

Thermal and Photoinduced Dissociation of CH₂I₂ on Cu(100) Surface

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The adsorption and dissociation of CH₂I₂ were studied at 90–250 K with the aim of generating CH₂ on the Cu(100) surface. The methods used included XPS, UPS, TPD, AES, and work function measurements. Adsorption of CH₂I₂ is characterized by a work function decrease (0.1 eV at the monolayer), indicating that adsorbed CH₂I₂ has a positive outward dipole moment. Two adsorption states were distinguished: a multilayer and an irreversibly adsorbed state. The adsorption of CH₂I₂ at 90 K is dissociative at the submonolayer but is molecular at higher coverages. Dissociation of the monolayer proceeded at 192–204 K, as indicated by a shift in the I(3d_{5/2}) binding energy from 620.5 to 619.7 eV. Illumination of the adsorbed CH₂I₂ at 90–95 K markedly enhanced the dissociation. The primary products are adsorbed CH₂ and I. CH₂ is characterized by a C(1s) binding energy of 283.9 eV and by a photoemission signal at 5.4–5.6 eV. CH₂ species reacted to form C₂H₄ at 160–230 K, which desorbed in a pseudo-first-order process with $T_p = 240$ K. The high peak temperature suggests the formation of a more strongly adsorbed, very likely di- σ -bonded ethylene. The self-hydrogenation of CH₂, observed on platinum metals, did not occur on Cu(100).

1. Introduction

The study of the chemistry of adsorbed CH_x species has a strong relevance to the better understanding of the role of reaction intermediates in the catalytic reactions involving hydrocarbons. The difficulty with CH_x fragments is that they are formed only in relatively small concentration, and as a result of the high temperature of catalytic reaction, their lifetimes are very short. To avoid this problem, attempts were made to generate CH_x species by decomposing the corresponding halide compounds, the dissociation of which produces CH_x fragments in a larger quantity.^{1–4} From the comparative studies on the reactivity of halogenated compounds it was found that iodide compounds are the most suitable substances for this purpose, since they dissociate at the lowest temperature.^{1–8} However, even the thermal dissociation of alkyl and alkene iodides on many solid surfaces requires elevated temperatures, where the decomposition of CH_x fragments may occur rapidly. The photolysis of the adsorbed layers provided a solution: the photodissociation of iodo compounds proceeded even at 90–100 K and yielded intact CH_x fragments.^{9–14} Another route to generate CH₃ radicals is the thermal decomposition of dimethyl azide.¹⁵ All these methods are now widely used, and the results obtained are documented in several recent reviews.^{5–8}

As regards the adsorption and dissociation of CH₂I₂ on metal single-crystal surfaces, the first detailed spectroscopic measurements were performed on the Pd(100) surface.¹⁶ The adsorption was dissociative at submonolayer coverage even at ~100 K and molecular at higher coverages. The primary products of the dissociation were adsorbed CH₂ and I. The CH₂ species is relatively unstable on Pd(100); it reacts at 160–230 K to give CH₄ on one hand and C₂H₄ on the other hand. Illumination of adsorbed CH₂I₂ enhanced the extent of dissociation even at 90–95 K and produced adsorbed ethylene in a larger concentration. Further study of the reaction of CH₂ on Pd(100) showed that CH₂ reacts readily with adsorbed O atoms above 150 K to give formaldehyde, which desorbed immediately after its formation.¹⁷

Similar features have been established on Rh(111).^{18,19} The products of the reaction of CH₂ were also H₂, CH₄, and C₂H₄. In this case the C₂H₄/CH₄ ratio was less than that for Pd(100). Characteristic vibration losses of adsorbed CH₂ were at 2940, 1190, 780, and 650 cm⁻¹. The formation of CH₂O species in the reaction of CH₂ with adsorbed O atoms was also observed.^{18–21} It was concluded that the CH₂ species, and not the undissociated CH₂I₂, is oxidized to CH₂O, since no CH₂O formation was observed by using CH₂Cl₂; this compound desorbs from Rh(111) without dissociation.¹⁸ The production of CH₂O in this case occurred only after the illumination of the coadsorbed layer, which induced the dissociation of CH₂Cl₂.¹⁸

The dissociation of CH₂I₂ (0.25 monolayers (ML)) on Mo-(110) proceeded at 200 K.²² Only a small amount of CH₂ hydrogenated to CH₄; the dominant reaction pathway was the decomposition to carbon and hydrogen at 450 K. No coupling of CH₂ into C₂H₄ was reported. As regards the interaction of CH₂I₂ with Cu surfaces, only few HREELS and TPD measurements have been carried out.^{23,24} The recombination of CH₂ species produced represented the major route of CH₂ reactions. The formation of CH₄ and the total decomposition to C were negligible.

The primary aim of the present paper is to obtain a more detailed picture of the adsorption and thermal dissociation of CH₂I₂ on clean Cu(100). The effects of the photolysis of adsorbed CH₂I₂ are also examined.

2. Experimental Section

Methods. The experiments were performed in standard ultrahigh vacuum systems with a background pressure of 5×10^{-10} mbar produced by turbomolecular, ion-getter, and titanium sublimation pumps. The chamber was equipped with an electrostatic hemispherical analyzer (Leybold-Heraeus LHS-10), a differentially pumped UV photon (He I, II) source for UPS, an X-ray source with an Al anode for XPS and an electron gun for AES measurements. The directions of the UV source and electron analyzer with respect to the surface normal were 70° and 16°, respectively. All binding energies are referred to the Fermi level with the Cu(2p_{3/2}) peak at 932.4 eV. Collection

