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Photon Stimulated Desorption of C_6H_6 on Rutile TiO_2(110): Hole or Electron Regulated?

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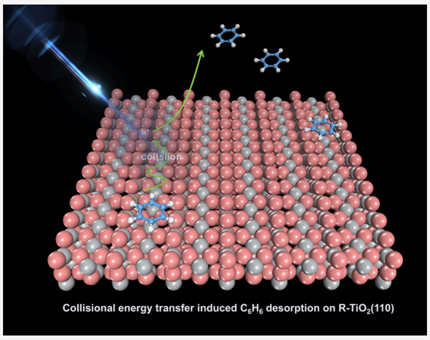
ABSTRACT: The photodesorption of benzene (C_6H_6) from rutile (R)-TiO_2(110) is a useful method to investigate the interfacial charge/energy transfer processes between adsorbates and R-TiO_2(110), which may further provide useful information for understanding the photochemical processes of C_6H_6 photodegradation with a TiO_2-based photocatalyst. With different kinds of electron acceptors (Cl_2, O_2, O atom), electron donor (CH_3OH), and neutral molecule (H_2O), the photodesorption of C_6H_6 from R-TiO_2(110) has been investigated systematically. Under ultraviolet irradiation, the electron donors/acceptors dramatically change the initial rate of the photon-stimulated desorption (PSD) of C_6H_6. In the presence of Cl_2 and O atoms, the photodesorption of C_6H_6 is largely enhanced. Conversely, the coadsorption of O_2, CH_3OH, and H_2O results in inhibition of the photodesorption of C_6H_6. In addition, the translational energy of the desorbing C_6H_6 at 257 nm is much higher than that at 343 nm, indicating that more photon energy transfers into the translational energy of the desorbing C_6H_6 at a shorter wavelength. Further analysis suggests that the photodesorption of C_6H_6 on R-TiO_2(110) is more likely to occur via collisions between C_6H_6 and hole trapped O_b^- rather than via interfacial electron/hole transfer. The collisional energy transfer process may be universal in photochemical processes on TiO_2.



■ INTRODUCTION

Titanium dioxide (TiO_2), as a widely used photocatalyst, has been applied in various fields.[1−6] In photocatalytic reactions, interfacial charge transfer between TiO_2 and adsorbates usually plays a vital role. Although rutile (R)-TiO_2(110) has been extensively utilized as a model for investigating interfacial charge transfer in photocatalysis,[7−10] the fundamental mechanisms of this process remain elusive, largely due to a scarcity of experimental techniques capable of directly or indirectly probing the charge transfer process between TiO_2 and adsorbates. Photon stimulated desorption (PSD) and electron stimulated desorption (ESD) are two powerful methods.[11−15] By coadsorbing proper electron donor/acceptor or changing photon energy, the interfacial charge transfer induced photodesorption process on R-TiO_2(110) can be significantly affected, which can provide useful information in understanding the charge carrier transfer process at the adsorbates/TiO_2 interfaces.

With different adsorbates on R-TiO_2(110), the microscopic mechanism for the PSD process varies significantly. Early, the photodesorption of CH_3X (X = I and Br) molecules on R-TiO_2(110) is proposed to be initiated via the interfacial electron transfer from TiO_2 to CH_3X molecules[16] following an Antoniewicz desorption mechanism,[17] forming CH_3X^- ions, and then the back electron transfer from CH_3X^- to TiO_2 leads to the desorption of the CH_3X. However, the photodesorption of O_2 on R-TiO_2(110) is considered as a hole mediated desorption process,[11,18] in which the transfer of photogenerated holes to the negatively charged O_2 neutralizes the O_2, resulting in the ejection of O_2 molecules from the surface. In addition, a recent study reports that the photodesorption of CO can be initiated by the recombination of photogenerated holes and electrons contributed from the surface bridging oxygen (O_b) defects, leading to the rearrangement of the surface atoms and the ejection of the weakly bound CO molecule.[19] Although photogenerated charge carriers are directly or indirectly involved in the PSD processes, the detailed role of photogenerated holes/electrons and the possible energy transfer in the process are still ambiguous.

Benzene (C_6H_6) is not only an important raw material in the chemical industry but also one of the carcinogenic volatile organic compounds (VOCs). Thus, the removal of C_6H_6 via photodegradation with TiO_2-based photocatalysts is very meaningful and may be initiated by the interfacial charge

