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SPECTROSCOPY OF ADSORBATES BY TRANSIENT LASER
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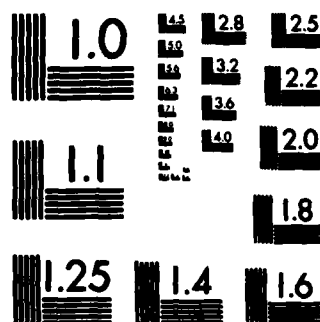
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Spectroscopy of Adsorbates by Transient Laser Calorimetry

by

**H. Coufal
T. J. Chuang
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Spectroscopy of Adsorbates by Transient Laser Calorimetry

H. Coufal, T. J. Chuang, and F. Träger*

IBM Research Laboratory
5600 Cottle Road, K34/281
San Jose, California 95193 U.S.A.

Abstract

The status of photothermal surface spectroscopy is reviewed. The importance of real time compensation techniques is underlined. Most recent results demonstrating sensitivities of hundredths of a monolayer of adsorbate are reported.

1. Introduction

In photothermal spectroscopy, the sample under investigation is excited with a modulated or pulsed light source [1-3]. Via radiationless decay part of the absorbed light is released in the sample as heat. With the incident energy being either modulated or pulsed the heat generation will also show a corresponding time dependence. Thermal waves are therefore generated and due to thermal expansion acoustic waves are induced. These waves can be detected with suitable transducers, such as pyro- or piezoelectric transducers. Only the *absorbed*, and *via* radiationless decay into heat converted fraction of the incident light energy contributes towards the photothermal signal. The fact that the absorbed energy is determined directly and not as the difference of incident and reflected or transmitted light energy makes photothermal techniques particularly suitable for weakly absorbing samples, such as adsorbates. Combined with laser excitation this detection method therefore offers a unique combination of advantages such as high sensitivity, high spectral resolution, high time resolution and instrumental simplicity.

For adsorbates on an ideal, not light absorbing substrate, be it a perfect mirror or a completely transparent substrate, the amount of adsorbate that is detectable is in principle only limited by the available light intensity: the incident light intensity has to be made large enough to generate a detectable increase in temperature in the sample. Nonlinear optical processes and even more so non-ideal substrates, reduce, however, the sensitivities obtainable in a typical experiment. The signal from a non-ideal substrate can be greatly suppress by real time compensation techniques, making this technique applicable to many combinations of adsorbates and substrates in various environments. This detection method permits recording of vibrational or electronic spectra at coverages of a fraction of a monolayer under well-controlled UHV conditions, *in situ* in an electrolyte, at atmospheric conditions or under high pressure. Despite the complicated signal generation process involving optical and thermal, and in the case of acoustic detection even acoustic properties of the sample, these techniques offer many advantages over conventional

*Permanent address: Physikalisches Institut der Universität Heidelberg,
Philosophenweg 12, D-6900 Heidelberg, Federal Republic of Germany.

surface analytical methods because of their sensitivity and simplicity and their time- and spectral resolution.

2. Experiments and Results

2.1 Detector

In this report the experimental considerations to obtain high surface sensitivity and some recent results are presented. Ferroelectric ceramic or polymeric materials were used as transducer materials. Discs made from PZT 5A® or SONOX P51® ceramics with a diameter of 10 mm and a thickness of 1 mm, metallized on both sides and sealed around the perimeter with a glass film to prevent outgassing served as detectors in UHV experiments requiring high temperatures during bakeout or annealing. PVF₂ films (Pennwalt KYNAR®) with a thickness of 9 μm were employed in the most recent experiments [4,5]. These films were coated with an adhesion layer of Al and on top of that an Ag thin film electrode. Due to its organic nature this material can sustain only temperatures up to 100°C and is therefore only of limited use in UHV experiments. The excellent time resolution of the organic thin film detector - tens of nanoseconds have been achieved [4], as compared to typically microseconds for ceramic materials [2] - makes this material, however, a prime candidate for pulsed excitation or time resolved experiments.

