Title

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The Photoassisted Reaction of Gaseous Water and Carbon Dioxide Adsorbed on the $SrTiO_3$ (111) Crystal Face to Form Methane

by

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Abstract

The photosynthetic reaction cf gas phase water and carbon dioxide molecules adsorbed onto strontium titanate surfaces that are in contact with platinum foils is reported. The dominant reaction product detected at 15 torr partial pressures of the reactant gases is methane. The reaction takes place without any externally applied potential (between the foil and $SrTiO_2$) and in the absence of liquid electrolyte, when the clean, reduced $SrTiO_3$ (111) crystal face is illuminated with light of energy greater than the band gap. A thermal process, which produces methane, when the $SrTiO_3$ - Pt sandwich is heated in CO_2 and water, is also observed. The photo and thermal processes are easily distinguished by the use of filters.

Introduction

In this letter we report the first observation of the photosynthetic reaction of water and carbon dioxide molecules from the gas phase to form methane, when adsorbed on clean single crystal strontium titanate surfaces of (111) orientation which are in contact with platinum foil. This process occurs without any applied potential between the strontium titanate and the platinum and in the absence of liquid electrolytes.

Ever since the report of photoassisted decomposition of liquid water by Fujishima and Honda (1), there has been much work on photoassisted reactions in aqueous solutions using various semiconductors (2-10). In some of these systems a small external potential (less than the $\Delta\varepsilon°$ of 1.23 volt for the decomposition of water) had to be applied, in others no potential was necessary for the detectable generation of hydrogen at the metal counter-electrode and oxygen at the illuminated semiconductor photoanode. In all cases, photons of energy greater than or equal to the band gap of the semiconductor electrode had to be used to initiate and sustain the chemical reactions.

The photon assisted reaction requires four distinct processes to take place at the active solid surface: 1) photoelectron-hole pair generation by light, charge separation and trapping, 2) oxidation and reduction reactions of the adsorbates with the aid of the photogenerated charges, 3) rearrangement and other surface reactions of intermediates, and 4) removal of the products and regeneration of the surface. It appeared to us that it should be possible to find surfaces that carry out all these functions while in contact with only gaseous reactants. Thus an electro-chemical cell may not be necessary to perform photon assisted chemical reactions.

There are distinct advantages in carrying out chemical reactions other than the dissociation of water. Although thermodynamically uphill, the reactions of CO_2 and water to produce a variety of hydrocarbons (methane or methanol, for example) require less energy input per electron transferred (have lower $\Delta\varepsilon°$ values) than that needed to dissociate water.

1. $CO_2(g) + 2H_2O(g) \rightarrow CH_4(g) + 2O_2(g)$ $\Delta\varepsilon° = 1.037$ev
2. $CO_2(g) + 2H_2O(g) \rightarrow CH_3OH(g) + 3/2\ O_2(g)$ $\Delta\varepsilon° = 1.19$ev

By appropriate choice of the catalytic surface and the reactant molecules, unique chemical reactions may be performed to obtain diverse products, selectively and with high reaction probability.

There are also many advantages in carrying out photon assisted reactions in the vapor phase over solid-liquid systems. Working in the gas phase at low pressures (less than 10^{-4} torr) allows the direct application of the various analytical tools of modern surface science to monitor the composition, structure and electronic states of both substrate and adsorbates. By utilizing the detailed information available from such studies the reaction mechanism can be discovered. At high pressures ($1\text{-}10^3$ torr) one may also be able to optimize the rates of product formation without concern for the problems involved in using an electrochemical cell. In the absence of the electrolyte the surface temperature can be changed over a broader range and the absorption of light by the electrolyte is avoided.

