

# TPD-MS

## APPLICATION NOTE

### Photocatalytic Studies Using Temperature Programmed Desorption Mass Spectrometry (TPD-MS)

Thermal analysis consists of many techniques for the exploration of the physical properties of different substrates and adsorbents. Samples are subjected to programmed temperature exposure, and data is represented as a function of temperature. Thermal analysis methods are increasingly important in many industries including, but not limited to, quality control and industrial research on products such as polymers, pharmaceuticals, clays and minerals, food packaging, and metals and alloys.<sup>1</sup>

Extrel is a recognized leader in technology designed for Temperature Programmed Desorption (TPD) or Thermal Desorption Spectrometry (TDS). TPD is a way of characterizing the surface composition of a substrate. With this type of analysis, one can study the kinetics of adsorption through the dissociation of adsorbed gases on surfaces. By heating a sample contained within the vacuum chamber, desorption occurs when a molecule gains enough energy to overcome the activation barrier.<sup>2</sup> The temperature rises, causing adsorbents to leave the observed surface in gas form; the adsorbents are then analyzed by the mass spectrometer.

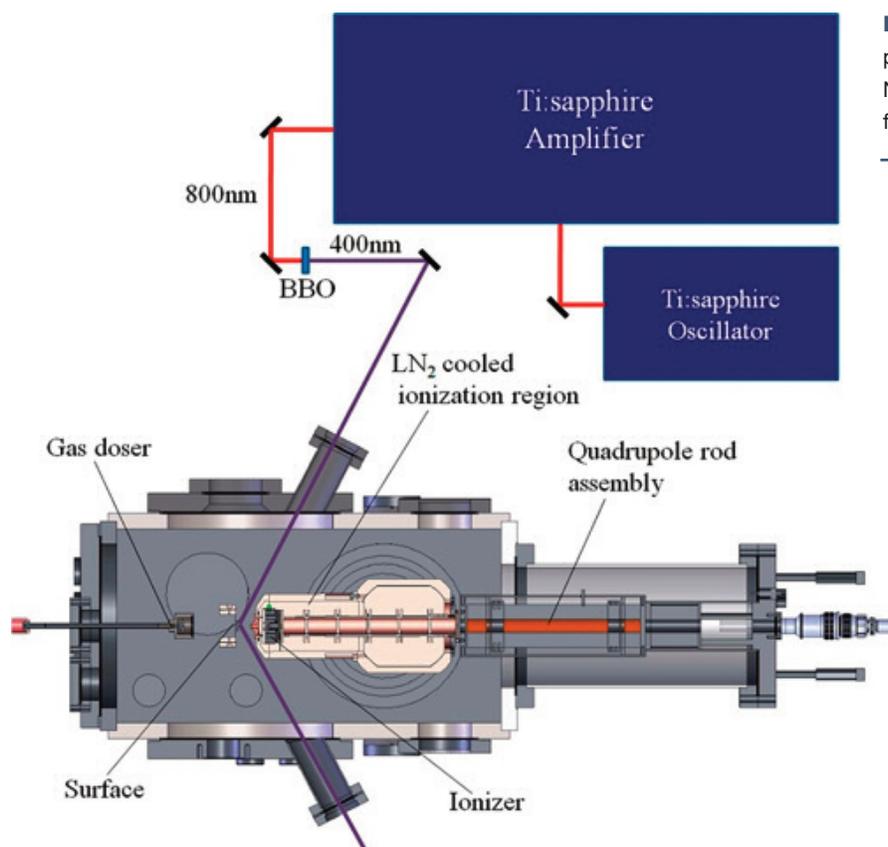
Mapping the temperature ramp while monitoring the mass spectrum allows the user to:

- identify the temperatures at which desorption occurs, and
- target analytes' binding energies.

Studying the resulting spectra can offer quantitative and qualitative information of the atomic and molecular species that have been annealed upon the surface of the examined substrate. TDS can be used to focus on analyzing and quantifying data from known adsorbents, as well as attempting to identify the presence of trace impurities within a sample matrix.

