Selective collision-induced desorption: Measurement of the $\pi$-bonded $C_2H_4$ binding energy on Pt$\{111\}$ precovered with atomic oxygen

D. Velic and Robert J. Levis

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

(Received 20 November 1995; accepted 13 February 1996)

Collision-induced desorption (CID) is used to selectively probe the well depth of one particular adsorbate–surface potential energy surface in the presence of multiple adsorbates. Ethylene adsorbed at saturation coverage on Pt$\{111\}$ precovered with atomic oxygen represents a system with three adsorbates: oxygen and two different adsorption forms of ethylene. Both the $\pi$-bonded ethylene ($\pi$-C$_2$H$_4$) and di-$\sigma$-bonded ethylene (di-$\sigma$-C$_2$H$_4$) species are formed at coverages of 0.25 ML preadsorbed atomic oxygen and 0.15 ML ethylene on Pt$\{111\}$ at 100 K. Deconvolution of Al K$\alpha$ x-ray photoelectron (XP) spectra suggests that C(1$s$) XP binding energy is 283.1 eV for $\pi$-C$_2$H$_4$ and is 283.7 eV for di-$\sigma$-C$_2$H$_4$. The C(1$s$) XP spectra together with the CID result reveal that the coverage ratio of $\pi$-C$_2$H$_4$ and di-$\sigma$-C$_2$H$_4$ at saturation at 100 K is $\sim$1:1. The selectivity of CID is demonstrated by desorbing only $\pi$-C$_2$H$_4$ using a neutral Xe atomic beam with translational energies ranging from 2.1 to 4.1 eV. In this translational energy range, di-$\sigma$-C$_2$H$_4$ remains intact on the O/Pt$\{111\}$ surface. The threshold energy for CID of $\pi$-C$_2$H$_4$ was determined by extrapolation to the Xe energy where the CID cross section is equal to zero. The threshold of 2.4±0.1 eV can be related to the $\pi$-C$_2$H$_4$–Pt binding energy using classical collision mechanics. An upper limit for the $\pi$-C$_2$H$_4$ binding energy on O/Pt$\{111\}$ is calculated to be 0.95±0.04 eV from the CID threshold measurement, using a Pt effective mass of 1.5 Pt atom. © 1996 American Institute of Physics.

I. INTRODUCTION

The collision-induced desorption (CID) experiment employs a hyperthermal, neutral, noble gas atom to eject an adsorbate from a surface into the gas phase. Applying gas phase molecular collision dynamics, the CID experiment can be used to nonthermally probe the potential energy surface (PES) of adsorbate–surface systems. Zeiri et al. first suggested that analysis of the desorbate angular and kinetic energy distributions could be useful for determining an adsorbate–surface binding energy. Beckerle et al. measured the cross section for CID of physisorbed methane on Ni$\{111\}$ as a function of both the kinetic energy and angle of incidence of the hyperthermal Ar atom. Szulczewski and Levis proposed that the threshold energy for CID is directly proportional to the adsorbate–surface binding energy and the methane–Ni$\{111\}$ binding energy was calculated using a hard sphere/cube model. In this calculation, the mechanism of CID was approximated by three steps. The first step is a binary collision between the incident hyperthermal atom and the adsorbate. The second step is a subsequent impulsive interaction between the adsorbate and the surface. The third step assumes desorption of the adsorbate from the surface if the momentum component of the adsorbate translational energy directed away from the surface exceeds the binding energy. We have subsequently investigated the CID of the chemisorbed systems: ammonia on Pt$\{111\}$ (Ref. 5) and di-$\sigma$-bonded ethylene on Pt$\{111\}$ (Ref. 6) which represent systems with one chemical bond and two chemical bonds per adsorbate with the surface, respectively.

In this paper the use of CID is extended to investigate a multiadsorbate system. Ethylene adsorbed on Pt$\{111\}$ precovered with atomic oxygen (C$_2$H$_4$/O/Pt$\{111\}$) represents a system with three adsorbates as shown in scheme 1.

These adsorbates are atomic oxygen and two different forms of ethylene, $\pi$-C$_2$H$_4$ and di-$\sigma$-C$_2$H$_4$. The $\pi$-C$_2$H$_4$ adsorbate is, presumably, more weakly bound on O/Pt$\{111\}$ than the di-$\sigma$-C$_2$H$_4$ adsorbate, because the temperature programmed desorption (TPD) peak temperature is 185 K for $\pi$-C$_2$H$_4$ as compared with 265 K for di-$\sigma$-C$_2$H$_4$. Thus, the C$_2$H$_4$/O/Pt$\{111\}$ system, having two C$_2$H$_4$ adsorbates with clearly different binding energies, was chosen to investigate the selectivity of the CID technique. The $\pi$-C$_2$H$_4$ species is formed on Pt$\{111\}$ only under specific conditions. In the present study, $\pi$-C$_2$H$_4$ is formed in the presence of preadsorbed atomic oxygen at 100 K. The coexistence of $\pi$-C$_2$H$_4$ with di-$\sigma$-C$_2$H$_4$ has been previously demonstrated using high resolution electron energy loss spectroscopy (HREELS) at the C$_2$H$_4$ saturation coverage when 0.23 monolayer (ML) of...
atomic oxygen was preadsorbed on Pt(111) at 92 K. In that study, a band measured at 720 cm⁻¹ was assigned to the CD₂ wagging mode of π-bonded ethylene by comparing the EELS spectra at 92 and 280 K. Ultraviolet photoelectron spectroscopy⁸ (UPS) binding energies have been assigned for C₂H₄/O/Pt(111) as π₁C–C at 4.2 eV, π₁CH₂ at 6.6 eV, σ₁C=O/π₁C–C at 8.9 eV and π₁CH₂ at 9.9 eV supporting the formation of π-C₂H₄. Near edge x-ray absorption fine structure (NEXAFS) features¹⁰ in the spectrum of C₂H₄/O/Pt(111) were also assigned as π² at 285 eV and σ¹C from a range from 294 to 301 eV using synchrotron radiation at an angle of 50° incidence.

