

# Thermal and photo-induced dissociation of $(\text{C}_2\text{H}_5)_2\text{Zn}$ to yield $\text{C}_2\text{H}_5$ on the Pd(100) surface

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The adsorption and dissociation of  $(\text{C}_2\text{H}_5)_2\text{Zn}$  was studied on Pd(100) surface. The methods used included photoelectron spectroscopy (XPS, UPS), electron energy loss spectroscopy (EELS) in the electronic range, temperature-programmed desorption (TPD), and work function measurements. Diethyl zinc adsorbs predominantly irreversibly on Pd surface. At submonolayer it dissociates even at 90 K. Thermal dissociation of adsorbed monolayer occurs at 170–230 K. Illumination of molecularly adsorbed layer at 90–95 K enhances the extent of the dissociation. The primary products of the thermal and photodissociation,  $\text{C}_2\text{H}_5$  and Zn, were characterized by a C(1s) binding of 284.0 eV and by Zn( $2p_{3/2}$ ) binding energy of 1021.0 eV. The  $\text{C}_2\text{H}_5$  reacted to form  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ . Coupling reactions to  $\text{C}_4\text{H}_{10}$  and  $\text{C}_4\text{H}_8$  were also observed. On the basis of He I, He II, and EELS data, energy levels of electron orbitals for  $(\text{C}_2\text{H}_5)_2\text{Zn}$ –Pd(100) system have been calculated.

## I. INTRODUCTION

Study of the interaction of metal alkyl compounds with solid surfaces is of importance for at least two reasons. First, metal organic chemical vapor deposition is an important method for the growth of thin films of compound semiconductors.<sup>1</sup> The nature of the ligands is to be expected to influence the properties of the metal films, though these effects have not yet been explored. Secondly, the fragments  $\text{C}_x\text{H}_y$  are important reaction intermediates in hydrocarbon synthesis, in the catalytic dimerization of methane, and also in olefin polymerization.<sup>2</sup>

Recently we examined the thermal stability and reactions of  $\text{CH}_2$ ,<sup>3</sup>  $\text{CH}_3$ ,<sup>4</sup> and  $\text{C}_2\text{H}_5$  (Refs. 5 and 6) species on Pd(100) surface. These hydrocarbon moieties have been produced by thermal and photo-induced dissociation of corresponding halogenated compounds. In the present paper we gave an account on the adsorption of  $(\text{C}_2\text{H}_5)_2\text{Zn}$  on the same Pd surface. The adsorption of  $(\text{C}_2\text{H}_5)_2\text{Zn}$  was investigated so far on ZnO,<sup>7</sup> GaAs(100),<sup>8</sup> and Si(100) (Ref. 9) surfaces.

## II. EXPERIMENT

### A. Methods

The experiments were performed in a ultrahigh vacuum system with a background pressure of  $5 \times 10^{-8}$  Pa, produced by turbomolecular, ion-getter and titanium sublimation pumps. The system was equipped with an electrostatic hemispherical analyzer (Leybold-Heraeus LHS-10), a differentially pumped ultraviolet (UV) photon (He I, II) source for ultraviolet photoelectron spectroscopy (UPS), an Al  $K\alpha$  x-ray anode for x-ray photoelectron spectroscopy (XPS) and an electron gun for Auger electron spectroscopy (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 Pd( $3d_{5/2}$ ) peak at 335.1 eV. Collection times for UPS and XPS were 15 and 30 min, respectively. XPS spectra were smoothed by fast Fourier transform method. For temperature-programmed desorption (TPD), the sample was heated resistively at 5 K/s. In the case of the desorption of Zn, the heating rate was 7 K/s. Changes in work function were obtained by measuring the secondary electron cut off in the UP 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 sample normal.

### B. Materials

The oriented 4N9 purity, disk-shaped crystal (diameter 7 mm, thickness 1.5 mm) was mechanically polished with diamond paste. The sample was heated resistively by Ta wires and cooled to 90 K by a Ta plate spot-welded onto the side of the sample, which was in contact with a liquid nitrogen-cooled stainless steel tube. The temperature of the sample was measured by a Chromel–Alumel thermocouple spot-welded to the side of the crystal. The accuracy of temperature measurements was  $\pm 2$  K. The sample cleaning procedure consisted of cycles of argon ion bombardment (1.0 kV,  $2 \mu\text{A}/\text{cm}^2$ , 300–1100 K), annealing (1000 K), oxygen treatment ( $5 \times 10^{-7}$  mbar, 700 K) and short annealing (1100 K), which were sufficient to remove the surface carbon and other contaminations. The oxygen, sulphur, phosphorous, and carbon impurities on the cleaned surface were estimated to comprise less than 0.1% of a monolayer.  $(\text{C}_2\text{H}_5)_2\text{Zn}$  was obtained from Fluka. It was degassed and purified by freeze–pump–thaw cycles prior to use, and stored in glass vials shielded from light to prevent photodecomposition.

## III. RESULTS

### A. Adsorption of $(\text{C}_2\text{H}_5)_2\text{Zn}$

The adsorption of  $(\text{C}_2\text{H}_5)_2\text{Zn}$  (further DEZn) was followed first by x-ray photoelectron spectroscopy (XPS).

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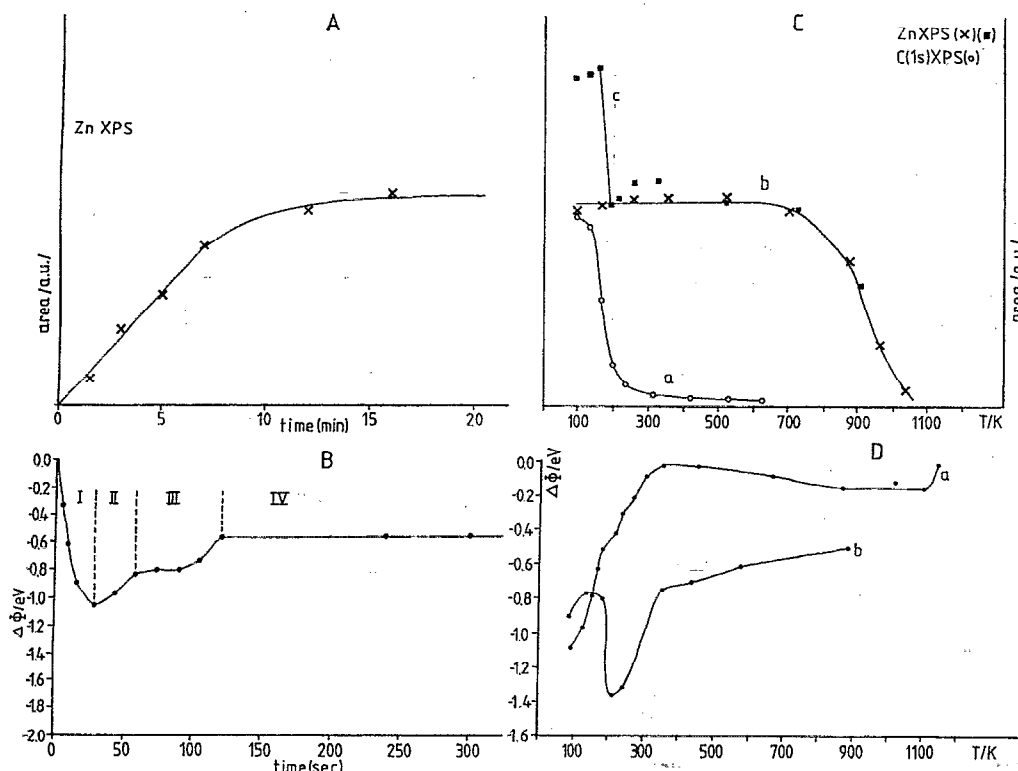


FIG. 1. Intensity of the  $Zn(2p_{3/2})$  XPS signal (A) and changes in the work function ( $\Delta\phi$ ) of Pd(100) (B) as a function of exposure time of  $(C_2H_5)_2Zn$  at a pressure of  $10^{-5}$  Pa at 90 K, and annealing temperature (C) and (D). In (C) the intensity of C(1s) signal is also plotted. The exposure time was 10 min for a and b, 25 min (at a pressure of  $3 \times 10^{-5}$  Pa) for c in (C), 45 s for a and 16 min for b in (D).