Extrel has developed a range of instruments and systems for accurate and reproducible TPD measurements. The Veraspec TDS is one example of a turnkey system featuring sample introduction, controlled thermal management, and high sensitivity detection. Extrel's custom TPD systems are also used for more dedicated and specific research, such as the one installed at the State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, China. This particular system features Extrel's most sensitive MAX-50 quadrupole analyzer and is used to study surface chemistry—specifically photocatalytic activity involving rutile TiO<sub>2</sub> surfaces, and its reactions with methanol and water. “Rutile and anatase TiO<sub>2</sub> materials have often been used in the study of hydrogen (H<sub>2</sub>) production from photocatalytic water splitting.”<sup>9</sup> Although some details of the experiment will be discussed for general understanding of the concept, the Ti:sapphire laser and the specifics of the photocatalysis reactions are subject matter for another paper. Here, the focus will be placed on the data and results obtained by Extrel's mass spectrometer which allowed the quantitative and qualitative results of the study to be analyzed.

# Instrument Introduction



**Figure 1.** Schematic diagram of the photocatalysis-TPD mass spectrometer. Note that the laser source did not come from Extrel.<sup>3</sup>

This highly sensitive TPD spectrometer was designed for photocatalytic process studies on a single crystal. It is an ultra-high vacuum (UHV) system whose main probing chamber operates at a base pressure of  $6 \times 10^{-11}$  Torr.<sup>3</sup> Above the main chamber, rests the vacuum system which includes the preparation and characterization chamber where the  $\text{TiO}_2$  (110) crystals (Princeton Scientific Corporation) are cleaned and checked for contamination.<sup>3-5</sup>

## Requirements of a TPD System Needs

- Relation of adsorbate concentration to partial pressure
- Analysis time relating to desorption rate
- Accurate desorption curves in order to relate to reaction kinetics