Examples of π-C₂H₄ bound to transition metals¹³ can be described by the Dewar–Chatt–Duncanson model or the πσ parameter¹² proposed by Stuve and Madix. For instance, the πσ parameter has been proposed as a measure of the rehybridization of carbon from sp² to sp³. The value of the πσ parameter for C₂H₄ in the gas phase was defined to be 0, representing sp³ hybridization with an undistorted π¹C–C bond. Zeise’s salt represents a Pt–π-C₂H₄ bond with electron density sharing between the π¹C–C bond and the Pt atom and the πσ parameter is 0.38. For the C₂H₄/Pt(111) system at 100 K the πσ parameter is 0.92, representing sp³ hybridization with two strong C–Pt bonds.⁶ The π-C₂H₄ species was not formed on Pt(111) at 100 K, although this species has been formed and characterized by TPD and EELS on (1×1) Pt(110),¹³ (2×1) Pt(110),¹⁴ and on Pt(210).¹⁵ This formation of π-C₂H₄ species for metallic coordination of 7 and below¹⁶ was supported by extended-Hückel calculations. The π-C₂H₄ species has been observed on Pt(111) only at temperatures below 52 K as characterized by TPD and UPS.¹⁷,¹⁸ At temperatures above 52 K the π-C₂H₄ transformation into di-σ-C₂H₄ occurred. Calculations¹⁹ revealed no barrier between π-C₂H₄ and di-σ-C₂H₄ on Pt(111). The π-C₂H₄ species has been observed at 100 K on O/Pt(111),⁷–¹⁰ on Pt(111) precoated with cesium,⁶,¹⁷ on Pt(111) precoated with potassium⁸,¹⁰,²⁰–²² and on Pt(111) precoated with potassium and oxygen.²³ All predeposited elements were in a subsurface layer coverage and, presumably, their role was to perturb the Pt PES. This perturbation is typically described by electrostatic and donation/back donation models²² and results in the formation of the π-C₂H₄ species. In this paper CID is investigated for C₂H₄ on Pt(111) precoated with atomic oxygen. Oxygen has been observed to adsorb molecularly on Pt(111) as a peroxo species below 150 K (Ref. 24) with a saturation coverage θ₀₂=0.44 ML.²⁵ Molecular oxygen was observed to partially desorb at 160 K and partially dissociate into atomic oxygen. The dissociation can take place even at lower temperatures (~92 K) when the molecular oxygen coverage is below the saturation coverage.²⁵ In the 150–500 K temperature range²⁴ atomic oxygen is present with a saturation coverage θ₀₂=0.25 ML and forms a (2×2) low energy electron diffraction (LEED) pattern. In the 1000–1200 K temperature range²⁴ a subsurface oxide may form associated with surface impurities.⁹

In the experiments reported in this paper, selective CID was used to collisionally desorb only the π-C₂H₄ adsorbate, leaving the di-σ-C₂H₄ adsorbate intact on the O/Pt(111) surface. In addition to investigating the selectivity of the CID technique we also use CID to determine the π-C₂H₄–Pt(111) binding energy. The CID experiment is one of the few techniques including TPD,²⁶ isosteric measurements,²⁷ and microcalorimetry,²⁸ capable probing adsorbate-surface chemical binding energies. As a nonthermal tool this method can also shed some light on the desorption energy measurements²⁶,²⁸ made using thermal techniques.

The remainder of this paper is organized as follows. In Sec. II we briefly describe the experimental apparatus. In Sec. III the preparation of C₂H₄/O/Pt(111) system is described, as well as the characterization of the π-C₂H₄ and di-σ-C₂H₄ species using x-ray photoelectron spectroscopy (XPS). The difference in C(1s) XP binding energy between the π-C₂H₄ and di-σ-C₂H₄ species is used to monitor the π-C₂H₄ surface coverage to demonstrate the selectivity of CID. In Sec. IV the binary collision energy transfer model is used to relate the threshold Xe energy for CID of π-C₂H₄ to the π-C₂H₄–Pt chemical binding energy. Sections V and VI provide a discussion and a summary of the findings, respectively.

II. EXPERIMENT

Experiments were performed in an ultrahigh vacuum (UHV) chamber, with a base pressure of 2×10⁻¹⁰ torr, coupled to a hyperthermal neutral atomic beam source. The experimental apparatus has been described previously.⁵ Briefly, the UHV system contains facilities for electron-beam heating, liquid nitrogen cooling, ion sputtering, quadrupole mass spectroscopy (QMS), and XPS. All of the XP spectra reported here employed 230 W of Al Kα radiation at 1486.7 eV. The O(1s) XP spectra were used to verify a constant coverage of atomic oxygen. The C(1s) XP spectra were monitored to differentiate π-C₂H₄ from di-σ-C₂H₄ and to quantify the π-C₂H₄ coverage before and after CID as described subsequently. The desorbed ethylene was monitored in the gas phase by comparing the QMS cracking pattern of backfilled C₂H₄ with the QMS signal of collisionally desorbed C₂H₄. The Pt(111) crystal was cleaned by cycles of argon sputtering (5 kV) and annealing at 1200 K. Between individual experiments, residual surface carbon was removed by oxygen treatment (10⁻⁷ torr) at 1000 K and afterwards the crystal was flashed to 1200 K. No impurities were detected at the XPS detection level (~1%). Except where noted, all the experiments were performed with the sample maintained at a temperature of 100 K.

The CID experiment is performed using a hyperthermal Xe beam produced via a supersonic free-jet expansion from a heated nozzle.²⁹ The nozzle system is constructed from a sealed molybdenum tube with a 100 μm diameter conical orifice. A mixture of Xe seeded in (either 1/2% or 1%) H₂ was used to form the supersonic beam. Note that control experiments employing only the H₂ carrier gas revealed no change of the initial C(1s) and O(1s) XP spectra for the C₂H₄/O/Pt(111) system. The atomic beam nozzle could be heated up to 1200 K to vary the beam translational energy.
The temperature of the nozzle was measured by chromel-alumel thermocouple attached to the outside of nozzle tube. The beam travels through a 1 mm diameter skimmer placed 2 cm away from the nozzle. The translational energy of the Xe beam was varied from 2.1 to 4.1 eV and was determined by a time-of-flight (TOF) technique using a quadrupole mass detector as described previously. The QMS was used to determine the flux and translational energy distribution of the Xe beam prior to each experiment. For instance, a typical flux for the atomic beam at 3.0 eV of translational energy was $8 \times 10^{14}$ Xe atoms/sec cm$^2$. Three angles of incidence, $0^\circ$, $30^\circ$ and $45^\circ$, were used to investigate the angular dependence of CID for C$_2$H$_4$/O/Pt[111].

