



NEXAFS measurements indicating a tilted molecular orientation for methyl halides on GaAs(110)

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Abstract

The orientation of methyl halides (CH_3X , $\text{X} = \text{Cl}, \text{Br}, \text{I}$) molecularly adsorbed at 80 K on GaAs(110) has been investigated by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at the carbon K edge. Analysis of the angular dependence of the $\text{C-X } \sigma^*$ resonance indicates that the molecules are oriented with the C-X axis tilted with respect to the surface normal. In the first monolayer, the molecules are inclined in the $[0\bar{1}]$ direction, the C-X axis approximately 45° from the surface normal. In the second monolayer the molecules are inclined in the opposite $[01]$ direction from the surface normal. Correlations between the orientation results obtained from these studies and other observations on these same surface adsorbate systems are discussed.

Keywords: Bromine; Chlorine; Gallium arsenide; Iodine; Methyl halides; Near edge extended X-ray absorption fine structure (NEXAFS); Single crystal surfaces; Surface structure; Thermal desorption spectroscopy

The determination of adsorbate molecular orientation on surfaces by near-edge X-ray absorption fine structure (NEXAFS) has been well established [1]. Tunable, polarized X-rays from a synchrotron source provide a convenient method for probing dipole transitions between core levels and unoccupied molecular orbitals of adsorbates [2]. While a number of NEXAFS studies have investigated the effects of chemisorption on adsorbate electronic structure and have determined molecular orientations on metal surfaces [3–5] relatively little is known directly about the orientation of adsorbed (either chemi- or ph-

ysisorbed) molecules on semiconductor surfaces [6–8].

The stable, well-characterized GaAs(110) surface provides a model substrate for investigating the effects of a highly corrugated, covalent surface on adsorbate orientation and thus is an interesting system for both fundamental and technical reasons [9]. Prior TPD studies have shown that the methyl halides adsorb on GaAs(110) at 80 K without dissociation [10]. In addition, the gas-phase properties of these highly polar molecules are well known. Moreover, the $\text{C-X } \sigma^*$ and $\text{C-H } \sigma^*$ orbital structure of the methyl halides, which is well documented from the gas-phase inner shell electron energy loss (ISEELS) spectra [11], can also be clearly seen in the NEXAFS spectra of the adsorbed species in the region of the

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carbon K edge. The variation of the intensity of the C–X σ^* resonance signal with the angle of incidence of polarized X-rays allows determination of the orientation of methyl halides on GaAs(110).

These measurements are of particular relevance because recent time-of-flight (TOF) measurements of methyl fragments from photostimulated dissociation of methyl halides on GaAs(110) have shown a distinct angular distribution, which has been interpreted as due to a tilted orientation of the adsorbate molecules on the surface [12]. In particular, it has been found that methyl fragments with a kinetic energy of ~ 1 eV are ejected from the surface in the $[0\bar{1}]$ direction and strongly peaked about an angle of -45° from the surface normal. The energetics and tight angular distribution of these ejected methyl fragments suggest that the adsorbed methyl halide molecules do not have time to reorient during the dissociation event and that the angular distribution of the ejected methyls thus reflects the orientation of the adsorbed methyl halides, i.e. adsorbed molecules are oriented with their C–X axes tilted at $\sim 45^\circ$ with respect to the surface normal in the $[0\bar{1}]$ direction, and that the halogen is closest to the surface. Several factors, however introduce some uncertainty into this interpretation. For example, the methyl halide photodissociation dynamics on GaAs(110), as well as on metal surfaces, suggests that these fast methyls are produced by the capture of hot electrons which are essentially photoemitted in the first monolayer and cause dissociation in a manner similar to gas-phase dissociative electron attachment (DEA) [13,14]. It is thus the orientation of the CH_3X^- ion which determines the fragment angular anisotropy. While one can argue convincingly that the anion and the neutral should have the same symmetry [15,16], and that the DEA process occurs on a time scale which precludes reorientation of an adsorbate molecule after electron capture, it is possible that the cross section for electron capture is highly dependent upon the molecular orientation and that adsorbates tilted at -45° from the surface normal, while not the dominant species, are the species detected in these TOF studies. On the other hand, modelling of thermal desorption profiles suggests, albeit indirectly, that the neutral molecules do have a tilted orientation on the surface [10].