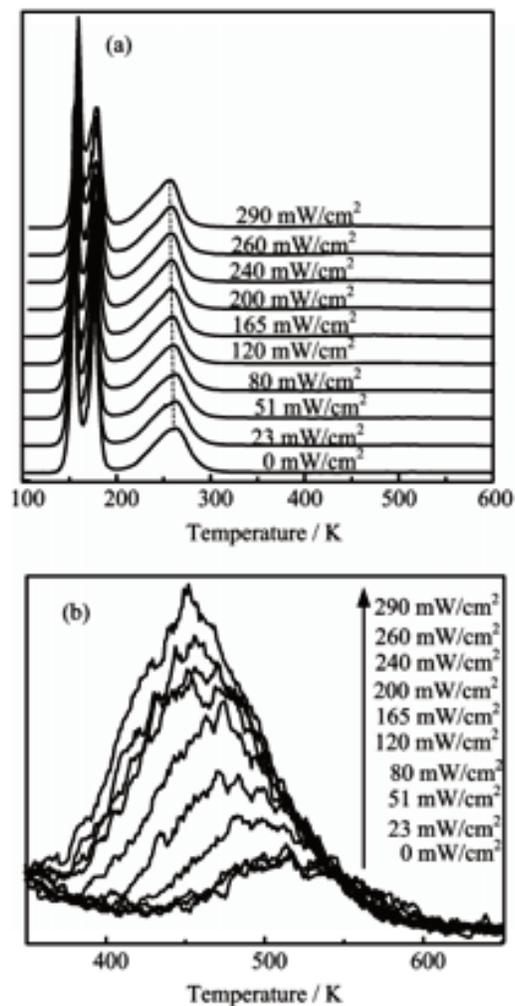
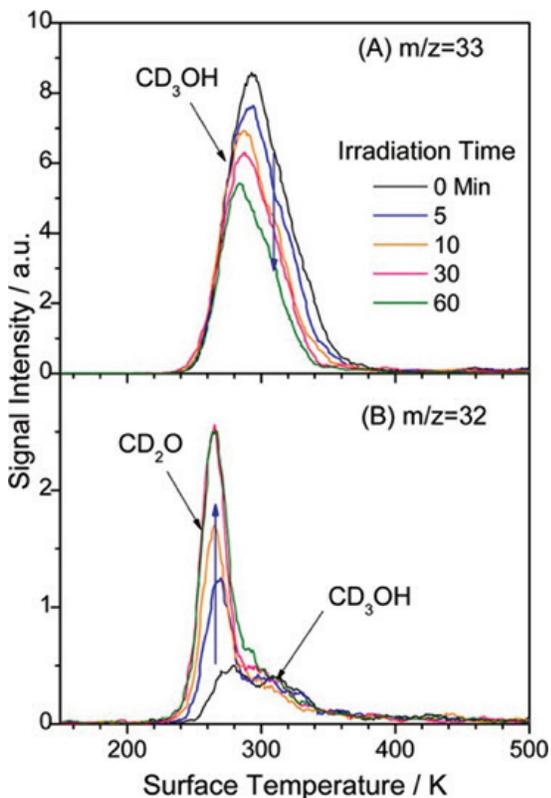
Extrel's MAX-50 quadrupole mass spectrometer utilizes an electron impact (EI) ionizer in a region that is maintained at an extremely high vacuum of  $1.5 \times 10^{-12}$  Torr.<sup>6-7</sup> The experiments were conducted using 2-3 mA of emission current and 60-70 eV electron energy. The ionization region was surrounded by a copper shield cooled by a double-layer liquid nitrogen cryopump to depress outgassing from chamber walls and adsorb low vapor pressure residual species.<sup>8</sup> The ionization chamber is connected to the main chamber by a 4 mm pinhole from the front of the ionizer, and a 5 mm pinhole leads ions to the quads from the back of the optics region. A titanium sublimation pump (Varian), surrounded by a double-layer liquid nitrogen Dewar, was used to achieve better vacuum by pumping high vapor pressure residual gasses. Utilizing these additional pumps allowed the experimenters to reduce background anywhere from 6-200 times, depending on the mass selected to analyze and increase detection of residual gases and radical species.

## Experimental

**Figure 2.** (a) Here the TPD spectra of the 2.9 ML H<sub>2</sub>O dosed TiO<sub>2</sub> (110) surface is shown as a function of pre-irradiated power with 266 nm for 90 s. (b) Close up view of the change in the 500 K peak as a function of pre-irradiated power.<sup>8</sup>

In this experiment, researchers dosed the TiO<sub>2</sub> (110) surfaces with CD<sub>3</sub>OH (Aldrich, 99.9%), purified by several freeze/pump/thaw cycles, and introduced to the surface with a calibrated molecular beam doser<sup>3,5,6,8,9</sup> before exploiting to laser irradiation.

The sensitivity of the mass spectrometer is clearly evident from the data shown in Figure 7 as the various water TPD states are easily manipulated by the photon flux. The increase in peak area within figure 2 (b) indicates an increase in the concentration of O-vacancy with an increase in photon flux.<sup>8</sup>

