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Dielectric measurements of adsorbed krypton on lamellar halides

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Résumé. — Les isothermes d’adsorption et les isothermes diélectriques pour le krypton adsorbé sur des halogénures lamellaires ont été mesurées simultanément. La comparaison entre les deux isothermes montre que la méthode diélectrique est bien adaptée pour caractériser la formation des multicouches. L’évolution des propriétés diélectriques d’un système bi-dimensionnel vers le système tri-dimensionnel est également obtenue.

Abstract. — We present simultaneous measurements of adsorption isotherms and dielectric isotherms for krypton on lamellar halides. The comparison between the two isotherms shows that dielectric method is well adapted to characterize the multilayer formation. The evolution of dielectric properties from a two-dimensional system towards the bulk is also obtained.

1. Introduction. — The study of adsorbed phases is the subject of a very important and still growing activity [1]. The existence of adsorbents with uniform surface gives now the opportunity to observe monolayers formation and transitions in a monolayer. A large number of experimental methods has been used to characterize the adsorbed phases. They are quite fruitful to describe the transitions occurring in such two-dimensional (2D) systems or the multilayers formation.

Dielectric measurements have not yet been fully exploited for such a study. It is the goal of this work to show that dielectric isotherms should effectively be quite useful to characterize adsorbed phases properties. A great deal of experiments has been performed to get the dielectric properties of polar or non polar molecules in adsorbed phases [2, 3]. However, in all cases, the substrates were rather heterogeneous and no step-like adsorption isotherms were observed. The theoretical postulates were rather unsatisfactory although a great number of equations was proposed [4-6]. In this paper we present dielectric measurements and adsorption isotherms for krypton adsorbed on appropriate substrates. We intend to show that dielectric measurements give a good characterization of the main features during the adsorption : transitions, layer completion etc... We expect that such measurements on well defined substrates should shed some light on the dielectric behaviour of 2D system and its evolution towards bulk system (3D).

In the second section we describe the experimental apparatus. The third section is devoted to the experimental results. In the last section we discuss these results and present some concluding remarks as well as perspective of use of dielectric method for adsorbed phases.

2. Experiment. — 2.1 Experimental set. — The goal of this experimental work is to measure simultaneously adsorption and dielectric isotherms. We use a capacitive method to measure the dielectric properties of the adsorbed krypton. The geometry of the experimental cell is essentially determined by the choice of the capacitance. We must be able to detect very small relative variation of capacity when amount of krypton corresponding to a fraction of monolayer is introduced. The best sensitivity of detection of this method implies :

— the largest nominal value for the empty capacity,
— the greatest surface adsorption area between the two condenser plates, to increase the number of adsorbed atoms corresponding to a given fraction of monolayer.

These two conditions bring us to use a cylindrical capacitor. Two coaxial brass cylinders are used. Each cylinder is 5.7 cm height and 1.4 mm thick. Their average diameters are respectively 6.60 cm and 7.32 cm. They are set on a plate of teflon which is used to hold them in position. The entire system is inside the experimental cell which is a copper cylinder of 7.87 cm diameter and 7.33 cm height.
Between the two coaxial cylinders of the condenser we introduce the material of large surface adsorption area on which the krypton is adsorbed. The choice of this adsorbent material is crucial. It should not only have a large surface adsorption area but also present a uniform surface so that we can observe monolayer formation with adsorbed krypton. In that respect it is well known that graphite and lamellar halides are well suited [7, 8]. We choose two insulating materials as adsorbent. First of all we take CdI$_2$ powder. The commercial product is crushed and then heated at 250 °C during 48 hours under a pressure $\approx 10^{-6}$ torr. Its specific surface adsorption area is 0.11 m$^2$/g. We introduce 53.1 g between the coaxial cylinders which gives a total surface adsorption area of 5.74 m$^2$.

The second product that we use is PbI$_2$. In that case the product was either sublimated at Saclay [9] or obtained by precipitation in order to check the influence of the substrate treatment on the dielectric isotherm. The same general features are observed for the various treatments. We present in this work the results obtained for sublimated PbI$_2$ of specific surface adsorption area of 1 m$^2$/g.