The NEXAFS results reported here provide a

direct measurement which confirms that the methyl halides do indeed have a tilted orientation in both the first and second monolayers, supporting some of the conclusions of previous studies.

The experiments were conducted at the U1A station of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in a UHV chamber with a nominal base pressure of 5×10^{-10} Torr and equipped with Auger, LEED, a quadrupole mass spectrometer, and an ion gun for sputtering the sample. The $1 \text{ cm} \times 1 \text{ cm} \times 0.5 \text{ mm}$ GaAs(110) sample was mounted on a thin piece of Mo foil which was heated resistively and was capable of being cooled to < 80 K. The surface was prepared by three cycles of sputtering at room temperature with 500 eV Ar^+ ions for 20 min followed by 30 min anneals at 840 K, which has previously been shown to give a sharp (1×1) LEED pattern [10]. It should be noted that this surface cleaning procedure differs in a small but significant way from that used for the TOF studies reported in Ref. [12]. In that work, the surface sputtering was carried out at 750 K. While both procedures produce a surface with a sharp (1×1) LEED pattern, the high temperature sputter gives rise to methyl radical TOF peaks in two opposite directions. In the case of the low temperature sputter, one TOF peak (the ~ 1 eV peak at -45° in the $[0\bar{1}]$ direction) dominates [17], and it is on this type of surface that the studies here were performed. Possible reasons for the variability of the second TOF channel (e.g. a high cross section for methyl halides at a small number of specific surface defects introduced by high temperature sputtering) are still being investigated.

The GaAs sample was cut from a wafer whose surface orientation had previously been determined by LEED analysis [18] and mounted such that the manipulator allowed rotation about an axis parallel to the $[1\bar{1}0]$ vector on the surface. As shown in Fig. 1, this axis of rotation is parallel to the Ga and As “zig-zag chains” in the (110) surface. The electric field vector of the incident polarized X-ray radiation is in the plane defined by the surface normal and the $[01]-[0\bar{1}]$ surface vector, so that the NEXAFS spectra reported here probe the tilt of the adsorbate molecules in this plane, i.e. perpendicular to these “chains”. The molecular tilt angle (α) is defined as the angle between the surface normal and the C–X

bond axis, along which lies the C–X σ^* orbital. The incident angle of the X-ray radiation (ϕ) is defined by the angle between the surface normal and the electric field vector (E), so that the E vector is parallel to the molecular tilt angle in this plane when $\alpha = \phi$. All angles are defined relative to the surface normal with positive angles in the [01] direction.

The methyl halides were adsorbed by cooling the sample to ~ 80 K and backfilling the chamber to a pressure of 5×10^{-8} Torr for the time necessary to achieve the desired exposures. The adsorbate coverage was calibrated by temperature programmed desorption (TPD), with the onset of a second lower temperature peak in the TPD spectrum being used to establish saturation of the first monolayer. The formation of a second layer was assumed to be completed at twice the exposure of the first layer, as indicated by a previous, more extensive TPD analysis [10]. Fig. 2 shows typical TPD spectra for coverages of one to two monolayers. TPD spectra were also taken after collecting NEXAFS spectra to confirm that the coverage did not change significantly during the X-ray irradiation.

