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A new approach to adsorption microcalorimetry based on a $LiTaO_3$ pyroelectric temperature sensor and a pulsed molecular beam [☆]

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Abstract

A novel method of measuring heat of adsorption of gases on metal films is described. The method is based on use of a $LiTaO_3$ pyroelectric crystal to monitor surface temperature changes of a film which are brought about by adsorption of gas from a pulsed molecular beam generated in a quasi-effusion source. Calibration of the calorimeter is performed by pulsed laser radiation. Advantages of this approach are briefly discussed and its potentialities outlined.

Keywords: Calorimeter; Heat of adsorption; Lithium tantalum oxide; Microcalorimetry; Pulsed molecular beam; Pyroelectric; Temperature sensor

1. Introduction

Heat released in chemisorption of gases on solids is one of the most important experimental quantities characterizing this surface process. When properly interpreted, it can furnish information on the strength of the formed chemisorption bonds, on the occurrence and extent of dissociation of the parent gas molecule, on

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interactions between the surface species and on their mobility, on reconstruction of the surface, etc.

Despite the heat of chemisorption being an equilibrium quantity, its magnitude is closely related to the kinetics and mechanism of surface processes. In general, it can be experimentally determined (a) by calculation from the adsorption equilibrium data; (b) by calculation from data on the kinetics of desorption; (c) by calorimetric measurement. Each of these three methods involves certain limitations. The two former methods are confined to reversible processes only. However, calorimetric measurement is applicable both to reversible and irreversible processes, but adsorption calorimetry with single crystal materials has not been feasible until recently. Moreover, when the kinetics of the adsorption heat evolution are slow, the measurement is only possible with granulated and finely divided materials, but not with cleaner and better defined surfaces such as vacuum-evaporated films, annealed metal filaments and single crystals.

In an endeavor to find new advanced technical solutions which would enable the microcalorimetric method to be ranked among the tools of up-to-date surface science, two novel approaches have recently been developed. King and co-workers at the University of Cambridge have designed and put into operation an adsorption microcalorimeter for studies on well-defined single crystal surfaces under ultrahigh vacuum conditions [1–4]. Supersonic molecular beam pulses of gas having a width of 5×10^{-2} s and a repetition rate of 0.5 Hz have been dosed onto metal single crystal films about 2000 nm thick. The evolved heat has been determined by monitoring the infrared radiation from the back face of the crystal, using a photoconductive mercury cadmium telluride infrared photon detector located at a distance of a few millimeters from the sample. This calorimeter has already provided detailed heat-coverage curves on single crystal surfaces of controlled cleanliness.

Fully independently, a novel microcalorimeter set-up for determining heats of adsorption of vacuum-evaporated films has been designed in this laboratory [5,6]. It is based on using the pyroelectric properties of $LiTaO_3$ single crystal to monitor the surface temperature changes of a metal film deposited onto the pyroelectric sensor and exposed to a pulsed molecular beam of gas generated in a quasi-effusion source, with a pulse width of 0.5–1 s and a repetition rate of about 2 Hz. The method has been discussed in detail in Ref. 6. The present communication only briefly outlines the main features of this approach and points out its potentialities.

2. The calorimeter set-up

Pyroelectric sensors have proved to be a remarkably versatile means of measuring surface temperature changes (see references cited in Ref. 6). This has stimulated us to apply a pyroelectric sensor to the determination of heats of adsorption of gases on metal surfaces. Of a range of available pyroelectric materials of different properties [7], we have selected $LiTaO_3$ crystal because of its high Curie temperature (893 K) enabling it to be baked out during the necessary outgassing of ultra-high vacuum adsorption apparatus. In order to achieve a maximum increase in the $LiTaO_3$ crystal temperature by the delivered adsorption heat, we have used it in the form of a very thin polished plate having dimensions $8 \times 8 \times 0.8$ mm^3. This plate was coated from both sides by an evaporated thin layer of gold serving as electrodes. In this way a parallel plate capacitor was formed. Temperature changes of the $LiTaO_3$ crystal due to adsorption heat brought about changes in its polarization, and hence in the voltage across the parallel capacitor and in the current flowing through an electrical circuit wired to the capacitor by means of feedthroughs in the apparatus wall. The $LiTaO_3$ plate was rotated by a manipulator into the particular positions for (i) evaporation of a film of the studied metal; (ii) calibration by pulsed laser radiation; (iii) determination of the molecular beam flux; (iv) an actual adsorption experiment.