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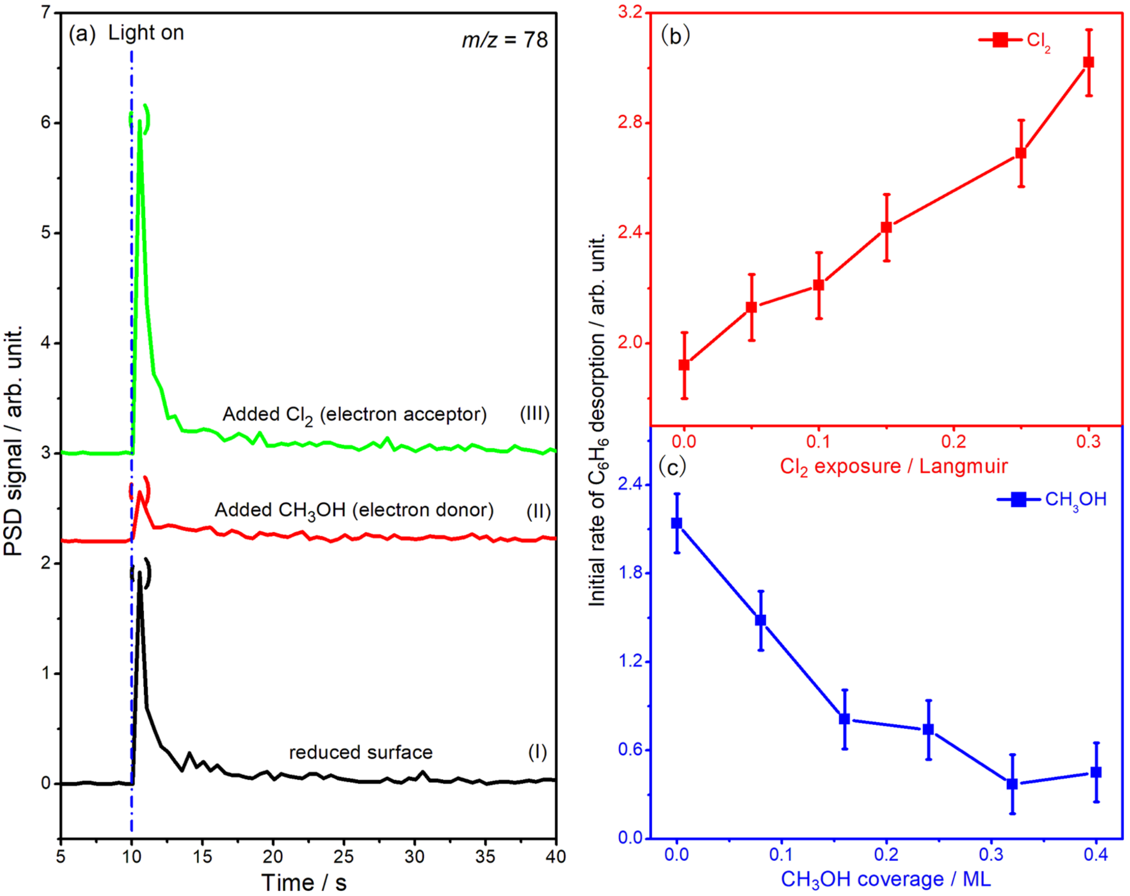

Figure 1. (a) Typical PSD spectra collected at $m/z = 78$ ($C_6H_6^+$) on the 0.2 ML of C_6H_6 covered (I) reduced R-TiO_2(110) surface and (II) in the presence of 0.4 ML of CH_3OH and (III) 0.3 langmuir of Cl_2 with 355 nm at 100 K. The photon flux is 7×10^{16} photons cm^{-2} s^{-1}. (b, c) Initial rate of C_6H_6 desorption as a function of Cl_2 (red lines) and CH_3OH (blue lines) exposures. The first point acquired at 0.5 s is used to measure the initial rate of C_6H_6 desorption.

transfer process. In addition, the adsorption of C_6H_6 on R-TiO_2(110) is very different from those of O_2 and CO. The temperature-programmed desorption (TPD) spectra reveal that the adsorption of C_6H_6 on the five-coordinated Ti^{4+} sites (Ti_{5c}) on R-TiO_2(110) is considerably more stable than that of CO and O_2,[20,21] as evidenced by its higher desorption temperature on the surface. However, the scanning tunneling microscopy (STM) images of CO[22] and O_2[23] show that the stable adsorption of these two species on the Ti_{5c} sites can be observed at 80 K. Conversely, the stable adsorption of C_6H_6 on the Ti_{5c} sites can be only observed at about 40 K.[24] Even at 50 K, the one-dimensional motion of C_6H_6 along the Ti_{5c} row is too fast for STM imaging,[24] indicating that the adsorption of C_6H_6 on R-TiO_2(110) at 100 K is very different from those of CO and O_2. As a result, a new pathway for the photodesorption of C_6H_6 may exist, which is essential for understanding the charge/energy transfer between adsorbates and TiO_2. In this work, the photodesorption of C_6H_6 on R-TiO_2(110) has been systematically studied with PSD, TPD, and time-of-flight (TOF) methods. In the presence of different kinds of coadsorbed electron acceptors (Cl_2, O_2, O atom), electron donor (methanol, CH_3OH), and neutral molecule (water, H_2O)), the initial rate of C_6H_6 photodesorption on R-TiO_2(110) changes dramatically. Moreover, the energy of the charge carrier/photon can be transferred into the translational energy of the desorbing C_6H_6 efficiently. The results not only suggest the photodesorption of C_6H_6 on R-TiO_2(110) is most likely to occur via the collisions between C_6H_6 and hole trapped O_b^- but also illustrate that PSD and TOF methods are useful tools to study photochemical processes on R-TiO_2(110).

■ METHODS

Experiments of TPD, PSD, and TOF were performed in an apparatus with a base pressure of approximately 6×10^{-11} Torr. Details of the apparatus have been described in the previous work.[25] The crystal surface of R-TiO_2(110) ($10 \times 10 \times 1$ mm^3, Princeton Scientific Corp.) underwent preparation through a series of Ar^+ sputtering followed by 850 K annealing at UHV. The ordering of the surface was validated using low-energy electron diffraction (LEED), while the cleanness was assessed by Auger electron spectroscopy (AES). Additionally, TPD of H_2O facilitated the calculation of bridge-bonded oxygen vacancies (O_v), revealing an concentration of 7−8% of R-TiO_2(110). C_6H_6 (Sigma, >99.5%), CH_3OH (Sigma, >99.5%), and H_2O (Sigma, >99.5%)) were purified through multiple freeze−pump−thaw cycles prior to their introduction to the R-TiO_2(110) surfaces using a home-built calibrated molecular beam doser.

