

ISOTOPIC ORDERING IN ADSORBED HYDROGEN MONOLAYERS

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The mass difference between the molecular isotopes hydrogen (H₂), deuterium hydride (HD) and deuterium (D₂) leads to very different liquid-vapor critical and liquid-vapor-solid triple points in both three and two dimensions. This effect is due to the importance of the zero point kinetic energy in these quantum systems. The zero point kinetic energy also manifests itself in the freezing of binary isotopic mixtures by the observation of bulk quantum fractionation, i.e. the separation at freezing of a liquid rich with the lower mass isotopic molecule, and a solid rich in the larger mass isotope.

The same quantum mass effect should also induce an isotopic ordering at low temperature in the bulk solid phase. Isotopic phase separation was predicted a long time ago by Prigogine^[1]. It was observed for ³He-⁴He mixtures but never for isotopic hydrogen solid solutions, although it has been predicted to occur at temperatures as high as ≈ 4 K.

Isotopic phase separation should be expected also in an adsorbed single layer of an isotopic hydrogen mixture. The reduced dimensionality and coordination number in a monolayer with respect to its three-dimensional counterpart makes the relative contribution of the zero-point kinetic energy to the total energy larger than in bulk. This is responsible, among other things, for a substantial difference in the molar areas of H₂ and D₂ at solidification and at monolayer completion. The difference in molar areas lifts the chemical equivalence of the isotopes and can be the driving force which may lead to phase separation.

This was the major motivation of our work on binary mixtures H_{2(x)}-D_{2(1-x)} or HD_(x)-D_{2(1-x)} of the hydrogen isotopic molecules H₂, D₂ and HD adsorbed on graphite, searching for the possible fractionation at solidification and for the expected isotopic phase separation in the solid phase at lower temperature^[2-4]. Neutron scattering is well suited for such investigations, taking advantage of the large difference in the coherent and incoherent cross sections of the various hydrogen isotopes. Indeed, the contribution to a diffraction process of all three isotopic molecules is large since the coherent scattering length of both H ($b_H = -3.742$ fm) and D ($b_D = +6.674$ fm) are comparable in magnitude. On the other hand, the large incoherent scattering length of H (especially in the HD molecule which does not undergo ortho-para conversion at low temperatures)

is particularly useful in quasielastic neutron scattering measurements.

We performed three kinds of neutron scattering experiments at various hydrogen surface densities (ρ), molar isotopic concentrations (x) and temperatures (T) :

-Diffraction experiments were performed on H₂-D₂ mixtures to identify long range ordering in the solid phases and its possible evolution with temperature.

-Small angle neutron scattering (SANS) investigations were carried out on monolayer H₂-D₂ mixtures. SANS is sensitive to the temperature dependence of the short and medium range structural and compositional order within the mixture. We were thus looking for small clusters of D₂ and H₂.

-Quasi-elastic neutron scattering (QENS) experiments were performed on HD-D₂ mixtures to determine the self-correlation function of the HD molecules in the fluid phase at high temperature (15...30K) and hence the corresponding diffusion coefficient.

The major part of the experiments was performed at the LLB on G6.1 and MIBEMOL ; it was complemented by measurements at the ILL on D1B and D16.

The diffraction measurements mapped portions of the ρ , T , x parameter space. The most meaningful results stem from intensity measurements of the (10) diffraction line at low temperature because they can distinguish between a compositionally disordered adlayer (random mixture) according to

$$I \propto [xb_H + (1 - x)b_D]^2 \quad (1)$$

and a fully phase-separated system, as given by

$$I \propto xb_H^2 + (1 - x)b_D^2 \quad (2)$$

The calculated intensity is represented in Fig. 1 (full line) for the random mixture ; it reaches zero for $x = 0.64$ as a result of the opposite signs of b_H and b_D , respectively. The dashed line represents eq. 2, i.e. the fully phase-separated system.

Two sets of experimental results are reported in Fig. 1, as well. One, for coverage $\rho = 1$, corresponds to the so-called commensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. The intensities of the (10) lines fit very well the

calculated intensities of a compositionally disordered mixed crystal. The commensurate solid remains a random mixture down to 3K.

