Electronically Excited Photodissociation and Desorption of Adsorbates: CH_2I_2 on Al_2O_3 and Ag Surfaces

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CH_2I_2 molecules adsorbed on Al_2O_3 and Ag surfaces are excited by a uv laser and the desorption behavior associated with photofragmentation is studied by time-of-flight mass spectrometry and x-ray photoemission and thermal desorption spectroscopies. The desorption yields as well as the mass and kinetic energy distributions are determined as functions of surface coverage and laser fluence. The results clearly reveal the characteristic electronic, thermal, and "explosive" desorption effects.

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Ultraviolet laser have been often used to induce gas-surface interactions, in particular, for applications to photochemical etching of solids and vapor deposition on surfaces.[1] There exist, however, few mechanistic studies on well characterized surfaces, and the basic photochemical processes involving the electronic excitation of adsorbates remain largely unknown. In a study of CH_3Br adsorbed on a LiF crystal excited by an excimer laser,[2] photofragmentation and desorption of CH_3 radicals were observed along with desorption of a large amount of CH_3Br parent molecules. The latter process was attributed to the uv absorption by the crystal and the generation of shock waves. In other studies, the photolysis of $Cd(CH_3)_2$ to deposit Cd atoms on metal particles,[3] the photodecomposition of aromatic molecules on roughened Ag surfaces,[4] and the photodesorption of neutrals and ions from molecular solids or deposited films[5,6] were reported. We have chosen CH_2I_2 molecules adsorbed on Al_2O_3 (sapphire crystal) and Ag (film) surfaces as a model system to investigate the uv-excited surface processes. The molecule is readily pumped by a XeCl excimer laser into its first excited and antibonding state which dissociates into CH_2I radicals and I atoms with a unit quantum yield in gas phase.[7,8] We have observed some very interesting phenomena not reported in any previous studies, namely, the characteristic electronic excitation effect, the clear molecular selectivity in photodesorption associated with fragmentation, and the "explosive" desorption behavior at high surface coverages.

The experiments are carried out in a UHV chamber equipped with x-ray photoemission (XPS), Auger, and thermal desorption (TDS) spectroscopies as well as time-of-flight (TOF) mass spectrometry similar to that used in our prior study.[9] An XeCl laser at 308 nm (20-nsec pulse width) is gently focused onto the substrate at 75° from the surface normal with an irradiation area of

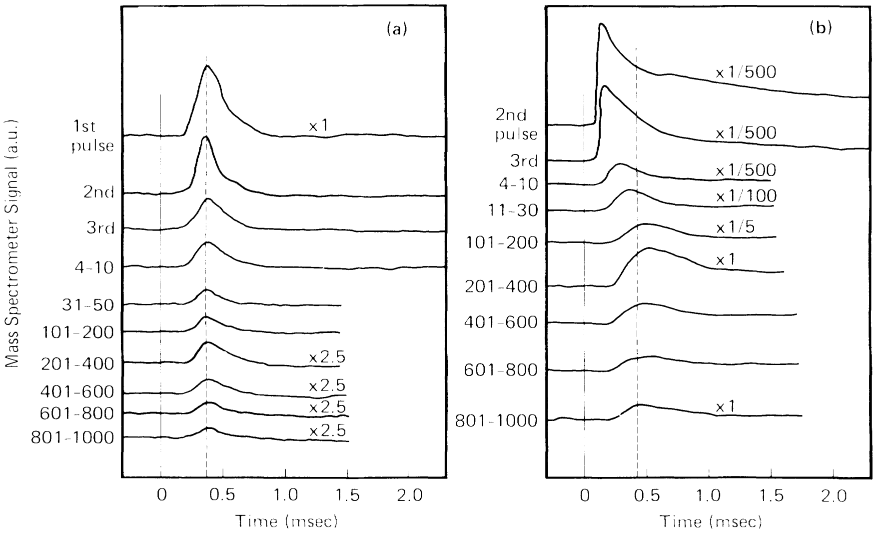

FIG. 1. TOF signals of CH_2I radicals from the first pulse to the thousandth pulse for CH_2I_2 adsorbed on Al_2O_3 (90 K) at the surface coverages of (a) $\Theta=1$ and (b) $\Theta=25$ monolayers, both excited by 308-nm laser pulses at $F=250$ mJ/cm^2.

about 7 mm^2. The desorbed species are detected by the mass spectrometer along the surface normal with a TOF distance of 11.7 cm. The transient TOF signals are recorded with a high-speed signal averager. The sample surface is cleaned by Ar^+-ion bombardment and cooled to 90 K before the exposure to CH_2I_2 gas. The surface coverages and the adsorption characteristics are determined by XPS and TDS. The photodissociation and desorption behavior are studied as functions of laser fluence (F) and surface coverage (Θ).