The NEXAFS spectra reported here were taken by measuring the partial electron yield ($E_r = 200$ V) with a channeltron situated directly above the inci-

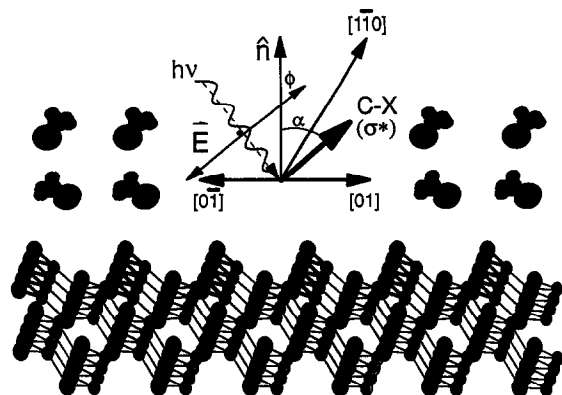


Fig. 1. Schematic diagram depicting the top four atomic layers at the GaAs(110) surface and a tilted orientation for methyl halides adsorbed on the surface in the first and second monolayers. In the substrate, the large balls represent As and the small balls Ga, and the “zig-zag chains” referred to in the text are highlighted by thicker lines. The surface relaxation results in a rotation of the topmost As atoms upward at $\sim 27^\circ$ relative to the Ga atoms. The incident irradiation (ϕ) and molecular tilt (α) angles are shown as defined in the text.

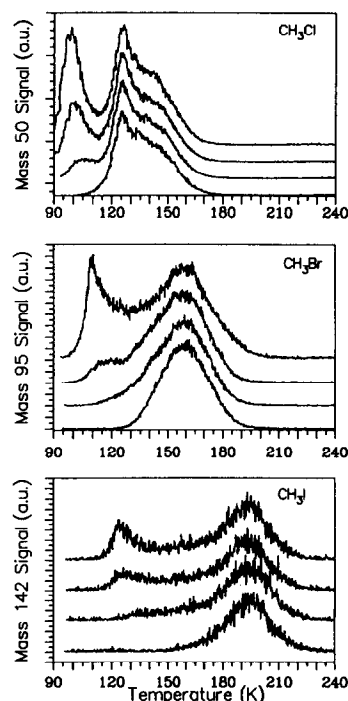


Fig. 2. Typical TPD spectra of methyl halides from GaAs(110) used to calibrate adsorbate coverages. Note that the beginning of the formation of a second monolayer is readily observed by the presence of the low temperature peak.

dent beam, approximately 10 cm from the sample. The incident X-ray energy was scanned from 275 to 320 eV, and the beam was approximately 4 mm^2 when incident normal to the GaAs surface. While the C–X σ^* resonances for all three methyl halides are in the 285–290 eV region, measurements were made of the “pre” and “post” edges of the carbon K-edge step in order to compare the total carbon adsorption. Thus, in the interest of time, many spectra were taken scanning only from 280–295 eV and 310–320 eV. Fig. 3 shows complete NEXAFS spectra for multilayer ($\theta > 50$ ML) absorption which clearly exhibit the C–X σ^* and C–H σ^* resonances similar to those seen in gas-phase ISEELS spectra [11]. The peak positions of the C–X σ^* (287.9 eV for CH₃Cl, 287.2 eV for CH₃Br, and 286.1 eV for CH₃I) in the NEXAFS spectra of the condensed phase are only approximately 0.5 eV higher than those of the gas-phase molecules, which is within the error of the absolute energy calibration for the monochromator on this system.

Comparison of the multilayer NEXAFS spectra and the gas-phase ISEELS thus allows unambiguous assignment of the C–X σ^* resonance which is used to establish the molecular orientation in the one and two monolayer NEXAFS spectra. In the first and second monolayers, the C–X σ^* peak resonance positions (287.7 eV for CH₃Cl, 287.0 eV for CH₃Br, and 285.9 eV for CH₃I) are only about 0.3 eV higher than their reported gas-phase values. These small shifts of the C–X σ^* peak positions in both the adsorbed (one and two monolayer coverages) and condensed (> 50 ML coverage) states are due to screening effects from the surrounding polarizable medium and are indicative of weak molecular adsorption [19].

