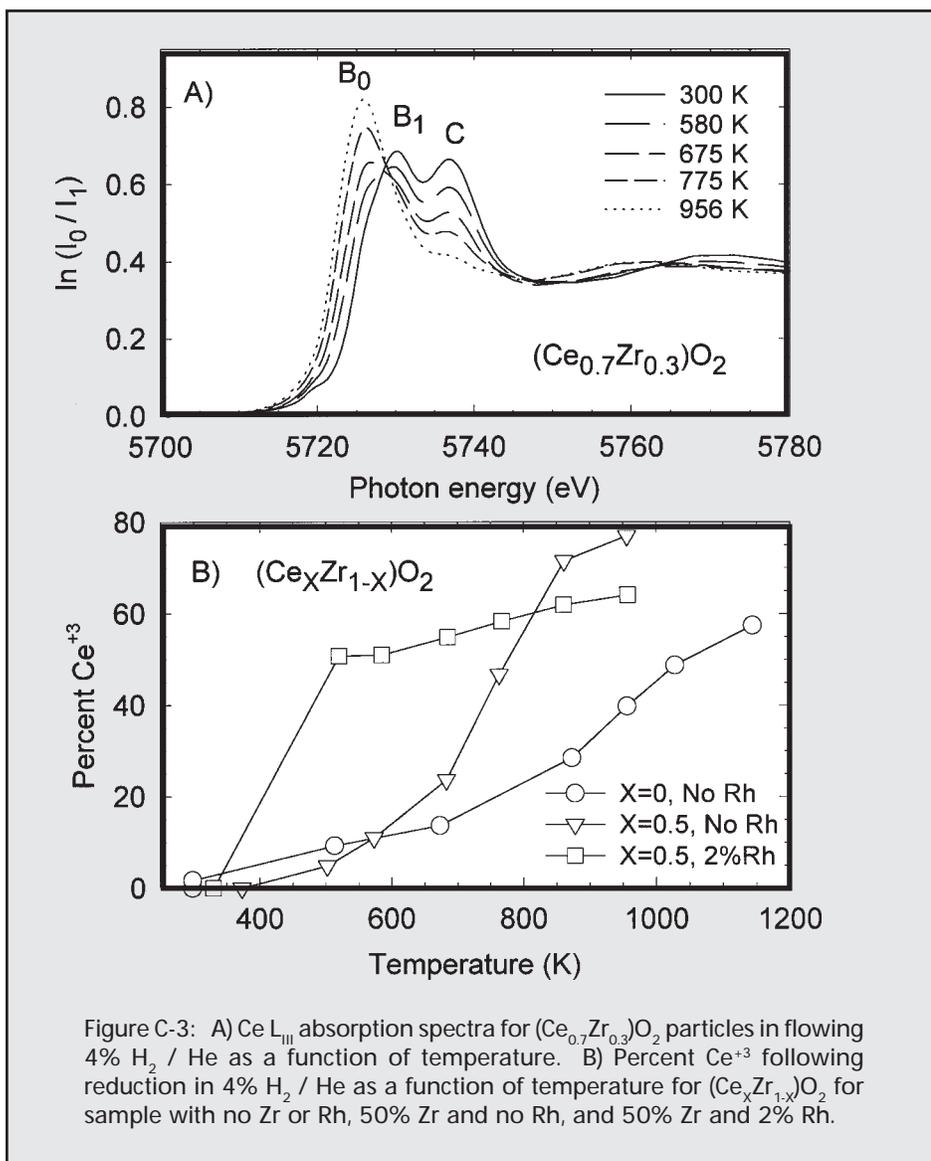
The degree of reduction can be determined from several features in the Ce L_{III} XAS.^[5] As shown in **Figure C-3a**, Peak C is associated with Ce⁺⁴ and it decreases as the sample is heated in the H₂/He atmosphere. Peak B₀ is associated with Ce⁺³ and its intensity increases during reduction. CeF₃ and reagent grade CeO₂ were used as standards for Ce⁺³ and Ce⁺⁴ spectra, respectively.

The reduction of CeO₂, Ce_{0.5}Zr_{0.5}O₂ and Rh/Ce_{0.5}Zr_{0.5}O₂ is shown in **Figure C-3b**. It can be seen that the addition of Zr enhances the extent of reduction at a given temperature while the addition of Rh reduces the temperature at which reduction occurs. ■

Acknowledgment

Research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. under contract number DE-AC05-96OR22464.

