will result in multiply interlocked [2]-catenanes (two singly, doubly, triply, etc. interlocked rings from one, three, five, etc. metals, respectively).

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Photodissociation of Intraadsorbate Bonds at Adsorbate–Metal Interfaces

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While photochemistry of gases and liquids is a mature research field[1,2] and photochemistry on semiconductors is relatively well-studied,[3] photochemistry at metal surfaces is a newly emerging area.[4-14] This Account describes the status of our current research on the surface science of photochemistry at *adsorbate–metal* interfaces; it forms part of an expanding, worldwide effort to understand, for metals,[4-14] semiconductors,[3] and insulators,[15] the role of the surface on the mechanistic and dynamical aspects of photon-driven surface processes. Our work, summarized in Table I, has focused on *intraadsorbate* bond-breaking processes. Particular examples, illustrating important points, are discussed below.

When a molecule is near a metal surface, its chemical and optical properties are altered, and the metal substrate itself can play a direct photochemical role by absorbing light and serving as a source of energy for activating the adsorbate. It can also quench excited adsorbates. Thus, we expect gas- and liquid-phase photo processes to change qualitatively and quantitatively at surfaces. For example, it is well-known that fluorescence, a nanosecond phenomenon, is very strongly quenched near metal surfaces,[16-18] an effect attributed to nonradiative energy transfer.[17,19] For adsorbed molecules, electronic quenching can proceed through charge transfer,[19,20] which occurs on a time scale from a few femtoseconds (fs = 10^{-15} s) for resonant electron tunneling[20,21] to $\sim 10^2$ fs for Auger neutraliza-

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Table I
Photochemistry at Adsorbate–Metal Interfaces: Summary of Systems Studied by White Group[a]

Systems Showing Photon-Driven Chemistry

metal	adsorbate	observations	ref
Pt(111)	CH_2CO	postirradiation TPD and SIMS evidence of C–C bond cleavage	48
	CH_3Cl	wavelength-dependent cleavage of C–Cl bond, correlation between rate coefficient and photoelectron yield, larger cross section for monolayer than for multilayer	34, 50
	CH_3Br	C–Br bond cleavage at longer wavelengths than CH_3–Cl bond	31, 50
	CH_3I	slower dissociation rate of C–I bond in monolayer than in multilayer, and than C–Br bond in CH_3Br	23
	C_2H_5Cl	C–Cl bond cleavage, accumulation of C_2H_5(a) and Cl(a)	33
	ClC_2H_4Br	Both C–Cl and C–Br bonds break at longer wavelengths than does CH_3–Cl bond	35
	O_2	dissociation, desorption and conversion between adsorption states, different wavelength dependence for dissociation and desorption	40, 41
	Cl_2CO	dissociation to Cl(a), CO(a), and CO(g), direct excitation dominates below 290 nm, and substrate excitation dominates above 290 nm	46
C/Pt(111)	CH_3Cl	constant dissociation rate coefficient from submonolayer to multilayer, correlation between rate coefficient and photoelectron yield, lower rate coefficient for submonolayer than on Pt(111)	34
	CH_3Br	C–Br bond cleavage, smaller dissociation cross section and higher photon energy threshold than on Pt(111)	32
Ag(111)	Cl_2CO	dissociation to Cl(a) and CO(g), enhancement and red shift of photodissociation for monolayer compared to gas phase	24
	C_2H_5Cl	C–Cl bond cleavage, retention of all Cl and a fraction of C_2H_5; red shift and enhancement more significant for monolayer than for multilayer	38, 39
	CH_3Br	C–Br bond cleavage, retention of all Br and a fraction of CH_3; red shift and enhancement more significant for monolayer than for multilayer	38, 39
	CH_3I	C–I bond cleavage, retention of all I and a fraction of CH_3; red shift for monolayer only; slight quenching for monolayer photodissociation	38
	ClC_2H_4Br	Same wavelength dependence for both C–Cl and C–Br bond cleavage, lower threshold than for C_2H_5–Cl bond cleavage	53
	C_6H_5Cl	C–Cl bond cleavage, accumulation of Cl and phenyl	52
	OCS	dissociation to S(a) and CO(g); red shift and enhancement compared to gas phase	55
	SO_2	monolayer photodesorbs	54
	CH_2CO	slow C–C bond cleavage	49
Ag(110)	02	desorption of O_2 and dissociation to O(a); substrate excitation responsible for photochemical processes; desorption activated by dissociation	40
Ru(001)	CH_3Br	C–Br bond cleavage, retention of CH_3 and Br	51
Cu/Ru(001)	CH_3Br	C–Br bond cleavage, retention of CH_3 and Br	51

