Raman spectra of hydrogen and deuterium adsorbed on a metal–organic framework

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Abstract

The Raman spectra of H_2 and D_2 adsorbed on metal–organic framework-5 at various pressures (H_2: 12.8 and 30.3 bar; D_2: 2.2–24.5 bar) and temperatures (H_2: 298 K; D_2: 40–300 K) have been recorded. The shifts observed in the vibrational modes of the gases indicate that physisorption is responsible for the attractive interactions between the gas and the framework; these interactions are larger with respect to those detected for carbon materials.
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The lack of a suitable and cost effective means of storing hydrogen [1–4] is one of the main unsolved challenges that prevents its use as a fuel on a global scale. Although several approaches for storing hydrogen are being pursued, the development of sorbent materials capable of reversible uptake and release offers key advantages if suitable gravimetric and volumetric uptake can be achieved [5]. A promising new class of materials in this regard are metal–organic frameworks (MOFs) [6–11]. This class of extended solids possesses extremely high surface areas with tunable pore sizes. In fact, very encouraging results have been obtained using these materials as reversible hydrogen sorbents. For example, MOF-5 (more recently termed IRMOF-1 [7]), produced by linking 1,4-benzenedicarboxylate with zinc oxide clusters (Fig. 1), and several other MOFs have displayed large gravimetric uptake [8,9].

Understanding the intermolecular interactions responsible for gas sorption (e.g., hydrogen) in solids (e.g., MOFs, carbon based materials, etc.) is fundamentally important to the development of new materials with improved gas sorption properties and geometries. The perturbation of the intramolecular potential resulting from intermolecular interaction with an adsorbing surface suggests that vibrational spectroscopy in general, and especially Raman spectroscopy, may turn out to be a useful technique to investigate the physical phenomena that take place because of these interactions [12–16]. Here, we present Raman spectra of H_2 and D_2 adsorbed in MOF-5 [17].

Let us consider a pure diatomic gas: the intermolecular interactions (attractive and repulsive) with other gas molecules perturb the intramolecular potential [12,14–16], thus affecting the stretching frequency of the molecule. If attractive forces prevail, lines will be down

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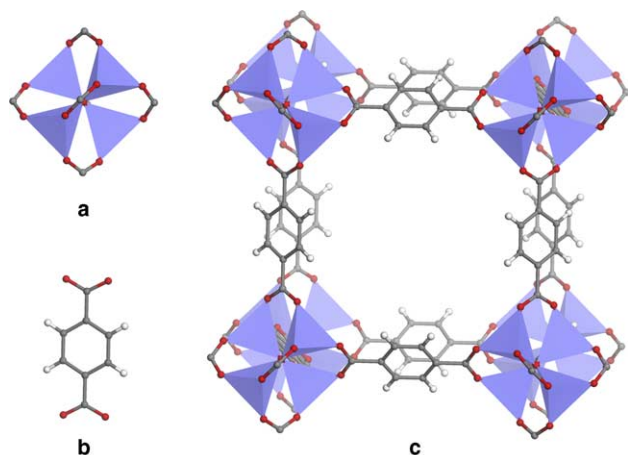
Fig. 1. MOF-5 construction: (a) zinc oxide cluster, (b) 1,4-benzenedi-carboxylate, (c) one of the framework cavities.
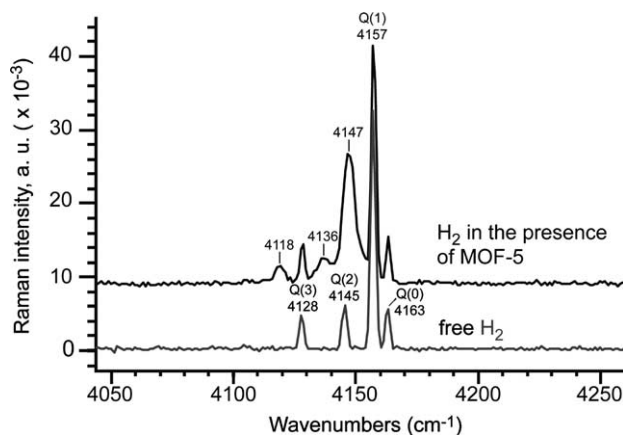

Fig. 2. Raman spectra of hydrogen as a free gas and in the presence of MOF-5 at room temperature and 30.3 bar (baseline correction was applied to remove the fluorescence background).

shifted (with respect to an isolated molecule); if repulsive forces dominate, they will cause an up-shift of the lines [12,14–16].

