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On the involvement of the shallow core 5d level in the bonding in HgO

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Abstract

Oxygen K shell X-ray emission spectroscopy has been used to demonstrate the covalent involvement of shallow core 5d electrons in the bonding in HgO. The extent of core hybridisation with the O-2p levels is much more pronounced in HgO than in ZnO or CdO and shows an inverse correlation with the atomic binding energy of the shallow core state. Band structure calculations confirm the importance of mixing between Hg-5d and O-2p states in HgO. However, the assumption that direct intra-atomic mixing between Hg-6s and Hg-5d orbitals determines the linear stereochemistry in HgO is shown to be incorrect.

Orthorhombic HgO adopts an unusual structure based on planar zig-zag Hg–O–Hg–O– chains [1]. The Hg–O–Hg bond angle of 107° is close to the tetrahedral value, but the coordination about Hg is essentially linear with two nearest neighbour O atoms at 203 pm. The four next nearest oxygen neighbours are much more distant at about 280 pm. By contrast ZnO adopts the zinc blende structure with tetrahedral metal coordination, whilst CdO crystallises in the rocksalt structure with regular octahedral coordination about Cd. The conventional textbook explanation [2,3] of the linear stereochemistry found in HgO and other mercury compounds is that this coordination environment promotes intra-atomic mixing between the filled shallow core Hg-5d$_{z^2}$ states and the nominally empty Hg-6s states, thus lowering the internal electronic energy of the Hg(II) ions through a second order Jahn–Teller effect. The onsite hybridisation with the shallow core-level is assumed to be more pronounced in Hg compounds than in Zn or Cd compounds because of the pattern of *empirical* atomic binding energies shown in Table 1 [4]. Here it is seen that the Hg-5d binding energy is *lower* than Cd-4d and Zn-3d binding energies, while the Hg-6s level lies at *higher* binding energy than the Cd-5s and Zn-4s levels. Thus the *difference* in energy between 6s and 5d levels in Hg is very much lower than corresponding separations in Zn and Cd. The atomic energy levels in Hg are strongly modified by relativistic effects, whose influence may be quantified in terms of differences in orbital eigenvalues between Hartree–Fock and Dirac–Fock calculations. Such a comparison [5] reveals that relativistic effects lower the energy of the highly penetrating Hg-6s electrons by 1.82 eV. Relativistic contraction of the core subshells leads to increased screening of the weakly penetrating Hg-5d orbitals. Additionally, the spin–orbit

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Table 1
Empirical atomic binding energies in Zn, Cd and Hg [4]

	Zn ($n = 3$)	Cd ($n = 4$)	Hg ($n = 5$)
$(n + 1)$s	9.39	8.99	10.43
$n\mathrm{d}_{5/2}$	17.17	17.58	14.84
$n\mathrm{d}_{3/2}$	17.50	18.27	16.70
nd (av)	17.30	17.86	15.58
nd(av) − ns	7.91	8.87	5.15

All values in eV.

interaction splits the Hg-5d levels with the overall consequence that in Dirac–Fock calculations the Hg-5$\mathrm{d}_{5/2}$ level is shifted *up* in energy by 3.80 eV relative to the Hartree–Fock limit [5]. The corresponding shift for the Hg-5$\mathrm{d}_{3/2}$ level is 1.74 eV giving a spin–orbit splitting of 2.06 eV. At the same time it is generally recognised that HgO (like other Hg compounds) is highly covalent with strong mixing between Hg-6s and O-2p orbitals. This in turn implies that there should be significant covalent mixing between Hg-5d and O-2p levels. To date, this presumption has not been tested experimentally.

Oxygen K shell X-ray emission spectroscopy provides a direct way of probing mixing between Hg-5d and O-2p states in HgO. An O-1s core hole is of course strongly localised on oxygen and radiative transitions into the hole are governed by a strict O-2p to O-1s dipole selection rule. It thus follows that if there were no mixing between Hg-5d and O-2p states, transitions from Hg-5d states would be absent from oxygen K shell emission spectra. Covalent mixing between Hg-5d states and O-2p states will give bonding and antibonding hybridised states. Wavefunctions for the lower bonding states may be written schematically as $((1/N)(a|\mathrm{Hg5d}\rangle + b|\mathrm{O2p}\rangle))$, where N is a normalisation constant and the mixing coefficients are such that $a > b$. Transitions from the bonding states are now allowed, with an intensity proportional to b^2/N^2: the O-K shell emission spectrum is therefore determined by the O-2p partial density of states. We exploit this simple idea here to demonstrate that there is indeed strong mixing between O-2p and Hg-5d states in HgO, and that this mixing is much stronger than the corresponding mixing in ZnO or CdO.