Systems Showing No Photon-Driven Chemistry

metal	adsorbate	ref
Pt(111)	NO	56
	H_2O	56
	NH_3	57
Ag(111)	C_6H_6	58
	H_2O	59
	$(CH_3)_2CO$	59
	CH_3OH	59

[a] Photon energies ≤5.3 eV.

tion.[22] On this time scale, significant bond-length changes occur on repulsive potential energy surfaces, and photon-driven intraadsorbate bond breaking competes strongly with quenching.[4,5,10,11,23,24]

Optical Excitation Mechanism

There has been considerable recent discussion of the mechanism(s) by which photon-driven adsorbate–metal processes are initiated.[6,7,9,11,21] These can be discussed in terms of photon absorption by (1) bulk metal, (2) bulk adsorbate (physisorbed multilayer), and (3) adsorbate–metal complex containing the chemisorbed monolayer adsorbate and at least the first layer of metal. As described below, there is evidence for all three kinds of photon absorption leading to intraadsorbate bond breaking.

Indirect adsorbate excitation mediated by the bulk metal must always be considered. For adsorbate coverages less than several monolayers, the overlayer is optically thin even if it absorbs. Therefore, most of the incident light passes through the adsorbate layer and is reflected and absorbed by the metal. Energetic electrons and holes are produced by absorption, and a nonthermalized fraction can migrate to the adsorbate–metal interface and activate the complex indirectly by electron or hole attachment. Analogous hole formation[25] and electron attachment processes occur in the gas phase.[26]

Photon absorption by the bulk adsorbate or the adsorbate–substrate complex is a direct electronic excitation process, the extent and wavelength dependence of which are determined by the relevant transition dynamic dipole.[11,21,24] Because of substrate interactions, the optical absorption properties of the adsorbate–substrate complex may be more like those of organometallics[27] than either gas-phase or bulk adsorbate.[11,21,24]

In deciding which kind of absorption dominates, we can make some progress by varying the incident angle and polarization of the light. The known optical con-

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stants of the metal describe the angular and polarization dependence of bulk substrate absorption. Direct bulk adsorbate excitation can be estimated from gas- and solution-phase molecular properties. Photoabsorption by the adsorbate–substrate complex, which is of great interest in our work, will involve (1) electromagnetic fields, **E**, just inside and just outside the plane of the surface nuclei, and (2) transition dipole vectors, μ, of the adsorbate–substrate complex. These fields and vectors are unknown for transition metals and chemisorbed adsorbates and present a significant challenge for future research. Considering the field problem, theoretical work on a model system, jellium and an adsorbate, indicates that the field strengths 0.1 nm outside the jellium surface are adequately described by classical electromagnetic theory.[28] For real metals, and in the absence of an adsorbate, the mean square field strengths some distance outside the metal are usually calculated by using Fresnel's equations.[29] These equations assume a step-function change in optical properties in passing from the vacuum to the metal. Since the adsorbed molecule defines a very short length scale (10^{-1} nm) and resides at an ill-defined position with respect to the step function discussed above, the assumption is questionable. If the direct excitation is weak and localized within a physisorbed molecule lying well outside the metal, then the excitation should follow $\langle \mu \cdot \mathbf{E} \rangle$ where μ is a molecular property and **E** is based on Fresnel's equations applied to the pure metal surface.