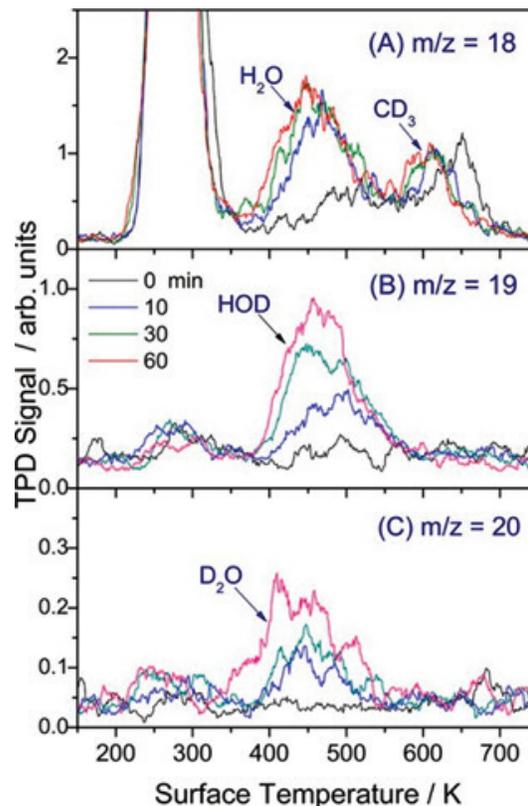


**Figure 3.** A) TPD spectra at  $m/z = 33$  ( $CD_2OH^+$ ). It can be seen that peak intensity decreased with increased laser irradiation times. Conversely, in (B),  $m/z = 32$  ( $CD_2O^+$ ) signal increases with laser irradiation time.<sup>3</sup>

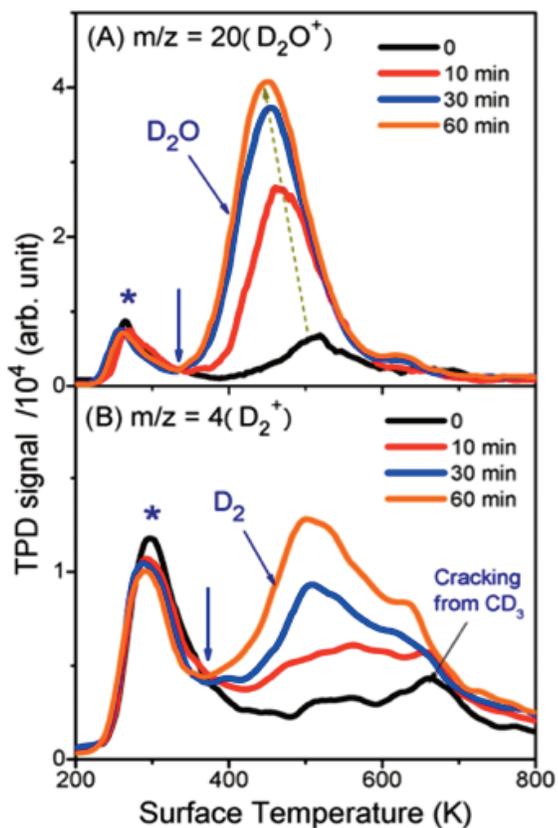
The peak in (A) is the result of dissociative ionization of the desorbed parent molecule, CD<sub>3</sub>OH.<sup>3</sup> The spectrum in (B) is thought to arrive from three possible sources. CD<sub>2</sub>O is the most intense peak around 270 K. The remaining lump in the spectrum is result of CD<sub>3</sub>OH and CD<sub>3</sub>OD, both of which are desorbed around 300 K.

**Figure 4.** TPD spectra of  $m/z = 18$  ( $\text{H}_2\text{O}^+$ ,  $\text{CD}_3^+$ ), 19 ( $\text{HOD}^+$ ), and 20 ( $\text{D}_2\text{O}^+$ ) showing photocatalysis of  $\text{CD}_3\text{OH}/\text{TiO}_2$  over varied laser exposure.<sup>3</sup>

The resulting TPD spectra are found to be similar to the TPD peak of  $\text{H}_2\text{O}$  which is a product of H atoms known to adsorb on the bridge-bonded oxygen (BBO) sites of the  $\text{TiO}_2$  (110) surface.<sup>4</sup> Based on this, it is suggested that the TPD signals of the water isotopologues, in Figure 4, have come from H and D atoms dissociating from BBO sites.



