

Photocalorimetric spectroscopy and ac calorimetry of thin surface films

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Photocalorimetric spectroscopy is demonstrated as a sensitive technique for recording the vibrational and electronic spectra of weakly absorbing films on surfaces. The method employs a low-temperature microcalorimeter which may also be used to monitor enthalpy changes associated with processes in surface films. The calorimeter is sufficiently sensitive to determine growth rates during film deposition, enthalpies of surface adsorption, and the heat capacity of the surface film. Therefore, it becomes possible to correlate spectroscopic data from surface films with thermodynamic information from the same sample. Preliminary results from studies of pyridine films on evaporated metal films are reported.

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I. INTRODUCTION

The study of surface adsorbates is of interest because the adsorbate layer influences many of the chemical and physical properties of the surface. Adhesion, lubrication, chemical corrosion, catalytic activity, and photoconductivity are a few of the many processes affected by surface adsorbates. Vibrational and electronic spectroscopy can provide information in great detail about the chemical and physical nature of adsorbed layers on surfaces. The infrared absorption properties of molecules are associated with their vibrational motions and therefore lead directly to structural information. In particular, frequency shifts in the infrared spectrum can be used to interpret the bonding character of an adsorbate.

The electronic spectrum of a weakly physisorbed molecule on a metal surface is likely to be similar to that of the free molecule, whereas the spectrum of a strongly chemisorbed species is expected to change dramatically. The intensities of the individual electronic transitions may alter considerably due to relaxation of selection rules based on molecule symmetry, or orbital and spin angular momentum. Additional transitions may be observed due to charge transfer between adsorbate and the metal substrate. Finally, linewidths may be modified to reflect either changes in relaxation time or the heterogeneity of the adsorbate sites occupied by the molecule.

Currently, the most detailed vibrational and electronic spectra of adsorbates on (single-crystal) metal surfaces are obtained by high-resolution electron energy-loss spectroscopy.¹ This technique, like several other important surface analysis methods, employs incident electrons and therefore requires at least moderate vacuum ($< 10^{-5}$ Torr). Additionally, the need for monoenergetic electron sources, analyzers, focusing systems, etc., contributes substantially to the cost and complexity of the technique.

The advantage of photon spectroscopy for surface analysis lies partly in the relative simplicity of the photon monochromators, polarizers, and lenses, and in the ready availability of intense, monochromatic photon sources. The difficulty encountered in spectroscopic studies of adsorbates with photons is the small absorption cross section, about 10^{-3} that for electrons. It is therefore necessary to devise

some method of improving sensitivity.

Several photon spectroscopies have been developed for the investigation of adsorbates on continuous surfaces. Two of the most advanced in their development are ellipsometry and reflectance/absorption spectroscopy. Absorbances (\approx absorption coefficient \times thickness) of $ad = 10^{-5}$ have been determined using IR ellipsometry² and it is estimated that a tenfold improvement is possible. Because of the large value of α associated with many electronic transitions, $\alpha d > 10^{-5}$ is frequently satisfied in the visible ultraviolet spectrum. This is less often true in the infrared, where only in special cases (e.g., carbon monoxide) is α sufficiently large that the condition $\alpha d > 10^{-5}$ is satisfied for monolayer surface coverage.

Photothermal spectroscopy provides an alternative approach to the spectroscopy of weakly absorbing surface films.³ The absorption of electromagnetic radiation by molecules adsorbed on the surface of a solid populates excited vibrational or electronic states of the adsorbate. Vibrational and electronic relaxation will proceed, in part, by transfer of energy to the substrate. Photothermal spectroscopy is based on the determination of the absorption spectrum of the surface adsorbate by detection of the heating of the substrate. The sensitivity of photothermal spectroscopy may exceed even that of fluorescence spectroscopy, since the yield for nonradiative processes usually exceeds that for radiative processes.

Generally, photothermal techniques result in high sensitivity because it is possible to suppress the unattenuated background signal by as much as two orders of magnitude. Values of $\alpha d \approx 10^{-7}$ have been measured in surface films using thermal deflection spectroscopy.⁴ This is comparable to the values of αd which may be determined by other thermal methods such as photoacoustic⁵ and thermal lens⁶ spectroscopy. All of these techniques are indirect photothermal methods which sense the temperature variation of the sample through the temperature dependence of a material property (e.g., refractive index, thermal coefficient of expansion, etc.). Alternatively, the variation in sample temperature may be followed directly with an attached thermometer.