- [1] K. C. Taylor, *Catal. Rev. - Sci. Eng.* **35**, 457, (1993).
- [2] J. G. Nunan, H. J. Robota, M. J. Cohn and S. A. Bradley, *J. Catal.* **133**, 309, (1992).
- [3] D. R. Mullins, S. H. Overbury and D. R. Huntley, *Surface Sci.*, submitted.
- [4] S. H. Overbury, D. R. Huntley, D. R. Mullins and G. N. Glavée, *Catal. Lett.*, submitted.
- [5] J. El Fallah, S. Boujana, H. Dexpert, A. Kiennemann, J. Majerus, O. Touret, F. Villain and F. Le Normand, *J. Phys. Chem.* **98**, 5522, (1994).



Dynamic Effects in Core Excitation of Small Molecules

B. Kempgens, A. Kivimaki, M.N. Piancastelli, K. Maier, H.M. Koppe, M. Neeb, U. Hergenhahn, and A. M. Bradshaw (Fritz-Haber-Institut, Berlin)

The high resolution capability of X1B has continued to give new insights into dynamic effects in core excitation of small molecules. As reported last year, excitation of the antisymmetric stretching mode by vibronic coupling was observed in the O 1s photoelectron spectrum in CO₂^[1]. A consequence of this effect is that the core hole dynamically localizes on one of the O atoms; the same phenomenon has been recently observed in the photoabsorption spectrum of hydrocarbon molecules containing equivalent C atoms^[2]. In the photoelectron spectrum of the ethane molecule (C₂H₆) the intrinsic C 1s bonding-antibonding splitting of ca. 105 meV has been established for the first time^[3]. New measurements of the vibrational fine structure of the C 1s and O 1s main lines have been made in CO, as shown in **Figure C-4**. From

an analysis of the Franck-Condon factors, the bond lengths of 1.079 Å and 1.167 Å can be determined for the C 1s and O 1s core-ionized states. This shortening and lengthening of the bond with respect to the ground state can be understood from the slightly antibonding and slightly bonding nature, respectively, of the C 1s and O 1s core states in CO^[4]. In another study, measurements of the photoelectron spectra above the C 1s threshold in the series C₂H₂, C₂H₄, and C₂H₆ have called into question the existence of shape resonances in the C 1s photoionization of these molecules^[5]. Shape resonances can be understood as enhancements of the photoionization cross section by angular momentum transfer to the photoelectron caused by its scattering on the molecular core. This picture implies that they are