When the pressure of  $DEZn$  was about  $10^{-5}$  Pa around the sample, the area of the  $Zn(2p_{3/2})$  peak changed only very little after exposure time of 15 min. However, we could not talk on saturation as applying a higher pressure ( $\sim 1 \times 10^{-4}$  Pa), we measured a significantly higher value for the area of  $Zn$  XPS peak [Fig. 1(C)] at 90 K.

The interaction of  $DEZn$  with the Pd surface was also followed by work function measurements. The adsorption of  $DEZn$  caused an almost linear decrease in the work function of Pd(100) at low exposure, as illustrated in Fig. 1(B). The maximum decrease,  $\Delta\phi \approx 1.05$  eV, was attained at a low exposure. Afterwards, the work function increased and reached a saturation value far below the exposure time required for saturation in Fig. 1(A);  $\Delta\phi$  in this case amounts to  $-0.55$  eV.

Thermal desorption of parent molecules was followed at a mass number of 122 amu. TPD curves for  $DEZn$  as a function of exposure are depicted in Fig. 2. No desorption of  $DEZn$  was seen at low exposure, where XPS and  $\Delta\phi$  measurements already indicated an uptake of  $DEZn$ . At higher exposures, a zero-order desorption peak starts to grow with a  $T_p = 175$ – $186$  K, which did not saturate even at high  $DEZn$  doses.

Figure 3 shows the XPS spectrum of Pd(100) as a function of  $DEZn$  exposure at 90 K. At low exposures, the binding energy of  $Zn(2p_{3/2})$ , which gives the most intense peak, was registered at 1021.0 eV. This shifted to higher values, up to 1023.2 eV, at high  $DEZn$  exposures. The FWMV value of  $Zn 2p_{3/2}$  is 2.1 eV. The split of  $Zn(2p_{1/2})$  and  $Zn(2p_{3/2})$  or-

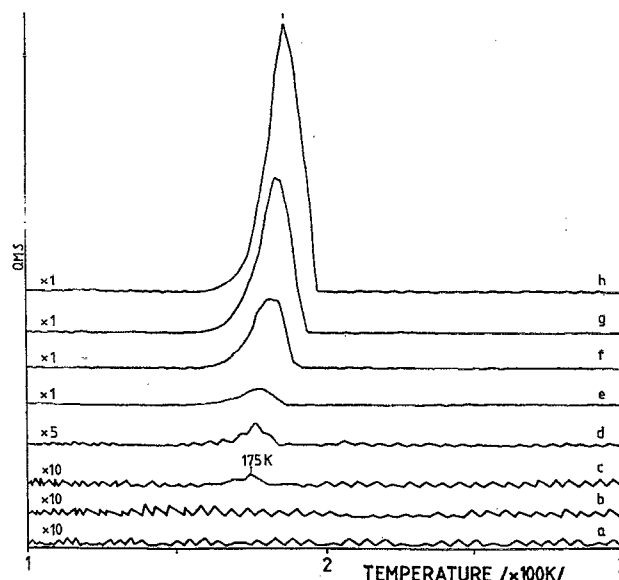
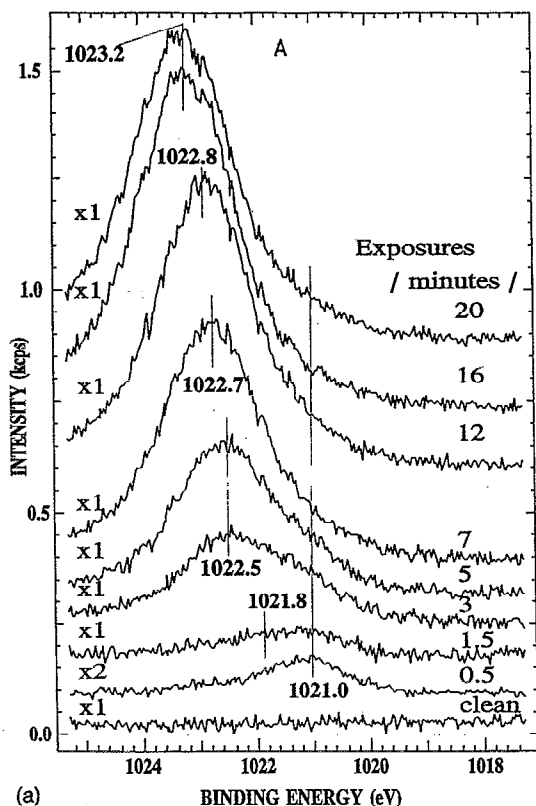
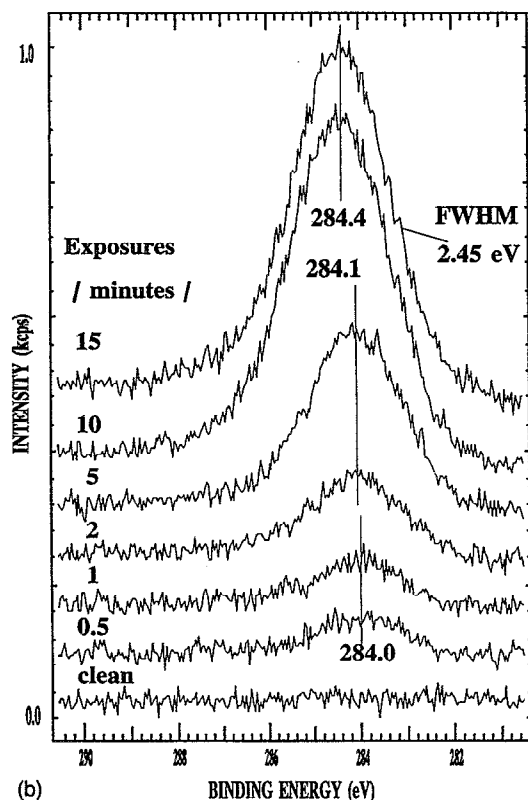


FIG. 2. Thermal desorption spectra of  $(C_2H_5)_2Zn$  following  $(C_2H_5)_2Zn$  adsorption on clean Pd(100) at 90 K. Exposure time at a pressure of  $1 \times 10^{-5}$  Pa (a) 5 s; (b) 15 s; (c) 25 s; (d) 45 s; (e) 90 s; (f) 180 s; (g) 360 s; (h) 1200 s.



(a)



(b)

FIG. 3. XPS spectra of Pd(100) for different exposure time of  $(C_2H_5)_2Zn$  at a pressure of  $1 \times 10^{-5}$  Pa at 90 K. (a) Zn ( $2p_{3/2}$ ); (b) C ( $1s$ ).

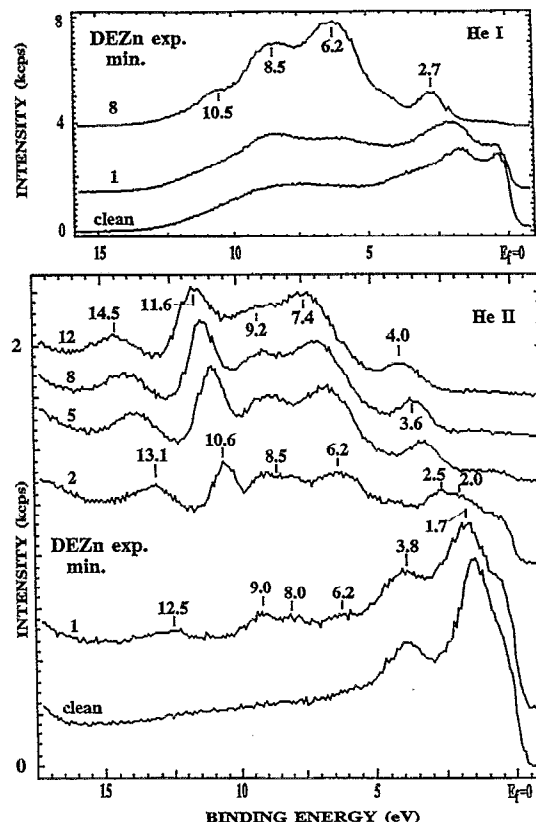


FIG. 4. He I and He II UPS spectra of Pd(100) for different exposure time of  $(C_2H_5)_2Zn$  at a pressure of  $1 \times 10^{-5}$  Pa at 90 K.

bitals is 23.0 eV, in a good agreement with the literature value.<sup>10</sup> As was shown in Fig. 1(A), plotting the areas of Zn( $2p_{3/2}$ ) peaks against exposure we obtained a saturation value at an exposure time of 15 min at a DEZn pressure of  $1.5 \times 10^{-5}$  Pa. We assume that this saturation corresponds to a monolayer (ML) formation.

