

Quantitative Technique for the Determination of the Number of Unoccupied d-Electron States in a Platinum Catalyst Using the $L_{2,3}$ X-ray Absorption Edge Spectra

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This paper describes a new technique to quantitatively extract the number of unoccupied d states in a material utilizing measurements of the L X-ray absorption edge spectra. A correlation between the area under each of the L_2 and L_3 X-ray absorption edges and d-band vacancies in platinum-containing materials which exhibit white lines is given for the first time. The technique is demonstrated with a platinum catalyst supported on silica as an example. The quantity determined is the fractional change of the d-band occupancy for the sample from that of bulk platinum.

I. Introduction

The $L_{2,3}$ X-ray absorption edges in the X-ray absorption spectrum $\mu(E)$ correspond to processes in which an X-ray photon is absorbed by promoting an electron from the 2p core states. The L_2 X-ray absorption edge arises from the $2p_{1/2}$ core states, while the L_3 X-ray absorption edge arises from the $2p_{3/2}$ core states and is at a lower energy.

One of the prominent features in many $L_{2,3}$ X-ray absorption edge spectra is the enhanced X-ray absorption or "white line" which has been observed at some L_2 and L_3 X-ray absorption edges. For example, in metallic Pt a white line is observed at the L_3 X-ray absorption edge but is almost absent at the L_2 X-ray absorption edge, while for a platinum oxide (α -PtO₂) a white line is observed at both the L_3 and L_2 X-ray absorption edges. This is shown in Figure 1.

A basic theory of white lines has been given by Mott,¹ Brown, Peierls, and Stern,² and Mattheiss and Dietz.³ Mott¹ has pointed out that for the L_1 X-ray absorption edge of platinum one neither expects nor finds any sharp line at the edge due to transitions into the empty d states, because the initial L_1 core states have s symmetry and thus would not have a significant transition probability to the empty d states because of the dipole selection rule. For the L_2 and L_3 edges, on the other hand, the initial core states have p symmetry. Furthermore, for a free Pt atom the empty states in the 5d shell only have a J value of $5/2$ and thus the transition probability should be affected by the J selection rule for the unoccupied d states (i.e., $\Delta J = 0, \pm 1$). One would therefore, expect a transition from the L_3 edge where the initial state has $J = 3/2$, but not from the L_2 edge where the initial state has $J = 1/2$, thus giving rise to a difference in the L_2 and L_3 near-edge X-ray absorption structure. This is, in fact, what one finds in the case where the spin-orbit coupling has not broken down. If it were broken down, the empty d states in the metal would be a mixture of the atomic states with $J = 3/2$ and $J = 5/2$, and both X-ray absorption edges would give lines of comparable strength. Experimental measurements of the L X-ray absorption edge spectra of Cauchois and Manescu⁴ and Coster and De Lang⁵ have confirmed that spin-orbit coupling is still valid and that significant differences in the L_2 and L_3 X-ray absorption edge spectra are observed. Brown, Peierls, and Stern² quantitatively discussed the white line at the L_3 X-ray absorption edge of platinum and its absence at the L_2 X-ray absorption edge. Using the tight-binding approximation for the unoccupied Pt d states including spin-orbit interactions, they showed that the final states are predominately those with total angular momentum $J = 5/2$, contributing about 14 times more to the final d states than those with total angular momentum quantum number $J = 3/2$. This ratio was then used

to calculate an experimental value for the total absorption contribution of the white line at the L_3 X-ray absorption edge of platinum. Finally, the authors² claimed that an excellent agreement was obtained when the experimental value was compared with the theoretical value. Mattheiss and Dietz³ applied the results of a relativistic tight-binding energy-band model for Pt and Au to calculate the one-electron contribution to various X-ray and energy-loss spectra involving 4f and 2p core states in these materials. These results show that the unoccupied states in the Pt 5d bands have predominantly $J = 5/2$ character such that the ratio of the unoccupied states ($h_{5/2}/h_{3/2}$) ranges from 3.5 within 0.5 eV of the Fermi level, E_f , to 2.9 over the entire unoccupied conduction band.

