

Adsorbate-Localized Excitation in Surface Photochemistry: Methane on Pt(111)

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Methane on Pt(111) dissociates or desorbs under irradiation by 193-nm photons. The polarization-dependent cross sections of the photochemical processes have been measured as a function of the incident angle by using postirradiation temperature-programmed desorption. The incident-angle dependence of the cross sections obtained with p polarization substantially deviates from that of the substrate absorbance. This clearly indicates that an adsorbate-localized excitation plays an important role in the photochemistry of methane.

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Photochemistry of molecules adsorbed on metal surfaces in the wavelength range from visible to UV is one of the current topics in surface science, and numerous adsorption systems have been studied [1–3]. However, in contrast to photochemistry of gas-phase molecules, the electronic excited states of adsorbed molecules responsible for the variety of photochemical processes are not well understood. Thus a central and fundamental question is how adsorbed molecules are excited with photon irradiation. A clear understanding of the excitation mechanism in surface photochemistry not only provides a solid basis for further exploration of nuclei dynamics following the excitation, but also casts a new light to gain insights on adsorbate-substrate interactions particularly for electronically excited adsorbates.

Basically, the excitation mechanisms in surface photochemistry are classified into two categories: adsorbate-localized (direct) excitation and substrate-mediated (indirect) excitation. In the former mechanism, we include photon adsorption associated with an electronic excitation localized in an adsorbate-substrate complex as well as strictly in an adsorbate. In the latter mechanism a hot carrier created via photon adsorption by the substrate is transferred to an adsorbed molecule to form a transiently charged species that undergoes photochemical processes. There have been several studies where direct excitation is claimed to play a role in surface photochemistry [4–9]. However, to our knowledge, none of them has conclusively established the adsorbate-localized photon absorption as a dominant excitation mechanism, particularly when adsorbate coverages are below one monolayer. An exceptional example where direct excitation has been firmly established is photodissociation of $\text{Mo}(\text{CO})_6$ on various metal and semiconductor surfaces [10–13]. In numerous other adsorbate systems, surface photochemical processes are thought to be initiated by substrate-mediated excitation. Thus it is widely believed that “direct photoexcitation of adsorbed molecules is, in most cases, overwhelmed by excitations in substrate” [1].

The insignificant contribution of direct excitation was interpreted as a result of rapid quenching of the electronic

excited state of the adsorbate due to strong interactions with the substrate [14]. If this were true, the direct excitation would be evident only for adsorbates whose electronic excited state interacts weakly with the substrate. For instance, direct excitation in the photochemistry of weakly adsorbed $\text{Mo}(\text{CO})_6$ has been confirmed from the close resemblance of the wavelength dependence of the photodissociation yield to that of gas-phase optical absorption. In other words, the electronic excited $\text{Mo}(\text{CO})_6$ also weakly interacts with the substrate. Thus the involvement of direct excitation is not unreasonable in this system. However, the direct excitation model has not been critically tested when adsorbate excited states significantly interact with the substrate.

Recently, we have found that methane adsorbed on Pt(111) can be readily dissociated to produce methyl and hydrogen adsorbates upon irradiation with 193 nm photons [15,16]. Interestingly, only those CH_4 adsorbates which are in close contact with the surface are photochemically active. The activation energy for thermal desorption of CH_4 on Pt(111) is 0.23 eV [16,17]; CH_4 absorbs weakly on Pt(111). CH_4 in the gas phase is transparent at this wavelength and shows appreciable absorption cross sections only above 8.5 eV (145 nm) [18]. Thus a large redshift (>2 eV) of the absorption band of CH_4 is required to account for the photochemistry with the direct excitation mechanism. Strong interactions in the excited state of CH_4 responsible for the large redshift would hamper photochemical processes initiated by direct excitation according to the concept cited above. However, in this Letter we show for the first time conclusive evidence of direct excitation in an adsorption system, where the electronically excited adsorbate strongly interacts with the metal substrate.