Direct photocalorimetric spectroscopy has a demonstrated sensitivity⁷ of $\alpha d \sim 10^{-7}$, but is instrumentally more

complicated because it requires the interconnection of the sample to a thermometer. Additionally, in order to obtain the sensitivity necessary for surface studies, low-temperature operation is necessary. The optical arrangement, however, is extremely simple, since the sample with attached thermometer is also the photodetector.

The apparatus for photocalorimetric spectroscopy is, in effect, a microcalorimeter which may also be used to determine the enthalpies associated with the adsorption, desorption, and phase transition of surface films. Furthermore, the calorimetric measurements may be used to quantitate the photon absorption cross sections of surface species and to determine the extent of surface coverage during deposition of a surface layer.

In the following sections, the application of photocalorimetric spectroscopy to the study of surface adsorbates is described. It is the additional purpose of the present work to demonstrate the utility of combining photocalorimetric spectroscopy with ac calorimetry⁸ for the study of surface adsorbates. When this is accomplished, it becomes possible to correlate changes in the vibrational and electronic spectrum of the surface adsorbate with thermodynamic information. Some preliminary thermodynamic and spectroscopic measurements on pyridine films are reported to illustrate the techniques discussed.

II. EXPERIMENT

A diagram of the experimental apparatus for the photocalorimetric spectroscopy of surface adsorbates in the visible and ultraviolet spectral regions is shown in Fig. 1. The sample substrate is mounted on a microcalorimeter contained within an evacuated chamber. The chamber is equipped with a number of ports and feedthroughs to permit optical access as well as dosing of the substrate. Radiation from a 900-W xenon arc lamp is monochromated by a 1/4 m, $f/9$ monochromator and then focused, at near grazing incidence (88°), on the adsorbate coated substrate. The incident radiation is

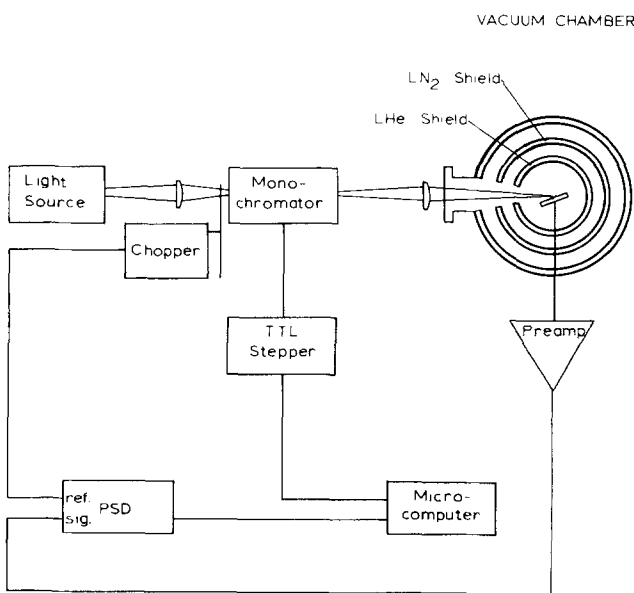


FIG. 1. Schematic representation of the experimental arrangement for photocalorimetry of surface adsorbates.

amplitude modulated at 33 Hz and the temperature variations of the substrate are detected using the combination of a high- Q , narrow bandpass, preamplifier and a synchronous phase-sensitive detector. The spectrum is recorded by monitoring temperature variations as a function of incident wavelength. The monochromator is interfaced to a microcomputer in order to improve base-line correction and general data analysis.

The calorimeter assembly consists of an adiabatically mounted sample, germanium resistance thermometer, temperature monitoring thermocouple, and calibration heater. Two types of samples are of interest: metal foils and metal films on refractory supports. The details of the configuration vary somewhat depending upon the nature of the sample to be studied, but a typical arrangement can be illustrated (Fig. 2).