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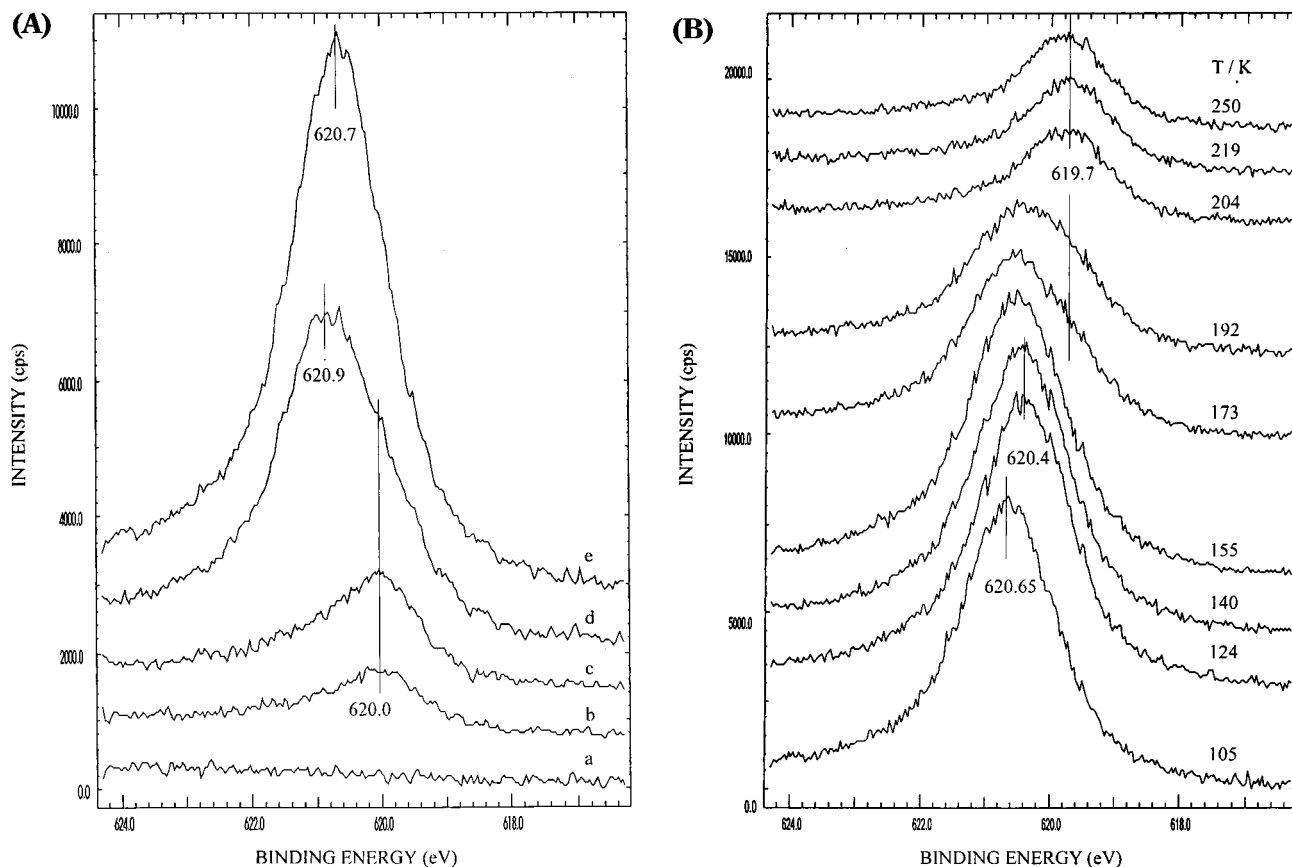


Figure 1. XPS spectra of Cu(100) as a function of CH₂I₂ absorption: (A) at 90 K; (B) after heating the adsorbed layer to different temperatures. Exposures for (A) are (a) 0.05, (b) 0.1, (c) 0.2, (d) 1.75, and (e) 3.75 L. Exposure for (B) is 1.5 L.

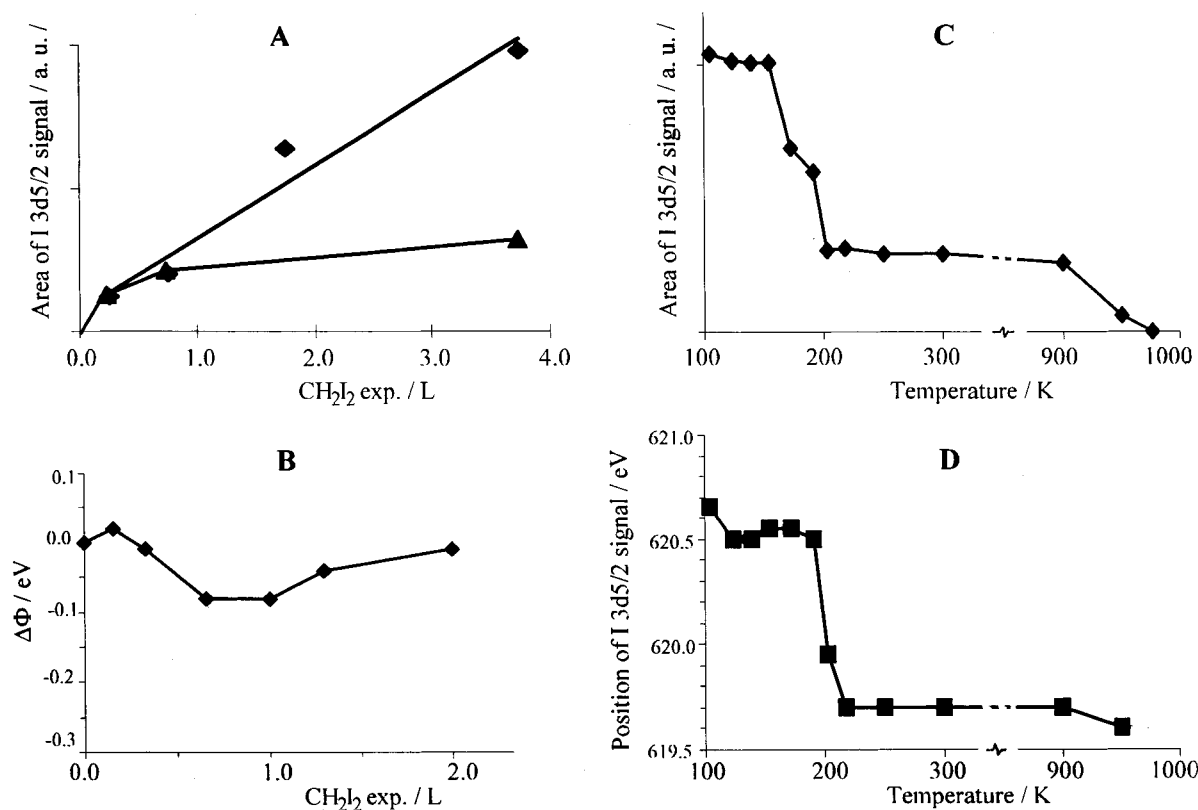


Figure 2. (A) Area of the iodine XPS signal at 100 K (◆) and after heating the adsorbed layer to about 350 K (▲) as a function of CH₂I₂. (B) Changes in the work function ($\Delta\phi$) of Cu(100) as a function of CH₂I₂ exposure at 90 K. Changes of (C) the peak area of the I(3d_{5/2}) peak and (D) the position of this peak as a function of annealing the adsorbed layer (0.75 L) to a higher temperature.

