displaces a π-bond in the interacting carbonyl group. LMO plots of the η^2-acyl bonds exhibit the true bidentate nature of this mode of bonding. The manganese–oxygen interaction is best described as the σ donation of the "π-type" lone pair orbital on the oxygen with vacant atomic orbitals on the metal. Although the η^2 interaction seems to be electronically favorable, the apparent strain present in the metallacycle works to diminish the stabilization.

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A Theoretical Study of the Bonding and XPS Spectra of Chromium Interacting with a Polyimide Model Compound

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Molecular orbital calculations have been performed on a complex of chromium with *N,N'*-diphenylpyromellitimide, a compound structurally similar to the PMDA part of the PMDA–ODA polyimide repeat unit. The PMDA/Cr complex investigated involving chromium located above the central benzene ring is one of several possible complexes formed under the experimental conditions of clean surfaces and ultrahigh vacuum. The calculated C 1s core levels, together with Koopmans' approximation, provide a reasonable fit to the carbon 1s XPS data, if it is assumed that the observed spectrum reflects a portion of both reacted and unreacted molecular species.

Introduction

Polymers such as PMDA–ODA polyimide, shown in Figure 1, have been the focus of recent interest motivated by technological applications that require thin film insulators with high thermal and mechanical stability.[1] Studies of the interface formed between such polymers and various metals have been performed to gain fundamental information about the interfacial metal–polymer bonding in an attempt to optimize relevant properties, e.g., adhesion.

The interpretation, at the molecular level, of data derived from spectroscopic studies such as XPS (X-ray photoelectron spectroscopy), is complicated by the presence of several different types of functional groups composing the PMDA–ODA polyimide polymer. It would be useful to distinguish the extent to which each of these groups interacts with the deposited metallic layer. To achieve a better understanding of metal–polymer interactions, we have studied the interaction of metal atoms with model compounds containing functional groups found in the polyimide polymer.

To investigate how the polymer might interact with deposited metal atoms, we have computationally investigated the interaction of a single metal atom with a fragment of the polyimide repeat unit. The present work will compare experimental XPS results and theoretical ab initio calculations of a PMDA model compound (*N,N'*-diphenylpyromellitimide) shown in Figure 1 (bottom). The PMDA model compound represents an excellent model for one part of the PMDA–ODA polyimide, Figure 1 (top), since it is structurally similar to the segment of the polymer that is found between two adjacent ether oxygens on a polymeric strand. By studying the PMDA model compound, information about one building block of PMDA–ODA polyimide is obtained, and certain details concerning the nature of metal–polymer interactions are revealed.

The approach that we will use is one in which the transition-metal–PMDA model compound is treated as an organometallic complex. We will look for analogies between the orbital interactions of the PMDA model compound with the transition-metal atom and similar orbital interactions in stable organometallic complexes that have been previously investigated.

Computational Methods

All calculations performed are ab initio and carried out with the GAMESS series of programs.[2] For first- and second-row atoms, an STO-3G basis set[3] was employed. Since it is well-known that the 3d orbitals of transition-metal atoms cannot be represented by a single exponent, an STO-3G expansion[4] for each of the two Slater orbitals obtained by Clementi[5] for the Cr atom was used. This had the effect of allowing the 3d orbitals of Cr to have a double-ζ expansion. The 4s and 4p orbitals of chromium were also expanded in an STO-3G basis with exponents taken from Pietro et al.[4]

For the present work, bond lengths, bond angles, and dihedral angles for the PMDA model compound were chosen from the X-ray structure of 4,4'-bis(phthalalimide) diphenyl ether.[6] The dihedral angle between the phenyl

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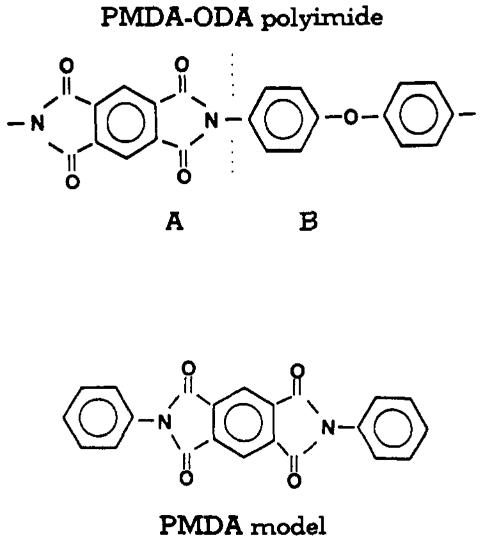
PMDA-ODA polyimide

PMDA model

Figure 1. Top: PMDA–ODA polyimide repeat unit. The PMDA part (A) and ODA part (B) are separated by the dotted line. Bottom: PMDA model compound.

