

Raman Spectroscopic Investigation of CH₄ and N₂ Adsorption in Metal–Organic Frameworks

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The adsorption behavior of CH₄ and N₂ (298 K, 30 bar) in a series of isorecticular metal–organic frameworks (IRMOFs) was investigated by Raman spectroscopy. For CH₄, the ν_1 vibrational mode shifted to lower frequency by 7.6, 8.4, 11.0, 10.3, and 10.1 cm⁻¹ from 2917 cm⁻¹ when adsorbed to IRMOF-1, -6, -8, -11, and -18, respectively. Along this same series, the adsorbed N₂ stretch exhibited smaller shifts of 2.7, 3.1, 4.2, 4.1, and 3.7 cm⁻¹. These shifts arise because of interactions within the framework pores, and not with the outer crystal surface. In all cases, Raman spectra at pressures up to 30 bar showed that saturation of the sorption sites does not occur. The observed shifts of the vibrational modes for each gas indicate different chemical environments within different IRMOFs, pointing to the important role the linkers play in the adsorption of gases.

1. Introduction

Metal–organic frameworks (MOFs) are extended crystal-line porous structures with extraordinary surface areas that enable unprecedented adsorption phenomena.^{1–3} A MOF consists of a metal ion or metal cluster linked together by organic units to give a well-defined periodic structure.^{4,5} By systematically varying the organic linker, we can synthesize a series of MOFs with controlled chemical and physical properties without altering the underlying topology. Such a series has been created on the basis of the cubic topology of MOF-5, wherein a Zn₄O cluster is used in conjunction with the linear organic linker benzene-1,4-dicarboxylate,¹ giving rise to isorecticular metal–organic frameworks (IRMOFs). As the parent structure, MOF-5 is designated as IRMOF-1.²

The high surface areas and tunable porosities exhibited by IRMOFs make them attractive for adsorption processes. The application of IRMOFs as media for gas storage has become especially appealing because of the possibility of these serving as hosts to alternative fuels such as CH₄ or H₂. The difference in adsorption affinities of IRMOFs for these and other gases has been reported.^{2,6} Given the emerging applications of IRMOFs as gas storage materials,

it is important to develop an understanding of the adsorbate/adsorbent behavior in the pores, an area that remains largely unexplored in MOFs. Within each framework, there are two distinct sites where the gas molecules may adsorb: the metal cluster and the organic linker. A series of low temperature and pressure inelastic neutron scattering (INS)^{7,8} and X-ray diffraction⁹ experiments have implicated the metal cluster as primary binding sites. Computational studies^{10,11} have corroborated these observations and led to the prevailing belief that adsorption to the linkers is a minor contributor to gas uptake. Here, we investigate this hypothesis with Raman spectroscopy at room temperature and elevated pressure to determine if this behavior holds under conditions more relevant to storage applications. This analysis method is a powerful technique for probing the adsorbate/adsorbent interactions offering facile detection of perturbations to the vibrational modes of the gaseous guest created by interactions with the framework.¹² In the present paper, we investigate the Raman spectra of CH₄ and N₂ adsorbed in samples of IRMOF-1, -6, -8, -11, and -18 (Figure 1). This series, which is built from a common metal cluster motif, offers a range

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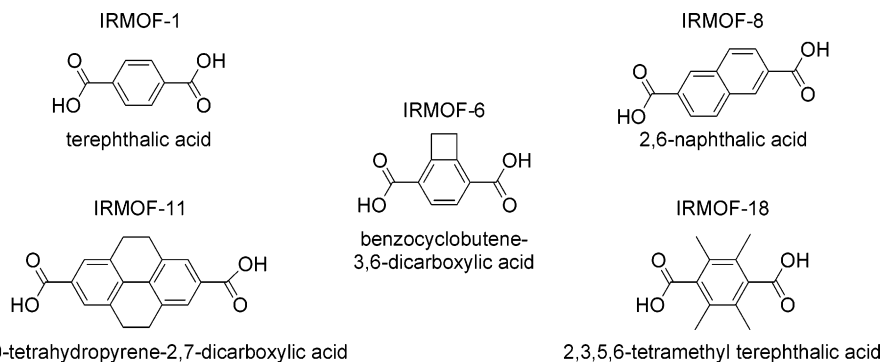


Figure 1. Dicarboxylic acid forms of the linkers used for the synthesis of IRMOF-1, -6, -8, -11, and -18.

of pore sizes, surface areas, and chemical environments across which to compare the binding of gases to determine if the linker contributes substantially to gas sorption behavior. IRMOF-1, -6, and -18 are similar in the dimensions of the pores, but differ in the nature of functional groups adorning the interior: hydrogen atoms on the benzene ring in IRMOF-1, methyl groups for IRMOF-18, and a cyclobutenyl group for IRMOF-6. The influence of expanded pore size is investigated with the remaining two IRMOFs, which relate to IRMOF-1 by substitution of the benzene ring with naphthalene (IRMOF-8) or 4,5,9,10-tetrahydropyrene (IRMOF-11).

