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ADSORPTION CALORIMETRY IN SURFACE CHEMISTRY

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ABSTRACT

The measurement of the energy of interaction of a molecule with a surface as a function of coverage provides information on the state of the surface and on the thermodynamic characteristics of the adsorption process.

Access to $\Delta_{ads}H$ is usually obtained on polycrystalline materials by means of a microcalorimeter connected to a dosing device which enables the simultaneous measurement of small uptakes and related heats. Small increments in the adsorbate from the lowest coverage to saturation can thus be evaluated. Successive adsorption-desorption cycles allow the separation of effects due to reversible and irreversible phenomena.

The adsorption of the same adsorptive onto variously pretreated solids or on materials of different origin yield evidence of differences in the state of the surface.

The application of this technique in various fields of surface science will be reported and the usefulness of joint use of microcalorimetry with other techniques will be stressed.

INTRODUCTION

Calorimetry in surface science is somehow an "old" subject. Pioneering work on the heat of adsorption by Beebe (1), Garner and coworkers (2), Beeck (3), Morrison and coworkers (4) have in fact reported results still valid presently. At those days, however, the measuring devices only allowed to gain an overall information on the phenomena under study. A significant improvement took place some twenty years ago, when, by the introduction of very sensitive flow microcalorimeters, it had become possible to measure in detail the energy of an adsorption system as a function of coverage, thus studying either induced or structural heterogeneity, and identifying in this latter case the type, population and energy of different adsorbed species.

Adsorption calorimetry as a surface technique still bears some peculiarities with respect to more recently developed techniques such as the various spectroscopies, surface analysis and microscopical investigations. It has the merit of being doubly quantitative, as both adsorbed amounts and evolved heats have to be measured simultaneously; the information gained, however, may often be rather generic, because every concomitant phenomenon contributes to the heat evolution. In this respect, it may be opposed to the many new techniques, which are able to monitor only some aspects of the overall surface reaction. Combined use of calorimetry with any of these latter, when possible, is usually very successful, as it provides a complete description of the surface phenomena.

The classical field of adsorption calorimetry has been so far that of catalytic systems and excellent reviews in the field by P.C. Gravelle have appeared in

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the early seventies (5). It has also included fundamental studies on the adsorption itself such as physisorption, as developed in Marseille by J. and F. Rouquerol (6) or adsorption on metals (7,8).

Other accounts of research in the field have also appeared more recently (5, 6, 9-11). The technique, however is not as widely employed as the importance of energy data would require.

The present paper illustrates some improvements in the technique and in the elaboration of experimental data. Few recent examples of succesful application in different fields of surface chemistry will be reported, which have been developed in our laboratory over the last decade.

TECHNIQUE

The main features of the experimental equipment are schematized in figure 1. A Tian-Calvet microcalorimeter is connected to a volumetric apparatus which enables the evaluation of adsorbed doses and equilibrium pressure.

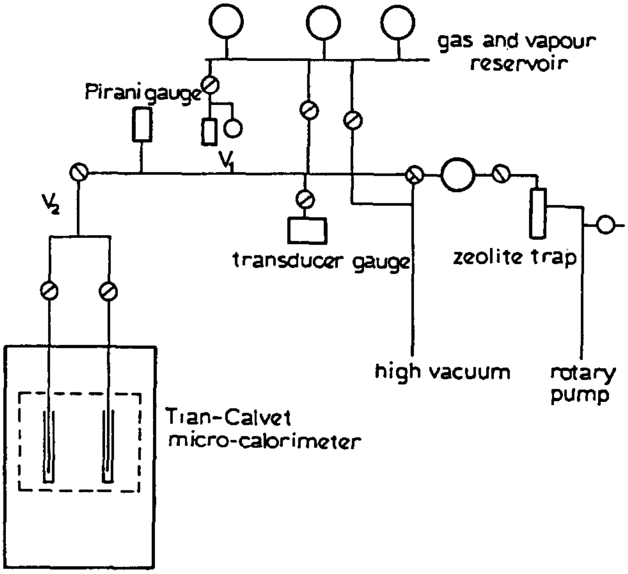

Fig. 1. Equipment for the measure of the heat of adsorption in gas-solid systems: a Tian-Calvet microcalorimeter connected to a volumetric dosing device.

