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Photoelectron Spectroscopy

Analysis of the Broadening of X-ray Photoelectron Spectroscopy Peaks for Ionic Crystals**

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Dedicated to the Fritz Haber Institute, Berlin, on the occasion of its 100th anniversary

X-ray photoelectron spectroscopy (XPS) is one of the most widely applied and powerful surface-sensitive investigative tools in heterogeneous catalysis research and yields, mainly by analyzing the area and the position of XP peaks, quantitative and element-specific information on the various stages in a catalyst's life, for example, surface speciation of precursor materials, activation, aging and poisoning, and electronic structure of the active site.[1] Recently, strong evidence has been provided that the flexibility of the geometric arrangement of atoms in the active sites of a catalytic system strongly influences the system's activity and selectivity.[2] This flexibility is intimately connected to the phonon structure of materials. The so-called polaronic distortion of thin films has been discussed as an important factor in thin-film oxide systems, which have recently been shown to stabilize charge transfer from the metal substrate through the oxide film to the adsorbed molecule or metal.[3] The g-tensor properties of O_2^- spontaneously formed on a thin MgO(100) film on Mo(100) and investigated with ESR spectroscopy under ultra-high-vacuum conditions directly revealed the polaronic distortion upon charge transfer.[4] Another way of investigating vibrational properties is to look at the broadening in photoelectron spectra. This broadening is natural and easy to observe in X-ray photoelectron spectra, which are routinely measured for oxide films on metal supports. However, there has not been a way to relate the broadening of the XPS peaks to the chemical and catalytic activity of the oxide films. For the first time we demonstrate, by comparing experiments on MgO thin films with ab initio calculations, that the changes in bond lengths between the initial ground state and the core-hole ionized states are directly related to the extent of the vibrational broadening. It is reasonable to expect that changes in the initial-state polaronic distortion will significantly affect the final-state changes in bond length. In this context, it is also important to recall that charge-transfer processes have been postulated and shown to affect the catalytic properties of thin-film oxide systems.[5] In this work on the Franck–Condon vibrational broadening of the XPS peaks of MgO, we have compared the extreme charging cases of core holes on an Mg cation, which is doubly positively charged, and on an O anion, which is doubly negatively charged.

It has been known for some time that vibrational excitations lead to broadening, and sometimes even distinct structure, in XPS and photoabsorption spectroscopies (XAS).[6–11] This broadening is due to the change in the equilibrium nuclear geometry between the initial ground state of a system and the final excited or ionized state. The broadening is commonly referred to as Franck–Condon (FC) broadening.[12] Vibrational structure and FC broadening have been observed for isolated molecules[6,10] as well as for adsorbed molecules[9,11] and condensed systems, especially ionic crystals. The theoretical treatments that have been used for molecular spectra follow, in large measure, the work of Cederbaum and Domcke.[13] For the XPS of ionic crystals, the theory is based on methods developed for optical excitations in solids.[14] This theory depends on parameters for the dielectric constants and the longitudinal optical modes.[7,8] Unfortunately, neither of these approaches gives insight into the chemical changes and chemical bonding that lead to the observed FC broadenings. Herein, we present a new conceptual approach that focuses on the chemical interactions and that provides the foundation for understanding chemical effects that account for potential changes in the broadenings between bulk, surface, and thin films of oxides and other ionic materials. We also present new experimental results that demonstrate that such changes do indeed exist. Our work now makes it possible to use the FC broadening as a feature that will allow us to gain new qualitative insight and, hence, greater understanding of materials properties and processes relevant for catalysis. We consider specifically a theoretical formulation for cubic oxides, for example, MgO and MnO, although the extension to other geometries is straightforward. We first discuss the FC broadening in bulk MgO and then extend the model to a monolayer MgO film supported by

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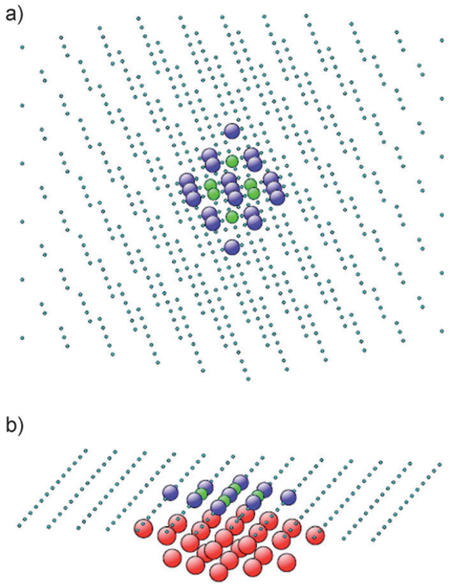

Figure 1. a) The MgO_6Mg_{18} cluster with representative point charges used to model the Madelung potential of MgO. Mg cations blue, O anions green. b) Cluster model of adsorption of monolayer MgO/Ag(100); Ag atoms red, Mg cations blue, O anions green.