We have examined the excitation mechanism by measuring the polarization-dependent photochemical cross section as a function of the incident angle γ . This technique has been reviewed and widely used [3]. Briefly, both light absorbance by metal substrates and electric field strengths at surfaces can be evaluated by Fresnel's equations. Figure 1 shows the calculated results of the bulk

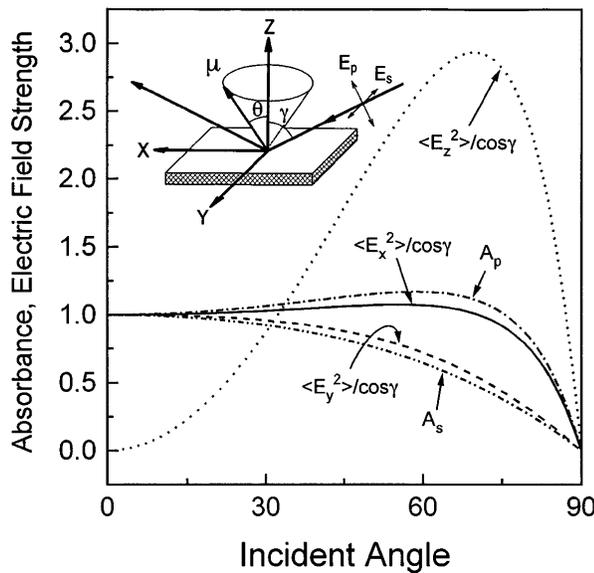


FIG. 1. Dependence of the electric field strengths and substrate absorbance on the incident angle for p - and s -polarized light ($\lambda = 193$ nm) impinging on a platinum surface. The results are calculated from Fresnel's equations. The inset shows a schematic drawing of the optical geometry and the orientation of a transition dipole μ at the metal surface.

absorbance and the mean square electric field strengths for platinum at $\lambda = 193$ nm. Here published optical parameters [19] were used in the calculations. If a photochemical process is induced by the substrate-mediated excitation, the cross section of the process, σ_j ($j = p, s$), will be scaled with the polarization dependence of light absorbance by the substrate, A_j . On the other hand, if the process is induced by adsorbate-localized excitation, the cross sections will be proportional to $|\boldsymbol{\mu} \cdot \mathbf{E}|^2$, where $\boldsymbol{\mu}$ is the transition dipole moment of an adsorbate-substrate complex and \mathbf{E} is the electric field vector at the surface boundary. For a system with rotational symmetries $\geq C_3$, the cross sections can be described as [3,20]

$$\sigma_p \propto [0.5 \sin^2 \theta \langle E_x^2 \rangle + \cos^2 \theta \langle E_z^2 \rangle] / \cos \gamma, \quad (1)$$

$$\sigma_s \propto [0.5 \sin^2 \theta \langle E_y^2 \rangle] / \cos \gamma, \quad (2)$$

where θ is the angle of the transition dipole moment with respect to the surface normal. Note that the factor of $1/\cos \gamma$ should be included to compare the experimental data normalized to the intercepted irradiance at the surface [21]; this was neglected in previous studies [8,22,23]. As pointed out by Richter *et al.* [21], it is practically impossible to distinguish between the two excitation mechanisms with this method if the transition dipole moment lies in the plane parallel to the surface. Thus distinction between the two mechanisms can be made only if adsorbed molecules have a nonzero component of the transition dipole moment perpendicular to the surface plane, μ_{\perp} .