In the C( $1s$ ) region, the adsorption of DEZn at low exposure yields a broad peak centered at 283.9–284.0 eV, which shifted to higher binding energy (maximum to 284.4 eV). The large FWHM value (2.45 eV) suggests that the peak is the result of two overlapping peaks. Curve resolution of the spectrum revealed that it could be fitted to two Gaussian-type peaks centered at 285.3 and 284.0 eV corresponding to each of the carbon atoms in the molecule. The intensities of the two peaks were equal with a FWHM value of 1.9 eV. The same feature was observed following the adsorption of ethyl iodine on Pd(100) surface.<sup>5</sup>

The surface concentration of adsorbed DEZn at a monolayer was calculated from XPS results. The calculation is based on the comparison of the C( $1s$ ) signal with that obtained at saturation CO coverage on Pd(100). In this way we obtained a value of  $0.33 \times 10^{15}$   $(C_2H_5)_2Zn$  molecules/cm<sup>2</sup>. For CO saturation, a value of  $1.06 \times 10^{15}$  CO molecules/cm<sup>2</sup> was taken into account.<sup>11</sup>

He II photoelectron spectra of Pd(100) under the same experimental conditions are displayed in Fig. 4. At low exposure we obtained very weak signals which grew with the

TABLE I. Binding energies (in eV) of species formed by adsorption and dissociation of  $(C_2H_5)_2Zn$  on the Pd(100) surface.

|                | UPS                       |       | XPS   |                        |
|----------------|---------------------------|-------|-------|------------------------|
|                |                           |       | C(1s) | Zn(2p <sub>3/2</sub> ) |
| $(C_2H_5)_2Zn$ | 4.0, 7.4, 9.2, 11.6, 14.5 | He II | 284.4 | 1023.1                 |
|                |                           | He I  |       |                        |
| $C_2H_5(a)$    | 6.2, 8.0, (9.0) 12.5      | He II | 284.0 | ...                    |
| Zn             | 9.4                       | He II |       | 1021.0                 |

increase of the exposure; the positions of photoemission signals were 6.2, 8.0, 9.0, and 12.5 eV. With the increase of DEZn exposures these photoemission signals intensified and gradually shifted to higher energies. The final positions of the signals attained are 4.0, 7.4, 9.2, 11.6, and 14.5 eV. In the He I photoelectron spectra photoemission lines appeared at 5.9 and 8.4 eV at low exposure, and at 2.7, 6.2, 8.5, and 10.5 eV at high exposures. Note that the relative intensities of the corresponding peaks in He I and He II spectra are different in comparison to the intensity of Pd-*d* band for the clean surface.

The adsorption of DEZn on Pd(100) also caused a shift of the Pd *d*-band maximum towards higher binding energies, and decreased its intensity. A summary of observed binding energies of adsorbates is given in Table I.

In order to obtain informations on the electronic structure of adsorbed DEZn some EELS (in the electronic range) measurements have been performed. The EEL spectrum of clean Pd(100) exhibits loss features at 4.4, 6.4, 14.5, and 21.8 eV (Fig. 5). Adsorption of DEZn at 90 K caused a significant change in the spectrum: loss features appeared at 5.6 (shoulder) (a), 6.8 (b), 10.8 (c), and 13.5 (d) eV.

An attempt was made to increase the amount of Zn atoms on the surface by repeated adsorption/decomposition cycles. In this way the Zn(2p<sub>3/2</sub>) XPS signal was grown maximum by about 25%–30%. TPD area for Zn was enhanced by the same factor. The  $T_p$  value for Zn, however, remained unaltered and no low temperature desorption of Zn was observed.

## B. Effects of annealing of adsorbed layer

The work function of the annealed layer depended on the initial exposure [Fig. 1(D)]. At low coverages (0.15 ML), the work function increased between 100 and 300 K approaching the value of the clean surface with a 0.05 eV. At higher coverages, first a decrease in the work function occurred at 210–220 K, when the minimum value of –1.33 eV was obtained. Above 230 K, the work function sharply increased up to 300–350 K ( $\Delta\Phi = -0.7$  eV). A slight increase in the work function was further observed and the value of the clean surface was attained only above 1150 K.

TPD measurements revealed that the main products of the decomposition of adsorbed DEZn are  $C_2H_4$ ,  $C_2H_6$ ,  $C_4H_8$ , and  $C_4H_{10}$  (Fig. 6). At low coverages, when no molecular desorption of DEZn was observed, the peak temperature of  $C_2H_4$  evolution was 293–303 K. With an increase of the coverage, the amount of ethylene desorbed at this temperature did not change, but new low temperature  $C_2H_4$  peaks developed with  $T_p = 178$  and 207 K [Fig. 6(a)].  $C_2H_6$  desorbed in peaks with  $T_p \sim 189$  and 212 K [Fig. 6(b)]. The most interesting feature of the TPD measurements is the detection of butene and a small amount of butane (mass number 56 and 58). Butene desorbed in three peaks with a  $T_p = 145$ , 175, and 215 K. Its amount increased with the increase of DEZn coverage [Fig. 6(c)]. Desorption peaks for butane

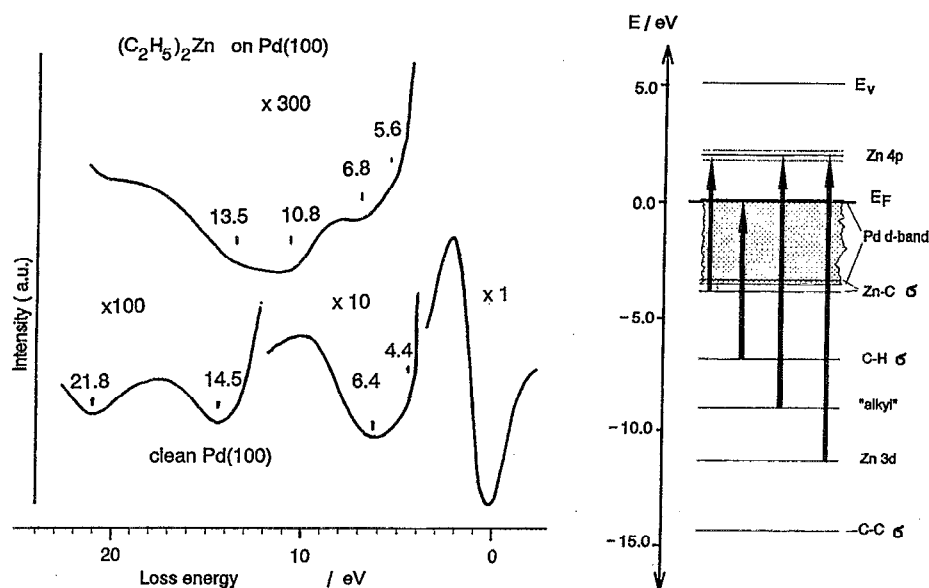


FIG. 5. EEL spectrum of clean and  $(C_2H_5)_2Zn$  covered (1.0 ML) Pd(100) at 90 K (A). Energy levels of electron orbitals in  $(C_2H_5)_2Zn$ -Pd(100) system (B).

