

Unusual extramolecular relaxation-polarization shifts of low-lying orbitals in the uv photoemission spectra of adsorbed organic molecules*

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Previous uv photoemission (UPS) measurements have shown that extramolecular relaxation-polarization shifts (ERPS) of the valence molecular orbitals of adsorbed organic molecules (i.e., shifts in orbital binding energies from free-molecule values) are essentially the same for all adsorbate orbitals of a given molecule-surface system (except for those high-lying orbitals directly involved in forming the chemisorption bond to the surface). There now exists much experimental evidence, compiled in this paper, for this pattern of essentially uniform ERPS. Although not understood on theoretical grounds, the observed uniformity of ERPS is very important, and perhaps crucial, to the use of UPS in surface chemistry. Also, we report here the first significant deviations from the pattern of uniform ERPS, which occur for a few deeper-lying valence orbitals of several organic molecules. These anomalies can be understood on the basis of the atomic-orbital character of the molecular orbitals, as determined by a straightforward molecular-orbital calculation. Furthermore, it appears that such calculations make it possible to predict which orbitals of which molecules might exhibit anomalous ERPS. Thus these anomalies do not represent a serious impediment to UPS studies of surface chemistry via the uniform-ERPS assumption. Finally, the interpretation of an anomaly for chemisorbed formaldehyde (H_2CO) appears to resolve a long-standing controversy between theory and experiment regarding the ordering of orbitals in the free molecule.

I. INTRODUCTION

In studies of unsaturated and saturated hydrocarbons on Ni(111), Demuth and Eastman¹ demonstrated clearly that uv photoemission spectroscopy (UPS) measurements of organic molecules adsorbed on solid surfaces can be used (i) to determine the chemical identity of molecularly adsorbed species, (ii) to distinguish the orbitals directly involved in forming the chemisorption bond, and (iii) to estimate interaction strengths for chemisorption from observed orbital shifts measured relative to gas-phase UPS spectra. These conclusions were greatly facilitated by the observation¹ that adsorption caused essentially the *same* shift, toward smaller binding energy, for all adsorbate molecular orbitals not directly involved in forming a chemisorption bond to the surface. This uniform shift was associated with extramolecular relaxation-polarization effects which include both initial-state polarization (chemical) effects and final-state relaxation of charge about the hole created in the photoionization process.¹ Considerably different shifts observed for high-lying (small binding energy) π orbitals of unsaturated hydrocarbons were attributed to the direct participation of these orbitals in chemical bonding to the surface; these bonding shifts, toward larger binding energy, were then used to estimate interaction strengths for chemisorption.¹

As indicated by this example, the uniformity of extramolecular relaxation-polarization shifts (ERPS) plays a crucial role in realizing the full po-

tential of UPS as a tool for studying a broad range of surface reactions involving organic molecules. The UPS spectrum for the adsorbed molecule constitutes a valuable "fingerprint" of the molecular identity of the adsorbate because the nonbonding valence orbitals of the molecule—those not directly involved in chemical bonding to the surface—all shift toward smaller binding energy by the same amount upon adsorption, thus preserving most of the characteristic shape of the spectrum. Orbitals which shift relative to the nonbonding orbitals in the rest of the spectrum can then be identified as contributing strongly to forming the chemisorption bond because they exhibit significant additional shifts (toward larger binding energy) associated with chemical bonding to the surface. Thus orbital bonding mechanisms can be distinguished from relaxation-polarization effects and in some cases interaction strengths can be estimated.

The motivation for this paper arises from the important role played by the uniformity of ERPS in making UPS a valuable tool for surface chemistry. We attempt to assess the extent of applicability of the uniform ERPS approximation from a compilation of previous work and from new results presented here. This assessment seems especially needed because, at this time, there exists no satisfactory theoretical explanation for the degree of uniformity of measured ERPS nor realistic calculations of both initial- and final-state contributions to the total ERPS of adsorbed organic molecules.

Since chemisorption bonding usually involves un-

TABLE I. Uniform ERPS. uv photoemission spectra for the following surface-adsorbate systems (Refs. 1–11 in text) all display *uniform* extramolecular relaxation-polarization shifts of all valence molecular orbitals not clearly and directly involved in chemisorption bonding, with the *exception* of the few cases underlined [which involve one of the “anomalous” adsorbates H_2CO , $\text{H}(\text{CH}_3)\text{CO}$, or $(\text{CH}_3)_2\text{SO}$]. Since each surface-adsorbate system represents 4–8 well-defined adsorbate orbitals and 1 or 2 phases (e.g., chemisorbed and/or condensed), this compilation demonstrates that the statistical evidence for the uniform ERPS approximation is very strong.