The Tian-Calvet microcalorimeter is a twin cell flow calorimeter thus practically isothermal, very sensitive and stable, so that heat evolution either rapid or lasting many hours can be recorded with satisfactory precision (12).

The volumetric apparatus connected to a high vacuum manifold consists in a dosing volume (V_1), where the dose of the adsorptive is prepared and measured, and an expansion volume (V_2), where the dose is contacted with the adsorbent placed in the microcalorimeter. The pressure is recorded by means of a transducer gauge (Baratron MKS) and by a Pirani gauge. The sample undergoes chemical and thermal pretreatments in situ outside the calorimeter: the cell is subsequently inserted into the calorimeter and connected to the dosing device without exposure to the atmosphere. Two identical calorimetric cells are employed, of which only one contains the sample, in order to obtain a calorimetric output free from contributions due to compression or expansion of the gas phase. Further details are reported in ref. 10.

PROCEDURE

A typical procedure for the characterization of a given gas-solid system, largely described in previous work (10, 13 - 15) is as follows. Appropriate doses of the adsorbate are successively admitted onto the adsorbent up to the desired coverage. Each dose is left in contact until equilibrium is attained: this is revealed both by the constancy of the pressure over the adsorbent and by the absence of any drift in the calorimetric baseline. This first adsorption run (ads 1) is followed by desorption, which may be performed either step by step or by simple evacuation of the cell. The heat of desorption is measured and again the end of desorption is monitored by the stability of the calorimetric baseline. Desorption being a process always kinetically activated - at least an activation energy barrier equal to the heat of adsorption has to be overcome - the process is slower than the adsorption of the same amount of gas. A second adsorption run (ads 2), usually employing similar doses as in the first run, is performed in order to evaluate the part of the adsorption which is reversible at the adopted temperature.

Adsorption of a single dose yields simultaneously equilibrium and kinetic data. The heat evolved (ΔQ^{int}), the adsorbed amount (Δn_a) and the equilibrium pressure are entities of the former kind; the rate of adsorption (uptake vs time) and the heat flow as a function of time (thermogram shape) of the latter kind. The thermograms are strongly influenced by the inertia of the calorimeter but, in most cases, fast and slow phenomena can be easily distinguished by mere visual inspection of the peak shape.

In more complicate cases a semilogarithmic plot of the calorimetric output can be used (fast processes yield exponential decay of output (10)or a partial integration of the peak (Q^{int} vs t) (5) and, if necessary, a computer deconvolution of the curves (16, 17). In any case, however, the comparison between heat and uptake evolution allows a distinction between activated chemisorption (both evolutions are slow) and reactions occurring at the surface following adsorption (fast kinetics and slow thermokinetics). This latter case is typical of reactions occurring via a molecular precursor such as water in hydroxylation of surfaces (10, 14) or dioxygen in the surface oxydation of a low valency ion (18) or metal (19). Such system can be usefully described by classical potential energy diagrams: structural and induced heterogeneity can play a crucial role in the variation of adsorption kinetics with coverage (10, 20).

The equilibrium data available at any coverage examined are: the total adsorbed amount (n_a, uptake), the total evolved heat (Q^{int}) and the equilibrium pressure (p). Following the kind of gas-solid systems under examination and the information required, various elaborations and representations of the equilibrium data can be employed, which are schematically reported in figure 2.

The merit and use of each kind of representation, widely illustrated in previous reviews (10, 20),are the following.

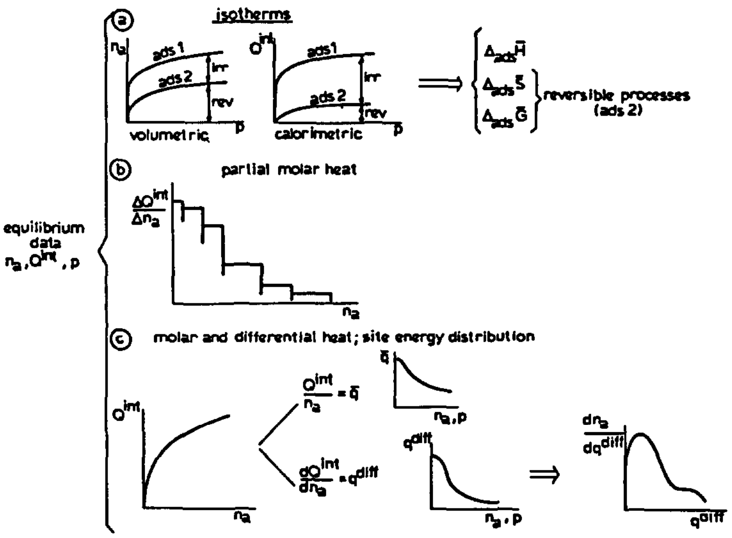

Fig. 2. Scheme of data representation.