### III. RESULTS: XPS CHARACTERIZATION AND SELECTIVE CID

The ratio of $\pi$-C$_2$H$_4$ and di-$\sigma$-C$_2$H$_4$ is dependent on the atomic oxygen surface coverage, therefore the preparation of a constant O/Pt[111] system was essential. The atomic oxygen coverage was interrogated by XPS and was consistent with previously reported XPS characterizations. The following procedure was used to prepare the atomic oxygen on the Pt[111] surface. The clean Pt[111] surface was saturated with 6 L (1 L = $10^{-6}$ Torr sec) of molecular oxygen at 100 K forming $\theta_o = 0.44$ ML. The sample was then annealed to 170 K to convert the molecular oxygen into atomic oxygen. The initial saturation coverage of $3.8 \times 10^{14}$ oxygen atoms/cm$^2$ can be approximately doubled using extended temperature cycling or external atomization. Therefore, the O$_2$ exposure and annealing process was performed only once to maintain the constant atomic oxygen coverage. Control experiments were performed to ensure that neither the ionization gauge nor the quadrupole mass spectrometer altered the atomic oxygen coverage. CID experiments were performed only when $\theta_o / \theta_3 = 0.25/0.44 = 0.57 \pm 5\%$. In Fig. 1, the O(1$s$) XP spectra for the (a) $\theta_3$, and (b) $\theta_o$ are shown. An atomic oxygen coverage of 0.25 ML, as shown in Fig. 1(b), was used in all CID experiments. After the atomic oxygen monolayer was prepared, the crystal was cooled to 100 K and C$_2$H$_4$ was then adsorbed on the surface. To determine whether the Xe beam would desorb atomic oxygen from C$_2$H$_4$/O/Pt[111], the O(1$s$) XP spectra were monitored before and after the CID experiments. The typical O(1$s$) XP spectra for C$_2$H$_4$/O/Pt[111] system before and after CID are shown in Figs. 1(c) and 1(d), respectively. No change in the O(1$s$) XP spectra was observed between Figs. 1(c) and 1(d). This suggests that no CID of atomic oxygen occurred at the energies used in this study. As another control experiment we used a Xe atomic beam with translational energy of 4.1 eV to collisionally prepare a monolayer of atomic oxygen on Pt[111] from a saturation coverage of molecular oxygen as shown in Fig. 1(a), at 100 K. The spectrum is shown in Fig. 1(e) and is almost identical with the thermally prepared atomic oxygen in Fig. 1(b) normally used in all experiments. This also supports the observation that the atomic oxygen adsorbed on Pt[111] at 100 K is collisionally stable in the CID experiments.

To calibrate the C$_2$H$_4$ coverage on O/Pt[111], the C(1s) XP spectra were first recorded as a function of C$_2$H$_4$ exposure as shown in Fig. 2. In each spectra the background due to the Pt 4d$_{5/2}$ feature has been subtracted. The integrated intensity of the C(1s) XP feature is plotted as a function of C$_2$H$_4$ exposure in Fig. 3. Steininger et al. reported that the saturation coverage of C$_2$H$_4$ adsorbed at 92 K on Pt[111] precovered with 0.23 ML atomic oxygen was reduced to 60% of the saturation coverage on clean Pt[111]. The saturation exposure for C$_2$H$_4$ on O/Pt[111] was measured to be approximately 1.3 L as shown in Fig. 3. This value is consistent with 60% of the 2.2 L saturation exposure reported for the C$_2$H$_4$ adsorption on clean Pt[111]. The C$_2$H$_4$ saturation coverage on clean Pt[111] was reported to be 0.25 ML. Assuming constant sticking coefficient and using our measured 60% coverage value, the C$_2$H$_4$ saturation coverage on O/Pt[111] was estimated to be 0.15 ML.

Steininger et al. demonstrated the coexistence of $\pi$-C$_2$H$_4$ and di-$\sigma$-C$_2$H$_4$ on 0.23 ML O/Pt[111] at 92 K at C$_2$H$_4$ saturation coverage using EELS and TPD. At low C$_2$H$_4$ coverages no desorption feature was observed for the more weakly bound $\pi$-C$_2$H$_4$ species and only at about 300 K did the di-$\sigma$-C$_2$H$_4$ species desorb. The TPD data demonstrated that with increasing ethylene coverage, the di-$\sigma$-C$_2$H$_4$ desorption feature saturated and became broader, eventually
formed a doublet. At high C₂H₄ coverages the desorption of π-C₂H₄ occurred. At the saturation coverage, π-C₂H₄ desorbed at 185 K and di-C₂H₄ desorbed at 265 K. This di-C₂H₄ desorption temperature was in good agreement with subsequent TPD measurements ranging from 235 K ~ Ref. 9 to 275 K ~ Ref. 8. Using EELS, Steininger et al. 7 concluded that π-C₂H₄ was the initial form of adsorbed C₂H₄ on O/Pt[111]. The fact that no π-C₂H₄ desorbed at low C₂H₄ coverages was attributed to a thermal conversion into di-σ-C₂H₄ which consequently desorbed at higher temperatures. 7

Some insight into the surface reaction chemistry of C₂H₄ on O/Pt[111] can be obtained by analyzing both the C(1s) XP binding energy shift and the change in the full width at half maximum ~FWHM~ of the C(1s) XP spectra as a function of C₂H₄ exposure. The C(1s) XP binding energy slightly shifts from an initial value of 283.3 to 283.4 eV at C₂H₄ saturation. The FWHM changes from 1.9 to 2.2 eV as the C₂H₄ exposure is increased, as shown in Fig. 4. This is consistent with the presence of two C₂H₄ species on O/Pt[111]. Figure 2 displays the deconvolution of the spectra corresponding to 0.3, 0.5, 0.7, 1.0, and 1.3 L C₂H₄ exposure. The low coverage spectrum shown in Fig. 2 ~a~ represents the initially adsorbed C₂H₄ species and was fit with a 1.9 eV FWHM Gaussian. The spectrum shown in Fig. 2 ~b~ reveals an increase in the C₂H₄ surface coverage with no change of FWHM indicating the presence of only the initially formed C₂H₄ species. At 0.7 L exposure, as shown in Fig. 2(c), a measurable increase in the FWHM was observed. This increase is consistent with the presence of two C₂H₄ species: π-C₂H₄ and di-σ-C₂H₄. At 1.0 L exposure, shown in Fig. 2(d), the FWHM of C(1s) XP feature further increases due to the additional formation of the second C₂H₄ species. Figure 2(e) shows the C(1s) XP spectrum of the saturation C₂H₄ coverage, deconvoluted into two peaks. Using Steininger’s suggestion 7 of initial C₂H₄ formation on O/Pt[111], we can assign the initially formed C₂H₄ species as π-C₂H₄. The di-σ-C₂H₄ formation contribution was then observed at 0.7 L exposure suggesting a stepwise formation: first π-C₂H₄: second di-σ-C₂H₄. Therefore the two features of C(1s) XP spectrum shown in Fig. 2(e) are assigned for di-σ-C₂H₄ at 283.7 eV and for π-C₂H₄ at 283.1 eV. This
formation mechanism can be rationalized using donation/back donation mechanism. On clean Pt(111) at 100 K, C$_2$H$_4$ exclusively adsorbs as di-σ-C$_2$H$_4$ species as soon as atomic oxygen is preadsorbed the Pt(111) PES is perturbed. This perturbation is described by the electronegative oxygen withdrawing of electrons from the Pt(111) surface. The adsorbing C$_2$H$_4$ can either donate σ electrons into Pt d band and form the π-C$_2$H$_4$ species or get back donation from the Pt d band into the π* orbital and form the di-σ-C$_2$H$_4$ species. In a case of 0.25 ML O/Pt(111) the Pt surface electron deficiency is presumably high and forces C$_2$H$_4$ to donate electrons resulting in the initial π-C$_2$H$_4$ formation. As soon as the lowest energy adsorption sites are titrated by π-C$_2$H$_4$, the formation of di-σ-C$_2$H$_4$ is possible. Zhou et al. investigated C$_2$H$_4$ adsorption at 100 K on Pt(111) precovered with potassium. This study showed the increasing π-C$_2$H$_4$/di-σ-C$_2$H$_4$ ratio as a function of potassium coverage. At low (less than 0.5 L) C$_2$H$_4$ exposures on 0.06 ML K/Pt(111) the π-C$_2$H$_4$ species thermally desorbed at 145 K. No di-σ-C$_2$H$_4$ desorption was observed, which was attributed to the di-σ-C$_2$H$_4$ thermal decomposition. At C$_2$H$_4$ exposures higher than 0.5 L, the di-σ-C$_2$H$_4$ desorption was observed at 285 K and the TPD features of both species increased steadily with C$_2$H$_4$ exposure. This experiment together with the EELS investigation suggested an almost simultaneous formation of both ethylene species on 0.06 ML K/Pt(111). The perturbation of the Pt(111) electronic structure caused by electronegative atomic oxygen and electropositive potassium are clearly different. The fact that both C$_2$H$_4$/O/Pt(111) and C$_2$H$_4$/K/Pt(111) systems form π-C$_2$H$_4$ suggests that the adsorption mechanism is determined by more than one process. Since the π-C$_2$H$_4$/di-σ-C$_2$H$_4$ adsorption chemistry as a function of C$_2$H$_4$ and preadsorbate surface coverages is complex, we focus on CID investigations at C$_2$H$_4$ saturation coverage on O/Pt(111). At this coverage, both π-C$_2$H$_4$ and di-σ-C$_2$H$_4$ coexist as clearly shown using EELS (Ref. 7) and our XPS measurements.

