Symmetry Controlled Surface Photochemistry of Methane on Pt(111)

Jun Yoshinobu, Hirohito Ogasawara, and Maki Kawai
The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama 351-01, Japan

(Received 12 April 1995)

Adsorbed states of methane on Pt(111) and subsequent processes photoinduced by ArF laser irradiation (193 nm) have been studied by infrared reflection absorption spectroscopy. Adsorption degrades the symmetry of first layer methane from T_d to C_{3v}, but the overlayer methane keeps T_d. Only the C_{3v} CH_4 in the first layer is photodissociated into CH_3 and H species. These reaction products modify the surface in such a way as to make the remaining CH_4 molecules photochemically inactive, and thus the reaction becomes self-limiting. The lifted degeneracy controls the surface photochemistry.

PACS numbers: 68.35.Ja, 82.50.Fv, 82.65.Pa

Carbon-hydrogen bonds, especially those of saturated (sp^3) carbons, are normally regarded as being chemically inert. When a saturated hydrocarbon molecule such as methane is adsorbed on metal surfaces, it is possible to distort to a lower symmetry, regardless of small adsorption energy (i.e., physisorption). Methane adsorption on Pt(111) is indeed such a case, in which the T_d symmetry of the molecule may be distorted. In this Letter, we report the details of adsorbed states of methane on Pt(111) at low temperature using infrared reflection absorption spectroscopy (IRAS) and demonstrate that the *deformed* methane on Pt(111) is selectively dissociated by ArF laser irradiation (193 nm).

Thermal activation of methane dissociation on transition metal surfaces is the rate-limiting step in catalytic steam reforming of methane [1], and many surface science experiments have been reported to elucidate the mechanism by means of thermal kinetic studies [2–4], molecular beams [5–8], and so on [9,10]. Recently, Gruzdkov *et al.* have reported the photodissociation of methane on Pt(111) by the ArF laser irradiation [11]. In every case, the adsorption of methane is the first step to interacting with metal surfaces and an entrance channel for the dissociation. However, in spite of the importance of adsorbed states of molecular methane, the detailed information has been very sparse [12].

The experiments were carried out in an ultrahigh vacuum chamber, which was equipped with a three-grid retarding-field analyzer for low energy electron diffraction and Auger electron spectroscopy, a quadrupole mass spectrometer for thermal desorption spectroscopy (TDS), and a pulsed gas delivering system. The base pressure was $\sim 4 \times 10^{-11}$ Torr. The details of the apparatus have been published elsewhere [13]. The Pt(111) clean surface was prepared by Ar-ion bombardment, annealing, oxidation, and flashing cycles. The defect density was estimated to be less than 0.5% according to the titration of adsorbed CO on Pt(111) [14]. The sample was cooled down to 25 K by a cryogenic refrigerator and was heated up to 1400 K by electron bombardment from the rear. Gaseous CH_4 or CD_4 was introduced onto the sample through a pulsed gas delivering system. The exposure was precisely controlled by the duration time and the gas pressure behind the valve. The coverage was determined from the integrated area of the TDS peak, assuming that the fractional coverage of the first layer CH_4 is 0.32 ML [1 monolayer (ML) $= 1.5 \times 10^{15}$ molecules cm^{-2}] [15]. The IRAS spectra were taken with a Fourier transform infrared spectrometer (Mattson RS-1) using a mercury-cadmium-telluride detector (or an InSb detector). The Pt(111) clean surface served as a background reference for an absorption spectrum. The ArF laser (193 nm) irradiates the surface through a BaF_2 window with the incident angle normal to the surface.