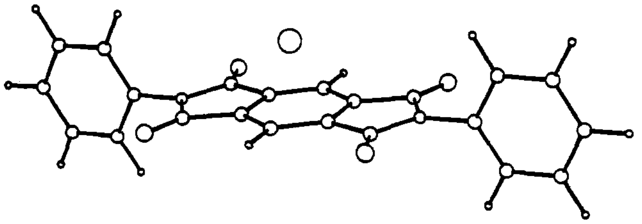

Figure 2. View of the PMDA model compound showing the Cr atom above the central benzene ring.

group and the planar bis(phthalimide) group was chosen as 60° to parallel the experimental data.[6] All phenyl groups were chosen as idealized structures with all angles equal to 120° and C–C and C–H bond distances equal to 1.39 and 1.10 Å, respectively.

The energies of the calculated core orbitals are related to the experimental C 1s XPS spectra by Koopmans' theorem.[7] Each of the calculated one-electron core energy levels is Gaussian broadened by the same amount (1.8-eV full width) in fitting the experimental data.

For purposes of comparing experimental and calculated C 1s core level shifts in the PMDA model compound, the following convention is adopted. C 1s (C═O) indicates the carbon 1s ionization energy of the carbonyl carbon atoms. The symbols Ar (arene) and Ph (phenyl) are taken to represent the central and terminal benzene rings, respectively, of the PMDA model compound shown in Figure 1 (bottom). Thus, C 1s (Ar—C═O) and C 1s (Ar—H) represent C 1s energies of the central benzene carbon atoms attached to the carbonyl groups and to the hydrogen atoms, respectively, while C 1s (Ph—N) and C 1s (Ph—H) represents C 1s energies of phenyl carbon atoms bonded to nitrogen and hydrogen atoms.

The model complex we have chosen to investigate has the Cr atom centered above the central benzene ring of the PMDA model compound as shown in Figure 2. This model complex is adopted both for computational efficiency (it has C_2 symmetry) and for its similarity to dibenzene chromium(0). In the model complex, the Cr atom is placed 1.61 Å above the midpoint of the central benzene ring. This distance corresponds to the distance found for the experimentally determined structure of the bis(benzene)chromium complex.[8]

Table I. Calculated Carbon 1s Core Level Positions (eV) with Respect to the C 1s (Ph–H) Binding Energy for PMDA Model Compound

carbon atom	core level position[a]
C(Ph—H)	+0.00
C(Ar—C═O)	+0.98
C(Ar—H)	+1.09
C(Ph—N)	+1.25
C(C═O)	+4.05

[a] All values are relative to 300.5 eV.

The PMDA model compound/Cr molecular complex is coordinatively unsaturated and does not obey the effective atomic number (EAN) rule. There is experimental evidence that gas-phase reactions of transition-metal ions with cyclic hydrocarbons yield $M(C_6H_6)^+$ ions for M = Fe^+, Co^+, and Ni^+,[10] providing some support for coordinatively unsaturated arene complexes. Moreover, all calculations performed on this complex were for a low-spin d^6 system in which the d electrons are paired. Chemical reaction of Cr with the PMDA model compound in UHV may yield oxides, cross-linking, as well as the possible formation of an organometallic complex. Nevertheless, cocondensation of Cr and arene vapors have yielded $Cr(\eta^6\text{-arene})_2$ complexes, in analogy to the PMDA model compound–Cr complex that we have investigated.[9]