Surface	Adsorbates
MoS_2 ^a	C_6H_6 , $\text{C}_5\text{H}_5\text{N}$, <u>H_2CO</u> , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$
$\text{ZnO}(1\bar{1}00)$ ^b	C_6H_6 , $\text{C}_5\text{H}_5\text{N}$, C_2H_2 , $(\text{CH}_3)\text{CCH}$, C_6H_{12} , <u>H_2CO</u> , <u>$\text{H}(\text{CH}_3)\text{CO}$</u> , $(\text{CH}_3)_2\text{CO}$, <u>$(\text{CH}_3)_2\text{SO}$</u> , CH_3OH , $\text{C}_2\text{H}_4\text{O}$
$\text{Ni}(111)$	C_6H_6 , ^c C_2H_2 , ^c $(\text{CH}_3)\text{CCH}$, ^d C_2H_4 , ^c C_6H_{10} , ^d 1, 3 butadiene, ^d propylene, ^d C_2H_6 , ^e C_3H_8 , ^e C_4H_{10} , ^e C_6H_{12} , ^e cyclopropane, ^e <i>n</i> -hexane, ^d CH_3OH , ^f <u>H_2CO</u> , ^f $(\text{CH}_3)_2\text{CO}$ ^f
$\text{Pd}(111)$	C_6H_6 , ^d C_2H_2 , ^d $(\text{CH}_3)\text{CCH}$, ^d C_2H_4 , ^d C_6H_{10} , ^d 1, 3 butadiene, ^d propylene, ^d C_2H_6 , ^d C_3H_8 , ^d C_4H_{10} , ^d C_6H_{12} , ^d cyclopropane, ^d CH_3OH ^f
$\text{Pd}(\text{poly})$ ^g	C_6H_6 , C_6H_{12} , <u>H_2CO</u> , <u>$\text{H}(\text{CH}_3)\text{CO}$</u> , $(\text{CH}_3)_2\text{CO}$, CH_3OH , CH_3OCH_3
$\text{Ni}(\text{poly})$	C_6H_6 , ^{h, i} C_2H_4 ^h
$\text{W}(110)$ ^j	C_2H_2 (from C_2H_4 dehydrogenation)
$\text{Cu}(\text{poly})$	C_6H_6 , ^d C_2H_2 , ^{d, k} cyclopropane, ^d CH_3OH ^d
$\text{Cu}(100)$ ^d	C_6H_6 , C_2H_2 , C_2H_4 , CH_3OH
$\text{Au}(\text{poly})$ ^d	C_2H_2
$\text{Fe}(\text{poly})$ ^k	C_2H_2 , C_2H_4

^a Reference 10.

^b Reference 11.

^c Reference 1.

^d Reference 7.

^e Reference 2.

^f Reference 9.

^g Reference 8.

^h Reference 5.

ⁱ Reference 4.

^j Reference 3.

^k Reference 6.

saturated π or lone-pair molecular orbitals which appear at relatively small binding energies (“high-lying” orbitals), and since one cannot at present make an unambiguous separation of ERPS and bonding shifts for orbitals directly involved in forming the chemisorption bond, the uniformity of ERPS for adsorbed organic molecules is best investigated by concentrating primarily on adsorption-induced binding-energy shifts of “low-lying” nonbonding valence molecular orbitals. In the discussion which follows, therefore, the uniformity of ERPS is considered only with respect to orbitals not clearly and directly involved in chemisorption bonding; in practice, these are all those except perhaps the highest-lying one or two orbitals (the majority of the nonbonding orbitals are low-lying valence orbitals).