Both types of materials can be used in a pyroelectric mode, detecting only the thermal wave, or in the piezoelectric mode, detecting sound waves. Thermal waves are critically damped diffusive waves, *i.e.*, within one wavelength the amplitude is attenuated by $e^{-2\pi}$. A typical value for the wavelength of a thermal wave with a frequency of 1 MHz is 1 μm [2]. A thermal wave detector has, therefore, to be in direct contact with the sample; a delay line will delay and at the same time also attenuate the signal appreciably. Sound waves of the same frequency have wavelengths in the order of mm and are basically unattenuated. Taking the acoustic impedance of various materials into account transmission lines can, therefore, be utilized to couple the sound wave from the sample, where it is generated, over a long distance to a detector. Sample and detector can be separated in this detection mode and can be at different temperatures, pressures, *etc.* Furthermore the transmission line introduces a time delay between excitation and detection, allowing to distinguish between electromagnetic interference during the excitation, which propagate with the velocity of light, and the acoustic signal. A purely thermal detector is insensitive to acoustic noise and vibrations. No mechanical resonances occur and therefore a ringing free signal is observed. In addition a thermal detector can easily be calibrated in absolute units using conventional calorimetry. These virtues of the pyroelectric detector [4] make it an interesting alternative to piezoelectric detection. In both detection modes the sample under study is a thin film deposited on a substrate. In the pyroelectric mode the detector itself serves as substrate, whereas in the piezoelectric mode the substrate is for example a sapphire rod used as a transmission line to the detector.

The sample under study was mounted in an UHV system (1×10^{-10} Torr) equipped with an ESCA-Auger spectrometer or a quartz microbalance to determine the amount of surface coverage. Simultaneous photoacoustic and X-ray photoemission or microbalance measurements allow after a suitable calibration to evaluate the photoacoustic signal as a function of surface coverage.

2.2 CW-Excitation

CW CO₂-lasers line-tunable in the infrared spectral region between 9 and 11 μm with an output power in the order of 1 W were used to excite vibrational transitions of adsorbed molecules. The unfocused beam was incident at 80° from the surface normal and covered the entire sample area about 7 mm in diameter. The light beam was intensity modulated at frequencies of typically 10 Hz. The signal was detected by two-phase lock-in analyzers (EG&G 5206). Without employing signal averaging techniques a sensitivity corresponding to a surface coverage of 0.002 of a monolayer of SF₆ on silver was achieved. That high a sensitivity can be readily obtained for nonabsorbing, highly reflecting or transparent substrates using a *stabilized laser* of sufficient output power. Time dependent phenomena like the adsorption/desorption cycle of SF₆ on silver [6] or the adsorption of NH₃ [7] were readily observed. In addition, vibrational spectra from submonolayer to multilayer coverages have been obtained; they indicate distinctive adsorbate-substrate interactions and a nonlinear relation between PA-signal and coverage.

2.3 Pulsed Excitation

For pulsed excitation and highly time resolved studies an Excimer laser pumped dye laser system (Lambdaphysik EMG 201, FL 2002) and suitable transient digitizers (Dataprecision D6000, Tektronix 7912) were employed. The laser system provided pulses with up to 60 mJ pulse energy at 12 ns half width, tunable over the wave length range 575 nm - 605 nm. A Raman cell is being prepared to shift this output into the IR. For the time being only electronic spectra of Nd₂O₃ in the wavelength domain covered by the existing system can be reported [4]. As shown in Fig. 1 for a sample containing 0.8×10^{15} Nd₂O₃ molecules isolated in a 10- μm -thick poly(methyl methacrylate) matrix, corresponding approximately to a one monolayer coverage of Nd³⁺-ions, a spectrum can be obtained at a sensitivity of hundredths of a monolayer with the existing system.