The sample is prepared in the form of a thin (0.1 mm), $5 \times 5 \text{ mm}^2$ plate and attached to the adiabatic support wires. A germanium resistance thermometer and a thin-film nichrome resistance heater are located on the mounting side of the substrate and are connected to external instrumentation through thermally anchored, 2×10^{-4} -mm-diam gold wires. The thin-film heater is used to calibrate the photocalorimeter and for temperature-programmed desorption (TPD) of surface adsorbates. The copper-constantan thermocouple pair is useful for measuring temperature over broad extremes during thermal desorption and annealing experiments.

The photocalorimeter assembly is supported by a liquid-helium cooled, variable-temperature cold finger within a high-vacuum chamber. The temperature of the sample may

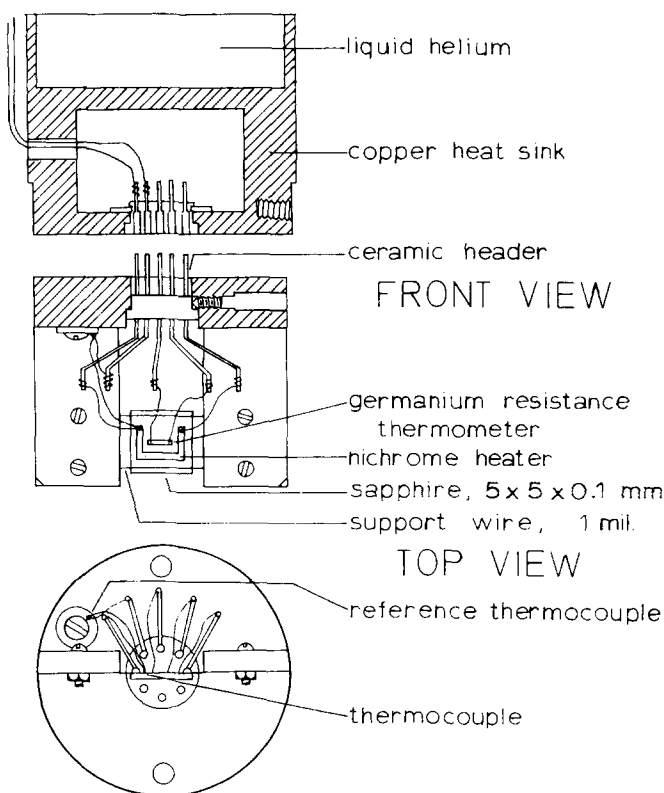


FIG. 2. Microcalorimeter assembly detail.

be regulated and rapidly cycled between 500 and 5 K by passing a small heating current (~ 200 mA) through the heater.

III. RESULTS AND DISCUSSION

A. Theory

The details of the measurement circuit are illustrated schematically in Fig. 3 and the following analysis refers to this diagram. The preamplifier consists of a biquad active filter with a $Q = 22$, band pass = 1 Hz, and gain = 88. The absorption of radiation and its degradation to heat causes a power dissipation $P_s(t)$ in the calorimeter. For calibration and calorimetric measurements, the signal power is derived from the integral, thin-film, resistive heater. In addition to the signal power, the thermometer circuit dissipates a power P_e in the calorimeter, so that the total power dissipated is $P_s + P_e$. Letting C represent the heat capacity of the calorimeter and G the thermal conductance between the calorimeter and heat sink at temperature T_0 , the heat balance equation for the assembly may be written:

$$C \left(\frac{d\Delta T}{dt} \right) = P_e(t) + P_s(t) - G\Delta T, \quad (1)$$

where ΔT is the temperature rise above the ambient. Since the resistance of the thermometer is a rapidly varying function of temperature, the electrical power dissipated in the calorimeter will vary with signal power.

The calorimeter response time (τ_c) may be written⁹

$$\tau_c = \tau \left[1 - \frac{\alpha P_e (R_L - R)}{G (R_L + R)} \right]^{-1}, \quad (2)$$

where $\tau = C/G$ is the usual thermal time constant, and α is the temperature coefficient of resistance.