The experiments reported here were performed in an ultrahigh vacuum apparatus (base pressure $\leq 1 \times 10^{-10}$ Torr) that has been described in detail elsewhere [24,25]. The sample could be cooled to 40 K with a closed-cycle He refrigerator and resistively heated above 1200 K. Exposures of CH_4 were carried out at the surface temperature 55 K to make a saturated first layer (saturation coverage 0.33 ML [16]). An ArF excimer laser beam ($\lambda = 193$ nm) was directed onto the surface at 40 K. The laser beam was expanded with a beam expander to irradiate the entire surface uniformly. Then the collimated laser beam was polarized with a polarizer composed of five pairs of UV-grade fused quartz plates placed at the Brewster angle at 193 nm. Laser pulses (2 mJ/cm^2 , 15 ns) at the repetition rate of 10 Hz did not raise the time-averaged surface temperature over 50 K during photon irradiation. The maximum transient temperature jump due to pulse-laser heating was estimated to be 7 K [26] at the incident angle of 0° , which does not exceed the desorption temperature (see below). Thus thermal effects were negligible. Standard cleaning and annealing cycles were necessary after repeated photolysis experiments owing to accumulation of small amounts of carbon supplied from photofragments of CH_4 adsorbates. Postirradiation temperature-programmed desorption (TPD) was used to quantify the photoreacted fraction of CH_4 as a function of the number of accumulated photons incident on the unit surface area, N_{ph} .

Methane on Pt(111) desorbs completely at ~ 70 K (α peak), and no thermal dissociation takes place. When the CH_4 -precovered surface is irradiated with 193 nm photons, the α desorption peak becomes smaller and a new desorption peak of CH_4 appears at ~ 260 K [15]. This new desorption peak denoted as β is attributed to recombination of CH_3 and H on Pt(111) [17,27,28]. A typical post-irradiation TPD is shown in the inset of Fig. 2. Thus the TPD result clearly indicates that CH_4 is dissociated to CH_3 and H adsorbates by the 193 nm photon irradiation. Post-irradiation TPD measurements were repeated as a function of N_{ph} at various incident angles for the impinging laser beam polarized parallel (p polarization) and perpendicular (s polarization) to the plane of incidence. Representative results are plotted in Fig. 2. While the integrated area of the α peak intensity I_{α} decreases, that of the β peak I_{β} increases with N_{ph} . However, both I_{α} and I_{β} level off with more extensive irradiation. Post-irradiation XPS and TPD confirmed that about one-half of the CH_4 adsorbates are ultimately either dissociated or desorbed, but the other half remains unreacted on the surface. The plausible origin of the quenching of the photochemical processes has been discussed elsewhere [16].

Least-square fits to the equations

$$I_{\alpha}(N_{\text{ph}}) = [I_{\alpha}(0) - I_{\alpha}(\infty)] \exp(-\sigma_j N_{\text{ph}}) + I_{\alpha}(\infty), \quad (3)$$

$$I_{\beta}(N_{\text{ph}}) = I_{\beta}(\infty) [1 - \exp(-\sigma_j N_{\text{ph}})] \quad (4)$$

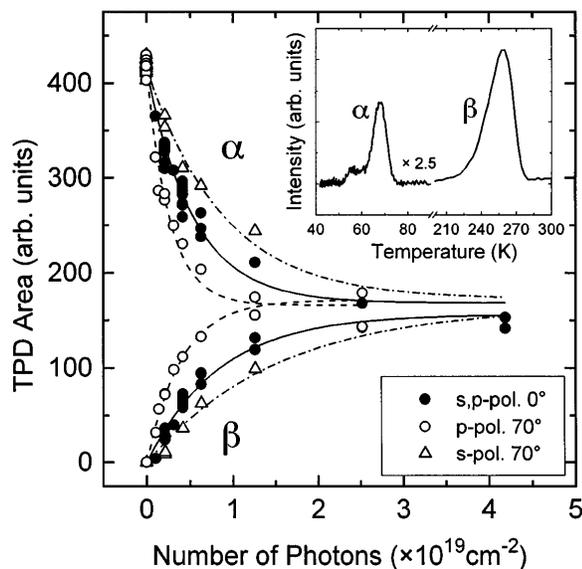


FIG. 2. Representative plots of the integrated areas of the CH₄ desorption peaks originating from CH₄ molecularly adsorbed (α peak) and originating from the photoproducts of CH₃ and H via associative desorption (β peak) as a function of the number of 193 nm photons incident on the surface. The Pt(111) surface saturated with CH₄ was irradiated with either *p*- or *s*-polarized 193 nm photons. Incident angles are 0° (solid circles) and 70° (*p*: open circles; *s*: triangles) with respect to the surface normal. Curves are the results of fittings to Eqs. (3) and (4). The total depletion cross section at 0° is $1.5 \times 10^{-19} \text{ cm}^{-2}$. The inset shows a typical post-irradiation TPD result revealing the α - and the β -desorption peaks.