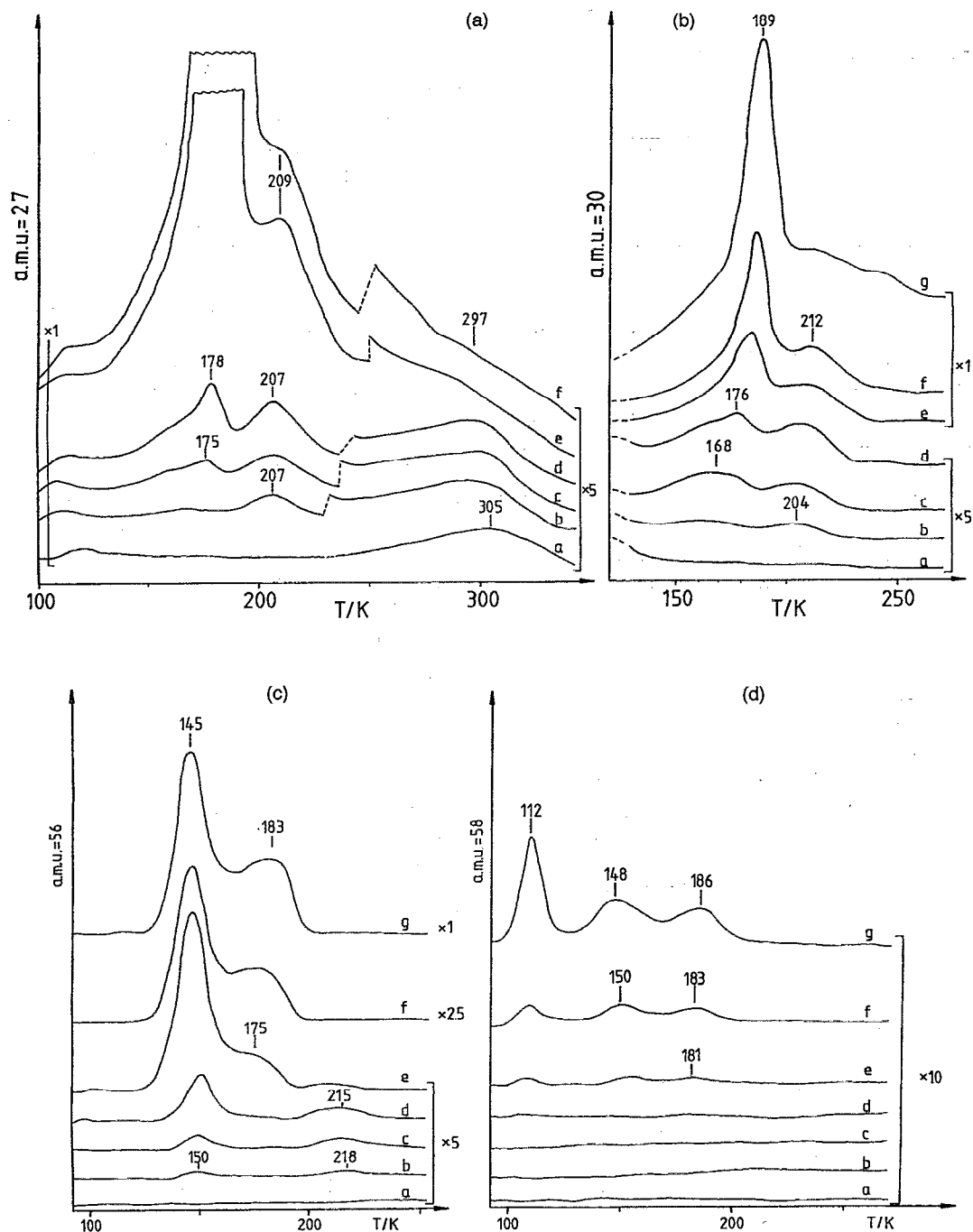


FIG. 6. Thermal desorption spectra of  $C_2H_4$  (a),  $C_2H_6$  (b),  $C_4H_8$  (c), and  $C_4H_{10}$  (d) following the adsorption of  $(C_2H_5)_2Zn$  on Pd(100) at 90 K. Exposure time at a pressure of  $1 \times 10^{-5}$  Pa; (a) 5 s; (b) 15 s; (c) 25 s; (d) 45 s; (e) 180 s; (f) 360 s; (g) 1200 s.

were observed at 112, 148, and 186 K [Fig. 6(d)]. Note that no increase in the amount of  $H_2$  desorbed was measured compared to the blank experiment. The desorption of Zn occurred in one peak,  $T_p = 1100$  K, the position of which was practically independent on the coverage.

Taking into account the sensitivity of MS to hydrocarbons, the fragmentation pattern of  $DEZn$ , and the peak temperatures of the desorption of hydrocarbons, we came to the conclusion that the desorption occurring at around 172–190

K is the result of the fragmentation of  $DEZn$ . On the basis of this, we obtain the following ratios for desorption products at monolayer: 1.0:4.6:6.3:8.5 for butane:ethane:ethylene:butene.

Selected XPS spectra of adsorbed layers annealed at different temperatures are displayed in Fig. 7. Annealing the adsorbed layer at submonolayer coverage (0.2 ML) resulted in a very little change in the position and intensity of the  $Zn(2p_{3/2})$  binding energy up to about 765 K [Fig. 7(a)]. The

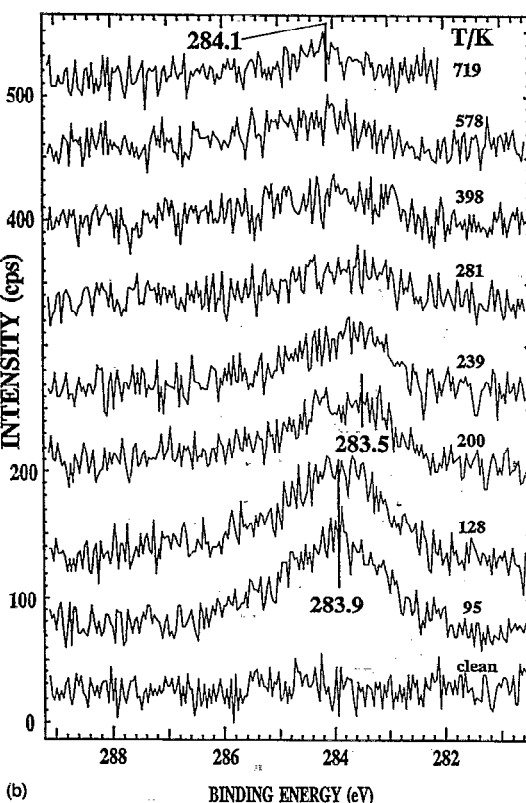
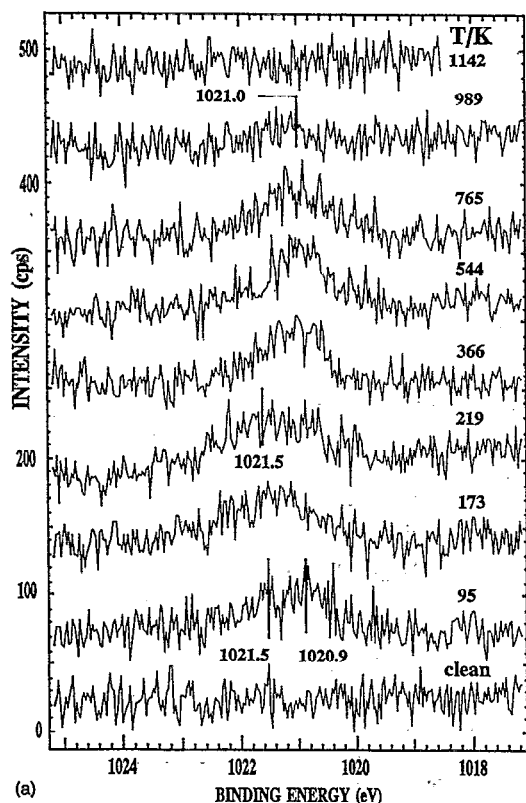


FIG. 7. XPS of Zn and C(1s) of adsorbed  $(C_2H_5)_2Zn$  at 0.2 ML after heating the adsorbed layer to different temperatures. (a) Zn( $2p_{3/2}$ ); (b) C(1s).

Zn signal was eliminated only at 1142 K. As regards the C(1s) peak, its intensity somewhat decreased at 128–200 K and became broader. Above 239 K the C(1s) signal at 284.0 eV was very weak, but could be detected even at 719 K.

Annealing a monolayer exhibited a much more complex picture (Fig. 8). No significant change occurred between 105–115 K. Above this temperature the development of another Zn peak can be observed which became dominant above 173 K. The position of this new peak was 1021.5 eV at 222 K and 1021.15 eV at 517 K. In harmony with the exposure dependence of the C(1s) signal, the location of BE for C(1s) was at 246.6 eV for this coverage. A significant attenuation of C(1s) peak occurred up to 166 K. The next decrease in its intensity was observed at 198–236 K. Above this temperature the C(1s) peak centered at 284.5 eV. A weak C(1s) signal at 283.6 eV was detected even at 626 K. Changes in the intensities of Zn( $2p_{3/2}$ ) and C(1s) peaks are plotted in Fig. 1(C). This demonstrates that while the intensity of Zn peak (at lower exposure) is practically constant up to 700 K, a sharp decrease in the intensity of C(1s) peak occurs between 130–200 K, corresponding to the desorption of various hydrocarbons formed in the surface reactions. Using a larger DEZn exposure, when TPD measurements indicated the formation of weakly adsorbed DEZn, a well measurable decrease in the Zn XPS signal was observed at 160–185 K [Fig. 1(C)].

