Infrared-Laser Photoacoustic Spectroscopy for Surface Studies: SF_6 Interaction with Silver Films

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(Received 29 September 1982)

Infrared-laser photoacoustic spectroscopy has been applied to surface studies at submonolayer coverage under ultrahigh-vacuum conditions. The adsorption of SF_6 on silver films at 90 K was investigated. Simultaneous x-ray photoelectron measurements show that 0.1 of a monolayer can be readily detected with the photoacoustic technique. Photoacoustic spectra from submonolayer to multilayer surface coverages have been obtained and show characteristic SF_6 vibrational bands.

PACS numbers: 78.20.Hp, 68.45.Da, 78.20.Nv, 78.30.-j

In the last few years vibrational spectroscopies have become an important tool for surface studies.[1] They can be used to investigate the interaction of adsorbed molecules with the bulk substrate and with each other.[2] The techniques commonly applied for such studies are, e.g., infrared absorption reflection spectroscopy, surface enhanced Raman scattering, or electron energy-loss spectroscopy. All these methods have certain strengths and limitations with regard to sensitivity, spectral resolution, ambient and instrumental requirements, as well as general applicability. Photoacoustic spectroscopy[3-6] has also been applied to adsorbed species. However, experiments seemed to be restricted to either powders and porous substances[7-11] or heavily exposed samples such as corroded[12] or anodized surfaces.[13,14] These surfaces were not well characterized and the presence of contaminants rendered the observed spectra difficult to interpret. Of course, the full potential of a new surface analytical method can only be realized when spectra of well-defined systems, preferably at submonolayer coverage, are available. Naturally, this requires the development of an acoustic transducer suitable for stringent UHV conditions (bakable, no outgassing), but also *in situ* preparation and characterization of the substrate and an independent determination of the surface coverage, e.g., by x-ray photoelectron spectroscopy (XPS).

In this Letter we report on the application of photoacoustic spectroscopy (PAS) to well characterized surfaces under UHV conditions. Submonolayer detection sensitivity for SF_6 on silver films is demonstrated and vibrational spectra are obtained.

In optoacoustic or photoacoustic spectroscopy, the sample under investigation is excited with a modulated or pulsed light source.[3-6] Subsequent radiationless decay causes local heating. Because of thermal expansion, sound waves are generated. They can be detected with an acoustic transducer. The photoacoustic (PA) signal reflects the optical, thermal, and acoustic properties of the sample. For a gas-solid system, the adsorption of molecules on a bulk material can change the optical properties and therefore induce changes in the PA signal. Thus, PAS can be applied to surface studies. Of course, the signal of the adsorbed molecules will be superimposed on a signal originating from the substrate. However, an inherent advantage of PAS is that this background only results from the light *absorbed* by the substrate (typically several percent of the incident light intensity), whereas in infrared absorption reflection spectroscopy, for example, the *reflected* light (nearly 100%) creates a much higher background signal. Thus, PAS should have a high surface sensitivity.

The experimental apparatus is shown in Fig. 1. Basically, it consists of a cw CO_2 laser and a UHV chamber (base pressure 2×10^{-10} Torr) equipped with an ESCA-Auger spectrometer, a sputter ion gun, a silver evaporation source, and a mass spectrometer. The x-ray photoemission spectrometer with an Al anode, a double-pass cylindrical-mirror analyzer, and on line with an IBM/System 7 computer was described previously.[15] The CO_2 laser is line tunable in the 9–11 μm region and provides 0.1–0.7 W output power depending on the laser line. The unfocused beam is incident at 75° from the surface normal and covers the entire sample surface area about 7 mm in diameter. A piezoceramic disc with 10 mm diameter and 1 mm thickness is used as a PA transducer. The disc is metalized on both sides and its perimeter is coated with a glass film to prevent outgassing. One of the electrodes is polished and coated with a 1-μm-thick silver film. An additional silver film is deposited *in*

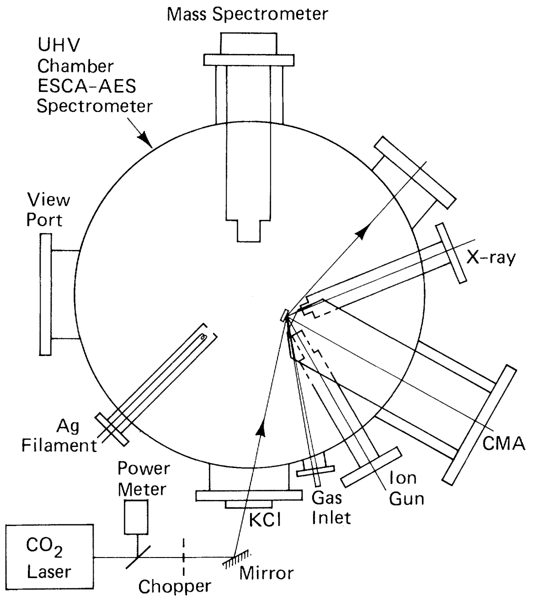

FIG. 1. A schematic diagram of the experimental apparatus for simultaneous XPS and PAS experiments.

situ and cleaned periodically by Ar$^+$ ion bombardment. The sample is attached to a manipulator and can be cooled to 90 K with liquid nitrogen. The SF_6 exposure is controlled with a leak valve and a small copper tubing directly facing the sample. The amount of surface coverage is determined from XPS analyses of the adsorbate and the Ag substrate. At 90 K, SF_6 can be adsorbed but not permanently condensed on the cold Ag surface. Thus, PAS and XPS measurements are performed simultaneously. The laser beam is intensity modulated with a chopper at 11 Hz and the amplitude of the PA signal is monitored with a lock-in amplifier the output of which is connected to a strip-chart recorder.