Experimental

Our experiments were carried out at $\sim$30 torr total pressures in an isolation chamber located in the middle of an ultra high vacuum system. The apparatus is shown in Fig. 1. The UHV system is a commercial Varian surface analysis chamber with low energy electron diffraction, and Auger electron spectroscopy capabilities. The chamber also has a quadrupole mass spectrometer for gas analysis and an ion gun for crystal cleaning. A diffusion pump and cryobaffle were added to the standard ion pump and titanium sublimation pump to handle the extra gas loads when the isolation cell is opened after an experiment. The system base pressure is $\sim 1 \times 10^{-9}$ torr. The isolation cell consists of a cylinder, mounted on a bellows, which can be raised up over the sample by a screw drive. The vacuum seal is made with a gold o-ring. With the cell closed gases are introduced into the cell through connections to an external gas loop. During an experiment the gases are circulated through the cell and the loop, which is external to the vacuum system, by a metal bellows pump. Also in the external loop are: a capacitance manometer (MKS 170M-6B) and the gas sampling valve for the gas chromatograph that is equipped with a flame ionization detector (HP 5720A). The sampling volume for the gas chromatograph is 0.25 ml. The total volume of the cell plus the external loop is $\sim$90ml. This isolation cell allows us to run batch type reactions on well characterized single crystal surfaces.

The strontium titanate single crystals were obtained from National Lead Company. The samples were small disks of $\sim 1\ \text{cm}^2$ area if (111) orientation (determined by Laue x-ray diffraction) and 1 mm thick.

The samples to be studied were reduced in a hydrogen furnace for two hours at 1000°K. The reduced sample was black in color and showed relatively high dark conductivity (∿1(ohm cm)$^{-1}$). The $SrTiO_3$ crystal was then mounted on a disk of .01 inch thick platinum foil and was held in place by two straps of Pt foil (∿1 mm wide) that were spot welded to the Pt foil backing (see Fig. 2). The sample was then mounted in the UHV chamber.

After evacuation the sample was cleaned by Argon ion bombardment and short periods of heating in oxygen. The main initial surface impurities were carbon and sulfur on both the oxide and the metal surfaces. After cleaning, Auger electron spectra (AES) that are characteristic of the clean surfaces were obtained and the spectrum for the oxide crystal face is shown in Figure 3. The oxygen (510ev)/titanium (381ev) and strontium (76ev)/titanium (381ev) peak ratios were 1.4 and 2.8 respectively, indicating that the oxide surface was oxygen deficient, as compared to unreduced samples which have been studied previously in our laboratory (11). The surface was disordered when viewed by low energy electron diffraction (LEED). At this point the isolation cell was closed and pressurized with the reactant gases. The CO_2 was Matheson Research Grade and was used without further purification. It contained a small methane impurity which was negligible compared to the methane produced. The pure water was obtained from Scientific Products and was used after several cycles of outgassing by freezing with liquid nitrogen while pumping on the sample. No impurities were detectable in the water by gas chromatography.

Band gap radiation was provided by a 500 watt high pressure mercury lamp in a water cooled housing. Light from the lamp was collimated and focussed on the sample with two quartz lenses. An infrared filter consisting of a quartz cell filled with $NiSO_4$ solution was placed between the mercury lamp and the reaction cell, to adsorb the heat and transmit the near U.V.. With this arrangement we were able to obtain a photon flux of $\sim 10^{17}$ photons/sec on the 1 cm^2 crystal surface.