The typical TOF signals of CH_2I radicals produced from the uv excitation of CH_2I_2 adsorbed on Al_2O_3 which is optically transparent at 308 nm are shown in Fig. 1. The important observations at a monolayer surface coverage or less (i.e., $\Theta \leq 1$) are the following: (1) The dominant desorbed neutral species as determined by the mass spectrometer are CH_2I and I, with a small amount of CH_2 which is most likely from the cracking of CH_2I by the ionizer of the spectrometer. No molecular CH_2I_2 (parent), I_2, or any ionic species are detected in a large range of laser fluences. This is in great contrast to the CH_3Br/LiF system studied by Bourdon *et al.*,[2] in which the vast majority (99%) of the desorbed species was CH_3Br. The mass distribution under laser irradiation is very different from that produced in the thermal desorption (TDS) of CH_2I_2 from Al_2O_3. In TDS, CH_2I_2, CH_2I, and I are the main species when CH_2I_2 is thermally desorbed at 230 K and cracked by the ionizer. (2) At a given F, the desorption yield of CH_2I increases almost linearly with the coverage up to about $\Theta = 0.8$ [Fig. 2(a)]. At a given Θ, the yield increases linearly with F from 0 to 500 mJ/cm^2. There is no apparent laser threshold for the photodissociation and desorption process. (3) The peak positions and the shapes of TOF signals remain the same from the first pulse to the thousandth pulse [Fig. 1(a)], even though the signal intensity decreases gradually with the number of pulses fired at 1-Hz pulse rate. This means that the kinetic energy (KE) distribution of desorbed CH_2I is independent of Θ. Furthermore, this energy distribution is found to be independent of F up to at least 500 mJ/cm^2. The kinetic energy corresponding to the peak of the TOF signal is $E_m = 0.095 \pm 0.009$ eV [Fig. 2(a)]. (4) XPS measurements of the surface coverages before and after laser irradiation show that the quantum yield for photodissociation based on the measured absorption coefficient is about 0.01–0.1, a value much less than the yield in the gas phase. This indicates the rapid electronic relaxation of excited $CH_2I_2^*$ even on an insulator surface. Since C(1s) XPS spectra do not show any chemical shift or broadening after laser excitation, no significant polymer or carbon deposit is present to influence the relaxation rate.

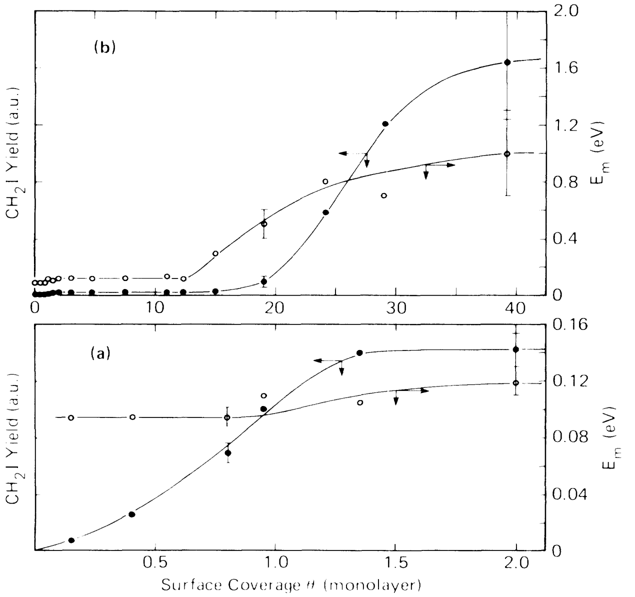

FIG. 2. CH_2I desorption yields (solid circles) as a function of surface coverage for CH_2I_2/Al_2O_3 (90 K) excited at 350 mJ/cm^2: (a) $\Theta = 0$ to 2 monolayers and (b) $\Theta = 0$ to 40 monolayers. The corresponding kinetic energies (E_m, open circles) are also displayed.