As the first step in the experiments, the adsorption behavior of SF_6 on Ag films at 90 K is studied with XPS. When the clean Ag surface at 90 K is exposed to SF_6, the intensities of the Ag($3d$) core-level peaks decrease and the F($1s$) and S($2p$) peaks appear in the XPS spectrum. The attenuation of the Ag($3d$) peaks and the intensity of the F($1s$) peak can be used to determined the surface coverage (θ) according to the simple formulas[16,17] generally adopted for XPS. In the estimation of the SF_6 coverage with XPS, we use 35 Å as the electron escape depth for photoelectrons at 1.1 keV kinetic energy. This value tends to be on the high side[17] and is used in order to reduce the possibility of underestimating the amount of surface coverage. The F($1s$) spectra exhibit fine structure depending on the amount of SF_6 coverage on the Ag surface. Below a monolayer, the F($1s$) signal shows a single peak at 688.5 eV with the Ag($3d_{5/2}$) binding energy taken to be 368.2 eV.[18] The full width at half maximum (FWHM) is about 2.1 eV. For $\theta > 1$, a second peak appears near 693 eV, whose intensity increases with coverage clearly indicating the formation of multilayer SF_6. The overall SF_6-Ag adsorption behavior is quite similar to the SF_6-Ru(001) system also studied with XPS by Fisher *et al.*[17] Since the F($1s$) XPS peak for the first monolayer is well separated from the multilayer F($1s$) peak, we can also use the F($1s$) spectrum for our estimation of the surface coverage. It is in fact experimentally observed that the high-binding-energy peak near 693 eV appears when θ estimated from the attenuation of the integrated Ag($3d_{5/2}$) and Ag($3d_{3/2}$) signals is about 1. This consistency shows that the uncertainty of our determination of the SF_6 coverage is considerably less than 50%.

As mentioned earlier, the PA signal is recorded simultaneously with the Ag($3d_{5/2}$) XPS signal during a given gaseous exposure. Since the gas dosing is accomplished through a small copper tubing directly facing the sample, for $\theta \leq 1$ the base pressure of the vacuum system does not rise above 1.5×10^{-9} Torr during each exposure associated with an adsorption-desorption cycle. It should be noted that under these experimental conditions, a clean Ag surface remains clean even after many exposures at 90 K. A typical result of such an adsorption-desorption experiment is shown in Fig. 2 with the CO_2 laser tuned to $\nu = 940.6$ cm^{-1}. Clearly, during the exposure the XPS signal of Ag decreases as a result of adsorption of SF_6. At this laser frequency, the light is absorbed by the chemisorbed SF_6 and the PA signal increases. Similarly, when the gas exposure is stopped and the SF_6 surface coverage decreases, the Ag($3d_{5/2}$) XPS signal increases and the PA signal decreases accordingly. When the experiment is repeated with the laser at 1033.5 cm^{-1}, clearly out of resonance with SF_6 vibrational bands, no PA signal due to SF_6 absorption is detected. From the signal-to-noise ratio of the PA signal and the SF_6 coverage (see Fig. 2) we estimate that for SF_6 on Ag the PAS surface sensitivity is better than 0.1 of a monolayer. To ensure that the PA signal is not saturated by the laser power (I), the intensity dependence of the PA signal is studied at various laser wavelengths. Within the used power range (0.1–0.7 W), the PA signal is found to have a linear dependence as

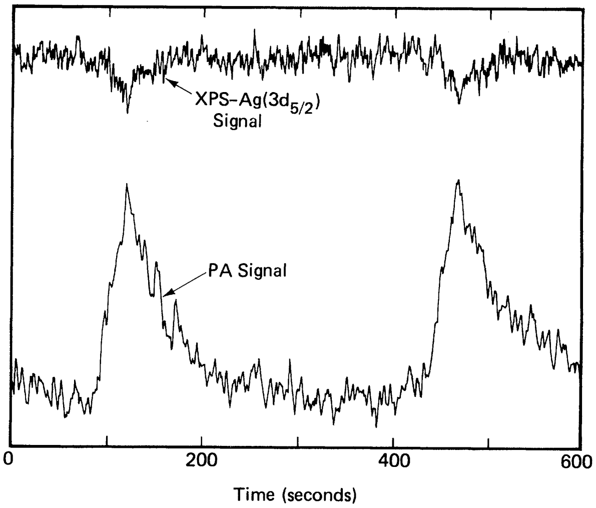

FIG. 2. Time dependence of PA and XPS-Ag($3d_{5/2}$) signals recorded during two successive SF_6 adsorption-desorption cycles. The peak SF_6 coverage on Ag is about $\theta = 0.2$ monolayer. The CO_2 laser is tuned to $\nu = 940.6\ cm^{-1}$ with $I = 0.67$ W.