Since the C 1s \rightarrow C–X σ^* transition involves excitation of an electron from a spherically symmetric core state to the σ^* molecular orbital, which is predominantly along the C–X bond axis [20], the measured intensity of this resonance will be greatest when the incident E vector is along this bond axis, i.e. when the incident angle ϕ is the same as the molecular tilt angle α . The variation of the intensity

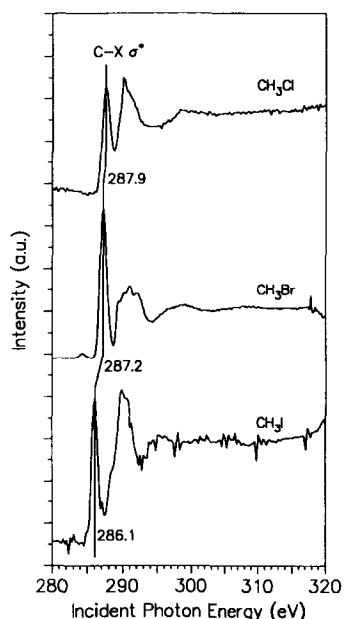


Fig. 3. NEXAFS spectra measuring partial electron yield (PEY) for multilayer ($\theta > 50$ ML) coverages of methyl halides on GaAs(110). These spectra exhibit electronic structure (C–X σ^* and C–H σ^*) similar to the gas-phase ISEELS spectra given in Ref. [11].

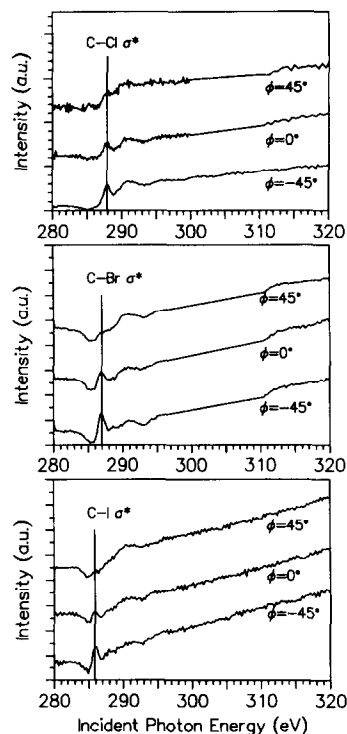


Fig. 4. NEXAFS spectra measuring partial electron yield for one monolayer coverages of methyl halides on GaAs(110) taken at three different angles. In each case the C–X σ^* resonance is most intense when the polarization of the incident X-ray beam forms an angle (ϕ) of -45° with the surface normal.

of the C–X σ^* resonance peak with the angle of the incident polarized irradiation thus clearly establishes the molecular orientation. Considering first measurements at approximately one monolayer coverage for all three molecules, the C–X σ^* peak height is greatest with an incident irradiation angle of -45° , thus indicating that the molecules are tilted, on average, at about -45° , i.e. in the $[0\bar{1}]$ direction. This orientation is even qualitatively exhibited in the angular dependence of the raw partial electron yield NEXAFS spectra shown in Fig. 4.

A more quantitative analysis of the results requires that several factors be taken into account. First, in the region of the carbon K edge, the X-ray intensity incident on the sample was energy dependent, i.e. it varied significantly as the monochromator was scanned from 280 to 295 eV. This behavior was evident from monitoring the electron-yield signal of a gold reference grid which showed a signifi-

cant increase between 285 to 286 eV due to residual X-ray adsorption of spurious carbon-containing compounds on the grid in this energy region. Since these same carbon-containing impurities were most likely adsorbed on surfaces throughout the monochromator and lensing regions of the chamber, their absorption of the incident X-ray intensity between 285 to 286 eV was significant enough to cause a decrease in the X-ray intensity which was incident on the sample. This absorption caused the “dip” visible at ~ 285.5 eV in the one and two monolayer NEXAFS spectra. Since this intensity variation was present at a fixed level for all experiments, it does not significantly effect the orientational interpretation of the results; however it does lead to a smaller C–I σ^* signal intensity and a slightly asymmetric peak shape in the methyl iodine spectra because the “dip” position overlaps the low energy side of the C–I σ^* resonance peak.

