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# Photofragmentation of $CH_3Br$ on Br/Ni(111): Cross Section and Competitive Processes

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Photolysis of $CH_3Br$ on a brominated Ni(111) surface was observed. Cross-section values are reported for 0.5-, 1-, 2-, 3-, and 10-monolayer coverages. The observed cross sections and photofragment times of flight indicate that complete quenching of the photolysis does not take place, and that the photodynamics is strongly perturbed.

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Surface photochemistry has received a great deal of attention in recent years because of its applications in semiconductor fabrication and in catalysis.[1] The photochemistry of an adsorbed molecule should be perturbed by the presence of metal or semiconductor substrate, even to the point of complete inhibition.[2] Comparison of both photolysis cross sections of adsorbed molecules and the velocity distributions of resulting fragments with similar gas-phase data should yield insight into the perturbations induced by the surface. The photolysis cross section can be determined by measurement of the photofragments produced as a function of photon exposure. This, however, requires a detailed knowledge of the product angular distributions, the fate of any photoproducts which remain on the surface, and knowledge of other nonphotolysis fragmentation processes. Alternatively, a total cross section for the removal of molecules can be determined simply by our measuring the number of molecules that remain after irradiation, using thermal desorption spectroscopy (TDS). In this Letter we report studies of $CH_3Br$ on a Ni(111) surface in the presence of coadsorbed Br, the measured cross sections (via TDS), and time-of-flight (TOF) distributions of ejected $CH_3$, and discuss possible mechanisms for the observed perturbations.

These experiments were done under ultrahigh-vacuum conditions in a previously described chamber.[3] The Ni(111) crystal was cooled to 40 K with a closed-cycle refrigerator, and dosed with a molecular beam ($6 \times 8$-$mm^2$ spot size with negligible penumbra). The adsorbed molecules were photodissociated by 193-nm excimer laser radiation, 74° from the surface normal. The laser spot size was defined by imaging of an aperture onto the crystal. In cross-section studies, a $9 \times 9$-$mm^2$ spot was used, and in the TOF studies a $3 \times 3$-$mm^2$ spot size was used. The laser power was measured every shot and was spatially uniform to within 10%. To avoid significant surface heating, low laser fluences [2 to 4 $mJ/cm^2$] were used. The laser was pulsed at 5 Hz for between 100 and 2000 shots. The photofragments were detected with a time-resolved quadrupole mass spectrometer (ionizer-crystal distance, 6.9 cm; ion flight time for $CH_3$, 8.8 $\mu s$). The surface was monitored with Auger spectroscopy and TDS, and was cleaned when needed by argon sputtering and radiative heating.

TDS indicated that on clean nickel, $CH_3Br$ adsorbed dissociatively, or was thermally decomposed before desorption could take place. This was evident from the near lack of a desorption peak until the surface was passivated with Br from $CH_3Br$ decomposition. The bromine remained on the surface forming a highly stable layer,[4] with a desorption peak at 1100 K. The methyls recombined and were ejected as ethane during the period of deposition (even at 40 K). Similar ethane production has been seen for $CH_3Br$ on Mg(0001).[5] Thus all photolysis experiments were carried out on a brominated surface which no longer dissociated $CH_3Br$. The surface was passivated by dosing of a clean surface with 1 monolayer of $CH_3Br$ at 65 K and heating to 550 K (to desorb any $CH_3Br$); then the procedure was repeated twice more. The surface was cleaned (C, Br, and S coverages less than 1%) and rebrominated after each run with the laser. The saturation concentration of bromine, after this passivation procedure, was estimated to be 0.6 monolayer from Auger spectroscopy.[6] The residual carbon coverage after passivation was determined to be 0.15 monolayer by calibration of the carbon-to-Ni Auger signal with a CO-saturated surface. When the surface was brominated as noted above it was completely passivated and would not longer promote the decomposition of $CH_3Br$. However, the surface was not Br saturated: Br fragments produced in photolysis were able to bind to this surface in a new lower-energy binding site. This new surface state could be seen growing in, with increasing photon exposure, as a shoulder on the Br TDS peak with a desorption maximum at 875 K. The integrated Br TDS signal showed a maximum of 35% increase after photolysis (due to this new adsorption state); this increase was typically kept between 1% and 10% for cross-section and TOF measurements. Measurements taken at 0.5 monolayer showed no apparent variation in the $CH_3$ TOF distributions with increasing initial Br coverage.