a) Volumetric and calorimetric isotherms: quantitative and energetic values at any defined equilibrium pressure, evaluation of reversible and irreversible adsorption, direct access to thermodynamic functions ($\Delta_{ads}H$, $\Delta_{ads}S$, $\Delta_{ads}G$) in the case of reversible processes (ads 2) (22-25).

b) Partial molar heat as a function of successive increments in the adsorbate: it is the most classical representation (5), a direct picture of the interaction energy of successively covered patches of the surface is given.

c) Integral vs uptake plot. In the particular case in which the heat of interaction is constant with coverage (see e.g. figures 3,6) a straight line through the origin is found, whose slope gives the $\Delta_{ads}H$ value. In any case from this plot the molar heat $\bar{q}^{int} = Q^{int}/n_a$ and, by differentiation, the differential heat $q^{diff} = dQ^{int}/d\,n_a$ are obtained, the latter being the most adequate for the picture of the variation of the interaction energy with coverage or equilibrium pressure.

In presence of irreversible adsorption often data from the first and second run originate separate curves in the q^{diff} vs n_a plot and fall on the same curve on the q^{diff} vs p one. By subsequent differentiation of the q^{diff} vs n_a curve ($d\,n_a/dq^{diff}$) the site energy distribution can be obtained (26, 27).

APPLICATION OF ADSORPTION MICROCALORIMETRY TO VARIOUS FIELDS OF SURFACE CHEMISTRY

The use of adsorption calorimetry by our and other research groups has been mainly in the field of heterogeneous catalysis: it consists in the evaluation of the population and strength of active sites making a wide use of differential heat and site energy distribution plots obtained by adsorption of probe molecules.

Few examples of less usual applications of the technique will be reported here in order to show the possible use in various fields of surface chemistry,such as hydrophobicity of powdered materials or dust toxicity, and illustrate the advantages resulting from the combined use with other techniques.

1) Evaluation of the free metal surface in multiphase catalysts.

The free metal surface in multiphase catalysts, which is obviously related to catalytic performance, is traditionally measured either by electron microscopy or by adsorption of an appropriate gas assumed to react only with the metal surface (28). The surface area is then related to uptake. This latter procedure sometimes yields uncertain results, because the gas can be adsorbed in different forms on the metal surface, can also interact with the support phase and finally may partly react with the bulk. The parallel measure of the heat of interaction of the gas with the catalyst reveals the occurrence of the above inconveniences, which show up in the differential heat vs uptake plot (interaction with substrate, adsorption in different forms) and on the thermokinetics (reaction with the bulk). This is the case of the measure of the copper surface in Cu/ZnO catalysts for methanol synthesis, where O_2 or N_2O are traditionally employed (29-31). The oxydation of copper at room temperature proceeds in different ways with the two gases, in that O_2 yelds surface and bulk oxidation and N_2O decomposes at some sites and only causes a partial oxidation at the surface (30%). Evidence of bulk reaction with oxygen is given by thermokinetics (19, 32) and a clear cut definition of the monolayer is consequently not easily found. To the contrary, the heat of interaction of N_2O with copper does not vary with coverage or with copper loading, as it can be seen in the integral heat vs uptake plot in figure 3 (32), where data concerning three different copper loading and pure Cu fall on a single straight line passing through the origin, whose slope furnishes, as interaction enthalpy, 317 kJ mol^{-1}. We have thus proposed that the evaluation of the heat released upon contact of copper containing catalysts with an excess of N_2O, can be used as a precise and quick measurement of the copper surface area (32).

2) Hydrophilicity and hydrophobicity of powdered materials.