Second, for a quantitative determination of the molecular tilt angle (α), the NEXAFS spectra were analyzed by subtracting the signal from a clean surface, obtained by annealing the sample to 840 K. This procedure was done for each angle in order to eliminate effects due to variation of the clean surface signal of the substrate or the detector with incident angle. Note that prior to the subtraction, all spectra were normalized by the pre-edge to account for different beam intensities. The results after this normalization and subtraction are shown in Fig. 5. The C–X σ^* intensity variation in these spectra exhibits the same angular dependence as the raw PEY data of Fig. 4. Unlike resonant core-level photoemission [21], in this energy region, the photoemission from the clean surface, or any impurities on it, does not have an appreciable angular variation. It should also be noted that normalization by division of the clean surface spectra produces almost identical variation of the C–X σ^* intensity with incident irradiation angle as the spectra normalized by subtraction of the clean surface. Subtraction was used for quantification in this analysis in order to establish the orientation of molecules in the second monolayer as described below.

Although spectra are shown for only three angles in the figures, for the case of methyl bromide, spectra were taken at least every 15° while varying the incident angle from -60° to 60° . Fig. 6 shows the

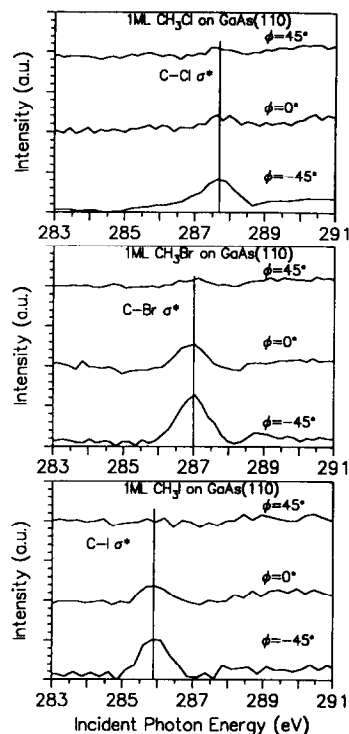


Fig. 5. The C–X σ^* region of the NEXAFS spectra of Fig. 4 after “quantification” by normalization using the pre-edge (280–283 eV) intensity and subtraction of the NEXAFS spectra (also normalized) obtained from the clean GaAs(110) surface at the same angle of incident irradiation.

angular variation of the “quantified” (after subtraction of the clean surface) C–X σ^* signal intensity. There is a clear maximum at $-45^\circ \pm 5^\circ$. The variation of the “quantified” C–X σ^* intensity can be approximately fit, within experimental error, by $\cos^2(\alpha - \phi)$ where ϕ is the angle of the incident polarization and α is, again, the molecular tilt angle, both defined relative to the surface normal (as in Fig. 1). Since the C 1s \rightarrow C–X σ^* transition probability is zero when the electric field vector is perpendicular to the σ^* orbital, if the adsorbed molecules are all tilted at -45° and the incident beam is truly linearly polarized, the C–X σ^* intensity should vanish at 45° . The presence of a residual signal at an incident angle of 45° in Fig. 6 may indicate that a small fraction of molecules are adsorbed with an opposite or random orientation, perhaps on defect sites [22], or possibly hindered vibration of the adsorbate molecules at 80 K [23]. But more likely, this residual

signal at 45° is due to the elliptical polarization of the incident X-rays which results in a small electric field component ($\sim 15\%$) perpendicular to the $[01]-[0\bar{1}]$ axis. When the beam is nominally incident at 45° , this gives rise to a constant background due to some tilt of the adsorbate molecules in this plane.