Equation (1) may be rewritten in the following form with the aid of Eq. (2).

$$\frac{d\Delta T}{dt} = \frac{P_s(t)}{C} - \frac{\Delta T}{\tau_c}. \quad (3)$$

The time dependence of the temperature fluctuation of the calorimeter is obtained by integration of Eq. (3) and will depend upon the form of $P_s(t)$. For ac calorimetry, a sinusoidally modulated resistive heating is employed and for photocalorimetric spectroscopy, a sinusoidally modulated radiation source is used. In either case,

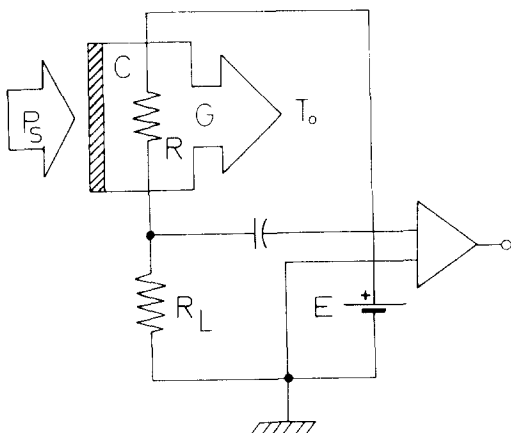


FIG. 3. Schematic of thermometer circuit.

$$P_s(t) = \frac{1}{2} P_s^0 (1 - \sin \omega t). \quad (4)$$

The solution of Eq. (3) may then be obtained in the form

$$\Delta T(\omega) = \Delta T_{dc}(\omega) + \Delta T_{ac}(\omega). \quad (5)$$

The ΔT_{ac} part is related to the heat capacity of the calorimeter as

$$\Delta T_{ac} = \frac{P_s^0}{2\omega C} \left(\frac{e^{-t/\tau_c}}{1 + (\omega\tau_c)^{-2}} + \frac{\sin(\omega t + \phi)}{\sqrt{1 + (\omega\tau_c)^{-2}}} \right). \quad (6)$$

ϕ is the phase angle between $P_s(t)$ and the thermal response, and is given by $\tan^{-1}(\omega\tau)$.

The dc portion of the solution is

$$\Delta T_{dc} = \frac{P_s^0}{2G} (1 - e^{-t/\tau_c}). \quad (7)$$

Both portions of the solution are useful in experimental measurements in certain limiting forms.

For the condition $\omega\tau_c \ll 1$ and $t \gg \tau_c$, Eqs. (6) and (7) yield

$$\Delta T_{dc} = \Delta T_{ac} = P_s^0/2G \quad (8)$$

from which G may be determined by measuring ΔT_{ac} for a known (electrical) P_s^0 . When $\omega\tau_c \gg 1$ and $t \gg \tau_c$ are satisfied, the ac solution becomes

$$\Delta T_{ac} = P_s^0/2\omega C \quad (9)$$

from which the heat capacity C may be determined by measuring $|\Delta T_{ac}|$ for a known (electrical) P_s^0 . This result forms the basis for ac calorimetry.⁸

The temperature fluctuation is related to the signal voltage by the parameters of the electrical circuit. The voltage variation across the thermometer, ΔE , is simply related to ΔT_{ac} .

$$\Delta E = [\alpha E R R_L / (R + R_L)^2] \Delta T_{ac}. \quad (10)$$

B. Photocalorimetric spectroscopy of surface adsorbates

The absorption of radiation by a dielectric film supported on a metal surface depends critically upon the variation of the electric field near the metal surface as radiation, incident upon the film, is reflected and refracted by it. Therefore, in order to optimize the sensitivity of photocalorimetric spectroscopy for the measurement of the absorption spectra of thin films on metal surfaces, the influence of the metal surface on the optical electric field must be considered. The simplest model of the metal surface is that of a semi-infinite, smooth surface having a local dielectric constant different from that of the bulk metal and covered by a thin adsorbate layer of uniform thickness. This model has proved adequate for the absorption of s -polarized radiation, for which the electric field varies slowly in the surface region, but a poorer description for p -polarized radiation for which the electric field varies sharply across the surface. For this case the local surface dielectric function is invalid. The role of nonlocality of the dielectric response at the surface has been clarified by Feibelman,¹⁰ Brodskii and Urbakh,¹¹ and Bagchi and Rajogopal *et al.*¹²