The hydrophilicity or hydrophobicity of a powdered solid is of vital importance in various fields such as ceramics, electronics etc. It also plays a central role in determining the interaction of dusts with biological system (33). When dealing with liquids this property is readily measured by miscibility and enthalpy of mixing. The situation is more complicated with solid surfaces. The shape of the adsorption isotherm of water (34), the heat of immersion (35) and contact angle measurements (36) have been proposed so far as criteria for assessment of hydrophilicity/hydrophobicity. All these methods are valuable tools particularly when dealing with highly hydrophobic solids (e.g. carbons (34)) or with highly hydrophilic ones, e.g. hydroxides. When at the same surface both hydrophobic and hydrophilic parches are present, the detection and evaluation of both kind of sites is not easy to achieve. We propose a general way to estimate the extent of

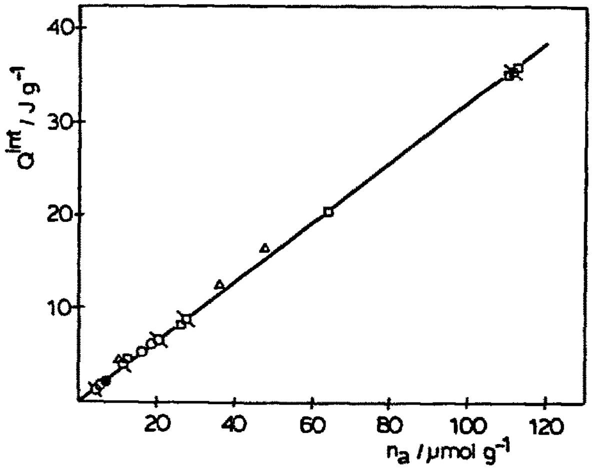

Fig. 3. Integral heat vs oxygen uptake from N_2O decomposition (O ∅ Cu-ZnO 3%; Δ, Cu-ZnO 15% □ Cu-ZnO 30%, ● pure Cu)Percentage indicate the mole fraction of Cu. Data are from ref. (32).

hydrophilicity/hydrophobicity by means of the evolution of the heat of adsorption of water vapour with coverage. A schematic representation of three possible cases is reported in figure 4. The differential heat of adsorption are compared with the latent heat of liquefaction of water. Following a definition proposed by Klier and Zettlemoyer (37,38), we consider hydrophilic any site interacting with water with an energy higher than or equal to the latent heat of liquefaction (44 $kJ\cdot mol^{-1}$), hydrophobic any site whose interaction energy with H_2O is below 44 kJ mol^{-1}. The figure reports three possible cases: the extreme case in which all the surface is hydrophobic and homogeneous (e.g. pyrogenic silica outgassed at or above 673 k (27); the other extreme in which the surface is wholly hydrophilic and heterogeneous (e.g. alumina (10)); an intermediate case in which some hydrophilic sites are present, which are filled up first, together with hydrophobic ones on which water adsorbs at a later stage (e.g. partially dehydrated silicas (27): correspondingly the heat of adsorption falls below the latent heat of liquefaction. An approximate measure of the extent of hydrophilic patches is given by the number of sites adsorbing water with $q^{diff} > 44$ kJ mol^{-1}. This intermediate case is often found when dealing with partially covalent oxides such as SiO_2, TiO_2 etc pretreated at high temperature (39). Figure 5 reports isotherms and differential heat vs pressure curves obtained with a low surface area silica prepared by precipitation. The material outgassed at 423 K is entirely hydrophilic: upon increasing the outgassing temperature hydrophobicity shows up. At 1073 k most silanols will have condensed into siloxane bridges, leaving only isolated silanols at the surface: both these kind of sites are hydrophobic.

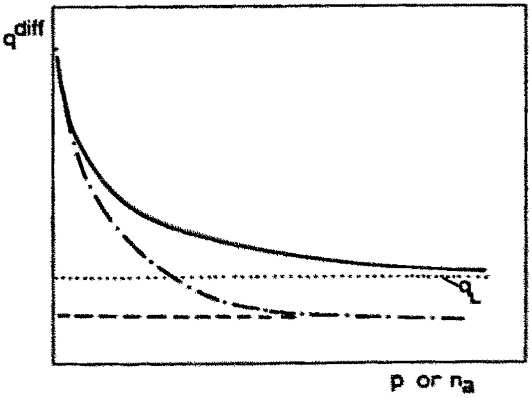

Fig. 4. Schematic representation of criteria for the assessment of hydrophilicity/hydrophobicity on the same surface,based on the heat of adsorption of H_2O. Full line: fully hydrophilic solid; dashed line: fully hydrophobic solid; dot-dash line: partially hydrophilic solid. Dotted line: latent heat of liquefaction.