Results and Discussion

The amount of methane produced as a function of time in a typical experiment is shown in Fig. 4. This experiment consisted of illuminating the cleaned sample in ∿15 torr CO_2 and ∿17 torr H_2O with $NiSO_4$ filtered radiation from the mercury lamp. The temperature of the sample was monitored by a thermocouple and was always less than ∿315°K. The initial rate of methane production corresponds to ∿1 molecule of methane for each 10^4 photons incident on the crystal. As shown in Figure 4, the rate of methane production decreases over a ∿10 minute period, due to a reaction inhibition process. The CH_4 production was not renewed by pumping out the gases and refilling the cell with fresh CO_2 and H_2O. This indicates that the decrease in CH_4 production was in fact due to a poisoning and not the result of the establishment of a steady state concentration of CH_4./ However, the CH_4 production was regenerated by repeating the cleaning process described above. The main impurities on the sample surface after reaction, as determined by Auger electron spectroscopy, were Cl (from an unknown source) on the $SrTiO_3$ crystal face and about a monolayer of carbon on the Pt surface. No carbon deposit was ever found to accumulate on the $SrTiO_3$. The total amount of methane produced is ∿5-10 times the number of surface sites on the $SrTiO_3$ crystal, indicating that a catalytic reaction is taking place. However, in the absence of a steady state rate of production of methane it is still uncertain whether the reaction is truly catalytic or whether a photoassisted stoichiometric reactionbetween the reduced $SrTiO_3$ crystal and CO_2 and H_2O is responsible for the CH_4 production. Studies aimed at a detailed understanding of the poisoning and to obtain irrefutable proof of the catalytic nature of the reaction are underway at present.

Several "blank" experiments were carried out to probe the nature of the photoassisted process. The following experiments all produced no detectable amounts of CH_4:

1. The $SrTiO_3$-Pt sample with only CO_2 (no H_2O) in the presence of light and by heating the sample to 450°K.
2. The $SrTiO_3$ crystal without the Pt foil using CO_2 and H_2O mixtures and illumination.
3. The Pt foil alone using CO_2 and H_2O mixtures both with illumination and by heating the Pt foil to 450°K.
4. The $SrTiO_3$-Pt sample in a CO_2 and H_2O mixture using illumination with the light of energy <u>less</u> than the band gap of $SrTiO_3$. (Light with energy less than the band gap was obtained by placing a corning glass filter (CS3-74) between the $NiSO_4$ solution filter and the reaction cell).

The last "blank" experiment indicates that band gap radiation is necessary for the photoassisted production of CH_4 from CO_2 and H_2O. This is consistent with the observed necessity for band gap radiation to dissociate H_2O in the electrochemical cell experiments.

It was found that heating the cleaned $SrTiO_3$-Pt sandwich at 420°K in 15 torr CO_2 and 17 torr H_2O produced CH_4 at rates comparable to the photoassisted reaction. This thermal reaction was also observed to poison. It should be noted that heating the reduced (conducting) $SrTiO_3$ sample will thermally generate electrons in the conduction band which should behave chemically identically to the photogenerated electrons obtained by using band gap radiation. With this in mind a thermal reaction is also expected in addition to the photoassisted reaction.

The purpose of this letter is to describe the phenomena, the discovery of a photosynthetic reaction that takes place at the solid-vapor interface using an oxide-metal sandwich. A better understanding of the reaction mechanism requires further experiments. A discussion of the elementary reaction steps will be presented in a forthcoming paper. Studies in this laboratory using TiO_2 and $SrTiO_3$ crystal surfaces indicate the importance of Ti^{3+} surface ions for the dissociative adsorption of water and the importance of band gap illumination to regenerate Ti^{3+} after being oxidized in the presence of water. (11-13) The accumulation of carbon only on the platinum surface during the photochemical reaction indicates that much of the carbon chemistry that includes hydrogenation is likely to take place on the metal. The accumulation of carbon at the surface can also be one reason for the poisoning of the methane production rate. Perhaps the rate of CO_2 decomposition is faster than the rate of rehydrogenation of the carbon that was formed.

It should be noted that products other than methane may also be produced by the photoassisted reaction. Hydrogen, oxygen, formic acid, and other hydrocarbons may also form under appropriate circumstances. Our detection system at present has very low sensitivity for oxygen and for hydrogen. Although methane is the dominant detectable product under our experimental conditions, experiments will also be carried out to obtain other molecules by photoassisted reactions.

Acknowledgment

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Figure Captions

Fig. 1 Schematic of ultra high vacuum surface analysis chember equipped with an isolation cell for carrying out reactions up to 1 Atm total pressure.