The TDS peak areas accurately give the relative surface coverage (with use of the $CH_3Br$ desorption peak). The coverage was strictly proportional to exposure from 0.1 to 10 monolayers. To measure the cross section the surface was dosed with $CH_3Br$. The adsorbed molecules were then thermally desorbed to measure the initial coverage $I_0$. The surface was then redosed and irradiated, and the number of molecules remaining on the surface was again measured with TDS, and defined as $I$. The number of molecules removed was kept small (0 to 20%) so that the cross section could be measured at roughly constant $CH_3Br$ coverage. The photolysis cross section was determined from the slope of a plot of $\ln(I/I_0)$ versus the number of photons per square centimeter. The number of photons per square centimeter was corrected for the change in field at the surface (calculated with Maxwell's equations). For unpolarized light incident at 74° from the surface normal, the ratios of the intensity at the surface to that of the incident beam are 0.073 and 0.59 for $s$- and $p$-polarized light, respectively. The cross sections were also corrected for exposure to a small constant background $CH_3Br$ pressure during the period of laser firing. Figure 1 shows examples of the data taken at 0.5-, 1-, 2-, 3-, and 10-monolayer coverages. This yielded cross sections of $(3.5 \pm 0.3)$, $(8.4 \pm 0.6)$, $(7.2 \pm 0.5)$, $(11 \pm 1)$, and $(3.9 \pm 0.4) \times (10^{-20}\ \mathrm{cm}^2)$, respectively.

These cross sections are 4 to 12 times smaller than for gas-phase photolysis ($4.2 \times 10^{-19} \mathrm{cm}^2$).[7] At *high* coverages the photolysis should resemble that seen in matrices; thus caging effects would be expected to reduce the cross section as already seen for 10-monolayer coverages. Figure 2 shows the number of molecules removed at constant fluence versus coverage. This shows a plateau after 3 monolayers, suggesting that caging is already very effective by that coverage.

Our TOF distributions described below show ejection of $CH_3Br$, comparable in yield to the $CH_3$ and Br fragments, for coverages above 1 monolayer. The fast photofragments of $CH_3$ and Br both have enough energy to eject neighboring molecules, and will increase the effective cross section for multilayers.[3]

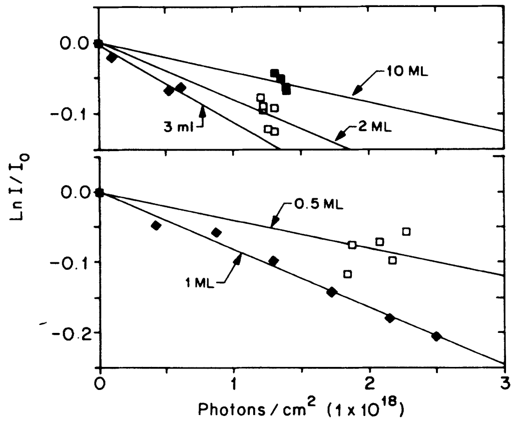

FIG. 1. Photolysis cross-section determination, for coverages of 0.5, 1, 2, 3, and 10 monolayers of $CH_3Br$ on Ni(111). The cross sections are given by the negative slope of the best-fit line.

Two important observations can be made about the photolysis taking place at coverages of 1 monolayer or less: first, that photolysis *does* take place on this surface; both $CH_3$ and Br photofragments are observed. This indicates that quenching is not complete. Second, the low cross sections indicate that the process is *highly* perturbed. This implies that a full understanding of the surface photochemistry will only come from an understanding of these perturbations. These conclusions are reinforced by very recent work on $CH_3Br$ photolysis on Pt(111).[8]

Insight into these perturbations is gained from the TOF distributions for ejected $CH_3$ radicals, shown in Fig. 3. At 1 monolayer and below, the distributions have a high-velocity *limit* which is the same as seen for gas-phase photolysis,[7] and extend to much lower velocities. This strongly suggests that the process began with gas-phase-like photofragmentation, and in the 20 fs or so needed to fragment,[9] energy was removed. At the highest multilayer coverage, a very narrow peak appears precisely at the gas-phase case velocity. This is likely due to those molecules on the topmost layer, with their $CH_3$ ends oriented outward. This orientation would lead to collision-free ejection, and the adsorbate-substrate spacing would eliminate perturbations. The very broad component should be due to collisionally slowed fragments from underlying layers. The broad peak near 100 μs is from the mass spectrometer "cracking pattern" of ejected molecular $CH_3Br$.