This experimental cell is mounted in a liquid nitrogen cryostat. The capacitance is one arm of a General Radio 1615 A capacitive bridge. A sinusoidal signal of 10 V amplitude at a frequency of 6 kHz feeds the bridge. The unbalanced signal is detected with a PAR 124 amplifier used as voltmeter. We adjust the calibrated capacitance of the bridge to obtain a balance. A change of $10^{-4}$ pF is detectable corresponding to $10^{-7}$ V variation on the voltmeter. The stability of the capacity value gives a resolution of $2 \times 10^{-4}$ pF. So for the standard capacitance in our experiments which is $\approx 200$ pF, we detect relative variations of capacity $\approx 10^{-6}$.

The adsorption isotherm is determined simultaneously. The experimental cell is connected to room temperature circuits by a filling capillary of 4 mm inside diameter, ended by a valve at the cryostat output. The pressure in the experimental cell is measured with a Baratron (MKS Baratron [10]).

The relative accuracy on pressure measurements is 0.5 % while the resolution is $10^{-4}$ torr.

2.2 EXPERIMENTAL PROCESS. — The temperature range for our experiments must be lower than the 2D critical temperatures, $T_{2c}$, of krypton adsorbed on the given substrate. It has been shown [8] that $T_{2c}$ is $\approx 91$ (K). We choose to work at $T \approx 84$ (K) where the formation of the two first layers is perfectly well characterized by adsorption isotherms [8].

We first introduce at room temperature helium gas at a pressure $\approx 10$ torr in the cell. This cell is then cooled down in our liquid nitrogen cryostat and reaches the chosen temperature after one day. The helium gas is used to increase the cooling speed of all elements in our cell and above all to make sure that temperature is uniform inside the cell. The temperature is measured with calibrated platinum resistors.

One of them is fixed outside and on the experimental cell. The other one is located inside the cell directly on the inner cylinder of the capacitor. The temperature is regulated using a S.E.I.N. bridge [11]. The stability over the entire experiment which can last for three days is better than $3 \times 10^{-2}$ K. The helium gas is then pumped off and the pressure inside the cell reduced below $10^{-4}$ torr. No detectable variation of temperature or capacity, which could be related at a adsorbent temperature variation, is observed during this operation. Each experimental point is then obtained in the following way. We introduce a given pressure of krypton gas in a calibrated volume at room temperature. This gas is then adsorbed in the experimental cell at low temperature. The equilibrium pressure obtained usually after 10 min. is measured as well as the new capacity value. The amount of adsorbed gas is easily deduced from the initial and final pressure measurements.

3. Experimental results. — 3.1 ADSORPTION OF KRYPTON ON CdI$_2$. — 3.1.1 Adsorption isotherm. — The adsorption isotherm obtained at 84.30 K is presented figure 1a. The absolute uncertainty on temperature is 0.02 (K). We observe two steps respectively at a pressure $P_1 = 0.12$ torr and $P_2 = 3.72(5)$ torr. The pressure corresponding to saturation is $P_s = 6.65$ torr. The localization of the first layer on that substrate and at this temperature agrees with results previously obtained by Lahrer [8].

Fig. 1. — a) Adsorption isotherm of Kr/CdI$_2$ at 84.30 K. b) Dielectric isotherm of Kr/CdI$_2$ at 84.30 K. Capacitance variations $\Delta C$ vs. the number of adsorbed atoms $N$.

From the magnitude of the first step (Fig. 2a) we get the specific surface of CdI$_2$ using the classical method in adsorption isotherm [8]. Taking for krypton atoms in the first layer the solid density we find that the area occupied by such atom is 14.34 Å$^2$ [8]. The total number of adsorbed atoms being

$$N = 41.75 \times 10^{18},$$

we get a surface adsorption area of 5.99 m$^2$ in our experiment. As the mass of adsorbent is 53.1 g we find
Fig. 2. — a) Adsorption isotherm of Kr/CdI$_2$ at 84.30 K in the first step range. b) Dielectric isotherm of Kr/CdI$_2$ at 84.30 K. Capacitance variations $\Delta C$ vs. the number of adsorbed atoms $N$ in the first step range (full line). Imaginary part of the dielectric constant $\varepsilon''$ vs. the number of adsorbed atoms $N$ for Kr/CdI$_2$ in the first step range (dashed line).