times for UPS and XPS were 15 and 30 min, respectively. XPS spectra were smoothed by the fast Fourier transform method. For TPD, the sample was heated at 8 K/s from 100 K to a

selected temperature. The mass spectrometer was in line of sight. Changes in work function were obtained by measuring the secondary electron cutoff in the He I UV photoelectron

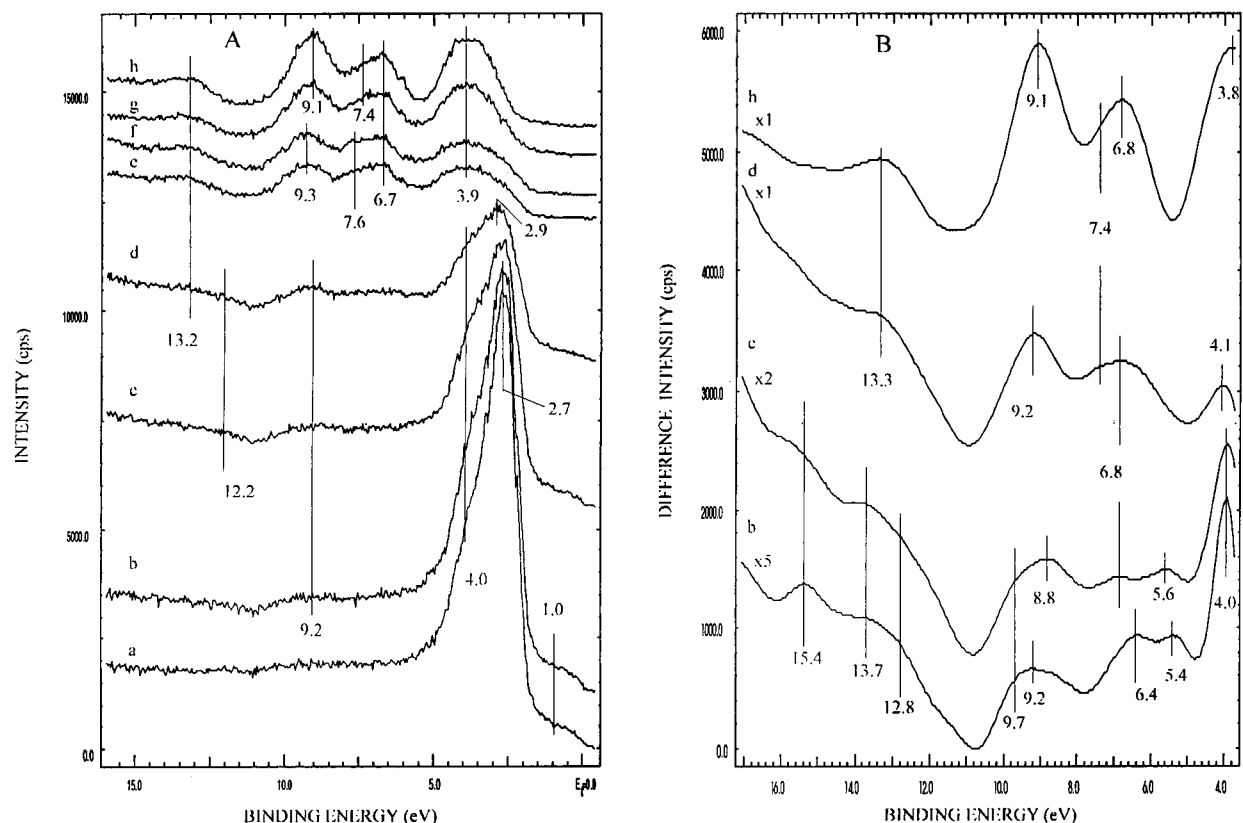


Figure 3. He II UPS of Cu(100) as a function of CH₂I₂ exposure at 90 K: (A) direct spectra with (a) clean Cu and exposures (b) 0.1, (c) 0.3, (d) 0.6, (e) 1.2, (f) 2.0, (g) 3.0, and (h) 6.0 L; (B) difference spectra with exposures (b) 0.15, (c) 0.4, (d) 0.6, and (h) 6.0 L.

TABLE 1: Photoemission Signals of Adsorbed CH₂Cl₂, CH₂I₂, and CH₂ on Different Metals

surface	adsorbed species	conditions	products	C(1s) XPS (eV)	He II UPS (eV)	ref
Co (poly)	CH ₂ Cl ₂	100 K				1
Co (poly)	CH ₂	190 K		284.9	5.5	1
Ni (poly)	CH ₂ Cl ₂	100 K				1
Ni (poly)	CH ₂	190 K		285.0–285.2	5.5–5.8	1
Pd(110)	CH ₂	130 K	CH ₄ , C ₂ H ₄ , H ₂ , C	283.6		26
Pd(100)	CH ₂ I ₂	multilayer, 100 K		285.5	3.8, 6.3, 8.8, 13.0	16
Pd(100)	CH ₂ I ₂	monolayer, 100 K		285.3	4.0, 6.7, 9.2, 13.0	16
Pd(100)	CH ₂	~200 K or <i>hν</i>	CH ₄ , C ₂ H ₄ , C	283.9	5.8–6.2	16
Cu(100)	CH ₂ I ₂	TDS	C ₂ H ₄			23
Cu(100)	CH ₂ I ₂	multilayer, 100 K		285.3	3.8, 6.8, 7.4, 9.1, 13.3	present work
Cu(100)	CH ₂ I ₂	monolayer, 100 K		285.6	3.9, 6.7, 7.4, 9.1, 13.2	present work
Cu(100)	CH ₂	~200 K or <i>hν</i>	C ₂ H ₄ , (C ₂ H ₅)?	283.8	5.4–5.6	present work

spectra with the sample at -9 V relative to earth. The UV light source was a focused 30 W Hg lamp. The light passed through a high-purity sapphire window into the vacuum chamber. The incident angle was 30° off the surface normal.