Results

PMDA Model Compound without Chromium. Table I lists the calculated C 1s energies relative to the lowest binding energy C 1s (Ph–H) levels. It is seen that the core binding energies of the carbon atoms composing the central benzene ring of the PMDA model compound, C(Ar—C═O) and C(Ar—H), are shifted to within less than 0.3 eV of the C 1s (Ph–N) energy levels. On the scale of instrumental resolution, the C 1s (Ar—H), C 1s (Ar—C═O), and C 1s (Ph-N) energy levels will appear as a single peak. The C 1s (Ph–H) energies are found to be approximately 1 eV lower in binding energy than this closely spaced group of three levels. For comparison with experiment, each of the calculated C 1s levels has been assigned equal intensity, shifted by a constant energy, Gaussian broadened by 1.8 eV (full width) and then summed to yield a calculated energy distribution curve. The calculated energy distribution curve (solid line) and experimental ESCA spectrum (dotted line)[11] are shown in Figure 3. The dashed curves in Figure 3 contain groups of calculated C 1s levels close in energy. The dashed curve at highest binding energy (peak 1) contains the C 1s (C═O) levels. The middle curve (peak 2) includes C 1s (Ar—C═O), C 1s (Ar-H), and C 1s (Ph-N) levels. The lowest binding energy curve (peak 3) is composed of a number of C 1s (Ph–H) levels which are sufficiently close in energy to be grouped together as a single peak. Both relative intensities and positions of the two main peaks for the theoretical (solid) and experimental (dotted) curves are in good agreement. The broad peak at higher binding energy is attributed to a shake-up transition in the experimental ESCA spectrum. This peak

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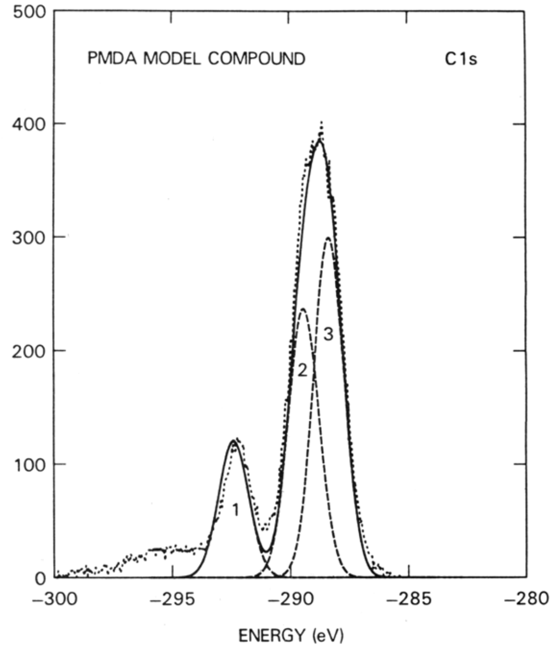

Figure 3. The calculated energy distribution curve (solid line) and experimental XPS spectrum (dotted line) of the PMDA model compound. The dashed curves contain groups of calculated C 1s levels close in energy.

is not accounted for by the calculations.

PMDA Model Compound with Chromium. Prior to discussing the results obtained for Cr interacting with the PMDA model compound, we will examine results obtained for a simpler system, namely, for one Cr metal atom interacting with benzene.[12–14] Results of a similar analysis for the PMDA model compound/Cr complex will then be given. Figure 4 shows an interaction diagram for $Cr(C_6H_6)$ constructed from the valence molecular orbitals of benzene. The relative strengths of interactions for orbitals given in Figure 4 are based on ab initio calculations and yield results that are in qualitative agreement with previous semiempirical calculations.[12,13] The benzene orbitals are on the left of the diagram, and the metal Cr 3d, 4s, and 4p orbitals are on the right. The a_{2u} benzene π orbital is stabilized by the metal s and p_z orbitals whereas the benzene e_{1g} π orbitals are stabilized by both the (d_{xz}, d_{yz}) and (p_x, p_y) orbitals. The metal $d_{x^2-y^2}$ and d_{xy} orbitals are stabilized by the benzene π^* orbitals of e_{2u} symmetry to yield the $1e_2$ degenerate set. The a_{1g} benzene π^* orbital, not shown in Figure 4, is very high in energy and has the wrong symmetry to interact with the d_{z^2} orbital. The a_{1u} π orbital lies in the nodal region of the d_{z^2} orbital, and,