2. Experimental Section

IRMOF-1, -6, -8, -11, and -18 were synthesized as detailed earlier.^{2,6} Microcrystalline samples were placed in a high-pressure Raman cell (HPRC) containing a chamber capable of simultaneously holding multiple samples. The HPRC was evacuated to $<1 \times 10^{-6}$ bar prior to charging with a fixed pressure (typically 30 bar) of the gas to be investigated and the internal pressure was monitored during the experiment with a liquid-filled gauge. Raman spectra were collected at room temperature through a glass window located above the chamber platform.

A Renishaw inVia Raman microscopy system equipped with a 785 nm diode laser and a 1200 lines/mm grating was used for spectrum collection through an Olympus SLMPlan 20 \times objective (0.35 numerical aperture). The slit width of the collection aperture was kept at 50 μ m. All spectra were obtained in extended scan mode in the range of 3200–100 cm^{-1} for analysis of framework bands, 3050–2750 cm^{-1} for analysis of the ν_1 band of CH_4 , and 2500–2200 cm^{-1} for monitoring the N_2 stretch. Calibration of the laser was performed in static scan mode using a silicon standard.

For assignment of peak positions, spectra were obtained for four samples of each IRMOF, all under the same conditions, and analyzed with the Peak Fitting feature in ACD/SpecManager version 8.11 (ACD/Labs). The peak shape was determined by a Gaussian–Lorentzian function, with width limits in the range 10–20 cm^{-1} , depending on peak broadness. Each spectrum exhibited two peaks, one belonging to the free gas (ν_{free}) and the second arising because of adsorbed gas (ν_{adsorbed}) (Figure 2). The difference in frequency between these two peaks, given by $\Delta\nu = \nu_{\text{free}} - \nu_{\text{adsorbed}}$, was calculated and an average shift was determined for each IRMOF. This shift in frequency was found to be independent of laser power (see the Supporting Information). CH_4 (99.999%, Matheson Trigas) and N_2 (99.999%, Cryogenic Gases) were used without additional purification.

Adsorption isotherms were measured via the static volumetric method in an HPA-100 (high-pressure analyzer) from the VTI

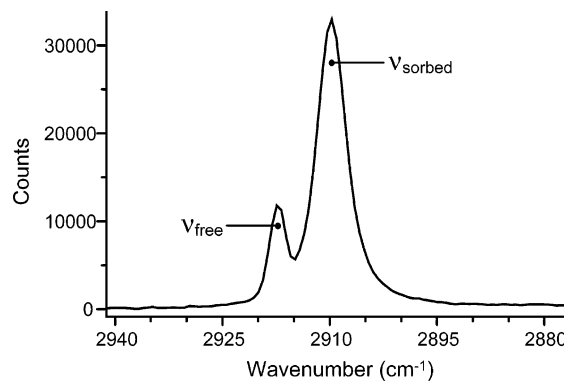


Figure 2. Raman spectrum of CH_4 (298 K, 30 bar) adsorbed in IRMOF-1.

Corporation (www.vticorp.com) at 298 K and pressures up to 90 bar. The dosing manifold was isolated from the sample cell and maintained at 318 K, whereas the sample cell temperature was maintained at 298 K via a recirculating bath. Prior to sorption measurements, IRMOF-1 was activated as previously described,⁶ charged into the sample cell, and then evacuated to $<1 \times 10^{-9}$ bar. The void volume of the cell was determined by expansion of a known amount of He gas from the dosing manifold into the sample cell. Accurate gas-phase compressibility factors (Z_{He} , Z_{N_2}) are required to calculate the correct number of moles of gas since $Z(p, T)$ is a function of temperature and pressure. Incorporated into the HPA software are the equations of state from the NIST reference fluid thermodynamic and transport properties (REFPROP version 7.0), which allow the determination of the compression factors of the gas both in the dosing manifold and in the sample cell. A N_2 isotherm was then constructed from adsorption data collected from 0 to 90 bar and from desorption data from 80 to 4 bar.