Materials. The oriented 4N9 purity, disk-shaped crystal (diameter 7 mm, thickness 1.5 mm) was mechanically polished with diamond paste. The crystal was mounted to a copper sample holder, and the sample was heated from the rear by the radiation of a tungsten filament. The temperature was measured with a chromel alumel thermocouple junction fastened to the side of the crystal. The sample-cleaning procedure consisted of cycles of argon ion bombardment (1.0 kV, $3 \mu\text{A}/\text{cm}^2$) and annealing at 970 K for some minutes, which was sufficient to remove the surface carbon and other contaminations. The oxygen, sulfur, phosphorus, and carbon impurities on the cleaned surface were estimated to comprise less than 0.1% of a monolayer. CH₂I₂ were obtained from Fluka; it was degassed by freeze–pump–thaw cycles prior to use. The O₂ was obtained from Messer-Griesheim.

3. Results

3.1. Adsorption of CH₂I₂. Figure 1 shows the XPS spectrum of Cu(100) in the iodine region as a function of CH₂I₂

exposure at 90 K. At low exposures, up to 0.5 layer (L), the binding energy of I(3d_{5/2}) was registered at 620.0 eV, which shifted to higher values, up to 620.9 eV, at high CH₂I₂ exposures. In the C(1s) region, we obtained a peak at 285.6 eV, which moved to 285.3 eV at higher CH₂I₂ dose. The fwhm value (1.8 eV) suggests that all carbon atoms are uniform.

Figure 2A shows the area of the XPS signal for I(3d_{5/2}), which increased continuously as a function of CH₂I₂ exposure at 100 K; saturation was not attained. When the adsorbed layer was heated first to 350 K, above the desorption temperature of CH₂I₂, much lower values were obtained, which saturated at an exposure of 0.8 L (Figure 2A).

The interaction of CH₂I₂ with the Cu surface was also followed by work function measurements. The adsorption of CH₂I₂ caused a gradual decrease in the work function of Cu(100), as illustrated in Figure 2B. The maximum decrease, $\Delta\phi = 0.1$ eV, was attained at an exposure of only 0.8 L. Taking into account the results obtained for other metals,^{16,19} we assume that the monolayer of adsorbed CH₂I₂ is completed at around this exposure.

He II photoelectron spectra of Cu(100) under the same experimental conditions are displayed in Figure 3. At a very

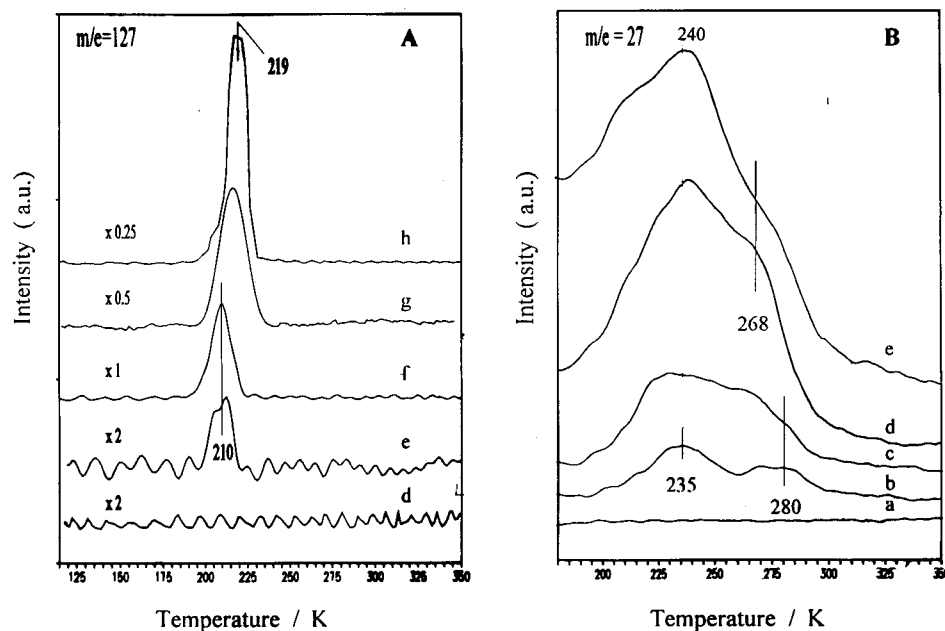


Figure 4. Thermal desorption spectra of (A) CH_2I_2 and (B) C_2H_4 following the adsorption of CH_2I_2 on $\text{Cu}(100)$ at 90 K.

