# Ambient-pressure photoelectron spectroscopy for heterogeneous catalysis and electrochemistry

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### ARTICLE INFO

### ABSTRACT

We describe the design and capabilities of a new ambient-pressure X-ray photoelectron spectroscopy system at the Stanford Synchrotron Radiation Lightsource. A unique feature of this system is that samples are illuminated at grazing incidence and with a tightly focused beam, which allows a 50 μm aperture to be placed in the first differential pumping stage of the lens system of the electron spectrometer. The low conductance of the aperture enables surface-sensitive electron spectroscopy of solid surfaces, liquids, and solid–liquid interfaces to be performed *operando* at pressures as high as 100 Torr. The instrument can also be used to obtain polarization-resolved X-ray absorption spectra using Auger-electron-yield detection. Results for Pt surfaces in ambient-pressure gas environments and for liquid water are presented.

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## 1. Introduction

X-ray photoelectron spectroscopy (XPS) has many advantages compared with other techniques that probe surface chemistry and heterogeneous catalysis [1–4]. It is, for example, element specific and provides information about the chemical state of systems through chemical shifts [5]. Importantly, XPS is also surface sensitive, because photoelectrons with kinetic energies between 100 and 1400 eV typically have inelastic mean free paths less than 20 Å in condensed media. A related disadvantage, however, is that conventional XPS measurements require ultra-high vacuum conditions ($P < 1 \times 10^{-8}$ Torr) to minimize scattering of emitted photoelectrons by gases and to prevent discharges on the electrostatic lens elements and the detectors, whereas many processes of interest in catalysis and electrochemistry take place at elevated pressure (>760 Torr) and temperature. This limitation was partially circumvented by the development of ambient-pressure XPS (APXPS), which began in the early 1980s [6] but later accelerated with the advent of third-generation synchrotron facilities [4]. Today, several synchrotron-based instruments allow XPS measurements at gas pressures of up to a few Torr. Concomitant improvements in conventional X-ray sources have also led to recent efforts to develop laboratory-based instruments for ambient-pressure spectroscopy [7,8].

The basic design principle of ambient-pressure electron spectrometers is straightforward: a small aperture limits the conductance between a gas cell containing the sample and a differentially pumped electron-energy analyzer. Samples are placed very close to the aperture to reduce the path length of the emitted photoelectrons through the ambient-pressure gas environment; typically, the sample is separated from the aperture by ~0.1–0.5 mm, which ensures that the local pressure at the sample is the same as the background pressure in the gas cell [9].

To date, three different electrostatic focusing schemes have been employed for the lens system of ambient-pressure spectrometers: (i) a conventional lens configuration optimized for fixed working distances (typically ~40–50 mm) [7]; (ii) an additional focusing electrostatic lens in the differential pumping scheme [10,11]; (iii) a pre-lens section incorporated into a conventional lens design [12]. In comparison with (i), the latter two methods provide more space between the sample and the spectrometer, so that additional differential pumping stages can be incorporated without losing detection efficiency. These design considerations and related studies performed in the early development stages of the technique have been reviewed in detail [9,10,13] and will not be recapitulated here.

In the past decade, APXPS has been primarily used to investigate solid surfaces in near-ambient gas environments [14–17]. The unique capabilities of APXPS are exemplified by recent studies of

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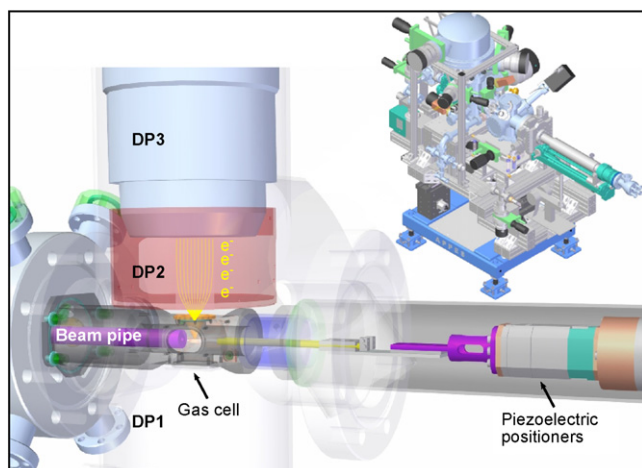*E-mail address:* sarpkaya@slac.stanford.edu (S. Kaya).

**Fig. 1.** The gas cell and the first three differential pumping sections (DP1, DP2, and DP3) of the APXPS system at BL 13-2 at SSRL. The first differential pumping section (DP1) is the measurement chamber that houses the gas cell. The second differential pumping section (DP2) is separated from the gas cell by a small opening that limits gas conductance. The first lens element of the electron spectrometer is located between the second and third differential pumping stages. The tube in the center of the gas cell (purple) is the X-ray beam pipe and a $Si_3N_4$ window separates the beam line components from the gas cell environment. The alignment of the sample is performed through piezoelectric positioners. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Fig. 2.** Top and side views of the measurement geometry with a table showing important parameters. Shaded area between the aperture and the sample in the side view image demonstrates the volume in which beam and emitted photoelectrons are going through. The images are not in-scale in order to only to introduce the concept. Important geometrical parameters are tabulated and pressures in the first and the second differential pumping sections as a function of the diameter of the apertures are shown on the right.

