



Hydrogen isotope separation in metal-organic frameworks: Kinetic or chemical affinity quantum-sieving?



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ABSTRACT

Recently we reported hydrogen isotope separation by quantum sieving in metal-organic framework MFU-4l, a framework exhibiting gates of about the same size as the molecular radii of D₂ and H₂. Due to its smaller effective particle size, D₂ penetrates preferentially through the framework, resulting in remarkable selectivity. Surprisingly, MFU-4l, a material of very similar composition, but with substantially larger gate openings, shows appreciable hydrogen isotopologue selectivity. This selectivity occurs at low temperature and is smaller compared to earlier reported CPO-27, a framework exhibiting open metal sites. We show that this is caused by different adsorption enthalpies which are the result of quantum effects. It turns out that two independent hydrogen isotope separation mechanisms have been reported for MOFs: while kinetic quantum sieving works at cryogenic temperatures for materials with small pores, different adsorption energies allow chemical affinity quantum sieving. This effect is maximized by strong adsorption centers, which allow high selectivity at high temperatures (100 K and above), and is more appropriate for the rational design of isotope separation membranes.

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1. Introduction

Successful and efficient separation of hydrogen isotopologues H₂, D₂, HD and variants involving tritium in metal-organic frameworks (MOFs) has recently been reported by various groups [1–4], and explained by the difference of host–guest interactions due to quantum-mechanical effects of the hydrogen isotopes. One mechanism is kinetic quantum sieving (KQS), a method first proposed by Beenakker et al., who have shown that D₂ has a shorter de Broglie wave length, and thus a smaller effective radius than H₂. In consequence, it penetrates easier through small openings [5]. KQS shows higher mobility of heavier hydrogen isotopologues and hence acts opposite to the tunnel effect, where the opposite phenomenon would be expected, and also to classical diffusion, where light-weight species have higher velocities. In a different mechanism, strongly attractive interaction

sites of MOFs preferably adsorb heavy hydrogen isotopologues due to their smaller zero-point energy (ZPE) and resulting in a stronger adsorption enthalpy. We will call this effect, in analogy to KQS, chemical affinity quantum sieving (CAQS). Remarkably, for CPO-27(Co) this effect has been found to be strongest at relatively high temperatures (above 100 K), which is explained with the fact that at this condition only the strongly binding and hence strongly selective adsorption sites are occupied [4]. CAQS can be employed in a temperature swing process [4], but is also suitable for diffusion-based separation in membranes, as the lower diffusion coefficients of the heavier isotopologues are further, significantly, reduced by the CAQS.

This work is motivated as we have observed appreciable isotope selectivity in MFU-4l, a framework that neither shows strong adsorption sites nor gates that could act as quantum sieve. Thus, sizeable CAQS is possible in systems without uncoordinated metal centers which are typically more water-stable and less affected by poisoning with residual gases. However, the selectivity in MFU-4l is smaller than for CPO-27 and thus requires lower temperature for operation as effective isotope separation membrane.

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2. Experimental section and computational details

The metal-organic frameworks, MFU-4 and MFU-4l, have been provided by the group of Dirk Volkmer, Augsburg University, and the details on the synthesis have been published previously [7,8]. The TDS experiments were performed in a home-made device with few mg of MFU-4 and MFU-4l powder. In the UHV sample chamber the sample holder was screwed tightly to a Cu block, which could be cooled using a liquid He cryostat and heated using a heating spiral. The samples were activated at 420 K. In order to quantify the mass-spectrometer signal, the TDS device was calibrated using a PdCe alloy. In this type of measurement, the selectivity is given as the ratio between the amounts of desorbed D₂ to H₂.

Density functional theory (DFT) was applied on large finite molecular clusters of MFU-4l, using B-LYP/def-TZVP as was previously verified for MFU-4 [1]. The treatment of London dispersion has been changed from D2, as used in Ref. [1] to Grimme's more recent D3 approach [6] that considers the chemical environment in the choice of dispersion parameters. Symmetry constrains have been applied if appropriate. Details of the thermodynamic models for calculating ZPE and adsorption properties are the same as reported earlier (Oh et al. [4]) and are outlined in the [Supporting information](#).