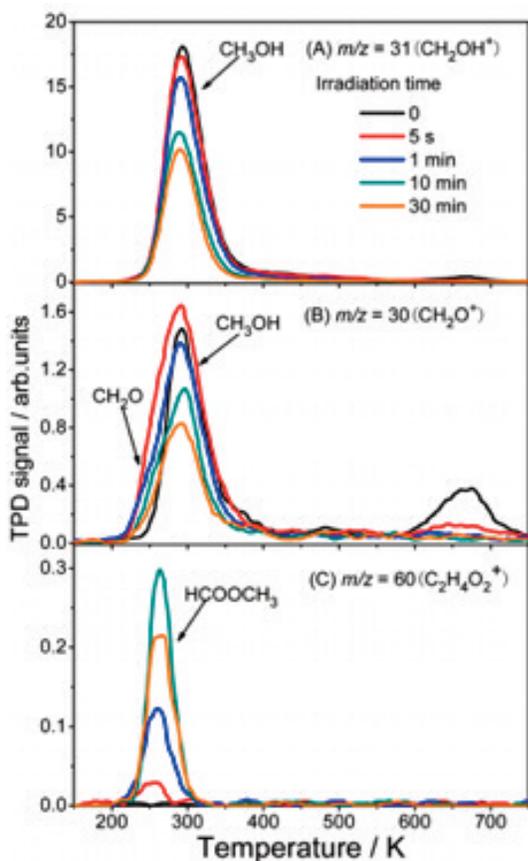
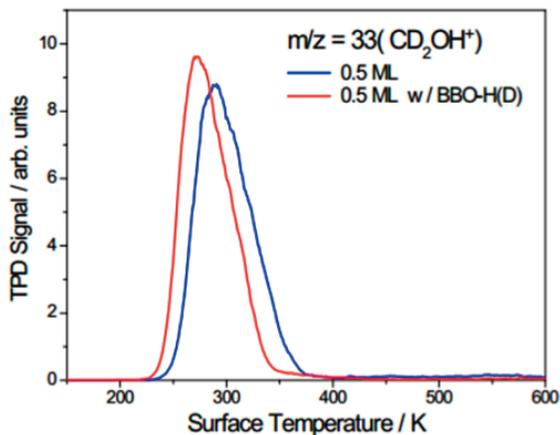
**Figure 5.** (A) TPD spectra of  $m/z = 20$  ( $\text{D}_2\text{O}^+$ ) collected after 400nm laser irradiation at different times. The peak near 300 K (marked with \*) is said to be the dissociative ionization signal of molecular adsorbed  $\text{CD}_3\text{OD}$ . (B) TPD spectra of  $m/z = 4$  ( $\text{D}_2^+$ ).<sup>5</sup>



**Figure 6.** TPD spectra at  $m/z = 33$  ( $\text{CD}_2\text{OH}^+$ ).<sup>6</sup>

Figure 6 highlights the ability of the mass spectrometer to differentiate between two  $\text{TiO}_2$  (110) surfaces. The graph depicts how the binding of Hydrogen or Deuterium atoms to the BBO sites affects the TPD spectra of  $\text{CH}_3\text{OH}$ . The red peak was plotted with the BBO sites saturated; the methanol signal is shifted approximately 20 K lower in the presence of BBO-H(D).