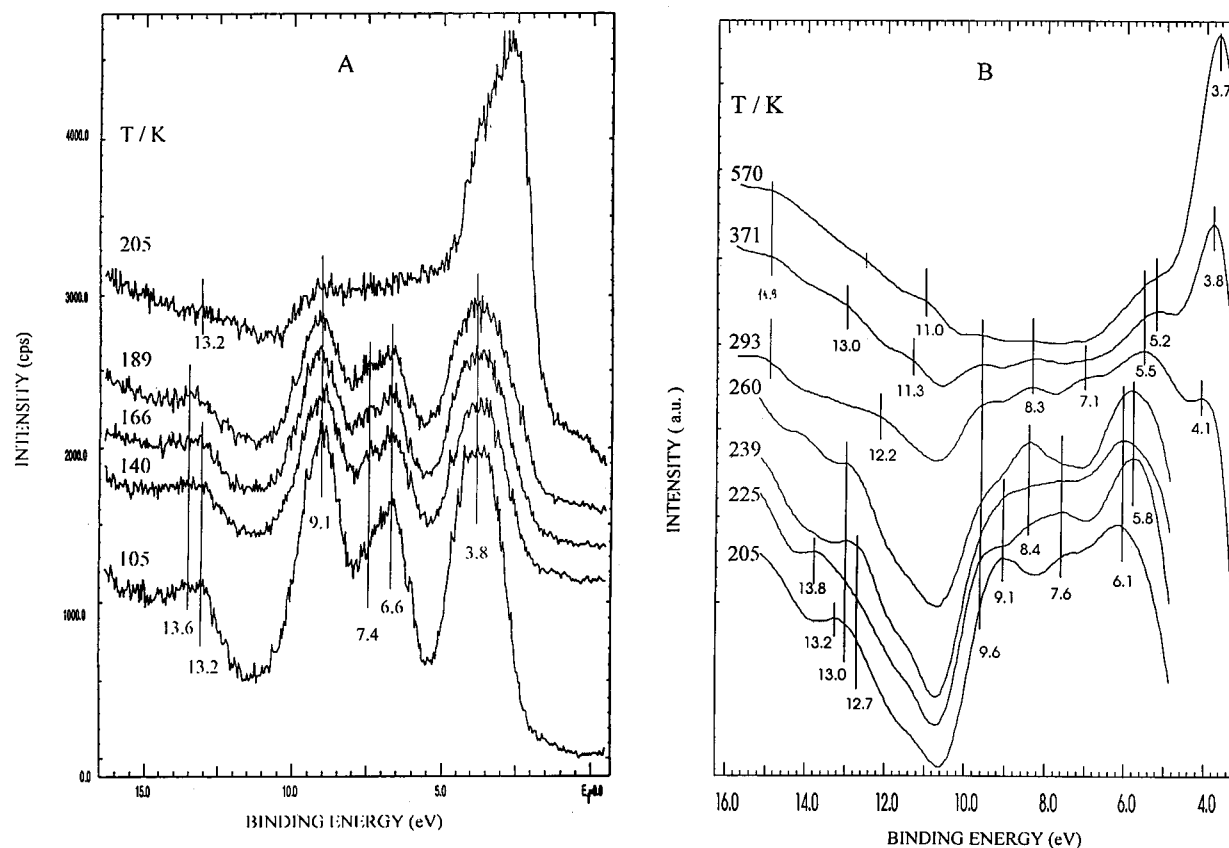


Figure 5. (A) He II UPS of adsorbed CH_2I_2 after heating the adsorbed layer to different temperatures. CH_2I_2 exposure was 2.5 L. (B) Difference spectra.

low exposure (~ 0.1 L) we obtained only a signal at 9.2 eV. At the same time the intensity of the Cu 3d band decreased and moved from 2.7 to 2.9 eV. At higher exposure the positions of the photoemission signals were 3.9, 6.7, 7.6, 9.3, and 13.2 eV (Figure 3A). In the magnified difference spectra, taken at lower coverages, more detailed features can be observed (Figure 3B). At 0.08 and 0.25 L exposures, the peaks are at 4.0, 5.4–5.6, 6.4–6.8, 8.8–9.2, 9.7, 12.8, 13.7, and 15.4 eV (spectra b and c in Figure 3B). The UPS features in spectrum d are very close to the positions for the multilayer. In the He I photoelectron spectra (not shown) the signals associated with the

adsorbed CH_2I_2 are seen at 3.6, 4.2, 6.7, 7.5, and 9.1 eV. A summary of observed binding energies of adsorbates is given in Table 1.

Thermal desorption curves following CH_2I_2 adsorption on the $\text{Cu}(100)$ surface are depicted in Figure 4. No desorption of CH_2I_2 was experienced below an exposure of 0.3 L. At and above this exposure, a CH_2I_2 peak appeared with $T_p = 210$ K. This peak is denoted by α . On increase of the CH_2I_2 exposure, the amount of desorbed CH_2I_2 increased and the T_p shifted to 219 K. The peak could not be saturated, and no new low-temperature peak developed at higher exposures.

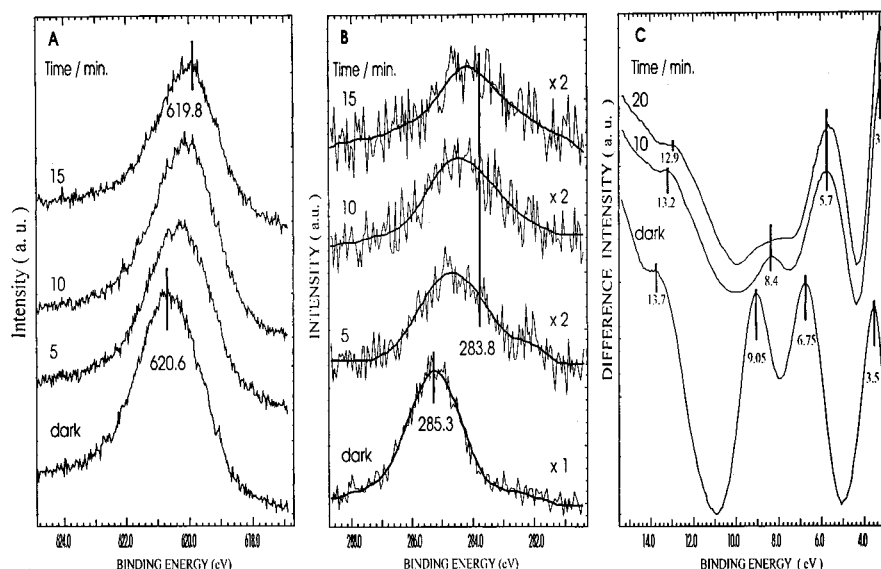


Figure 6. Effects of illumination on the XPS of (A) $\text{I}(3d_{5/2})$ and (B) $\text{C}(1s)$ and on (C) UPS of adsorbed CH_2I_2 on $\text{Cu}(100)$ at 100 K. CH_2I_2 exposure was 1.5 L.

3.2. Effects of Annealing of Adsorbed Layer. XPS spectra of adsorbed layers annealed at different temperatures are displayed in Figure 1B. When a multilayer was annealed up to 192 K, only a slight shift occurred in the BE of $\text{I}(3d_{5/2})$ to lower energy. The peak became appreciably wider at 173 K. Above 192 K, a significant decrease in the intensity of the $\text{I}(3d_{5/2})$ signal was observed. This was accompanied by a large shift in the binding energy of $\text{I}(3d_{5/2})$ from 620.5 to 620.6 to 619.7 eV. The position and the intensity of the $\text{I}(3d_{5/2})$ signal remained unaltered above this temperature up to 900 K, the temperature of the onset of iodine desorption. Changes in the area and the position of the $\text{I}(3d_{5/2})$ peak are displayed in Figure 3. The intensity of the $\text{C}(1s)$ peak also underwent an attenuation at 192 K and shifted from 285.3 to 285.5 eV. The fwhm value became somewhat larger, 2.2 eV, indicating that more than one type of carbon is on the surface. Above 220 K, the $\text{C}(1s)$ signal became very weak.