A specific surface area for CdI$_2$ of 0.113 m$^2$/g. This figure is in reasonable agreement with the value obtained by Thomy and Duval [12].

The existence of a small fraction of the adsorption isotherm convex towards the positive ordinates, below the first step and the fact that the portion BC of the isotherm is not strictly horizontal indicate some residual heterogeneity and a proportion of lateral faces on the adsorbent crystals. Finally we notice that the two steps (Figs. 2a and 3a) are not strictly vertical. The origin of this effect is usually attributed either to the adsorbent crystals which are not all identical or to temperature gradient in the sample. Anyway this adsorption isotherm shows a very good characterization of the adsorbed phase and will make possible to compare and discuss the dielectric isotherm.

### Dielectric isotherm.

We present figure 1b the variation of capacity vs. the number of adsorbed atoms $N$. Two significatives features are observable on this curve:

- The introduction of krypton gas gives first a decrease of the capacity value, which ends around the beginning of the first step, i.e. the first monolayer formation.
- After this point the addition of krypton atoms always increases the capacity. The curve is then represented by five different sections, four of them being linear with different slopes. The characteristic points defined by slope change in the dielectric isotherm and characteristic points of the adsorption isotherms (Fig. 1a) are clearly correlated.

The beginning of the curve up to the first layer completion is presented in a more detailed way figure 2b. Also we give figure 2b our experimental results for the imaginary part of the dielectric constant $\varepsilon''$ which is related to the conductance that we measure with our General Radio bridge. We find that correlated to the capacity decrease, $\varepsilon''$, which describes dissipative mechanisms, is also reduced. This behaviour stops at point A, corresponding to a given amount of adsorbed krypton. The initial value of the capacity before introducing any krypton being $C_i = 157.8825$ pF at this temperature the observed reduction $\Delta C = -3.36 \times 10^{-2}$ pF represents $\approx 2 \times 10^{-4}$ as relative variation. Meanwhile we detect that the final value of $\varepsilon''$ represents only $3 \times 10^{-2}$ of the initial one.

Above the point A, increasing the amount of adsorbed atoms does not affect $\varepsilon''$ which remains always constant. Along the first layer formation we find that the variation of capacity is not rigorously linear with $N$. The point A is not exactly equivalent to the beginning of the first monolayer, deduced from the adsorption isotherm.

Above this point, $\varepsilon''$ remains constant and so dissipative mechanisms do not affect the analysis any longer. We notice that a good characterization of the first monolayer completion, i.e. the position of B is then obtained through the slope change in the dielectric isotherm.

It seems easy to determine accurately this completion from dielectric measurements particularly in the case of the second step which is not strictly vertical.

The first linear section in the dielectric isotherm represents, from the adsorption isotherm, the adsorption on lateral faces. The slope of this section BC, see figure 1b, is

$$s_1 = 2.56 \times 10^{-22} \text{ pF/at}. $$

The points C and D corresponding respectively to the beginning and completion of the second layer are also connected in the two isotherm curves figures 3a and 3b. They also are easy to determine from the dielectric isotherm.
The slope of this linear section is then
\[ s_2 = 1.39 \times 10^{-22} \text{ pF/at} \].

The slope of the next linear section DE, figure 1b is
\[ s_3 = 3.125 \times 10^{-22} \text{ pF/at} \].

No special feature is detectable for the point E on the adsorption isotherm. However we observe that the amount of adsorbed krypton for point E roughly corresponds to three layers.

Finally the last linear section starting from point E up to saturation has a slope
\[ s_4 = 2.08 \times 10^{-22} \text{ pF/at} \].

It is then bulk krypton properties which are measured as will be shown in the discussion.

3.2 ADSORPTION OF KRYPTON ON PbI₂.

3.2.1 Adsorption isotherm. — The adsorption isotherm obtained at 85.05 (K) is presented figure 4a. We observe two steps respectively at a pressure \( P_1 = 0.18 \text{ torr} \) and \( P_2 = 5.4 \text{ torr} \). Again these results agree with the isotherms obtained for krypton on PbI₂ in the literature [8]. From the magnitude of the first step we estimate the specific surface of PbI₂ in the same way than for CdI₂. We get a surface adsorption area in this experiment of 3.15 m² which for 3.1 g of PbI₂ gives a specific surface area of 1.02 m²/g. Here again our adsorption isotherm, the two steps of which are presented with more details figures 5a and 6a, gives a very good characterization of the multilayers formation of the adsorbed krypton.