The coverage dependence of the behavior of the adsorbed layer was also exhibited in the He II UP spectra (Fig. 9). At a submonolayer region the spectrum remained unaltered up to 155 K. The photoemission signals of DEZn disappeared at 160–196 K leaving behind an intense and very stable peak at 9.3–9.5 eV. This was eliminated only above 1100 K, which strongly suggests that it is associated with Zn adatoms.

At high coverage of DEZn, an attenuation and a shift of photoemission lines occurred above 140 K; remaining signals at 189 K were at 1.8, 3.5, 6.2, 9.3, and 10.9 eV. Further heating of the sample led to an additional decay in the intensity of the signal at 10.9 eV and marked enhancement of the peak at 9.3 eV. At the same time the lines due to Pd *d*-band are restored. At 237 K the line at 6.2 eV shifted to 5.8 eV. At 297 K a broad, overlapped band occurred at 3.5–6.0 eV; the maximum of the covering curve is at 4.3 eV. Above 297 K, the only photoemission signal (besides those of Pd) is seen at 9.4, which could be eliminated only above 1150 K.

### C. Effects of illumination

In Fig. 10 we present XPS spectra for Zn( $2p_{3/2}$ ) region obtained before and after irradiation of adsorbed layer with a full arc of mercury lamp at 90 K. Before irradiation we registered two peaks for Zn( $2p_{3/2}$ ) at 0.1 ML; a small one at 1022.4 eV and a more intense one at 1021.1 eV. With the increase of irradiation time, the intensity of high energy peak gradually decreased, and completely disappeared after 45–60 min of irradiation. In contrast, no change occurred in the position of the low energy peak at 1021.1 eV. As regards the C(1s) signal, illumination of adsorbed layer caused a

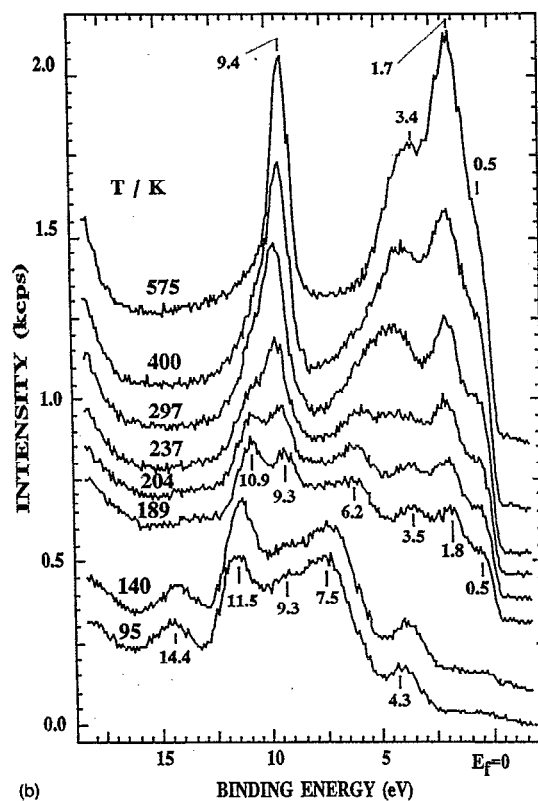
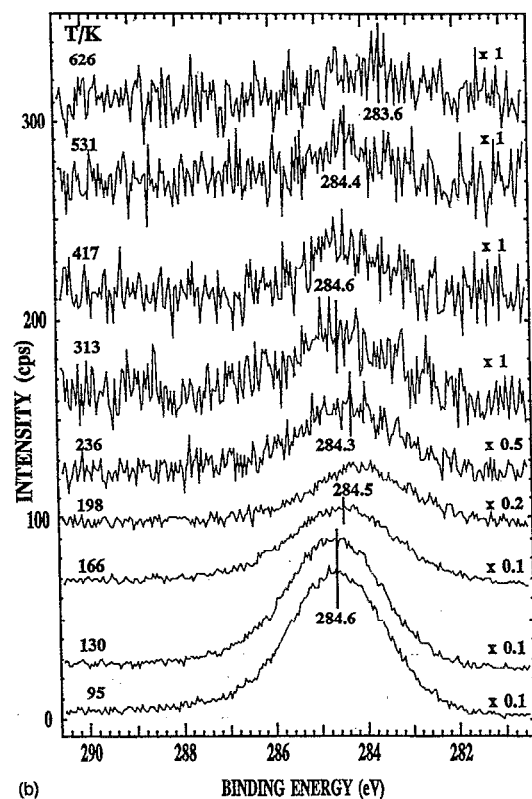
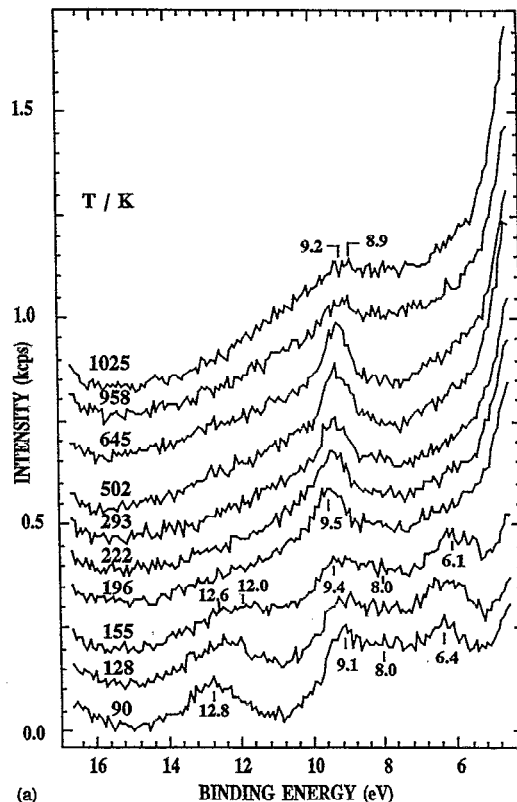
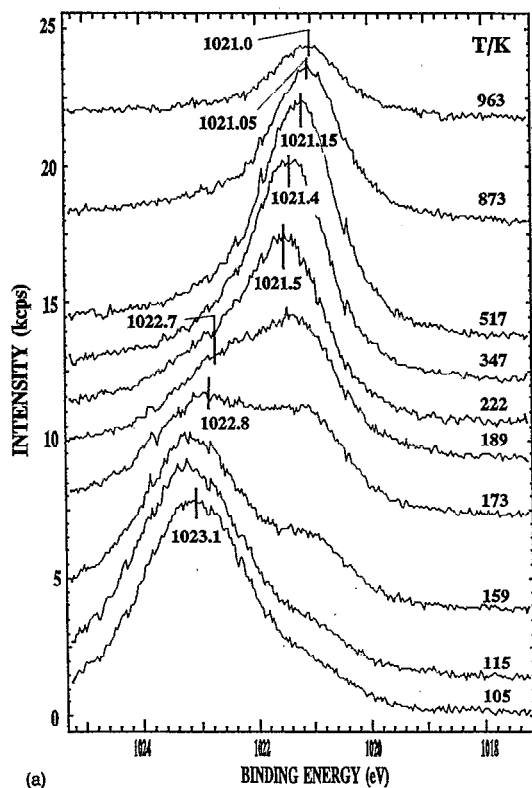
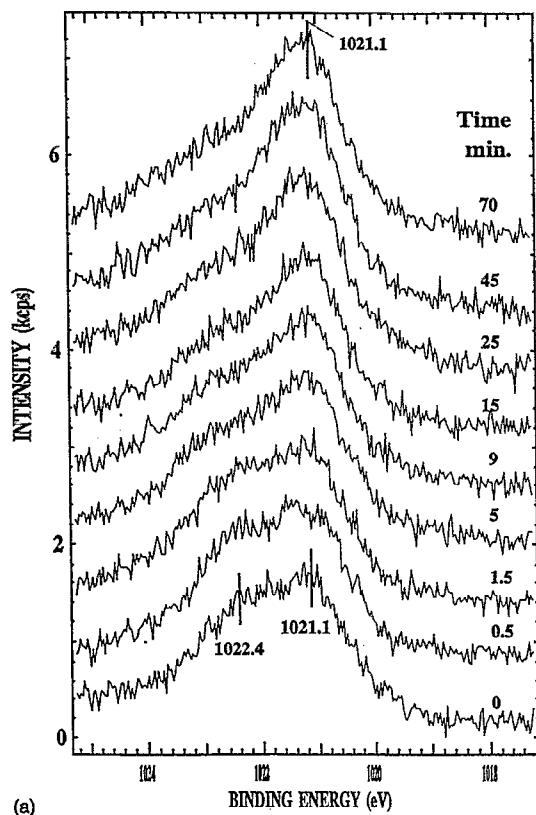
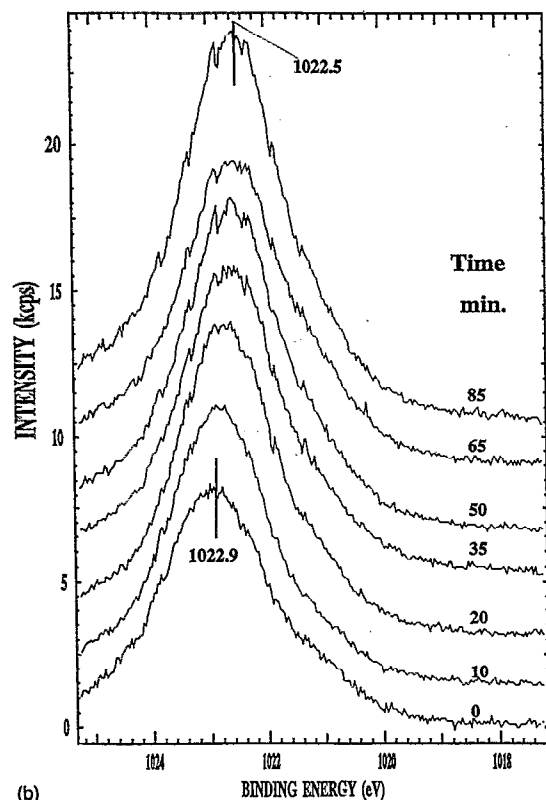