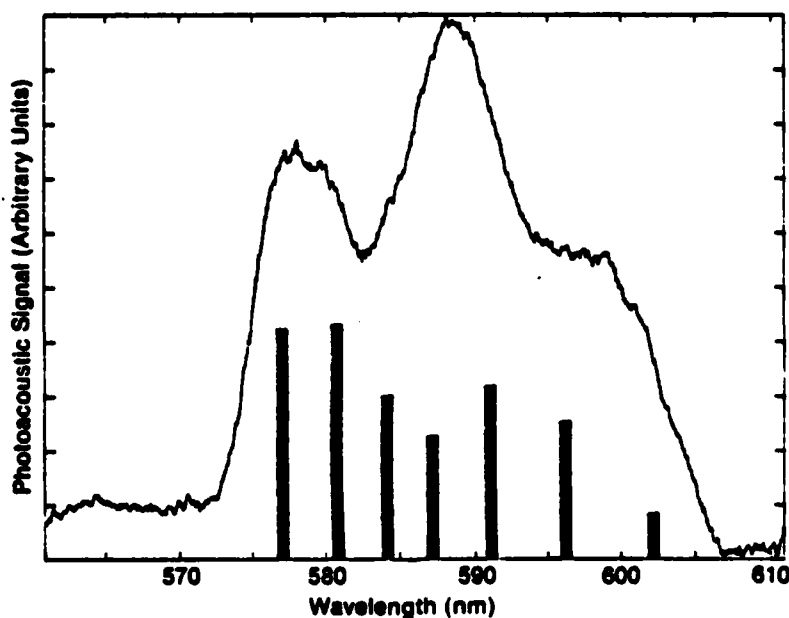


Fig. 1: Photothermal absorption spectrum of 0.8×10^{15} Nd₂O₃ molecules isolated in a 10 μm thick PMMA matrix.

2.4 Compensation Techniques

With absorbing substrates, and at high enough a sensitivity every substrate starts to absorb an appreciable fraction of the incident light intensity, a background signal due to the substrate is superimposed on the signal originating from the material on the surface. Fluctuations of the incident light intensity translates then directly into fluctuations of the background signal *i.e.*, noise. This effect limits the detection of adsorbed species on the surface of a light absorbing substrate. This background problem cannot be overcome by electronic techniques like zero suppression. If one, however, could suppress this background signal the detection sensitivity could be largely enhanced or an unstabilized light source could be used.

We have, therefore, explored a new scheme of general applicability which permits almost complete background suppression for a large variety of experimental purposes [8]. It has been shown [9] to permit ultrahigh sensitive photoacoustic probing (0.002 of a monolayer) of adsorbate materials on light absorbing substrates. Substrate and adsorbate are excited by a suitable modulated light source thus generating a thermal wave; a second source with an appropriate amplitude and phase is used to generate a thermal wave with an amplitude identical to that one due to the substrate but with a 180° phase shift. This second thermal wave adds to the first thermal wave. Contributions due to the substrate therefore result in a DC heating of the sample and cannot contribute to the AC signal detected by a lock-in amplifier. The thermal wave due to the adsorbate, however, still causes an AC signal which is no longer buried by the background originated from the substrate. Amplitude and phase adjustment of the compensation source is achieved by zeroing the signal of the uncovered substrate.

In the pulsed mode another approach proved successful. It is not possible to generate heat pulses with different polarities. It is, however, no problem to generate two identical heat pulses in two identical samples and detect them with two pyroelectric detectors with opposing polarizations, but otherwise identical properties. The electric signals from both detectors have identical amplitude and pulse shape, but different polarities. Both signals cancel and the difference signal is zero. If this symmetry is disturbed, for example by a thin film on one of the substrates a net signal is observed.

Several versions of these compensation scheme have been tested successfully illustrating that the scheme can be realized in many different ways to achieve the same goal *e.g.*, by applying a single light beam or in a two beam arrangement. In addition, different physical principles can be used to generate a second heat source.