More recently, Stern and Rehr have considered many-body effects on the near-edge structure in X-ray absorption.⁶ They show, in general, that the most natural single-particle states to describe the system are not the usual Hartree-Fock states but a set of states which has the excited photoelectron state orthogonal to all initially occupied states and the resulting core hole orthogonal to all finally occupied states. In the case of a material such as platinum, which has a nearly filled band, they show that the problem reduces to an effective single-particle problem for which the density of states of the initial system should be used.

Because of these advances in our theoretical understanding of the X-ray absorption white lines, several studies have used the L_3 X-ray absorption edge spectra to characterize the chemical state of the absorbing atom. Lytle et al.^{7,8} have shown that the intensity of the peak at the L_3 X-ray absorption edge is proportional to the d-electron vacancies. In their studies, they used the L_3 X-ray absorption edge spectra of the elements iridium, platinum, and gold in the pure metallic state and in a variety of compounds. They claimed that when the normalized L_3 X-ray absorption edge spectrum of the metal is subtracted from that of the metal compound, the resulting difference spectrum is related to differences in the electronic structure of the absorbing atom in the two different types of environments. Gallezot et al.⁹ studied the L_3 X-ray absorption edge spectra of platinum in various catalyst samples as a function of crystallite size and support effects. From evaluation of the area under the normalized L_3 X-ray absorption edge spectrum, they concluded that the electronic properties of very small particles change with size and environment.

However, the studies mentioned above have only considered the L_3 X-ray absorption edge spectrum. Furthermore, there was not any quantitative determination for the d-band vacancies nor even any systematic definition of the areas that they were studying. Instead, their conclusions were only qualitative. We have extended these ideas to include both the L_2 and L_3 X-ray absorption edge

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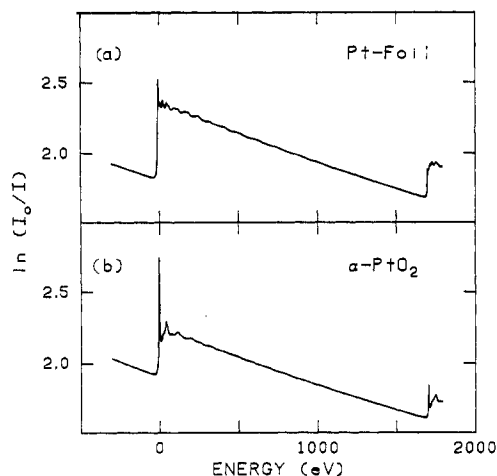


Figure 1. $\ln(I_0/I)$ is plotted vs. photoelectron energy for a thin (2.5 μm) platinum foil (a) and an $\alpha\text{-PtO}_2$ sample (b).

spectra for the first time to develop a technique to quantitatively extract the number of holes in the d bands of Pt-containing materials. The basic theoretical concepts which are required in order to account for the experimentally observed L₃ X-ray absorption edge spectra are reviewed in the next section. The details of the method for extracting the number of unoccupied d states from the white lines are presented in section III and an application of the technique to a supported Pt/SiO₂ catalyst is given in section IV.

II. Theoretical Considerations

The probability per unit time for a transition from an initial state $|i\rangle$ to a final state $|f\rangle$ by the action of a perturbation H' is given by the golden rule¹⁰

$$W = (2\pi/\hbar) |\langle f|H'|i\rangle|^2 \rho(E_f)$$

where W = transition probability per unit time, and $\rho(E_f)$ = the density of final states. The perturbation here is an X-ray photon (i.e., $H' = A \exp(ikr)$). In the dipole approximation the transition is restricted by the following selection rules:

$$\begin{aligned} \Delta L &= \pm 1 \\ \Delta J &= 0, \pm 1 \end{aligned}$$

where L = the orbital angular momentum quantum number and J = the total angular momentum quantum number ($J = L \pm 1/2$). Therefore, the L₂ X-ray absorption edge makes transitions to empty s_{1/2}, d_{3/2}, and d_{5/2} states above the Fermi level. The contributions from the final s states can be assumed to be negligible² since the density of s-symmetric final states is normally small and spread over a wide energy range, the radial part of the dipole transition matrix element for s states is approximately 1 order of magnitude smaller than that for d states, and the d-symmetric portion of the density of final states is large and narrow. Furthermore, we assume that no significant hybridization occurs and that the major features in the L_{2,3} X-ray absorption edge spectra are explained by single-electron effects in the cases that we are studying here.⁶ Therefore, the L₂ X-ray absorption edge probes those final states which are characterized by a total angular momentum quantum number $J = 3/2$, while the L₃ X-ray absorption edge probes those states with total angular momentum quantum numbers $J = 3/2$ and $J = 5/2$. This is depicted schematically in Figure 2a.

To completely understand the observed L_{2,3} near-edge X-ray absorption structure we must also account for the splitting of the final d states due to spin-orbit coupling. In a spherically symmetric field, the magnitude of this splitting, E_{so} , is given by

$$\Delta E_{\text{so}} = (5/2)\xi_d$$

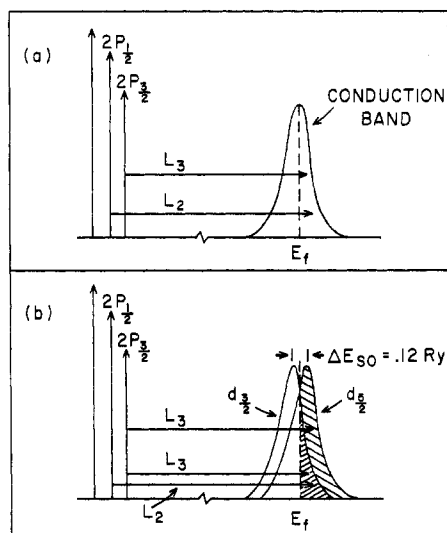


Figure 2. (a) A rough sketch of the density of states is plotted vs. energy for the L₂ edge, L₃ edge, and conduction band excluding spin-orbit coupling for the conduction band. (b) Same as part a but including spin-orbit coupling.

where ξ^d = the spin-orbit parameter for the d states. The d_{5/2} states are shifted toward higher energies, while the d_{3/2} states are shifted toward lower energies. Using Herman-Skillman atomic wave functions for Pt, Mattheiss and Dietz³ estimated that $\Delta E_{\text{so}} = 0.115$ Ry. Since this splitting is significant when compared with the d bandwidth, 0.6 Ry, it is necessary to separate the total density of final states into partial densities corresponding to each value of the total angular momentum quantum number, J , as shown in Figure 2b.

In addition, the results of a fully relativistic, tight-binding energy-band model³ for metallic Pt, using a linear combination of atomic orbitals, have shown that in the unoccupied region above the Fermi level, the density of final states is characterized predominantly by a total angular momentum quantum number of $J = 5/2$. It is the existence of those unoccupied states with $J = 5/2$ that accounts for the occurrence of an enhanced X-ray absorption, or white line, at the L₃ X-ray absorption edge of metallic Pt. This has been verified by experimental measurements¹¹⁻¹⁵ and calculations^{2,3} which indicate that L X-ray absorption edge white lines are limited to compounds with unoccupied d states above the Fermi energy.

An exact description of the relationship between the L₂ and L₃ near-edge X-ray absorption structure and the number of d-band holes around the absorbing atom depends on many-body effects which have been discussed extensively in the literature.¹⁶ Recently, Materlik et al.¹⁷ in a study of the L edge absorption spectra of rare-earth compounds claimed that a one-electron picture describes the white-line and near-edge structure quite well; however, there is not a simple relationship between the area under the white line and the unoccupied d states because of the strong energy dependence of the matrix element. This statement is a general conclusion which does not specifically consider the limit of an almost filled band discussed by Stern and Rehr.⁶ The relationship developed here is restricted to the case of Pt for which the appropriate density of states is that of the initial system. Based on these general theoretical ideas, a new technique will be proposed

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which systematically extracts the number of unoccupied d states from the experimental L_2 and L_3 X-ray absorption edge spectra. An outline of this method is presented in the next section.