It is important to identify the precise mechanism responsible for the dramatic effects on the cross sections and the velocity distributions seen at 1 monolayer coverage or less. Several possibilities are discussed below. Though our results do not completely identify which is dominant, they place some reasonable limits on some and

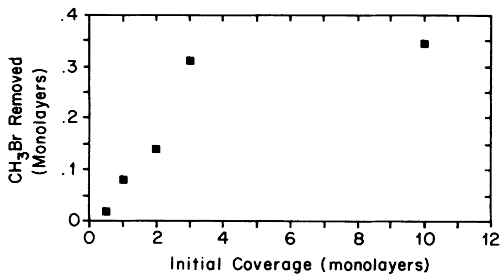

FIG. 2. $CH_3Br$ removed during photolysis vs initial coverage (monolayers). The amount of $CH_3Br$ laser desorbed is in monolayers, calculated for a fluence of $5 \times 10^{18}$ photons/cm$^2$ with the experimentally determined cross sections for each coverage.

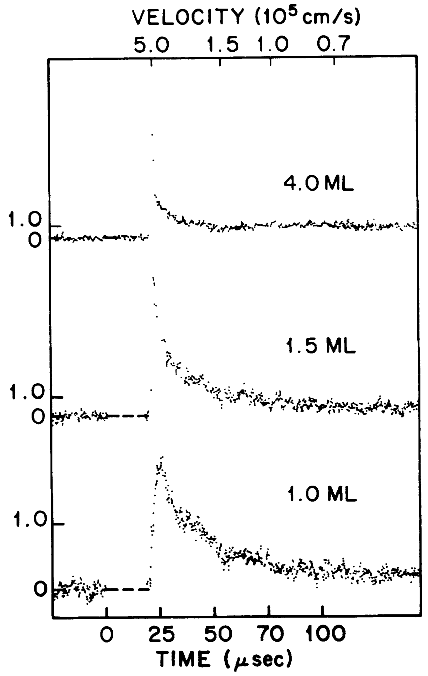

FIG. 3. Time-of-flight distributions for $CH_3Br$ photolysis, measuring signal from $CH_3$ fragments with a Transiac transient digitizer and signal averaging for 100 sweeps with 0.1-s channel time.

eliminate others.

One possibility is that the process is not photolysis at all, but dissociative electron attachment. Since the photon energy is greater than the Ni work function, many electrons are produced[9]; and $CH_3Br$ dissociates upon electron attachment in the gas phase.[10] Though the electron quantum yields and attachment cross sections are not known exactly, our preliminary estimates[9] suggest they may be important at the lowest coverage. However, the $CH_3$ fragment velocities extend too high to be compatible with electron attachment. To the extent that electron attachment *is* important, this would reduce our estimate for the photofragmentation cross section, and imply even higher perturbations.

Image-dipole quenching[11] could both prevent photolysis and remove energy from the photofragments. The quenching rate for a molecule adsorbed on a surface a distance $Z$ away[12] ($1\,\text{Å} < Z < 500\,\text{Å}$) is

$$R_q = A_s^*(\lambda/2\pi Z)^3 nk/[1+\epsilon]^2, \tag{1}$$

where $A_s$ is the spontaneous emission rate, $n+ik$ is the complex refactive index, and $\epsilon$ is the complex dielectric coefficient for Ni ($n=1.01$, $k=1.46$).[13] $A_s$ determined from the absorption spectrum[7] via the Einstein relations is $(270\text{ ns})^{-1}$. At $z=3$ and 1 Å this gives $R_q$ of 1400 and 50 fs, respectively. Even at the unreasonably short distance of 1 Å, image dipole quenching is *not* fast enough to dominate a 20-fs photofragmentation. This should be true for most other cases of directly repulsive surface photolysis, except where $A_s$ is very large [as for $Cd(CH_3)_2$].