Oxygen K shell emission spectra were measured at beamline 7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, USA. This beamline is equipped with a spherical grating monochromator. Emission spectra were recorded using a Nordgren-type grazing-incidence spherical grating spectrometer with an energy resolution of 0.4 eV at the O-K edge [6,7], leading to an overall resolution of 0.85 eV. Phase-pure orthorhombic HgO (Aldrich 99.999%) was heated ex situ at 100 °C for 24 h to minimise surface contamination by water or carbonates and was then pressed into In foil. Experiments were performed with the samples held at room temperature. Pressures during the measurements were below 5.0×10^{-9} Torr. Al-Kα excited X-ray photoelectron spectra of similarly prepared samples measured on the Scienta XPS spectrometer at the NCESS facility of Daresbury Laboratory, UK, confirmed that no core lines due to contaminant atoms were observed other than a very weak C-1s signal with a C-1s/O-1s intensity ratio of around 1/100. XES is very much less surface sensitive than XPS and this low level of C contamination is essentially negligible.

The oxygen K shell emission spectrum of HgO is shown in Fig. 1, along with comparable data previously published for ZnO and CdO [8]. In each case the spectra are dominated by a broad band straddling the region between 522 and 530 eV photon energy. This is associated with states of dominant O-2p atomic character, i.e. the oxygen valence band states. For analysis of the band intensity it is possible to make a heuristic fit of this region using three Voigt components. At lower photon energy there is further weak but well-defined structure associated with states of dominant metal nd atomic character. This region may be fitted with a single Voigt peak for ZnO and CdO, but for HgO the d shell structure shows a distinct shoulder due to spin–orbit splitting and the curve fit demands the use of two components. The intensity ratio between nd structure and the O-2p structure corrected to take account of the number of electrons involved (i.e., 6 for the O-2p band, 10 for the Zn-3d or Cd-4d band, 6 for the Hg-5$\mathrm{d}_{5/2}$ band and 4 for the Hg-5$\mathrm{d}_{3/2}$ band) is plotted in Fig. 2 against the atomic nd binding energy. This plot provides clear evidence that the extent of interatomic mixing of shallow core nd states is much more pronounced in HgO than in ZnO and CdO. For the Hg-5$\mathrm{d}_{5/2}$ level the intensity ratio is about 0.12. The extent of O-2p mixing into the more tightly bound Hg-5$\mathrm{d}_{3/2}$ subshell is less pronounced with a normalised intensity ratio of around 0.07.

For comparison with the experimental data, density functional theory as embodied in the Vienna Ab-initio Simulation Package (VASP) [9,10] was used to calculate the electronic structure of HgO. The calculations included explicit treatment of the spin–orbit splitting of the Hg-5d levels. The crystal wave functions were expanded in terms of a plane wave basis set using periodic boundary conditions with a plane wave cutoff of 500 eV and a K-point grid density of 4 × 4 × 6. The generalised gradient approximation (GGA) parameterization of Perdew et al. [11] was used with the projector augmented wave method [12] employed to represent the valence–core interactions (Hg: [Xe], O: [He]). These fixed core states were generated from all-electron scalar relativistic calculations.

Calculations on a free Hg atom show a 1.83 eV splitting of the 5d states and a separation of 2.43 eV between the 5$\mathrm{d}_{5/2}$ and 6s levels. These are in reasonable agreement with the Dirac–Fock calculations indicating that the spin–orbit approach in addition to the relativistic