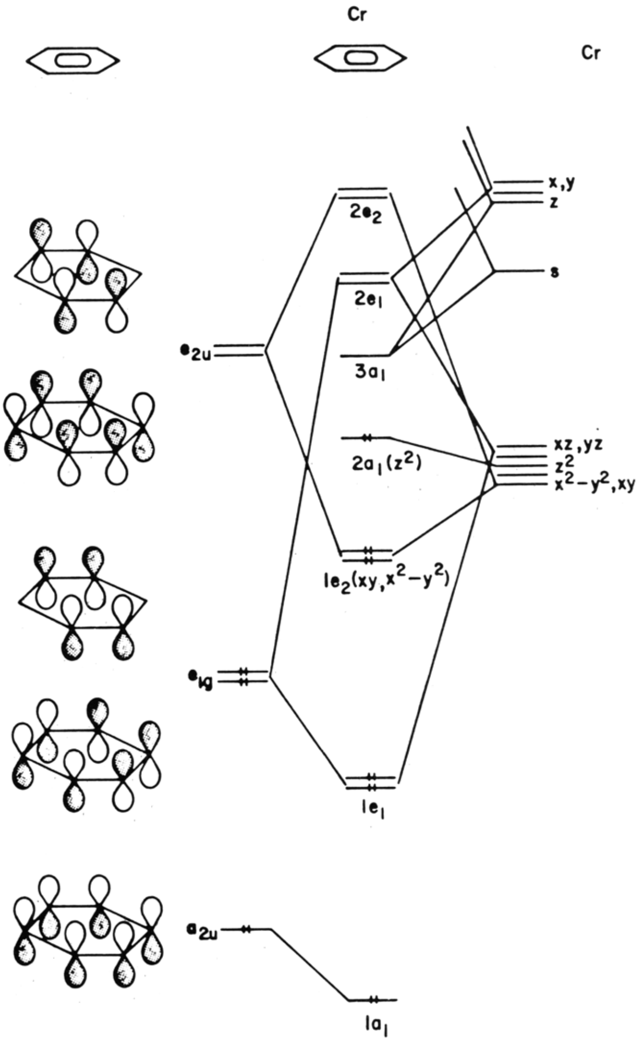

Figure 4. An interaction diagram for C_6H_6–Cr showing the construction of valence orbitals.

therefore, the $2a_1$ molecular orbital has essentially total metal d_{z^2} character. The $Cr(C_6H_6)$ complex has three empty low-lying orbitals. The $3a_1$ orbital is a mixture of s and z orbitals localized on Cr and hybridized away from the a_{2u} orbital. Similarly, the $2e_1$ orbitals consist of metal *xz* and *yz* orbitals and are also hybridized away from the benzene e_{1g} orbitals. The orbitals $3a_1$ and $2e_1$ are hybridized out and away from the benzene toward the missing ligand positions.

When the benzene molecule is replaced by the PMDA model compound, both the e_{1g} and e_{2u} orbitals are split since the neighboring C=O groups lower the symmetry to C_{2v} by interacting with the central benzene orbitals shown at the left of Figure 5. The e_{2u} orbital splits into the a_2 and a_1 orbitals shown in **1** and **2**, respectively. The amplitudes on the C(C=O) carbon atoms for the a_2 orbital were increased slightly to circumvent a cutoff for orbital contours in the plotting program. In addition to delocalization over the central benzene portion of the molecule, the molecular orbitals are also delocalized over the imide fragments. The interaction of the PMDA model compound with Cr as shown to the right of Figure 5 is similar to $Cr(C_6H_6)$, but there are important differences. The unoccupied a_1 and a_2 orbitals stabilize the d_{xy} and $d_{x^2-y^2}$ orbitals, but the lower lying a_2 orbital now interacts more strongly with the d_{xy} orbital resulting in a larger stabilization. The d_{xy} orbital on the PMDA/Cr molecular complex consists of a mixture of the pure metal Cr d_{xy} orbital and the lowest unoccupied a_2 molecular orbital of the

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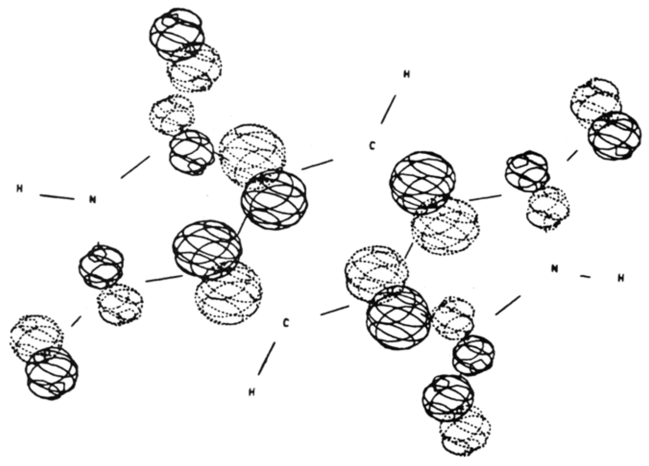