III. Quantitative Technique for the Determination of d-Electron Character

The absorption of an X-ray photon results in a photoelectron being emitted with some kinetic energy, E . This kinetic energy is given by

$$E = h\nu - E_b$$

where E_b = the initial binding energy of the electron and $h\nu$ = X-ray photon energy. In this process, the absorption coefficient can be expressed as

$$\mu x = \ln(I_0/I)$$

where μ = the linear absorption coefficient, x = the absorber thickness, I_0 = the incident X-ray intensity, and I = the transmitted X-ray intensity. Therefore, in a transmission experiment, μx is determined from the experimentally measured quantities I_0 and I . The absorption coefficient is measured as a function of the X-ray photon energy to obtain the X-ray absorption spectrum.

The total X-ray absorption coefficient, μ , may be written as

$$\mu = \mu_{L_i} + \mu'$$

where μ_{L_i} is the absorption coefficient due to the initial-state electrons (corresponding to the L_2 or L_3 edges) and μ' is the absorption coefficient due to all other electrons in the system and is presumed to be monotonically decreasing over the energy region around the edge being studied. Isolation of μ_{L_i} from μ' is accomplished by using the preedge fitting procedures described in section IV. It is then assumed that μ_{L_i} may be written as

$$\mu_{L_i} = \mu_{d_i} + \mu_{s_i}$$

where μ_{d_i} is the contribution to μ_{L_i} due to the unoccupied d states and μ_{s_i} is the contribution due to the s states. Neglecting significant hybridization, the unoccupied d states will be in a narrow band with a high density of states while the s states have a small density of states spread over a wide range of energy. Thus, it is expected that μ_{d_i} will be a sharply peaked function whose area is proportional to the total number of unoccupied states contributing to the absorption by that subshell while μ_{s_i} should consist of the absorption edge, broadened by lifetime effects, but containing no other significant features.

In order to apply the technique described here, μ_{d_i} must be isolated from μ_{L_i} . This is done by approximating the form of μ_{s_i} and subtracting it from μ_{L_i} . Two types of approximations are typically used. One can assume that μ_{s_i} has the form of an arctangent.¹⁸ However, this is difficult to apply in practice because of the complication of choosing the appropriate parameters since it is only μ_{L_i} which is observed and not μ_{s_i} . The other approximation is to use an appropriate L edge of another element which has no significant structure (e.g., the Au L_2 edge). While there is still some uncertainty in scaling and positioning the threshold energy of this edge, we have found that it can be done by comparing the cross sections in the extended X-ray absorption fine structure (EXAFS) region. Details of aligning μ_{s_i} and defining the areas are described in section IV. Then the areas A_2 and A_3 which are derived from μ_{L_i} and will be used to extract the information about unoccupied states are, therefore, defined by