surface-oxide growth on catalytically active metal surfaces [18–20], the interaction of water with metal and metal-oxide surfaces [21–23], the surface electronic-structure of operating solid-oxide fuel cells [24], and compositional changes of bimetallic nanoparticles in oxidizing and reducing atmospheres [25]. In addition, ambient-pressure spectrometers have been used to perform X-ray absorption spectroscopy (XAS) at the *K* edges of C, N and O, and at the *L* edges of 3*d* transition metals [26]; these studies provide information about the geometric structure of adlayers in equilibrium with near-ambient gas environments. It is noteworthy, however, that few of the *in situ* APXPS studies outlined above yielded significant additional information beyond what had been obtained from the corresponding *ex situ* measurements performed in UHV. These observations have encouraged researchers to improve the performance of APXPS systems, *e.g.*, by extending the working pressure range.

In the present article, we demonstrate the capabilities of the new APXPS system now operating at beamline 13-2 at the Stanford Synchrotron Radiation Lightsource (SSRL). Although the working principle is comparable to other instruments in use around the world, the design of the gas cell allows us to perform *in situ* measurements at pressures of up 100 Torr. The design of the new spectrometer will be described in Section 2, and applications of the new spectrometer to adsorbate systems and fuel-cell reactions will be presented in Section 3.

## 2. Materials and methods

### 2.1. The ambient-pressure photoelectron spectroscopy instrument

The instrument, shown in Fig. 1, is composed of two separate chambers: a preparation chamber, in which surface cleaning (sputtering, annealing, *etc.*) and sample preparation can be performed in UHV; and a spectrometer chamber that houses a titanium gas cell with an entrance aperture to the differentially pumped lens elements of the electron-energy analyzer. The first three of five differential pumping sections are shown in Fig. 1. A sample is mounted
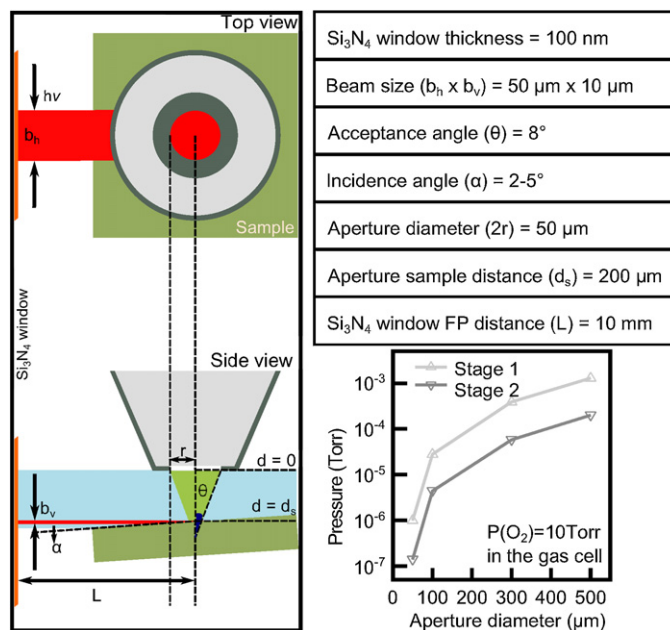
on a rod and can be transferred between the preparation chamber and the gas cell by a manipulator. When the sample is introduced into the gas cell, the transfer rod engages with the gas-cell opening assuring a vacuum-tight sealing. Inside the gas cell, the lateral and vertical alignment of the sample can be adjusted by using three piezoelectric positioners (Attocube; two ANPx101 attoFLEX and one ANPz101 attoFLEX) that are used for precise positioning of the samples close to the aperture and also for lateral sample scanning in order to prevent beam induced effects. While the electron spectrometer (VG Scienta, SES 100) is customized to incorporate differential pumping units, it does not contain any pre-lens section or additional electron-focusing lens elements. Gases are introduced into the gas cell through variable leak valves. The composition of the gas that effuses through the aperture and into the differentially pumped section can be monitored by means of a quadrupole mass spectrometer (Thermo, 201 HAL). A heater attached to the gas cell allows the temperature of the gases in the cell to be controlled; temperatures as high as 150 °C can be achieved.

The APXPS instrument is connected to beamline 13-2, which is an elliptically polarized undulator (EPU) beamline at SSRL that covers the photon energy regime between 150 and 1300 eV with resolving power of $E/\Delta E > 5000$. The 13-2 branch line is equipped with Kirkpatrick–Baez (KB) refocusing optics that tightly focus the X-ray beam onto the center of the APXPS gas cell; the full-width at half-maximum (fwhm) of the focal spot of the X-ray beam is smaller than 10 μm (vertical) × 50 μm (horizontal).

### 2.2. Measurement geometry

A close-up view of the measurement geometry—specifically, the incidence angle of the X-ray beam and the acceptance angle of the emitted electrons—is shown in Fig. 2. The sample is illuminated at grazing incidence to minimize the signal from gases relative to that from surface species. The ratio of signals arising from gaseous and surface species is controlled principally by two factors, provided