The results show that at $\Theta \leq 1$, a vast majority of excited $CH_2I_2^*$ molecules on Al_2O_3 decay back to the ground state even though they are photoactivated into antibonding states. Since the photodissociation rate is higher than 10^{13}/sec,[7] the electronic relaxation rate must be higher than 10^{14}/sec. The fraction of excited molecules which undergo dissociation and desorption exhibits the characteristic electronic effect, namely, the linear yield dependence on F and the invariance of the KE distribution with respect to F over a large fluence range. Since no desorption of CH_2I_2 is detected, we expect the photoexcitation process to be molecularly selective. To test the hypothesis, we coadsorb NH_3 with CH_2I_2 as a 1:1 mixture on Al_2O_3 at 90 K with $\Theta = 1$. NH_3 molecules do not absorb 308-nm light. Again, only CH_2I and I species are detected when the mixture is excited by laser pulses. Desorption of NH_3 is not observed even though in the conventional TDS, NH_3 desorbs at a much lower temperature (150 K) than CH_2I_2. It should be pointed out that in the CH_3Br and Xe/LiF systems studied earlier,[2] Xe desorption was observed even though the atom was not electronically excited. Our results suggest negligible thermal or other contributions (such as shock waves) to the observed CH_2I and I desorption.

When the coverage on Al_2O_3 is raised above a monolayer ($\Theta > 1$), the CH_2I yield increases but reaches a constant value for $2 \leq \Theta \leq 12$ at a given F. E_m is almost constant in this coverage region. When Θ exceeds fifteen monolayers, the yield rises drastically and the KE of CH_2I radicals as expressed by E_m is also very high. The typical TOF signals at $\Theta = 25$ are shown in Fig. 1(b). The yield and E_m dependences on Θ at a given F

are shown in Fig. 2. The yield per pulse in the high-coverage region can be 2 to 3 orders of magnitude higher than that at $\Theta = 1$, and E_m can be greater by more than a factor of 10 (i.e., $\gtrsim 1$ eV). The quantum yields for the top few monolayers can exceed unity. The desorption behavior at $\Theta > 15$ can be described as "explosive," and when this occurs, a large amount of CH_2I_2 desorption is also detected. In this regime, CH_2I and CH_2I_2 yields as well as their E_m values increase nonlinearly with F. For a multilayer CH_2I_2 and NH_3 mixture ($\Theta \gg 1$) on Al_2O_3, NH_3 desorption is also observed at moderate fluences even though only CH_2I_2 is excited. The molecular selectivity in desorption diminishes under this condition. Discussion of this explosive desorption behavior is given below.

For CH_2I_2 adsorbed on an Ag film at 90 K with $\Theta \leq 1$, no desorption of any species is detected for F up to about 50 mJ/cm^2. Above 80 mJ/cm^2, both CH_2I and CH_2I_2 desorption are observed with their yields and KE's increasing nonlinearly with F. This is mainly due to the laser-induced thermal desorption because unlike Al_2O_3, the Ag substrate absorbs a large portion of uv light. The lack of any desorption signal at $\Theta \leq 1$ and $F \leq 50$ mJ/cm^2 is most likely due to the rapid electronic relaxation and/or the spectral shift and the reduced oscillator strength at 308 nm because of the strong electronic interaction between CH_2I_2 and Ag. When Θ is higher than a monolayer, desorption of CH_2I is observed at $F \leq 50$ mJ/cm^2. Clearly, CH_2I_2 on the top layer not in direct contact with the metal can be effectively excited by the laser. Under the irradiation condition at $2 \leq \Theta \leq 10$, no significant CH_2I_2 desorption is detected and the CH_2I yield increases linearly with F. Furthermore, the KE ($E_m \simeq 0.095$ eV) of CH_2I is independent of F, again showing the characteristic electronic effect. For $F \geq 80$ mJ/cm^2, the laser-induced substrate-heating effect becomes important.

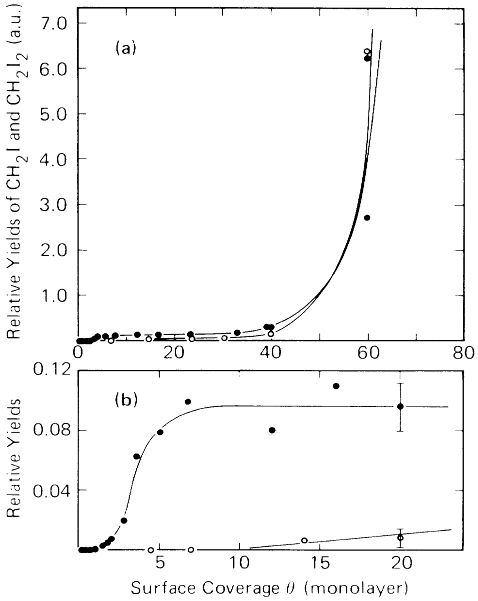

FIG. 3. Relative desorption yields of CH_2I (solid circles) and CH_2I_2 (open circles) as a function of surface coverage for CH_2I_2/Ag (90 K) excited at 38 mJ/cm^2: (a) $\Theta = 0$ to 20 monolayers (expanded scales) and (b) $\Theta = 0$ to 60 monolayers.