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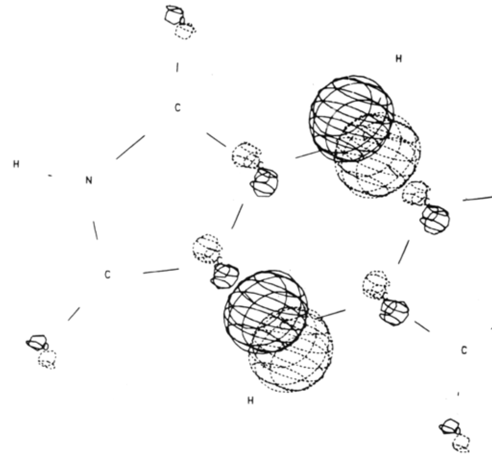

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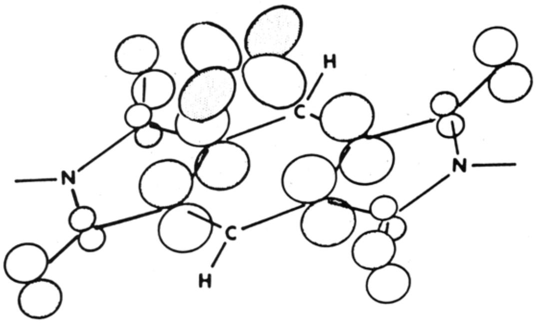

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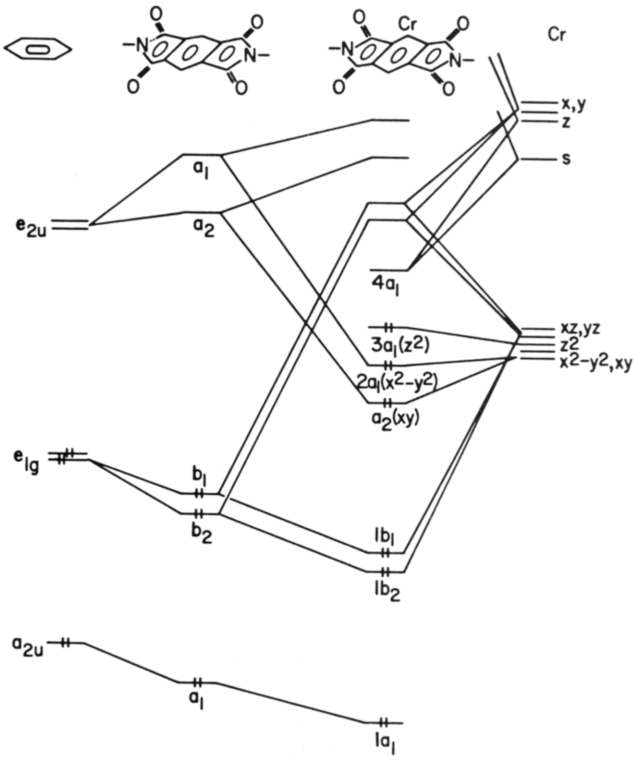

Figure 5. An interaction diagram for the PMDA model compound/Cr complex showing the construction of valence orbitals.

Table II. Selected Atomic Charges for PMDA Model Compound with and without Chromium

atom	without Cr	with Cr
C(Ar—H)	−0.04	−0.05
C(Ar—C═O)	−0.02	−0.13
C(C═O)	+0.31	+0.30
O	−0.24	−0.29
C(Ph—N)	+0.10	+0.11
C(Ph—H)	−0.06	−0.06

Table III. Calculated Carbon 1s Core Level Positions (eV) with Respect to the C 1s (Ph-H) Binding Energy for PMDA Model Compound with Chromium

carbon atom	core level position[a]
C(Ph—H)	+0.00
C(Ar—C═O)	−0.54
C(Ar—H)	+1.56
C(Ph—N)	+1.19
C(C═O)	+3.24

[a] All values are relative to 300.2 eV.

