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ELECTRON TRANSFER REACTIONS AT SEMICONDUCTOR SURFACES: DYNAMICAL STUDIES

ABSTRACT

In the last year we have focused our experimental measurements of surface dynamics on the study of the fundamentals of electron transfer reactions at semiconductor-adsorbate interfaces. Our work is unique since we have provided the first dynamical or energy-resolved measurements of these reactions at the atomic *scale*. Thus we have strong evidence to suggest a specific orbital pathway by which electrons leave the semiconductor surface and enter the overlying adsorbate molecule. Our experimental approach is to use tunable UV and visible lasers to study translational-energy resolved fragmentation on single-crystal semiconductor surfaces under UHV conditions with time of flight (TOF) and other surface probes.

During this year we have observed and understood the central phenomena of adsorbate photochemistry of semiconductor-adsorbate interfaces. In particular, it was observed that a major channel of photochemistry on a semiconductor surface is through the transfer of photoexcited substrate electrons to the adsorbed molecules. In contrast, photochemical processes by direct intra-adsorbate excitation are largely quenched for molecules in direct contact with the surface. The electron-transfer mediated process leads to both desorption and intra-adsorbate bond cleavage. The transfer may be by hot electrons or thermalized electrons in the conduction band. The dynamics of the electron-transfer reaction vary greatly for molecules in the first and second layer and for molecules of different orientations in the first layer. While molecules in the second layer can be dissociated only through the transfer of hot electrons or direct intra-adsorbate bond cleavage, those in the first layer react by thermalized electrons as well as hot electrons, depending on the orientation of the molecules. The two processes are differentiated experimentally by the different characteristic energy and angular distribution of the photofragments. In addition, we have discovered that reaction self-quenching can be an

important process in thermalized electron-induced reactions on semiconductor surfaces. This behavior stems from the effects on the lifetime of the thermalized carriers by the reaction products left on the surface. Finally, we have found that the importance of electron-transfer-induced reactions at surfaces arises in part from the shift in the lowering of the unoccupied electronic orbitals of the adsorbates in the image region of the semiconductor surfaces. This latter effect is also largely responsible for a red shift observed for photochemical processes on surfaces.

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INTRODUCTION

Previous research by our and other groups has shown that a surface can provide new channels for enabling UV photodissociation or photoreactions, and that such studies may provide a useful route to understanding electron transfer. In particular, the results on metal surfaces have suggested that photoemitted electrons or hot carriers may be a major surface dissociation channel.¹⁻⁶ Such effects are particularly important as the irradiating photon energy approaches 4-5 eV, since the work function of many metal surfaces falls in this range. While the previous work has mostly focused on metal surfaces, photochemistry on semiconductor surfaces has not been as extensive. Given the observed importance of photoelectron induced processes on metal surfaces and the different relaxation dynamics of excited electron in semiconductors and metals, $\sim 10^{-9}$ - 10^{-3} sec for the former versus⁷ $\sim 10^{-12}$ sec for the latter⁸ photochemistry on semiconductor surfaces may be significantly different. Further, semiconductor surfaces are also better systems to the study of site dependence of the surface photochemistry due to covalent bonding between surface atoms and the resultant high corrugation.

Following our group's previous work on Cl_2 and CCl_4 on GaAs(110),^{9,10} we have focused our experimental work on adsorbed CH_3X on the same surface. The choice of this molecule was made because it is an ideal model system since its gas-phase chemistry is well known and there have been earlier studies of its photodissociation on single-crystal metal surfaces. The GaAs(110) surface is of interest because it can be prepared readily with a stable stoichiometry and because its electron and atomic structure is clearly defined and well understood, even for normally unoccupied bands. In our work, we have identified and observed for the first time several chemical processes which control photochemistry on semiconductor surfaces. A summary of the processes which we have considered are contained in the J. Phys. Chem. feature article which we include in the appendix of this report. In brief, at coverages $> 1\text{ML}$, we find that hot electron and intra-adsorbate photon excitation leads to molecular dissociation.¹¹ However, for coverages $< 1\text{ML}$, a separate channel by thermalized electrons is seen in addition to the process induced by hot electrons.¹¹ This reaction channel arises from the