3. Results and Discussion

Globally, IRMOFs have two very chemically different sites: namely, the zinc oxide unit and the organic linker. For IRMOF-1, inelastic neutron scattering (INS) at 10 K has shown that H_2 adsorbs to both sites, with the zinc cluster site being preferred at lower partial pressures.⁷ Similar behavior was demonstrated for both IRMOF-8 and -11.⁸ Single-crystal X-ray diffraction studies performed at 30 K for N_2 and Ar in IRMOF-1 have also proven that adsorption takes place at both sites.⁹ However, for CH_4 , the preferred sorption sites have not been determined. Raman spectroscopy provides a viable way to investigate adsorption interactions by analyzing the vibrational modes of both the gas and the adsorbent. Furthermore, if connections between spectroscopic

features and gas sorption strength or capacity can be drawn, Raman spectroscopy has the potential for being an effective analytical method for nondestructively screening new MOFs on the microscale.

CH₄ has four fundamental vibrational modes in the gaseous state, two of which are Raman active: (1) the C–H symmetrical stretching mode ν_1 at 2917 cm⁻¹, and (2) the out-of-plane degenerate deformation ν_2 at 1526 cm⁻¹. The N₂ stretch can be found at 2330 cm⁻¹. Upon adsorption, the intermolecular interactions between adsorbent and gas alter the intramolecular potential of the gas molecules, causing displacements of the vibrational modes.^{13,14} These shifts may occur either to higher frequency (upshift: negative $\Delta\nu$) or to lower frequency (downshift: positive $\Delta\nu$). A positive $\Delta\nu$ is indicative of bond strength weakening within the gas molecule.^{15,16} A number of studies have established that CH₄ and CO₂ adsorption in NaA, CaA, and NaX zeolites,^{13,17} CH₄ in ion-exchanged ZSM zeolites,¹⁸ and *p*-xylene in ZSM-5¹⁶ all produce positive $\Delta\nu$'s.

The adsorption behavior of CH₄ and N₂ in IRMOFs was investigated by monitoring the vibrational modes of the gases. When CH₄ is in the pores of IRMOF-1, the high intensity ν_1 vibrational mode is perturbed to lower frequency by 7.6 cm⁻¹ (Figure 2). Comparison of the two bands reveals that the adsorbed gas peak is broader than the free gas peak, suggestive of multiple sorption sites participating in gas binding.^{19,20} Adsorption of N₂ in IRMOF-1 revealed smaller shifts in the stretching frequency of the gas ($\Delta\nu = 2.7$ cm⁻¹) than were observed for CH₄. Previous work with zeolites has also revealed smaller shift magnitudes for N₂.¹³

The possibility that the observed shift is due to interactions between the gas and the IRMOF-1 crystal surface, as has been implicated in IR spectroscopic studies of H₂ adsorbed in this MOF,²¹ was ruled out by exposing samples of the dicarboxylic acid form of the linker, as well as crystals of a chemically similar but nonporous zinc compound (Zn₄O[O₂-CC₆H₅]₆)²² to 30 bar of CH₄ gas. Raman spectroscopy of these samples in the range 3000–2800 cm⁻¹ is marked by the singular presence of the free gas. This suggests that the

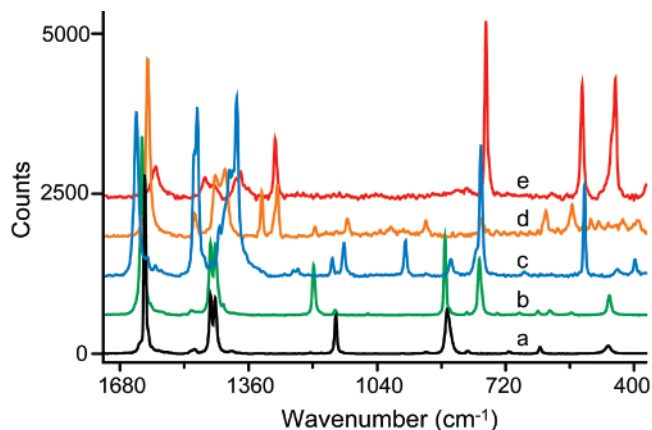


Figure 3. Room-temperature Raman spectra of (a) IRMOF-1, (b) IRMOF-6, (c) IRMOF-8, (d) IRMOF-11, and (e) IRMOF-18.

bands observed for adsorbed CH₄ in IRMOF-1 are the result of the interaction between the gas and the inside walls of the frameworks and not with the outer surface of the IRMOF.²³