give effective total depletion cross sections of the photochemical processes, σ_j ($j = p, s$). The fittings were made for the two desorption peaks independently. Figure 3(a) shows the γ dependence of σ_s . The γ dependences of the cross sections obtained from the two peaks agree with each other to within the experimental errors. The dashed and the dash-dotted curves represent the calculated A_s and σ_s , respectively. The observed cross sections are in excellent agreement with the two calculated curves. Figure 3(b) shows the γ dependence of σ_p . In contrast to the γ dependence of σ_s , σ_p is peaked at $\gamma = 70^\circ$. Moreover, note that it deviates significantly from A_p drawn by the dashed curve. This deviation clearly demonstrates that the photochemical processes cannot be accounted for only by substrate-mediated excitation; direct excitation with the transition dipole component perpendicular to the surface must be taken into account.

Although CH₄ adsorbs on Pt(111) weakly, the symmetry of the adsorbate is reduced to at least C_{3v} from the T_d symmetry of gaseous CH₄ according to IR absorption measurements [29]. Thus we assume that transition dipoles are not distributed isotropically, but rather oriented in such a way that they possess the same or higher rotational symmetry as the substrate, i.e., $\geq C_3$.

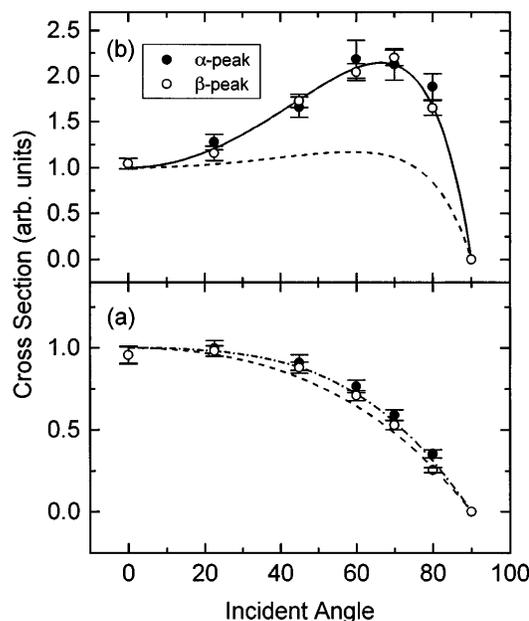


FIG. 3. Incident angle (γ) dependence of photochemical cross sections determined by using the α (solid circles) and the β (open circles) desorption peaks in post-irradiation TPD with various numbers of photons incident on the surface. The impinging light was polarized (a) perpendicular (*s* polarization) and (b) parallel (*p* polarization) to the plane of incidence. The dashed curves are calculated absorbance of the platinum substrate. The dash-dotted curve in the lower panels is $\langle E_y^2 \rangle / \cos \gamma$. The solid curve in the upper panel represents the best fitting result to Eq. (1), resulting $\theta = 66^\circ$ at $|\epsilon_{\text{eff}}| = 1$.

Some cautions are needed to apply Eq. (1). When the surface is covered with an adsorbate coverage of one monolayer or less as in this study, effects of the adlayer on the reflection and refraction of light can be neglected, since the thickness of the adlayer is sufficiently small [11]. However, the assumption of a step function for the electric field normal to the surface used in the macroscopic treatment is certainly not valid on a microscopic scale. Instead of a step function, the electric field normal to the surface is expected to change smoothly from E_z to E_z/ϵ_s , where ϵ_s is the dielectric constant of the substrate. Thus we describe the microscopic field as $E_z/\epsilon_{\text{eff}}$ at the vacuum side near the surface.