long lifetime of the these electrons at and near semiconductor surfaces, a direct consequence of the characteristic energy gap in these materials. The observation of both hot electron and thermalized-electron-induced processes for molecules at $< 1\text{ML}$ coverage indicates that the detailed dynamics of the electron transfer process depends sensitively on the site of adsorption and structure of the substrate-surface complex (see below). An important characteristic of thermalized electron-induced reactions on semiconductor surfaces is the self-quenching behavior stemming from the effects on the lifetime of the thermalized carriers by chemisorbed reaction products.¹²

TPD of CH_3Br and CH_3Cl on $\text{GaAs}(110)$

Temperature programmed desorption (TPD) indicates that CH_3Br on $\text{GaAs}(110)$ is rather weakly molecularly adsorbed. Up to 1 ML, TPD of CH_3Br exhibits a broad desorption peak, as well as a peak temperature that decreases with increasing coverage, as shown in Fig. 1. The shifting to a lower desorption temperature with increasing coverage is a result of repulsive dipole-dipole interaction between adsorbates, an observation in agreement with the behavior of other CH_3X molecules on other surfaces. We have used a simple numerical model¹³ to describe the coverage- dependent variation in the desorption temperature and found it to show good agreement with the experimental results. The model is based on the increased repulsive dipole-dipole interaction energy as coverage increases. The model implies that molecules are oriented with their dipoles preferentially pointed in the same direction. The fit to our data is shown in Fig. 1. The conclusion that the dipoles are aligned preferentially in the same direction is also born out by the results of our measurements on the angular distribution of the photofragments (to be shown in a later section). Note that the observation of a single TPD peak precludes adsorption of molecules with large differences in the binding energy.

Similar results are also obtained and shown in Fig. 2 for the case of CH_3Cl on $\text{GaAs}(110)$. However, in this case, the model seems to be valid only to about $1/2\text{ ML}$ coverage. Above $1/2$ monolayer, the peak desorption temperature remains fixed at 135 K. A possible

explanation is that additional molecules adopt antiparallel configurations as the coverage increases further.

Figure 1. TPD of CH_3Br on GaAs(110) at or below 1 ML and the fit with a coverage-dependent activation energy for desorption that includes a repulsive dipole-dipole interaction. The fitting follows a procedure used in Ref. 13. We have evidence that the disagreement on the higher temperature side is due to desorption from periphery of the sample.

Figure 2. TPD of CH_3Cl on $\text{GaAs}(110)$. Note the peak temperature shift with coverage in the two coverage ranges above and below $1/2$ ML. We believe this is an indication that the CH_3Cl assumes a parallel position and antiparallel position respectively in these two coverage ranges.

Dissociative electron attachment of CH_3Br on $\text{GaAs}(110)$

Irradiation of CH_3Br on $\text{GaAs}(110)$ at various wavelengths leads to the ejection of CH_3 radicals, indicating photoinduced dissociation. The kinetic energy (KE) of these fragments was measured by TOF, a series of which is shown in of the CH_3 radicals clearly indicates that the initial photon absorption occurs within the substrate. Direct adsorbate excitation would necessarily result in KE varying with photon energy due to the relatively small number of

Figure 3. TOF spectra of the photoejected CH_3 measured at various wavelengths for one monolayer CH_3Br coverage. The data were normalized by the actual number of photons adsorbed by the substrate. Different total irradiation was used in order to compensate for the low signal at longer wavelengths.

internal degrees of freedom involved. The absence of CH_3 ejection at 870 nm places the threshold of the process between 840 and 870 nm. Given the uncertainty in our laser wavelength readout, i.e. ± 20 nm, the observed threshold suggests that dissociation is induced by photoexcited *bandedge* carriers ($\lambda_g = 825$ nm at 80 K for GaAs).