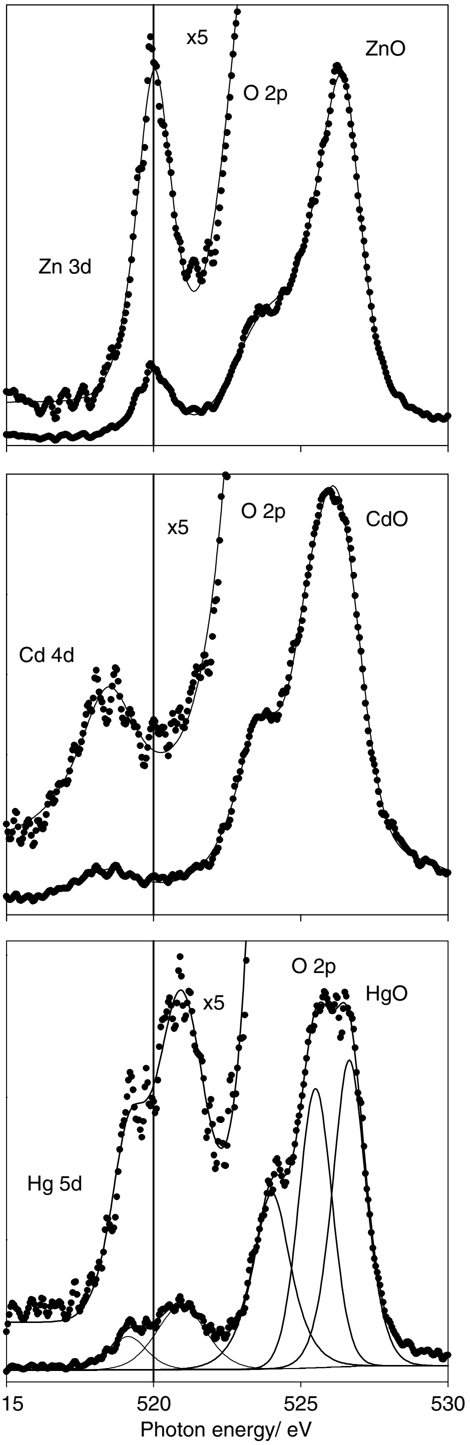

Fig. 1. Oxygen K shell X-ray emission spectra of HgO($h\nu = 570$ eV) with data for ZnO and CdO shown for comparison. Experimental spectra have been fitted to three Voigt functions in the O-2p band and to one (ZnO and CdO) or two (HgO) components in the shallow core *n*d region. The fitted components are shown for HgO. The solid lines represents the sum of the fitted components for ZnO and CdO. For ZnO a peak at 516 eV due to Zn-L_3 emission following excitation of Zn-2p electrons with second order radiation was also fitted, but for clarity this component has been subtracted from the spectra. The data for ZnO and CdO are taken from [8]. The vertical lines are added to emphasise the alignment of peaks in the three spectra.

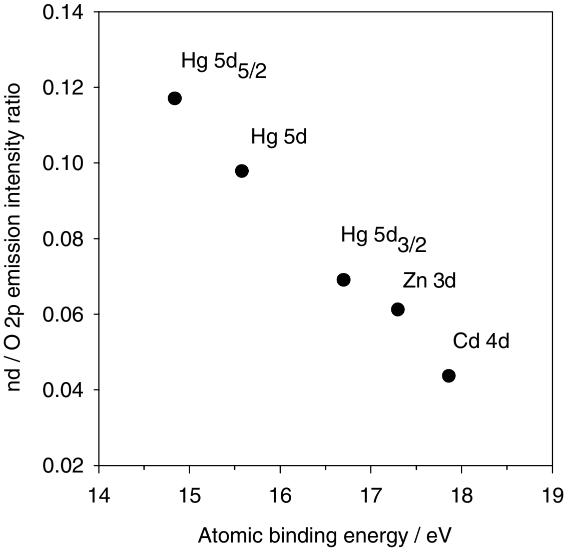

Fig. 2. Normalised intensity of O-K shell emission from levels of nominally metal *n*d character relative to O-2p valence band emission intensity plotted against empirical *n*d shallow core atomic binding energy. For ZnO and CdO both the emission intensity and the binding energies represent averages of values for $d_{5/2}$ and $d_{3/2}$ spin orbitals, but for HgO it is possible to determine both the average value and separate values for the $5d_{5/2}$ and $5d_{3/2}$ levels.

frozen core electrons and their subsequent effect on the valence electrons give rise to a good representation of the relativistic effects in Hg. Structural optimisation of HgO gave cell parameters $a = 674.4$ pm, $b = 567.7$ pm and $c = 368.0$ pm. The percentage deviations from the experimental values are respectively +2.0%, +2.8% and +4.4%. The nearest neighbour Hg–O bondlength was calculated to be 207 pm, which is only 2.0% greater than the experimental value of 203 pm.