The apparent uniformity of extramolecular relaxation-polarization shifts for valence molecular orbitals (MO) of organic molecules has been further documented in succeeding UPS studies on metal surfaces,^{2–9} on surfaces of inert layer compounds,¹⁰ and on active surfaces of semiconducting metal oxides.¹¹ These investigations encompass a wide variety of organic molecules (saturated and unsaturated hydrocarbons, aldehydes, ketones, al-

cohols, aromatics, ethers, and N- and S-substituted derivatives of such compounds). They include both chemisorbed and condensed molecules, the latter either directly on the surface (physisorbed) or in multilayers which may be on top of other, chemisorbed species. We summarize these results in Table I, which documents the currently strong evidence for expecting *uniform* (to within ~ 0.2 eV) ERPS in the general case. As indicated above, this empirical and statistically well-founded result is very valuable for studying surface chemistry by UPS. However, it is especially surprising in view of the different geometrical relation between the surface and the different molecular orbitals of an oriented, adsorbed molecule. The observed uniformity thus represents a challenging theoretical problem.

We have observed and report here the first significant deviations from the pattern of uniform ERPS for adsorbed organic molecules. We find that the adsorption-induced shifts of a few low-lying valence MO's of a few organic molecules on both metal and semiconductor surfaces deviate considerably (~ 0.5 – 1.0 eV) from the ERPS common to the other orbitals of the same adsorbate molecules. We show that these shifts are of two types,

both of which can be understood *and their possibility predicted* from a knowledge of the character of the molecular orbital(s) involved and its relation to the character of high-lying orbitals directly involved in chemisorption bonding. This demonstrates that even these unusual deviations from uniform ERPS, by far the largest yet observed, do not greatly diminish the utility of the uniform ERPS approximation for surface chemistry. In fact, understanding of these anomalies makes it possible to identify some of these orbitals in the UPS spectrum of the free molecule and in particular allows us to resolve a significant and long-standing controversy concerning the ordering of orbitals in the gas-phase UPS spectrum of formaldehyde.

II. EXPERIMENTAL TECHNIQUES

The UPS measurements of adsorbed molecules were carried out primarily at $h\nu = 40.8$ eV using the HeII line from a differentially pumped He resonance lamp. Photoelectron kinetic energies were analyzed with a double-pass cylindrical mirror analyzer in an electron counting mode with an energy resolution of ~ 0.35 – 0.40 eV. UPS measurements of the free molecules in the gas phase were carried out at $h\nu = 40.8$ and 21.2 eV in a similar way with essentially the same geometric orientation between light source and electron energy analyzer, and at the same resolution. This presents an optimal situation for accurately comparing orbital binding energies of the free and adsorbed molecules, since experimental geometries (except for orientation of the adsorbed molecules) and analyzer transmission factors are the same.

The ZnO measurements were performed on "as-grown" nonpolar (1100) "prism" faces which were cleaned in the ultrahigh vacuum system [operating pressure $(1-3) \times 10^{-10}$ Torr] by direct electrical heating to $\sim 700^\circ\text{C}$.¹¹ Clean Pd surfaces were prepared by evaporation from Pd wire (0.25 mm diam) onto the ZnO crystals used as substrates.⁸ Sample temperatures were monitored by a Au-Ni thermocouple fused to the ZnO. H_2CO (formaldehyde) gas was prepared from paraformaldehyde crystals as described by Yates *et al.*,¹² while other gases [$\text{H}(\text{CH}_3)\text{CO}$, $(\text{CH}_3)_2\text{CO}$, $(\text{CH}_3)_2\text{SO}$] were obtained from the equilibrium vapor pressure of reagent-grade liquids at 300 K. Residual- and adsorbate-gas partial pressures were monitored with a quadrupole mass spectrometer.

III. EXPERIMENTAL RESULTS: FORMALDEHYDE

The UPS "difference curves" ($h\nu = 40.8$ eV) showing the change in electron emission intensity due to adsorbed formaldehyde (H_2CO) on ZnO(1100) and

on evaporated Pd surfaces are given in Fig. 1. Such difference curves are obtained by measuring the emission spectrum (number of photoemitted electrons versus binding energy) for an adsorbate-covered substrate and subtracting a properly normalized spectrum of the clean substrate alone, as described previously.^{1,11} The difference curve then is a representation of the change in emission due to the presence of the adsorbed molecules, so that adsorbate molecular orbitals appear as peaks in the difference curve.

The spectrum for moderate exposure [10 langmuirs ($1 \text{ L} = 10^{-6}$ Torr sec)] of H_2CO on ZnO at 120 K is given in Fig. 1(a) and that for additional surface coverage produced by measuring in an ambient (1×10^{-7} Torr) at 120 K is given in Fig.