In the first one an adsorbate on a metallic substrate was studied. A particular surface property was used here: the difference in absorption between s- and p-polarized light is different for the substrate and the adsorbate. Therefore, by illuminating the substrate with alternating polarizations (*i.e.*, s- and p-polarized light waves phase shifted by 180°) the relative amplitude of the electric field vector for the two polarizations was adjusted in such a way as to obtain a zero substrate signal. With the intensities for s- and p-polarization being different this results in an overall intensity modulation which causes a photoacoustic signal originating only from the adsorbate layer. Figure 2 shows the photothermal signal as a function of time as ammonia molecules are slowly adsorbed on a silver substrate at 90 K. The *unstabilized* CW CO_2 laser is tuned to a wavelength of $9.30\text{ }\mu\text{m}$, corresponding to the ν_2 mode of NH_3 . The laser power at the sample is approximately 1 W. Simultaneously the microbalance reading is recorded. The ammonia partial pressure in the system is 8×10^{-9} Torr during the dosage. The maximum coverage as determined from the change in the frequency of the microbalance and independently from partial pressure and sticking probability, is 0.8 of a monolayer. From the signal to noise ratio a sensitivity of a few thousandths of one monolayer is estimated.

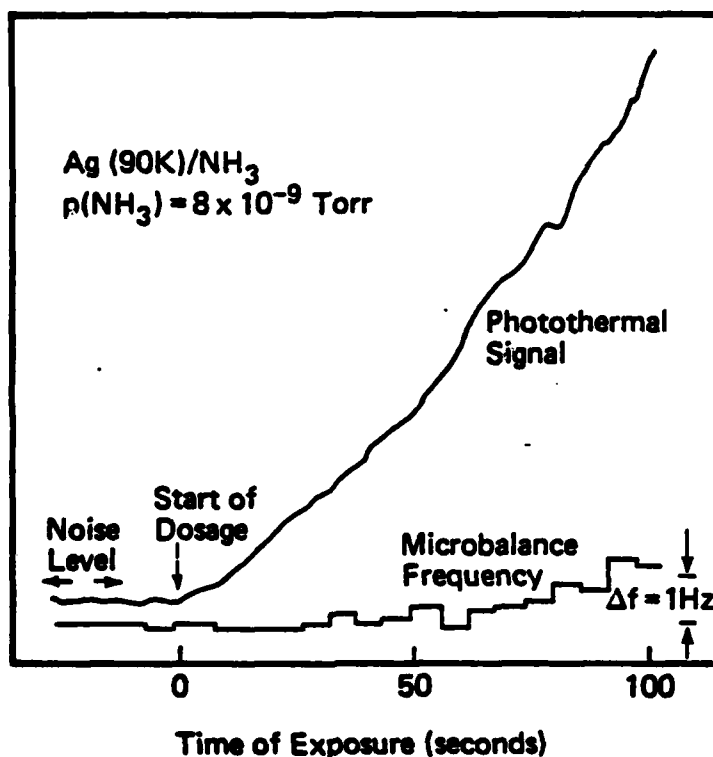


Fig. 2: Photothermal signal and microbalance read out as a function of time as ammonia molecules are slowly adsorbed on the cold silver substrate. A 1 Hz change in the microbalance reading corresponds to a coverage of 0.7 monolayers.

In another experiment the thermal wave due to the substrate was cancelled by a second thermal wave generated at the backside of the sample with a suitable amplitude and phase shift to achieve zero substrate signal. The thermal wave from the adsorbate on the front side, however, is not cancelled and causes a photoacoustic signal. Using the same laser to excite both thermal waves eliminates long term drifts efficiently and therefore lowers the requirements for laser stabilization. Using two lightsources with different wavelengths [10] does not have this advantage but instead allows to take advantage of differences in the absorption of substrate and adsorbate and to measure deposition rates differentially. Preliminary experiments on conducting substrates showed that instead of undergoing the formidable task of stabilizing a laser essentially the same sensitivity can be achieved by resistance heating of the substrate. The phase of the current and the gain of the feed back loop is adjusted prior to the adsorption; during the exposure the fluctuations of the laser are compensated efficiently by the feed back loop.

3. Conclusion

In conclusion, the feasibility of photothermal spectroscopy at submonolayer coverages and under ultrahigh vacuum conditions has been demonstrated. It has been shown that these sensitivities can be obtained with CW or pulsed excitation. This new surface analytical technique, alone or in combination with the compensation schemes that are under further development, is not only able to provide important information at high sensitivity and spectral resolution but should also have a high potential for applications to chemical systems in various environments, whether in vacuum or not.

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