The electric field amplitude of the s -polarized radiation is dramatically reduced at the surface of the metal. The field

of the *p*-polarized radiation does not vanish at the surface and is strongly dependent upon the angle of incidence. Near grazing incidence maximizes the amplitude of the *p*-polarized electric field at the surface and results in the greatest excitation of the surface film. Calculations based on the optical model introduced by Greenler¹³ suggest that the absorbance of *p*-polarized, grazing incidence, radiation near electronic resonance by an organic film on a metal surface is about 10^{-3} to 10^{-4} .

The equations given by Greenler¹³ and Heavens¹⁴ were used to estimate the 2600-Å absorbance of a thin ($d = 10$ Å) surface film of pyridine supported on gold. This calculation requires the values of both the real and imaginary parts of the complex refractive indices of the pyridine film and the gold surface at 2600 Å. The values used for pyridine were for the bulk liquid ($n = 1.0$, $k = 0.187$) and for gold ($n = 1.3$, $k = 1.2$). For an 80° angle of incidence, the absorbance of the *s*- and *p*-polarized waves was computed to be 3.3×10^{-4} and 0.18, respectively. Since the model employed does not treat nonlocal dielectric effects and neglects surface roughness, the numerical result is best regarded as a zeroth-order estimate, probably low, of the surface absorbance.

The monochromated radiation source produced 3.5×10^{-6} W of power in the *p*-polarized field incident upon the calorimeter. A fractional absorbance of 0.18 would result in a signal power (P_s) of 6.3×10^{-8} W. For the experimentally determined $G = 7 \times 10^{-4}$ J sec K, the resulting temperature rise of the calorimeter from Eq. (8) is calculated to be 9×10^{-5} K. The signal voltage, $\Delta E = 100$ μ V, calculated using Eq. (10) with $\alpha = 0.240$, $R = 4$ K, $R_L = 15$ K and $E = 29$ V, is typical of the signal levels observed in our experiments. The total noise background currently limits detection to monolayer coverages. The major contribution to the background noise is instabilities in the light source used and improvement here would significantly improve the detection limits.

We have obtained electronic spectra of pyridine thin films on gold and nickel which illustrate the spectroscopic application of the microcalorimeter. Pyridine chemisorbs weakly on gold, copper, and silver surfaces,¹⁵ desorbing (under vacuum) from these metals at temperatures below 290 K. On Ag(111) surfaces, pyridine undergoes a structural phase transition from being π -bonded, with the molecular plane parallel to the metal surface, to an *N*-bonded compressional phase in which the surface interaction is decreased by ~ 2 kcal/mole.¹⁶ This behavior indicates that intermolecular interactions are comparable to the surface interactions. In fact, the sublimation temperature of crystalline pyridine is comparable to the desorption temperature of chemisorbed pyridine.

Pyridine vapor at room temperature was allowed to deposit on a freshly evaporated gold surface held at ~ 8 K, until approximately 100 monolayers had been deposited. It was anticipated that the resulting surface film would be highly disordered and the extremely broad, featureless spectrum recorded photocalorimetrically is in agreement with this expectation [Fig. 4(c)]. The film was cycled to successively higher temperatures and spectra were recorded after completion of each cycle when the temperature had returned

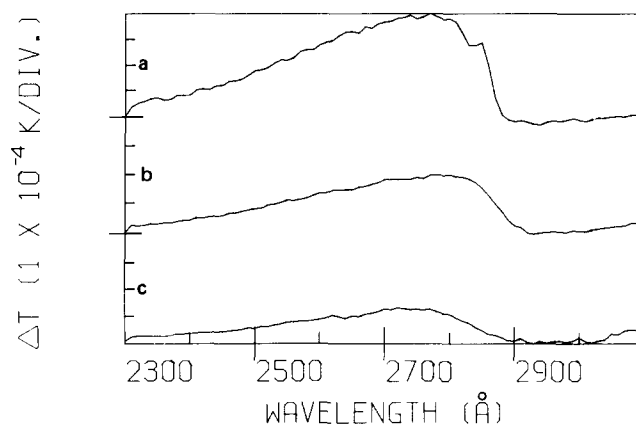


FIG. 4. Photocalorimetric spectra of a multilayer pyridine film on gold: (a) top, 150–190 K, (b) center, 100–120 K, (c) bottom, as deposited at 10 K.

to 8 K. Little change in the spectrum is observed until the maximum cycle temperature exceeds 100 K, at which point a shift in the spectrum and the development of vibrational structure is observed [Figs. 4(a) and 4(b)].

