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STRUCTURE AND EVOLUTION OF DIFFERENT ICE SURFACES AT LOW TEMPERATURE ADSORPTION STUDIES

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RESUME : Des mesures d'adsorption de N_2 et Ar ont été faites à 77K et 87K sur différents types de poudres de glace. Un fort champ dipolaire est trouvé à la surface des glaces Ih broyées. Ce caractère polaire de la surface persiste après recuit à plus haute température malgré une importante diminution de la surface développée par les échantillons. Pour les glaces amorphes obtenues par condensation de vapeur d'eau à 77K on a trouvé une structure très poreuse. Le mécanisme de base de leur formation semble être une agrégation de molécules H_2O à laquelle s'ajoute des effets de recuit liés à la vitesse et à la température de condensation.

ABSTRACT : N_2 and Ar adsorption measurements at 77K and 87K are done on different types of ice powders. A strong dipole field is found at the surface of crushed hexagonal ice and this polar nature persists after annealing at higher temperature, despite of a very large decrease in surface area. For amorphous ice obtained by vapour deposition at 77K, a very porous structure is found. The basic mechanism for its formation seems to be a random aggregation of H_2O molecules together with annealing effects depending on both condensation rate and temperature.

INTRODUCTION

The structure and dynamics of ice surfaces is the purpose of many studies, especially at temperatures near the melting point. In comparison at low and very low temperatures relatively little work is done.

However, in addition to fundamental relevances ices formed and stored at these temperatures are important for astrophysical problems such as evolution of cometary nuclei and molecule formation on icy interstellar grains.

For these purposes, fundamental studies are needed to determine the structure and dynamics of ices at low temperature in relation with their formation processes and the different kinds of evolution or alteration that they may have experienced.

Adsorption studies are generally considered to be a powerful approach for characterization of both surface and powder structures. Historically, Karasz and al [1] were the first to study N_2 and Ar adsorption at 77K on very thin films of ice. Since, several studies have been done for N_2 adsorption on various ice powder samples [2 to 8]. The adsorption features of these different samples show great dependence on preparation conditions and thermal history : the total spread of the net BET heat of adsorption lies between 0.1 and 3.7 kJ/mol with powders having surface areas from 0.1 to 400 m²/g. On the other hand a single adsorption study has been done with Ar and CO gases at 77K [8].

In the present study we first investigate gas-surface interactions and their evolutions for nitrogen and argon on freshly and annealed crushed Ih monocrystals. Secondly we start a systematic study of adsorption properties and structure of amorphous ice obtained by slow water vapour deposition at low temperature [9].

EXPERIMENTAL PROCEDURES

The first type of ice samples was obtained by crushing Ih monocrystals under vacuum (10^{-6} torr) in a stainless steel container at 77K. Before the first measurement, the sample was always maintained at this temperature. The powders obtained with this method are very fine and without any sintering.

Amorphous snow samples were obtained by condensation of water vapor at 77K under vacuum. Water vapor is obtained either from bubble free artificial monocrystals or deionized water (electrical resistivity : 18 M Ω /cm at 300K). This water was outgassed by several freeze-thaw cycles under pumping. The condensation took place directly from the glass vessel maintained at a desired temperature to the glass sample holder at liquid nitrogen temperature. The condensation rates used lie between $2 \cdot 10^{-7}$ and 10^{-8} mol cm $^{-2}$ s $^{-1}$ and samples thickness varie from 50 μ to 900 μ with 7 hours deposition time.

In order to measure adsorption isotherms at 77K on surfaces as low as 1 m 2 we have improved an apparatus of volumetric type entirely immersed with its pressure gauge at the adsorption temperature. A second pressure gauge (Datametrics 590A) at room temperature allows us to calibrate each equilibrium pressure, read with the immersed gauge (Celesco P1A), with an accuracy of 0.02% [9]. After non ideal gas corrections and dead space calibrations, an accuracy higher than 0.1m 2 is reached for surface area determination.