The effect of annealing of the adsorbed layer was also exhibited in the UPS spectra (Figure 5). Up to 189 K, mainly the intensity ratios of the 6.6 and 7.4 eV peaks changed, and the 13.2 eV peak moved to 13.6 eV. When the adsorbed layer was heated to 205 K, a relatively strong photoemission line remained at 9.1 eV and the signals of the 3d and 4p orbitals of Cu were restored. Weak photoemission lines were also seen in the magnified difference spectra at 6.1, 7.6, 9.1, and 13.2 eV (Figure 5B). Further annealing caused some changes in the positions of these signals. Above 260 K, only weak lines can be detected.

TPD measurements revealed that the only product of the reaction of CH_2 on $\text{Cu}(100)$ is the ethylene. Its formation occurred parallel to the desorption of the parent molecule (Figure 4B). At low coverages, when no molecular desorption of CH_2I_2 was observed, the peak temperatures of C_2H_4 evolution were 235 and 280 K. With the increase of the coverage, the amount of ethylene increased and the majority of ethylene desorbed in a peak with $T_p = 240$ K. Two shoulders can be distinguished at $T_p = 210$ and 268 K (Figure 4B). Note that neither methane and ethane nor hydrogen was identified in the desorbing products. Attempts to identify desorbing CH_2 radicals were not successful. The desorption of iodine began above 900 K.

3.3. Effects of Illumination. The primary aim of the illumination study was to promote the generation of CH_2 at low temperature (~ 100 K), where its decomposition and secondary reactions are minimal.

The effect of illumination was exhibited by changes of the positions of the $\text{I}(3d_{5/2})$ and $\text{C}(1s)$ signals in the XPS (Figure 6A). At a monolayer, the $\text{I}(3d_{5/2})$ peak clearly shifted from 620.6 to 619.8 eV even after a relatively short (5–10 min) irradiation, which was accompanied by a slight decrease of the peak area. At the same time, the $\text{C}(1s)$ signal at 285.3 eV moved to lower energy and became wider and a new shoulder developed at 283.8 eV (Figure 6B.)

Illumination of the adsorbed layer caused a dramatic alteration in the He II photoelectron spectrum of CH_2I_2 (Figure 6C). After photolysis, photoemission signals characteristic of the adsorbed CH_2I_2 almost disappeared and a very intense signal appeared at 5.7 eV.

Postirradiation TPD measurements showed that the amount of CH_2I_2 desorbed decreased with the rise of irradiation time (Figure 7A). No desorption of CH_2I_2 was detected after 20 min of illumination. In contrast, the irradiation somewhat increased the amount of ethylene produced (Figure 7B).

4. Discussion

4.1. Adsorption of CH_2I_2 . The adsorption of CH_2I_2 on $\text{Cu}(100)$ caused a relatively slight decrease in the work function at low exposure. The same feature was observed for $\text{Pd}(100)$ and $\text{Rh}(111)$ surfaces.^{16,19} In these cases, however, we measured a somewhat larger decrease in the $\Delta\phi$, 0.85 and 0.75 eV, respectively. These results suggest that CH_2I_2 adsorbed on metals has a positive outward dipole moment. The fact that at higher exposures an increase in the work function occurred is very likely due to the less ordered arrangement of permanent dipoles in the second layer.¹⁶ An alternative explanation is a change in the molecular orientation of adsorbed CH_2I_2 . With regard to the bonding characteristics of adsorbed alkyl halides, it is very likely that CH_2I_2 bonds through the halogen atoms.^{5–8}

Following the uptake of CH_2I_2 by XPS measurements, we found that the area of both the $\text{I}(3d_{5/2})$ and $\text{C}(1s)$ peaks increased continuously with the rise of CH_2I_2 exposure. As regards the nature of the adsorption of CH_2I_2 at 100 K, the position of $\text{I}(3d_{5/2})$ provides important information; the binding energy of $\text{I}(3d_{5/2})$ for atomically adsorbed I is always lower, 618.5–619.7 eV, than that for molecularly adsorbed iodo compounds, ≥ 620.5 eV.^{6–8,17} As appeared in Figure 1, the position of the $\text{I}(3d_{5/2})$ peak at very low exposure appeared at 620.0 eV and at higher exposures at 620.7–620.9 eV. This latter value is characteristic

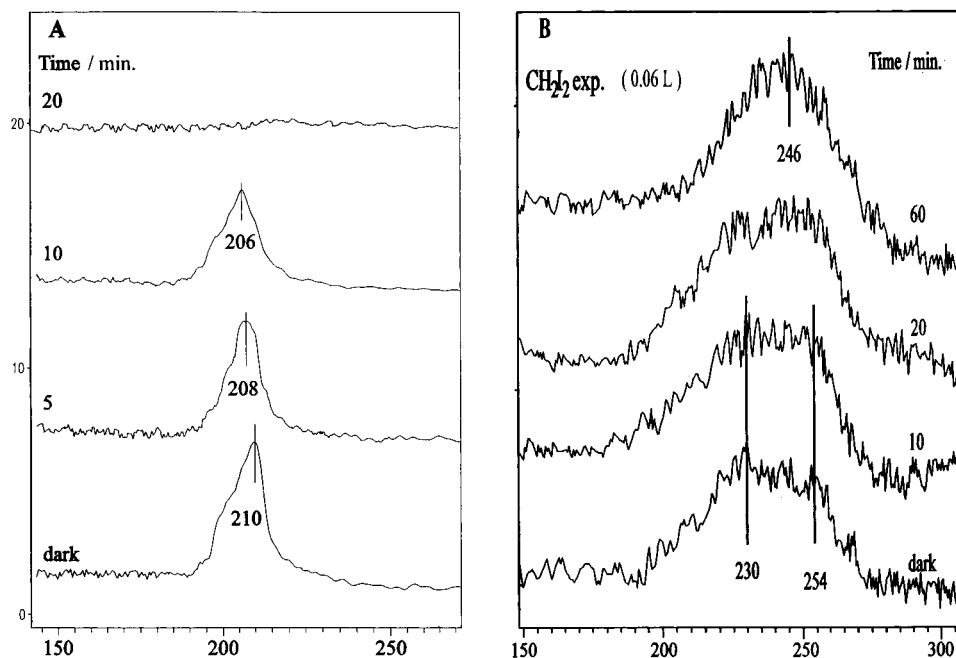


Figure 7. Postirradiation TPD spectra for adsorbed CH_2I_2 : (A) CH_2I_2 ; (B) C_2H_4 .