A film of the studied metal was evaporated in ultra-high vacuum onto one face of the $LiTaO_3$ plate covered by gold electrode. Because pyroelectric sensors react on a change in temperature rather than on its level, gas was delivered onto the metal film in a pulsed molecular beam. Pulses of the produced adsorption heat gave rise to pulses of current in the electrical circuit which was amplified, converted into voltage, filtered using a low-pass filter with a cutoff frequency of approximately 1 Hz, digitized and fed to a personal computer.

To test the applicability of a $LiTaO_3$ sensor to the measurement of adsorption heat in the outlined way, we have designed a simple molecular beam apparatus (Fig. 1). The molecular beam was generated in a quasi-effusion source consisting of a 12 l gas reservoir (pressure 10^2 Pa), an adjustable leak valve and a 0.5 mm capillary. The beam was sequentially collimated by a system of capillaries located in differentially pumped chambers and finally arrived at the metal adsorbent kept at a background pressure in the 10^{-8} Pa range. The beam was modulated by a simple mechanical

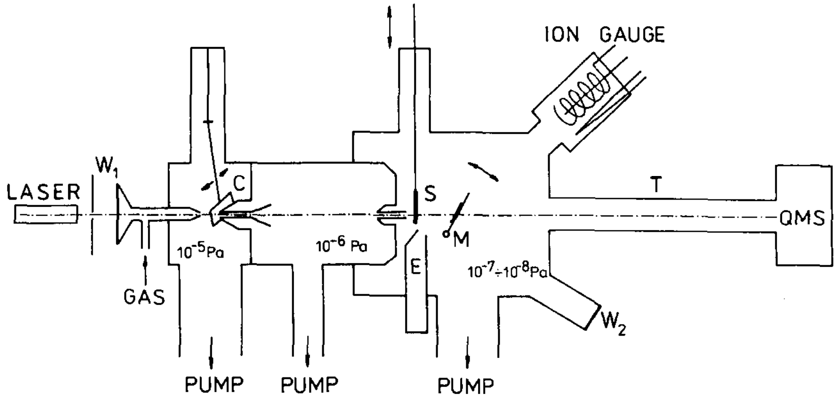

Fig. 1. Scheme of an adsorption microcalorimeter with pyroelectric sensing of temperature changes and supply of gas in a pulsed molecular beam. W_1, entrance window; W_2, window for the film reflectivity measurement; E, evaporator of the metal; C, mechanical chopper; M, manipulator; S, beam stopper (glass flag); T, tube connecting the sample chamber with quadrupole mass spectrometer; QMS, quadrupole mass spectrometer.