The case of a gas adsorbed on a material becomes more complex, and we should consider at least three kinds of intermolecular perturbations due to interactions between: (i) adsorbed and gaseous molecules, (ii) adsorbed molecules and the material, (iii) molecules in the adsorbed layer. If we express the perturbing intermolecular potentials in the form of Lennard–Jones [12] we obtain that the line shift will be determined by the action of the various terms of the intermolecular potentials:

$$\Delta v_{\text{H–H}} = \frac{K^{\text{REP}}_{\text{H}_2(\text{ads})-\text{H}_2(\text{gas})}}{r^{12}_{\text{H}_2(\text{ads})-\text{H}_2(\text{gas})}} - \frac{K^{\text{ATT}}_{\text{H}_2(\text{ads})-\text{H}_2(\text{gas})}}{r^{6}_{\text{H}_2(\text{ads})-\text{H}_2(\text{gas})}}$$
$$+ \frac{K^{\text{REP}}_{\text{H}_2(\text{ads})-(\text{material})}}{r^{12}_{\text{H}_2(\text{ads})-(\text{material})}} - \frac{K^{\text{ATT}}_{\text{H}_2(\text{ads})-(\text{material})}}{r^{6}_{\text{H}_2(\text{ads})-(\text{material})}}$$
$$+ \frac{K^{\text{REP}}_{\text{H}_2(\text{ads})-\text{H}_2(\text{ads})}}{r^{12}_{\text{H}_2(\text{ads})-\text{H}_2(\text{ads})}} - \frac{K^{\text{ATT}}_{\text{H}_2(\text{ads})-\text{H}_2(\text{ads})}}{r^{6}_{\text{H}_2(\text{ads})-\text{H}_2(\text{ads})}}. \quad (1)$$

For the study of adsorption of hydrogen in MOF-5, crystals were prepared as described earlier [7], evacuated for 18 h in a Raman cell, and exposed to an atmosphere of H_2 (30.3 bar). Room temperature Raman spectra were collected with a Renishaw inVia Raman Microscope in extended scan mode between 3900 and $4400 \, \text{cm}^{-1}$. A 25 mW 514.5 nm argon-ion laser with a 1800 lines/mm grating was employed along with an SLMPlan 20× objective from Olympus. Calibration of the system was accomplished with a silicon standard. Because of the high fluorescence exhibited by MOF-5 in the region of H_2 stretching, the samples were bleached for 14 h prior to collection.

Fig. 2 shows the Q-branch of free hydrogen as well as the spectrum of H_2 adsorbed on MOF-5. For free

hydrogen, the peak at $4163 \, \text{cm}^{-1}$ can be assigned to the $Q(0)$ transition whereas those at 4157, 4145 and $4128 \, \text{cm}^{-1}$ belong to $Q(1)$, $Q(2)$, and $Q(3)$, respectively [18]. Upon adsorption in MOF-5, the $Q(1)$ frequency shifts $10 \, \text{cm}^{-1}$ to $4147 \, \text{cm}^{-1}$, a peak which overlaps with free $Q(2)$ and sorbed $Q(0)$. It is also evident that the $Q(2)$ and $Q(3)$ frequencies shift by $10 \, \text{cm}^{-1}$, pointing to a systematic shift to lower energy of all the vibrational frequencies of gaseous hydrogen upon adsorption. In addition, the shifted lines are slightly broadened.

Conducting the experiments at lower pressure (12.8 bar) reveals the same $10 \, \text{cm}^{-1}$ shifts in these lines (not shown). Moreover, the intensities of the lines of both free and adsorbed molecules do increase with increasing pressure, thus suggesting that saturation of adsorption has not yet been achieved.