Temporal Evolution of Excited Adsorbate

Intraadsorbate bond breaking requires a sufficiently long excited-state lifetime. Population of antibonding orbitals and/or depopulation of bonding orbitals often leads to bond cleavage unless relaxation (quenching) processes intervene on a femtosecond time scale. For example, the lowest lying empty orbital in methyl chloride is antibonding with respect to the C–Cl bond, and we expect that both direct photon absorption and indirect excitation by substrate electron attachment lead to bond breaking, but with reduced probability near a metal. The dissociation process can be even more complex, because during the excited-state lifetime, bond lengthening will occur and quenching (assuming a Franck–Condon transition) will leave the molecule in a vibrationally excited form of its electronic ground state. Dissociation can follow, particularly on transition metals where strong metal–fragment bonds provide a thermodynamic driving force.

Experimental Considerations

All experiments were performed in ultrahigh-vacuum chambers with base pressures of 10^{-11}–10^{-10} Torr. The samples were cooled to $\leq$100 K with liquid nitrogen or He refrigeration. The UV light source (in several cases polarized) was a conventional high-pressure Hg arc lamp, which generates photons distributed in a broad energy range (230–900 nm). Either band-pass or cutoff filters were used to vary the photon energy distribution. The adsorbate–metal system was continuously irradiated and analyzed during irradiation or afterward with conventional surface science tools, including mass spectrometry, temperature-programmed desorption (TPD), high-resolution electron energy loss spectroscopy (HREELS), X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS), and work function change ($\Delta\Phi$). Our experiments do not provide information on the dynamics of the surface photochemical processes; this requires a pulsed UV light source and a time-resolved detection system, and there are excellent examples.[6,7,9]

Alkyl Halides on Pt(111) and Ag(111)

The UV photochemistry of gas-phase alkyl halides is relatively simple.[1,2] Absorption is continuous, indicating carbon–halogen bond cleavage, and shifts to shorter wavelengths in the order iodide > bromide > chloride. Qualitatively, the same kind of wavelength-dependent, molecule-specific, photon-driven chemistry occurs for alkyl halides adsorbed on metals (Table I), but as indicated below, much of the excitation is indirect and involves substrate electron attachment to the adsorbate.

For example, these molecules adsorb molecularly on Pt(111) and C/Pt(111) at or below 100 K. In subsequent TPD, only iodides decompose; the others desorb intact.[30] UV irradiation drives the nonthermal dissociation of carbon–halogen bonds; all halogen atoms and a fraction of the alkyl fragments are retained. For methyl and ethyl halides, strong metal–CH_3 and metal–C_2H_5 bonds were identified by HREELS,[31-33] and metal–halogen bonds by XPS.[23,34,35] In postirradiation TPD, significant amounts of small hydrocarbons and hydrogen were observed; in some cases, surface carbon was present after TPD.[31,35] As none of them appeared without irradiation, and since only carbon–halogen bond breaking occurs during low-temperature illumination, these products are the expected result of metal-catalyzed thermal reactions of the photolysis products.

As an example of wavelength and molecule dependences, monolayer (ML) CH_3Cl on Pt(111) photodissociates only when the incident light is below 300 nm, but CH_3Br is easily photodissociated out to 360 nm. On the basis of gas-phase optical properties,[1] we expect no photodissociation of CH_3Cl since the cross section is $\sim 10^{-24}$ cm^2 at $\lambda \sim 230$ nm, the shortest wavelength from the Hg arc. Thus, typical of the alkyl halide systems in Table I, the photochemistry is red-shifted compared to the gas phase and depends strongly on the halogen present.

At least for CH_3Cl (and consistent with related work[7]), we have good evidence that the red shift is due to substrate photoelectrons. In the process, CH_3Cl^- species, known to dissociate in the gas phase,[26] form and dissociate on Pt(111) and C/Pt(111). Measuring both

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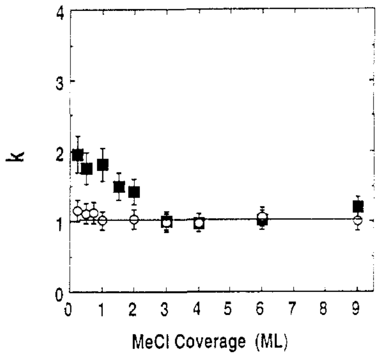

Figure 1. Rate coefficients, showing a first-order reaction with respect to CH_3Cl and electrons, versus CH_3Cl coverage on Pt(111) (solid squares) and carbon-covered Pt(111) (open circles). From ref 34a.