$$A_2 = \int [\mu_{L_2}(E) - \mu_{s_2}(E)] dE$$

$$A_3 = \int [\mu_{L_3}(E) - \mu_{s_3}(E)] dE$$

These areas are related to the number of final states through³

$$A_2 = C'(R_d^{2p_{1/2}})(1/3h_{3/2}) \quad (1)$$

$$A_3 = C'(R_d^{2p_{3/2}})(6h_{5/2} + h_{3/2})/15 \quad (2)$$

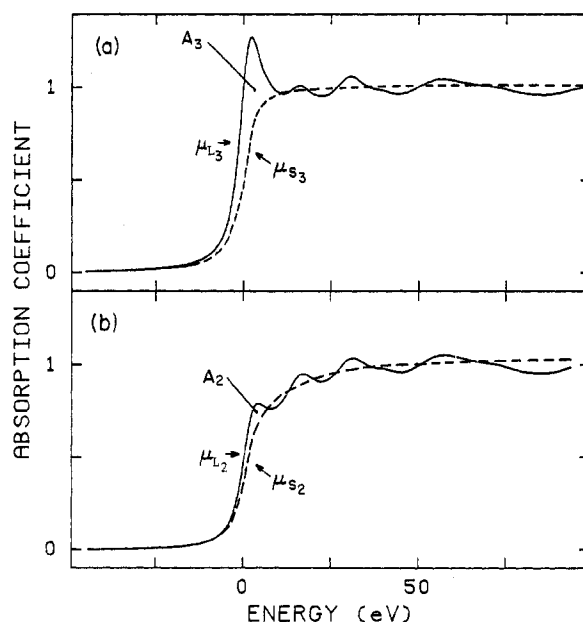


Figure 3. (a) The normalized L_3 X-ray absorption edge of platinum (solid) overlotted on a roughly sketched edge with no white line (dash). (b) The normalized L_2 X-ray absorption edge of platinum (solid) overlotted on a roughly sketched edge with no white line (dash).

where $R_d^{n'l'j'}$ = the radial part in the dipole transition matrix element connecting the core states ($n'l'j'$) with the d states, h_j = the number of unoccupied d states that are characterized by total angular momentum quantum number J , and C' = a numerical constant which depends on the element whose edge is being studied, but not on the chemical state of that element. (See Figure 3.)

Since the degeneracy for the $2p_{3/2}$ states is twice that for the $2p_{1/2}$ states, one would expect a factor of 2 difference in the edge heights or areas before normalization. However, it is found that the L_2 X-ray absorption edge spectrum should be multiplied by 2.22 in agreement with the previous results³ so that the L_2 and L_3 X-ray absorption edge spectra would align at high energies where any difference in the edge spectra should have disappeared. The variation from the value 2 results from differences in the radial part of the dipole transition matrix element. Using the factor of 2.22 between the areas for the L_2 and L_3 X-ray absorption edges, we can write eq 1 and 2 in a simpler form

$$A_2 = (1/3)Ch_{3/2} \quad (3)$$

$$A_3 = (1.11/15)C(6h_{5/2} + h_{3/2}) \quad (4)$$

where

$$C = C'(R_d^{2p_{1/2}})^2$$

Solving eq 3 and 4 for $h_{3/2}$ and $h_{5/2}$, we can express $h_{3/2}$ and $h_{5/2}$ in terms of the areas A_2 and A_3 by

$$h_{3/2} = 3A_2/C \quad (5)$$

$$h_{5/2} = (2.25A_3 - 0.5A_2)/C \quad (6)$$

Then the sum h_T , the total density of unoccupied states with d character, is defined by

$$h_T = h_{3/2} + h_{5/2} \quad (7)$$

In terms of the areas A_2 and A_3 , the sum h_T is given by

$$h_T = 2.25(A_3 + 1.11A_2)/C$$

In principle, eq 5-7 form a complete solution for $h_{3/2}$, $h_{5/2}$, and h_T . However, in practice it is difficult to determine the areas A_2 and A_3 explicitly. Therefore, $h_{3/2}$, $h_{5/2}$, and h_T cannot be determined. The complexity in determining the areas A_2 and A_3 arises because the functional formula of $\mu_{s_i}(E)$ is neither well-defined nor measurable experimentally. Furthermore, to determine

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the value of the constant C in the above-mentioned equations, an accurate band structure calculation is required. To minimize these effects the method proposed here does not attempt to find the total number of unoccupied states but instead determines the fractional change in the number of d-band vacancies relative to a reference material. This quantity f_d is defined as

$$f_d = \Delta h_T / h_{Tr} \quad (8)$$

where

$$\Delta h_T = h_{Ts} - h_{Tr}$$

s refers to the sample being studied, and r refers to the reference material. Using eq 5-7, we express f_d in terms of the areas A_2 and A_3 by

$$f_d = (\Delta A_3 + 1.11\Delta A_2) / (A_{3r} + 1.11A_{2r}) \quad (9)$$

where the changes in the areas of the sample relative to the reference compound are $\Delta A_3 = A'_{3s} - A'_{3r}$ and $\Delta A_2 = A'_{2s} - A'_{2r}$ with the primes denoting the total area due to d and s states (i.e., under μ_L and not μ_d).