The CID scheme was used to further differentiate the two C$_2$H$_4$ species and to selectively quantify the π-C$_2$H$_4$ surface coverage. The TPD measurements for the C$_2$H$_4$/O/Pt(111) system suggest that the π-C$_2$H$_4$–Pt binding energy is weaker than the di-σ-C$_2$H$_4$–Pt binding energy. Therefore, we assume that a Xe atom having translational energy lower than the threshold for CID of di-σ-C$_2$H$_4$ will selectively desorb only π-C$_2$H$_4$. Obviously, the Xe atom must also have translational energy above the threshold for CID of π-C$_2$H$_4$. Using these assumptions and knowing the translational energy threshold for CID of di-σ-C$_2$H$_4$/Pt(111) of 5.2 eV (Ref. 6) we should be able to use a range of Xe translational energies less than 5.2 eV to effectively desorb the π-C$_2$H$_4$ species, presumably leaving the di-σ-C$_2$H$_4$ species intact on the O/Pt(111) surface. Note that since we have not measured the di-σ-C$_2$H$_4$ binding energy on O/Pt(111), we used the TPD temperature to provide some indication of the bond strength. The peak temperatures in the TPD spectra for di-σ-C$_2$H$_4$ in C$_2$H$_4$/O/Pt(111) and C$_2$H$_4$/Pt(111) are 265 and 280 K, respectively. This suggests that the di-σ-C$_2$H$_4$ binding in the C$_2$H$_4$/O/Pt(111) system is slightly weaker than in the C$_2$H$_4$/Pt(111) system. To be conservative, we used Xe translational energies of 4.1 eV and lower. As will be seen, these energies do not effect di-σ-C$_2$H$_4$. Figure 5(a) shows the saturation coverage of C$_2$H$_4$ adsorbed at 100 K on O/Pt(111). This coverage was used as an initial coverage in all CID experiments. As described previously, background subtraction, peak integration and deconvolution were used to identify at least two C(1s) XP features as shown in Fig. 2(e). Figure 5(a) shows the C(1s) XP spectrum of the initial state of C$_2$H$_4$/O/Pt(111) deconvoluted into the π-C$_2$H$_4$ and di-σ-C$_2$H$_4$ features; this XP spectrum is identical with that shown in Fig. 2(e). Figure 5(b) represents the C(1s) XP spectrum as a result of 600 s of collision-induced desorption of the C$_2$H$_4$/O/Pt(111) system shown in Fig. 5(a), the incident Xe atoms had 4.1 eV of translational energy. This spectrum shows a depletion of π-C$_2$H$_4$ feature, as assigned from Fig. 2(e), while the di-σ-C$_2$H$_4$ feature remains unchanged. The virtually complete depletion of π-C$_2$H$_4$ feature is shown in Fig. 5(c). This spectrum represents a total of 1800 s of CID of the C$_2$H$_4$/O/Pt(111) system shown in Fig. 5(a) using 4.1 eV of Xe translational energy. The fit of Fig. 5(c) was done using a 1.9 eV FWHM Gaussian at 283.7 eV and is consistent with the di-σ-C$_2$H$_4$ feature in Fig. 5(a). Subsequent exposure of the system shown in Fig. 5(c) to 4.1 eV Xe atoms results in no measurable change in the C(1s) XP spectrum. We also note that the result shown in Fig. 5(c) is consistent with the hypothesis that Xe atoms of 4.1 eV translational energy have insufficient energy to collisionally desorb the di-σ-C$_2$H$_4$ species from O/Pt(111) at 100 K.

The assignment of C(1s) XP binding energies as 283.7 eV for di-σ-C$_2$H$_4$ and 283.1 eV for π-C$_2$H$_4$ as shown in Fig. 2(e) is consistent with the result of the selective CID experi-

![Figure 5](http://ojps.aip.org/jcpo/jcpcr.jsp)
ment. An additional thermal experiment described subsequently confirmed this observation. Note that a C(1s) XP binding energy of 283.4 eV for di-σ-C₂H₄ was reported for the C₂H₄/Pt[111] system. Cassuto et al.¹⁰ reported C(1s) XP binding energies for C₂H₄/K/Pt[111] at 95 K. In that experiment, high potassium coverages resulted in average C(1s) XP binding energies of 283.7 eV for di-σ-C₂H₄ and 285.8 eV for σ-C₂H₄. Those values are not in agreement with our C(1s) XP binding energy values, perhaps because of different initial and final state effects when C₂H₄ is adsorbed on O/ and K/Pt[111].