A mixture of Cl_2 (2%)/Ar was exposed to the reduced surfaces to prepare the Cl atom covered surfaces. The O_2 covered R-TiO_2(110) surfaces were prepared through preadsorption of 2 langmuirs of O_2 at 100 K; the O atom covered R-TiO_2(110) surfaces were prepared by adsorption of

12 langmuirs of O_2 at 300 K. The hydroxylated R-TiO_2(110) surface was prepared by exposing the reduced surface to 1 ML of H_2O at 100 K and then flashed to 400 K to remove the H_2O molecule at Ti_{5c} sites, leaving bridging hydroxyl (OH_b) groups on the surface. The PSD spectra were acquired from a picosecond 355 nm laser. The pulse duration and repetition rate were 160 ps and 2 MHz, respectively. The beam had an average power output of 20 mW, resulting in a photon flux of 7×10^{16} photons cm^{-2} s^{-1}. The TOF spectra were recorded using either the third (343 nm) or fourth (257 nm) harmonic of a Coherent 1030 nm Flare NX laser. The pulse duration is 1.5 ns with a repetition rate of 200 Hz. With an output power of 5 mW, the photon flux for 343 nm was 1.6×10^{16} photons cm^{-2} s^{-1}, while it was 1.2×10^{16} photons cm^{-2} s^{-1} for 257 nm. TPD spectra were collected at a heating rate of 2 K/s.

■ RESULTS

Figure 1 shows the typical PSD spectra of mass-to-charge ratios (m/z) of 78 collected on the 0.2 ML (1 ML = 5.2×10^{14} atoms/cm^2) of C_6H_6 covered (I) reduced R-TiO_2(110) surface, (II) CH_3OH, and (III) Cl_2 predosed R-TiO_2(110) surfaces. According to previous results,[26] Cl_2 molecules will dissociatively adsorb on reduced R-TiO_2(110), forming the Cl atom covered surface. With the coadsorption of CH_3OH molecules (hole acceptor) and Cl atoms (electron acceptor), the initial rate (during the first 0.5 s photon exposure) of C_6H_6 desorption changes dramatically. In the presence of Cl atoms, the initial rate of C_6H_6 desorption is largely enhanced. In contrast, the initial rate of C_6H_6 desorption is largely inhibited with the coadsorption of CH_3OH molecules (electron donor or hole trap), indicating that the surface modification with different coadsorbates significantly affects the charge/energy transfer process, while the initial rates of C_6H_6 desorption with various Cl_2 and CH_3OH exposures are plotted in Figures 1b and 1c. Consistent with previous PSD and ESD works about O_2 desorption on R-TiO_2(110),[11,15] the initial rate of C_6H_6 desorption increases with the Cl_2 exposure. Conversely, the initial rate of C_6H_6 desorption decreases to near zero with 0.4 ML of CH_3OH coverage. The same trends of the initial rates of C_6H_6 and O_2 desorption indicate that the desorption of C_6H_6 is likely to be a hole mediated process as well.

Further, the initial rates of C_6H_6 desorption on the O atom and the O_2 molecule covered R-TiO_2(110) surfaces were also obtained (Figure 2). The O atom covered R-TiO_2(110) surface was prepared by exposing the reduced surface to 12 langmuirs of O_2 at 300 K,[27,28] leading to the formation of Ti_{5c}-bound O atoms on the surface via the dissociative adsorption of O_2 molecules at the O_v sites. The O_2 molecule covered surface was prepared by adsorbing 2 langmuirs of O_2 on R-TiO_2(110) at 100 K. Although both the O atom and O_2 molecules are electron negative when adsorbed on R-TiO_2(110), they have opposite effects on the initial rates of C_6H_6 desorption. O atoms enhance the C_6H_6 photodesorption (Figure 2b), consistent with the case of Cl_2 preadsorption (Figure 1, III). However, O_2 molecules decrease the initial rate of C_6H_6 desorption, while as the O_2 exposure increases, the initial rate of C_6H_6 desorption decreases gradually (see Figure S1 in the Supporting Information). According to previous works,[11,15,18] it has been widely accepted that the photodesorption of O_2 is a hole mediated process in which O_2 is neutralized through reaction with photogenerated holes and then ejects from the surface. If the C_6H_6 photodesorption is an electron mediated process, then the coadsorption of O_2 will consume the photogenerated holes. Thus, more electrons are available for C_6H_6 and enhance C_6H_6 photodesorption significantly. Conversely, C_6H_6 photodesorption is largely inhibited by coadsorbed O_2. Therefore, the electron mediated C_6H_6 desorption on R-TiO_2(110) can be ruled out, and the hole mediated C_6H_6 desorption seems to be the possible candidate. As a result, the photodesorption of O_2 will compete with that of C_6H_6, decreasing the hole availability for C_6H_6 desorption, inhibiting the rate of C_6H_6 desorption.

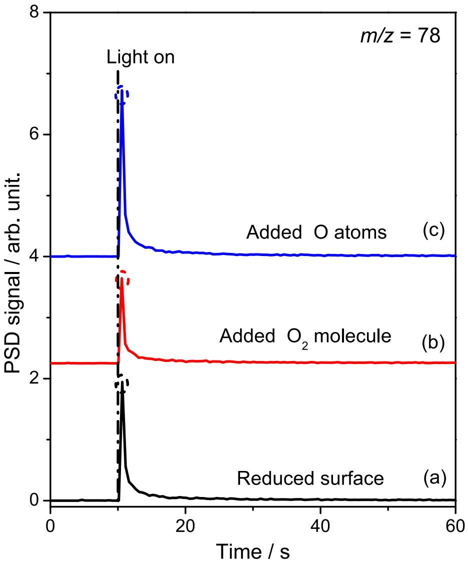

Figure 2. Typical PSD spectra collected at m/z = 78 ($C_6H_6^+$) on the 0.2 ML of C_6H_6 covered (a) reduced R-TiO_2(110) surface (black lines), (b) O_2 molecule predosed surface, and (c) O atom predosed R-TiO_2(110) surface with 355 nm at 100 K. The photon flux is 7×10^{16} photons cm^{-2} s^{-1}. The O atom covered R-TiO_2(110) surface was prepared by exposing the reduced surface to 12 langmuirs of O_2 at 300 K. The O_2 molecule covered surface was prepared by adsorbing 2 langmuirs of O_2 on R-TiO_2(110) at 100 K.