RESULTS

Freshly crushed hexagonal ice : Nitrogen and argon adsorption isotherms at 77K on freshly crushed samples fit the BET equation in the 0.03 to 0.21 relative pressure range for N $_2$ and in the 0.05 to 0.25 range for Ar.

In table I, we have summarized the following parameters : samples weight We, mono-layer capacity Vm, BET constant C and the net heat of adsorption ΔQ derived from BET theory. Specific surface area Sw measured with N $_2$ (Adsorbate cross section : 16.2 $\text{\AA}^2$ at 77K) and Vm(N $_2$)/Vm(Ar) ratio are also listed.

Table I

Sample N°	Weight g	Ta °K	Vm cm 3 STP/g		C		ΔQ J/mol		Sw m 2 /g	$\frac{Vm(N_2)}{Vm(Ar)}$
			N $_2$	Ar	N $_2$	Ar	N $_2$	Ar		
4	24.53	77	0.262	0.226	64.8	12.4	2680	1620	1.140	1.160
6	24.5	77	0.378	0.329	68.7	12.3	2710	1610	1.645	1.150
11	24.31	77	0.317	0.272	66.2	12.7	2690	1630	1.380	1.165
"	"	87	0.304	0.285	40.6	9.8	2680	1650	"	1.070

Figure 1: N $_2$ and Ar isotherms at 77K on crushed Ih monocrystals

We can see that the BET C values are approximately the same for a given gas despite of differences of about 40% in specific surface areas. Moreover, the isotherms relative to V_m are virtually the same for N_2 and Ar respectively (figure 1). These results indicate that ice-crushing at 77K provides powders with good reproducibility of their adsorption properties. Comparisons between measurements at 77K and 87K show that nitrogen monolayer density has the same temperature dependence than liquid.

On the other hand, argon monolayer capacities have low values and an opposite temperature dependence. This leads to abnormally high $V_m(N_2)/V_m(Ar)$ ratios.

Isosteric heats of adsorption q_{st} and differential molar entropies ΔS for N_2 and Ar were measured for different surface coverages (figure 2). For argon, a steady decrease in isosteric heat takes place during the monolayer completion. A mean net heat of adsorption of 1650 J/mol is calculated from the isosterics heats, this value is in good agreement with the BET one. The entropy of adsorbed argon molecules is slightly greater than that for the bulk liquid. A quite different behaviour is observed with nitrogen : the isosteric heat first slightly decreases until a coverage of about 0.8 monolayer is reached and then falls more abruptly to a very low value (≈ 800 J/mol).

The corresponding entropies have large negative values and show an increase around the monolayer to the liquid bulk value. A mean value of 3500 J/mol, 30 % greater than the BET one, is deduced for the monolayer net heat of adsorption.

Aged crushed hexagonal ice : Freshly crushed ice showed great stability at 77K, no isotherm changes has been recorded at this temperature over more than 15 days.

On the other hand, irreversible changes occurred when the samples were annealed by bringing them to a temperature higher than 77 K for a desired time. After each annealing the samples were recooled to 77 K for adsorption measurement. For example, figure 3 shows successive adsorption isotherms for argon on a sample annealed at 213.2K. During the evolution, the monolayer capacity falls irreversibly while the relative isotherms, the $V_m(N_2)/V_m(Ar)$ ratios and the net heats of adsorption remain unchanged, and this for annealing times as long as 2000 hours and temperatures between 190K and 215K.

Amorphous ice : Ice condensed at 77K with a very low condensation rate is assumed to be amorphous [10]. As deposition proceeds, ice samples are transparent until a thickness of some micrometers is reached, then they become progressively opaque and finally have the appearance of white powders.

These powders have large nitrogen and argon adsorption capacities, but these capa-

Figure 2: Net isosterics heats and differential molar entropies of adsorption (crushed Ih).

Figure 3: Ar isotherms on hexagonal ice freshly crushed and annealed at 213.2K for different times.

cities depend on condensation rates and in a different way for these two gases. Moreover, a slight decrease in these quantities is observed with time although samples are maintained at 77K between each adsorption measurement. This behaviour is even more pronounced at 87K. Therefore, a straightforward comparison between N_2 and Ar monolayer capacity values is impossible, but we can estimate the $V_m(N_2)/V_m(Ar)$ ratio from several successive isotherms.