The projected partial densities of states for HgO (assuming radii of 165 pm and 155 pm for Hg and O, respectively) emerging from our calculations are shown in Fig. 3. There are two peaks with dominant Hg-5d character present between −4 and −8 eV, labelled IV and V in the figure. To a first approximation these correspond to the spin–orbit split shallow core Hg states, although integration reveals that some of the $5d_{5/2}$ states must have shifted to lower energy and are located within the region dominated by $5d_{3/2}$. A second region with dominant O-2p character is present between −4.25 eV and the Fermi level. This region is found to contain three peaks labelled I, II and III, in good agreement with the X-ray emission spectra. As is usual [14], the overall spread of energies within the O-2p band is smaller in the density functional calculations (4.25 eV) than is found experimentally (6.25 eV).

On closer examination of the partial densities of states the two Hg-5d peaks IV and V can be seen to contain a significant amount of O-2p character (12% and 21%, respectively). This indicates that a strong interaction be-

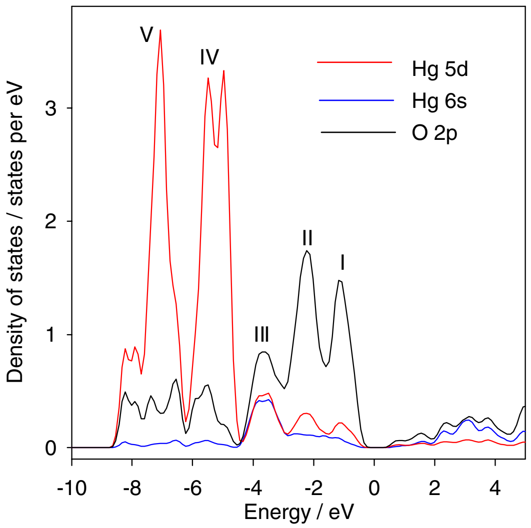

Fig. 3. Partial densities of states for HgO calculated using the VASP code. Energies are referenced to the Fermi energy, which is taken to be defined by the top of the O-2p valence band.

tween with O-2p orbitals takes place for both the Hg-5d$_{5/2}$ and Hg-5d$_{3/2}$ spin orbitals. The region between −4 and 0 eV is found to contain 18% Hg-5d and 12% Hg-6s character in addition to the dominant O-2p contribution, again demonstrating the covalent nature of HgO. The distribution of Hg-6s character is of particular interest. There is in fact very little direct mixing between Hg-6s and Hg-5d states: the occupied states IV and V have negligible Hg-6s character and the unoccupied states of dominant Hg-6s character above the Fermi level have correspondingly little Hg-5d character. By contrast peak III at bottom of the O-2p valence band is associated with states having very pronounced Hg-5d *and* Hg-6s character simultaneously. Qualitatively therefore we have found that mixing between Hg-6s and Hg-5d states is mediated by mixing with O-2p states. This scenario is at variance with the simple textbook viewpoint discussed above, which essentially ignores the highly covalent nature of mercury compounds and considers only intra-atomic hybridisation. The situation is in some ways similar to that for PbO. Here the asymmetric coordination environment found for Pb is conventionally attributed [2] to direct intra-atomic mixing between the occupied Pb-6s level and an empty Pb-6p level. This mixing becomes possible only if the Pb ions occupy a non-centro-symmetric site and is expected to gives rise to an asymmetric electron density around Pb. However, we have recently shown [13] that the Pb-6s states mix strongly with O-2p states to give a lower in-phase combination of dominant Pb-6s character and an upper out-of-phase combination of dominant O-2p character. The asymmetric electron density derives mainly from mixing of the latter with the empty Pb-6p levels, rather than from direct on-site mixing between Pb-6s and Pb-6p states.

The current observations are of significant interest in relation to mercury-containing cuprate superconductors, including $HgBa_2\ Ca_2\ Cu_3\ O_{8+x}$. This compound exhibits the highest known superconducting transition temperature of any material [15–17]. It is usually assumed that hole doping is entirely confined to the CuO_2 planes [18] and that from an electronic point of view the Hg cations are simply spectators. However, the present work demonstrates that in Hg oxide phases there must be significant Hg-5d character in the O-2p bands. Thus valence band holes necessarily introduce some Hg-5d hole character. In other words p-type doping is associated with partial oxidation of Hg. This hitherto overlooked effect provides a mechanism for introduction of a weak but possibly important electronic coupling between the doped CuO_2 sheets. Further work is needed to explore the possible impact of this effect on the superconductivity.

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