The characteristic Raman frequencies of IRMOF-1 were also monitored throughout the addition and removal of gas, to ensure framework integrity as well as to determine the nature of the adsorption process. Addition of the gas did not affect the framework peaks significantly, an indication that physisorption dominates rather than chemisorption. Previous powder X-ray diffraction studies and multiple cycles of adsorption and desorption have unequivocally proven that at low pressures, inclusion and evacuation of guests does not alter the IRMOF scaffolds.⁶ At high pressures, integrity of the framework has been verified for H₂ in IRMOF-1,^{14,24} but little data exist for the more strongly adsorbing N₂, or CH₄. A reversible adsorption process was confirmed by inspection of the framework Raman spectra (Figure 3), before and after gas exposure, which revealed the absence of both significant shifts and of new peaks.

Raman spectra collected at various pressures for both CH₄ and N₂ showed that the intensities of the free and adsorbed bands increased with pressure, indicating that saturation of the adsorption sites does not occur below a pressure of 30 bar. This observation was confirmed by high-pressure N₂ sorption experiments carried out at 298 K. A typical N₂ isotherm is shown in Figure 4 for IRMOF-1. The adsorption branch clearly shows that saturation uptake of N₂, which would manifest itself as a plateau in the isotherm, is not achieved even at pressures of 90 bar. The Raman spectra collected at various pressures also demonstrated that the difference in frequency between free and adsorbed gas remains fairly constant as a function of pressure (see the Supporting Information).

For IRMOF-8, the ν_1 vibrational band of CH₄ is displaced by 11.0 cm⁻¹ in the same direction as in IRMOF-1, followed

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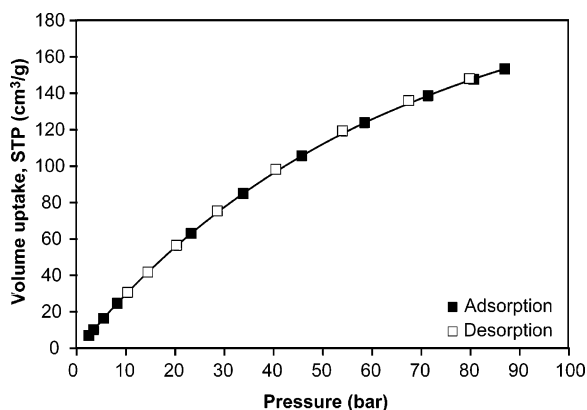


Figure 4. High-pressure gas adsorption isotherm for N₂ in IRMOF-1, measured at 298 K. Filled symbols, adsorption; open symbols, desorption.

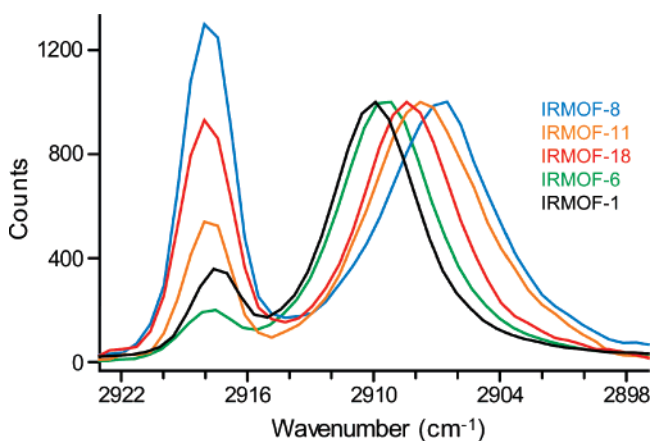


Figure 5. Normalized room-temperature Raman spectra of CH₄ (30 bar) adsorbed in IRMOF-1, -6, -8, -11, and -18.

Table 1. Raman Frequencies of the Vibrational Transitions of N₂ and CH₄ Adsorbed on IRMOF-1, -6, -8, -11, and -18 at 30 bar ($\Delta\nu = \nu_{\text{free}} - \nu_{\text{adsorbed}}$); Peak Positions are Accurate to within 0.1 cm⁻¹

sample/sorbent	CH ₄		N ₂	
	ν_1 (cm ⁻¹)	$\Delta\nu_1$ (cm ⁻¹)	ν (cm ⁻¹)	$\Delta\nu$ (cm ⁻¹)
IRMOF-1	2909.9	7.6	2327.0	2.7
IRMOF-6	2909.2	8.4	2326.7	3.1
IRMOF-8	2906.9	11.0	2325.8	4.2
IRMOF-11	2907.5	10.3	2326.0	4.1
IRMOF-18	2907.8	10.1	2326.4	3.7