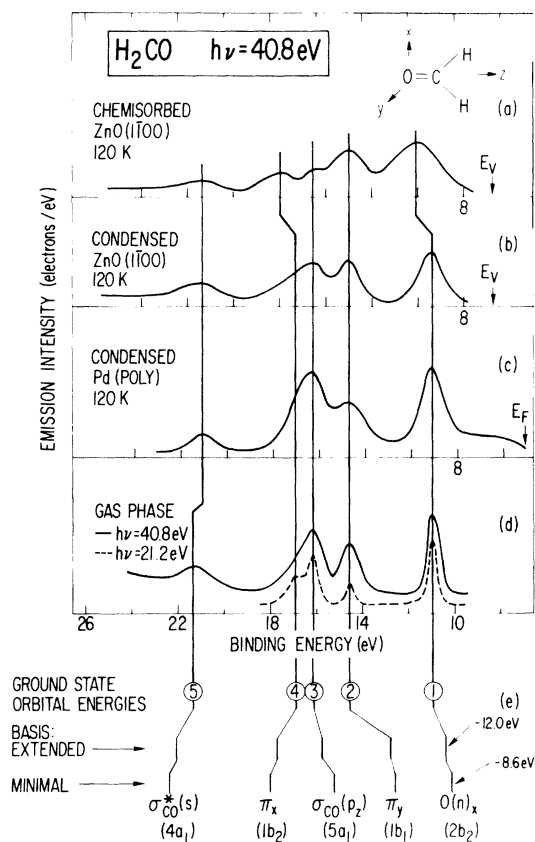


FIG. 1. UPS spectra at $h\nu = 40.8$ eV for H_2CO : (a) chemisorbed on ZnO(1100) at 120 K, exposure 10 langmuirs ($1 \text{ L} = 10^{-6}$ Torr sec); (b) condensed on ZnO(1100) at 120 K, 10^{-7} Torr ambient; (c) condensed on evaporated Pd at 120 K, 10^{-7} Torr ambient; (d) gas phase at $h\nu = 40.8$ and 21.2 eV; (e) ground-state orbital energies calculated by *ab initio* Gaussian-70 calculations with minimal (STO-3G) and extended (4-31G) basis sets. Energy scales of spectra have been shifted to show correspondence between orbitals, and the most reasonable correspondence between calculated and measured orbitals is shown in (e).

1(b).¹¹ The difference curve resulting from exposing an evaporated Pd film to an ambient (1×10^{-7} Torr) pressure of H_2CO at 120 K is shown in Fig. 1(c).⁸ Figure 1(d) depicts for comparison the gas-phase H_2CO photoelectron spectra at $h\nu = 40.8$ (solid curve) and 21.2 eV (dashed curve), as measured in our laboratory. The four spectra in Figs. 1(a)–1(d) have been rigidly shifted along the energy axis (as was done in Ref. 1) to optimally align all MO's with the exception of the highest-lying orbital (the oxygen lone-pair) in Fig. 1(a), which participates strongly in chemisorption bonding in this case. This alignment accounts for uniform ERPS relative to the gas phase, which is somewhat different in magnitude for adsorption on Pd than on ZnO.

The distinct similarity between the spectra in Figs. 1(b), 1(c), and 1(d) for the orbitals labeled 1, 2, and 3 (and the region near 4 as resolved in the gas phase at $h\nu = 21.2$ eV) leads us to conclude that the exposures of ZnO [Fig. 1(b)] and Pd [Fig. 1(c)] at 120 °K to an H_2CO ambient produce a condensed layer of adsorbed molecules on the surface. The molecular orbitals of these molecules show uniform (to ~0.1 eV) ERPS (except for orbital 5) but no orbital shifts associated with chemical bonding. The low-exposure phase of H_2CO on ZnO at 120 K [Fig. 1(a)] exhibits a (chemisorption) bonding shift (~1 eV) of the oxygen lone-pair orbital (1)

which is accompanied by a simultaneous downward shift (to larger binding energy) of orbital 4, making it now well-resolved at $h\nu = 40.8$ eV from orbital 3. All three phases [chemisorbed, Fig. 1(a); and condensed, Figs. 1(b) and 1(c)] display an anomalous upward shift (to smaller binding energy) of orbital 5, larger in magnitude than the uniform ERPS of the other valence orbitals. This behavior of orbital 5 is also seen in the data for H_2CO condensed on the chemically inert surface of MoS_2 ,¹⁰ while similar anomalous behavior of both orbitals 4 and 5 has also recently been observed in chemisorbed and condensed phases of H_2CO on Ni(111).⁹ The departures of valence orbitals 4 and 5 from uniform ERPS are what we seek to understand in this paper.