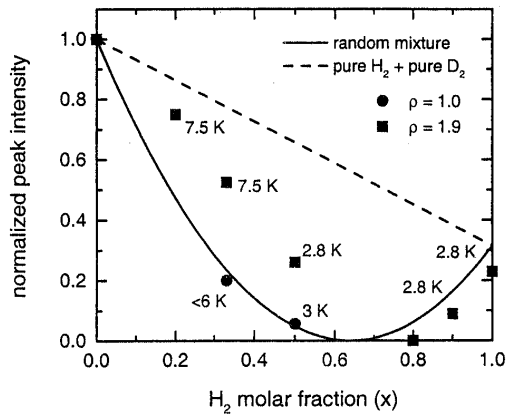


Figure 1. Behaviour of the (10) adlayer diffraction peak intensity

The other coverage $\rho = 1.9$ corresponds to a complete, very dense, incommensurate monolayer ($\rho \approx 1.5$) with, in addition, 30% of a second adsorbed layer (other experiments, not reported here, for $\rho \approx 1.5$, look qualitatively the same). In that case, the measured intensities for $0.2 < x < 0.5$ are intermediate between the calculated intensities of a random mixture and a fully phase-separated system. Hence, a partial phase separation is observed at monolayer completion for these isotopic molar concentrations.

The small clusters of D_2 or H_2 should be observed by SANS. We have measured the variation of the SANS intensity from 20 to about 3K by decreasing the temperature step by step for $x = 0.5$ and 4 coverages ($\rho = 1.92, 1.54, 1.2$ and 1.0). The results are represented in Fig. 2 as the difference of the recorded intensity at 3K, $I(3K)$ and at 20K, $I(20K)$, in order to eliminate the contribution of the beam adsorption due to the hydrogen condensation on the graphite surface.

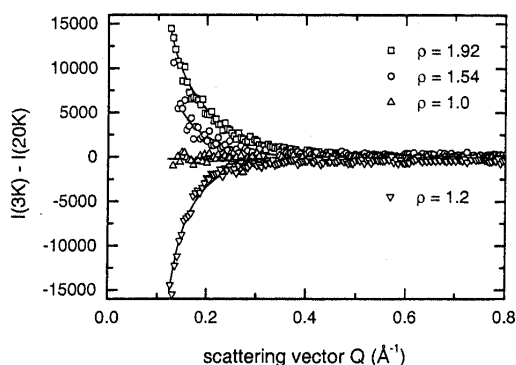


Figure 2 SANS results

At $\rho = 1.92$ and 1.54 , we measure at low temperature an increase of the intensity at small scattering vector which is readily interpreted as the signature of an isotopic clustering in the mixture. Hence, the trend towards phase separation observed by diffraction is confirmed by SANS for these coverages.

The interpretation of the decrease of the SANS intensity at low temperature, observed for $\rho = 1.2$, is not as straightforward. It suggests that more ordering occurs in the adsorbed layer at low temperature. This is also suggested by diffraction measurements because a superstructure peak is observed for this coverage at 3K.

In the vicinity of the commensurate solid ($\rho = 1$), the SANS intensity is essentially constant between 20 and 3K. No change in the ordering is detected between these temperatures ; this means that the adsorbed layer remains compositionally disordered down to 3K, as already seen by diffraction measurements.

At higher temperature, in the solid-liquid transition range, we looked, by QENS, for a possible ordering or phase separation at freezing in an isotopic hydrogen mixture adsorbed on graphite. We did not observe any indication of fractionation during the layer solidification but instead a rather unexpected effect : by substituting one half of HD by the heavier molecule D_2 in an adsorbed monolayer, we measured an enhancement of the hydrogen mobility with respect to the pure HD layer in the fluid phase just above the melting temperature. This effect is represented in Fig. 3. It can be interpreted in terms of a strengthening of the bonding of the lighter molecule, resulting from its larger quantum motion. Indeed, the lighter molecule has a larger vibrational amplitude and it tends to experience more strongly the repulsive part of the Van der Waals potential ; this effect stabilizes the lighter isotope adlayer.

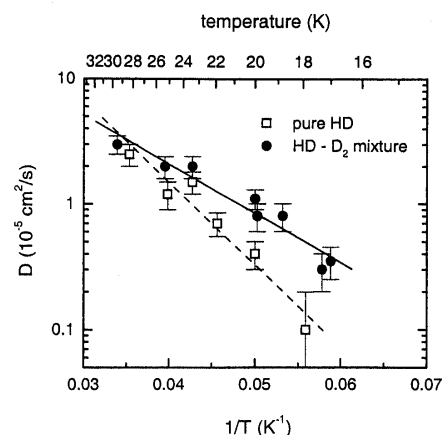


Figure 3. Diffusion coefficient of HD molecules deduced from QENS results

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