Ag(100) (Figure 1). The results are compared to experimental XPS spectra obtained for MgO/Ag(100) thin films of different thickness. Results for MnO, not included herein, show the generality of our broadening analysis.

The logic of the FC broadening is shown schematically in Figure 2. We show the ground state (GS) and ionic (Ion) potential curves for three cases: Case I for $r_e(\mathrm{Ion}) \approx r_e(\mathrm{GS})$; case II for $r_e(\mathrm{Ion}) < r_e(\mathrm{GS})$; and case III for $r_e(\mathrm{Ion}) > r_e(\mathrm{GS})$, where r_e is the equilibrium Mg–O distance. On the GS curve, we show the $\nu = 0$ energy level as a horizontal line. Vertical lines are drawn at the classical turning points of the $\nu = 0$ energy level, and the intersection of the vertical lines with the hole-state potential curve represents the range of energies of excited vibrational levels that are allowed.[12,15] For case I, there will be very little vibrational broadening; in the limiting case that the two curves have the same shape, only $\nu = 0 \rightarrow 0$ transitions will have intensity. For case II, the bond length in the ion is shorter than that in the ground state. This bond shortening will occur because of the greater electrostatic interaction between a core ionized metal cation and the oxygen anions, drawing them closer to the cation. For case III, the bond in the ionic state lengthens, as would occur when an oxygen anion is ionized, thus reducing its negative charge and hence its electrostatic attraction to the metal cation. This logic is the same as that used by Iwan and Kunz;[8] however, we are able to directly determine the changes in M–O bond length Δr, and we are able to take into account changes in the harmonic vibrational frequency ω_e between the GS and the hole states. Our formalism makes it possible to relate the FC broadenings to the chemical bonding in the material. To demonstrate the application of our approach, we report results for the XPS of MgO.

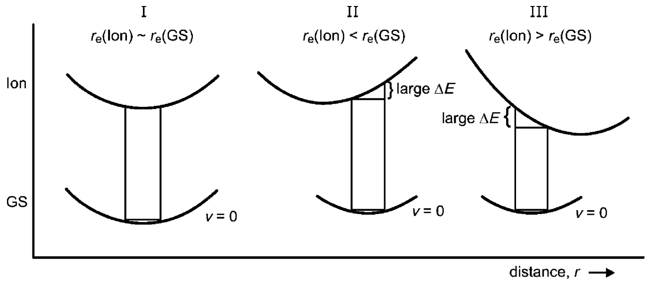

Figure 2. The Franck–Condon vibrational broadening ΔE for three cases of different equilibrium distances for the ground-state (GS) and hole-state (Ion) potential-energy curves. See text for details.

The cluster model for bulk MgO (Figure 1 a), the cluster wavefunctions, the breathing mode for the Mg–O vibrations, and other computational details are described in the Supporting Information. We present in Table 1 the calculated r_e and ω_e values for the ground and Mg 2p hole state for the MgO_6Mg_{18} cluster model; for the 2p hole, we include the broadening of the XPS peak arising from the FC vibrational excitations, as described above. For the ground state, we compute an equilibrium distance of 2.09 Å, which is very close to the experimental value for the MgO crystal of 2.11 Å.[16] The frequency of 620 cm^{-1} is in reasonable agreement with the measured longitudinal optical phonon mode, $\omega_{LO} = 727\ \mathrm{cm}^{-1}$.[17] The change in the r_e for the 2p hole state is large, approximately 0.1 Å. The ω_e for the hole state is less than 10% larger than the ω_e for the GS. This modest increase in ω_e is consistent with an increase in the Pauli repulsion at the shorter distances for the hole states but without any bond being formed.[18] The shift of r_e leads to a large FC broadening of the 2p XPS peaks. An important measure of the size of the Δr_e is that the vibrational excitations are to quite high levels ($\mathrm{v} = n$). Assuming harmonic frequencies $\omega(n) = (n + 1/2)\omega_e$, then for the 2p hole, the main intensity will go to final-state vibrational levels with n between 7 and 17. The results for the properties and the FC broadening for the Mg 2s and 1s hole states are quite similar to those for the 2p hole discussed above and are presented in the Supporting Information. This similarity is not surprising and indicates that the main force driving the changes in r_e, ω_e, and the FC broadening is the increased electrostatic attraction in this nearly ideal ionic compound.[19] Similar calculations for the O 1s and O 2s hole states of an O-centered embedded OMg_6O_{18} cluster are also discussed in the Supporting Information.