3. Results

MFU-4l represents the first example of MFU-4-type frameworks featuring a large 9.1 Å pore aperture, in contrast to a small pore with aperture of 2.5 Å for MFU-4. MFU-4 and MFU-4l are constructed by [Zn₅Cl₄]⁶⁺ coordination units, stitched together with [BBTA]²⁻ and [BTDD]²⁻ organic ligands, respectively (Fig. 1) [7,8]. The chemical composition of both frameworks differs only by the additional rings in the linkers, but the structure is strongly different. Two pore types are found in MFU-4, a small one (A) and a large one (B). Both pores are separated by gates, formed by the four chlorine atoms. Gas diffusion through the MOF is only possible by penetration through the gate between the A and B pores. The pore has been found to be small, so that hydrogen and its isotopologues can only enter the framework at higher temperatures [1]. In contrast, the MFU-4l gates are large and the framework can be loaded with larger gas molecules without any penetration barriers [9]. As we will show in this work, both frameworks are suitable for hydrogen isotopologue separation; however, the separation mechanisms are unrelated to each other. Isotopologue separation

in MFU-4 has been studied experimentally, and the results have been backed up by a theoretical analysis [1]. In summary, the gates in MFU-4 are too narrow for hydrogen penetration at very low temperature. Only above ~50 K, D₂ and also H₂ can enter the framework, assisted by the first thermally excited lattice vibrations. Those slightly open the gates between A and B pores. D₂ preferentially enters as it is smaller than H₂ – a genuine QoS effect as proposed by Beenakker et al. [5]. A second supporting property of D₂ is its stronger adsorption enthalpy to the MFU-4 surface, caused by the smaller repulsive zero-point energy, which results in the blockade of the gates for H₂ by the heavier isotopologues [1].

Based on this reasoning, one would expect that extending the linker, thus opening the gate that is acting as quantum sieve, would annihilate the selectivity for dihydrogen isotopologues. Instead, we observe that also MFU-4l shows a remarkable selectivity, again favoring D₂ adsorption.

Fig. 2 shows the results of a thermal desorption spectroscopy (TDS) experiment on both frameworks, exposed to a 1:1H₂/D₂ mixture at 40 K and 10 mbar. The general appearance of both spectra is not comparable. However, both frameworks show a significantly different adsorption towards D₂ and H₂. In MFU-4, less gas is present in the framework material, caused by the fact that the gates are barely opening due to the low exposure temperature of 40 K. H₂ and D₂ desorption starts at about 50 K and shows a maximum rate just above 60 K, as gate opening occurs at this point and the gas molecules can leave the framework. A strong selectivity of 6.9 is obtained based on the integration of the signals from 40 to 100 K.

In contrast, the TDS of MFU-4l shows very different features. Due to the open pores and lower mass density, the material is able to adsorb significantly more gas. However, the significant peak is observed at a lower desorption temperature. The total selectivity, that is, integrating the TDS spectrum from 20 K to 75 K, gives a relatively poor selectivity of 1.7. The total selectivity at 50 K, predicted with DFT is 1.7 which is in a perfect agreement with the experiment. An interesting feature of MFU-4l is the D₂ signal at 50 K and above, when most of the H₂ molecules are removed from the host framework, but D₂ still remains inside, resulting in very high selectivity (higher than 17 by integrating the desorption signal from 50 K to 75 K).

The MFU-4l TDS spectrum shows three distinct adsorption sites, thus dihydrogen shows a similar adsorption as heavier noble gases [9]. These three sites have been identified by our London dispersion corrected DFT calculations as linker, metal and cup sites, which in

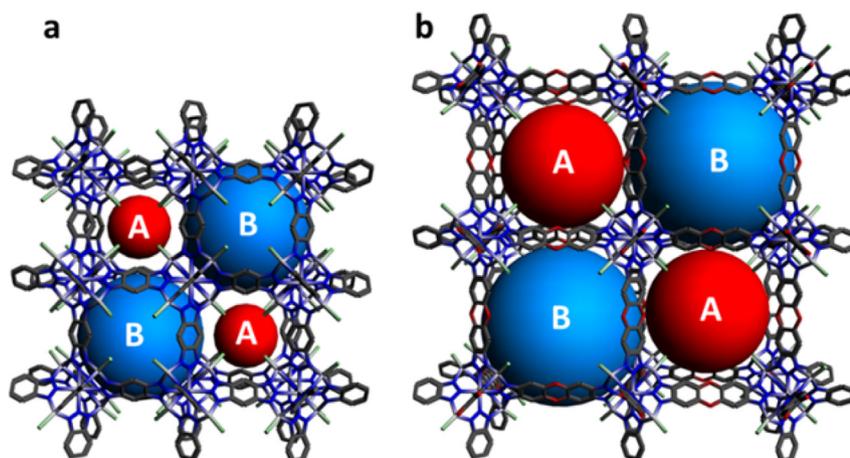


Fig. 1. Structures of MFU-4 (a) and MFU-4l (b); A – small pore and B – large pore; Color scheme: White – Zn, Green – Cl, Gray – C, Red – O, Blue – N; Hydrogen atoms omitted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