It is important to note that although the framework integrity of MOF-5 has been unambiguously demonstrated after evacuation [6], no such data is available at very high pressures. However, inspection of Raman spectra of the framework before gas exposure and after depressurisation reveals the absence of shifts or of new peaks, indicating a reversible process.

To gain further insight into the nature of gas sorption in MOF-5, variable temperature studies were conducted. The Raman spectra, at low temperatures, were recorded in a back scattering geometry using a custom made Raman cell (placed on a cold finger of a cryostat) that can operate from room temperature to very low temperatures (40 K) and both in high vacuum or at high pressure (up to 100 bars). The adsorbing material was evacuated in dynamic high vacuum (10^{-6} mbar) overnight before introducing the gas into the cell. The description of the experimental apparatus is given elsewhere [12].

Although MOF-5 shows a strong fluorescence with green and blue exciting lines, acceptable spectra could

be recorded with a red exciting line (632.817 nm). We did not succeed to quench the residual fluorescence of the amount of material used in our experiments (macro Raman). With the exciting line used, the spectrometer can record a maximum Raman shift of about 3300 cm^{-1} thus denying the possibility of recording the roto-vibrational Q-branch of H$_2$ (at ∼4160 cm^{-1}). Therefore, D$_2$ (Q-branch ∼3000 cm^{-1} of Raman shift) was employed as the adsorbing gas.

Raman spectra of D$_2$ (99.999%) adsorbed on MOF-5 were recorded with a Dilor XY double monochromator in double subtractive configuration that, with an exciting line of 632.817 nm (He–Ne), can achieve a resolution of 0.6 cm^{-1} in the frequency range near 3000 cm^{-1} of Raman shift. For calibration, Ne emission lines in the proximity of the deuterium Q-branch were employed [19].

It is important to underline that the properties of H$_2$ and D$_2$ are different, every gas has its own critical temperature ($T^{critical}$(H$_2$) = 32.8 K and $T^{critical}$(D$_2$) = 38.2 K) and its nuclear statistics. It is known that the different nuclear statistics affect the Raman spectra because they determine the degeneracy of the rotational levels; this problem will not be treated here [20,21].

The spectra of D$_2$ adsorbed on MOF-5 at 40 K as a function of pressure (Fig. 3) show two distinct sets of lines: the Q-branch near 2990 cm^{-1} (also found in the case of the pure gas alone) and other broad lines down shifted near 2980 cm^{-1}. It is interesting to note that, the intensity of the Q-branch increases as the pressure increases (Fig. 3) while the integrated area of the down shifted lines is almost constant.

Obviously the Q-branch is ascribed to free D$_2$ and it becomes logical to assign the down-shifted lines to adsorbed gas. Because the temperature is very near the critical temperature of deuterium the additional weak feature near 2985 cm^{-1} could originate from D$_2$ in the liquid phase.
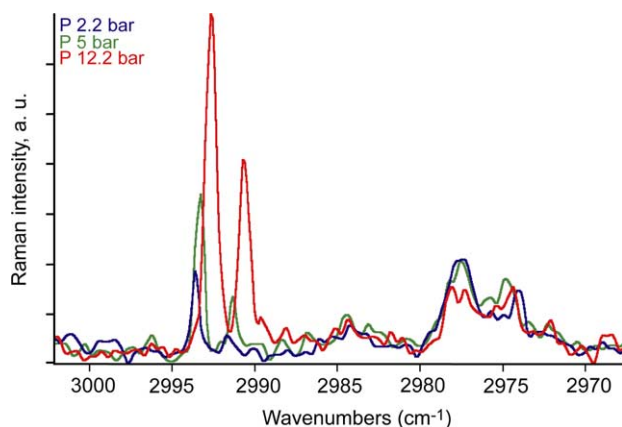