Figure 1 shows the IRAS spectra of adsorbed CH_4 on Pt(111) at 25 K as a function of coverage. Up to the saturation of the first layer (0.32 ML), three peaks have developed at 2997, 2882, and 1295 cm^{-1}. With increasing the coverage further, two new peaks develop at ≥ 3007 and 1305 cm^{-1}. However, the intensity of the 2882 cm^{-1} peak is saturated at the completion of the first layer (0.32 ML). The assignment of observed bands is referred to the vibrational spectra of gaseous CH_4 [ν_1(symmetric stretch) = 2917 cm^{-1}, ν_2(degenerate deformation) = 1534 cm^{-1}, ν_3(degenerate stretch) = 3019 cm^{-1}, ν_4(degenerate deformation) = 1306 cm^{-1}] [16]. The observed bands between 2997 and 3008 cm^{-1} are assigned to the CH degenerate stretching mode, the band at 2882 cm^{-1} to the CH symmetric stretching mode, and the bands between 1295 and 1305 cm^{-1} to the CH degenerate deformation mode. The ν_2 mode is not observed within the detection limit of the present experimental condition.

In the case of gaseous CH_4, only two F_2 modes of ν_3 and ν_4 are infrared (IR) active due to the T_d symmetry of the molecule. When the tetrahedral T_d symmetry is broken and lowered to C_{3v} symmetry containing a single threefold axis, six modes become IR active in gas phase: two A_1 modes and one E mode in the CH stretching region, one A_1 mode and two E modes in the deformation region. According to the surface dipole selection rule, only A_1 modes are observable by IRAS. The observed three absorption bands for the first layer CH_4 on Pt(111)

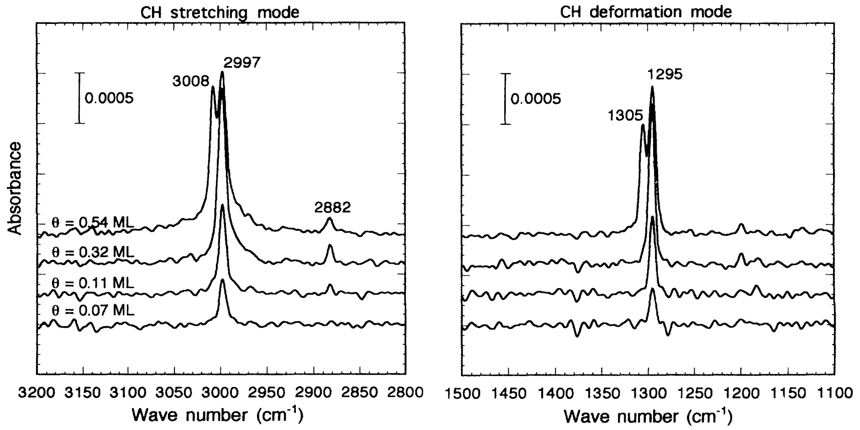

FIG. 1. IRAS spectra of CH_4 on Pt(111) at 25 K as a function of coverages. The spectra were taken with 4 cm^{-1} resolution using a *p*-polarized filter.

can thus be assigned to three A_1 modes of a C_{3v} methane molecule, two CH stretching modes at 2997 and 2882 cm^{-1}, and one deformation mode at 1297 cm^{-1}. If the symmetry is C_{2v}, C_s, or C_1, five or more A_1 modes should be observed. However, we cannot exclude completely the possibility of C_{2v}, C_s, or C_1, because the dynamic dipole moment of other modes may be too small to be observed.

Overlayer CH_4 keeps T_d symmetry with little perturbation, judging from the similarity of its vibrational wave numbers to those of gaseous CH_4. When the multilayer CH_4 on Pt(111) is heated to 50 K, the 3008 and 1305 cm^{-1} peaks, which are assigned to overlayer CH_4, disappear, and the peaks assigned to the first layer CH_4 (2997, 2882, and 1295 cm^{-1}) remain. A further heating to 80 K makes all these peaks disappear. These results are consistent with the facts that thermal desorptions of overlayer and the first layer CH_4 occur at ~40–50 and ~65–75 K, respectively [9,11].