Fig. 2 Schematic of the $SrTiO_3(111)$ - Pt foil sample.

Fig. 3 Auger electron spectrum obtained from the clean reduced $SrTiO_3$ surface.

Fig. 4 Methane produced as a function of illumination time.

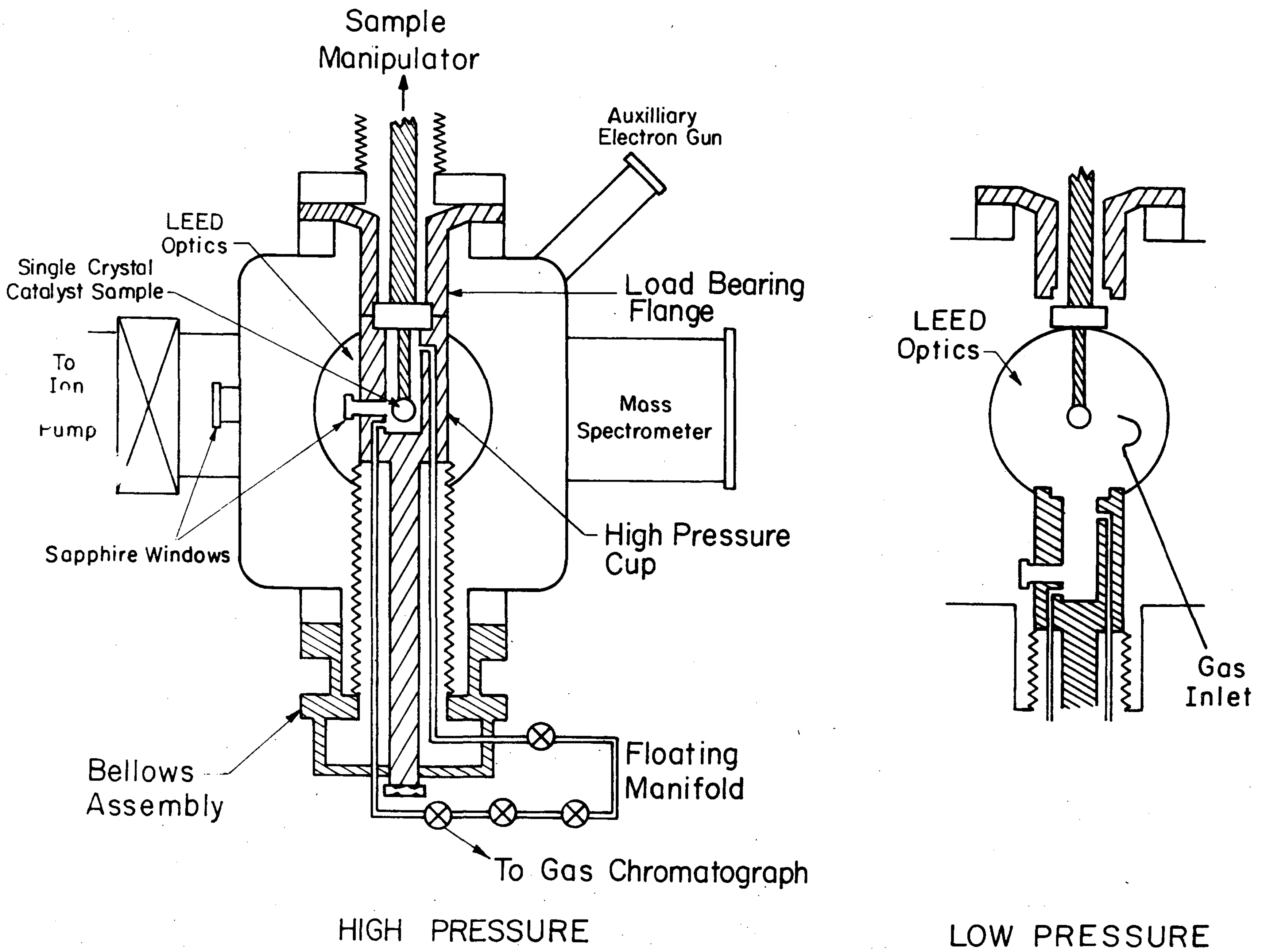

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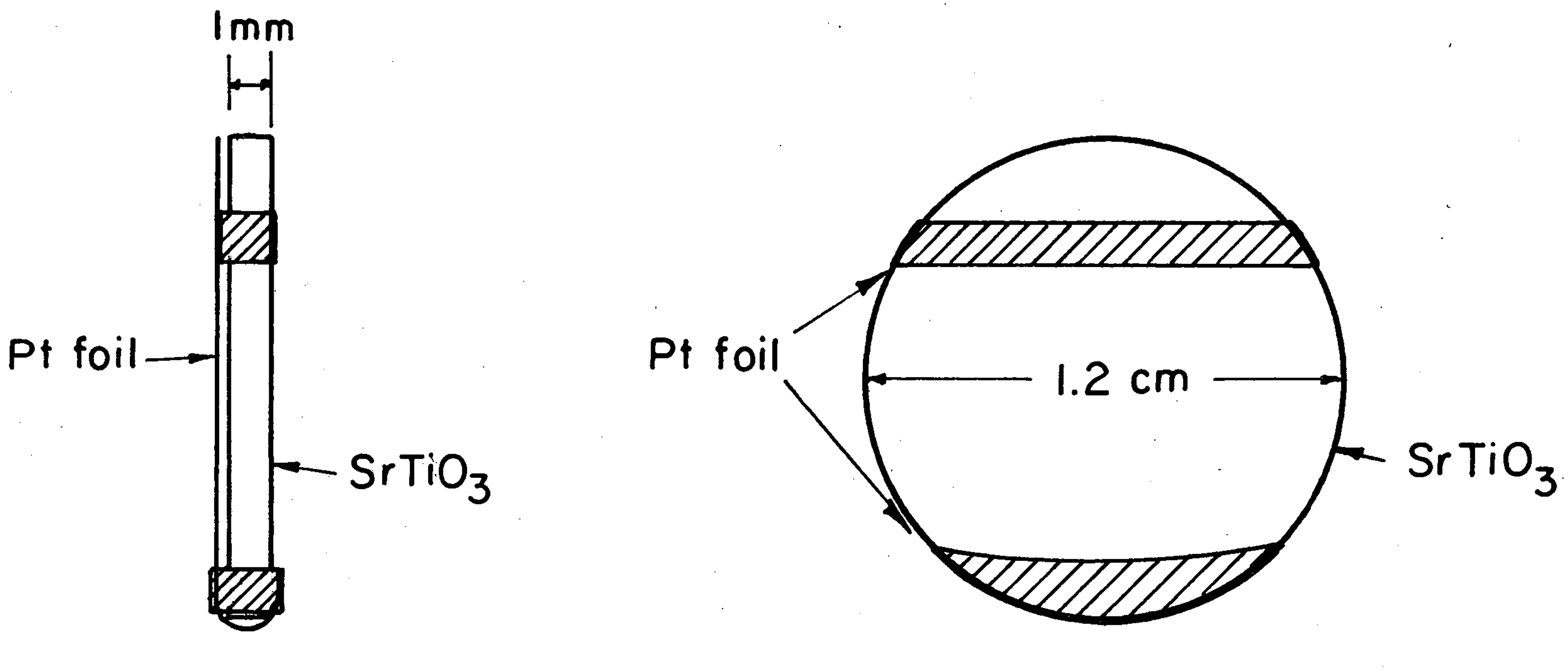
Fig. 1