IV. DISCUSSION AND ANALYSIS: FORMALDEHYDE

In an effort to understand these departures from the usual case of uniform ERPS, we consider the character and relative energies of ground-state orbitals of the free H_2CO molecule using readily available MO calculations. The ground-state orbital energies for the free H_2CO molecule obtained by *ab-initio* self-consistent-field (SCF)–MO Gaussian-70 calculations¹³ using both the minimal (STO-3G) and extended (4-31G) basis sets of Slater-type orbitals are shown in Fig. 1(e). The calculated or-

TABLE II. Amplitudes (normalized to unity) of significant atomic-orbital components of valence molecular orbitals in H_2CO and $\text{H}(\text{CH}_3)\text{CO}$ obtained from Gaussian 70 *ab initio* SCF-MO calculations at STO-3G (minimal basis). Molecular geometries for H_2CO and $\text{H}(\text{CH}_3)\text{CO}$ are depicted in Figs. 1 and 2, respectively.

H_2CO										
Number	1	2	3	4	5					
Type	$\text{O}(n)_x: 2b_2$	$\pi_y: 1b_1$	$\sigma_{\text{CO}}(p_z): 5a_1$	$\pi_x: 1b_2$	$\sigma_{\text{CO}}^*(s): 4a_1$					
	$\text{O}(2p_x)$	$\text{O}(2p_y)$	$\text{O}(2p_z)$	$\text{C}(2p_x)$	$\text{C}(2s)$	-0.86	0.74	-0.69	-0.66	0.65
	$\text{H}(1s)$	$\text{C}(2p_y)$	$\text{O}(2s)$	$\text{O}(2p_x)$	$\text{O}(2s)$	0.34	0.67	0.50	-0.53	-0.50
	$\text{H}(1s)$		$\text{C}(2p_z)$	$\text{H}(1s)$	$\text{H}(1s)$	-0.34		0.45	0.37	0.30
				$\text{H}(1s)$	$\text{C}(2p_z)$				-0.37	0.30
					$\text{C}(2s)$					0.25
					$\text{C}(2s)$					-0.21
$\text{H}(\text{C}'\text{H}'_3)\text{CO}^a$										
Number	1	2	3	4	5	6	7			
Type	$\text{O}(n)_x$	π_y	$\sigma(p_z)$	$\sigma(p_{z,x})$	$\sigma_{\text{C}'\text{H}'_3}(p_y)$	π_x	$\sigma_{\text{CO}}^*(s)$			
	$\text{O}(2p_x)$	$\text{O}(2p_y)$	$\text{O}(2p_z)$	$\text{C}'(2p_x)$	$\text{C}'(2p_y)$	$\text{C}(2p_x)$	$\text{C}(2s)$	-0.84	-0.71	0.55
	$\text{H}(1s)$	$\text{C}(2p_y)$	$\text{C}'(2p_z)$	$\text{H}'(1s)$	$\text{H}'(1s)$	$\text{O}(2p_x)$	$\text{O}(2s)$	0.33	-0.59	0.41
	$\text{C}'(2p_x)$	$\text{C}'(2p_y)$	$\text{C}(2p_z)$	$\text{O}(2p_z)$	$\text{H}'(1s)$	$\text{C}'(2p_z)$	$\text{H}(1s)$	-0.28	0.23	-0.37
		$\text{H}'(1s)$	$\text{H}'(1s)$	$\text{O}(2s)$	$\text{C}(2p_y)$	$\text{O}(2s)$	$\text{C}'(2s)$		0.22	-0.34
		$\text{H}'(1s)$	$\text{O}(2s)$	$\text{C}(2p_z)$	$\text{O}(2p_y)$	$\text{O}(2p_z)$	$\text{C}(2p_x)$		-0.22	-0.33
			$\text{H}(1s)$	$\text{C}(2p_x)$		$\text{H}'(1s)$	$\text{C}'(2p_x)$			-0.23
			$\text{H}'(1s)$	$\text{O}(2p_x)$		$\text{H}'(1s)$	$\text{C}'(2p_y)$			0.21
						$\text{C}(2s)$	$\text{H}(1s)$			0.22
						$\text{H}(1s)$				-0.21