We have studied the effect of ArF laser irradiation on CH_4 on Pt(111). About two layers (~0.6 ML) of CH_4 were adsorbed on Pt(111) at 25 K, and the laser (3.5 mJ/cm^2, 10 Hz) continuously irradiated the surface. The temperature rise during the irradiation was less than 5 K, and the laser induced thermal desorption was negligible. Figures 2(a), 2(b), 2(c), 2(d), and 2(e) show the IRAS spectra of two layers of CH_4 on Pt(111) before the irradiation and after 300, 600, 1200, and 1800 s irradiation, respectively. Further irradiation induced little change. With the increase of irradiation time, the intensities of both 2997 and 1295 cm^{-1} peaks decrease. The 2882 cm^{-1} peak is broadened and its integrated absorbance increases. On the other hand, the peaks due to second layer CH_4 (~3007 and 1305 cm^{-1}) do not change upon irradiation. These results clearly show that only a certain amount of the first layer CH_4 is affected by the irradiation.

The 50 K heating after the 1800 s irradiation induces thermal desorption of second layer CH_4, and the 3008

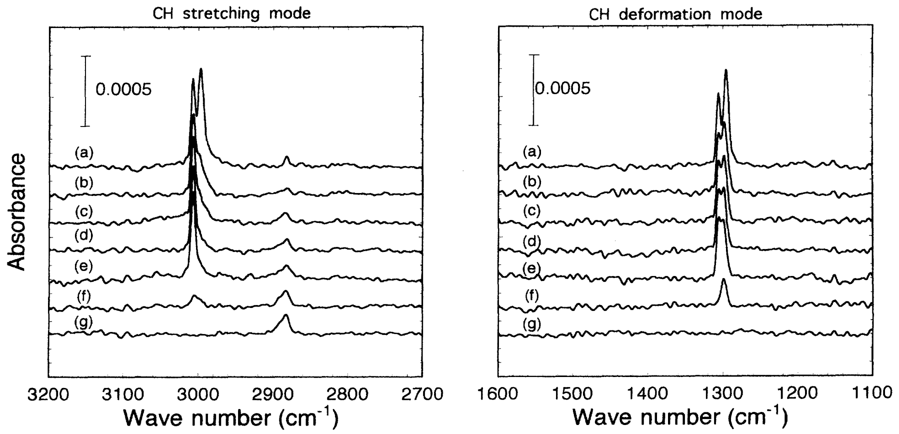

FIG. 2. IRAS spectra of 0.6 ML CH_4 on Pt(111) at 25 K, (a) before irradiation, and after (b) 300 s, (c) 600 s, (d) 1200 s, (d) 1800 s ArF irradiation (3.5 mJ cm^{-2}, 10 Hz) (f) followed by 50 K heating, and (g) 80 K heating. The spectra were taken with 4 cm^{-1} resolution.

and 1305 cm^{-1} peaks disappear [Fig. 2(f)]. The heating to 80 K induces thermal desorption of first layer molecular CH_4 unaffected by the irradiation, and only the 2882 cm^{-1} peak remains [Fig. 2(g)]. The amount of unaffected CH_4 is estimated to be about a half of the initial amount (~0.15 ML). This peak remains unchanged up to ~200 K heating. The remaining species are assigned to adsorbed CH_3 on Pt(111). Adsorbed CH_3 species on Pt(111) have been studied by the direct adsorption of CH_3 radical from the pyrolysis of gaseous $(CH_3)_2N_2$ and thermal decomposition of adsorbed CH_3I. The IRAS studies by Trenary and co-workers [17,18] show that the symmetric stretching mode of CH_3 on Pt(111) is observed between 2880 and 2885 cm^{-1} without any other normal mode. They have concluded that CH_3 species have a local symmetry of C_{3v} with the threefold axis normal to the surface.

The present IRAS study clearly demonstrates that a certain amount of first layer CH_4 is dissociated to produce CH_3 species on Pt(111). The decomposed CH_3 and H species recombine and desorb at ~250 K, which is observed by TDS [9,11]. According to the x-ray photoelectron spectroscopic (XPS) study of this process [15], not only photoinduced dissociation but also photoinduced desorption have been observed simultaneously, where 43% of the first layer CH_4 is dissociated, 12% is desorbed, and 45% remains intact after enough irradiation. Note that when a small amount of CH_4 (< 0.15 ML) is initially adsorbed and then irradiated by the ArF laser, all the CH_4 species have been reacted.

