

Adsorption Isotherms of *ortho*- and *para*-Water

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The fundamental quantum property of a water molecule is its ability to exist in one of the two spin states *ortho* and *para* with parallel or antiparallel proton spins, respectively. Under normal conditions, the amounts of gaseous *ortho* and *para* molecules are in statistical 3:1 equilibrium. It is an intriguing challenge for researchers to separate a volume of water into two parts, each consisting of molecules of only one type: paramagnetic *ortho*-water and nonmagnetic *para*-water. Long ago, a similar problem was resolved for dihydrogen H₂.^[1] Properties of separate *ortho*- and *para*-water are at present completely unknown. However, accessibility of new forms of water could stimulate research in many branches of science.

Earlier, we demonstrated qualitatively different adsorption properties of gaseous *ortho* and *para* molecules on a solid surface.^[2] Here we report on the quantitative influence of this effect the individual adsorption isotherms of *ortho*- and *para*-water adsorbed on the hypercross-linked polystyrene MN-200.^[2]

We performed a conventional adsorption experiment in which water vapour mixed with nitrogen or argon as carrier gas is brought into contact with an adsorbent, and the amount of adsorbed water molecules is measured as a function of pressure at a fixed (room) temperature. The amount of adsorbed water molecules was determined indirectly by monitoring molecules lacking from the gaseous phase. To this end, the headspace above the adsorbent was sounded with a beam of electromagnetic radiation. The principal feature of the experiment is that the number densities of the *ortho*- and *para*-water molecules in the gas (partial pressures p_o and p_p) are measured separately. The used backward-wave-oscillator spectroscopic technique registers selectively the response (absorption) of *ortho* and *para* molecules at respective frequencies of 36.6 and 37.1 cm⁻¹ (radiation transitions 3₋₂-3₋₁ and 0₀-1₀ of the rotational spectrum of the isolated water molecule).^[3] Integral intensities of the *ortho* and the *para* absorption spectral lines I_o and I_p and the linewidths are measured during one frequency scan. The former are taken as representing the partial pressures $p_o \sim I_o$ and $p_p \sim I_p$. The latter, calibrated by electron manometer, give the total pressure P of the gaseous mixture.

Figure 1 shows the partial pressures p_o and p_p against the total pressure P for an empty cell and a cell filled with an adsorbent. In the first case, the dependences are straight lines starting at the origin with a slope of 3:1 (within an accuracy of a few percent). This corresponds to the normal *ortho*:*para* ratio

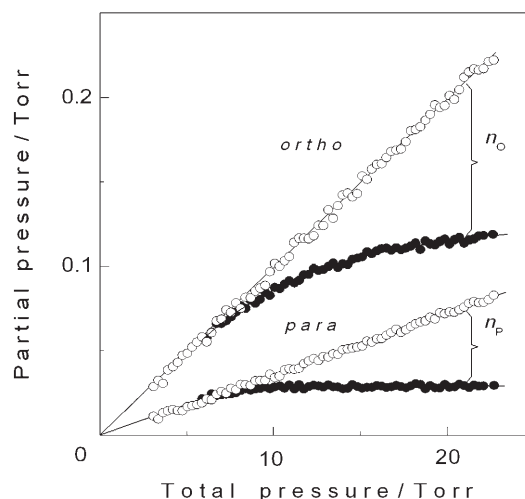


Figure 1. Partial pressures p_o and p_p of *ortho*- and *para*-water vapour in the cell versus total pressure P of the water/nitrogen (1/100) gas mixture a) without adsorbent in the cell (\circ , reference curves) and b) with the adsorbent MN-200 (\bullet). Wedge-shaped differences indicate amounts of lacking *ortho* and *para* molecules, n_o and n_p . The lines are the fit by simplest linear and exponential dependences, and the differences are given by Equation (1).

in gaseous water. In the second case, the curves turn down at higher pressures. Their progressively increasing deviation from the straight lines demonstrates that only part of the water molecules entering the cell remains in the gas and is responsible for radio absorption. We suggest that the portions of molecules n_o and n_p lacking in the gas (the wedge-shaped differences marked by n_o and n_p in Figure 1) are captured by the adsorbent. Of critical importance is that the p_o and p_p values, as well as their ratio p_o/p_p , do not relax at any fixed total pressure P . We found that p_o and p_p of the isolated gas-adsorbent system remain unchanged for hours. The transient processes that occur when the gas is let into the cell take no more than a few tens of seconds. Consequently, the pressure-changing process is essentially in equilibrium in our experiment. The straight and turned-down lines in the Figure 1 are perfectly fitted by the simplest linear and exponential expressions, respectively.

Figure 2 shows the data of Figure 1 recalculated into standard adsorption isotherms: fractions of lacking molecules n_o and n_p as functions of p_o and p_p . The graphs were brought to a unified scale by matching the reference straight curves. The isotherms are represented analytically as a difference of the aforementioned linear and exponential forms Equation (1):

$$n = \{A \ln[A/(A-p)] - p\}V/kT \quad (1)$$

where $n = n_{o,p}$ is the amount of lacking molecules (*ortho* or *para*), $p = p_{o,p}$ the pressure, T the temperature, V the volume of the vacuum system, k Boltzmann's constant and $A = A_{o,p}$ the only fitted parameter characterising adsorptive ability of the *ortho* and *para* molecules with reference to the given adsorbent. The coefficient A represents a characteristic pressure (an asymptote) of the indicative condensation-like $n(p)$ behaviour.