Fig. 3. Raman spectra of adsorbed deuterium on MOF-5 at 40 ± 2 K at pressures from 2.2 to 12.2 bar (baseline correction has been applied to remove the fluorescence background).
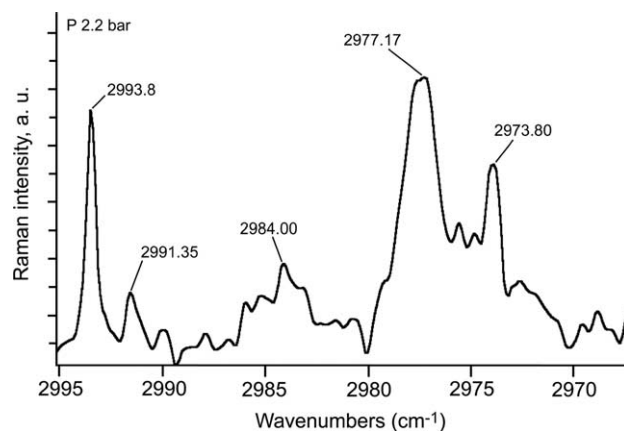

Fig. 4. Raman spectra of adsorbed deuterium on MOF-5 at 40 ± 2 K at a pressure of 2.2 bar (baseline correction was applied to remove the fluorescence background).

The saturation of adsorption is exactly what is expected for microporous materials characterised with a type I isotherm like MOF-5 [9]. In Fig. 4 the Raman spectrum of adsorbed D$_2$ on MOF-5 at 2.2 bar and 40 K is reported in detail. In spite of the noisy background, two structured and broad features appear; and at least three main peaks (at 2984.00; 2977.17; and 2973.80 cm^{-1}) stick out. The broad feature at the lower frequency is even more down-shifted with respect to the frequency of the pure liquid deuterium (see Table 1) and consequently must be generated by the interaction with the adsorbing material.

The lines due to the adsorbed gas are structured, very likely because the gas is adsorbed at different sites inside the cage with different binding energies, an observation that is in agreement with inelastic neutron scattering data collected at low temperature for H$_2$ adsorbed on MOF-5 [8]. In particular the down-shifting of the lines is non-negligible, and actually much larger than that observed for H$_2$ and D$_2$ adsorbed on carbon based materials [12,13]. This indicates the existence of a much more favourable (i.e., attracting) intermolecular potential of MOF-5 if compared with carbon based materials (even if the dispersion of frequencies in the same physical conditions is expected for D$_2$ to be smaller than that of H$_2$ [16] which has a larger zero point frequency).

The spectra of D$_2$ adsorbed on MOF-5 at 77 K (Fig. 5), show a broad down-shifted line approximately in the same frequency region of the spectra at 40 K; at this temperature also the Q(2) lines (of the free gas) appear

Table 1
Q(0), Q(1) Raman frequency of pure deuterium in the gaseous [18], liquid [22] and solid state [18]

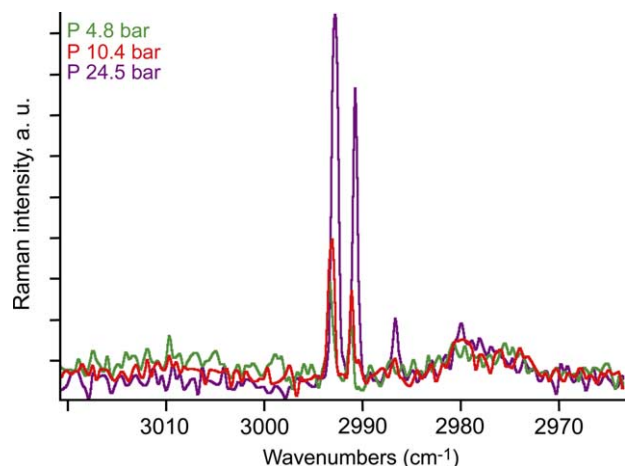|	Gas	Liquid	Solid
Q(0)	2993.548	2987.99	2985.46
Q(1)	2991.446	2984.58	2982.48

Fig. 5. Raman spectra of adsorbed deuterium on MOF-5 at 77 ± 2 K at pressures from 4.8 to 24.5 bar (baseline correction was applied to remove the fluorescence background).

due to the increase population of the $J = 2$ rotational level.

Again the intensity of the Q-branch increases with pressure, while the integrated area of the adsorbed gas is almost constant, thus indicating that the saturation of adsorption sites available for specific interactions is already reached at 5 atm (77 K).

