The adsorption of molecules within the nanopores of a sparse material and their low-lying excitations provide rich phenomena of fundamental interest that are seldom explored by first principles methods, even for molecules as simple as H$_2$. For example, one can ask how the well-known para–ortho transition of H$_2$ survives in a recognizable form in the presence of the rotational barriers and hindrances provided by the adsorbing material, and how it changes for different concentrations of H$_2$. The necessity of proper treatment of van der Waals interactions has foiled traditional density functional treatments. Here, by using the van der Waals density functional (vdW-DF) of Dion et al. [1], we are able to predict a picture of the low-lying excitations which provides a credible match for the results of inelastic neutron diffraction (INS) [2] for different hydrogen loadings in a nanoporous material of a type thought to provide a possible path toward future hydrogen storage technology.

The material studied here is a metal-organic framework (MOF) compound, namely the material that has been called MOF-74 [3], chosen because of recent inelastic neutron scattering measurements [2] with varying amounts of H$_2$ adsorption. More generally MOFs are a relatively new class of materials which are composed of metal clusters connected by organic ligands [4]. The search for a MOF structure with high binding strength to H$_2$ has become very active recently [5, 6]. The dynamical properties of the adsorbed dihydrogen such as vibrational and hindered rotational motion play a significant role in determining the H$_2$ binding energy, especially for caged structures with nanopores. This area is even less explored than the modeling of hydrogen uptake based only on the depth of the potential well. An attempt along this line studied the rotational transition of H$_2$ adsorbed over benzene molecule which is often a fraction of the organic linker in MOF materials [7]. However, the interaction between full MOF and H$_2$ usually differs significantly from that between a fraction of MOF and H$_2$ [8]. A very recent paper studied the rotational transition in another MOF (HKUST-1) with generalized gradient approximation (GGA) calculations [9]. However, GGA is known to fail for cases where the binding is dominated by van der Waals interactions, and only a preliminary theoretical picture was obtained.

Here using vdW-DF [1], implemented via the efficient algorithm of two of us [10], we calculated the dynamical properties as well as the binding energy of H$_2$ adsorbed in MOF-74 structure, which has been demonstrated to increase both the H$_2$ affinity [2] and hydrogen density [2] due to the unsaturated metal sites [2]. The primary binding sites associated with metal atoms are confirmed by our calculations with a binding energy of 130 meV, while the LDA and GGA results are 230 and 46 meV respectively [10]. The center-of-mass translation and molecular rotation of H$_2$ are found to attribute zero point energy (ZPE) of ~20 meV and ~10 meV, respectively, to the total energy of the MOF–H$_2$ system. As a result the effective binding is about 100 meV, which is close to the experimentally measured value of ~90 meV [2, 3].

Furthermore, we find that the adsorbed H$_2$ is a three-dimensional quantum rotor at both the primary and secondary binding sites. The original $J = 1$ triplet state splits into three nondegenerate levels, which imply three distinct para to ortho excitation energies. A good match between the calculated rotational transitions and the inelastic neutron scattering spectra [2] was obtained. As suggested in Ref. [11], MOF materials may be used to create artificial hydrogen nanocages. In addition to the confinement and short intermolecular distance, the temperature dependent preferential adsorbance [12] of ortho-H$_2$ due to the splitting of the triplet could give rise to unexpected properties as well.

To locate the binding site near the Zn atom, we used the experimental MOF structure. With one H$_2$ per primitive cell (1/6 H$_2$ per Zn), we calculated the MOF–H$_2$ interaction energy for various H$_2$ positions near the Zn atom. The contour map of the interaction energy is shown in Fig. 1. The minimum position has a binding energy of 130 meV and its distance to the Zn atom is 2.9 Å while the experimental value is 2.6 Å [2].
over-estimation of the bond length is typical in vdW-DF calculations [13].

Along with the strongest binding site near the metal atom (hereinafter referred to as the Zn site), a secondary site above the oxygen triangle was observed by neutron scattering measurements [2]. We again took the structure of Ref. 2 with a loading of 12 D2/cell. We performed a relaxation of the adsorbed dihydrogens with a fixed MOF host with the force converged to 12 meV/Å. We find that a H2 indeed positions itself above the oxygen triangle when its neighboring metal sites are occupied. In other words, a potential minimum is created at the O-triangle site due to the adsorbance of H2 at the metal site. The closest distance between sorbate and sorbent is 3.4 Å, while the distance between the O and Zn sites is 3.2 Å. These are each 0.3 Å larger than the respective experimental distances [2].

With the two binding sites located, we now turn to the dynamical properties of the adsorbed H2 at these sites, which are important in determining the zero-point energy correction to the total binding strength. In general, H2 has six degrees of freedom. We here focus on the translational and rotational motions where the H2 bond length is fixed at its equilibrium value. Even with fixed bond length, the full quantum mechanical treatment of the remaining five degrees of freedom is still beyond the scope of current letter. We make the approximation that rotation-translation coupling may be neglected to lowest order, so that the two motions can be treated separately. In the absence of intersite dynamical coupling, this would be exact to the extent that the H2 motions were small enough to be described by the harmonic approximation. Neither of these is exact, so that small deviations from the rotational spectra we calculate are to be expected, even though we use methods that do not explicitly assume the harmonic approximation’s validity.