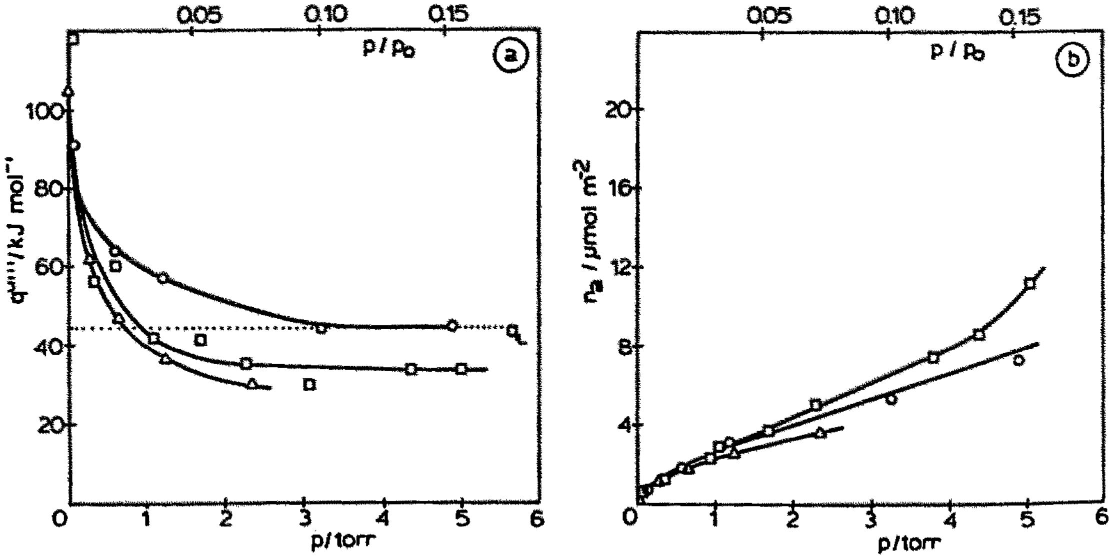

Fig. 5. Adsorption of water on silica outgassed at ○ 423 k, □ 673 k, Δ 1073 k.

3) Adsorption properties and effect of form on variously prepared Zinc Oxides

In order to investigate the relation between form of crystallites and adsorption properties of ZnO of various origin, Carbon monoxide, which is reversibly coordinated on unsaturated cations (27, 40), has been used as probe molecule. Figure 6 reports the isotherms and the integral heat vs uptake plot obtained on K-ZnO (ignition of Zn metal), C-ZnO and O-ZnO (decomposition of Zinc carbonate and oxalate respectively).

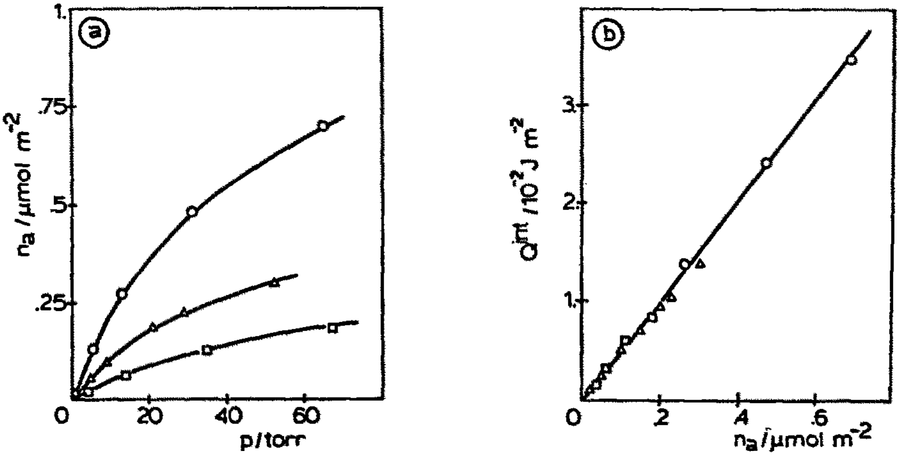

Fig. 6. Coordination of CO on K ZnO (O), C-ZnO (Δ) and O-ZnO(□).