The major advantage of using eq 9 for the analysis is that the areas ΔA_2 and ΔA_3 can be determined much more accurately than the absolute areas A_2 and A_3 because the reference compound is either the sample itself in a previous state or a related material (e.g., bulk metal vs. highly dispersed crystallites). The quantity $A_{3r} + 1.11A_{2r}$ is essentially the combined area per unoccupied d electron and is a constant for the type of element being studied. As shown by others^{3,19} it can be determined by assuming that the $h_{5/2}/h_{3/2}$ for the reference material is known. Equation 8 can then be rearranged to give

$$h_{Ts} = (1.0 + f_d)h_{Tr} \quad (10)$$

Therefore, h_{Ts} can be determined by assuming that h_{Tr} can be evaluated from a band structure calculation. Application of these equations to highly dispersed crystallites of platinum on silica is described in section IV.

IV. Data Analysis

In order to successfully apply the technique described above, care must be taken in analyzing the data and calculating the areas to avoid the introduction of systematic errors. The three critical components of the analysis include the removal of the background absorption, the alignment of the edges of the sample and reference data, and the normalization of the sample and reference edges. In order to discuss the details of this analysis and illustrate one area of application of this technique, the change in the unoccupied d states of a highly dispersed Pt catalyst relative to bulk platinum is presented. The catalyst consists of 2 wt % platinum supported on SiO_2 and is prepared by the ion-exchange technique.²⁰ The sample was calcined in the presence of oxygen at 623 K for 2 h and then reduced in the presence of H_2 at 473 K for 2 h. A 2.5 μm thick platinum foil was used for the measurements on the bulk material. The raw data near the L_3 X-ray absorption edge of platinum are shown in Figure 4a. The operations²¹ performed on the data in order to be able to make a valid comparison between the L_2 and L_3 X-ray absorption edges are described in the following paragraphs.

First, the energy scale is shifted so that the position of the edge, defined as the inflection point on the absorption edge step, corresponds to zero as shown by the dashed curve in Figure 4. However, the unoccupied states start at the Fermi energy for metals, and, to correctly compare two edges, their Fermi energies should be aligned. Pease²² first pointed out that the absorption edge is lowered below the Fermi energy, particularly if a sharp white line is present, because energy broadening either is introduced experimentally or is inherent in the lifetime of the excited state. The amount of lowering increases with the broadening and

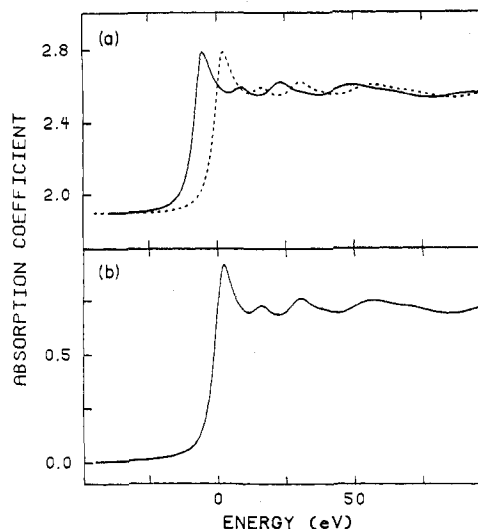


Figure 4. (a) $\ln(I_0/I)$ vs. photoelectron energy for the L_3 X-ray absorption edge of platinum foil (solid) overplotted on itself but with energy shifted so that the inflection point is assigned zero energy (dash). (b) Same as the dashed curve in part a but with preedge background subtracted.