PMDA model compound molecule which is delocalized over the C(Ar—C═O) and O atoms as shown schematically in **3**. Thus, placing two electrons in the $a_2(d_{xy})$ orbital of the PMDA model compound/Cr complex transfers charge from Cr to both the C(Ar—C═O) and O atoms. The unfilled a_1 orbital of the PMDA model compound also interacts with the metal $d_{x^2-y^2}$ orbital but yields less stabilization because it is higher in energy and consequently interacts less with the metal d orbitals. Less charge is, therefore, transferred from the Cr to the unfilled a_1 orbital, and, consequently, to the C(Ar–H) atoms. These results are summarized in Table II. One sees from examination of Table II that the four C(Ar—C═O) and O atoms gain electron density in the presence of the Cr atom. The C(C═O) and C(Ar—H) carbon atom charge densities are essentially unchanged upon interaction with the Cr atom which is consistent with the character of the LUMO, a_2. The calculated C 1s energies that result from the PMDA model compound interacting with Cr are given in Table III. A comparison of the broadened calculated C 1s energy level spectrum for the PMDA model compound with and without Cr is given in Figure 6. The broadening has been chosen to simulate the resolution expected from the XPS experimental data. Peaks 1 through 5 along with the solid curves represent theoretical contributions to the XPS spectrum. The C 1s (Ar) energy levels (peaks 3 and 4) are at approximately the same position in the PMDA model compound but split as a result of interaction with Cr. One peak appears at lower binding energy [C 1s (Ar—C═O) levels] and the other at approximately the same position as found in the absence of Cr, [C 1s (Ar-H) levels]. A comparison of the results given in Tables I and III shows that the C 1s (C═O) component peak moves to lower binding energy relative to the C 1s (Ph—H) peak by about 0.8 eV as a result of Cr interaction. These results are consistent with the idea that Cr bonded to the central benzene ring of PMDA model compound selectively in-

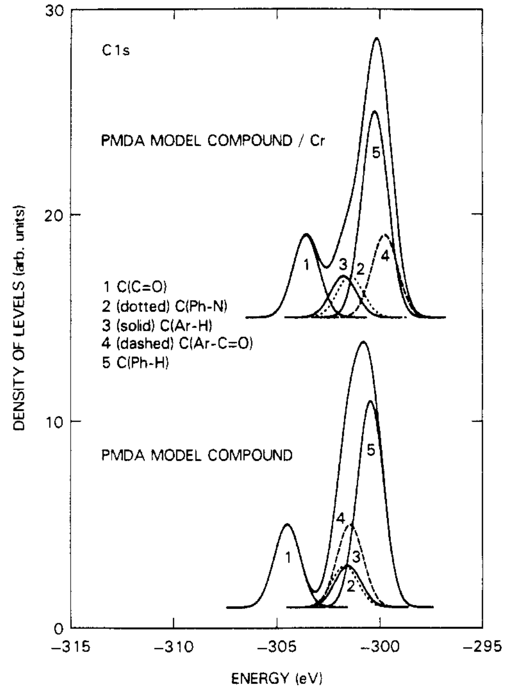

Figure 6. Broadened calculated C 1s energy levels for the PMDA model compound with and without chromium.

creases electron density at the C(Ar—C=O) sites and at the carbonyl oxygen atom sites. The atomic populations in Table II shown an increase in electron density at the C(Ar—C=O) carbon and at the carbonyl oxygen positions with Cr present. This, in turn, will induce lower C 1s binding energies which is in accord with the calculated results for these atoms. The C(C=O) atoms, on the other hand, show very little change, ΔQ, in the atomic populations since the amplitude at these sites is small for the $a_2(d_{xy})$ orbital as is shown in 3.

The change in binding energy, ΔE_B, of a carbon atom in going from the PMDA model compound to the PMDA model compound/Cr molecular complex can be represented by the expression given in eq 1. In eq 1, k is a

$$\Delta E(A)_B = k\Delta Q_A + \sum_{i\neq A} 14.4\frac{\Delta Q_i}{R_i} \qquad (1)$$

constant approximately equal to the one-center repulsion integral between a C 1s electron and valence electron on atom A,[16c] ΔQ_A is the change in atomic population on center A on which the C 1s level is located, and R_i is the distance between atom i and atom A. A comparison of changes in XPS binding energies for selected carbon atoms using calculated atomic populations incorporated into eq 1 and binding energies obtained from ab initio calculations on the PMDA model compound with and without Cr is given in Table IV. As previously discussed, the change in atomic populations, ΔQ, for the C(Ar—H) and C(C=O) atoms is essentially zero. However, as Table IV shows, the two-center term of eq 1 can produce changes in binding energies consistent with the ab inito results. Thus, the C(C=O) atoms are adjacent to O and C(Ar—C=O) atoms which gain electronic charge upon interaction with Cr. This charge decreases the C 1s binding energies of the neighboring C(C=O) atoms. The small positive shift in binding energies of the C(Ar-H) atoms upon Cr interaction is the result of the close proximity of these sites to the positively charged Cr atom.