When Θ on Ag is greater than 15, some CH_2I_2 desorption is observed even at $F < 50$ mJ/cm^2. In fact, as shown in Fig. 3, explosive desorption characterized by the desorption of both CH_2I and CH_2I_2 species, the very large yields, the high KE's, and the very nonlinear dependences of the yields and KE's on F occurs. The most striking observation of the phenomenon is that there exists a laser threshold fluence for explosion and the threshold value depends on the coverage. For instance, as in Fig. 4, the CH_2I yield at $\Theta = 8$ is a linear function of F up to 120 mJ/cm^2 and above that, explosive desorption takes place, whereas at $\Theta \gtrsim 100$, the explosion happens near 1.4 mJ/cm^2! The nonlinear dependence of CH_2I yield on F in the explosive regime cannot be due to the multiphoton excitation effect because the threshold fluences for explosion at high coverages are simply too low for nonlinear absorption process to be important. The fluence between 1.4 and 120 mJ/cm^2 is in the linear (yield *versus F*) range for $\Theta = 8$, but is clearly in the nonlinear region for $\Theta \geq 100$. If explosion were caused by multiphoton absorption $\Theta \geq 100$, it should also occur at $\Theta = 8$. This is obviously not the case.

The explosive desorption at high coverages on both Al_2O_3 and Ag surfaces is somewhat similar to the "photoablation" of organic polymers excited by uv lasers. Very high ablation yields per pulse and high KE's of ejected particles were observed in polymer systems.[10] From the present results, it appears that in the thick layer many excited molecules beneath the surface may not dissociate because of the repulsive interaction and collisions with neighboring molecules as the CH_2I-I bond distance expands in the excited state. In the deexcitation process, the electronic energy may be converted into translational energy for the molecules involved. This can generate particles with high kinetic energies. If the excited molecules dissociate, they can also quickly recom-

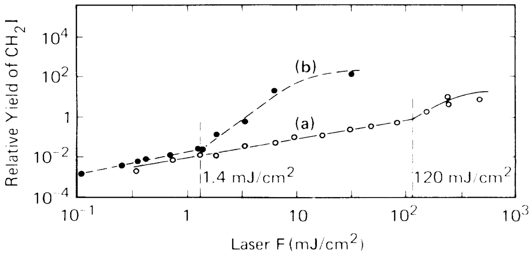

FIG. 4. CH_2I desorption yields as a function of laser fluence for CH_2I_2/Ag (90 K) at the surface coverages of (curve *a*) $\Theta = 8$ and (curve *b*) $\Theta > 100$ monolayers.

bine because of the "cage" effect of surrounding molecules,[11] and release the absorbed 4.0-eV photon energy. This energy may again be directly transformed into kinetic energy or it may relax to create local heating leading to drastic thermal expansion and explosion. There seems little doubt about the importance of the thermal effect in the explosion process. In particular, it can cause molecules to desorb with medium and low KE's [see the long tails in some of the TOF signals shown in Fig. 1(b)]. The combined effects of electronic and thermal activation can thus cause the quantum yields to exceed unity. The data in the intermediate-coverage region, where CH_2I yields are nearly constant with respect to Θ (Figs. 2 and 3) and are essentially a linear function of F over a large range [Fig. 4, curve *a*], indicate that the electronic effect dominates in this regime, even though some thermal effect may be present. By comparison of the behavior between the thin and the thick layers, it is also clear that a critical amount of energy absorbed per unit time (i.e., density and rate of excitation times volume) is needed for the explosive desorption to happen. Since the optical penetration depth is about 150 Å,[12] the volume of optical excitation and the total energy absorbed in a thick layer are much larger than in a thin layer. Thus, explosion can occur more readily in a thick layer. From a thermal point of view, the good thermal conductivities of Al_2O_3 and Ag substrates can also reduce the thermal effect in a thin layer. Clearly, the overall desorption behavior is determined not only by the optical-absorption coefficients but also by the thermal properties of the adsorbate-solid system.

In short, the present study shows the electronic excitation effect and the clear molecular selectivity in photodissociation and desorption at a monolayer coverage or below. Electronic relaxation of the excited adsorbate is apparently very rapid on both Al_2O_3 and Ag surfaces resulting in low quantum yields for dissociation. The study also elucidates the thermal contribution and the "explosive" desorption behavior in high-coverage regime.

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