At 125 K considerable pyridine desorption occurs, as indicated by the sudden rise in the pressure of the experimental chamber (see Fig. 5), and the base-line spectrum is recovered. Although there is evidence¹⁵ that pyridine chemisorbed on gold films does not desorb until about 300 K, we were unable to detect spectroscopically any residual pyridine above 125 K.

A sequence of spectra similar to those shown in Fig. 4 was obtained from pyridine adsorbed on evaporated nickel films. Therefore, the spectral changes which occur in the spectrum of the film below 150 K are independent of the substrate and are associated with crystal growth in the thin film. Large thermal transients are observed in the as-deposited unannealed films. These have been reported previously in adsorbed films of cryopumped gases¹⁷ and are thought to arise in the collapse of unstable microstructures at temperatures well below the melting point of the bulk material.

The spectrum of pyridine shown in Fig. 4(a) is, in most aspects, identical to that of crystalline pyridine, except that its origin is shifted approximately 0.37 eV to lower energy and is nearly coincident with the position of the vapor phase origin. A qualitatively similar result has been reported by Harris¹⁸ from his studies of pyridine and pyrazine physi-

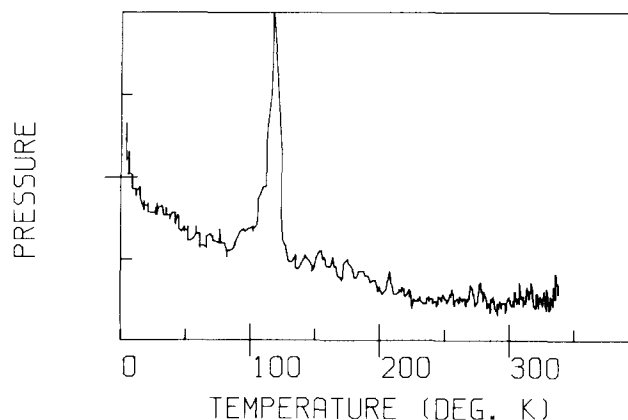


FIG. 5. Temperature-programmed desorption of pyridine on gold.

sorbed on clean, well-characterized Ni(111) using ellipsometric spectroscopy. Harris has suggested that these spectral changes are associated with a substantial modification of the local pyrazine environment, perhaps as a consequence of epitaxial crystal growth on Ni(111).

Since the observed long wavelength spectral shift of pyridine on evaporated nickel films, is, within our experience, independent of the structure of the substrate, it cannot be associated with epitaxy. It seems possible, however, that it results from a different crystalline structure of the physisorbed material than that exhibited in the bulk phase. Furthermore, it appears likely that the structure is a direct result of surface effects in microcrystals formed by diffusion-limited crystal growth on the low-temperature substrate surface.¹⁹

The spectrum of the terminal chemisorbed layer on evaporated nickel films could be observed and is shown in Fig. 6. It is identical to that recorded by Harris for pyridine on Ni(111) using ellipsometric techniques. The spectrum was obtained at the limit of sensitivity of the current instrumentation and is comparable in signal-to-noise ratio to the ellipsometrically obtained spectrum.

C. Enthalpies and heat capacities of surface adsorbates

In the case of resistive heating, $P_s(t)$ is known exactly and the absolute heat capacity may be determined. The heat capacity is composed of two parts, the (addendum) heat capacity of the calorimeter and C_s , that of the sample (surface film). It is possible to reduce the addendum heat capacity to as little as 5×10^{-8} J/K.²⁰ The variation in C_s associated with order-disorder phenomena is on the order of 5×10^{-9} J/K for each monolayer or about 10% of the heat capacity of the calorimeter.