Table 1: Properties of the ground state and the Mg 2p hole state for bulk MgO.

	GS	2p hole	Δ[a]
r_e [Å]	2.09	1.97	−0.12
ω_e [cm^{-1}]	620	671	+51
FC-FWHM[b] [eV]	–	0.78	–

[a] Difference between hole and GS values. [b] Franck–Condon broadening; FWHM = full width at half maximum of the Franck–Condon broadening.

To examine the broadening of the XPS peaks for an ultrathin MgO(100) film supported on a Ag(100) substrate, we studied a cluster model of a monolayer of MgO on a Ag(100) substrate, represented by the $Ag_{25}MgO_4Mg_8$ cluster shown in Figure 1 b. The MgO_4Mg_8 adsorbate is embedded in an extended set of point charges representing the anions and cations not explicitly included; this embedding insures that the cluster model for the adsorbate gives an accurate description of the extended monolayer, especially for ionic MgO. According to standard practice, the MgO lattice constant was contracted by 3 % so that the O anions are directly over surface Ag atoms and the Mg cation is placed above the four-fold site of the Ag cluster.[20,21] As for our above work for bulk MgO, we determined potential-energy curves for the GS and for the hole states for the breathing motion of the nearest-neighbor O atoms with respect to the central Mg atom of the MgO overlayer. The optimized Mg–O bond length for the GS, r_e(Mg–O) = 2.056 Å, is close to the ideal value of r(Mg–O) = 2.043 Å, which arises when the O atoms are placed directly above surface Ag atoms.[20,21] This agreement is consistent with our choice of the ideal spacing for the embedded MgO_4Mg_8 model of the MgO monolayer. In our calculations of the monolayer of MgO/Ag(100), we have not included rumpling, since it is known to be small for MgO,[20] consistent with our preliminary results. We report results for the vibrational broadening arising from O breathing for the MgO monolayer at 4.6 bohrs (2.43 Å) above the surface; this distance is consistent with the distance reported from a slab-model band structure calculation.[20] We have looked at other distances and find that the FC broadening is not sensitive to the distance of the MgO monolayer in this region. The results for r_e, ω_e, and the FC broadening are given in Table 2. The vibrational broadening for the monolayer is significantly smaller than for the bulk (see Table 1). In Figure 3 we report experimental Mg 2p XPS spectra of 1 and 14 monolayer (ML) MgO/Ag(100) (Figure 3 a) as well as the dependence of the measured FWHM on the film thickness (Figure 3 b). A core-level shift to lower binding energy for thinner MgO films has been observed previously and is due to reduced Coulomb and charge-transfer energies for thinner films and not to charging of the thicker films.[22] The FWHM of the Mg 2p peak is approximately 1.45 eV in the limit of 1 ML MgO/Ag(100) and reaches a constant value of approximately 1.60 eV for MgO films of 10 ML and thicker. The experimentally observed reduction in the broadening is much smaller than the predicted one based on pure FC broadening. If we assume that additional instrumental broadenings, as determined by the width of the X-ray line of the unmonochromatized Al K_α radiation and the spectrometer resolution, are Gaussian and have a FWHM of 1.0 eV, then adding the vibrational broadening, also assumed to be Gaussian, would give a total broadening of 1.27 eV (bulk) and 1.08 eV (monolayer). The reduction of the FWHM from bulk to a monolayer is now close to the observed value of 0.15 eV.

Table 2: Properties of monolayer MgO/Ag(100); see Table 1.