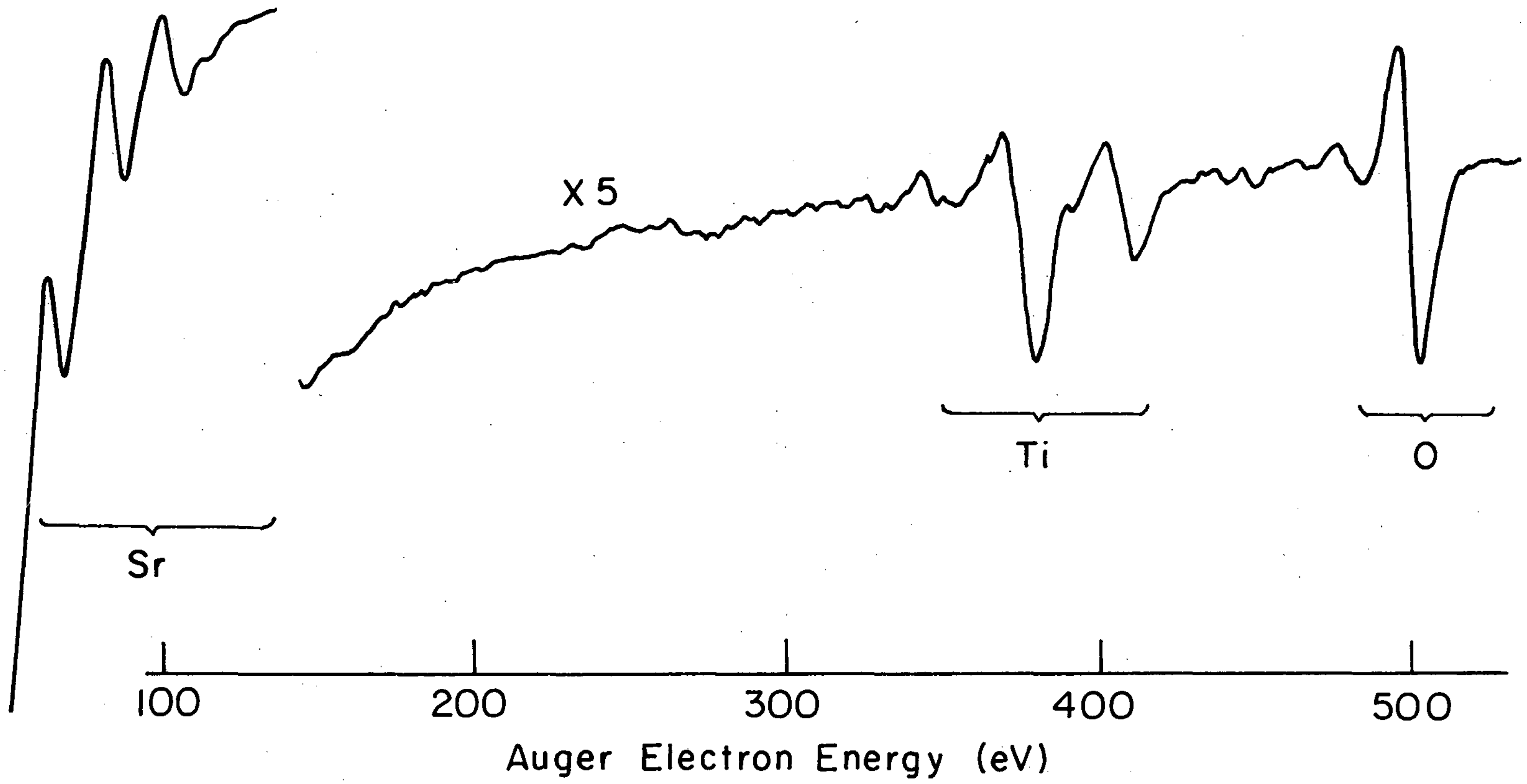


Side View

Front View

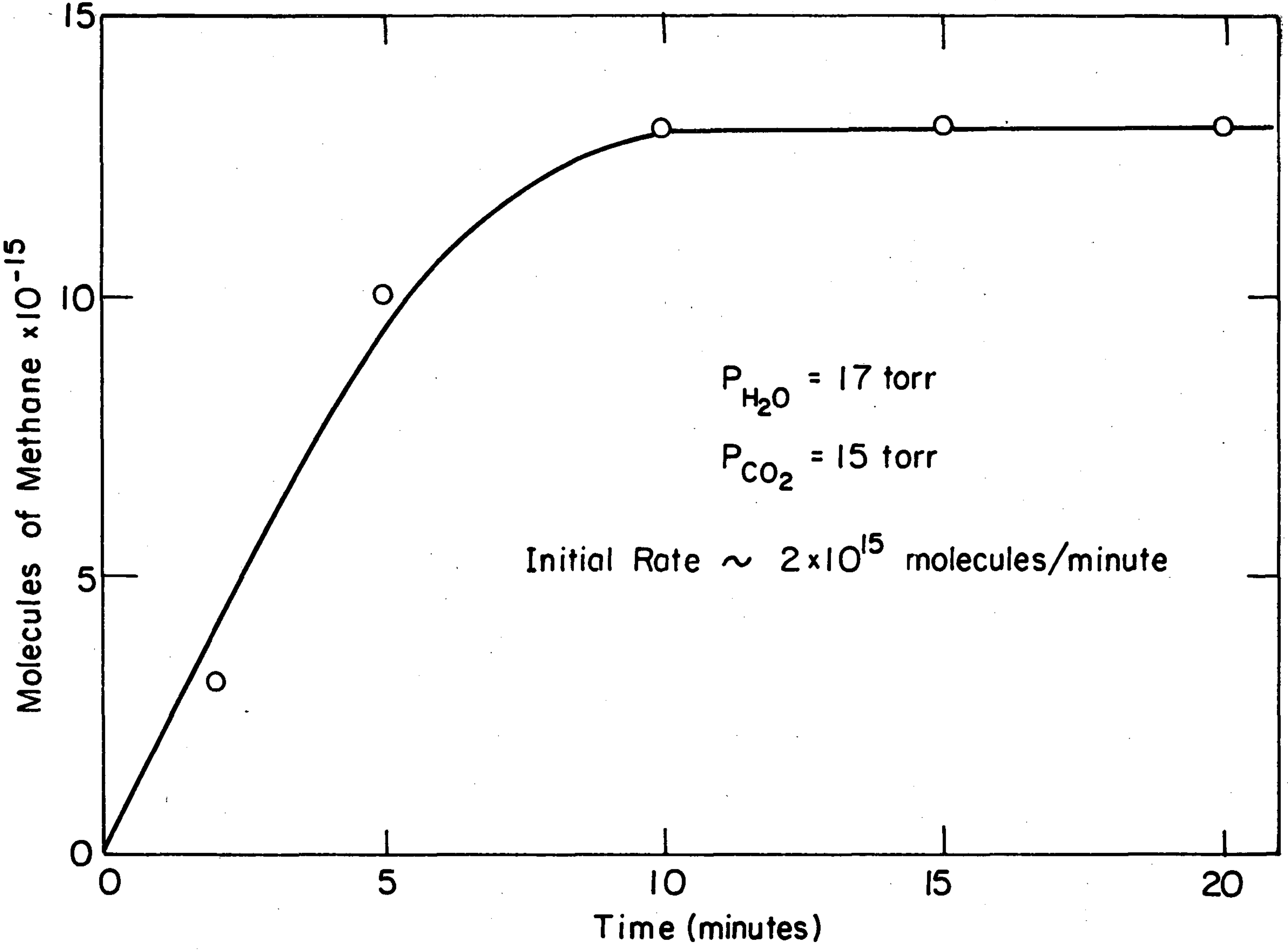
XBL783-4778

Fig. 2



XBL 783-4779

Fig. 3



XBL 783-4759

Fig. 4

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