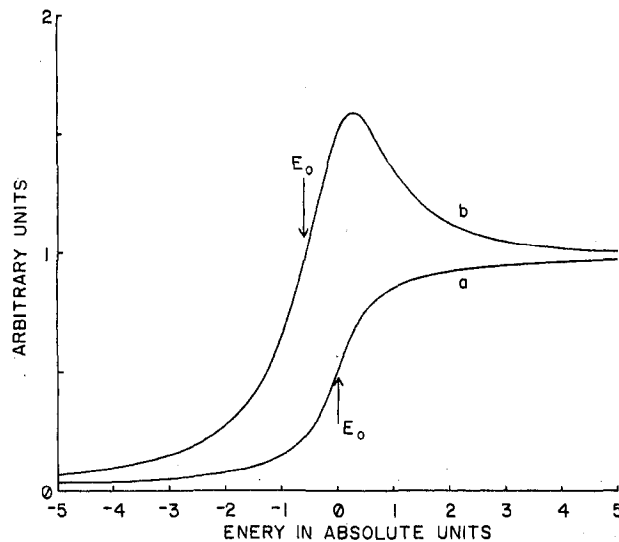


Figure 5. Schematic of the shift of the inflection point to lower energy because of the presence of a sharp white line. E_0 indicates the position of the inflection point. Curve a represents an arctangent function; curve b represents the sum of curve a and a Lorentzian distribution function.

the white-line strength as illustrated schematically in Figure 5. Thus, the use of the inflection point for edge alignment does not guarantee that the Fermi energies have been properly aligned but it does provide a systematic approach to the problem. Next, a preedge background is subtracted from the entire range of the data to remove the contribution of all other electrons to the X-ray absorption spectrum, thus isolating the partial cross section being studied (i.e., μ_L). This background is obtained by fitting the preedge data to the Victoreen formula, $C/E^3 - D/E^4$, where E is the energy and C and D are constants which must be determined. To ensure that there is no contribution from the X-ray absorption edge being studied, the fitting is done in a region well separated from the edge. It is preferable to use the same region for preedge fitting for all samples to be compared. For Pt data, the region used for fitting the preedge background extends from 300 to 70 eV below the X-ray absorption edge. The fitted Victoreen function is then extrapolated and subtracted from the entire data. The X-ray absorption spectrum with preedge background subtracted is shown in Figure 4b.

Then, the L_2 absorption edge is aligned by adjusting the energy scale so that the EXAFS oscillations in both the L_2 and L_3 absorption edges align horizontally with each other as shown in

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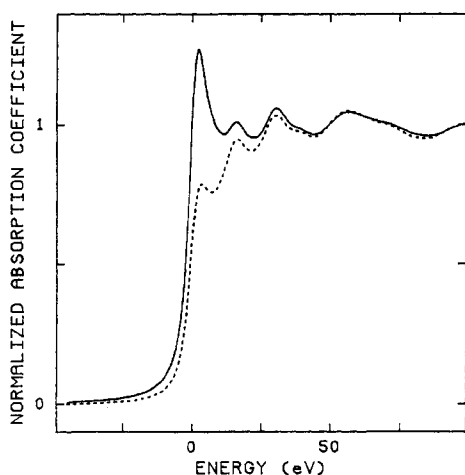


Figure 6. Normalized L_3 X-ray absorption edge of the Pt foil (solid) overlotted on the normalized L_2 X-ray absorption edge (dash).

Figure 6. This procedure is used because the EXAFS data for both edges should be the same. If the sample to be studied and the reference material have similar crystallographic structures, then the same procedure is also used to align the L_2 and L_3 absorption edges of the sample being studied with the L_2 and L_3 absorption edges of the reference material, respectively.

Next, the data are normalized so that the EXAFS of both edges align or symmetrically overlap one another at energies greater than 40 eV above the edge, as shown in Figure 6. This criterion is used because we expect the amplitude of the extended X-ray absorption fine structure on the high-energy side of an X-ray absorbing atom in a given environment to be independent of the absorption edge being probed. For samples with different atomic arrangements, the smoothly varying EXAFS background beyond the near-edge structure is used to normalize the data. The normalization value is chosen as the absorbance at the inflection point of one of the EXAFS oscillations. A spectrum is normalized by dividing each data point by the normalization value. The minimum at the foot of the white line should not be used as the normalization value, as has been done by Gallezot et al.⁹ since the absorbance at that point depends on the shape of the white line.