Calculations by Feibelman [30] based on a jellium model demonstrated that the macroscopic description is a reasonable approximation for distances greater than about 1 Å outside the jellium edge. In this approximation, i.e., $|\epsilon_{\text{eff}}| = 1$, the satisfactory fit to Eq. (1) drawn by the solid curve in Fig. 3(b) gave $\theta = 66^\circ$; $\mu_\perp : \mu_\parallel \approx 4:9$. If the classical treatment cited above is not appropriate, $|\epsilon_{\text{eff}}|$ takes the value between 1 and $|\epsilon_s|$ (3.38 at 193 nm). Although the data of σ_p were fitted with two free parameters, $|\epsilon_{\text{eff}}|$ and θ , they could not be determined independently from the fitting. Thus we set $|\epsilon_{\text{eff}}| = |\epsilon_s|$

as the other extreme case. An equally satisfactory fitting was obtained, resulting in $\theta = 34^\circ$.

Although CH_4 in the ground state interacts weakly with the substrate, we can treat the adsorbate system as an adsorbate-substrate complex. A possible excitation scheme might be an excitation of the complex that couples wave functions predominantly associated with surface states to unoccupied CH_4 levels. The excited states relevant to the excitation scheme would be correlated with CH_4^- states in the gas phase. The CH_4^- state responsible for the lowest Feshbach resonance was found at 8–10 eV above the vacuum level, but no low-lying CH_4^- states below the resonance state were confirmed [31]. Therefore the excited state is hardly accessible with 193 nm (6.4 eV) photons from surface states below the Fermi level even if the CH_4^- state is stabilized near the surface by the image-charge interaction and so forth.

The first excited state of gaseous CH_4 ($1t_2 \rightarrow 3sa_1$) 1T_2 is known to be at 10 eV above the ground state [18]. The excited-state orbital is essentially a $3s$ Rydberg-type orbital. With decreasing the distance between the adsorbate and the surface, in contrast to the ground state configuration, the excited state is likely shifted and its width is broadened by hybridization with orbitals of the substrate, since the excited-state configuration has the open shell structure. As a result of the interactions the symmetry of the adsorbate in the excited state is also reduced to the lower symmetries from T_d as in the ground state. Thus the excited state of the adsorbate-substrate complex is split to the states with symmetries of $A_1 + E(C_{3v})$ or $A_1 + N_1 + B_2(C_{2v})$, etc. Therefore both perpendicular and parallel transitions originating in $A_1 \leftarrow A_1$ and $E(B_1, B_2) \leftarrow A_1$, respectively, are allowed; this accords with the observed results. Consequently, electronic excitation from the electronic state predominantly associated with the CH_4 ground state to the excited state of the adsorbate-substrate complex is likely responsible for the 193 nm photochemistry of CH_4 , where the strong interactions with the substrate in the excited state manifest themselves in a large redshift of >2 eV from the onset of the absorption band of gaseous CH_4 .

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[1] X.-Y. Zhu, *Ann. Rev. Chem. Phys.* **45**, 113 (1994).

[2] W. Ho, in *Desorption Induced by Electronic Transitions, DIET IV*, edited by G. Betz and P. Varga (Springer, Berlin, 1990), p. 48.