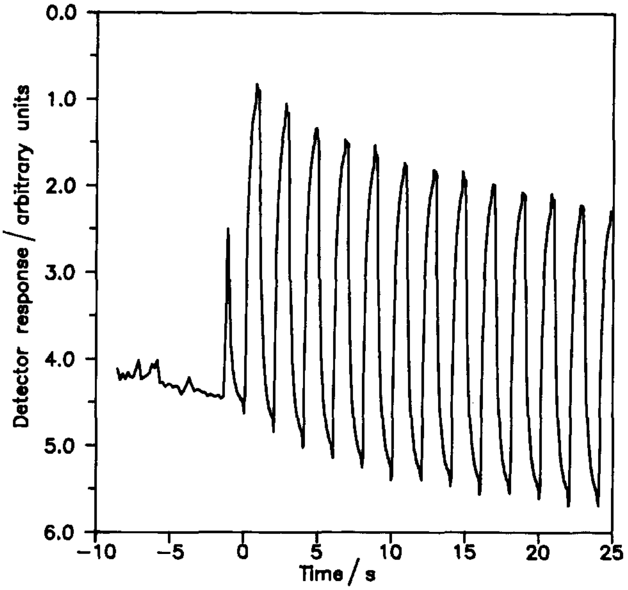

Fig. 2. Response of $LiTaO_3$ sensor (pulses of current) to pulses of oxygen striking a film of dysprosium. Beam pulses have an intensity of 3×10^{13} molecules cm^{-2} s^{-1}, a pulse width of 0.93 s and a repetition period of 2 s.

chopper consisting of a steel ribbon deflected by means of an electromagnet actuated by a circuit for setting the desired width and repetition rate of the beam pulses. The system of collimating capillaries was manufactured from quartz to prevent their deformation by temperature changes. The other parts of the apparatus were of glass.

In the outlined apparatus, a molecular beam of 10^{13} to 10^{14} molecules s^{-1} cm^{-2}, a pulse width between 0.5 and 1 s, and repetition period around 2 s were typically obtained. The spot size of the beam on the sample surface was 0.04 cm^2. As a result, a beam pulse hitting this area was of the order of 10^{12} molecules.

Fig. 2 shows response of the $LiTaO_3$ sensor to pulses of oxygen beamed on a film of dysprosium. The large pulse width and long repetition period allowed filtering of the primary current signal to be performed, resulting in an excellent signal-to-noise ratio.

3. Determination of the molar heat of adsorption

To obtain the required molar heat of adsorption Q, the measured heat amount q should be divided by the number of adsorbed moles n or molecules N

$$Q = \frac{1}{n} q = \frac{N_{\mathrm{Av}}}{N} q$$

where N_{Av} is the Avogadro number.

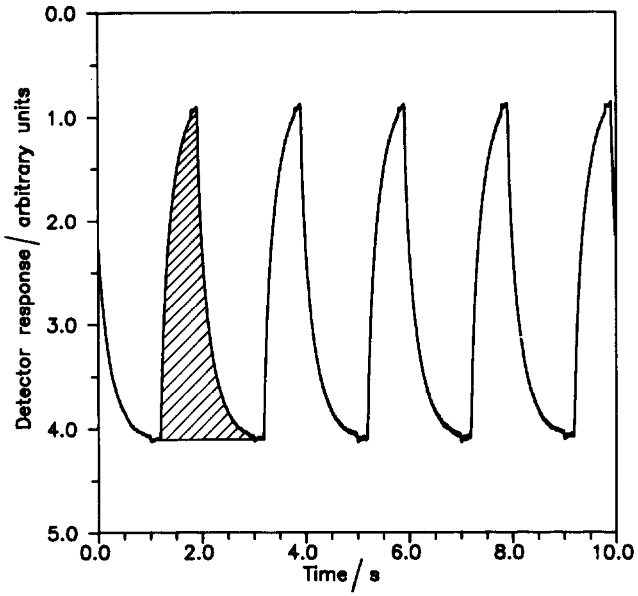

Fig. 3. Response of the $LiTaO_3$ sensor (pulses of current) to the pulsed laser beam. The peak area (hatched for the first pulse) represents the response to 2.63×10^{-6} J absorbed per pulse by a dysprosium film deposited on the sensor.

Usually, q can be determined more easily than n or N. The $LiTaO_3$ sensor responds to a heat pulse released on its surface by a current peak of area A. From this area, the released heat q was obtained for each pulse by comparing it with an area brought about by laser beam pulses. We used a laser source furnishing radiation of a wavelength of 670 nm with an output power adjustable between 0 and 0.8 mW. The laser beam was chopped into pulses in the same way as a molecular beam, passed through the collimator capillaries and illuminated the same area of the adsorbent surface as the molecular beam itself. The width, repetition period and power of the laser pulses were set as close as possible to the pulsed molecular beam in adsorption experiments (Fig. 3). From the incident laser power and reflectance of the film, the power absorbed in each pulse was determined. Fig. 4 shows the calibration curve obtained.