Fig. 4 shows TOF spectra observed for 2 ML, which are in clear contrast to the ones at 1 ML spectra. Three distinct peaks were detected at 0.25, 1.1 and 2.5 eV for CH_3 desorption. The

Figure 4. TOF spectra of the photoejected CH_3 measured at various wavelengths for 2 ML CH_3Br coverage. The data were normalized by the actual amount of substrate absorption. Note that different irradiation times were used in order to compensate for the low signal and longer wavelengths.

highest energy peak at ~ 2.5 eV, seen at 193 nm only, has been shown in our previous work to be due to direct photodissociation¹⁴ of CH_3Br , which is strongly quenched for the 1 ML case. As in the case for 1 ML, the wavelength-independent KE of the 0.25 and 1.1 eV peaks indicates that the dissociation in both cases is mediated by substrate absorption. However, different wavelength thresholds are seen for the two features, indicating different mechanisms; the 0.25 eV peak requires above-band-gap photon energies while the 1.1 eV peak is seen only with UV

radiation. The wavelength threshold at λ_g for the 0.25 eV feature again suggests transfer of thermalized carriers. Since thermalized electron transfer can only occur through tunneling because the surface barrier lies above the conduction band minimum, and thus the process is much less probable for molecules in the second layer, we believe that the 0.25 eV peak arises from dissociation of molecules in the first layer, just as the 0.6 eV peak does at 1 ML. The ejection of the CH₃ fragments through the second layer occurs because of the relatively high KE of the fragments and the relatively loose intermolecular binding of the adsorbates. A threshold of slightly below 3.5 eV (351 nm) for the 1.1 eV feature originating from the second ML indicates a process driven by hot or photoemitted electrons.

We have observed no Br desorption that can be associated with the electron induced dissociation processes in the first ML. This observation suggests that Br atoms were retained on the surface after the process of photoexcited carrier-mediated dissociation. We conclude that both the thermalized and the hot-carrier processes proceed via DEA with substrate electrons and, as such, would result in a CH₃ radical and a Br⁻ ion, the latter of which is then trapped on the surface due to charge-image interaction (see below). In its isolated state, CH₃Br dissociates readily into CH₃ and Br⁻ through DEA with low-energy (0.57 eV) electrons.¹⁵

To reach an adsorbed molecule, an electron at the surface must either tunnel or be photoemitted into the adsorbate layer. Our photon energy threshold for the 1.1 eV feature is ~3.5 eV, well below the 5.6 eV photoemission threshold for clean GaAs (110), indicating that coupling to molecules in the second layer occurs by internal photoemission. This threshold value is reasonable when we consider two factors. First, the external photoemission threshold of GaAs(110) should be reduced substantially upon CH₃Br adsorption. For example, the work function is reduced by 1.5 eV in the case of CH₃Br on Pt(111).¹⁶ Second, internal photoemission requires lower photon energy than external photoemission due to image-charge reduction of the surface barrier, an important effect for the first 1-2 monolayers, and the polarization response by the adsorbates.^{15,17,18} The difference can be as large as 1-2 eV.

The long lifetime of these carriers is critical to achieve measurable amounts of the

surface reactions which are initiated by the photogenerated electrons at the CBM, since a long lifetime allows multiple electron-surface collisions. Thus the probability of tunneling into the adsorbate is significant even though the probability per interface collision is small. This is an important difference in electron chemistry between semiconductors and metals, a consequence of the different band structure on the dynamics of relaxation of electronic excitations in these two different types of substrates. Additionally, the small density of states at the CBM limits the detachment from the ion intermediate, since the available final semiconductor states are then very small. Finally, upon formation, the *potential* energy of the negative ions decreases and, as a result, for detachment to occur the electrons have to be transferred back into bulk states within the gap. Since, by definition, such states do not exist, detachment is prevented from occurring. All three of these effects enhance the yield by DEA.