^a The primes simply denote which C and H atoms in the following table are those associated with the methyl group.

bital energies have been shifted rigidly somewhat to display best the correspondence with the gas-phase photoelectron (ionization) spectrum. The amplitude coefficients of the significant atomic orbitals comprising the valence molecular orbitals are given in Table II for the minimal basis calculation. The z direction is taken along the C–O bond direction, with x and y , respectively, in and perpendicular to the molecular plane, as depicted in Fig. 1. Inspection of the atomic-orbital components of the MO shows that, unlike the other valence orbitals, orbital 4 (an in-plane π_x) involves a large component of O($2p_x$) (amplitude -0.43 in the minimal basis set), which is the dominant component (amplitude -0.88) of orbital 1 (the oxygen lone-pair). Both orbitals also share H($1s$) components (amplitude $\sim \pm 0.3$) as well. We observe that when (and only when) orbital 1 is perturbed and shifted in forming the chemisorption bond [Fig. 1(a)], orbital 4 undergoes a simultaneous additional shift downward (toward larger binding energy) relative to the other orbitals. Thus the anomalous shift of orbital 4, coupled to the bonding shift of orbital 1, can be related to the strong similarity of these orbitals, both having strong O($2p_x$) [and some H($1s$) atomic-orbital components. This shift of orbital 4 most likely represents an initial-state (chemical) effect.¹⁴

The additional shift of orbital 4, simultaneous to that of orbital 1 in chemisorption, might be visualized in two ways. First, when the oxygen lone-pair (orbital 1) is perturbed by its direct participation in forming the chemisorption bond, a self-consistent solution for the molecular orbitals requires that the other orbitals respond in some way (in this sense they “share” in the chemisorption bond). In the usual case of uniform ERPS, this response would appear as an initial-state (chemical) effect which contributes to the total ERPS in approximately the same way for all orbitals. In the case of H₂CO, however, the response of orbital 4 may be considerably larger than that of the other orbitals. Since the atomic-orbital components of orbital 1 are very similar to those of orbital 4, the latter would be much more sensitive to perturbations of orbital 1 than are the other molecular orbitals.

An alternative viewpoint is that the symmetry of bonding to the surface strongly perturbs molecular orbitals containing a large O($2p_x$) component, i.e., orbitals 1 and 4 in the case of H₂CO. This would suggest that the chemisorption bond affects primarily a particular atomic-orbital component and thus selectively and strongly affects all molecular orbitals which are substantially comprised of this particular atomic orbital.

We turn now to the behavior of orbital 5. Table

II shows that this is the highest-lying orbital which involves no appreciable atomic p character; it is comprised of approximately equal amounts of O($2s$) and C($2s$), antibonding and with some H($1s$) admixture. This orbital may behave rather more like a core level with respect to ERPS, perhaps because the absence of atomic p character results in a more localized orbital. Since ERPS for core levels are generally larger than for valence (predominately $2p$) orbitals,^{5,15-17} it is not surprising that an orbital (like orbital 5) having a character intermediate between that of valence orbitals and core levels should show ERPS larger than for the other valence orbitals. In this case, either initial- and/or final-state effects may cause the ERPS to be larger than for the other valence orbitals.

This example demonstrates that observed deviations from uniform ERPS can be understood on the basis of simple MO calculations. Alternatively, by carrying out such calculations in advance for molecules to be studied, possible deviations from uniformity can be anticipated.