At 160 K the spectra of free D_2 also show the $Q(3)$ line, the dispersion of frequency with pressure is reduced and starts to become negligible in the pressure range analysed; at this temperature not much information can be deduced from the spectra of D_2 adsorbed on MOF-5 (not shown); the broad lines, if any, are strongly disturbed by noise. Analogous reasoning can be applied to the spectra at 300 K (not shown).

In conclusion, we have recorded the Raman spectra of adsorbed H_2 and D_2 at different temperatures and as a function of pressure. We observed lines down-shifted substantially with respect to the lines of the free gas; necessarily the down-shifted lines must originate from the adsorbed gas. The lines of the adsorbed gas are broadened and structured probably because of different adsorption sites. The down-shifted lines suggest that the attracting potential is certainly stronger than for carbon based materials. With this Letter, we show that the Raman spectrum turns out to be a useful physical probe for understanding the interactions inside the pores. The down-shifted lines are evidence of the existence of different interactions sites inside the materials with different chemical groups, which are able to polarise and attract the guest molecule. Therefore, one promising approach in the effort of increasing the stor-

age capacity of the adsorbing material should focus on sorbents able to strongly polarise hydrogen.

References

[1] M. Hirscher, M. Becher, M. Haluska, F. von Zeppelin, X.H. Chen, U. Dettlaff-Weglikowska, S. Roth, J. Alloy. Compd. 356 (2003) 433.
[2] A. Züttel, Mater. Today 6 (2003) 24.
[3] F. Schüth, W. Schmidt, Adv. Mater. 14 (2002) 629.
[4] M. Hirscher, M. Becher, J. Nanosci. Nanotechnol. 3 (2003) 3.
[5] FreedomCAR Initiative, See Solicitation Number DE-PS36-03GO93013. US Department of Energy, 2003.
[6] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Nature 402 (1999) 276.
[7] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keefe, O.M. Yaghi, Science 295 (2002) 469.
[8] N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi, Science 300 (2003) 1127.
[9] J.L.C. Rowsell, A.R. Millward, K.S. Park, O.M. Yaghi, J. Am. Chem. Soc. 126 (2004) 5666.
[10] L. Pan, M.B. Sander, X.Y. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath, J.K. Johnson, J. Am. Chem. Soc. 126 (2004) 1308.
[11] H.K. Chae, D.Y. Siberio-Perez, J. Kim, Y. Go, M. Eddaoudi, A.J. Matzger, M. O'Keeffe, O.M. Yaghi, Nature 427 (2004) 523.
[12] A. Centrone, L. Brambilla, G. Zerbi, Phys. Rev. B 71 (2005) 245406.
[13] K.A. Williams, B.K. Pradhan, P.C. Eklund, M.K. Kostov, M.W. Cole, Phys. Rev. Lett. 88 (2002).
[14] A.D. May, G. Varghese, H.L. Welsh, J.C. Stryland, Can. J. Phys. 42 (1964) 1058.
[15] P. Lalleman, P. Simova, J. Mol. Spectrosc. 26 (1968) 262.
[16] E.C. Looi, J.C. Stryland, H.L. Welsh, Can. J. Phys. 56 (1978) 1102.
[17] The vibrational modes of MOF-5 have recently been investigated by Raman spectroscopy: S. Bordiga, C. Lamberti, G. Ricchiardi, L. Regli, F. Bonino, A. Damin, K.P. Lillerud, M. Bjorgen, A. Zecchina, Chem. Commun. (2004) 2300.
[18] B.P. Stoicheff, Can. J. Phys. 35 (1957) 730.
[19] D.R. Lide (Ed.), Handbook of Chemistry and Physics, CRC Press, Boston, 1990.
[20] G.H. Herzberg, Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules, Van Nostrand Company, New York, 1950.
[21] A. Centrone, R. Scotti, Morazzoni, G. Zerbi (in preparation).
[22] S.S. Bhatnagar, H.L. Welsh, E.J. Allin, Can. J. Phys. 40 (1962) 9.