Reactions by thermalized electrons

Careful measurements show that the TOF intensity arising from the thermalized electron mechanism decreases drastically as the surface is exposed to irradiation. Fig. 5 shows the CH₃ TOF signal vs the irradiation exposure for 1-ML coverage at 658 and 351 nm. For both wavelengths, the signal intensity of the desorbed CH₃ decays rapidly as the surface is exposed to irradiation. Further, the decay is much faster at 351 nm than at 658 nm. The number of absorbed photons leading to the decay is sufficiently small that the decay cannot be attributed to depletion of the adlayer coverage. This is further confirmed by comparing pre- and post-irradiation TPD of CH₃Br, which showed no change in the CH₃Br coverage within experimental error, *i.e.* $\pm 5\%$, indicating that at most a few percent of the adlayer is dissociated. Measurement on the production of another product, GaBr, of the photodissociation also showed decay. Since no Br desorption is seen in TOF, the photogenerated Br atoms must be retained on the surface. Thus, a post-irradiation TPD of GaBr, which is the only Br-containing reaction product, is an accurate measure of total photoreaction. Fig. 6 gives a plot of the GaBr signal and the *time-integrated* CH₃ signal for different irradiation exposure, *i.e.* number of pulses. For both data,

Figure 5: Mass-15 flux versus number of photons absorbed by the substrate for irradiation at 658 nm and 351 nm and at 1-ML CH₃Br coverage. The substrate absorption is calculated using the measured laser fluence, the actual incident angle, and the known optical constants of GaAs. Each point is averaged over 100 to 400 pulses.

the leveling-off or the decrease in the slopes represents the decay of the *rate with increasing*

irradiation exposure. The good correlation between the two different measurements clearly indicates that the overall photoreaction rate decreases as the surface is exposed to increased irradiation.

The rapid decrease in the photoreaction rate results from the fact that the reaction is induced by thermalized photoexcited electrons at the CBM,¹¹ whose lifetimes are affected by the formation of surface recombination centers. Specifically, in our case, as the photoreaction occurs, Br atoms react with the surface atoms to form the surface states. A recent study of chemisorbed¹⁹ Br on GaAs(110) shows the formation of such surface states within the GaAs bandgap. Although in this case adsorption was from gas-phase Br₂, we believe that the Br in our experiments is likely to be bound to the same sites, since the reaction product in either case is surface monobromination.

Figure 6: Total GaBr (mass 69) signal from postirradiation TPD plotted together with the total CH₃ (mass 15) signal from the TOF measurements versus photon exposure at 1-ML CH₃Br coverage. The GaBr TPD is that obtained after subtraction of the "dark" signal, *i.e.* that acquired without irradiation.

To verify directly the occurrence of the surface Br-induced reduction of the CBM-electron lifetime, we measured the photoluminescence (PL) yield as a function of irradiation

Figure. 7: Photoluminescence signal versus number of photons absorbed by the substrate for 633 and 325 nm under cw illumination at 1-ML CH_3Br coverage. No decay is seen for a bare (undosed) surface at either of the two wavelengths.

time; detection of the intensity of PL allows direct measurement of the change in the lifetime of band edge carriers. Since GaAs is a direct-gap material, this PL signal is readily observable. Fig. 7 shows the PL signal versus irradiation time for 1 ML coverage at two different wavelengths, 325 and 633 nm, using a cw HeCd and HeNe laser, respectively. Note that the short absorption depth of UV light is well known to lead to a PL yield which is more surface sensitive than that of longer-wavelength visible light.²⁰ In this experiment, the cw laser served both to dissociate the CH₃Br and to excite photoluminescence; thus the cw laser drives *both* the chemistry and the photoluminescence through the formation of electron-hole pairs. The decrease in the PL signal with irradiation time shows clearly that there is a reduction in the lifetime of the band edge carriers in the presence of surface irradiation. Further, the dependence of the decay rate of the PL signal on the laser wavelength is consistent with the TOF data shown in Fig. 5. Specifically, at 325 nm the time-varying PL signal declined faster than that at 633 nm. Further confirmation of the proposed origin of the reduction in the photoreaction rate is seen in the observation that the TOF signal can be recovered by annealing to but not below the temperature 650 K, at which GaBr desorbs.