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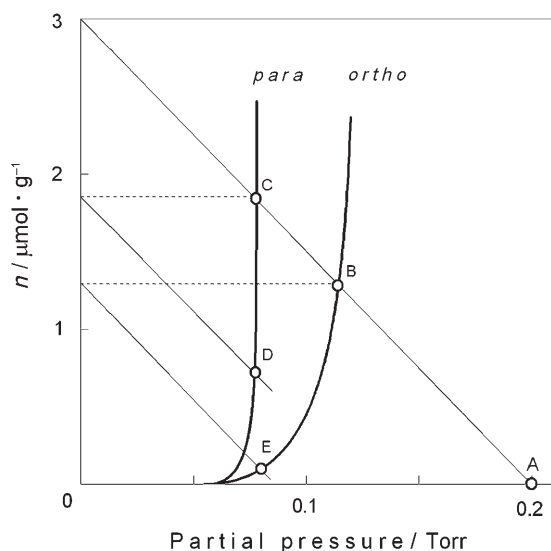


Figure 2. Fractions n_o and n_p of molecules lacking in the gas versus partial pressures p_o and p_p (bold rising lines). Thin straight lines show possible distributions of the fixed fractions of water molecules in the cell between the gas and the adsorbent. Point A corresponds to a nonequilibrium state when the vapour of *ortho*- and *para*-water molecules is let into the cell containing MN-200 adsorbent ($3 \mu\text{mol}$ of each sort per gram of MN-200). The intersection points B–E denote stable states. Their coordinates show the *ortho:para* ratio in gaseous and condensed water at thermodynamic equilibrium between a gas and an adsorbent.

The graphs conclusively demonstrate that, within the experimental accuracy, the $n(p)$ isotherms for *ortho*- and *para*-water do not coincide. The critical partial pressure for *ortho* water ($A_o = 0.12 \pm 0.01$ Torr) is half as much again as the critical partial pressure for *para* water ($A_p = 0.08 \pm 0.01$ Torr): $A_o/A_p = 1.5$.

There are two ways to explain the enhancement of *ortho* molecules in the gaseous phase: either by rapid generation of additional *ortho* molecules on a surface or by preferential adsorption of the *para* molecules with conservation of spin state on a surface. We can not decide at present: the spin states of water molecules on a surface are still unknown.

In either case, the experiment provides direct evidence for *ortho/para* separation and its long-term conservation in the gaseous phase. In addition, the second case, where the *ortho*- and *para*-water molecules have distinctly different adsorption capabilities, offers the possibility to accumulate in the adsorbent the molecules lacking in the gas. An independent challenge would be to investigate the spin states of the adsorbed water molecules.

The idea is illustrated in Figure 2 by additional inclined straight lines. They represent possible distributions of the portion of water molecules between gas and adsorbent in a closed volume. The slope of the lines depends on the volumes of the gas and of the adsorbent (the graphs roughly correspond to the conditions of the experiment). The intersections of the lines with the isotherms correspond to the thermodynamic equilibrium in the gas/adsorbent system. Position A refers to a moment at which equal portions of *ortho*- and *para*-water molecules (1:1 ratio) are quickly let into the cell containing dry adsorbent. The A state is not stable; adsorption

transfers it to the equilibrium, but to different positions B and C for the *ortho* and *para* molecules, respectively. The equilibrium *ortho:para* ratios (the ratios of the abscissas and ordinates of points B and C) appear to be noticeably different from the value of 1:1, both in the gaseous and, formally, in the condensed phase. Quick removal (pumping out) of the gas from the cell results in fast desorption of water from the adsorbent (transient process) and transition of the gas/adsorbate system from the B and C states to the new equilibrium states D and E. Here, the *ortho:para* ratio in the gas (the ratio of the abscissas) returns to the initial, but now stable, 1:1 value. At the same time, in accordance with the shape of the $n(p)$ graphs, further enhancement of the amount of *para* water occurs in the adsorbent (the ratio of ordinates is 1:7). Thus, small variations of the *ortho:para* ratio observed in gaseous phase may indicate a very large deviation of the 3:1 ratio in the adsorbent. Recently, in an analogous adsorption experiment, a similar dependence of p_o/p_p on P was observed by diode-laser spectroscopy.^[4] However, additional direct measurements of the *ortho/para* ratio in the condensed phase are required.

In summary, adsorption isotherms were measured separately for *ortho*- and *para*-water. For the hydrophobic adsorbent MN-200 a condensation-like regime was revealed which occurs at different critical partial pressures for *ortho*- and *para*-water. In a closed volume filled with MN-200 adsorbent the equilibrium gas-phase *ortho:para* ratio is noticeably shifted from 3:1 in favour of the *ortho* component. Correspondingly, condensed (adsorbed) water is formally strongly *para*-enriched. The deviation from 3:1 ratio in the isolated gas–adsorbent system exhibits long-term stability. This makes it possible to consider the gas and perhaps the adsorbent as potential accumulators and storers of spin-modified water. The remaining challenges are to develop accessible *ortho/para* diagnostic techniques (primarily NMR) and to elucidate the origin of the *ortho/para* water-separation phenomenon.

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