FIG. 8. XPS of Zn and C(1s) of adsorbed  $(C_2H_5)_2Zn$  at 1.0 ML after heating the adsorbed layer to different temperatures (a) Zn( $2p_{2/3}$ ); (b) C(1s).

FIG. 9. He II UPS of adsorbed  $(C_2H_5)_2Zn$  after heating the adsorbed layer to different temperatures. (a) 0.15 ML; (b) 1.0 ML.



(a)



(b)

FIG. 10. Effects of irradiation time on the XPS spectra of  $Zn(2p_{3/2})$  for adsorbed  $(C_2H_5)_2Zn$  at 90 K. Full arc was used. (a) 0.1 ML; (b) 1.0 ML.

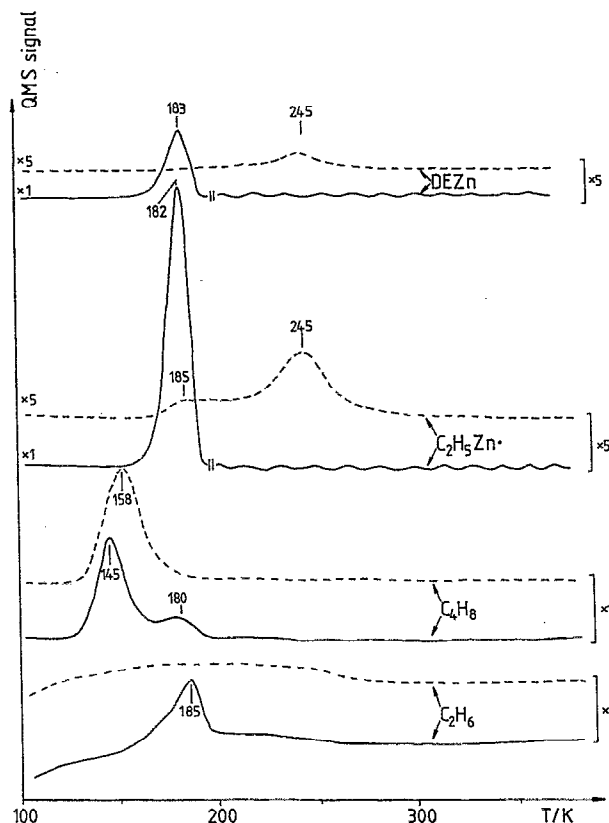


FIG. 11. Post-irradiation TPD spectra of  $(C_2H_5)_2Zn$  at 1.0 ML coverage. Illumination was performed at 90 K for 60 min.

slight decay in its peak area, the position of the peak was clearly at 283.9 eV, FWHM=2.35 eV; the component curves were practically unaltered.

At about monolayer of DEZn we obtained a  $Zn(2p_{3/2})$  peak at 1022.9 eV. Illuminating of this layer the position of the peak shifted to lower energy; after 85 min to 1022.5 eV.

Post irradiation TPD spectra are presented in Fig. 11. At submonolayer coverages no change was observed in the spectra. At monolayer the reversibly bonded DEZn characterized with  $T_p \approx 182$  K disappeared or reduced to a very low value. Interestingly, a new small peak developed at  $T_p = 245$  K. This is more clearly seen at mass number 93 ( $C_2H_5Zn$ ), which is an intense fragment of DEZn. A slight increase in the amount of butene desorbed with  $T_p = 158$  K can be established.

## IV. DISCUSSION

### A. Adsorption of DEZn

DEZn adsorbs strongly and irreversibly on the Pd(100) surface at low coverage; no, or only very limited molecular desorption is observed. With increase of the coverage, a more weakly bound layer develops, which desorbs in a zero-order process with  $T_p = 175$ –186 K. This weakly adsorbed state is considered as a physisorbed DEZn. The activation energy of the desorption is 51.3 kJ/mol, which is clearly higher than the heat of evaporation (36.7 kJ/mol).<sup>12</sup> Note that the formation of condensed DEZn was observed only for



Si(100);<sup>9</sup> its desorption temperature was about 150 K. With regard to the bonding characteristics of adsorbed alkyl halides, it is very likely that the strongly adsorbed DEZn bonds through the Zn atom.

In the XPS, the DEZn adsorbed at monolayer is characterized by a  $Zn(2p_{3/2})$  binding energy of 1023.2 eV. This is exactly the same value as observed for the molecular adsorption of DEZn on the GaAs(100) surface.<sup>8</sup> In the  $C(1s)$  region of the XPS, a broad peak is observed at 284.4 eV, which is resolved into two Gaussian-type peaks of equal intensity centered at 284.6 and 284.0 eV, each with a FWHM of 1.9 eV (Fig. 3). The higher value is associated with the methyl group C, and the lower value with the C bound to the Zn. Two C peaks, at 284.7 and 285.3 eV, were also observed following  $C_2H_5I$  adsorption on the same Pd(100) surface.<sup>5</sup>

At submonolayer coverage, photoemission peaks in the UPS emerge at 6.2, 8.0, 9.0, and 12.5 eV. When a monolayer is formed, the peaks lie at somewhat higher energy, at 4.0, 7.4, 9.2, 11.6, and 14.5 eV (Table I). If the gas-phase photoelectron spectrum of DEZn and the gas-phase ionization potentials are considered,<sup>13</sup> these latter peaks can be assigned to the two, not resolved  $Zn-C \sigma_u$  and  $Zn-C \sigma_g$  orbitals, to the  $Zn(4s)$  band mixed with the  $C(2p)$ , to the more or less resolved emissions of the  $C-H \sigma$  bonds, to the "alkyl" substituent and to the  $Zn(3d)$  levels.<sup>13</sup> When the work function and relaxation effects are taken into account, the peak at 14.5 eV (which is outside the energy range sampled in the gas-phase spectrum) can be readily assigned to the  $C-C \sigma$  bond similarly as for other  $C_2$  compounds.<sup>5,7</sup> These assignments are supported by the strong dependence of the valence-level intensities between the He I and He II photon spectra. This effect was earlier observed for compounds  $R_nM$  ( $R=CH_3$ ,  $C_2H_5$ , and  $M=Zn, Cd, Hg$ ), where the most prominent features were the large relative cross sections of the  $d$  levels in the He II, and of the  $C-H \sigma$  bonds in the He I photoelectron spectra.<sup>13</sup>

The position of the topmost band below the Fermi level reveals a strong dependence ( $\sim 0.9$  eV) on the energy of photon excitation. It appears that the highest-lying orbitals ( $Zn-C \sigma_u$  and  $Zn-C \sigma_g$ ) are strongly perturbed, very probably due to bonding with the Pd surface. A similar feature was established in the interaction of  $CH_2I_2$  with the Pd(100) surface.<sup>7</sup>

The observed shift (1.0–1.5 eV) in the He II photoelectron spectrum to higher binding energy with increase of the surface concentration of DEZn {which persists after correction with the substrate work function [ $\Phi_{Pd(100)} + \Delta\Phi_{DEZn/Pd(100)}$ ]} is attributed to the final state extra atomic relaxation on the part of the neighboring DEZn molecules in the adsorbed layer. Similar shifts are observed for all valence-level bands of DEZn in the He I excited UPS and core-level orbitals of  $Zn(2p_{3/2})$  and  $C(1s)$ . This relaxation effect results in values of  $0.6 \pm 0.1$ ,  $1.5 \pm 0.3$ ,  $0.6 \pm 0.1$ , and  $0.5 \pm 0.1$  eV for the He I, the He II UP spectra, and  $Zn(2p_{3/2})$  and  $C(1s)$  in the XP spectra, respectively.