	GS	2p hole[a]	Δ
r_e [Å]	2.06	1.96	−0.11
ω_e [cm^{-1}]	567	570	+3
FC-FWHM [eV]	–	0.42	–

[a] Weighted average of ionizing Mg 2pσ and 2pπ.

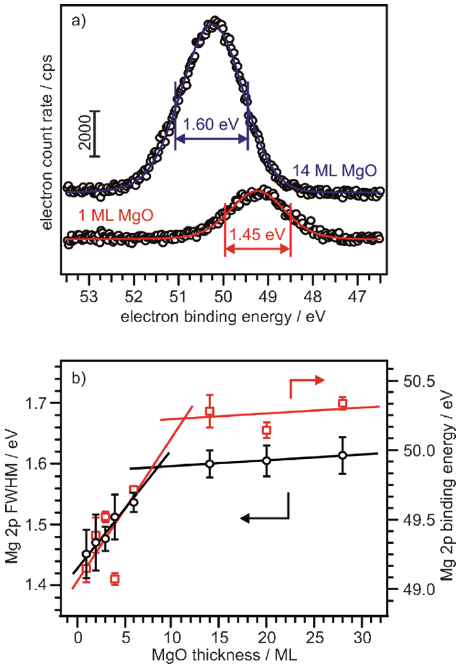

Figure 3. a) Experimental Mg 2p XPS spectra of 14 ML and 1 ML MgO/Ag(100). b) MgO thickness dependence of Mg 2p FWHM and binding energy.

The changes in the FC broadenings for the MgO monolayer from their bulk values arise because of several differences between bulk MgO and monolayer MgO in contact with and interacting with a metal support: 1) The equilibrium Mg–O distance r_e is different for bulk and monolayer MgO; this is true for both the GS and 2p hole potential curves. 2) The curvature of these potential curves, as measured by ω_e, is different between bulk and monolayer, again for both GS and 2p hole potential curves. And, 3) the final-state relaxation, or screening, for the 2p hole state is expected, and found, to be larger for the monolayer, because the polarizable metal responds to the Mg 2p hole. The results for the 2p hole states given in Table 1 and Table 2 are based on the ΔSCF method, which takes screening effects fully into account.[23] Cluster models of modest size describe, with reasonable accuracy, the relaxation of the metal conduction band charge in response to charged species in the bulk, at the surface, and as adsorbates.[18,24,25] With our cluster model, we are able to use Koopmans' theorem (KT) to rigorously separate final-state effects from initial-state effects.[23] We have computed KT potential curves for Mg–O breathing and find that the screening effects are important for the FC broadening only for the adsorbed MgO monolayer but, even here, they only lead to a 15 % change in the broadening. The largest change in the FC broadening between bulk and adsorbed monolayer MgO films arises from the initial-state bonding of the film with the Ag surface. Since it is the bonding of the MgO monolayer to Ag(100) that changes the FC broadening, the broadening of the Mg XPS for bulk, for surface, and for isolated monolayer MgO should be similar. The differences in the FC broadening of the Mg 2p XPS for these three cases, which reflect the different coordination of bulk, surface, and monolayer atoms, are approximately 10%, in strong contrast to the change of almost a factor of two between bulk MgO and monolayer MgO/Ag. This connection of the FC broadening to the bonding of the monolayer to the surface is precisely the correlation that we need in order to use the FC broadenings to provide information about the flexibility that is present for MgO monolayers on metal surfaces.

In summary, we have demonstrated a new way to use XPS broadening to investigate the flexibility of thin oxide films. Specifically, we find a pronounced decrease of the line widths of MgO ionizations when the corresponding line widths from single crystals or thick MgO films are compared with results on an ultrathin MgO film supported on Ag(100). We provide herein a simple explanation based on chemical intuition of the observed results, which is based on the concept of a Franck–Condon analysis. It is shown by quantitative cluster calculations that the decrease in the FC broadening of the Mg 2p ionization from a single layer of MgO on Ag(100) is connected to the binding of the O atoms in contact with the Ag substrate. The binding leads to changes in the Mg–O spacing and in the harmonic vibrational frequencies of the Mg–O breathing mode. As a result of this analysis, the concept of flexibility influencing catalytic activity may be further studied using photoelectron spectroscopy, a technically generally available and applicable technique.

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