To further probe the identity of the C(1s) XP feature at 283.7 eV, a saturated C₂H₄/O/Pt[111] system identical to that shown in Fig. 5(a) was annealed to 240 K. The result of this experiment is shown in Fig. 5(d). This C(1s) XP spectrum has the same FWHM and XP binding energy as the di-σ-C₂H₄ feature in Fig. 5(a) strongly suggesting that the spectrum shown in Fig. 5(d) represents the di-σ-C₂H₄ species. This observation is also consistent with Steininger’s⁷ result that π-C₂H₄ thermally converts into di-σ-C₂H₄. Note that the shift of C(1s) XP binding energy is expected after annealing to temperatures higher than 240 K due to formation of CO. The amount of thermally prepared di-σ-C₂H₄ shown in Fig. 5(d) represents about 2/3 of initial saturation C₂H₄ coverage shown in Fig. 5(a). This suggests that approximately 1/3 of the initially adsorbed C₂H₄ desorbed upon heating. This observation is in quantitative agreement with Steininger’s TPD areas corresponding to π-C₂H₄ and di-σ-C₂H₄ desorption. Note that at low C₂H₄ coverages the π-C₂H₄ species does not desorb upon heating, but is converted into the di-σ-C₂H₄ species. Recall that at the C₂H₄ saturation coverage both thermal desorption and conversion into di-σ-C₂H₄ is observed. This observation can be rationalized by assuming that, at C₂H₄ saturation coverage, the sites for conversion of π-C₂H₄ into di-σ-C₂H₄ are saturated, hence, the thermal desorption of π-C₂H₄ is observed. As soon as the π-C₂H₄ species desorbs, the thermal conversion of π-C₂H₄ into di-σ-C₂H₄ may occur. The difference between spectra of Figs. 5(c) and 5(d) essentially represents the amount of π-C₂H₄ which does not thermally desorb but reverts to form di-σ-C₂H₄. However, the deconvolution of C(1s) XP spectra shown in Figs. 5(a), 5(b), and 5(c) suggests that the coverage of di-σ-C₂H₄ remains constant during the CID experiments. Therefore we assume that the collision-induced cross section for π-C₂H₄ conversion into di-σ-C₂H₄ is much lower than the collision-induced cross section for π-C₂H₄ desorption. Within the limit of our XPS measurements we observed no collision-induced conversion of π-C₂H₄ into di-σ-C₂H₄. This observation is consistent with the assumption that the CID and TPD experiments access different reaction mechanisms, as will be discussed subsequently.

The coverage study and the CID experiment not only differentiate the π-C₂H₄ species from the di-σ-C₂H₄ species, but also quantify the surface coverage ratio of π-C₂H₄ and di-σ-C₂H₄ (θ_d/θ_p). Based on the adsorption study shown in Fig. 2, di-σ-C₂H₄ forms at a C₂H₄ exposure of 0.7 L which is at about 50% of the C₂H₄ saturation exposure. This fact and our XPS deconvolution of Fig. 2(e) suggest that θ_d/θ_p is approximately 1. Another estimate of θ_d/θ_p can be obtained from the results of selective CID experiment performed on the saturated C₂H₄/O/Pt[111] system. The estimate is obtained by comparing the C(1s) integrated area before CID as shown in Fig. 5(a) and after CID as shown in Fig. 5(c). In essence, this experiment suggests the complete depletion of π-C₂H₄. The θ_d/θ_p ratio calculated from this CID experiment is 0.98 and is consistent with the adsorption study shown in Fig. 2. Using the estimated θ_d/θ_p = 1, we propose that the π-C₂H₄ coverage is approximately 0.075 ML at the C₂H₄ saturation on O/Pt[111] at 100 K.

IV. CID BINDING ENERGY DETERMINATION

Our hypothesis is that the minimum Xe translational energy required to desorb π-C₂H₄ from the O/Pt[111] surface is proportional to the π-C₂H₄-Pt binding energy (BE). This minimum energy is defined as the threshold energy (E_t). To determine the threshold for CID, the cross section for CID must be measured as a function of Xe translational energy. A plot of the CID cross section as a function of the incident Xe energy reveals E_t. The determination of the cross section for CID begins with measurement of the integrated intensity of the C(1s) XP spectra before and after CID. Figures 5(a) and 5(b) display an example of the XPS analysis for a typical CID experiment. Figure 5(a) represents the C(1s) XP spectrum for the initial C₂H₄ coverage before CID and Fig. 5(b) represents the C(1s) XP spectrum for the final C₂H₄ coverage after 600 s of CID using a 4.1 eV Xe beam at 45° angle of incidence. Because a dissociation of C₂H₄ was not detected using either XPS or QMS, we conclude that the desorption of π-C₂H₄ is the main product channel. To calculate the absolute cross section for CID of π-C₂H₄, we first subtract the di-σ-C₂H₄ intensity from the C(1s) XP spectra shown in Figs. 5(a) and 5(b). The subtraction is based on the fact that θ_d/θ_p = 1 and allows us to obtain the absolute π-C₂H₄ coverage before (θ_p) and after (θ_f) CID. To determine the order of the CID process the logarithm of (θ_f/θ_p) was plotted as a function of the time allowed for CID (Xe flux). We observe a linear dependence suggesting that the CID process follows first order kinetics. The absolute CID cross section σ_CID is then calculated from

\[ \sigma_{\text{CID}} = \frac{-\ln(\theta_f/\theta_i)}{F_{\text{Xe}} t_{\text{CID}} \cos \phi}, \]

where θₖ is the initial and θₙ is the final surface coverage of π-C₂H₄, respectively. F_Xe is the flux of incident Xe atoms, tCID is the time of CID, and φ is the angle of incidence with respect to the surface normal. The factor of cos φ multiplied by F_Xe, measured perpendicular to the Xe beam axis, represents the number of Xe atoms that strike the Pt surface per unit surface area per unit time.

The measured cross sections for CID are plotted as a function of Xe translational energies in Fig. 6. The angular dependence of collisional energy transfer into the C₂H₄/O/Pt[111] system was investigated using 0°, 30°, and 45° angles of incidence. The similarity in the energy depen-
dence of the cross sections for the three angles of incidence suggests that the CID of \( \pi \)-C\(_2\)H\(_4\) proceeds via a total energy scaling mechanism.\(^6\) To determine the threshold for CID from Fig. 6 the following empirical function\(^33\) was used:

\[
\sigma_{\text{CID}} = S \left( \frac{E_i - E_{\text{th}}}{E_i} \right)^N,
\]

where \( E_i \) is the translational energy of the incident Xe atom, \( E_{\text{th}} \) is the Xe threshold energy for CID, and \( S \) and \( N \) are fitting parameters. The general form of Eq. (2) was derived from statistical theories\(^1\) for the simplest example of gas phase collision-induced dissociation: \( A + BC \rightarrow A + B + C \). This reaction represents Xe+-C\(_2\)H\(_4\)/O/Pt[111] \( \rightarrow \) Xe+C\(_2\)H\(_4\)+O/Pt[111] in this CID investigation. To obtain the threshold for CID of \( \pi \)-C\(_2\)H\(_4\) the data shown in Fig. 6 were fit using Eq. (2) convoluted over the Xe translational energy distributions.\(^5\) The fit resulted in \( E_{\text{th}} = 2.4 \pm 0.1 \) eV, where \( S = 0.165 \) and \( N = 1.65 \).