To determine the number of molecules adsorbed per pulse, it was necessary to know the number of molecules impacting the adsorbent surface per pulse, and the fraction of these impacts resulting in chemisorption, i.e. the sticking coefficient. The former quantity was estimated from the established beam flux F, using the relation

$$F = G\frac{\Delta P}{kT}$$

Here, G is the conductance of the tube connecting the chamber where the sample is located with the quadrupole mass spectrometer (Fig. 1), ΔP is the measured

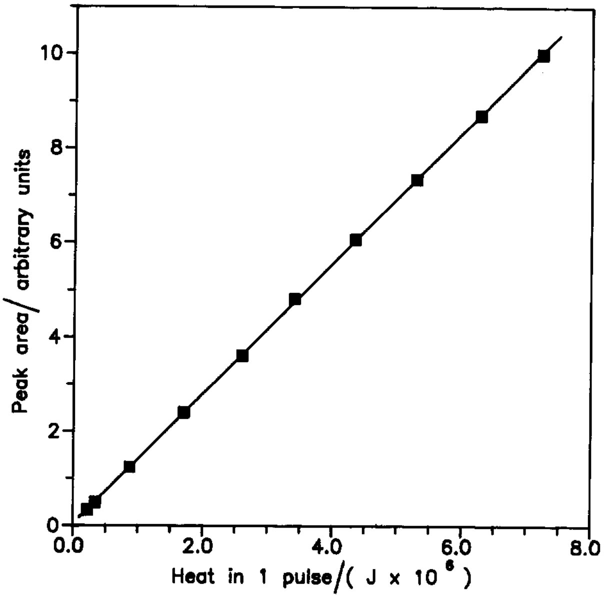

Fig. 4. Calibration curve showing a linear dependence of the area of the $LiTaO_3$ detector response (pulses of current) to the absorbed energy of a series of laser pulses having a width of 0.75 s and a repetition period of 2 s.

pressure difference between the two volumes. It is assumed that the molecular beam flows unperturbed through this tube without any scatter, and that its scattering occurs in the chamber of the quadrupole mass spectrometer; the scattered molecules then enter by molecular flow through the connecting tube back into the chamber with the sample. The intensity I of the beam at the sample surface is given by

$$I = \frac{F}{S}$$

where S is the area of the beam spot on the film surface. The sticking coefficient s was estimated for discrete pulses of gas using the method of King and Wells [8] based on measuring the increase in pressure brought about, respectively, by molecules scattered off the adsorbent and a glass stopper inserted into the path of the beam. This technique is known to be useful for determining $s > 0.02$.

4. Testing of the calorimeter set-up

Operation of the calorimetric set-up was preliminarily tested by determining heats of chemisorption of oxygen and carbon monoxide on dysprosium, known from our previous experiments using a Beeck-type calorimeter [9,10].

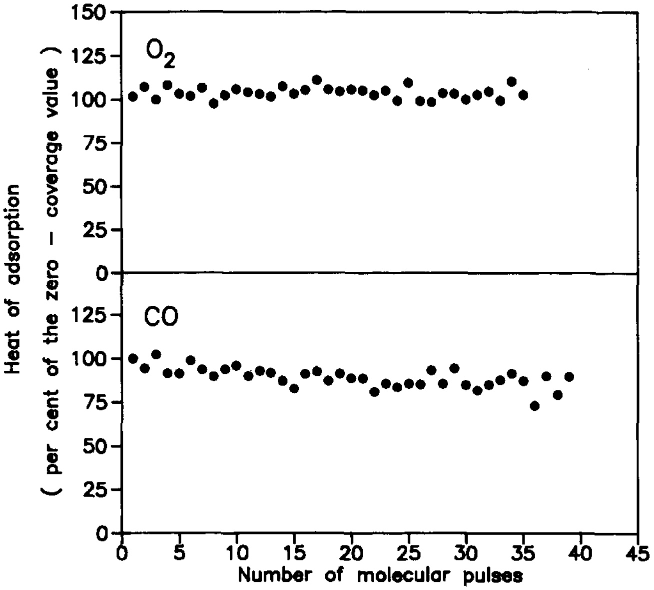

Fig. 5. The heat of adsorption as a function of the number of pulses of carbon monoxide and oxygen at a low coverage.