V. RESULTS AND DISCUSSION OF ANOMALOUS ERPS: OTHER CASES

A. Acetaldehyde

Both types of anomalous ERPS seen for H₂CO are also observed in the difference spectra for chemisorbed acetaldehyde [H(CH₃)CO] on evaporated Pd,⁸ and on ZnO(1100) at 120 K,¹¹ as shown in Figs. 2(a) and 2(b), respectively. Our measured gas-phase spectrum is shown in Fig. 2(c). Chemisorption bonding involving the oxygen lone-pair (orbital 1) is accompanied by a simultaneous anomalous shift of the low-lying in-plane π_x (orbital 6). The adsorption also produces a larger upward ERPS of the quasi-core-like antibonding O($2s$)-C($2s$) orbital (7). Both effects are somewhat different in magnitude for the Pd and ZnO surfaces, but follow the same trends outlined for H₂CO. In addition, the deviations from uniform ERPS in H(CH₃)CO are slightly smaller than in H₂CO. The character of the H(CH₃)CO MO's is given by the orbital coefficients listed in Table II. Clearly, replacement of one H atom in H₂CO by a methyl (CH₃) group in going to H(CH₃)CO complicates the orbitals considerably and reduces the similarity of atomic-orbital character in the MO's as seen, e.g., by the smaller proportion of O($2p_x$) character in the in-plane π_x orbital of H(CH₃)CO compared to that in H₂CO. One might expect this trend to suppress possible “anomalous” behavior of low-lying orbitals in larger organic molecules, at least as far as coupling of orbital shifts [like the π_x and O(n_x)] in chemisorption is concerned.

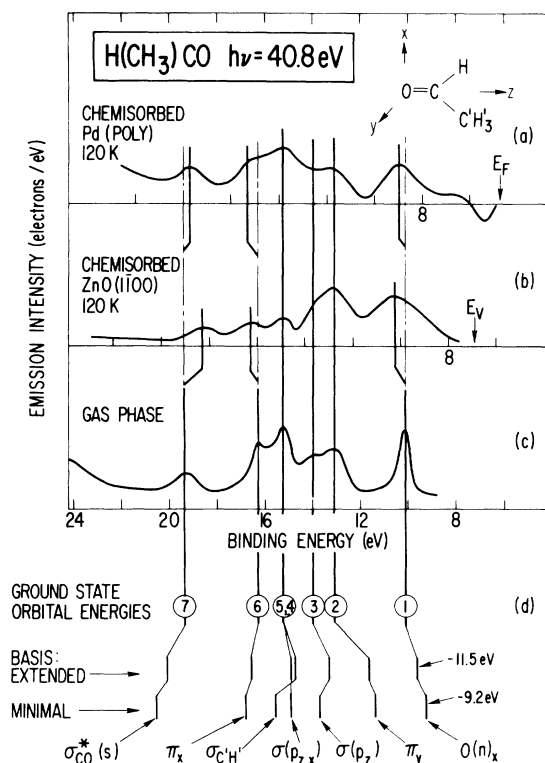


FIG. 2. UPS spectra at $h\nu = 40.8$ eV for $\text{H}(\text{CH}_3)\text{CO}$: (a) chemisorbed on evaporated Pd at 120 K, 68-lam-muirs exposure; (b) chemisorbed on $\text{ZnO}(1\bar{1}00)$ at 120 K, 5×10^{-8} Torr ambient; (c) gas phase at $h\nu = 40.8$ eV; (d) ground-state orbital energies obtained from *ab initio* Gaussian-70 calculations.

B. Larger molecules

In larger molecules, the mixing of atomic orbitals to form the molecular orbitals is even more thorough, and the complicated MO structure makes the identification of gas-phase UPS orbitals more difficult. Our measurements for chemisorbed acetone [$(\text{CH}_3)_2\text{CO}$] show only very small anomalies for the $\text{O}(2s)\text{-C}(2s)$ antibonding orbital. Furthermore, these data reveal no anomalous ERPS which can be assigned to an in-plane π , perhaps because the thorough mixing of atomic orbitals in the MO's averages out the response of the molecule in the formation of a chemisorption bond involving the oxygen lone-pair orbital.

Dimethyl sulfoxide [$(\text{CH}_3)_2\text{SO}$] bears a chemical resemblance to acetone in that the central C atom is simply replaced by a S atom. This produces a pyramidal rather than planar structure for the molecule, so that no real in-plane π_x orbital is present. Chemisorbed dimethyl sulfoxide, which we observed on $\text{ZnO}(1\bar{1}00)$,¹¹ exhibits an upward ERPS of the $\text{O}(2s)\text{-S}(3s)$ antibonding orbital [analogous to the $\text{O}(2s)\text{-C}(2s)$ antibonding orbital al-

ready discussed] which is ~ 1 eV larger than that of all other $(\text{CH}_3)_2\text{SO}$ orbitals seen in UPS at $h\nu = 40.8$ eV.