The threshold Xe energy for CID of \( \pi \)-C\(_2\)H\(_4\) can be related to the \( \pi \)-C\(_2\)H\(_4\)–Pt binding energy by accounting for energy transfer in two binary collision events as shown in Fig. 7. In our model the \( \pi \)-C\(_2\)H\(_4\)–Pt binding energy determination is based on energy conservation before and after the collision events. The initial and final energies of the system can be represented by the expression,

\[
E_{\text{Xe},i} = E_{\text{Xe},f} + \text{E}_{\text{Pt},em} + E_{\text{C}_2\text{H}_4,f} + \text{BE},
\]

where \( E_{\text{Xe},i} \) is the initial energy of the incident Xe atom before collision, \( E_{\text{Xe},f} \) is the final energy of Xe after collision with the \( \pi \)-C\(_2\)H\(_4\) adsorbate, \( E_{\text{Pt},em} \) is the energy transferred into the surface after collision with the \( \pi \)-C\(_2\)H\(_4\) adsorbate, \( E_{\text{C}_2\text{H}_4,f} \) is the final energy of the \( \pi \)-C\(_2\)H\(_4\) adsorbate after ejection from the O/Pt[111] surface, and BE is the binding energy of the \( \pi \)-C\(_2\)H\(_4\) adsorbate on O/Pt[111]. Our model for CID of \( \pi \)-C\(_2\)H\(_4\) from O/Pt[111] is shown in Fig. 7. Figure 7(a) represents the initial state of the system and all of the energy is contained in the translational energy of the incident Xe atom as measured using the time-of-flight (TOF) technique. Figure 7(b) represents the first binary collision event between the incident Xe atom and the \( \pi \)-C\(_2\)H\(_4\) adsorbate. We account for this energy transfer using the hard sphere approximation with head on collision (impact parameter=0). The energy of \( \pi \)-C\(_2\)H\(_4\) immediately after collision, with the incident Xe atom, \( E_{\text{C}_2\text{H}_4,i} \), is calculated using

\[
E_{\text{C}_2\text{H}_4,i} = E_{\text{Xe},i} - \frac{4m_{\text{Xe}}m_{\text{C}_2\text{H}_4}}{(m_{\text{Xe}}+m_{\text{C}_2\text{H}_4})^2},
\]

where \( m_{\text{Xe}} \) is the mass of Xe atom and \( m_{\text{C}_2\text{H}_4} \) is the mass of the C\(_2\)H\(_4\) molecule. The Xe atom impulsively transfers a quantity of energy into \( \pi \)-C\(_2\)H\(_4\) and Xe scatters away from the system with energy

\[
E_{\text{Xe,f}} = E_{\text{Xe},i} - E_{\text{C}_2\text{H}_4,i}.
\]

We assume that essentially no energy is transferred into the internal modes of \( \pi \)-C\(_2\)H\(_4\) at the threshold for CID. This assumption is based on the adiabaticity parameter, which is defined by the ratio of the collision time to the period of motion for a given internal mode.\(^1\) The hyperthermal Xe atom travels with a velocity of 1900 m/s at the threshold for CID and the interaction distance in the collision can be estimated to be approximately 2 Å. Therefore the collision time

![FIG. 6. The collision-induced desorption cross section as a function of Xe translational energy. The squares represent a data set for 30° incidence angle, the triangles represent a data set for 45° incidence angle, and the diamonds represent a data set for 0° incidence angle. The solid line is the empirical fit to the data using Eq. (2). The threshold energy is 2.4±0.1 eV, with the parameters \( S = 0.165 \) and \( N = 1.65 \).](image)

![FIG. 7. The selective CID scheme. Panel (a) represents the C\(_2\)H\(_4\)/O/Pt[111] system with the Xe atom as shown in Scheme 1. The gray spheres represent the Pt[111] surface. The black sphere represents the preadsorbed atom of oxygen. The white sphere of C\(_2\)H\(_4\) structure bound to Pt[111] through a single bond represents the \( \pi \)-C\(_2\)H\(_4\) adsorbate. The shadowed sphere of C\(_2\)H\(_4\) structure bound to Pt[111] through two bonds represents the di-\( \pi \)-C\(_2\)H\(_4\) adsorbate. The unfilled sphere in the gas phase above the C\(_2\)H\(_4\)/O/Pt[111] system represents the Xe atom. Panel (b) displays the collision between the Xe atom and the \( \pi \)-C\(_2\)H\(_4\) adsorbate. Panel (c) displays the collision between the \( \pi \)-C\(_2\)H\(_4\) adsorbate and the Pt[111] surface. Panel (d) displays the ejection of \( \pi \)-C\(_2\)H\(_4\) adsorbate from the O/Pt[111] surface into the gas phase.](image)
is approximately 100 fs. Comparison with the C–H vibrational period of 10 fs suggests that the collision is within the adiabatic limit. In this limit essentially no energy is transferred into the internal modes of π-C_{2}H_{4}. Further support for a hard sphere energy transfer can be found in simulations of CID of N_{2} from W[100] using an Ar beam. These calculations suggested that less than 4% of the incident translational energy channeled into internal energy at the threshold for CID. In addition we also note that, essentially no excitation of CH_{4} at threshold was evident during CID from Ni[111].

In the second collision represented by Fig. 7(c), energy is transferred from the translationally energetic π-C_{2}H_{4} adsorbate into the Pt surface. We treat the Pt lattice involved in the second collision as a particle of some effective mass, m_{eff} (see subsequent discussion). The energy transferred from the π-C_{2}H_{4} adsorbate into the Pt lattice, E_{Pt,em}, can be calculated from

\[ E_{Pt,em} = \frac{4m_{C_{2}H_{4}}m_{eff}}{(m_{C_{2}H_{4}} + m_{eff})^2}. \] (6)

The energy retained in the scattered π-C_{2}H_{4} molecule after collision with the surface, E_{C_{2}H_{4},2}, can be calculated from the difference of Eqs. (4) and (6):

\[ E_{C_{2}H_{4},2} = E_{Xe,f} \frac{4m_{Xe}m_{C_{2}H_{4}}}{(m_{Xe} + m_{C_{2}H_{4}})^2} \left( 1 - \frac{4m_{Xe}m_{eff}}{(m_{C_{2}H_{4}} + m_{eff})^2} \right). \] (7)

If the energy retained in the π-C_{2}H_{4} adsorbate is larger than the π-C_{2}H_{4}–Pt binding energy, the π-C_{2}H_{4} adsorbate can desorb from the O/Pt[111] surface as shown in Fig. 7(d). Therefore the π-C_{2}H_{4} final translational energy with which π-C_{2}H_{4} ejects from the surface is given by

\[ E_{C_{2}H_{4},f} = E_{C_{2}H_{4},2} - BE. \] (8)

At the threshold for collision-induced desorption of C_{2}H_{4} in the Pt lattice is exactly zero. If E_{C_{2}H_{4},f} is zero, Eq. (8) defines the binding energy of π-C_{2}H_{4} as being equal to E_{C_{2}H_{4},2}. Thus at threshold, we can substitute the value for E_{C_{2}H_{4},2} given by Eq. (7), into Eq. (8) to obtain the BE. Note that the value for E_{Xe,f} in Eq. (7) is simply the threshold energy of 2.4±0.1 eV experimentally determined from Fig. 6. We note that an identical solution can be obtained from Eq. (3) when E_{C_{2}H_{4},f} is set equal to zero and the values of E_{Xe,i}, E_{Xe,f}, E_{Pt,em} are employed. Using 1.5 Pt atom as m_{eff} of (1.5×195), m_{Xe} of 131, and m_{C_{2}H_{4}} of 28 the π-C_{2}H_{4}–Pt binding energy is calculated to be 0.95±0.04 eV.