In order to solve the question of why only a part of first layer methane is affected by ArF irradiation and to confirm that the deformation of methane is essential for the photoreaction on Pt(111), the following experiment was performed. First, adsorbed CD_4 (0.32 ML) was irradiated by an ArF laser until the saturation of the dissociation, followed by heating to 80 K to remove the intact CD_4 species and leave only CD_3 and D on the surface [Fig. 3(a)]. Then, CH_4 molecules were adsorbed on the CD_3/Pt(111) surface up to the saturation of the first layer [Fig. 3(b)]. In this condition, approximately 0.16 ML CH_4 molecules coexist with CD_3 and D in the first layer on Pt(111). Only one absorption band is observed at 2999 cm^{-1} in the CH stretching region, and no band is observed at ~2882 cm^{-1}. Note that the 2882 cm^{-1} peak is clearly seen in the spectrum of the corresponding amount of CH_4 on the Pt(111) clean surface [Fig. 3(c)]. This indicates that such first layer CH_4 species keep T_d symmetry and they are not deformed. The coadsorption with CD_3 and D affects the environment of adsorbed CH_4, and the interaction between CH_4 and Pt(111) has changed. Further irradiation did not affect the coadsorption system. Namely, the reaction products modify the surface in such a way as to make the remaining methane molecules inactive to the ArF irradiation, and the reaction becomes self-limiting. Thus, it is clearly revealed here that only the CH_4 species with C_{3v} symmetry is dissociated by the ArF irradiation. Note that the adsorption energy of the first layer molecular methane changes very slightly even after the irradiation, judging from the fact that the desorption temperature is still about 60–75 K [11].

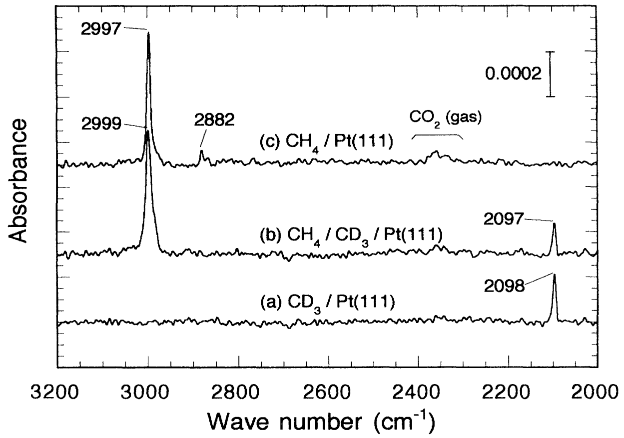

FIG. 3. IRAS spectra of (a) CD_3 on Pt(111) prepared by photodissociation and heating to 80 K (see text), (b) CH_4 on CD_3 preadsorbed Pt(111), and (c) 0.15 ML CH_4 on Pt(111). An InSb detector was used, and the spectral region was limited above ~1900 cm^{-1}. The spectra were taken with 4 cm^{-1} resolution using a p-polarized filter.

Two kinds of mechanisms have been proposed for photoinduced reactions of adsorbed molecules on metal surfaces [19]. One is the direct excitation of adsorbed molecules by photons. Another is the hot-electron mechanism, where hot electrons excited in the substrate by photons are transferred to the affinity level of the adsorbed molecule. The produced temporal negative ion undergoes reactions. In the case of gaseous CH_4 with the T_d symmetry, dissociation by the direct excitation with the photon is realized above ~8.3 eV [20]. Dissociative electron attachment of CH_4 is observed at the electron threshold energy at ~8 eV [21]. When the symmetry of methane changes from T_d to C_{3v}, the degenerate $1t_2$ occupied state splits into $1e$ and $3a_1$ states, and the $2t_2$ unoccupied state splits into $2e$ and $5a_1$ states [22]. Although the orbital energies are not known for the CH_4 on Pt(111), it is expected that the broken symmetry of the adsorbed methane leads to change in the electronic structure. Possibly, a direct transition to an antibonding state may be excited even by a 6.4 eV photon, inducing the photodissociation. Alternatively, in the case of the hot-electron induced reaction via a negative ion, the energy of the affinity level may decrease upon adsorption. The image potential attracting the negative ion to the metal surface may help increase the electron affinity of adsorbed methane. In either case, the broken symmetry of adsorbed methane on Pt(111) is associated with the photochemistry induced by ArF laser irradiation.