VI. APPLICATION TO ORBITAL ASSIGNMENTS IN FORMALDEHYDE

Because departures from uniform ERPS in the UPS spectra of small adsorbed molecules can apparently be understood on the basis of the MO character of the orbitals, observed anomalies can be used in favorable cases to help identify orbitals in the gas-phase UPS spectra. First, when relatively larger upward ERPS are observed for some orbitals, these may be predominately *s*-like MO's. Second, other anomalous ERPS which occur when and only when a chemisorption bonding shift is seen for a high-lying orbital are likely to be a result of a close similarity between the atomic components of these two MO's. This latter effect has special significance for the H_2CO molecule, a simple and important prototype for a large class of organic molecules.

There has been considerable controversy over the ordering of the third and fourth orbitals in the gas-phase UPS spectrum of formaldehyde [Fig. 1(d)]. From an analysis of the observed vibrational structure of these orbitals in the UPS spectrum of the free H_2CO molecule, orbitals 3 and 4 were identified as the in-plane π_x ($1b_2$) orbital and a σ_x -like ($5a_1$) orbital, respectively,^{18,19} while UPS studies of the "perfluoro effect" in H_2CO (F_2CO) were inconclusive in determining the relative ordering of these orbitals.²⁰ In contrast, calculations using *ab-initio* MO (GTO),²⁰ Hartree-Fock,^{21,22} or SCF $X\alpha$ scattered-wave (nonoverlapping spheres)²³ methods predict the reverse assignments, as do Green's-function techniques^{24,25} which include a theoretical analysis of vibrational structure. All of these are in apparent contradiction with inferences from the original gas-phase UPS experiments, although by employing overlapping spheres the SCF $X\alpha$ calculations²³ were found to reverse the ordering and thereby obtain agreement with the experimental conclusions.^{18,19}

Chemisorption bonding represents an experimental perturbation to the H_2CO molecule and its oxygen lone-pair orbital which now provides us with a new determination of the ordering of orbitals. The behavior of gas-phase orbitals 3 and 4 in Fig. 1 shows quite clearly that orbital 3 is unperturbed relative to the overall spectrum while orbital 4 exhibits an anomalous ERPS strongly correlated with the chemisorption bonding shift of the oxygen lone-pair (orbital 1). If indeed the unusual departure from uniform ERPS results from the coupling of MO's through a common atomic orbital, then the anoma-

lous shift of orbital 4—coincident with the bonding shift of the lone-pair—identifies the fourth orbital as the in-plane π_x ($1b_2$). Thus the unusual ERPS of this low-lying orbital (upon chemisorption) implies an ordering of H_2CO orbitals in agreement with most of the calculations and opposite to that inferred by the original analyses^{18,19} of vibrational structure in gas-phase UPS spectrum alone. The use of overlapping spheres in the SCF $X\alpha$ calculations,²³ which gives agreement with the original experimental conclusions, thus appears somewhat artificial and misleading.

The use of anomalous ERPS to help identify molecular orbitals in UPS spectra will clearly be restricted to perhaps a few small molecules which have fairly simple MO structure and which show clear deviations from the uniform ERPS assumption. In these cases, adsorption on a solid surface represents a more gentle and more understandable diagnostic perturbation than the perfluoro effect.

VII. CONCLUSIONS

There now exists much experimental evidence (Table I) that uniform (to ~ 0.2 eV) extramolecular relaxation-polarization shifts are the rule rather than the exception in UPS studies of adsorbed organic molecules. Although this uniformity and the details of initial- and final-state contributions to the ERPS are not satisfactorily understood on a theoretical basis at present, the empirical result makes the assumption of uniform ERPS very val-

uable in UPS studies of surface chemistry.

Furthermore, the rare significant exceptions to the rule of uniform ERPS, such as those examples given here, are likely to appear most often in smaller molecules, where the mechanisms for the anomalies can be understood on the basis of simple molecular-orbital calculations. Such calculations can be used to predict which orbitals in which molecules are subject to possible deviations from uniform ERPS. Alternatively, possible anomalies may also be anticipated from past experience with the same molecule on different surfaces. Thus the anomalies do not significantly detract from the utility of the uniform ERPS approximation. Instead, in some of these few cases, the anomalous ERPS may be useful in interpreting UPS spectra. We have shown this in the case of H_2CO , for which a new ordering of orbitals can be inferred from experiment to resolve a long-standing controversy between theoretical calculations and prior experimental conclusions.

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