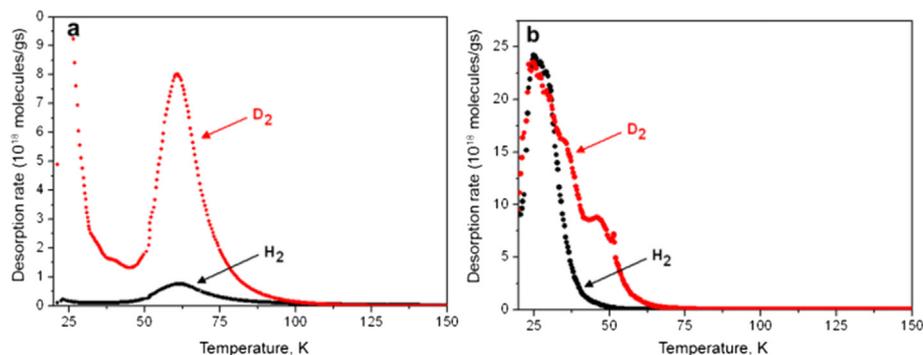


Fig. 2. TDS spectrum of an adsorbed 1:1 mixture of H₂ and D₂ in MFU-4 (a) and MFU-4l (b) at 40 K and 10 mbar. The strong D₂ signal at low desorption temperature (below 40 K) for MFU-4 is attributed to the adsorption at the outer framework surface – the signal remains for even lower temperatures [1].

this order show increasing adsorption enthalpy (Fig. 3). These three adsorption sites are all independent of each other and none of neighboring sites influences the H₂ adsorption. All different orientations of H₂ with respect to the main adsorption sites were taken into account (Fig. 3a–c).

The strongest H₂ binding of $-10.5 \text{ kJ mol}^{-1}$ is found for the cup site with H₂ being in linear orientation with respect to the central zinc atom of the secondary building unit (SBU). The most favorable H₂ position for the second, metal site is located on the Zn atom connected Cl. In this case H₂ is adsorbed in T-configuration with respect to Zn–Cl unit resulting in -8.7 kJ mol^{-1} . At the third and weakest linker site, the H₂ molecule is oriented in-plane of the phenyl ring along the oxygen atoms with the energy of -5.5 kJ mol^{-1} . All the energies are corrected for basis set superposition error (BSSE) including energy correction for framework deformation [10].

Adsorption enthalpies and related quantities at 50 K are given in Table 2. The linker site is weakly attractive with respect to the two other sites, that its adsorption signal coincides with the bulk signal of the adsorption in the pore volume and is hence not further discussed. The cup and metal sites show clear D₂ signals at 50 and 30 K, respectively.

The selectivities of the adsorption sites are given by the different adsorption enthalpies of the dihydrogen isotopologues due to the isotopic contributions to the ZPE and to the partition function. We follow the approach suggested by Sillar et al. for MOF-5 [11], that we have recently successfully applied to a similar problem in CPO-27(Co) [4]. The ZPE is the governing quantity discriminating between the adsorption properties of the isotopologues, and this quantity is directly related to the curvature of the potential at the

Table 1

Vibrational frequencies of H₂ relative to the surface of the MFU-4l $\Delta\omega(\text{H}_2\cdots\text{MFU-4l})$; Potential energy (ΔE) of H₂ in the main adsorption sites; Zero-point energy (ΔZPE) of adsorbed H₂ (D₂); Bond length $d(\text{H-H})$ of adsorbed H₂; All calculations have been done with BLYP-D3/def-TZVP. All energies are in kJ mol^{-1} .