NEXAFS measurements were also made at a coverage of two monolayers. As Fig. 7 shows, at positive angles of incidence, the C–X σ^* resonance signal is more intense in the 2 ML NEXAFS spectra than in the 1 ML case, indicative of the presence of adsorbed molecules which are either oriented more upright (α is smaller but still negative) or tilted in the $[01]$ direction. Assuming that the adsorption of a second layer does not effect the orientation of those molecules adsorbed in the first monolayer, the orientation of the molecules in the second monolayer can be investigated using the normalization and quantification procedure described above to subtract the first monolayer signal from the two monolayer spectra. In this case, and as shown qualitatively in Fig. 8, the molecules in the second layer appear also to have a tilted orientation, but in the $[01]$ direction which is opposite to the $[0\bar{1}]$

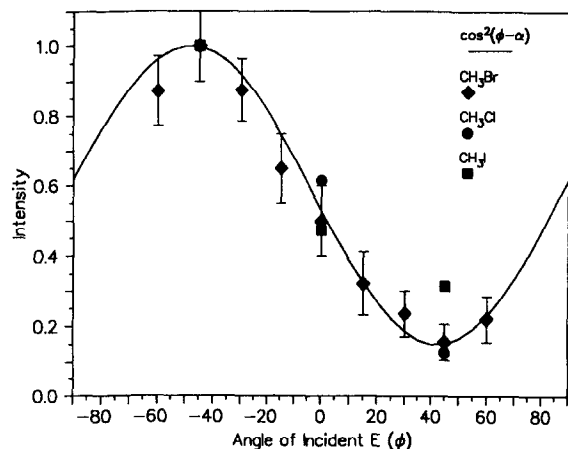


Fig. 6. Plot of the variation of "quantified" 1 ML C–X σ^* resonance intensity as a function of the angle of incident irradiation, ϕ . For methyl bromide, the data points are the average of several measurements and the error bars represent the variance of those measurements. For each methyl halide, the data have been divided by the maximum intensity for that species. The $\cos^2(\phi - \alpha)$ curve was obtained from a least squares fit of the methyl bromide data and has a maximum at $\phi = -48^\circ$, implying a molecular tilt angle, α , of -48° .

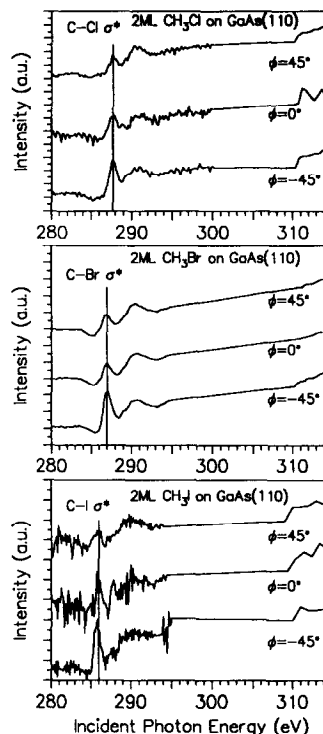


Fig. 7. NEXAFS spectra measuring partial electron yield for two monolayer coverages of methyl halides on GaAs(110) taken at three different angles. The spectra include contributions from molecules adsorbed in both the first and second monolayers; however, note that the C–X σ^* resonance signal is greater at positive angles of incidence than for the one monolayer spectra of Fig. 4.

direction along which the C–X bonds are oriented in the first monolayer.

The quantitative determination of the molecular tilt angle (α) for molecules in the second monolayer is complicated by the fact that this procedure is highly sensitive to the calibration of the coverage in the first monolayer spectra. If, for example, the coverage in the first monolayer spectra is actually only 0.95 ML, then upon subtraction, the normalized second monolayer signal will include some contribution from molecules which are actually in the first monolayer. Furthermore, because the one and two monolayer spectra were not taken immediately following one another and thus involved repositioning the sample after dosing, the normalized 2 ML spectra exhibit a poorer signal-to-noise ratio which precludes a significantly quantitative deconvolution of the first