Enthalpies of adsorption of molecules on surfaces may be determined from the temperature rise of the calorimeter if the total number of molecules deposited is known. We assume that surface adsorption may be described by a single potential well and a single molar adsorption enthalpy (ΔH_{abs}), which will be smaller in the case of physical adsorption and larger for chemisorption. Experiments are conducted using a known flux of molecules effusing from a source at temperature T_s . Let $n(t)$ be the number of molecules per

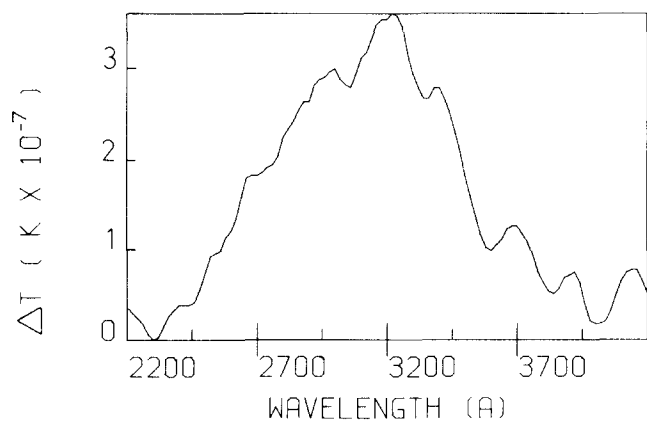


FIG. 6. Photocalorimetric spectrum of a chemisorbed monolayer of pyridine on nickel.

second deposited on the microcalorimeter surface. A unity sticking coefficient is assumed for low coverages on the cold surface. Molar enthalpies of adsorption for physisorbed molecules are in the range 5–25 kcal/mole and for chemisorption 25–100 kcal/mol.²¹ Therefore, for a room-temperature effusive molecular source, the power dissipated in the calorimeter is approximately

$$P_s(t) \simeq n(t) \Delta H_{\text{abs}} \quad (11)$$

since the thermal energy of the incident flux is negligible compared to ΔH_{abs} . For steady dosing, $n(t) = n_0$ and the temperature rise of the calorimeter when $t \gg \tau$ is obtained using Eq. (8):

$$\Delta T(t) \simeq n_0 \Delta H_{\text{abs}} / G. \quad (12)$$

Both C and G may be determined independently using the resistive thin-film heater on the calorimeter and employing Eqs. (8) and (9). Typically, $C = 2 \times 10^{-5}$ J/K and $G = 7 \times 10^{-4}$ J sec K (at 8 K). Therefore, even for weak physisorption (~ 5 kcal/mole), easily measurable temperature variations of ~ 1 mK are produced in the calorimeter.

Several measurements of the heat adsorption of pyridine on evaporated, polycrystalline nickel films were made. The ambient temperature of the nickel film substrate was about 8 K. For low (submonolayer) coverages the enthalpy of absorption was computed from the observed temperature rise (typically 1 K) to be 90 kcal/mole. At coverages in excess of one monolayer, the measured enthalpy dropped abruptly to approximately 2–3 kcal/mole. These enthalpies of adsorption are broadly representative of, in the first instance, chemisorption, and in the second, physisorption. The results demonstrate the marked variation in ΔH with completion of the chemisorbed monolayer. The results, although strongly ($\pm 50\%$) dependent upon sample history and method of preparation, demonstrate the practicality of this type of measurement on single, planar surfaces with low total area (0.25 cm^2).

IV. CONCLUSION

Photocalorimetric spectroscopy is a sensitive technique for the study of surface adsorbates. The photocalorimeter is easily adapted for a variety of simultaneous calorimetric measurements of surface processes. In a small surface area calorimeter (0.25 cm^2) it is possible to measure the enthalpy of adsorption, to determine the rate of deposition of a single monolayer of surface adsorbate, and to measure the enthalpy associated with structural phase changes in the surface layer. This information may then be usefully correlated with changes in the vibrational and electronic spectrum of the same surface sample. Finally, quantitative photon absorption cross sections may easily be determined for surface adsorbed molecules using the photocalorimeter as a radiometer, if the absolute intensity of the incident photon flux is known.

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