In the calculation of BE the effective mass is the only estimated parameter and represents a certain number of Pt atoms involved in the collision between π-C_{2}H_{4} and Pt surface. The effective mass of the Pt lattice during the scattering process is a complex function of incident particle energy, angle, particle–Pt PES and Pt–Pt PES. To model the effective masses as function of velocity and particle mass we use well-defined Ar–Pt[111] and Xe–Pt[111] scattering experiments. A simplification of the physics involved in determining a given effective mass was made by proposing that the velocity of the incident particle in comparison with the speed of sound in the Pt lattice governs the effective mass. At the CID threshold energy of 2.4 eV, the π-C_{2}H_{4} molecule obtains a velocity of 3100 m/s after the collision with the incident Xe atom. Since C_{2}H_{4} and Ar have a comparable mass (in comparison with Xe and C_{2}H_{4}, at least) we use the Ar scattering experiments to estimate the effective mass of the Pt lattice during the C_{2}H_{4}–Pt collision. At 3100 m/s the Ar scattering studies suggest that the Pt effective masses are calculated to be 1.5 Pt atom using simulations and 2.0 Pt atoms using scattering experimental results. We conclude that at the π-C_{2}H_{4} velocity of 3100 m/s the Pt effective mass is approximately 1.5 Pt atom. The π-C_{2}H_{4}–Pt binding energy is plotted in Fig. 8 as a function of Pt effective mass using Eq. (7). This functional dependence of BE and effective mass provides an estimate of the sensitivity of calculated BE to effective mass. The calculated π-C_{2}H_{4}–Pt binding energy varies on average by ±10% with a change in the estimated effective mass ±0.5 Pt atom. However, a reliable model for calculating the effective mass can increase the accuracy of CID adsorbate-surface binding energy determination.

V. DISCUSSION

The CID experiment can be used to determine the adsorbate-surface binding energy. This CID binding energy measurement is one of few techniques, including TPD, isosteric, measurements, and microcalorimetry capable of probing a chemisorption adsorbate-surface PES. We propose that TPD and CID/microcalorimetry can probe complementary portions of the π-C_{2}H_{4}–Pt PES and we will
show that the CID and microcalorimetry experiments reveal comparable binding energies for π-C₂H₄ on Pt surfaces. Stuck et al.²⁸ recently reported the first microcalorimetric measurement of a heat of reaction for an adsorbate bound to a single crystal surface. In that study the C₂H₄/Pt[110] (1×2) system was investigated at 300 K. The formation of π-C₂H₄ was observed to occur reversibly at above 0.6 ML coverage. The heats of reaction for π-C₂H₄ and di-σ-C₂H₄ were directly measured to be 120 kJ/mol=1.24 eV and 136 kJ/mol =1.41 eV, respectively. The π-C₂H₄ heat of reaction represents the amount of energy released due to π-C₂H₄ adsorption. Thus the heat of adsorption is analogous to the minimum translational energy required to desorb π-C₂H₄ in the CID experiment. Collision-induced desorption of π-C₂H₄ is similar to the microcalorimetry experiment, at the C₂H₄ coverage of 0.6 ML and above, in that the ethylene molecule is ejected intact into the gas phase without accessing alternative intermediate adsorbate states. In a thermally activated experiment such as TPD, alternative intermediate states are often accessed and one can not unambiguously determine the intermediates accessed prior to desorption. Hence, the determination of the activation energy for TPD is always model dependent.²⁸ For instance, the activation energy for thermal desorption is proportional to the TPD peak temperature for first order process. As an example of irreversible reactivity, we note that the TPD study of C₂H₄/Pt[110] (2×1) (Ref. 14) revealed three desorption temperatures for C₂H₄ of 220, 280, and 415 K. The desorption at 220 K was assigned to the π-C₂H₄ species. In the C₂H₄/Pt[110] (2×1) system, there is no doubt that multiple reaction pathways are accessed during the thermal desorption process, so a determination of the absolute binding energy for such a system would be difficult if not impossible.

One question that must be addressed involves the difference in the activation energy measured by TPD and the binding energy measured by CID. The TPD experiment provides an activation energy for desorption of an adsorbate. If there are no precursor states accessed during thermal desorption of the adsorbate-surface system, the measured activation energy should be equal to the binding energy. If there are precursor states, implying local minima in the PES of adsorbate-surface system, it is likely that the activation energy corresponds to the PES barrier for the deepest local minima for a nonequilibrium process. The binding energy or the bond dissociation energy is proposed to be proportional to the threshold energy measured by the CID experiment. Unlike TPD, excitation to a local minima has no contribution to the collision-induced desorption threshold energy because the frequency of excitation (roughly 1 Hz) is far slower than the rate of deexcitation from the local minimum. It is probable, then, that the TPD and CID experiments probe different portions of the PES. Differences in the CID and TPD measurements have been observed previously for the di-σ-C₂H₄/Pt[111] system. Using TPD, Salmeron and Somorjai²⁶ measured a desorption feature at 280 K which was attributed to the di-σ-C₂H₄ species. The activation energy for di-σ-C₂H₄ desorption from Pt[111] was then calculated to be (12.0±3.2) kcal/mol=0.52±14 eV. The TPD result is supported by extended-Huckle calculations³⁹ which suggested that the di-σ-C₂H₄ adsorption energy on Pt[111] is 15 kcal/mol=0.65 eV. However, Anderson⁴⁰ determined the di-σ-C₂H₄–Pt binding energy on Pt[111] using atom superposition and electron delocalization molecular orbital (ASED-MO) calculation method to be 2.04 eV. Using the CID (Ref. 6) experiment the di-σ-C₂H₄–Pt[111] binding energy has been measured at 100 K to be 2.1 eV. The CID result is then in good agreement with the ASED-MO calculation.⁴⁰ The discrepancy between the TPD and CID results was attributed to a local minimum of intermediate. For systems where no local minima are expected, the CID and TPD energetics agree. For instance, the TPD activation energy and CID binding energy for physisorbed CH₄ on Ni[111] are 0.125 and 0.118 eV, respectively.³⁴