the photoelectron yield and the initial photodissociation rate as a function of CH_3Cl coverage, and assuming a first-order dissociation reaction with respect to both CH_3Cl and the number of photoelectrons, we obtained the dissociation rate coefficient[34] (Figure 1). It is constant, as expected for this model, over the entire coverage range on C/Pt(111) and indistinguishable from that for >2 ML on Pt(111). Remarkably, the rate coefficient is *higher* for lower coverages on Pt(111), even though quenching, due to direct interaction with the metal, is expected. Among the possible causes,[34] but not yet demonstrated, is an additional dissociation channel due to direct excitation of the CH_3Cl–Pt complex. Adsorbate orientational effects may also be important. Another attractive possibility, analogous to quenching in electron-stimulated desorption,[36,37] involves a vibrationally excited ground state that dissociates. Clearly, the photochemistry of the chemisorbed first monolayer of CH_3Cl is unique, as it is for other metal–adsorbate systems.[24,32,38,39]

Methyl iodide is also distinctive. On the basis of gas-phase data,[1,2] CH_3I should dissociate more readily than CH_3Cl and CH_3Br. But using XPS to distinguish halogen atoms in CH_3X and in Pt–X,[23] we found that, compared to CH_3Br, monolayer CH_3I photodissociated much more slowly and *multilayer* CH_3I much more quickly. We conclude that quenching by the metal is significantly more competitive in *monolayer* CH_3I, as compared to CH_3Cl and CH_3Br. The same conclusion is reached for the methyl halides on Ag(111).[38]

Ag(111)–alkyl halide photochemistry (Table I) is like that on Pt(111), but the thermal chemistry of the retained photolysis products is different; Ag selectively catalyzes the recombination of alkyl groups to form hydrocarbons, which desorb, leaving no C or H.

Figure 2 compares photodissociation cross sections for chemisorbed C_2H_5Cl and CH_3Br on Ag(111) with the gas phase optical absorption cross sections, the latter assigned to n → σ^* transitions.[1,2] In contrast to the rapidly changing gas-phase cross section, the photodissociation cross sections of the adsorbed halides vary much less with photon energy. For example, reducing the photon energy from 5 to 3.5 eV lowers the cross section by only 1 order of magnitude. While we attribute a major part of these differences to substrate excitation and electron attachment processes described above, determining the relative contributions of substrate and direct excitation remains a formidable challenge.

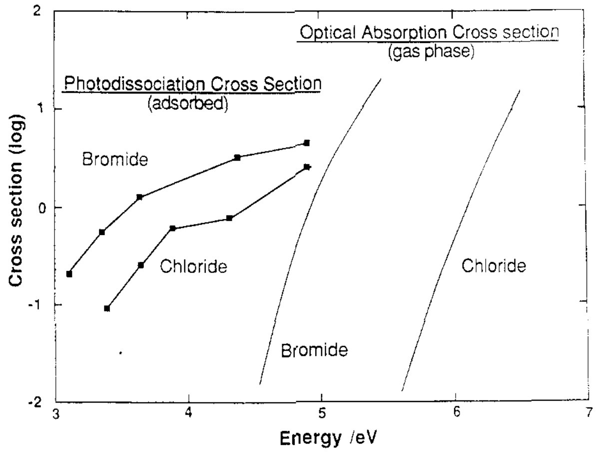

Figure 2. Comparison of gas phase absorption cross sections and photodissociation cross sections for 1-ML C_2H_5Cl and CH_3Br on Ag(111) (logarithmic scale). The 0 of the ordinate corresponds to a cross section of 10^{-20} cm^2. Reprinted with permission from ref 39. Copyright 1990 Elsevier (Amsterdam).