With regard to the UPS and EELS data for the  $Zn(0001)$  surface,<sup>14</sup> the losses of adsorbed DEZ observed in the EELS at 90 K (Fig. 5) can be attributed to the transition from  $Zn-C \sigma$  orbitals to an empty orbital above the Fermi level (loss a),

to the excitation from the  $C-H \sigma$  orbital to an unfilled orbital in the Pd  $d$ -band at  $E_f$  (loss b), and to the transitions from the "alkyl" orbital and from  $Zn(3d)$  to the empty orbital (losses c and d, respectively). This empty orbital is the same as for loss A, and it is located between the Fermi and vacuum levels at  $E=2.0 \pm 0.2$  eV. As concerns the data in the partial electron-level diagram of Zn [the distance between  $4s^2$  and  $4p$  is 5.8 eV (Ref. 15)], this empty orbital can be the  $Zn(4p)$  orbital. The energy levels of the electron orbitals for the  $(C_2H_5)_2Zn/Pd(100)$  system are shown in Fig. 5.

## B. Dissociation of DEZn

An important question to be answered is the dissociation of DEZn. This is to be expected at submonolayer coverage, during illumination and heating of a molecularly adsorbed layer.

Let us start with an examination of the Zn region of the XP spectrum, which is expected to be more sensitive to the environment than the  $C(1s)$  signal. The binding energy of  $Zn(2p_{3/2})$  is 1021.45 eV.<sup>10</sup> When Zn is deposited in an atomically adsorbed state on solid surfaces, the binding energy for  $Zn(2p_{3/2})$  lies between 1020.0 and 1021.0 eV.<sup>8,16</sup> We obtained a value of 1021.0 eV at low coverage and also when the monolayer was heated to above 500 K. At this temperature all the hydrocarbon fragments were desorbed. This strongly suggests that at submonolayer coverage DEZn dissociates to a Zn atom and  $C_2H_5$  even at 90 K. With increase of the coverage, molecular adsorption becomes the predominant adsorption pathway.

However, molecularly adsorbed DEZn dissociates during heating of an adsorbed layer to above the desorption temperature,  $\sim 172$  K, of weakly bound DEZn. This is clearly revealed in the formation of a new peak at 1021.4 eV [Fig. 8(a)]. The fact that the position of the  $Zn(2p_{3/2})$  peak remains practically unaltered above 222 K suggests that the dissociation is complete below this temperature. The slight change in binding energy observed above 347 K may be a result of the desorption of strongly bound hydrocarbon fragments formed in the reactions of  $C_2H_5$  species.

Accepting this interpretation we may also conclude that the  $C(1s)$  peak (at 283.9–284.0 eV) observed at low DEZn coverage [Fig. 7(b)] is associated with  $C_2H_5$  species formed in the surface dissociation process. Another possibility is that this binding energy value belongs to the decomposition fragments of  $C_2H_5$  moieties.

To decide between these alternatives we may take into account the BE values for  $C(1s)$  in  $C_2H_5$  species on different surfaces. Note that the BE for  $C(1s)$  of adsorbed  $CH_2$  and  $CH_3$  on Pd(100) were found to be 283.9 and 284.6 eV, respectively.<sup>3,4</sup> In the case of thermal dissociation of  $C_2H_5I$  on Ag(111), the  $C(1s)$  BE of 284.3 eV was attributed to adsorbed  $C_2H_5$ .<sup>17</sup> A similar value, 284.0 eV was registered when  $C_2H_5Cl$  was photolyzed on the Ag(111) surface.<sup>18</sup> In the case of the Pt(111) surface a BE of 283.9 eV (observed between 160–200 K) was associated with adsorbed  $C_2H_5$  fragment.<sup>19</sup> Following irradiation of adsorbed  $C_2H_5I$  at 90 K, where the further reactions of adsorbed  $C_2H_5$  was expected to be minimal, a BE of 284.1 eV for  $C(1s)$  was registered.<sup>5,6</sup>

Taking into account all these observations it is reasonable to conclude that the 283.9–284.0 eV BE value for C(1s) belongs to adsorbed C<sub>2</sub>H<sub>5</sub> species.

It should be pointed out that this value may be influenced by the presence of the electropositive zinc atom, which can modify the local surface electronic structure to such an extent that the C<sub>2</sub>H<sub>5</sub>-surface interaction is significantly perturbed relative to that for a zinc-free surface.

The above interpretation suggests that the work function decrease (1.05 eV) at submonolayer [stage I in Fig. 1(B)] is mostly caused by the dissociation products (C<sub>2</sub>H<sub>5</sub> and Zn) of DEZn. As such a small amount of Zn exerts a very slight influence on the work function of Pd(100) (~0.1 eV) [this can be judged from the high-temperature part of the curve in Fig. 1(D)], the 1.05 eV decrease is mostly due to C<sub>2</sub>H<sub>5</sub> fragment. When molecularly adsorbed DEZn is also produced on the surface [stages II and III in Fig. 1(B)] at higher DEZn exposures, the work function increases by about 0.5 eV. [The work function of the system is -0.55 eV lower than that of clean Pd(100).] In this case we have adsorbed C<sub>2</sub>H<sub>5</sub>, Zn, and DEZn on the surface. The above features demonstrate that molecularly adsorbed DEZn alone causes a relatively small work function decrease, in harmony with the small dipole moment of the molecule.<sup>12</sup>

The work function changes observed for annealed systems at low and high coverages [Fig. 1(D)] are in accord with the above picture. At submonolayer, the situation is simple: the desorption of hydrocarbons, which are assumed to be responsible for the large lowering of the work function, results in a significant increase in the work function. More complex behavior was obtained at the monolayer [curve b, Fig. 1(D)]. The sharp decrease observed at 210–220 K can be attributed to the dissociation of molecularly adsorbed DEZn and to the production of hydrocarbon fragments and Zn adatoms. As most of the hydrocarbons produced desorb below 220 K, this should lead to an increase in the work function above 220 K, as shown in Fig. 1(D). The data in this figure also suggest that the Zn adatoms at this coverage lower the work function of Pd(100) by about 0.5–0.6 eV. The slight changes observed above 500 K mainly result from the interaction of Zn with the Pd surface.

The different modes of adsorption of DEZn at low and high coverages give rise to only slight changes in the He II UP spectra (Fig. 3). In the submonolayer region, where the XPS results suggest the dissociation of DEZn, photoemission signals are registered at (6.2), 8.0, 9.0, and 12.5 eV. Very nearly the same signals, at 8.3, 9.0, and 12.3 eV, were found after the complete photodissociation of C<sub>2</sub>H<sub>5</sub>I on the Pd(100) surface at 90 K, which were associated with the C<sub>2</sub>H<sub>5</sub> species.<sup>5</sup> This strengthens the idea that C<sub>2</sub>H<sub>5</sub> remains intact at 90 K following the dissociation of DEZn.

### C. Thermal stability and reactions of adsorbed C<sub>2</sub>H<sub>5</sub> species

Analysis of TPD, UP, and XP spectra suggests that C<sub>2</sub>H<sub>5</sub> undergoes reactions parallel to its formation including dehydrogenation to ethylene and hydrogenation to ethane. As ethane does not adsorb on the Pd(100) surface above 120 K, we can conclude that the release of ethane is a reaction lim-

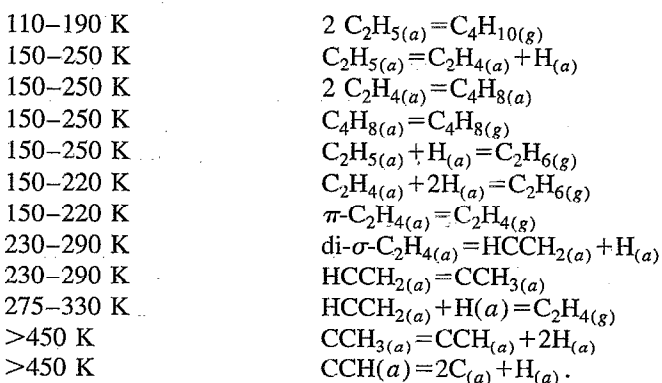
ited process. This is not valid for ethylene, which remains adsorbed after its formation. Taking into account the behavior of adsorbed ethylene on metal surfaces,<sup>20–26</sup> this desorbing ethylene, with a *T<sub>p</sub>* = 207 K, very likely corresponds to the weakly held II-bonded form.