In addition, as shown in Figure 3, the PSD spectra of m/z = 78 were collected on 0.2 ML of C_6H_6 covered R-TiO_2(110) surfaces as a function of irradiation power. As the laser power increases, the initial rate of C_6H_6 desorption obviously increases obviously. Moreover, the initial rate of C_6H_6 desorption scales linearly with the square root of the photon flux ($F_{h\nu}^{1/2}$) (the inset of Figure 3). Based on previous works of O_2 photodesorption[11] and C_2H_5OH photodecomposition on R-TiO_2(110),[29] the linear relationship illustrates that the photodesorption of C_6H_6 on R-TiO_2(110) is governed by the second-order electron−hole (e−h) pair recombination kinetics, and only one photon is involved in the desorption process.

Based on previous works of PSD and ESD of O_2 on R-TiO_2(110),[11,15,18] the different roles of Cl_2 and CH_3OH in the initial rate of C_6H_6 desorption may be explained by "band bending",[30] in which the Cl_2 adsorption results in an upward band bending, thus facilitating hole transfer from bulk to the surface and C_6H_6 photodesorption (Figure 4). Conversely, the CH_3OH adsorption leads to a downward band bending, thus depressing hole transfer from bulk to the surface (Figure 4). This seems to be reasonable. However, recent photoelectron spectroscopy studies about CH_3OH adsorption on R-TiO_2(110)[31] and anatase (A)-TiO_2(101)[32] have shown that the change of band bending at the interface after CH_3OH adsorption is very small (≤0.2 eV). Such a small band bending

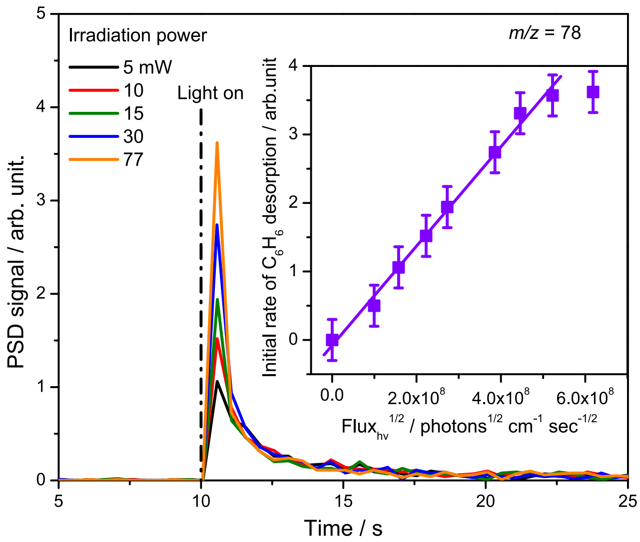

Figure 3. Typical PSD spectra collected at m/z = 78 ($C_6H_6^+$) on 0.2 ML of C_6H_6 covered R-TiO_2(110) surfaces after irradiating the surfaces with 355 nm at 100 K as a function of the laser irradiation power. The initial rate of C_6H_6 has a linear relationship with the square root of the incident light flux ($F_{h\nu}^{1/2}$), as shown in the inset of Figure 3.

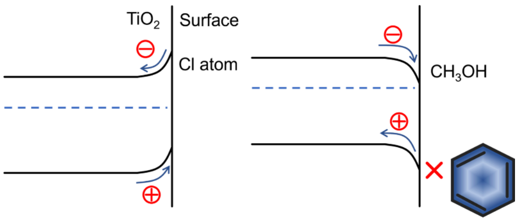

Figure 4. Schematic diagram of band bending effect on the hole transport causing the enhancement or the depression of C_6H_6 desorption with preadsorption of Cl_2 or CH_3OH molecules.

will not cause the obvious depression of hole transfer from the bulk to the surface, significantly inhibiting C_6H_6 photodesorption.

Although the coadsorption of CH_3OH only leads to slight downward band bending, CH_3OH can also act as a hole trap to decrease the surface hole concentration,[11] thus inhibiting C_6H_6 photodesorption via the possible hole mediated process. However, when H_2O coadsorbs on R-TiO_2(110), which is not a good hole trap,[7] the initial rate of C_6H_6 desorption also decreases dramatically as the H_2O coverage increases (Figure 5). Correspondingly, the remaining C_6H_6 increases with H_2O coverage (Figure S2), demonstrating that H_2O can also inhibit C_6H_6 photodesorption on R-TiO_2(110). Therefore, CH_3OH may not act as a hole trap in the photodesorption of C_6H_6 on R-TiO_2(110), and the photodesorption process may not be a hole mediated process.

DISCUSSION

According to previous works about photodesorption of adsorbates on R-TiO_2(110), five photodesorption pathways have been proposed: (1) transient heat induced desorption at high laser fluences,[16] (2) photogenerated electron mediated desorption,[16] (3) photogenerated hole mediated desorption,[11] (4) photodesorption induced by the rearrangement of the surface atoms and excess charges via the recombination of photogenerated holes and excess electrons,[19] and (5) the photodesorption induced by collisional energy transfer.[33] As shown in Figure 3, the photodesorption of C_6H_6 on R-TiO_2(110) is governed by the second-order e−h pair recombination kinetics, which is very different from the transient heat induced desorption at high laser fluences, indicating that the photodesorption of C_6H_6 does not occur via the pathway. In addition, the PSD signal of ethane (C_2H_6) was also collected on R-TiO_2(110) under the same experimental condition (Figure S3). Because the adsorption of C_2H_6 on R-TiO_2(110) is much weaker than that of C_6H_6, if the photodesorption of C_6H_6 is induced by transient heat at