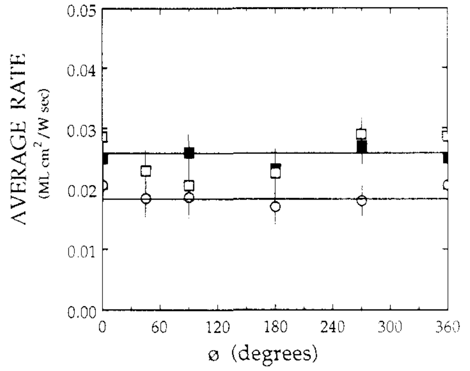

Figure 3. Azimuthal angle dependence of the photodissociation rate (open circles) and photodesorption rate (squares) for O_2 on Ag(111) at 100 K. The open symbols are from HREELS data while the squares are from TPD. Reprinted with permission from ref 40a. Copyright 1990 American Institute of Physics.

Oxygen on Pt(111) and Ag(110)

The photochemistry of strongly chemisorbed dioxygen on Pt(111) and Ag(110) provides some interesting contrasts to the weakly bound alkyl halides.[40,41] With UV irradiation are observed O–O photodissociation, O_2 photodesorption, and on Pt(111), photoinduced rearrangement of adsorbed dioxygen.

Since, on Ag(110), the O–O bond axis is parallel to the Ag(110) azimuth, the angle, ϕ, between this direction and **E** can easily be controlled by using polarized light at normal incidence. As shown in Figure 3, the rates of both photodissociation and photodesorption are independent of ϕ. For this to be the result of direct excitation requires a transition dipole moment vector that is invariant with ϕ, and since this is unlikely, we conclude that substrate excitation dominates. Further support comes from the fact that both incident angle

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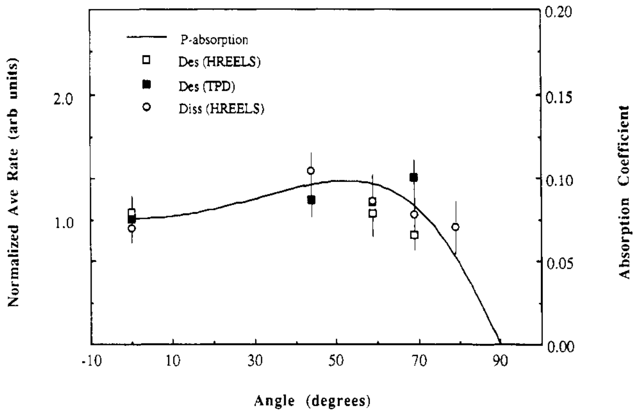

Figure 4. Average rates for photoinduced desorption by HREELS (open squares) and TPD (solid squares), and dissociation (open circles) as a function of incident angle for p-polarized light to the O_2-saturated Ag(110) surface. The solid curve is the calculated p-polarized metal absorption. See ref 40b.

dependences of photodissociation and photodesorption are adequately fit (Figure 4) by the substrate absorption of p-polarized light.[40] Although we cannot unequivocally rule out some contribution by direct excitation of the adsorbate–substrate complex, all the evidence indicates that dissociative attachment of hot subvacuum electrons is dominant.

Unlike O_2 on Ag(110) (Figure 4), photodissociation and photodesorption on Pt(111)[41] have different wavelength dependences, with thresholds of ~315 and ~450 nm, respectively. Increasing the incident angle of unpolarized UV light, we found that the dissociation rate decreases, while the desorption rate increases. These differences point to different excitation mechanisms, perhaps including contributions from both direct and substrate excitation. Interestingly, the thresholds agree with those for direct gas-phase photolysis of hydrogen peroxide and $[P(C_6H_5)_3]_2PtO_2$,[42] respectively.

Keeping in mind that proof is, as yet, lacking, direct and substrate excitation can be intuitively explained by the model in Figure 5. Adsorption of O_2 increases the work function of Pt(111) from 5.8 to 6.6 eV.[43] Upon adsorption, the degeneracy of $1\pi_g^*$ is removed;[44] the orbital parallel to the surface, π_n, is largely nonbonding with respect to Pt, while the one perpendicular to the surface interacts strongly with the d band (π_σ: d_{xz} and d_{yz}). The coupling of the latter results in a bonding, π_σ, and an antibonding, π_σ^*, orbital. Direct excitation from π_n to σ_u^*, as in H_2O_2,[1,2] would account for the dissociation. Excitation from π_n to π_σ^* would decrease the bonding between O and Pt and could lead to desorption. This model also accounts for the different dissociation and desorption thresholds. Substrate excitation can also contribute; for example, excitation of electrons from below E_F to σ_u^* might lead to dissociation. Clearly, O_2/Pt(111) is an interesting photochemical system, which we continue to study.