3.2.2 Dielectric isotherm. — We present figure 4b the dielectric isotherm. The same general features as for CdI₂ are observed. The first adsorbed atoms give a reduction of capacity and of \( \varepsilon'' \). However we notice that the loss reduction figure 5b ends now almost at the completion of the first layer. The corresponding relative decrease of capacity is \( 6.5 \times 10^{-3} \text{ pF} \). So our analysis with krypton on PbI₂ will be limited compared to the case of CdI₂.

We find also that once \( \varepsilon'' \) remains constant we get four linear sections in the dielectric isotherms. The slope breaks are correlated to the breaks in the adsorption isotherm. The first linear section represents only a part of adsorption on lateral faces as regard to the adsorption isotherm. Its slope is \( s_1 = 2.3 \times 10^{-22} \text{ pF/at} \). The point C gives the beginning of the second layer which is completed at point D. The slope of this linear section CD is \( s_2 = 6.7 \times 10^{-23} \text{ pF/at} \). The slope of the next linear section DE is \( s_3 = 2.5 \times 10^{-22} \text{ pF/at} \). No special feature on the adsorption isotherm is observable for the amount of adsorbed krypton corresponding to
the point E (Fig. 4a). The last linear section has a slope which is \( s_4 = 8.8 \times 10^{-23} \text{ pF/at} \).

4. Discussion and conclusion. — The most striking results of our experiments are:

— A reduction of the capacity with the first adsorbed atoms. Depending on the substrate this effect ends at the beginning or during the first step. This capacity decrease is directly related to a reduction of losses. As soon as the capacity starts to increase with added krypton atoms, the losses, i.e. \( \varepsilon'' \), remain constant.

— A strong correlation between slope changes in the dielectric isotherms and the layer formation or completion deduced from the adsorption isotherms. The previous observations which were made with various substrates [2, 3] also showed slope changes that suggested the first monolayer completion and even, but controversial, multilayer completion. However it is only the kind of experiment that we present which could unambiguously relate these slope breaks to multilayer formation. Effectively by comparison with the adsorption isotherm using the same appropriate substrate we find what these slope breaks mean.

Also we observe that slope breaks in dielectric measurements give a rather accurate determination of the transitions.

The reduction of capacity with the first adsorbed atoms is rather surprising, but this effect has already been observed for some dielectric isotherms [3]. It was attributed to the presence of OH radicals on the substrate and to the fact that the first atoms were adsorbed on it. There is however no satisfactory explanation to describe quantitatively the very first part of our dielectric isotherms. We believe that, then, the interaction between adsorbed atoms and substrate plays the dominant role for the dielectric properties of the total system. We assume that as soon as \( \varepsilon'' \) remains constant with added atoms this interaction is no more crucial and that we measure the dielectric properties of the composite system (substrate and adsorbed phase).

For such composite system various models [13, 4] have been proposed and we will use them to analyse our results for the dielectric isotherms. Of course because of the initial effect we only will look at relative capacitance variations for amount of krypton larger than the ones corresponding to the points A in figures 1b and 4b. The slope of the experimental curve is:

\[
\frac{dC}{dN} = \frac{d\varepsilon}{dN} \tag{1}
\]

where \( C_0 \) represents the parasite capacity. We then entirely fill the capacitor with liquid argon of dielectric constant \( \varepsilon_{ar} \) which is well known, and measure the capacity \( C_{ar} \) at \( T \). We have then:

\[
C_{ar} = \varepsilon_{ar} C_0 + C_p. \tag{3}
\]

From our measurements we find \( C_0 = 48.33 \text{ pF} \) and \( C_p = 10.911 \text{ pF} \). The apparent dielectric constant of the composite system is of course:

\[
\varepsilon = \frac{C - C_p}{C_0}. \tag{4}
\]

We will limit our discussion to two models. The first one discussed by O. Gröbner [13] is very simple but certainly too rough. It starts from the Clausius-Mosotti equation and assumes that the change of \( \varepsilon \) is only due to adsorbed molecules. He then finds that the relative variation of \( \varepsilon \) is in first approximation:

\[
d\varepsilon = \frac{4\Pi}{9}(\varepsilon_s + 2\gamma) dN \frac{\nu}{V} \tag{5}
\]

where \( \gamma \) is the volume average polarizability of adsorbed molecules which is assumed to be constant, \( \nu \) the atomic volume and \( V \) the total volume.