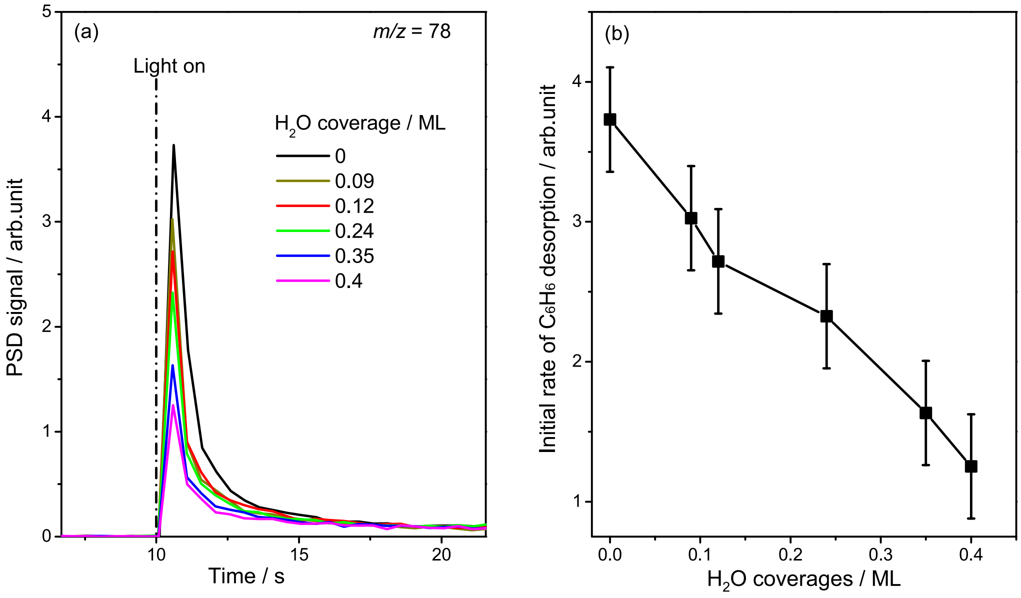

Figure 5. (a) Typical PSD spectra collected at m/z = 78 ($C_6H_6^+$) on the 0.2 ML of C_6H_6 covered H_2O predosed R-TiO_2(110) surfaces after irradiating the surfaces for 60 s with 355 nm at 100 K as a function of H_2O coverage. The photon flux of 355 nm light is 7×10^{16} photons cm^{-2} s^{-1}. (b) Initial rate of C_6H_6 desorption as a function of H_2O coverage.

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high laser fluences, then the obvious C_2H_6 desorption signal will also be detected. However, no obvious PSD signal of C_2H_6 desorption demonstrates that transient heat produced with a laser pulse does not induce C_6H_6 desorption here. Likewise, the result in Figure 2 also rules out electron mediated C_6H_6 desorption on R-TiO_2(110).

Theoretical results[21,24] suggest that a small charge transfer from C_6H_6 to R-TiO_2(110) occurs when C_6H_6 adsorbs on R-TiO_2(110). Because of the delocalized excess electrons contributed from O_v sites and subsurface Ti interstitials on reduced R-TiO_2(110),[34] part of the excess electrons may transfer to the unoccupied Ti 3d states of the Ti_{5c} sites. Therefore, when the reduced R-TiO_2(110) surface is oxidized by O_2 to heal the O_v sites, the excess electrons on the Ti_{5c} sites will be largely eliminated. The interaction between C_6H_6 and Ti_{5c} sites on the oxidized surface will be stronger than that on the reduced surface because of the charge transfer, forming slightly positively charged C_6H_6.[21,24] Correspondingly, the stronger adsorption of C_6H_6 on oxidized R-TiO_2(110) is observed (Figure S4). In contrast to the C_6H_6 adsorption on R-TiO_2(110), negatively charged O_2 is formed on R-TiO_2(110). In principle, if the photodesorption of C_6H_6 on R-TiO_2(110) is an electron/hole mediated process, the trends of C_6H_6 and O_2 photodesorption in the presence of an electron acceptor/donor should be different. However, the trends of C_6H_6 and O_2 photodesorption with the same electron acceptor (Cl_2) or donor (CH_3OH) are the same, indicating that the photodesorption of C_6H_6 on R-TiO_2(110) is not a simple hole mediated desorption process.

Moreover, the TOF results of the electron mediated CH_3I desorption[16] and the hole mediated O_2 desorption[12] show that the velocity distributions of CH_3I (257 and 320 nm) and O_2 (298, 335, and 360 nm) at different wavelengths are nearly the same, demonstrating that the photon energy is not transferred into the translational energy of the desorbing CH_3I and O_2 efficiently. Similarly, the velocity distributions of H_2O desorption on R-TiO_2(110)[35] are also wavelength independent in the range 250−310 nm. However, the TOF spectra of C_6H_6 desorption collected on 0.2 ML of C_6H_6 covered R-TiO_2(110) surfaces under 343 and 257 nm irradiation are very different (Figure 6). At 343 and 257 nm, the spectra have a peak arrival time at about 100 and 62 μs (from the R-TiO_2(110) surface to the ionizer), respectively. The big difference indicates that the translational energies of the desorbing C_6H_6 at these two wavelengths are very different, and the photon energy is transferred into the translational energy of the desorbing C_6H_6. Moreover, as the surface temperature increases, the peak arrival time in TOF spectra slightly increases under 257 nm irradiation (Figure S5), which is opposite to the result of O_2 photodesorption on R-TiO_2(110) at different surface temperatures.[12] This is quite contrasted with the results observed in desorption processes facilitated by electrons and holes, indicating that the C_6H_6 desorption is not likely induced by the interfacial electron/hole transfer.