In complementary work, the same three processes are found for O_2 adsorbed on Pd(111)[45] with desorption and dissociation setting in at different wavelengths.[5] Polarization analysis indicates that all three involve substrate excitation, at least at 6.4 eV.[45] Time-of-flight measurements indicate that desorption of molecular O_2 occurs through two channels, characterized by translational temperatures of 800 and 120 K.

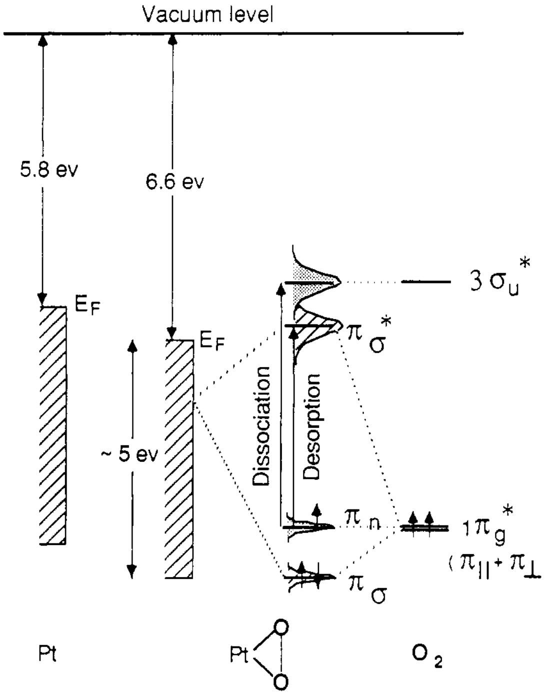

Figure 5. Schematic model of the interaction of O_2 with Pt(111), indicating possible dissociation and desorption channels. Reprinted with permission from ref 41. Copyright 1989 American Institute of Physics.

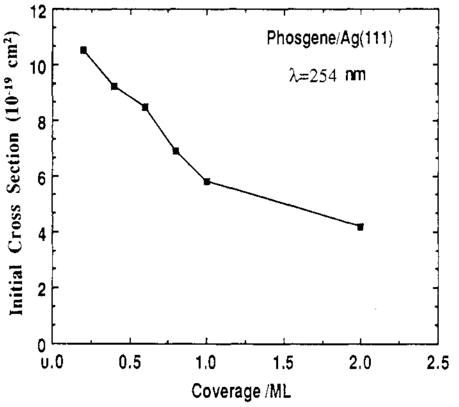

Figure 6. Initial cross section for photodissociation of Cl_2CO on Ag(111) versus initial Cl_2CO coverage at $\lambda = 254$ nm. Reprinted with permission from ref 24b. Copyright 1990 American Institute of Physics.

Phosgene on Ag(111) and Pt(111)

Because of its wavelength dependence, in particular on Pt(111), phosgene surface photochemistry provides an interesting contrast to O_2 and the alkyl halides. UV gas-phase absorption, starting at ~300 nm with a maximum at ~230 nm, is continuous and produces Cl atoms and CO molecules.[1] Adsorption on Ag(111) and Pt(111) at ~100 K is molecular, and there is no detectable thermal decomposition in TPD.[24,46] On these surfaces, photodissociation to Cl and CO occurs readily, with a higher cross section and lower photon energy thresholds than in the gas phase. For monolayers, all the Cl atoms are retained, but only a small fraction of

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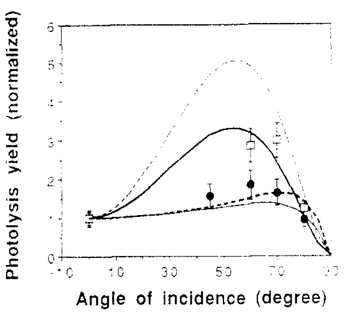

Figure 7. Photodissociation yield of Cl_2CO on Pt(111) versus incident angle for p-polarized light with 280-nm band-pass filter (open squares) and 315-nm cutoff filter (solid circles). The two lower curves are calculated metal absorbances at 280 (solid lines) and 365 nm (dashed line), respectively. The two upper curves are calculated on the basis of direct excitation of a surface transition dipole (see text) oriented at 50° (dashed) and 55° (solid) with respect to the surface normal. See ref 46.