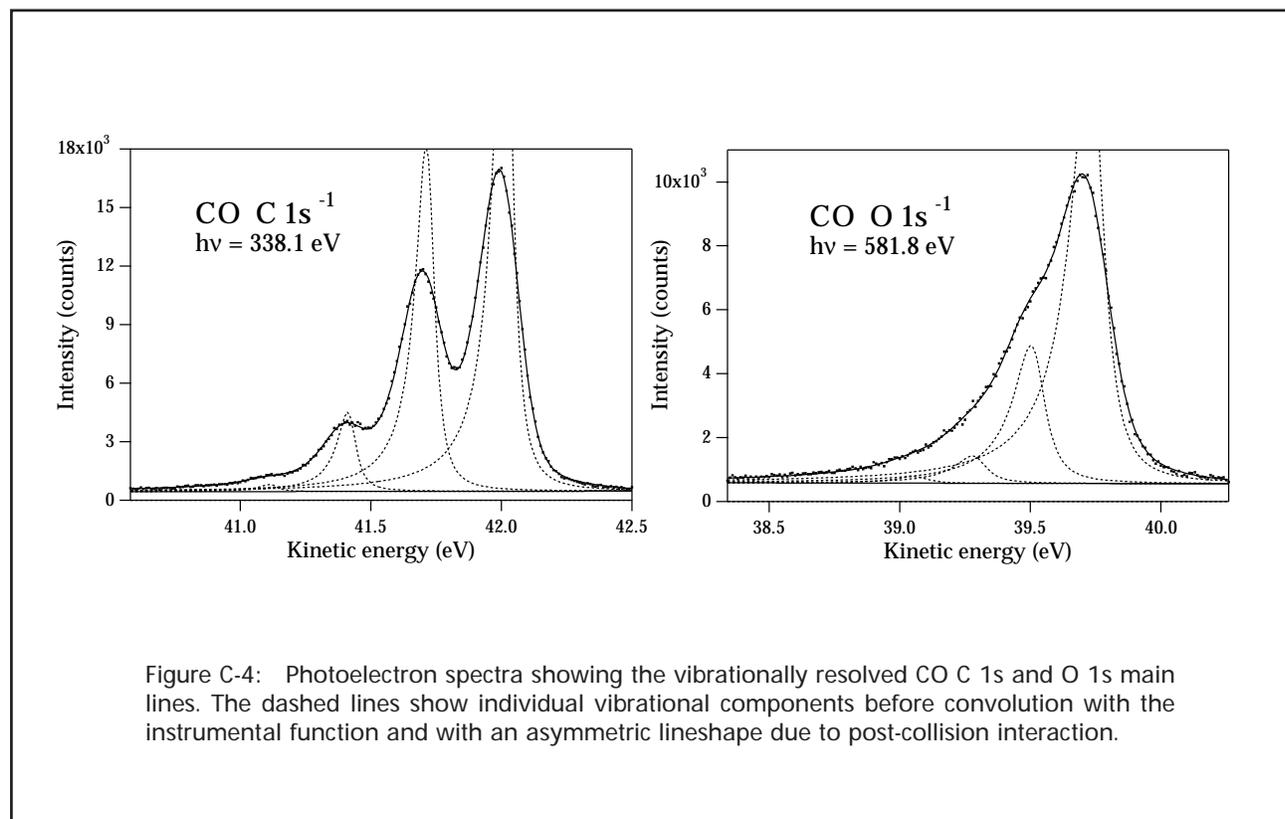


Figure C-4: Photoelectron spectra showing the vibrationally resolved CO C 1s and O 1s main lines. The dashed lines show individual vibrational components before convolution with the instrumental function and with an asymmetric lineshape due to post-collision interaction.

due to a single-particle phenomenon and should be visible in the single hole photoionization cross section. The C_2H_2 photoelectron spectrum in **Figure C-5a** depicts the C_2H_2 C 1s main line and its most prominent satellites, S1 and S0, pertaining to the triplet and singlet states, respectively, due to the valence $1(\pi)u \rightarrow 1(\pi)^*$ shake-up accompanying the C 1s photoionization. By analyzing a series of these spectra taken at photon energies over the presumed shape resonance position, it is shown that the cross-section of S0 is enhanced at a few eV above its threshold. The same is true for several other satellites, partly due to conjugate shake-up processes which involve the dipole excitation of the C 1s electron and the monopole ionization of a valence electron. Such an enhancement results in the peak around 310 eV in the photoabsorption cross-section in **Figure C-5b**. In contrast to that in the C 1s photoionization main line, no clear enhancement, as would be expected from a shape resonance, is observable. A similar phenomenon leads to a shoulder in the C 1s photoabsorption cross-section of C_2H_4 , which was also previously interpreted as a shape resonance by other researchers. This study raises the question as to whether there exists a simple linear correlation between shape resonance position and bond length, as has been proposed earlier both in gas phase spectroscopy and surface science. ■

[1] A. Kivimaki, *et al.*, *Phys. Rev. Lett.* **79**, 998, (1997).

[2] B. Kempgens, *et al.*, *Chem. Phys. Lett.* **277**, 436, (1997).

[3] B. Kempgens, *et al.*, *Phys. Rev. Lett.* **79**, 3617, (1997).

[4] B. Kempgens, *et al.*, *J. Phys. B* **30**, L741, (1997).

[5] B. Kempgens, *et al.*, *Phys. Rev. Lett.* **79**, 35, (1997).

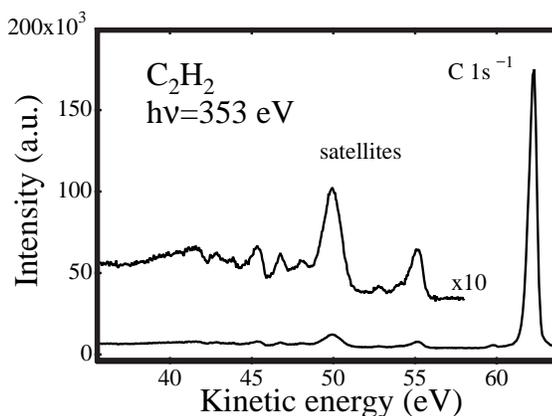


Figure C-5: (a) Photoelectron spectrum of C_2H_2 showing the main line and various satellite lines. (b) The photoabsorption and single-hole cross-sections of C_2H_2 above the C 1s threshold.