Besides, the roles of coadsorbed O_2 in the photodesorption of CO and C_6H_6 on R-TiO_2(110) are opposite. With O_2 coadsorption, CO photodesorption is largely enhanced on the surface (Figure S6), consistent with previous result.[13] In contrast, C_6H_6 photodesorption is largely inhibited (Figure 2), suggesting that C_6H_6 photodesorption on R-TiO_2(110) is not induced by the rearrangement of the surface atoms and excess charges via the recombination of photogenerated holes and excess electrons. In addition, a previous study[33] shows that surface hydroxylation can inhibit the O_2 photodesorption because surface hydroxylation can decrease the surface work function and change the surface dipole, leading to inhibiting the hole transfer process between the adsorbates and TiO_2. To investigate the role of the surface dipole in C_6H_6 photodesorption, the C_6H_6 photodesorption experiment was conducted on the reduced and hydroxylated R-TiO_2(110) surfaces. The hydroxylated surface was prepared by exposing the reduced surface to 1 ML of H_2O at 100 K and then flashed to 400 K to remove the remaining H_2O molecules at the Ti_{5c} sites, leaving bridging hydroxyl (OH_b) groups on the surface. As shown in Figure S7, the photodesorption signals of C_6H_6 on the reduced and hydroxylated surface are identical, indicating that local changes of the surface dipole did not play a significant role in C_6H_6 photodesorption, which is different from that of O_2.[33]

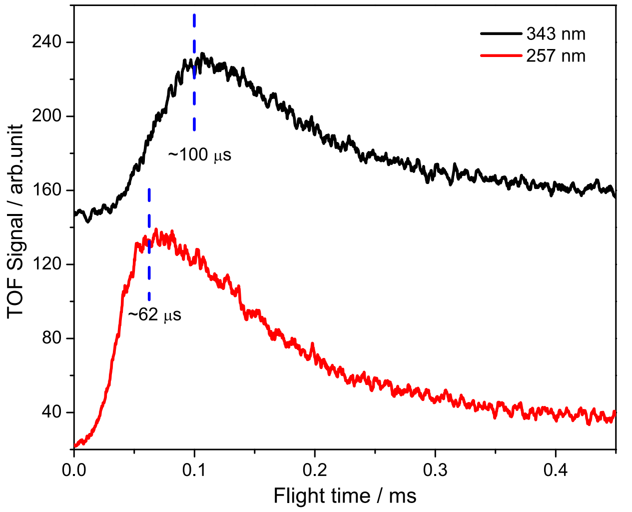

Figure 6. Typical TOF spectra collected at $m/z = 78$ ($C_6H_6^+$) on the 0.2 ML of C_6H_6 covered R-TiO_2(110) surfaces after irradiating the surfaces for 5 min with 343 and 257 nm at 80 K, respectively. The photon flux is 1.6×10^{16} photons cm^{-2} s^{-1} at 343 nm and 1.2×10^{16} photons cm^{-2} s^{-1} at 257 nm. The repetition frequency for both wavelengths is 200 Hz.

With the discussions, the pathways of C_6H_6 photodesorption on R-TiO_2(110) via the interfacial charge transfer process or the recombination of photogenerated holes and excess electrons can be ruled out. Namely, the transfer of photon energy into the translational energy of desorbing C_6H_6 on R-TiO_2(110) does not occur via these processes. Therefore, an energy transfer process via a collision process will be the candidate. As reported previously, the one-dimensional motion of C_6H_6 along the Ti_{5c} row on R-TiO_2(110) can occur even at 50 K.[24] Here, the surface temperature was kept at 100 K for experiments, and the movement of C_6H_6 along the Ti_{5c} row will be much faster than that at 50 K. As a result, the collision between C_6H_6 and the O_b atoms will occur easily. Under 355 nm irradiation, hole trapped O_b^- can be produced.[36−38] At a shorter wavelength, deeper hole trapped O_b^- can be produced. Then, the transfer of photon energy into the translational energy of the desorbing C_6H_6 could occur via the collision between C_6H_6 and hole trapped O_b^-. Because no interfacial charge transfer occurs, the collision can occur immediately after hole trapped O_b^- production, which can avoid energy dissipation via the fast relaxation of hot hole. As a result, more energy can be transferred into the translational energy of the desorbing C_6H_6 due to the production of deeper hole trapped O_b^- at a shorter wavelength. Similarly, previous studies show that photoinactive molecules like Kr, Ar, and N_2 can also be efficiently photodesorbed from the R-TiO_2(110) surface because of the collision with the photoexcited oxygen atoms on the Ti_{5c} sites.[34] The existence of O_2 and CH_3OH on R-TiO_2(110) may quench the hole trapped O_b^- via the photodesorption or possible proton-coupled electron transfer (PCET) process.[39] While for the case of H_2O, which is a neutral molecule and incapable of donating significant charge into the TiO_2 surface, the C_6H_6 photodesorption is also depressed. This may be due to the formation of stable hydrogen bonds between H_2O and R-TiO_2(110),[40,41] thus facilitating the energy transfer from O_b^- to H_2O and quenching the excited O_b^-. In contrast, the existence of Cl and O atoms on R-TiO_2(110) can eliminate the excess electrons on the surface by forming Cl^- and O^{2-} anions, thus facilitating the transfer of holes from the bulk to the surface and enhancing the hole trapped O_b^- formation. In addition, in combination with previous work,[34] the photodesorption of adsorbates induced by collisional energy transfer on R-TiO_2(110) may be universal. Further, the collisional energy transfer may also induce photocatalytic reactions for weakly bonded molecules on the surface.

■ CONCLUSIONS

In summary, the photodesorption of C_6H_6 on R-TiO_2(110) in the presence of an electron acceptor/donor has been systematically investigated. The results show that the photodesorption of C_6H_6 on R-TiO_2(110) is most likely to occur via the collisions between C_6H_6 and hole trapped O_b^- rather than via the interfacial electron/hole transfer, resulting in more energy transfers into the translational energy of the desorbing C_6H_6 at a shorter wavelength. The collisional energy transfer induced desorption under irradiation may be universal on TiO_2, which may also induce photocatalytic reactions on R-TiO_2(110) for weakly bonded molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.4c00648.

> PSD spectra of C_6H_6 as a function of O_2 exposure (Figure S1), TPD spectra of C_6H_6 after irradiation as a function of coadsorbed H_2O coverage (Figure S2), PSD spectrum of C_2H_6 (Figure S3), TPD spectra of C_6H_6 (Figure S4), TOF spectra of C_6H_6 as a function of surface temperature (Figure S5), PSD spectra of CO with different electron acceptors (Figure S6), and PSD spectra of C_6H_6 on the reduced and hydroxylated surfaces (Figure S7) (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Chen, X.; Mao, S. S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chem. Rev.* **2007**, *107*, 2891−2959.