Orbital 3 also shows C=O antibonding character which is consistent with electron energy loss (EELS) experiments[23] that indicate an initial softening of the C=O vibration and a subsequent disappearance of this peak with increasing metal coverage. The remaining C 1s (Ph-H) energy levels move to slightly lower binding energy with Cr but show no change in atomic population.

Table IV. Calculated Changes in Binding Energies (eV) for Selected Carbon Atoms from ΔE_B and SCF Calculations

atom	ΔE_B[a]	SCF
C(Ar—H)	+0.02	+0.47
C(Ar—C=O)	−1.54	−1.52
C(C=O)	−0.86	−0.81

[a] Calculated from eq 1; see text.

Several investigators have obtained C 1s energies of organometallic complexes[15–18] and have related these results to the structure and bonding of these molecules.[19,20] In order to assess the ability of the present calculations to reproduce correct relative C 1s ionization energies, we performed calculations on chromium–benzene organometallic complexes.[15,18] A comparison of experimental and theoretical results is presented in Table V. One interesting result seen in Table V is that the calculated C 1s shift is larger for the mono(benzene)chromium complex, $Cr(C_6H_6)$, than it is for the bis(benzene)chromium complex, $Cr(C_6H_6)_2$. This trend is carried over to the PMDA/Cr molecular complex and is due essentially to the electrostatic effect in which the charge transferred from the Cr is similar for both cases but is distributed over two C_6H_6 groups for the dimer as compared with one C_6H_6 for the monomer. Experimental C 1s energy shifts corresponding to the theoretical results for the PMDA model compound and related chromium complexes are not listed in Table V since both complexes are found in the solid state where charging as well as other effects make it difficult to obtain absolute C 1s energies.

It is important to point out that at the level of calculation performed for the complexes presented in this work, the ordering of the d levels is not the same as inferred from previous experimental photoelectron spectra on bis(benzene)chromium(0)[24] or obtained from previous theoretical calculations.[25] We believe this result is due to the neglect of final state effects. These effects can be obtained from SCF calculations performed on the positive ion as well, and the ionization energy is then determined by the difference in energy between the positive ion and the neutral ground state.[26] Nevertheless, we do not expect the d-level ordering to qualitatively affect the details of the charge transfer between the metal and the PMDA model compound previously discussed. For purposes of illustration, however, we have adopted the d-level ordering of that given in previous work.[12b,13]

Discussion

The XPS C 1s spectra of the PMDA model compound without Cr is shown in Figure 7a while the XPS C 1s spectrum after two 0.14 μg/cm^2 (2 Å) of chromium deposition[27] is shown in Figure 7b. Four Gaussian broadened levels, namely, peaks 1, 2, and 3, as well as a broad energy shake up peak have been fitted (solid curve) to the experimental data (dotted curve) shown in Figure 7a.

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Table V. Comparison of Theoretical and Experimental Shifts in C 1s Binding Energies for Benzene–Chromium Complexes

	C 1s (C_6H_6) energy shift,[a] eV	
	theory	expt
$Cr(C_6H_6)_2$	−0.05	+0.7,[b] −0.7[c]
$Cr(C_6H_6)$	−1.42	
$Cr(C_6H_6)(CO)_3$	+0.90	+0.3,[c] +0.64[d]

[a] The shifts in C 1s binding energies are taken relative to gas-phase experimental data on C_6H_6.[21] The geometries for $Cr(C_6H_6)$ and $Cr(C_6H_6)_2$ were taken from ref 8 while that for $Cr(C_6H_6)(CO)_3$ was obtained from ref 22. [b] Reference 15a. [c] Reference 15b, extrapolation to gas-phase value from solid state. [d] Reference 18.

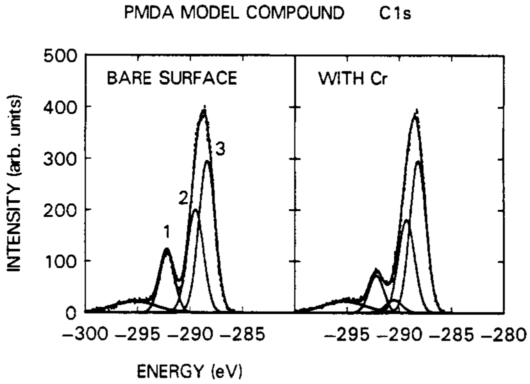

Figure 7. The XPS C 1s spectra (dotted lines) of the PMDA model compound before (left) and after (right) 0.14 μg/cm² (2-Å monolayer) of chromium deposition. The peaks 1, 2, and 3, along with the broad peak at high binding energy (shake-up transition) produce the fit of the spectrum (solid lines).