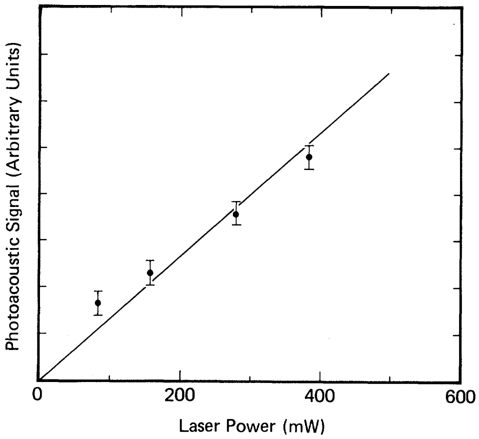

FIG. 3. The PA signal as a function of the laser power at $\nu = 940.6\ cm^{-1}$. SF_6 coverage on silver is about 0.4 monolayer.

shown in Fig. 3. This allows us to take the PAS data at the maximum laser power obtainable with every laser line in order to achieve optimum signal-to-noise ratio and subsequently normalize the data for each laser frequency. Figure 4, curves *a* and *b*, shows the normalized PA signal as a function of the laser frequency in the 920–960 cm^{-1} region at SF_6 surface coverages of about 0.2 and 0.4 monolayer, respectively. The error bars indicated in the figure represent one standard deviation of the normalized PA signal obtained during five subsequent adsorption-desorption cycles. The vibrational spectra of SF_6 at this submonolayer coverage as determined from PAS around 938 cm^{-1} appear to be quite broad (FWHM about 20 cm^{-1}). When the SF_6 surface coverage is increased to more than 1 monolayer, the vibrational spectrum sharpens considerably and the peak shifts toward 940 cm^{-1}. Figure 4, curve *c*, shows the vibrational spectrum at about 3 monolayers SF_6 coverage. The spectrum as determined by the photoacoustic technique resembles the ν_3 spectrum of solid SF_6 at low temperatures.[19]

The broadening of the measured vibrational spectrum of SF_6 at these submonolayer coverages on silver surfaces may be due to the existence of different adsorption sites and different chemical interactions between the adsorbed molecules and the metal film. The F(1*s*) XPS spectra also change considerably when the surface coverage is increased from submonolayer to multilayer coverages. We will continue to study this gas-surface system in order to better understand its chemical interactions and the technique of surface PAS as well. The results presented here clearly establish that the PAS method, as applied to well-characterized surfaces under UHV con-

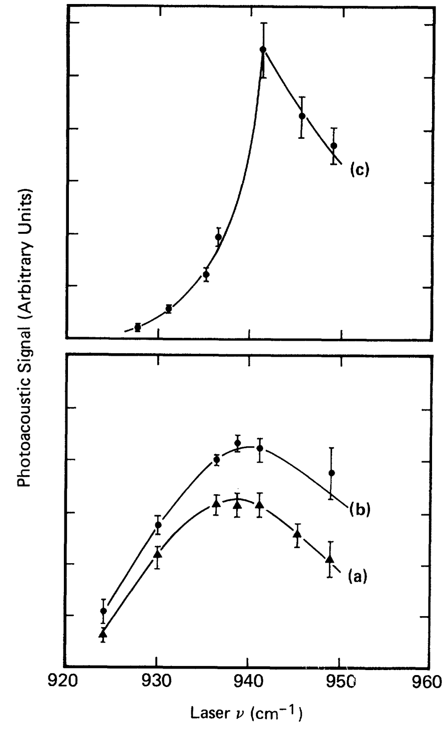

FIG. 4. ν_3 vibrational spectra of SF_6 adsorbed on Ag surfaces at 90 K determined by PAS: curve *a*, $\theta = 0.2$; curve *b*, $\theta = 0.4$; and curve *c*, $\theta = 3$.

ditions, indeed has submonolayer surface sensitivity.

In conclusion, photoacoustic spectroscopy provides important information about surface vibrations at submonolayer coverage. A number of obvious improvements are envisaged, which will increase the sensitivity of the technique even further. For example, the setup should be isolated against mechanical vibrations and the influence of power fluctuations on the PA signal can be minimized by stabilizing the laser intensity. Thus, laser surface photoacoustic spectroscopy offers advantages such as instrumental simplicity, high sensitivity, and high spectral resolution. Experiments in various environments, whether in vacuum or not, can be carried out. In addition, the method should have a high potential for applications to a wide variety of adsorbates and substrates.

The authors are grateful to R. G. Brewer for the loan of his CO_2 laser. They wish to thank J. Goitia for his assistance with the experimental setup and G. Castro for helpful discussions.

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