A comparison of the activation energy for thermal desorption for π-C₂H₄/O/Pt[111] measured using TPD with the binding energy measured using CID again suggests that these measurements probe different portions of the PES. To begin we note that the activation energy for thermal desorption has not been yet calculated for the C₂H₄/O/Pt[111] system although the data for such a calculation is available. This activation energy for π-C₂H₄ desorption from O/Pt[111] is calculated using the Redhead equation³¹ for a linear temperature sweep. In this calculation we input the π-C₂H₄ TPD (Ref. 7) peak temperature of 185 K, a heating rate of 15.5 K/sec, and an assumed frequency factor of 10¹². The activation energy for thermal desorption is then calculated to be 0.42 eV. This value is consistent with the 8 kcal/mol=0.35 eV value obtained from extended-Huckle calculations³⁹ for the π-C₂H₄–Pt[111] adsorption energy. In this paper, the C₂H₄/O/Pt[111] system was investigated using CID and the π-C₂H₄–Pt binding energy was determined to be 0.95 eV. The TPD activation energy for π-C₂H₄ desorption from O/Pt[111] is then approximately 50% of the binding energy determined by the CID technique, suggesting that TPD measurements probe only a portion of π-C₂H₄ PES.²⁸

We can compare the C₂H₄/Pt[110] (2×1) binding energy, as measured by microcalorimetry,²⁸ with the C₂H₄/O/Pt[111] binding energy, as measured by CID, by assuming that the TPD peak temperature is proportional to the binding energy. Using this assumption we can determine whether the binding energies measured by CID and microcalorimetry are consistent. Comparing the π-C₂H₄ TPD peak temperature of 220 K in C₂H₄/Pt[110] (2×1) (Ref. 14) and 185 K in C₂H₄/O/Pt[111] (Ref. 7) we expect that the π-C₂H₄–Pt binding should be weaker in the case of C₂H₄/O/Pt[111]. The π-C₂H₄ TPD peak temperature of 185 K in C₂H₄/O/Pt[111] is approximately 20% lower than the 220 K peak temperature measured for C₂H₄/Pt[110] (2×1). Assuming that the TPD peak desorption temperature is proportional to the binding energy, the π-C₂H₄–Pt[111] binding energy should be proportionally weaker than the π-C₂H₄–Pt[110] (2×1) binding energy. Microcalorimetry has been used to measure the π-C₂H₄–Pt[110] (2×1) heat of reaction (binding energy) equal to 1.24 eV.²⁸ We can then estimate the π-C₂H₄–Pt[111] binding energy which we would expect to measure if microcalorimetry was used on
the $\text{C}_2\text{H}_4$/O/Pt[111] system. Using the TPD peak desorption temperature ratio we calculate that a value of approximately 1.0 eV would be measured using microcalorimetry. This estimate is in good agreement with the CID determined $\pi$-$\text{C}_2\text{H}_4$--Pt[111] binding energy of 0.95 eV suggesting a consistency in the CID and microcalorimetric measurements. The energies from TPD, CID, microcalorimetry, and calculations are summarized in Table I.

The thermal reaction of $\text{C}_2\text{H}_4$/O/Pt[111] system is also a simple model for the catalytic combustion of hydrocarbons. The previous reaction studies come mainly from TPD (Ref. 26) supported by theoretical calculations (Refs. 19 and 39). Thermal activation of this system gives rise to $\text{H}_2$, $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, CO, CO$_2$, and $\text{H}_2\text{O}$, but the exact mechanisms of reaction, presumably involving precursor states, are not well resolved. The knowledge of the $\pi$-$\text{C}_2\text{H}_4$--Pt binding energy provides insight into the $\text{C}_2\text{H}_4$/O/Pt[111] system. This paper also suggests that the selectivity of CID can be a potential tool to probe such precursors by determining absolute binding energies.

### Table I. Binding energies from TPD, CID, microcalorimetry, and calculations.

<table>
<thead>
<tr>
<th>Binding Form</th>
<th>$\pi$</th>
<th>$\sigma$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPD temperature (K)</td>
<td>185 (Ref. 7)</td>
<td>220 (Ref. 14)</td>
<td>285 (Ref. 7)</td>
</tr>
<tr>
<td>Activation energy for desorption by TPD (eV)</td>
<td>0.42$^a$</td>
<td>0.52 (Ref. 26)</td>
<td></td>
</tr>
<tr>
<td>Binding energy by CID (eV)</td>
<td>0.95$^a$</td>
<td>2.1 (Ref. 6)</td>
<td></td>
</tr>
<tr>
<td>Heat of reaction by microcalorimetry (eV)</td>
<td>1.0$^a$</td>
<td>1.24 (Ref. 28)</td>
<td></td>
</tr>
<tr>
<td>Adsorption energy by extended-Huckel calculation (eV)</td>
<td>0.35 (Ref. 39)</td>
<td>0.65 (Ref. 39)</td>
<td></td>
</tr>
<tr>
<td>Binding Energy by ASED-MO calculation (eV)</td>
<td></td>
<td>2.04 (Ref. 40)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$This work.

### VI. CONCLUSION

At the exposure of 1.3 L $\text{C}_2\text{H}_4$ adsorbs on 0.25 ML atomic oxygen precovered Pt[111] at 100 K in two forms: $\pi$-$\text{C}_2\text{H}_4$ and di-$\sigma$-$\text{C}_2\text{H}_4$. In this paper both forms of $\text{C}_2\text{H}_4$ were characterized by XPS and C(1s) XP binding energies were assigned to be 283.1 eV for $\pi$-$\text{C}_2\text{H}_4$ and 283.7 eV for di-$\sigma$-$\text{C}_2\text{H}_4$.

The $\text{C}_2\text{H}_4$/O/Pt[111] system was chosen to investigate a selectivity of CID. To our knowledge we have demonstrated for first time the selective CID. The $\pi$-$\text{C}_2\text{H}_4$ adsorbate was selectively desorbed from O/Pt[111] by using a Xe translational energy which leaves the more strongly bound di-$\sigma$-$\text{C}_2\text{H}_4$ intact on the surface. The minimum Xe translational energy of 2.4 eV required to eject $\pi$-$\text{C}_2\text{H}_4$ from O/Pt[111] is related to the binding energy of chemisorbed $\pi$-$\text{C}_2\text{H}_4$ on O/Pt[111]. Using two classical binary collisions, the $\pi$-$\text{C}_2\text{H}_4$--Pt chemical binding energy of 0.95 eV was calculated.

### ACKNOWLEDGMENTS

The support of the National Science Foundation through a Young Investigator Award (R.J.L.) is gratefully acknowledged. The authors also acknowledge valuable discussions with Gregory Szulczewski.

---

41 P. A. Redhead, Vacuum 12, 203 (1962).