Site	$\Delta\omega(\text{H}_2\cdots\text{MFU4l}), \text{cm}^{-1}$	ΔE	ΔZPE	$d(\text{H-H}), \text{Å}$
		H ₂	H ₂ (D ₂)	
Cup	83, 99, 185 ^R , 226 ^R , 232, 4228	-10.5	1.8 (1.2)	0.7478
Metal	126, 153, 214, 253 ^R , 333 ^R , 4211	-8.7	2.1 (1.5)	0.7477
Linker	57, 69 ^R , 97, 224, 230 ^R , 4285	-5.5	1.9 (1.3)	0.7488

Free H₂: 4346 cm^{-1} ; Free D₂: 3075 cm^{-1} ; [R] Vibrations that correspond to rotations of H₂/D₂ with respect to a main adsorption site of MFU-4l.

equilibrium structure: strong adsorption sites with a steep potential form exhibit the strongest difference in ZPE for the different isotopologues and are thus showing the highest selectivity.

In the case of MFU-4l we have a very similar situation. Selective adsorption is possible for the adsorption sites. Despite the relatively low adsorption energy, a rather large selectivity is achieved, though the ZPE of adsorbed H₂ in MFU-4l is 4 times smaller than in CPO-27(Co) [4]. Separation can be achieved in a temperature swing process working around 50 K as described earlier [4], or in diffusion membranes, as the CAQS effect is further supported by the diffusion coefficient in the free gas.

Here we emphasize that two mechanisms of isotopologue separation in MOFs have been discussed that should not be confused with each other. The first one is based on kinetic quantum sieving (KQS). The material must include gates that perfectly fit the different molecular extensions of the isotopologues, which are

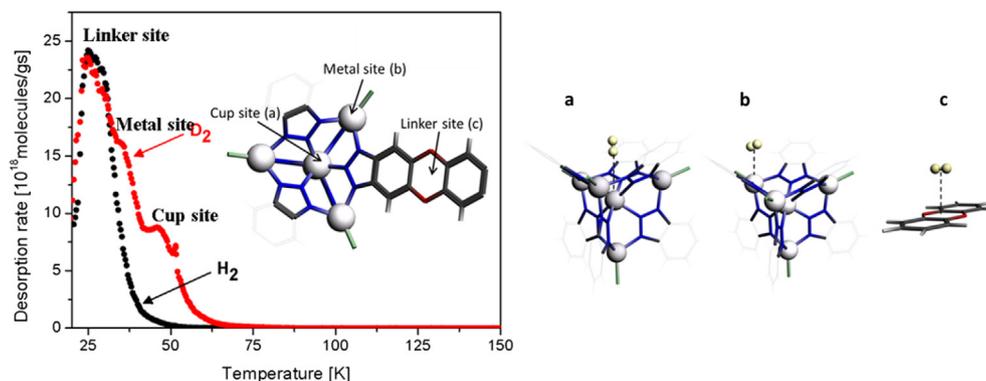


Fig. 3. Left: TDS spectra of main adsorption sites of MFU-4l: Cup site, Metal site and Linker site. Right: (a) Cup site: Linear orientation of H₂ with respect to central Zinc; (b) Metal site: T-shaped H₂ with respect to Zn–Cl unit; (c) Linker site: T-shaped orientation of H₂ in-plane of linker, along oxygen–oxygen axis.

Table 2
Enthalpy (ΔH) of adsorbed H_2 (D_2) at 50 and 77 K; Entropy (ΔS) of adsorbed H_2 (D_2) at 50 and 77 K; Gibbs energy (ΔG) of adsorbed H_2 (D_2) at 50 and 77 K. All calculations have been done with BLYP-D3/def-TZVP. All energies are in kJ mol^{-1} .

Site	ΔH_{50K}	ΔS_{50K}	ΔG_{50K}	ΔH_{77K}	ΔS_{77K}	ΔG_{77K}
	H_2 (D_2)					
Cup	-9.4 (-9.8)	3.8 (4.0)	-5.6 (-5.8)	-9.5 (-9.8)	6.1 (6.3)	-3.4 (-3.5)
Metal	-7.3 (-7.8)	3.9 (4.2)	-3.4 (-3.6)	-7.5 (-7.9)	6.4 (6.7)	-1.1 (-1.2)
Linker	-4.2 (-4.6)	3.7 (3.9)	-0.6 (-0.8)	-4.3 (-4.6)	5.9 (6.0)	1.6 (1.4)

reflected by their de Broglie wave lengths. This is a rather harsh geometrical condition that is only possible for few materials, among them MFU-4. Dihydrogen isotopologue separation in MOFs without such gates cannot be a kinetic effect. Instead, separation is achieved by chemical affinity quantum sieving (CAQS) due to different ZPE and contributions to the partition functions determining the adsorption enthalpy. The geometry of the adsorption sites can have a significant effect on the adsorption enthalpy differences and thus on the separation factors, while the adsorption enthalpy determines the temperature of desorption, and thus working temperature of a temperature swing process that could be implemented for D_2 production.