Reporting (5) in (1) we obtain that the slope is:

\[
s = \frac{4\Pi}{9} C_0(\varepsilon_s + 2\gamma) \frac{\nu}{V}. \tag{6}
\]

Everything being known the measured slope should give the volume average polarizability \( \gamma \) of adsorbed molecules.

The second model is an extension of Böttcher's treatment for a powder [14] to the case of finely divided solid and adsorbate [4]. As in our experiment the equilibrium gas pressure remains always low, \( \varepsilon \) is related to the volume average polarizabilities of substrate \( \varepsilon_s \) and krypton \( \gamma \) by:

\[
\frac{\varepsilon + 2}{3} - \delta_3 \frac{3\varepsilon}{2\varepsilon + 1} = \frac{\varepsilon_s - 1}{4\Pi\varepsilon_s} + \frac{\varepsilon - \varepsilon_s}{4\Pi\gamma} \tag{7}
\]

where \( \delta_3 \) is the volume fraction of the gas phase inside the capacitor:

\[
\delta_3 = \frac{V - NV - V_s}{V} \tag{8}
\]

where \( V_s \) is the adsorbent volume that we measure and \( \nu \) the atomic volume in the adsorbed phase.

Considering that only \( \varepsilon \) and \( \delta_3 \) change with \( N \) we get:

\[
s^{-1} = \frac{dN}{dC} = -\frac{V}{C_0\nu} \left( \frac{2\varepsilon + 1}{3\varepsilon} \right) \times
\]

\[
\times \left[ \frac{1}{3} - \frac{3\delta_3}{(2\varepsilon + 1)^2} - \frac{1}{4\Pi\gamma} \right]. \tag{9}
\]
We can compare the experimental slopes and those calculated from equations (9) and (6). First of all we find that the models only predict one slope. This is in contradiction with the experimental observation.

In a theoretical work Dignam and Rao [6] suggested that the existence of one break slope observed for some dielectric isotherms was the result of capillary condensation after the first layer formation. Such explanation is clearly not valid for our experiments where we observe many break slopes and where adsorption isotherms show that there is no capillary condensation but multilayers formation.

The fact that we find linear sections of different slopes can be interpreted as if the adsorbed molecules have an effective polarizability \( \gamma \) which depends on the considered layer. Our slopes will give us this effective polarizability using equation (9) or (6). We present Table I these effective polarizabilities. It is comforting to check that for three atomic layers, both models give the bulk krypton polarizability within a relative accuracy of ten percent: this result is expected as for thick adsorbed films we should recover the bulk dielectric properties.

It can lead to two conclusions:

- It suggests the validity of the models we use to describe the dielectric properties of adsorbed phases.
- The adsorbed phases present an effective polarizability different in the first layers than the bulk one. The bulk properties are obtained when the amount of adsorbed krypton represents more than 2 or 3 atomic layers. The understanding of this effective polarizability in the first layers remains an open problem, which is of course related to dimensionality.

It could also be connected to local field effects between neighbouring adsorbate molecules. Some aspects of this have been treated in connection with optical properties of adsorbed layers [16].

In conclusion this work has proven that dielectric isotherms could give a good characterization of monolayer formation and completion. Such a method should be quite useful for systems in which the pressure corresponding to the first layers is too low to give a good determination with adsorption isotherms. For instance we think that this method could be applied to helium films adsorbed at very low temperature.

We also believe that transitions occurring in a given layer could be studied by dielectric isotherms.

Not only does this method give information about transitions in adsorbed phases but also it gives new information about dielectric properties of the adsorbed phases. The present results clearly indicated the existence of an effective polarizability depending on the considered layer and more effort is needed to get a better understanding of dielectric properties in 2D system and their evolution towards 3D or bulk system.

Acknowledgments. — We are grateful to Y. Lahrer for helpful discussions.

Table I. — Volume average polarizability \( \gamma \) for the various linear section obtained from equations (6) and (9).

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References