Striking changes that occur in the observed spectra of the PMDA model compound with the addition of Cr include a decrease of C 1s (C═O) peak intensity, a broadening of this peak, and a filling in of the trough between this peak and main XPS peak. There is also a smaller decrease in the central band intensity composed of the C 1s (Ar—C═O) and C 1s (Ar—H) energy levels. Little change in the corresponding C 1s (Ph—H) energy levels suggests that the terminal phenyl groups do not participate in the bonding of the PMDA model compound to Cr.

All of these observed changes in the XPS spectrum upon chromium deposition cannot be explained by assuming that each spectroscopically observed molecule undergoes the same type of interaction with Cr as we have calculated. This is so for the following reason. The broadening of each type of C 1s level has been chosen to simulate the XPS instrumental broadening and is, therefore, expected to be relatively unchanged upon Cr deposition. Therefore, if each molecule interacts with Cr in the same manner, the various C 1s peaks of different origin will just be shifted about without any change in broadening. The apparent broadening of the C 1s (C═O) levels upon Cr deposition will then be unexplained. However, if we assume that the XPS measurements sample interacting as well as noninteracting molecules, the observed broadening of the C 1s (C═O) levels upon Cr deposition can be reproduced. A reasonable fit of the broadened calculated level distribution to the experimental spectrum can be obtained by employing a 50/50 mixture of reacted and unreacted PMDA model compound. This fit is shown in Figure 8. We should also mention that the fit we have obtained is not particularly sensitive to this choice of ratios of reacted to unreacted species. For the coverages used in these experiments (1-Å monolayer or greater), there are enough Cr atoms to interact with each of the PMDA model compound molecules exposed at the polymer surface. It may well be that the emitted photoelectrons that we have observed originate from regions near the surface that involve reacted complexes as well as regions sufficiently below the surface that are unreacted with Cr.

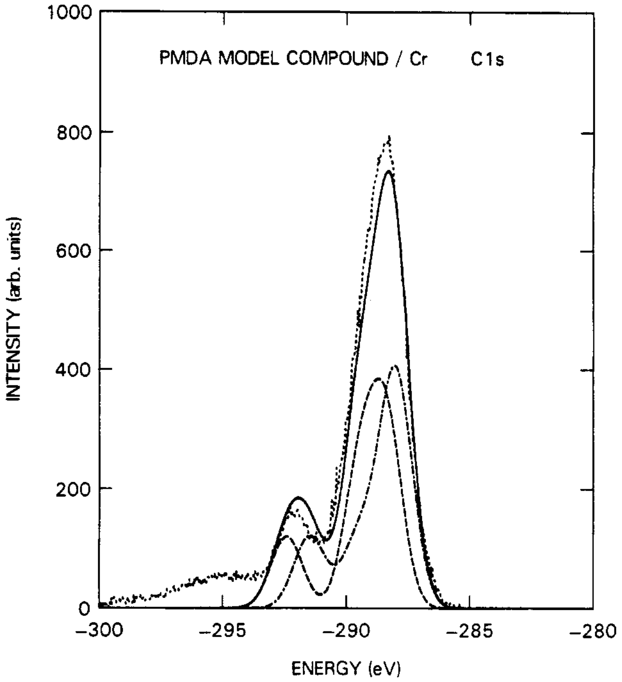

Figure 8. The experimental XPS C 1s spectrum (dotted line) and broadened calculated C 1s energy levels (solid line) of a 50/50 mixture of calculated unreacted (dashed line) and reacted (dot-dashed line) of PMDA model compound.

In conclusion, we should emphasize that the good fit between the calculated and experimentally observed XPS spectrum does not guarantee that the complex we have chosen to investigate is the actual complex responsible for the observed changes in the XPS spectrum up Cr deposition. It is certainly conceivable that one or more other complexes or reactions might affect the carbonyl carbon atom core level energies in a similar manner. Future work will be devoted to examining the consequences of other potential reactions that might occur at the interface between chromium and the PMDA model compound.

Registry No. PMDA, 6626-68-2; PMDA-ODA (SRU), 106359-25-5; PMDA-ODA (copolymer), 106359-24-4; Cr(PMDA), 106403-52-5; $Cr(C_6H_6)_2$, 1271-54-1; $Cr(C_6H_6)$, 61332-93-2; $Cr(C_6H_6)(CO)_3$, 12082-08-5.