Two experiments with oxygen yielded a heat of 706 and 635 kJ mol^{-1} at zero coverage, while 251 and 279 kJ mol^{-1} resulted in two experiments with carbon monoxide. The heat in the region of the low adsorbed amount was fairly constant both for oxygen and carbon monoxide, as shown in Fig. 5.

Initial heat values of both oxygen and carbon monoxide differed by ±5.3% from their respective averages. This average value represented respectively 70% and 73% of the value determined for oxygen and carbon monoxide in the Beeck-type calorimeter. This should be considered an acceptable result, if one bears in mind the problems with determining the adsorbed amount per pulse in the simple quartz-and-glass UHV apparatus which was available. The apparatus yielded a molecular beam of a relatively poor quality, and did not allow the beam intensity and the amount of gas adsorbed per pulse to be measured reliably. Furthermore, the beam spot amounted to 4×10^{-2} cm^2, while the area of the $LiTaO_3$ sensor covered by dysprosium was 64×10^{-2} cm^2. When the adsorbed amount was growing, sticking probability was decreasing and an increasing number of molecules were scattered from the beamed spot and readsorbed on other, less covered, parts of the surface. This effect, which was intensified by a limited pumping rate of the apparatus, gave rise to pressure pulses in the gas phase above the sample, and caused the continued response of the $LiTaO_3$ sensor to the pulsed beam even when a monolayer on the beam spot of the dysprosium film had already been attained. It is in principle possible to suppress or entirely eliminate this effect by reducing the area of the film outside the beamed spot (by modifying the evaporator geometry and/or by blocking that area by an inactive layer) and by increasing the pumping rate using an all-metal UHV apparatus. In such a way, absolute coverage values and a reliable heat-coverage curve are obtainable.

5. Conclusions

The outlined novel approach to the measurement of chemisorption heat on metal adsorbents provides a number of advantages which may be summarized as follows.

The $LiTaO_3$ single crystal temperature sensor is very well suited for microcalorimetric measurement in UHV adsorption systems due to its high Curie temperature, large sensitivity, favorable values and considerable invariancy of other relevant characteristics, which enable the sensor to be applied over a wide range of temperatures.

Metal film laid directly onto the pyroelectric sensor is in good thermal contact with it, whereby sensitivity and versatility of the method are increased. The small size of the sample and its location in the apparatus allow its dosing by molecular beam to be applied; this method is superior in many respects to that used in classical Beeck-type calorimeters. Moreover, the said arrangement allows the film to be characterized by LEED and AES methods, if they are available.

When a molecular beam generated in a quasi-effusion source strikes the pyroelectric sensor, no disturbing piezoelectric effects occur, as opposed to the more energetic supersonic beams. Moreover, molecular beams effusing from a source, when chopped into pulses of a relatively large width and low frequency, deliver an appropriate amount of gas onto the film. Thereby the primary pyroelectric signal can be electrically filtered to provide resulting current pulses with an excellent signal-to-noise ratio. The area of these pulses can thus be accurately determined and represents a very good measure of the released heat per pulse. Finally, calibration of the calorimeter by laser radiation has turned out to be most satisfactory.

As a result, a $LiTaO_3$ pyroelectric temperature sensor in conjunction with a pulsed molecule beam generated in a quasi-effusion source represents a promising novel method of considerable potential in adsorption microcalorimetry.

Acknowledgment

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