(2) Fujishima, A.; Zhang, X. T.; Tryk, D. A. TiO_2 Photocatalysis and Related Surface Phenomena. *Surf. Sci. Rep.* **2008**, *63*, 515−582.

(3) Chen, H.; Nanayakkara, C. E.; Grassian, V. H. Titanium Dioxide Photocatalysis in Atmospheric Chemistry. *Chem. Rev.* **2012**, *112*, 5919−5948.

(4) Henderson, M. A.; Lyubinetsky, I. Molecular-Level Insights into Photocatalysis from Scanning Probe Microscopy Studies on TiO_2(110). *Chem. Rev.* **2013**, *113*, 4428−4455.

(5) Ma, Y.; Wang, X.; Jia, Y.; Chen, X.; Han, H.; Li, C. Titanium Dioxide-Based Nanomaterials for Photocatalytic Fuel Generations. *Chem. Rev.* **2014**, *114*, 9987−10043.

(6) Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D. W. Understanding TiO_2 Photocatalysis: Mechanisms and Materials. *Chem. Rev.* **2014**, *114*, 9919−9986.

(7) Henderson, M. A. A Surface Science Perspective on TiO_2 Photocatalysis. *Surf. Sci. Rep.* **2011**, *66*, 185−297.

(8) Guo, Q.; Zhou, C.; Ma, Z.; Ren, Z.; Fan, H.; Yang, X. Elementary Photocatalytic Chemistry on TiO_2 Surfaces. *Chem. Soc. Rev.* **2016**, *45*, 3701−3730.

(9) Guo, Q.; Zhou, C.; Ma, Z.; Ren, Z.; Fan, H.; Yang, X. Elementary Chemical Reactions in Surface Photocatalysis. *Annu. Rev. Phys. Chem.* **2018**, *69*, 451−472.

(10) Guo, Q.; Zhou, C.; Ma, Z.; Yang, X. Fundamentals of TiO_2 Photocatalysis: Concepts, Mechanisms, and Challenges. *Adv. Mater.* **2019**, *31*, 1901997.

(11) Thompson, T. L.; Yates, J. T. Monitoring Hole Trapping in Photoexcited $TiO_2(110)$ Using a Surface Photoreaction. *J. Phys. Chem. B* **2005**, *109*, 18230−18236.

(12) Sporleder, D.; Wilson, D. P.; White, M. G. Final State Distributions of O_2 Photodesorbed from $TiO_2(110)$. *J. Phys. Chem. C* **2009**, *113*, 13180−13191.

(13) Petrik, N. G.; Kimmel, G. A. Off-Normal CO_2 Desorption from the Photooxidation of CO on Reduced $TiO_2(110)$. *J. Phys. Chem. Lett.* **2010**, *1*, 2508−2513.

(14) Zhang, Z.; Yates, J. T., Jr. Electron-Mediated CO Oxidation on the $TiO_2(110)$ Surface during Electronic Excitation. *J. Am. Chem. Soc.* **2010**, *132*, 12804−12807.

(15) Zhang, Z.; Yates, J. T., Jr. Effect of Adsorbed Donor and Acceptor Molecules on Electron Stimulated Desorption: $O_2/TiO_2(110)$. *J. Phys. Chem. Lett.* **2010**, *1*, 2185−2188.

(16) Kim, S. H.; Stair, P. C.; Weitz, E. UV-Induced Desorption of CH_3X (X = I and Br)/$TiO_2(110)$. *J. Chem. Phys.* **1998**, *108*, 5080−5088.

(17) Antoniewicz, P. R. Model for Electron- and Photon-Stimulated Desorption. *Phys. Rev., B Condens. Matter* **1980**, *21*, 3811−3815.

(18) Thompson, T. L.; Yates, J. T. Control of a Surface Photochemical Process by Fractal Electron Transport across the Surface: O_2 Photodesorption from $TiO_2(110)$. *J. Phys. Chem. B* **2006**, *110*, 7431−7435.

(19) Mu, R.; Dahal, A.; Wang, Z. T.; Dohnálek, Z.; Kimmel, G. A.; Petrik, N. G.; Lyubinetsky, I. Adsorption and Photodesorption of CO from Charged Point Defects on $TiO_2(110)$. *J. Phys. Chem. Lett.* **2017**, *8*, 4565−4572.

(20) Dohnálek, Z.; Kim, J.; Bondarchuk, O.; White, J. M.; Kay, B. D. Physisorption of N_2, O_2, and CO on Fully Oxidized $TiO_2(110)$. *J. Phys. Chem. B* **2006**, *110*, 6229−6235.

(21) Chen, L.; Zhang, S.; Persaud, R. R.; Smith, R. S.; Kay, B. D.; Dixon, D.; Dohnálek, Z. Understanding the Binding of Aromatic Hydrocarbons on Rutile $TiO_2(110)$. *J. Phys. Chem. C* **2019**, *123*, 16766−16777.

(22) Zhao, Y.; Wang, Z.; Cui, X.; Huang, T.; Wang, B.; Luo, Y.; Yang, J.; Hou, J. G. What Are the Adsorption Sites for CO on the Reduced $TiO_2(110)$-1 × 1 Surface? *J. Am. Chem. Soc.* **2009**, *131*, 7958−7959.

(23) Tan, S.; Ji, Y.; Zhao, Y.; Zhao, A.; Wang, B.; Yang, J.; Hou, J.G. Molecular Oxygen Adsorption Behaviors on the Rutile $TiO_2(110)$-1 × 1 Surface: An in Situ Study with Low-Temperature Scanning Tunneling Microscopy. *J. Am. Chem. Soc.* **2011**, *133*, 2002−2009.