In summary, we have studied adsorbed states of methane on Pt(111) by IRAS. The first layer methane is deformed to C_{3v} symmetry because of the direct interaction with the Pt(111) surface. On the other hand, the overlayer methane is still tetrahedral (T_d symmetry). Upon ArF laser irradiation, only the deformed (C_{3v}) first layer methane is photodissociated to produce CH_3 species on Pt(111), but the methane with the T_d symmetry is unaffected.

We acknowledge discussions with Professor Y. Matsumoto and his colleagues at the Institute for Molecular Science, and a Grant-in-Aid for Scientific Research on Priority Areas (photoreaction dynamics) from the Ministry of Education, Science and Culture.

[1] J.R. Rostrup-Nielsen, *Catalytic Steam Reforming* (Springer, Berlin, 1984).
[2] H. Winters, J. Chem. Phys. **62**, 2454 (1975); **64**, 3495 (1976).
[3] C.N. Stewart and G. Ehrlich, J. Chem. Phys. **62**, 4672 (1975).
[4] T.P. Beebe, Jr., D.W. Goodman, B.D. Kay, and J.T. Yates, Jr., J. Chem. Phys. **87**, 2305 (1987).
[5] C.T. Rettner, H.E. Pfnür, and D.J. Auerbach, Phys. Rev. Lett. **54**, 2716 (1985).
[6] M.B. Lee, Q.Y. Yang, and C.T. Ceyer, J. Chem. Phys. **87**, 2742 (1987).
[7] A.C. Luntz and D.S. Bethune, J. Chem. Phys. **90**, 1274 (1989).
[8] A.C. Luntz and J. Harris, Surf. Sci **258**, 397 (1991).
[9] V.A. Ukraintsev and I. Harrison, Surf. Sci. Lett. **286**, L571 (1993).
[10] S.T. Ceyer, Langmuir **6**, 82 (1990).
[11] Y.A. Gruzdkov, K. Watanabe, K. Sawabe, and Y. Matsumoto, Chem. Phys. Lett. **227**, 243 (1994).
[12] J.D. Beckerle, A.D. Johnson, Q.Y. Yang, and S.T. Ceyer, J. Chem. Phys. **91**, 5756 (1989).
[13] J. Yoshinobu, N. Takagi, and M. Kawai, Phys. Rev. B **49**, 16670 (1994).
[14] M. Tüshaus, E. Schweizer, P. Hollins, and A.M. Bradshaw, J. Electron Spectrosc. Relat. Phenom. **44**, 317 (1987).
[15] Y.A. Gruzdkov, K. Watanabe, K. Sawabe, and Y. Matsumoto (to be published).
[16] T. Shimanouchi, Report No. NSRDS-NBS39, 1972, Vol. I.
[17] D.H. Fairbrother, X.D. Peng, R. Viswanathan, P.C. Stair, M. Trenary, and J. Fan, Surf. Sci. Lett. **285**, L455 (1933).
[18] J. Fan and M. Trenary, Langmuir **10**, 3649 (1994).
[19] X.-L. Zhou, X.-Y. Zhu, and J.M. White, Surf. Sci. Rep. **13**, 73 (1991).
[20] R.W. Ditchburn, Proc. R. Soc. London A **229**, 44 (1955).
[21] L.G. Christophorou, D.L. MaCorkle, and A.A. Christodoulides, in *Electron-Molecules Interaction and their Application,* edited by L.G. Christophorou (Academic, 1984), p. 478.
[22] G. Herzberg, *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1966).