4. Discussions

We expect CAQS to be the more efficient process compared to QOS, as it shows excellent separation factors and operates at higher temperatures. Efficient CAQS materials are characterized by the presence of a high density of strong adsorption sites that provide a “free” metal site for guest molecules, where the adsorption strength defines the best temperature for separation and the potential curvature the selectivity. Moreover, CAQS might be employed in typical diffusion-based separation technology, as diffusion-related factors (higher velocity of lighter molecules) are enforced by the quantum adsorption effects.

5. Conclusions

In conclusion, we have found appreciable hydrogen isotopologue selectivity in MFU-4l, even though the material is neither suitable for kinetic quantum sieving, nor does it include strongly attractive open metal sites. Its selectivity is based on the small difference between ZPE of adsorbed H_2 and D_2 at a temperature of ~50 K. This effect, chemical affinity quantum sieving, was clearly identified and is suggested for exploitation in the rational design of new framework materials. Thus, we have shown that kinetic quantum sieving is possible in typical MOFs with large surface area, however, the operational temperature for effective separation of hydrogen isotopologues is significantly lower compared to those of frameworks with open metal sites, such as CPO-27.

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Appendix

The structure of MFU-4l was simulated by using a finite molecular cluster. A molecular cluster of the MFU-4l cavity was cut

from the experimental periodic structure and the dangling bonds were saturated with hydrogen atoms, resulting in molecular system of 380 atoms.

The interactions of H_2 with the main adsorption sites were calculated. Different initial configurations of dihydrogen were taken into account. All calculations have been performed with the Turbomole 6.5 [12]. The BLYP exchange-correlation functional has been applied in combination with the all electron triple-zeta def-TZVP atomic basis set [13] and the corresponding auxiliary basis sets [14] for the Resolution of Identity (RI) [15] approximation. The Grimme empirical scheme (denoted as DFT-D3) to account for the London dispersion forces has been used [6]. The m4 grid was used and the convergence criterion for the SCF cycle was set to 10^{-8} a.u. The geometries were optimized until the forces were smaller than 10^{-4} a.u./bohr and the energy changes between the geometry cycles less than 10^{-6} a.u. Vibrational frequencies were calculated numerically within the harmonic approximation following the approach of K. Sillar et al. [11]. A frequency analysis of adsorbed H_2 has been done in order to verify that the structure is a local minimum and to calculate the ZPE (Table 1).

Upon adsorption on a surface of a porous material, the three translational and two rotational degrees of freedom of gaseous H_2 are converted into five vibrational modes with respect to the adsorption site. However, the experimental work showed that H_2 retains its two rotational degrees of freedom in MOF-5 [16]. This approximation has been used in previous works, where the authors studied with ab initio methods the adsorption of H_2 in MOF-5 and D_2/H_2 separation in CPO-27(Co) [4,11]. Following this approach, the three translational and the stretching mode of adsorbed H_2 are treated as vibrations within the harmonic approximation, whereas the two rotational modes are excluded from zero-point energy and are treated as rotations (Table 1).

Based on calculated frequencies of adsorbed and free gas molecules the selectivity of D_2/H_2 from a gas phase x_{H_2}/x_{D_2} mixture is calculated by the Formula (1):

$$S_{D_2/H_2} = \frac{\theta_{D_2}/x_{D_2}}{\theta_{H_2}/x_{H_2}} \quad (1)$$

where θ_{H_2} , θ_{D_2} is the surface coverage in H_2 , D_2 and x_{H_2} , x_{D_2} refer to the gas phase mixture of H_2 , D_2 . The bulk phase of adsorbed molecules is described with a Langmuir-type isotherm (2a–c) by including the three ($X = 1,2,3$) main adsorption sites of MFU-4l:

$$\theta_{H_2/D_2}(X) = \sum_X n(X) \frac{K_{H_2/D_2}(X)P_{H_2/D_2}}{1 + K_{H_2}(X)P_{H_2} + K_{D_2}(X)P_{D_2}} \quad (2)$$