and second monolayer signals for the cases of methyl chloride and methyl iodide. However, for the case of methyl bromide, the signal-to-noise ratio is particularly good and the angular variation of the intensity of the C–X σ^* resonance signal from molecules in the second monolayer can be obtained, as is shown in Fig. 9. The tilt angle for molecules in the second monolayer is determined to be $35^\circ \pm 10^\circ$. In general, for all three methyl halides, the tilt angle (α) for molecules in the second monolayer appears to be slightly less than that of the first layer. This is reasonable if one assumes that the tilted orientation is due to surface–adsorbate interactions which are stronger in the first monolayer as discussed below. In any case, the orientation of molecules in the second monolayer as determined by NEXAFS is in general accordance with the orthorhombic crystal structures of the methyl halides where alternating layers along the c -axis are tilted in opposite directions [24,25].

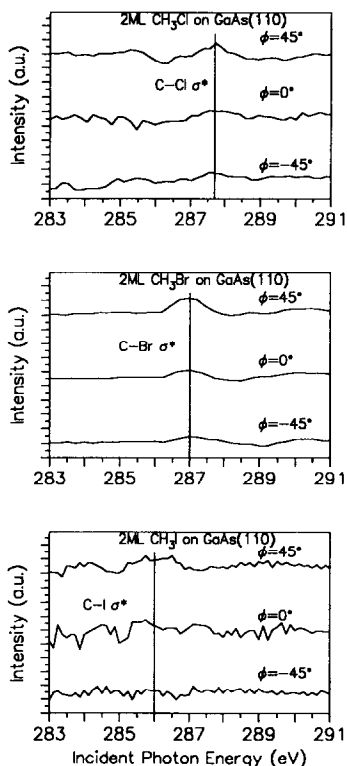


Fig. 8. The C–X σ^* region of the NEXAFS spectra of Fig. 7 after “quantification” by normalization using the pre-edge (280–283 eV) intensity and subtraction of the one monolayer NEXAFS spectra at the same angle of incident irradiation.

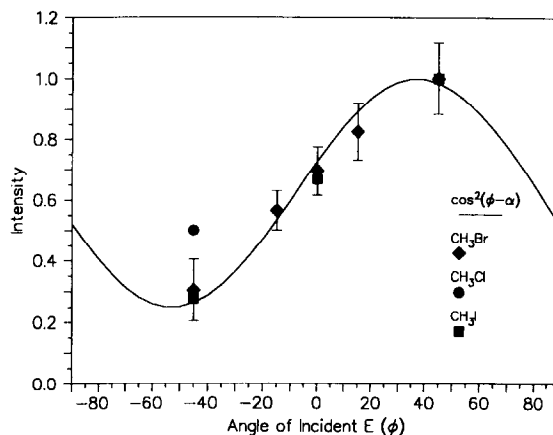


Fig. 9. Plot of the variation of “quantified” 2 ML C–X σ^* resonance intensity as a function of the angle of incident irradiation ϕ . The least squares fit of a $\cos^2(\phi - \alpha)$ curve to the methyl bromide data has a maximum at $\phi = 37^\circ$.

The angular dependence of the NEXAFS spectra, therefore, clearly indicates a tilted orientation for the methyl halides on GaAs(110). Furthermore, the small shifts of the C–X σ^* resonance positions relative to the gas-phase values, along with the low activation energy for desorption (~ 0.5 eV) of these molecules from GaAs(110) obtained from the TPD profiles [10], indicate weak molecular adsorption. As mentioned above, recent measurements using TOF techniques have suggested a tilted molecular orientation with the halogen end down on GaAs(110). Although the “halide down” alignment cannot be addressed by these NEXAFS measurements, it is consistent with methyl halide–metal systems. A decrease in the work functions of Ag and Pd upon adsorption of methyl halides is also indicative of an adsorbate orientation with the positive end of the dipole pointing away from the surface [26]. Furthermore, HREELS studies have shown that the C–X stretch frequency is more strongly perturbed than the C–H upon adsorption of CH_3Br or CH_3I on Cu due to a “halogen down” orientation [27,28]. The one monolayer desorption temperatures in TPD for these systems are close to those examined here, implying that the strength of the surface adsorbate interactions are of the same order. Thus it is proposed that the methyl halide molecules are adsorbed with the halogen closest to the surface on GaAs(110). While the previously mentioned TOF results are also consistent

with this orientation, investigation of the work function change upon adsorption would be desirable to further substantiate the direction of the adsorbate dipole moments.