by IRMOF-11, -18, and -6, with shifts of 10.3, 10.1, and 8.4 cm⁻¹ respectively (Table 1, Figure 5). For each of these compounds, saturation of adsorption sites was not observed below 30 bar, and integrity of the framework was confirmed during adsorption and desorption processes. Inasmuch as the magnitude of frequency shifts are correlated to the energy of interaction,^{17,18} it can be concluded that CH₄ molecules are able to more strongly bind to IRMOF-8 than for all other samples. This also implies that the CH₄-IRMOF-1 interaction is the weakest of all, with IRMOF-11, -18, and -6 having intermediate binding strengths, in descending order. The frequency shift, however, does not imply that the CH₄ capacity in the IRMOFs will follow this same trend because binding strength is not related to ultimate capacity.²⁴

Recent data suggest that IRMOF-8 may exhibit interpenetration,²⁵ whereas it is known that IRMOF-11 is doubly interpenetrated.² Interpenetration has long been perceived as a hindrance to transport and adsorption of molecules within porous media. However, it is now recognized that interpenetration can be beneficial by providing a higher density of adsorption sites with enhanced affinity, conditions that are ideal for adsorption of small molecules.²⁶ The Raman spectroscopy data presented here support this notion, as evidenced by the higher shifts experienced by CH₄ molecules when adsorbed in both IRMOF-8 and IRMOF-11. In turn, because IRMOF-8 has shorter linkers, and therefore smaller pores, a molecule adsorbing to interpenetrated IRMOF-8 will be more confined than if adsorbing to IRMOF-11. It should then be expected that the looser association experienced by this same molecule in IRMOF-11 will result in less interaction with the framework and smaller shifts to the vibrational modes of the gas. Experimentally, this is borne out.

It has been determined for H₂, D₂, N₂, and Ar that both the metal oxide unit and the organic linker can serve as adsorption sites for gas molecules. Although this has not been determined for CH₄, the same type of adsorption behavior might well be expected. In the limiting case of dominant adsorption to the zinc oxide unit, the CH₄ would experience the same $\Delta\nu_1$ shift independent of the IRMOF being studied. At room temperature and high pressure, conditions that are relevant to storage systems, adsorption is clearly not dominated by the metal cluster.²⁷ The disparate shifts observed for a series of IRMOFs, built with the same metal cluster but with chemically different linkers, leads to the conclusion that the CH₄ is in dramatically different chemical environments; similar behavior has been observed in a series of ZSM-5 zeolites, where the presence of different counterions allowed for the adsorbed gas to be perturbed uniquely, indicating adsorption of the gas in the vicinity of the cation.¹⁸ Thus, in the IRMOF series, the linkers are important sites of adsorption.

Adsorption of N₂ in these same IRMOFs reveals that the perturbations to the N₂ stretch are much smaller (Table 1). However, as observed for CH₄, IRMOF-8 is still able to more strongly perturb the vibrations of N₂, as evidenced by the greater $\Delta\nu$ (4.2 cm⁻¹), followed in magnitude by IRMOF-11, -18, -6, and finally IRMOF-1.

4. Conclusions

The perturbations in the vibrational modes of CH₄ and N₂ adsorbed in a series of IRMOFs have been investigated by Raman spectroscopy. The shifts in these frequencies yield information on the type and the strength of the adsorption interaction. Shifts for CH₄ ranged between 7 and 11 cm⁻¹, with IRMOF-8 inducing the greatest shift. A larger shift

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indicates that the interaction between CH₄ and IRMOF-8 is greater than for the other IRMOFs. For N₂, the shifts were smaller, in the range of 3–4 cm⁻¹, but, as observed for CH₄, IRMOF-8 induced the greatest frequency shift, followed by IRMOF-11, -18, -6, and IRMOF-1. The shifts in vibrational modes for both gases are a clear indication of the gas molecules adsorbing to the IRMOF linkers inside the framework cavities under conditions of temperature and pressure that are most relevant to a storage system. These results point to the critical role that the linkers play in the adsorption behavior of gases in MOFs, thus revealing that

selection of the appropriate linker with the highest affinity for gases will provide an optimal storage material.

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Supporting Information Available: Lists of Raman frequencies for the IRMOFs, and Raman spectra of CH₄ in the presence of IRMOF-1 as a function of pressure and laser power (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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