In Table II, we have summarized several features of amorphous condensates : sample weight, average thickness, condensation rate, N_2 and Ar monolayer capacity, their average ratio and the apparent specific surface area calculated with N_2 .

Table II

Sample N°	Weight g	Thickness μ	Condensation rate mol/cm ² s	Vm cm ³ STP/g		Sw m ² /g	$\frac{V_m(N_2)}{V_m(Ar)}$
				N_2	Ar		
13	0.52	50	$1.0 \cdot 10^{-8}$	59.2	74.0	258	0.80
12	5.13	500	$1.0 \cdot 10^{-7}$	26.4	31.4	115	0.84
15	9.39	900	$1.6 \cdot 10^{-7}$	8.1	9.2	35	0.90

Complete N_2 adsorption-desorption isotherm has been made with sample N°15 obtained with the highest condensation rate (Figure 4a). We can see a wide hysteresis loop, with a sharp shoulder at low relative pressure, which indicates a wide pore size distribution, with a large quantity of very small pores. Pores size and volume distributions have been calculated in the range of validity of Kelvin equation ($Radii > 18\text{\AA}$) using a numerical integration method [11] (figure 4b). For this calculation, crushed ice is taken as the non porous reference. For pores ranging between approximately 10 and $18\text{\AA}$ (modified Kelvin equation range) we can only estimate their total volume with the drop of the desorption curve around the shoulder at $P/P_s=0.42$.

Moreover, an estimation of the micropores volume ($Radii < 10\text{\AA}$) is obtained with Dubinin-Raduskevitch plot corrected from adsorption in larger pores [12].

For this sample we find that pores with radii less than $18\text{\AA}$ account for approximately 40% of the pore volume, that is to say $0.017 \text{ cm}^3/\text{g}$.

Preliminary results for amorphous ice obtained with lower condensation rates show that a smaller water vapour flow increases largely the monolayer capacity V_m but decreases appreciably the V_m ratio (table II). Moreover, the corresponding isotherms are more flat at high pressures. These behaviours are obvious in figure 5 (A crushed Ih ice sample is also shown for comparison). Adsorption measurements have also been done on these condensates after annealing at 190K for 10 minutes.

Figure 4: a) N_2 adsorption and desorption isotherm, b) Pores size ($\Delta V/\Delta R$) and volume (V) distribution of amorphous condensate. (condensation rate : $1.6 \cdot 10^{-7} \text{ mol/cm}^2 \text{ s}$).

Figure 5: N_2 and Ar isotherms at 77K on amorphous condensates (a: ech 13), (b: ech 15) and on hexagonal ice (c).

A very low final adsorption capacity corresponding to a value of less than $0.1 \text{ m}^3/\text{g}$ is measured. In addition, we have observed that large quantities of gases are occluded when annealing is done with preadsorbed gases (N_2 or Ar).

DISCUSSION

The abnormally high $V_m(N_2)/V_m(\text{Ar})$ ratio observed with crushed Ih ice cannot be explained with N_2 and Ar theoretical cross sections calculated from bulk liquid or solid. With an adsorbate cross section of $16.2 \text{ \AA}^2$ for N_2 a value of $18.8 \text{ \AA}^2$ is calculated for argon at 77K. The argon monolayer is then 30% less dense than the liquid. Several authors have already observed V_m ratios greater than unity, this high value going generally with a low argon BET constant [13]. Indeed when, as in our case for argon, the adsorption heat is sufficiently low, the adsorbate lateral mobility on the surface will tend to disrupt any tendency for an organized structure to develop and the adsorbed layer may appear more as a two dimensional gas [14]. The positive entropy of adsorbed argon molecules confirms their greater mobility relative to liquid state. The increase in monolayer capacity with rising temperature can then be explained in term of adsorbed film compressibility because the pressure needed to build the argon "statistical monolayer" is four times greater at 87K than at 77K.