The magnitude and direction of the molecular tilt angle is presumably influenced by the adsorption site, a combination of surface–adsorbate and interadsorbate forces, and the surface structure. Clearly experimental determination of the adsorption site requires more intensive investigation by XPS or perhaps X-ray standing wave analysis along with more appropriate theory. However, several tentative suggestions can be briefly outlined at this stage. For example, one would expect the halogen to be more strongly attracted to the more positive Ga atoms with their empty p orbitals. In such a case, interaction with the halogen valence orbitals might be responsible for the tilted orientation. Upon surface relaxation, the empty Ga p_z orbital can be visualized as protruding from the (110) surface at an angle of 63° , i.e. perpendicular to the 27° tilt angle between the topmost As and Ga atoms [29]. Since the halogen valence orbitals are sp^3 hybridized, maximum overlap with the empty Ga p_z orbital would occur when the molecules are tilted in the opposite direction at a $46^\circ (= 109^\circ - 63^\circ)$ angle.

However, as an explanation of methyl halides incommensurately physisorbed on insulators, thus precluding strong orbital interactions, both theoretically and experimentally based discussions have tended to favor an explanation of orientation based on a combination of electrostatic surface–adsorbate forces, which favor an orientation where the C–X axis is parallel to the surface, and interadsorbate forces (dipole–dipole repulsions) which favor an orientation where the C–X axes are perpendicular to the surface with an anti-parallel arrangement. Specifically, methyl halides on LiF, NaCl, and graphite surfaces have been extensively studied by He diffraction and modelled using Monte Carlo techniques [30,31]. At one monolayer coverages, where repulsive interadsorbate forces are apparently greater than surface–adsorbate ones in these systems, the C–X axis was found to be perpendicular to the surface, and the adsorbate overlayer was incommensurate with the surface, thus, as mentioned above, precluding orbital interactions. These studies also showed that at very low coverages, when the surface–ad-

sorbate interaction was dominant, the molecules adsorbed with the C–X axis parallel to the surface, which is the most energetically favored orientation for a single dipolar molecule on an ionic surface. Thus, in these physisorbed systems the adsorbate orientation is determined by the relative strengths of surface–adsorbate and interadsorbate forces. For methyl halides on GaAs(110), the surface–adsorbate interaction is stronger, due in part to the stronger image charge attraction for the high dielectric constant semiconductor, which might be responsible for the tilted orientation at one monolayer coverages [32]. Furthermore, the molecules are less tilted in the second monolayer where the surface–adsorbate interaction is weaker.

In conclusion, these NEXAFS results show that the methyl halides are weakly molecularly adsorbed on the GaAs(110) surface at 80 K and that in the first monolayer they are oriented with the C–X axis tilted approximately -45° from the surface normal, i.e. in the $[0\bar{1}]$ direction. Furthermore, molecules in the second monolayer, and most clearly CH_3Br , suggest an orientation with the C–X axis tilted in the $[01]$ direction, which is opposite those in the first monolayer, with a smaller tilt angle. Such a tilted orientation for the methyl halides had previously been proposed from analysis of TPD spectra as an explanation for the decrease of the effective dipole moment from the gas-phase value [10]. More importantly, the establishment of a tilted orientation in both the first and second monolayer also correlates well with the angular dependence of TOF measurements of methyl fragments from photodissociation. These fragments are ejected at -45° from the surface normal, in the $[0\bar{1}]$ direction for the first monolayer and, for substrate electrons photoemitted into the second layer, fragments are detected in the opposite direction. These NEXAFS results thus confirm that the initial state and orientation of the adsorbate molecule play a fundamental role in determining the dynamics of photoreactions on semiconductor surfaces.

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