CO is retained on Pt(111) and none on Ag(111). On Ag(111), the photodissociation cross section at 254 nm decreases with increasing coverage (Figure 6). This common characteristic[38,39] is a subject of current investigations. Possible explanations include rapid energy exchange among neighboring phosgene molecules and variation with coverage of the *local* electronic potential at each adsorption site.

The angular variation, using p-polarized light, of the phosgene decomposition rate on Pt(111) is very interesting.[46] As shown in Figure 7, there is a change in character between 280 and 315 nm. Whereas the angular dependence closely follows the predicted metal absorbance for $\lambda \geq 315$ nm, the results at 280 nm require an additional channel, assumed to be direct excitation, since the parent molecule absorption starts in this region.[1] With an oriented transition dipole on a surface of C_3 (or higher) symmetry, the angular dependence of the average transition rate, proportional to $\langle \mu \cdot \mathbf{E} \rangle^2$, is very sensitive to the transition dipole orientation. As indicated in Figure 7, a transition dipole vector at 55°, with respect to the surface normal, gives a reasonable fit, whereas a 60° orientation does not. To our knowledge, this is the first polarization evidence for a surface photochemical process that does not correlate with substrate absorption.

Photoinactive Adsorbate–Metal Systems

As shown in Table I, there are many cases where photodissociation of adsorbates is not observed. In the gas phase, NO, H_2O, CH_3OH, and NH_3 are transparent at $\lambda > 230$ nm.[1,2] This may also be the case for these molecules adsorbed on metal surfaces. Photolysis using higher energy photons will be interesting, and we already know that H_2O on Pd(111) is readily photolyzed at 193 nm but appears to involve substrate excitation.[6] On the basis of gas-phase data, we expect direct UV absorption by adsorbed $(CH_3)_2CO$ and C_6H_6, but there is no intraadsorbate bond breaking.[1,2,47] Finally, it is important to note that photon-driven molecular desorption, as opposed to intraadsorbate bond cleavage, is well-known in some of these systems, particularly NO.[8]

Concluding Remarks

As demonstrated in this paper, photodissociation of intraadsorbate bonds at adsorbate–metal interfaces often is competitive with traditionally expected substrate quenching. Although quenching does sometimes dominate, promotion of photodissociation also occurs. While dissociation due to substrate excitation is evident in a number of systems, direct excitation of the adsorbate or adsorbate–substrate complex can also make important contributions. The dominant excitation pathway is wavelength dependent and varies with the adsorbate–metal system. The role of metal band structure remains to be worked out. Clearly, Pt and Ag have very different electronic structures around the Fermi level, and these should be reflected in any substrate excitation process. Moreover, the question of the relative roles played by electrons and holes remains open.

An obvious application of photodissociation is the synthesis of interesting intermediates that are important in heterogeneous catalysis, e.g., alkyl fragments. Many have been proposed, but few are well-characterized because at operating catalytic conditions they are not stable enough to accumulate in large concentrations. Photodissociation at low adsorbate–metal temperatures provides the opportunity to prepare spectroscopically measureable concentrations of some of these intermediates.

As a newly emerging area, surface photochemistry has a bright future. Work will continue on the dynamics and mechanism(s) of photochemical systems. As has been established,[6,7,9,15] dynamic studies using a pulsed laser as the UV source, combined with time-of-flight mass spectrometry, laser-induced fluorescence, and multiphoton ionization, will provide much information on the energy content of the desorbing photofragments and on how the photofragments form and desorb. In addition to metal single crystals, supported metal thin films, from submonolayer to multilayer, are of interest. Since excited substrate electrons often play an important role, studying the low-energy electron-induced chemistry of adsorbate–metal systems, in parallel with the photochemistry, will be interesting and productive.

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