Finally, the edge areas are determined from the normalized data by numerical integration using Simpson's rule. For the example used here the areas are determined by using that part of the X-ray absorption spectrum which extends from 10 eV below the X-ray absorption edge to 13 eV above the X-ray absorption edge. Comparisons of the L_2 and L_3 absorption edges for the Pt/SiO₂ catalyst and the Pt foil are shown in Figure 7. The edge areas for the catalyst are $A'_{3s} = 17.94$ eV and $A'_{2s} = 12.34$ eV while those for the foil are $A'_{3r} = 17.47$ eV and $A'_{2r} = 11.24$ eV. The terms $\Delta A_3 = 0.47$ eV and $\Delta A_2 = 1.10$ eV were calculated from the differences in A'_3 and A'_2 for the catalyst and foil samples. The denominator in eq 9 ($A_{3r} + 1.11A_{2r}$) was determined following the procedure adopted by Brown, Peierls, and Stern.² The area A_{3r} was found by first calculating the difference between the areas under the L_3 and L_2 X-ray absorption edges over the range -10 to 40 eV. Second, this difference in area is then multiplied by the ratio $(h_{5/2} + h_{3/2})/h_{5/2}$ to correct roughly for white-line weight at the L_2 X-ray absorption edge. The area A_{2r} is estimated by multiplying the difference in area by the ratio $h_{3/2}/h_{5/2}$. The areas A_{3r} and A_{2r} were determined to be 7.37 eV and 0.49 eV, re-

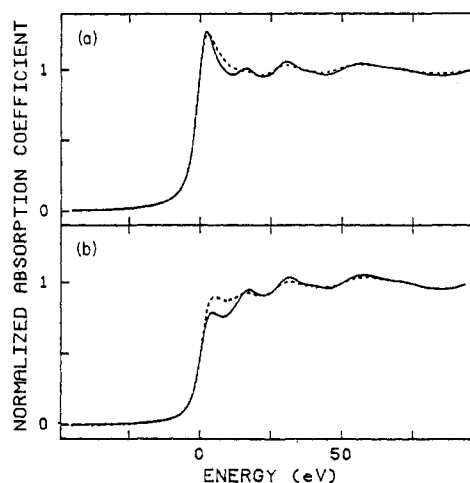


Figure 7. comparison of the L_3 edges (a) and L_2 edges (b) for the Pt/SiO₂ catalyst sample reduced at 473 K (dash) and the Pt foil (solid).

spectively. The areas are normalized² by multiplying by $\sigma\rho$ where σ is the X-ray absorption cross section at the edge jump and ρ is the density of the absorbing material. Values of 117.1 and 54.2 cm² g⁻¹ were used for the absorption cross sections at the platinum L_3 and L_2 absorption edges,²³ respectively. In terms of these normalized values and in units of eV cm⁻¹, $\Delta A_3 = 1.18 \times 10^3$, $\Delta A_2 = 1.28 \times 10^3$, $A_{3r} = 1.85 \times 10^4$, $A_{2r} = 5.70 \times 10^2$, and $A_{3r} + 1.11A_{2r} = 1.92 \times 10^4$. Substituting the above values into eq 9, one finds the value of f_d for the Pt/SiO₂ catalyst sample to be 0.14. Using eq 10 and the total number of unoccupied states for bulk platinum,² we estimate h_{T3} to be 0.34 hole as the total number of unoccupied states for the sample.

In conclusion, we must emphasize the importance of being consistent in the choice of the energy scale as well as in the choice of the normalization for the edges being compared. One should also be aware that significant changes may occur in the energy-dependent edge structure with no measurable change in the edge area. Thus, even with this technique we have not extracted all of the potential information that might possibly be obtained from X-ray absorption edge data. However, we believe that the technique does give more consistent and quantitative information from edge data for these systems than has previously been determined.

The technique has been applied here to metallic or almost metallic platinum compounds where the limit of a nearly filled d band appears to be valid. Studies are now under way to test its validity in gold and iridium compounds and on other compounds to see if a systematic demonstration of the breakdown of these approximations can be made.

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