(24) Zhou, J.; Dag, S.; Senanayake, S. D.; Hathorn, B. C.; Kalinin, S. V.; Meunier, V.; Mullins, D. R.; Overbury, S. H.; Baddorf, A. P. Adsorption, Desorption, and Dissociation of Benzene on $TiO_2(110)$ and Pd/$TiO_2(110)$: Experimental Characterization and First-Principles Calculations. *Phys. Rev. B* **2006**, *74*, 125318.

(25) Guo, Q.; Xu, C.; Ren, Z.; Yang, W.; Ma, Z.; Dai, D.; Fan, H.; Minton, T. K.; Yang, X. Stepwise Photocatalytic Dissociation of Methanol and Water on $TiO_2(110)$. *J. Am. Chem. Soc.* **2012**, *134*, 13366−13373.

(26) Diebold, U.; Hebenstreit, W.; Leonardelli, G.; Schmid, M.; Varga, P. High Transient Mobility of Chlorine on $TiO_2(110)$: Evidence for "Cannon-Ball" Trajectories of Hot Adsorbates. *Phys. Rev. Lett.* **1998**, *81*, 405−408.

(27) Lira, E.; Hansen, J. Ø.; Huo, P.; Bechstein, R.; Galliker, P.; Lægsgaard, E.; Hammer, B.; Wendt, S.; Besenbacher, F. Dissociative and Molecular Oxygen Chemisorption Channels on Reduced Rutile $TiO_2(110)$: An STM and TPD study. *Surf. Sci.* **2010**, *604*, 1945−1960.

(28) Sokolović, I.; Reticcioli, M.; Calkovsky, M.; Wagner, M.; Schmid, M.; Franchini, C.; Diebold, U.; Setvin, M. Resolving the Adsorption of Molecular O_2 on the Rutile $TiO_2(110)$ Surface by Noncontact Atomic Force Microscopy. *Proc. Natl. Acad. Sci. U. S. A.* **2020**, *117*, 14827−14837.

(29) Lai, Y.; Zeng, Y.; Chen, X.; Wang, T.; Yang, X.; Guo, Q. Photochemistry of Ethanol on Rutile $TiO_2(110)$: Breaking Two Bonds with One Hole. *J. Phys. Chem. C* **2023**, *127*, 1863−1869.

(30) Zhang, Z.; Yates, J. T., Jr. Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces. *Chem. Rev.* **2012**, *112*, 5520−5551.

(31) Dong, S.; Hu, J.; Xia, S.; Wang, B.; Wang, Z.; Wang, T.; Chen, W.; Ren, Z.; Fan, H.; Dai, D.; et al. Origin of the Adsorption-State-Dependent Photoactivity of Methanol on $TiO_2(110)$. *ACS Catal.* **2021**, *11*, 2620−2630.

(32) Setvin, M.; Shi, X.; Hulva, J.; Simschitz, T.; Parkinson, G. S.; Schmid, M.; Di Valentin, C.; Selloni, A.; Diebold, U. Methanol on Anatase $TiO_2(101)$: Mechanistic Insights into Photocatalysis. *ACS Catal.* **2017**, *7*, 7081−7091.

(33) Petrik, N. G.; Kimmel, G. A. Probing the Photochemistry of Chemisorbed Oxygen on $TiO_2(110)$ with Kr and Other Co-Adsorbates. *Phys. Chem. Chem. Phys.* **2014**, *16*, 2338−46.

(34) Minto, T.; Sanioo, Y.; Kim, Y.; Kato, H. S.; Aika, K.; Kawai, M.; Zhao, J.; Petek, H.; Huang, T.; He, W.; et al. The Electronic Structure of Oxygen Atom Vacancy and Hydroxyl Impurity Defects on Titanium Dioxide (110) Surface. *J. Chem. Phys.* **2009**, *130*, 124502−1-11.

(35) Xu, C.; Xu, F.; Chen, X.; Li, Z.; Luan, Z.; Wang, X.; Guo, Q.; Yang, X. Wavelength-Dependent Water Oxidation on Rutile $TiO_2(110)$. *J. Phys. Chem. Lett.* **2021**, *12*, 1066−1072.

(36) Zhou, M.; Wang, H. Optimally Selecting Photo-and Electro-catalysis to Facilitate CH_4 Activation on $TiO_2(110)$ Surface: Localized Photoexcitation Versus Global Electric-Field Polarization. *JACS Au* **2022**, *2*, 188−196.

(37) Wang, X.; Wan, L.; Wang, Z.; Liu, X.; Gao, Y.; Wang, L.; Liu, J.; Guo, Q.; Hu, W.; Yang, J. Identifying Photocatalytic Active Sites of C_2H_6 C-H Bond Activation on TiO_2 Via Combining First-Principles Ground-State and Excited-State Electronic Structure Calculations. *J. Phys. Chem. Lett.* **2022**, *13*, 6532−6540.

(38) Li, F.; Lai, Y.; Zeng, Y.; Chen, X.; Wang, T.; Yang, X.; Guo, Q. Photocatalytic Ethane Conversion on Rutile $TiO_2(110)$: Identifying the Role of Ethyl Radical. *Chem. Sci.* **2023**, *15*, 307−316.

(39) Migani, A.; Blancafort, L. Excitonic Interfacial Proton-Coupled Electron Transfer Mechanism in the Photocatalytic Oxidation of Methanol to Formaldehyde on $TiO_2(110)$. *J. Am. Chem. Soc.* **2016**, *138*, 16165−16173.

(40) Henderson, M. A. An HREELS and TPD Study of Water on $TiO_2(110)$: The Extent of Molecular Versus Dissociative Adsorption. *Surf. Sci.* **1996**, *355*, 151−166.

(41) Zehr, R. T.; Henderson, M. A. Influence of O_2-Induced Surface Roughening on the Chemistry of Water on $TiO_2(110)$. *Surf. Sci.* **2008**, *602*, 1507−1516.