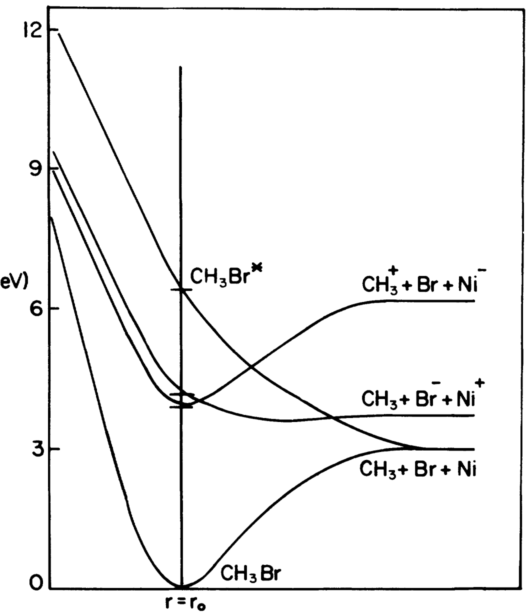

FIG. 4. $CH_3$-Br potentials, for ground, excited, and charge-transfer states, vs bond distance.

Charge-transfer processes very likely dominate the surface photochemistry. The excited $CH_3Br$ electron occupies an orbital which is degenerate with empty substrate orbitals, thus enhancing the electron tunneling probability between molecule and substrate. Also, the hole left by the promoted electron has a high electron affinity, and is resonant with filled substrate orbitals. Electron-transfer rates at similar energies have been examined via experiment and theory,[14] and the trend is for them to occur in 1 to 5 fs or less whenever energetically allowed. This is fast enough to compete with photofragmentation. The *outcome* of such a charge transfer is discussed below.

The rough potential-energy diagram for the photolysis process is shown in Fig. 4.[7] Also shown are two charge-transfer curves. The latter are estimated by the energy required to transfer an electron between a substrate orbital and the molecule (or, after dissociation, the fragments). To form positive or negative molecules, respectively, this should be approximately

$$\begin{aligned} E_{\text{pos}} &= P_{\text{mol}} - A_{\text{sub}} - (14.4\text{ eV Å})/4Z, \\ E_{\text{neg}} &= P_{\text{sub}} - A_{\text{mol}} - (14.4\text{ eV Å}/4Z, \end{aligned} \tag{2}$$

where $P_{\text{mol}}$ and $A_{\text{mol}}$ are the gas-phase molecular (or fragment) ionization potential and electron affinity, $P_{\text{sub}}$ and $A_{\text{sub}}$ are similar quantities for the substrate, and the $1/Z$ term is the image potential stabilization. The curves shown in Fig. 4 are those only for the maximum $A_{\text{sub}}$

and minimum $P_{\mathrm{sub}}$ possible (given by the substrate work function). These curves represent the lower edge of charge-transfer *continua.* (These curves are at least qualitatively correct, and will be fully discussed in Ref. 9.) *Resonant* charge transfer can occur for the 10 to 15 fs that the trajectory along the excited state lies imbedded in one or both of these charge-transfer continua.

Since the charge transfer could take up to 5 fs, the molecular fragments would still have gained considerable momentum. This could result in dissociation—however, with kinetic energies well below the unperturbed fragmentation. The "lost" energy would be found in the higher potential energy of the asymptotic state and in excited substrate electrons or holes. A double charge transfer would likely lead back to a ground-state molecule [but with high (1–2 eV) vibrational excitation]. As charge-transfer processes are expected to be fast enough and energetically accessible, and to lead to slow fragments or nonfragmentation, we suggest them as leading candidates for domination in this photochemistry.

In conclusion, we have measured cross sections and fragment times of flight for the photolysis of $CH_3Br$ adsorbed on a brominated Ni(111) surface. These measurements indicate that photofragmentation does take place, but that the photodynamics is strongly perturbed. The only process that could compete with photofragmentation on these time scales would be resonant charge-transfer and collisional processes. Collisional processes dominate much of the photodynamics at high coverage. This could also be important at low coverages, depending on the orientation of the adsorbate. By determining the adsorbate orientation, and by closing some of the charge-transfer channels available, we hope to determine the relative importance of these processes in future studies.

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