Self-quenching of *bandedge* carrier-induced photochemical reactions on semiconductor surfaces may be a common phenomenon, since the formation of surface states within the bandgap is a likely consequence of chemisorbed reaction products. Chemisorbed products of reactions on semiconductor surfaces perturb the bonding structure of the surface atoms, which can split off states from the surface band and push them into the band gap where they would enhance the recombination of electrons and holes and lower the lifetime of carriers at the band edges. In fact, the study of the photodissociation of both CCl₄ on GaAs(110)¹⁰ and O₂²¹ on InP has revealed similar light-exposure-dependent decreases in the reaction rate. We suspect that a similar effect is involved in both cases, although in neither case did the authors elaborate on possible explanations.

Site specific electron transfer initiated reactions

The angular variation in the TOF spectra at or below one monolayer shows that the photochemistry is considerably richer and more complicated than discussed above. Fig. 8 shows a series of TOF spectra, measured at 248 nm and at 1 ML at various desorption angles, with the detection plane defined by the surface normal and the [01] vector within the (001) surface, which is also perpendicular to the GaAs zig-zag chain on the surface. For up to 1 ML coverage, the angular distribution of the photoejected CH₃ fragments are characterized by two lobes with distinctly different angles, one with the most probable direction at 25° and the other at -45°, with respect to the surface normal. We have defined the angle such that the detection angle is +90° along the [01] direction and -90° along $[0\bar{1}]$. One important aspect of the result is that the desorption into both lobes exhibits a relatively narrow angular distribution. Note that the signal is normalized to reflect the desorbing probability per adsorbate and per photon absorbed by the substrate. At coverages less than 1ML, two similar angular lobes are observed but the angular width at 25° sharpens somewhat and the most probable angle shows a slight shift away from the surface normal with decreasing coverage.

As shown in the insert of Fig. 8, the CH₃ fragment desorbed into the two angular distributions is also characterized by different KE: 0.6 eV for desorption in the 25° direction, which is the one discussed above, and 1.1 eV in the -45° direction. Note that this 1.1 eV CH₃ feature is not the one discussed above, which is observed above 1 ML coverage and with a different desorption angle (+35°). However, we believe that the similar process is responsible for the 1.1eV CH₃ fragments under consideration, except that the molecule is located in the first layer. The evidence supporting this conclusion includes similar photon energy independent behavior and similar wavelength threshold.

Desorption into each of the two angular lobes was observed in the coverage range from 0.05 to 1 ML and the intensity for both increases monotonically with coverage. Based on this result, as well as the repeatability of angular direction and energies, we believe that the observed desorption is very unlikely due to dissociation on defect sites.

The fact that the two desorbed species desorb in two distinct angular lobes strongly

Figure 8. Angular dependence of the CH₃ TOF spectra of CH₃Br on GaAs(110) at 1 ML coverage. The Insert shows the details of the spectra for the two angular lobes. The two lobes are a result of photodissociation of CH₃Br of two different orientations.

suggests that we are observing photodissociation of CH₃Br of two differing orientations, most likely on different sites. The possibility that identical adsorbate molecules give rise to two desorption angles through two different dissociation processes can be excluded, since the

desorption angle should be very close to the bond orientation in the present case. The latter follows the fact that the time it takes for the bond to break is similarly very short, < 100 fs,²² and thus there is insufficient time for the C-Br bond to reorient. The latter is a consequence of the fact that the intramolecular potential is significantly more steep and repulsive due to the antibonding nature of the σ^* orbital than that of the adsorbate-substrates potential.

It is important to point out that the angle at which 0.6 eV CH_3 is desorbed is close to the direction of the p orbital on the Ga surface atom, a fact important to the understanding of the difference in the wavelength threshold between these two processes.

The CH_3Br TPD result indicates that CH_3Br is weakly and molecularly adsorbed on GaAs(110), as has been seen on other surfaces. Thus the electronic structure of the two molecules is expected to be similar. In light of this, the difference in the wavelength threshold is quite surprising between the two processes, both of which we believe are electron attachment initiated processes. We believe that in order to understand the electron energy necessary to transfer to an adsorbate, it is necessary to consider energy levels of the ion intermediate upon its formation, whose electronic configuration differs from that of the ground state molecules and thus, may vary by a large amount due to interaction with substrate atoms. This is unlike the electron attachment process in the gas phase where the ion intermediates are isolated.¹⁵ The site specific interaction is in addition to the effect on the energy of the ion intermediate on a solid surface due to the image-charge interaction, which is independent upon the specificity of substrate-adsorbates interaction. The significance of this ion intermediate-substrate atom interaction arises from the fact that the position in energy of the lowest occupied orbital is now most likely to be in the range for the unoccupied surface levels of the substrate. Thus electron delocalization may occur between the substrate atoms and the surface adsorbates, which can further stabilize the ion intermediates. This interaction may vary significantly from site to site depending on the extent of orbital overlap between the electron in the σ^* orbital on the CH_3Br - and an orbital on the substrate atoms.