The differences in uptake and the coincidence of the heats of interaction ($\Delta_{ads}H = 46$ kJ mol^{-1}) indicate that the same active sites are present on the three samples, whose abundance is closely related to the preparation procedure. On the basis of XRD and electron microscopy investigation it has been found that the higher surface reactivity on K-ZnO by comparison with ex-salt ZnO is not due to a preferential developement of crystal planes at the surface, as previously proposed (40-43) but to better defined morphology of single microcrystals with sharp edges (44).

4) Toxicity of inhaled dusts

This is a new field to surface chemistry: in spite of massive medical work, few studies have been performed on the physico-chemical properties of the dusts and on their possible role as carrier of adsorbed toxic agents into the lung (33).

The role of quartz in silicosis is a typical example. Quartz dusts are obtained by mechanical grinding in air which by cleavage of the Si-O bonds creates very reactive radical species ($Si^{\bullet}$, $SiO^{\bullet}$, $SiO_2^{\bullet}$ etc) and distorted siloxane and peroxobridges (45, 46). This is not the case of amorphous silicas chemically prepared (non toxic).

When initially contacted with water vapour, the active sites on quartz are revealed by a small fraction of H_2O strongly reacting, totally absent on amorphous silicas (see figure 7 from ref. 46). Possible reactions are also reported.

These reactive bridges, together with surface radicals evidenced by EPR, can be regarded as possible initiators of the biological response ending up in silicosis (47).

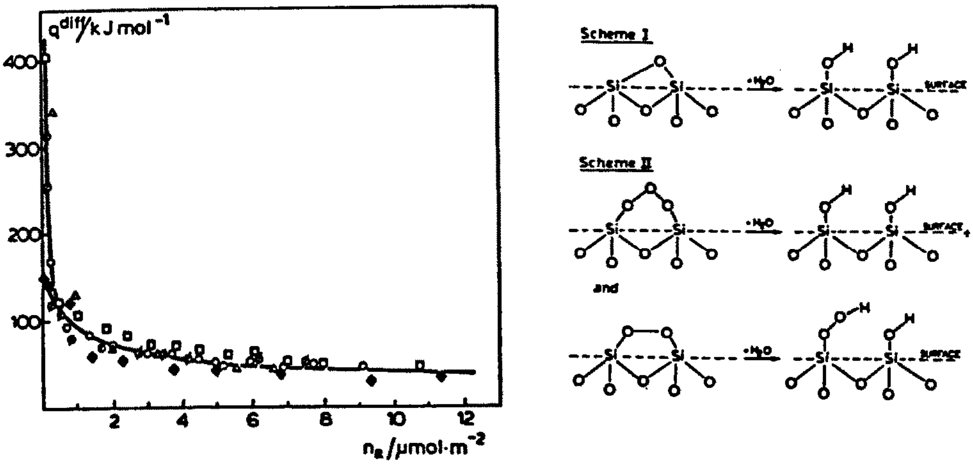

Fig. 7. Heat of adsorption of H_2O onto various crystalline samples (O; Ø, Δ, □) and amorphous silica (◆); differential heat (q^{diff}) vs. adsorbed amount (n_a). Possible reactions occurring on quartz.

QUALITATIVE AND QUANTITATIVE MEASUREMENTS: JOINT USE OF CALORIMETRY WITH OTHER TECHNIQUES

Beside the above reported results on the role of morphology in the surface properties of ZnO, we have obtained much advantages in the past and recent work, by the joint use of calorimetry with several spectroscopies, e.g. IR (25, 48, 51). UV-VIS reflectance (18), EPR (45-47, 52) or with a set of such techniques (53).

Infrared spectroscopy is particularly useful when more than one adsorbed species are formed, as from the knowledge of the kind and stability upon temperature and pressure of the various adspecies, energy values can be associated to each single species.

In some simple systems, IR data such as the stretching frequency ν of the admolecule can be closely related to the adsorption energy. When CO is adsorbed on unsaturated cations (Lewis acid) of non-d oxides (i.e. in the absence of backbonding), a well defined dependence of ν and of the extinction coefficient upon the interaction energy has been found over a series of several oxides (49).

The stretching frequency is bound to vary with coverage when the admolecule "feels" the presence of other molecules adsorbed at the surface. This occurs when the electronic perturbation induced by the adsorbed molecule on the solids is transmitted by the solid itself. An example of this is given by the adsorption of NO on the {100} of NiO microcrystals. A steady decrease in the heat of adsorption was measured with coverage which was found to parallel the decrease of the stretching frequency of NO (50).

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