of the molecularly adsorbed CH_2I_2 ^{16,18,19} and CH_3I .^{6–8,17} The lower value of binding energy for $\text{I}(3d_{5/2})$ suggests the occurrence of the dissociation of CH_2I_2 at submonolayer at 100 K. However, the fact that this binding value is somewhat higher than that obtained following the complete dissociation of CH_3I on $\text{Pd}(100)$ ¹⁴ may indicate that a substantial amount of undissociated CH_2I_2 also exists on the surface at low exposure.

The situation is somewhat more complex with the $\text{C}(1s)$ signal. At lower exposures, when partial dissociation of CH_2I_2 is assumed, a $\text{C}(1s)$ peak was detected at 283.8 eV. At high exposure, the $\text{C}(1s)$ binding energy was located at 285.6 eV. According to the previous consideration, it is reasonable to conclude that the $\text{C}(1s)$ value at 283.8 eV belongs to the isolated CH_2 species formed in the dissociation. This $\text{C}(1s)$ binding energy may be compared with previously reported ones determined on other surfaces. Steinbach et al.¹ reported a value of 284.9–285.2 eV, derived from the thermal dissociation of CH_2Cl_2 on polycrystalline Ni and Co. Monim and McBreen²⁶ obtained a much lower value, 283.6 eV, as a result of the dissociation of CH_2N_2 on a $\text{Pd}(110)$ surface. They argued that in the study of Steinbach et al.¹ the highly electronegative halogen atom modified the local surface electronic structure to such an extent that the CH_2 -surface interaction was significantly perturbed relative to that for a halogen-free surface. The perturbation was much less in their own case when only adsorbed nitrogen was present. A further shift could result from the extra-atomic relaxation shift due to the presence of adsorbed halogen. However, following the dissociation of CH_2I_2 on a $\text{Pd}(100)$ surface, we also determined a binding energy for $\text{C}(1s)$ at 283.9 eV.¹⁶ This suggests that the adsorbed iodine on Pd, and probably on Cu surfaces, too, exerts less influence, if any, on the position of $\text{C}(1s)$ binding energy. The high binding energies observed by Steinbach et al. may belong to an undissociated CH_2Cl_2 molecule.

Adsorption of CH_2I_2 on $\text{Cu}(100)$ gave very weak photoemission signals in He II photoelectron spectra at low coverage. At higher coverages, slightly above monolayer (spectrum e in Figure 3A), photoemission peaks emerged at 3.9, 6.7, (7.6) 9.3, and 13.2 eV. If the gas-phase photoelectron spectrum of CH_2I_2 and the gas-phase ionization potentials are considered, the above peaks can be assigned to the $(2b_1, 3b_2, 1a_2, 4a_1)$, $(2b_2, 3a_1)$, $1b_1$, and $2a_1$ orbitals. The differences in binding energies in

the adsorbed layer on $\text{Cu}(100)$ approximate well the values measured for gaseous CH_2I_2 .²⁵ From this finding, it may be concluded that the bonding of CH_2I_2 to $\text{Cu}(100)$ did not result in a strong distortion of its molecular electronic structure.

These photoemission lines were observed in the magnified difference spectra for submonolayer coverages at slightly different energies (Figure 3B). The most important difference is the appearance of a new peak at 5.4–5.6 eV, which we assign to CH_2 species formed in the dissociation process. In the UPS spectra of polycrystalline Ni and Co following the dissociative adsorption of CH_2I_2 , a photoemission line at 5.5–5.8 eV was also detected, which was attributed to adsorbed CH_2 species.¹ This signal was also seen in the He II photoelectron spectrum of adsorbed CH_2I_2 at submonolayer coverage on the $\text{Pd}(100)$ surface.¹⁶ Taking into account that in the present case the photoemission line at 5.4–5.6 eV appeared together with the signals of CH_2I_2 even at the lowest exposures, we may conclude that molecularly and dissociatively adsorbed CH_2I_2 coexist on the Cu surface in the first layer at 100 K.

According to the TPD measurements, we found only one adsorption state that desorbed at 210–219 K with an activation energy of 52–55 kJ/mol. The calculation was based on pseudo-first-order desorption kinetics assuming a preexponential factor of 10^{13} s^{-1} . Since we could not obtain a saturation of this peak even at very high exposures, we may conclude that this peak corresponds to the desorption of a multilayer. The value of T_p is somewhat higher than that observed for the desorption of a multilayer from $\text{Pd}(100)$ ($T_p = 177 \text{ K}$)¹⁶ and $\text{Rh}(111)$ ($T_p = 205 \text{ K}$).¹⁹ In these cases other adsorption states were also registered, desorbing at higher temperatures of $T_p = 200$ and 220 K , respectively.

4.2. Annealing of Adsorbed CH_2I_2 . Heating the adsorbed multilayer caused no appreciable changes in the XPS below 173 K (Figure 1B). At 173–192 K the $\text{I}(3d_{5/2})$ peaks broadened and a shoulder could be distinguished at 619.7 eV. The presence of this shoulder indicates that a fraction of the molecularly adsorbed CH_2I_2 underwent dissociation at this temperature. Above 192 K this shoulder became the dominant peak for $\text{I}(3d_{5/2})$, indicating the completeness of the dissociation process.