For nitrogen, its increased adsorption energy compared to argon can be explained if a high interaction between the quadrupole moment of nitrogen molecules and a dipole field at the surface of ice is considered. The quite negative entropy of nitrogen molecules in the first monolayer agree with this concept of oriented adsorption on a polar surface. This polar nature of the surface of crushed ice persists after annealing at higher temperature. Then the evolution process responsible for the decrease in surface area and the sintering of ice particles observed with time don't seem to influence on the surface structure.

The adsorption properties of amorphous ice obtained by vapour deposition at low temperature are characteristic of a porous structure with wide pore size distribution. The larger adsorption capacities and the more pronounced type I isotherms observed with the sample prepared at lowest condensation rate suggest that a narrower porosity develops when more isothermal conditions are used. Moreover, the low value of the $V_m(N_2)/V_m(\text{Ar})$ ratio is a further argument for the presence of large quantities of pores only a few molecular diameters wide. Indeed, the increased adsorption energy in micropores causes the condensation of argon in these very thin volumes (with probably solid density) while an argon monolayer is approximately 40%

less dense on a free surface. This "monolayer ratio" is then linked with the micropore ratio.

These properties of amorphous ice can be explained if a random aggregation mechanism is considered for the condensation of H_2O molecules at low temperatures. The structures obtained by this way are extremely porous with continuous pore size distribution [15,16], but are also very unstable. With our deposition conditions we must added annealing effects due to the thermal energy of molecules at 77K and the latent heat released during condensation (spot heating). The slight evolution observed after condensation show that a slow molecular rearrangement occurs even at this temperature, this great unstability of ice condensed at low temperature is at the origin of the large gas occlusion when samples were warmed at somewhat higher temperature.

CONCLUSION

Comparisons between adsorption behaviour of nitrogen and argon on both crushed Ih ice and condensed amorphous ice are shown to provide useful informations about the structure and the nature of their surfaces.

The polar nature observed for ice surfaces crushed at 77K must be compared to the only slightly polar surfaces observed by Adamson et al for two types of condensed ice [2,8]. This difference is probably linked with their different formation processes.

On the other hand, we have found that the main feature of amorphous ice condensates is a large porosity and that both temperature and condensation rate seem to be the first parameters determining its porosity and stability.

For astrophysical topics such as synthesis of hydrogen molecules on icy interstellar grains the presence of pores in which an increase in adsorption occurs at very low pressure is of particular importance. For this, a study of the porous structure of mixed ice condensates, and more particularly the micropore volume, is needed for temperatures below 20K. If the condensation mechanism of amorphous ices is a molecular aggregation process, then the very low temperatures and extremely low gas densities prevailing in space are ideal conditions for the formation of icy grains with large quantities of very narrow pores.

Some few results in cryopumping techniques litterature seem to prove that large quantities of hydrogen molecules are still adsorbed at temperatures near 20K on different kinds of ices (H_2O , CO_2 , CH_4 , ...) condensed at this temperature [17,18]. In addition, the evolution properties of amorphous icy condensates are probably the key of several processes such as gas occlusion, phase change, etc..., occurring when these aggregates are warmed. The composition and evolution of cometary matter will then strongly depend on the thermal history of ices before comet formation [19].

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COMMENTS

remark of J. DORE

The large volume of this material would make it ideal for study by small-angle scattering techniques with neutrons (SANS) or X-rays (SAXS). There is much interest in the characterization of porous networks in terms of a fractal representation. The SAS measurements would yield the fractal dimensionality and the way this varied with deposition conditions would provide valuable information on the way the molecules are laid down and build the surface structure.

Answer :

It would certainly be very interesting to do SAXS or SANS experiments on this type of amorphous ice in order to confirm our results. But these scattering techniques are also limited to minimal size of around 15 Å for pore size distribution determinations. On the other hand, the shape of the pores may probably be obtained with these experiments. The fractal dimensionality can easily be derived from the pores volume distribution. The relationship between this fractal dimension and the basic mechanisms of condensation are fairly well understood but when annealing effects occur in the same time, the problem is more complicated and it is necessary to perform computer simulation for explaining the detailed structure of these condensates.