In the absence of more specific knowledge of the surface adsorption site, it is difficult to

characterize the precise details of the molecule substrate interaction. However, the known electronic structure of GaAs(110) allows us to make several useful observations. In particular, during surface relaxation, GaAs(110) rehybridizes so as to leave one Ga p -orbital near the bottom of the conduction band unoccupied.²³ On the other hand, the surface state corresponding to the p orbital on the As atom is occupied and with its energy just below the valence band maximum.

Given the downward shift due to image charge interaction, the orbital is then close enough in energy to the Ga p -orbital so that the mixing between the two orbitals becomes important and the orbitals are no longer localized on the Ga or the CH_3Br^- . In other words, an electron from the conduction band can transfer by tunneling onto the CH_3Br , because the Ga p -orbital is in resonance with the conduction band minimum. This scenario calls for the molecules to be adsorbed in closer spatial proximity to Ga surface atoms. Further, given the symmetry for both the p orbital on Ga and the σ^* on CH_3Br^- , the orbital overlap or electron transfer becomes significant only when the C-Br bond is oriented close to the p orbital direction. In contrast, transfer requires higher energy electrons or hot electrons for CH_3Br on a different site or with a different orientation. This is consistent with our observation that the thermalized electron process ejects CH_3 along the p orbital of the Ga surface atoms. It can also be shown that a similar interaction is absent for CH_3Br on an As site and thus attachment would have to be a hot electron transfer process.

To summarize, we have observed two dissociation processes for CH_3Br on GaAs for coverage up to 1 ML. The two processes are both initiated by electron transfer from the substrate, but the transfer is to distinctly oriented molecules: molecules tilted in the $[01]$ orientation undergo bond cleavage via charge transfer from the conduction band minimum, while those pointing in the $[0\bar{1}]$ require photoemitted electrons to initiate the charge transfer process. The observations presented above can be interpreted most clearly as the interplay between charge-transfer mechanism and specific surface site or ad molecule orientation. Each of these two different processes exhibits a different photon energy threshold and gives off a

fragment with a different translational energy. The difference in the wavelength threshold can be explained by the significantly different interaction of the intermediates with the substrate atoms for CH₃Br of different orientation or on different sites. In the present case, the *p* orbital on the Ga provides a stabilization to the σ^* of the CH₃Br⁻ with the C-Br oriented along Ga *p*-orbital direction. Clearly, unambiguous interpretation of our TOF result will have to wait for experimental measurement on the CH₃Br orientations and adsorption sites on GaAs(110) by, for example, NEXAFS. The general implication of our observation is that the detailed dynamics of electron transfer to even physisorbed molecules may vary significantly for molecules of different orientation. This is due to different interaction between the substrate atoms and the ion intermediate, the variation of which is no longer to be characterized by physisorption and therefore can be large.

FUTURE WORK

Our work in the last year has shown that it is possible for the first time to measure the dynamics of electron-transfer reactions on semiconductor surfaces. It this next year, we wish to exploit this new discovery by expanding the scope of previous measurements and by developing a stronger quantitative understanding of the physics of the transfer process. In particular, we will seek to use independent techniques, primarily NEXAFS or He scattering, to determine the molecular orientation of methyl-halides on semiconductor surfaces; these results will be correlated with the fragmentation data from our TOF experiments. Second, we will expand our measurements to other semiconductor crystal-adsorbate systems so as to strengthen our understanding. Finally, we will continue to examine other photochemically initiated chemical phenomena on the same surfaces.