It is interesting that practically no shift occurred at that temperature range in the position of the $\text{C}(1s)$ signal. Accepting the previous consideration for the interpretation of the low

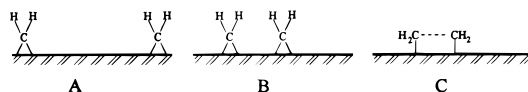


Figure 8. Scheme for the reaction of CH₂ molecules: (A) adsorbed CH₂ formed in the dissociation of CH₂I₂; (B) migration of CH₂; (C) coupling of CH₂.

binding energy of C(1s) in the CH₂ species, this feature may suggest that the CH₂ formed in the dissociation of CH₂I₂ at high temperature is transformed immediately into other adsorbed species. According to the TPD spectra, this species is adsorbed ethylene, which starts desorbing above 200 K with the main peak temperature of 240 K (Figure 4B). This suggests that the CH₂ formed in the dissociation of CH₂I₂ above 173 K is coupled into ethylene: CH_{2(a)}=C₂H_{4(a)}.

From the comparison of the dissociation temperature of CH₂I₂ and the peak temperatures for ethylene desorption, we infer that ethylene produced may remain adsorbed for a while on the surface. This idea is supported by UPS results: above the desorption of weakly bonded CH₂I₂, 205–210 K, weak photoemission signals at 6.1, 8.4 and 12.7 eV can be seen that are characteristic of adsorbed C₂H₄ on metal surfaces. Note that the nature of the interaction of ethylene with Cu surfaces differs from that established on platinum metals. Ethylene retains most of its π character upon adsorption on Cu(100), (110), and (111) surfaces.^{27,28} Unlike on other transition metal surfaces it binds with its molecular plane perpendicular to the surface and its C–C bond tilted away from the surface plane. The π -bonded ethylene does not transform into the di- σ -bonded form on Cu surfaces.

Following the adsorption of ethylene on Cu(100) and Cu-(110) surfaces, ethylene desorbed at $T_p = 160$ K at low coverages.^{23,24} This temperature is almost ~ 80 K lower than observed in the present case for ethylene desorption after CH₂I₂ dissociation. For the explanation of this difference several assumptions can be made: (i) the dissociation of CH₂I₂ is not complete at 204 K; (ii) the dissociation is complete, but the coupling of CH₂ is restricted perhaps because of its hindered diffusion by adsorbed I; (iii) the coupling of CH₂ species gives no π -bonded ethylene. This process proceeds through a transition surface complex that is not produced following ethylene adsorption on Cu(100). The formation of this surface species is illustrated by the reaction scheme presented in Figure 8.

Assumption (i) can be excluded as the shift in the binding energy of I(3d_{5/2}), indicating the cleavage of C–I bond, completed up to 204 K (Figure 1B). Above this temperature there is no change in the position of the I(3d_{5/2}) peak. In addition, there are no photoemission signals in the UPS above 205 K that would suggest the presence of undissociated CH₂I₂. If we accept the previous finding^{1,16} that adsorbed CH₂ is characterized by a photoemission line at 5.4–5.6 eV, then the UV photoelectron spectra presented in Figure 5 make proposal (ii) also unlikely. The most probable explanation is assumption (iii): adsorbed CH₂ species are transformed into more strongly adsorbed structure, like di- σ -bonded ethylene, which is known to desorb at higher temperatures. The fact that some weak photoemission signals remain in the He II spectra even after desorption of ethylene may indicate that the decomposition of a small fraction of the strongly bonded ethylene may also occur to other hydrocarbon species. Similarly, as in the case of Pd-(100),¹⁶ we may count with the transient formation of ethylidyne, CCH₃, which decomposes further to CH species and surface carbon. Photoemission lines (5.2, 9.6, 11.3, and 13.0 eV) detected at 371 K were also observed for Pd(100) above 250 K and were attributed to CCH₃ species.

It is an interesting feature of the behavior of adsorbed CH₂

on Cu(100) is that its decomposition and self-hydrogenation into CH₄ do not proceed to a detectable extent. This is in contrast to that on Pd(100), Rh(111), and Mo,^{16,18–22} where the formation of methane was the dominant reaction pathway, or, at least, was commensurable with the coupling of CH₂ species. This difference was used in the fabrication of an effective catalyst for the conversion of methane into C₂ compounds.³⁰ Addition of copper to a Rh/SiO₂ catalyst enhanced the selectivity of ethane and ethylene production by a factor of 5, which was attributed to the migration of CH_x fragments formed on Rh to the Cu, on which the coupling reaction of CH_x was favored.³⁰

4.3. Photolysis of Adsorbed CH₂I₂. Illumination of the adsorbed layer at 100 K caused a gradual shift in the position of I(3d_{5/2}) binding energy in the XPS. After 10–15 min illumination time the peak attained a value of 619.8 eV, which is considered a sign of dissociation of CH₂I₂ to a great extent. A significant shift in the binding energy of C(1s) is also indicative of the occurrence of the photodissociation of CH₂I₂. The area of the I(3d_{5/2}) signal decreased only by about 10%, indicating that only a small fraction of the adsorbed CH₂I₂ underwent a photoinduced desorption. A somewhat larger decrease was observed in the intensity of the C(1s) peak, which suggests the photoinduced desorption of hydrocarbon species.

This conclusion is supported by the UPS results. As shown in Figure 6C, the photoemission signals of adsorbed CH₂I₂ vanished or attenuated to a great extent and an intense signal at 5.7 eV, attributed to CH₂ species, appeared in the spectra. As a result of the illumination, the amount of CH₂I₂ desorbed around 210 K decreased and completely ceased after 20 min of illumination. At the same time, the formation of C₂H₄ did not change or even somewhat enhanced. This proves that the disappearance of the desorption peak of CH₂I₂ at 20 min is the result of the photoinduced dissociation of CH₂I₂ and not due to its photoinduced desorption.

5. Conclusions

- (1) CH₂I₂ adsorbs dissociatively at submonolayer coverage on Cu(100) surface at 90 K and molecularly at higher coverages.
- (2) The primary products of the dissociation are adsorbed CH₂ and I.
- (3) The most important feature of the adsorbed CH₂ on Cu-(100) is that CH₂ species are coupled into strongly adsorbed C₂H₄, very likely the di- σ -bonded form, which desorbs with a $T_p = 240$ K. No self-hydrogenation of CH₂ into CH₄ was observed.
- (4) Illumination of adsorbed CH₂I₂ with a Hg arc lamp enhanced the extent of dissociation even at 90–95 K.

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