- [3] X.-L. Zhou, X.-Y. Zhu, and J.M. White, *Surf. Sci. Rep.* **13**, 73 (1991).
- [4] S.A. Costello, B. Roop, Z.-M. Liu, and J.M. White, *J. Phys. Chem.* **92**, 1019 (1988).
- [5] K. Domen and T.J. Chuang, *Phys. Rev. Lett.* **60**, 1518 (1987).
- [6] E.P. Marsh, T.L. Gilton, W. Meier, M.R. Schneider, and J.P. Cowin, *Phys. Rev. Lett.* **61**, 2725 (1988).
- [7] W. Mieber and W. Ho, *J. Chem. Phys.* **91**, 2755 (1989).
- [8] X.-Y. Zhu, S.R. Hatch, A. Campion, and J.M. White, *J. Chem. Phys.* **91**, 5011 (1989).
- [9] X.-Y. Zhu and J.M. White, *J. Chem. Phys.* **94**, 1555 (1991).
- [10] Z.C. Ying and W. Ho, *J. Chem. Phys.* **93**, 9077 (1990).
- [11] Z.C. Ying and W. Ho, *J. Chem. Phys.* **94**, 5701 (1991).
- [12] S.K. So and W. Ho, *J. Chem. Phys.* **95**, 656 (1991).
- [13] M. Wolf, X.-Y. Zhu, J.M. White, T.H. Koschmieder, and J.C. Thompson, *J. Chem. Phys.* **97**, 7015 (1992).
- [14] B. Helling, *Surf. Sci.* **282**, 216 (1993).
- [15] Y.A. Gruzdkov, K. Watanabe, K. Sawabe, and Y. Matsumoto, *Chem. Phys. Lett.* **227**, 243 (1994).
- [16] Y.A. Gruzdkov, K. Watanabe, K. Sawabe, and Y. Matsumoto (to be published).
- [17] V.A. Ukraintsev and I. Harrison, *Surf. Sci. Lett.* **286**, L571 (1993).
- [18] G. Herzberg, *Molecular Spectra and Molecular Structure III* (Van Nostrand, New York, 1966), p. 526.
- [19] $n = 1.32$ and $k = 1.28$ at 193 nm; *Handbook of Optical Constants of Solids*, edited by E.D. Palik (Academic, Orlando, 1985).
- [20] X.-Y. Zhu, J.M. White, M. Wolf, E. Hasselbrink, and G. Ertl, *Chem. Phys. Lett.* **176**, 459 (1991).
- [21] L.J. Richter, S.A. Buntin, D.S. King, and R.R. Cavanagh, *Chem. Phys. Lett.* **186**, 423 (1991).
- [22] E. Hasselbrink, S. Jakubith, S. Nettesheim, M. Wolf, A. Cassuto, and G. Ertl, *J. Chem. Phys.* **92**, 3154 (1990); M. Wolf, E. Hasselbrink, J.M. White, and G. Ertl, *J. Chem. Phys.* **93**, 5327 (1990); M. Wolf, E. Hasselbrink, G. Ertl, X.-Y. Zhu, and J.M. White, *Surf. Sci.* **248**, L235 (1991).
- [23] S.A. Buntin, L.J. Richter, D.S. King, and R.R. Cavanagh, *J. Chem. Phys.* **91**, 6249 (1989).
- [24] K. Sawabe and Y. Matsumoto, *Chem. Phys. Lett.* **194**, 45 (1992).
- [25] K. Sawabe and Y. Matsumoto, *Surf. Sci.* **283**, 126 (1993).
- [26] R.B. Hall, *J. Phys. Chem.* **91**, 1007 (1987).
- [27] F. Zaera and H. Hoffmann, *J. Phys. Chem.* **95**, 6297 (1991).
- [28] D.H. Fairbrother, X.D. Peng, R. Viswanathan, P.C. Stair, M. Trenary, and J. Fan, *Surf. Sci. Lett.* **285**, L455 (1993).
- [29] J. Yoshinobu, H. Ogasawara, and M. Kawai, *Phys. Rev. Lett.* **75**, 2176 (1995).
- [30] P.J. Feibelman, *Prog. Surf. Sci.* **12**, 287 (1982).
- [31] J.B. Hasted and D. Mathur, in *Electron-Molecule Interactions and Their Applications*, edited by L.G. Christophorou (Academic, Orlando, 1984), Vol. 1, p. 403.