NEXAFS Determination of the Molecular Orientation on Surfaces

We have proposed to apply the NEXAFS technique available at Brookhaven National Lab. to determine the orientation of molecules such as CH_3X on GaAs(110) surface. The information of the orientation is to be obtained by measuring X-ray absorption near the carbon *K* edge by CH_3X as a function of two angles, (θ, ϕ) , between the surface normal and the polarization of the X-ray radiation. The angles at which the maximum absorption occurs would correspond to the C-X bond of the CH_3X molecules on the surface. In the case of CH_3Br , we expect to see two separate orientations of CH_3Br at 25° and -45° , with respect to the surface normal. The results of this experiment would allow us to verify independently our proposed model explaining the observed angularly resolved TOF results.

Similar measurements will also be carried out on CH_3Cl on GaAs(110). As discussed earlier, there is an indication from our TPD results that two different orientations of CH_3Cl exist on this surface. However, unlike in the case of CH_3Br , the two orientations seem to be obtained at two different coverage ranges, below and above 0.5 ML. NEXAFS would allow direct verification of this conclusion. Again, this information on the orientation of the adsorbate will

be combined with angular resolved TOF measurement to study the dynamics of photodissociation on CH₃Cl on GaAs(110).

Angular and Energy Resolved Measurement of Photofragment to Probe the Dynamics of Surface Photochemistry

As shown above, angular and energy dependence of the photofragments is a convolution of the molecular orientation and the dynamics of photodissociation events of the adsorbates on surfaces. We will extend our study to CH₃Cl on GaAs(110). According to our TPD results, the molecules adopt a parallel orientation below 0.5 ML, but the orientation changes to an antiparallel position above 0.5 ML, with respect to the molecules that are already present on the surface. We thus expect to see a change in the angular distribution of the photofragment above and below 0.5 ML. Again, different mechanisms may be expected for molecules with these two different orientations in the two coverage ranges. This will be studied by TOF measurement of the photofragment kinetic energy and the dependence of the photodissociation cross section on the radiation wavelength. In this study, we are particularly interested in looking at possibly different orbital overlap and its implication on the dynamics of electron-transfer process. The importance of orbital overlap depends on the energetics of the orbitals involved as well as orientations of the molecule, which is why independent measurement on the molecular orientation is needed.

Threshold Measurement for Electron Attachment Initiated Desorption Process

Electron transfer may induce both desorption and dissociation of adsorbates, via an Antoniewicz mechanism for the former and through the occupation of an antibonding orbital of the adsorbate for the latter. Thus the dynamics of electron-transfer-induced processes on surfaces, as well as the branching ratio for desorption and dissociation, depends on the electron energy or implicitly on the energy of the excitation photon. Obviously, the branching ratio will depend on the detailed potential energy surfaces involved in the electron attachment

transition. However, for adsorbates on a semiconductor surface, one generalization may be made, namely, that *bandedge* carriers may induce dissociation through carrier transfer but *not* desorption. In other words, the desorption may have a higher photon energy threshold than the dissociation process. This is counterintuitive since one would imagine that a more energetic process, photodissociation in this case, should have a higher energy threshold. For desorption to occur, a minimum amount of energy, namely the binding energy of the adsorbates on the surface, will have to be imparted to the adsorbate and surface bond. In an electron-transfer-induced process, this occurs when the electron detaches from the adsorbate and transfers back into the substrate. The desorption is a consequence of the motion of the nuclei when a molecule is on the upper potential curve of the substrate-molecule coordinate; in this case the adsorbate-substrate distance is greatly compressed. The electron can only transfer back to a substrate state with a lower electron energy. Thus if the initial transfer starts with a thermalized electron, back transfer would have to be into a nonexistent state within the bandgap and therefore would be forbidden. Thus the electron-induced desorption will require an energy threshold above the CBM. However, we have shown that electrons at CBM activate the dissociation of CH₃Br on GaAs(110) through dissociative electron attachment. In the coming year, we will use our excimer pumped dye laser set up to carefully measure the wavelength threshold for both the desorption and the dissociation processes to verify this proposed explanation.

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