Among the most interesting results is the appearance of butane and butene in the desorption products. The formation of butane indicates the dimerization of C<sub>2</sub>H<sub>5</sub> produced in the dissociation of DEZn. Butene may be formed through the coupling of two ethylene molecules or the dehydrogenation of butane formed in the recombination of C<sub>2</sub>H<sub>5</sub> species.

XP spectra suggest that adsorbed hydrocarbon fragments remain on the surface even above 236 K, as indicated by the weak and broad C(1s) peak at 284.6–284.4 eV. Similar feature was observed following the CH<sub>2</sub>I<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>I adsorption on Pd(100) and annealing the adsorbed layer to 250–290 K, and were attributed to the formation of C<sub>2</sub>H<sub>n</sub> species from the di-σ-bonded ethylene.<sup>3–5</sup>

Taking into account the reactions of di-σ-bonded ethylene on Pd and other surfaces we came to the conclusion that this highly stable hydrocarbon fragments is ethylidyne (CCH<sub>3</sub>).<sup>3–5</sup> This may ultimately decompose to CH fragments and surface carbon above 450 K.

On summing up we propose the following scheme for the reactions of adsorbed C<sub>2</sub>H<sub>5</sub> formed in the dissociation of DEZn:



As we did not detect the evolution of hydrogen in this temperature range, we may assume its dissolution in the palladium bulk.

Similarly as in the decomposition of CH<sub>3</sub>(a) and CH<sub>2</sub>(a) on Pd(100),<sup>3,4</sup> our sample does not accumulate surface carbon as a result of such processes because of very efficient surface to bulk transport of carbon at high temperature.<sup>21</sup>

### D. Effects of Zn adatoms on the reactions of C<sub>2</sub>H<sub>5</sub>

Features similar to those described above were observed when a C<sub>2</sub>H<sub>5</sub> species on Pd(100) was produced by the dissociation of C<sub>2</sub>H<sub>5</sub>I.<sup>5,6</sup> A comparison of the two systems indicates a striking effect of the presence of Zn; the production of C<sub>4</sub> compounds, not observed following C<sub>2</sub>H<sub>5</sub>I adsorption on Pd(100).

The formation of ethylene and ethane is also altered, whereas the C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio was 0.5 for the iodide-dosed Pd, the corresponding value in the present case is 1.4. Comparison of XPS and UPS results for the annealed systems

suggests that the stability of hydrocarbon moieties, existing on the surface above 300 K (see previous section), is significantly higher in the presence of Zn adatom.

### E. Photolysis of adsorbed $(C_2H_5)_2Zn$

In our previous studies on Pd(100) surface we found that illumination of adsorbed  $CH_3Cl$  and  $CH_3I$  with a full arc of mercury induces cleavage of both the C–Cl and C–I bond in alkyl halides,<sup>3–6</sup> and the presence of potassium adatoms further increases the extent of photolysis.<sup>27</sup> From a study of the wavelength dependence, it was concluded that optical excitation of the substrate to produce photoelectrons plays a dominant role in the photodissociation of C-halogen bonds.<sup>27</sup>

Although we did not perform detailed measurements in the present case, the effects of photolysis of adsorbed DEZn were established. (A heat effect can be excluded as the temperature of the sample during illumination was not higher than 90–95 K.) Illumination of a submonolayer at 90 K caused completion of the dissociation of DEZn, as indicated by a gradual elimination of the  $Zn(2p_{3/2})$  peak at 1022.4 eV. When a monolayer of adsorbed DEZn was irradiated, a shift in binding energy for  $Zn(2p_{3/2})$  also occurred. However, a complete dissociation for a monolayer was not achieved even after 85 min irradiation. This is in contrast with the behavior of  $C_2H_5I$ , where (under exactly the same experimental conditions) the complete photodissociation of adsorbed monolayer required only 7 min.<sup>6</sup> The effect of photolysis is also revealed by the postirradiation TPD spectra; the weakly bound DEZn is almost completely eliminated. The products of  $C_2H_5$  reactions are only slightly affected; there is an increase in the amount of butene formed.

As regards the mechanism of photocexcitation, we assume that, similar to the case of other alkyl halides on Pd(100),<sup>3,6,27</sup> the photoelectrons generated by illumination may play an important role in the enhanced dissociation of DEZn. The photoelectrons may attach to an adsorbed DEZn to form a partially negatively charged species that dissociates more easily. In the case of alkyl halides, this assumption was supported by the results obtained with the use of different cutoff filters. This process could occur easily in the present case taking into account the low-lying empty orbital  $[Zn(4p)]$  of DEZn [Fig. 5(b)]. The fact that the photolysis at monolayer was rather limited, compared to adsorbed  $C_2H_5I$ , indicates that the quenching process is much faster for DEZn. The lack of empty adsorption sites on Pd surface at monolayer coverage may also hinder the occurrence of the photodissociation. It is also possible that the primary product of the photodissociation at monolayer is  $C_2H_5Zn$ ; the binding energy for Zn in this compound is obviously higher than that for Zn metal. The formation of  $ZnC_2H_5$  intermediate was observed in the photolysis of DEZn in the gas phase.<sup>28</sup>

However, we cannot exclude the contribution of a direct photoexcitation of adsorbed DEZn. This route of photolysis is supported by the fact that the highest photon energy of the mercury lamp used in this study (5.3 eV) is almost the same as the energy level of the first excited state of DEZn (5.1 eV) in the gas phase photoabsorption spectrum.<sup>29</sup> The large absorption cross sections for organometallic compounds, in-

cluding zinc compounds,<sup>30</sup> may also strengthen this excitation process.

### F. Behavior of Zn on Pd(100) surface

The final product of decomposition of DEZn on the Pd(100) surface is metallic Zn. This allows both conclusions concerning its interaction with Pd, and a comparison with other Zn-containing systems. Zn adatoms (also produced by the decomposition of DEZn) interacted weakly with GaAs(100) and desorbed near 530 K.<sup>8</sup> From the Si(100) surface, Zn metal desorbed with  $T_p = 500$  K.<sup>9</sup> These relatively low desorption temperatures indicate that Zn interacts rather weakly with these surfaces. Zn atoms adsorb more strongly on transition metals. For the Zn/Ru system, the temperature of Zn desorption depended on the Zn coverage; it was 460 K for a multilayer, 490 K for the second layer, and 720 K for the first layer.<sup>16,31</sup> The large separation ( $\sim 250$  K) between the desorption of the monolayer and multilayer states indicated the existence of a very strong interaction between Zn and Ru.

TPD measurements show that Zn metal desorbs from the Pd(100) surface only at extremely high temperature,  $T_p = 1100$  K. This peak temperature displays no variance with the coverage attained by DEZn decomposition. We believe that this high desorption temperature is a result of alloy formation between Zn and Pd. As Zn-promoted Pd is an effective catalyst for several reactions, it seems worthwhile to perform a more detailed study of this system (including XPS, ELS, and AES measurements). This will form the subject of a separate publication.

### V. CONCLUSIONS

- (1)  $(C_2H_5)_2Zn$  adsorbs dissociatively at submonolayer coverages on the Pd(100) surface at 90 K, and molecularly at higher coverages. Molecularly adsorbed species dissociate at 170–230 K.
- (2) The primary products of dissociation are adsorbed  $C_2H_5$  and Zn.
- (3) The  $C_2H_5$  species undergoes dehydrogenation to yield  $C_2H_4$ , and also hydrogenation to  $C_2H_6$ . Coupling reactions to  $C_4H_{10}$  and  $C_4H_8$  occur too. The Zn produced in the dissociation interacts strongly with the Pd and desorbs only at around 1100 K.
- (4) Illumination of the adsorbed layer with a Hg arc lamp induced the desorption of weakly bound  $(C_2H_5)_2Zn$  and enhanced the extent of dissociation, even at 90–95 K.

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