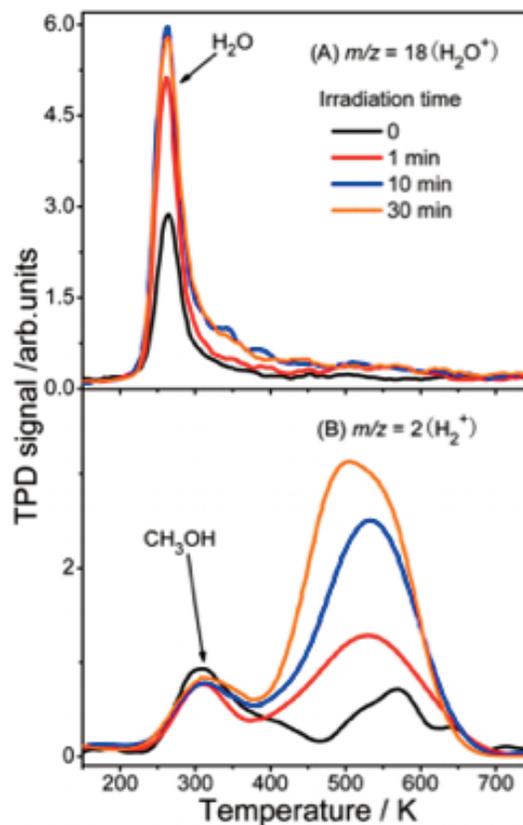
In their most recent study at the State Key Laboratory, researchers shifted their focus from the rutile (R)- $\text{TiO}_2$  (110) substrate to the anatase (A)- $\text{TiO}_2$  (101) material. The anatase form has been described as the most active polymorph in commercial applications for catalysts.<sup>10</sup> From the previous studies, the reaction process of methanol and water on the rutile surface has been pretty well defined. Researchers had been dissatisfied by the lack of efficiency of the R- $\text{TiO}_2$  (110) surface. It was determined that only about 7% of D-atoms on the BBO sites contribute to  $\text{D}_2$  formation with a majority recombining with BBO atoms to form  $\text{D}_2\text{O}$ . Here the photocatalytic chemistry of  $\text{H}_2$  formation on A- $\text{TiO}_2$  (101) is investigated.



**Figure 7.** (A) Spectra of  $m/z = 31$  ( $\text{CH}_2\text{OH}^+$ ). (B) Spectra of  $m/z = 30$  ( $\text{CH}_2\text{O}^+$ ). (C) Spectra of  $m/z = 60$  ( $\text{C}_2\text{H}_4\text{O}_2^+$ ) a signal of the parent ion signal of  $\text{HCOOCH}_3$ . Spectra were collected from a 0.38 ML of  $\text{CH}_3\text{OH}$  dosed A- $\text{TiO}_2$  (101) substrate plotted as a function of irradiation time with a photon flux of  $1.9 \times 10^{17}$  photons  $\text{cm}^{-2} \text{s}^{-1}$ .<sup>9</sup>

The spectra of the observed products are similar to those achieved in earlier studies on the R- $\text{TiO}_2$  (110) surface, suggesting that its formation follows similar photocatalytic mechanisms. Following the mechanism from A to B to C, dissociated H atoms are transferred to the BBO sites, setting up the reaction conditions for the formation of molecular  $\text{H}_2$  as a thermally-driven reaction.

**Figure 8.**(A)TPD spectra of  $m/z = 18$  ( $\text{H}_2\text{O}^+$ ) and (B)  $m/z = 2$  ( $\text{H}_2^+$ ) at varied laser irradiation times.<sup>9</sup>



## Extrel's Excellence in Thermal Desorption

### Needs

- Relation of adsorbate concentration to partial pressure
- Analysis time relating to desorption rate
- Accurate desorption curves in order to relate to reaction kinetics

### Strengths

- The high accuracy and sensitivity of Extrel systems allow for detection of minimal signal fluctuations.
- Often temperature ramps are in the 1 K/sec to 10 K/sec "range:" Extrel's mass spectrometer allows for fast, real-time analysis in order to relate to accurate temperature relations.
- Extrel's mass spectrometers allow for the desorption curves to be used to target binding energies.

## Conclusion

Extrel's mass spectrometry systems offer users the abilities:

1. to study the surface composition of a substrate and the kinetics of adsorption through the dissociation of adsorbed gases on surfaces.
2. to maintain high sensitivity and exceptional confidence for the resulting data and mass spectrum.

Extrel's analyzers and turnkey systems for TPD are trusted by many of the world's leading researcher groups. With controlled temperature ramping to 1200°C, and featuring Extrel's industry leading MAX-CS range of quadrupole mass spectrometer analyzers, both off the shelf and custom solutions address individual research needs without compromise.

### Sources:

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