Here we denote: as (1) the Cup site, (2) the Metal site and (3) the Linker site, where $n(X) = N_X/N$ is the fraction of the specific adsorption site per molecular cluster; $P_{i,j}$ is the partial gas pressure and $K_{i,j}$ is the equilibrium constant for the adsorption process of each isotope, which is calculated as:

$$K_{H_2} = \frac{q'_{H_2}^s}{q'_{H_2}^g} e^{-\frac{D_{H_2}^0}{RT}} \quad (3a)$$

and

$$K_{D_2} = \frac{q_{D_2}^s}{q_{D_2}^g} e^{-\frac{D_{D_2}^0}{RT}} \quad (3b)$$

where q_{H_2, D_2}^s and q_{H_2, D_2}^g are the overall partition functions of H_2 , D_2 in solid and gas phase, respectively. To compute zero-point energies and thermodynamic energies of adsorbed H_2 and D_2 , the partition functions have to be calculated. As was mentioned above, the translational degrees of freedom are lost upon adsorption and only the vibrational and rotational contributions of adsorbed molecules have to be considered, Eq. (4a–d):

$$q_{H_2}^s = q_{H_2, vib}^s q_{H_2, rot}^s \quad (4a)$$

$$q_{D_2}^s = q_{D_2, vib}^s q_{D_2, rot}^s \quad (4b)$$

$$q_{H_2}^g = q_{H_2, vib}^g q_{H_2, rot}^g q_{H_2, trans}^g \quad (4c)$$

$$q_{D_2}^g = q_{D_2, vib}^g q_{D_2, rot}^g q_{D_2, trans}^g \quad (4d)$$

The exponential factor in Eq. (3a,b) is the potential energy of a system corrected with zero point energy of a system:

$$D_{H_2}^0 = E_{H_2}^{Pot} + \Delta ZPE_{H_2} \quad (5a)$$

$$D_{D_2}^0 = E_{D_2}^{Pot} + \Delta ZPE_{D_2} \quad (5b)$$

where $\Delta ZPE_{H_2, D_2} = ZPE_{H_2, D_2}^s - ZPE_{H_2, D_2}^g$ is the change in zero point energy of the adsorbed molecule, ZPE_{H_2, D_2}^s is the zero point energy of the molecule in the bulk phase (which does not include the modes that correspond to rotations) and ZPE_{H_2, D_2}^g is the zero point energy of the molecule in the gas phase.

The individual partition functions of Eq. (4a–d) are evaluated:

Vibration:

$$q_{vib} = \sum_i^{N_{vib}} \frac{1}{1 - e^{-\frac{\epsilon_i^{vib}}{T}}}, \quad \text{where} \quad \theta_i^{vib} = \sum_i^{N_{vib}} \frac{hc\omega_i}{K_B} \quad (6)$$

Translation:

$$q_{trans} = \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \frac{N k_B T}{P} \quad (7)$$

Rotation in the gas and solid phase is written as:

$$q_{rot} = \sum_{\text{even}}^{\infty} g_o(2J+1) e^{-\theta_{rot} \frac{(J+1)}{T}} + \sum_{\text{odd}}^{\infty} g_p(2J+1) e^{-\theta_{rot} \frac{(J+1)}{T}} \quad (8)$$

where J is rotational quantum number, θ_{rot} is rotational temperature.

To describe the system accurately, the ortho-, para-hydrogen has to be considered. In case of a fermion nucleus of H_2 we obtain half-integer-spin:

$g_o = (S+1)(2S+1)$, for the symmetric nuclear spin functions (S) coupled with odd J .

$g_p = S(2S+1)$, for the antisymmetric nuclear spin functions (S) coupled with even J .

In case of a boson nucleus of D_2 we obtain integer-spin:

$g_o = S(2S+1)$, for the antisymmetric nuclear spin functions (S) coupled with odd J .

$g_p = (S+1)(2S+1)$, for the symmetric nuclear spin functions (S) coupled with even J .

Summation is done over the first 1000 rotational levels.

Based on quantum mechanical calculations and formulas listed above, the thermodynamic properties and selectivities of adsorbed D_2/H_2 have been calculated at 50 and 77 K and the results are reported in Table 2.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.micromeso.2015.03.017>.

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