Fig. 1 shows the orientational dependence of the interaction energy at Zn site. The maximum point in this figure corresponds to H2 bond aligned toward the Zn atom, which is the weakest binding orientation, while the preferential bond direction of the adsorbed dihydrogen is in the plane perpendicular to the Zn–H axis. The O site, however, is quite different from the Zn site. The H2 tends to line up toward the oxygen triangle and the preferential orientation is inside a conical region (figure not shown). The maximum variation of the rotational potential at each of the two sites is ~27 meV and ~18 meV, respectively. Due to this variation, the adsorbed hydrogen molecule exhibits hindered rotation behavior at these two sites. As a result, the energy levels of the free H2 rotor (E = BJ(J + 1), B = 7.35 meV) will be lifted and, in particular, three nondegenerate states emerge from what was the J = 1 level with m = 0, ±1, respectively. The transition between the singlet and triplet states is the well-known para-ortho transition. A spin flip is required to satisfy the antisymmetry requirement of the total wave function. To compare with INS data [2], we calculated the rotational spectrum by solving the rigid rotor Schrödinger equation for H2. We first fitted the orientational potential E(θ, φ) to a summation of spherical harmonics and then diagonalized the Schrödinger equation with a spherical harmonics basis. The results are shown in Table I, where three spectra with different loadings are calculated for Zn site and one set for the O site, which is mostly unoccupied at low loading.

In Table I we first observe that the ground state energies (zero point energies) are about 10 meV at both sites, and it increases by about 3 meV at Zn site as the loading is increased. The excited state of J = 1 splits into three nondegenerate states for all four cases considered theoretically, showing the hindered three-dimensional quantum rotor character of the adsorbed dihydrogen at the two sites. For the Zn site with 1 H2/cell loading, the three para-ortho transitions are 10.6, 14 and 21.6 meV, which we assign to the main INS peaks at 8.3, 11.1, and 20.9 meV in Fig. S2 of Ref. 2, whose points we replotted in Fig. 3 for easy comparison. In addition to the three major peaks, two small peaks at 14.2 and 18.6 meV are
also observed experimentally in the INS spectrum. Their strength increases substantially as the loading increases so that the second site begins to be occupied, and they move to slightly higher energies (14.5 and 19.2 meV, respectively). This result is in surprisingly good agreement with our calculations which show that the O site gives two transitions at 15.6 and 18.5 meV. Moreover, the experimental peak at 11.1 meV significantly increases in strength with a shoulder appearing under high H2 loading; this feature probably consists of two peaks with one of them due to the second site and the other due to the Zn site. This result is again consistent with our findings that H2 at the O site has a para-ortho transition at ∼11 meV. From Table I we also see that the predicted transition energies at Zn site shift as loading increases, especially for the Zn-3 transition, which changes from ∼22 to ∼26 meV while the other two shift downward only by ∼1 meV. Experimentally, there is a smaller corresponding shift to about 23 meV for higher loading (9.6 H2/cell). For the loadings of 7 and 9.6 H2/cell, we assign Zn-3′ to the contribution from the sites where the neighboring O site is empty, while assigning Zn-3 to the case where it is occupied. Theoretically there are no empty O sites at the 12 H2/cell loading, while presumably at the 7 H2/cell loading, none of the 5 Zn-3 sites with empty O sites would show the large shift that would be caused by a filled adjacent O site.

In Table I we show, for different sites and loadings, the translational energies along normal coordinate directions, obtained from the forces induced by small displacements. The energies were obtained by using these harmonic normal coordinates to extend the results approximately into the anharmonic quantum-mechanical regime, by first displacing the H2 along these normal directions and then substituting the resulting potential into the Schrödinger equation to get the energies $\mathcal{E}$, and hence the transition frequencies. The frequencies determined by this method deviate as much as ∼10% from the harmonic frequencies, although for most cases the deviation is less than 5%. Table I shows that the translational frequencies are remarkably close to the rotational transitions shown in Table I and could lead to a complex INS spectra. However, the scattering probability for para-ortho transition is proportional to the incoherent cross section ($\sigma_i$) of atomic hydrogen while the para-para scattering is proportional to the coherent cross section ($\sigma_c$) [14]. These cross sections have been tabulated [15] and one finds that $\sigma_i \gtrsim 40\sigma_c$. Therefore the INS spectra would be dominated by the para-ortho transitions with little direct contribution from translational motions. Simultaneous excitation of rotational and translational excitations may appear as shoulders or sidebands of the major para-ortho transition peaks, which are not necessarily weak. Although two possibilities are labeled (T-1 and T-2) in Fig. 3 an unambiguous assignment is difficult. The majority of such double excitations would be predicted to occur at frequencies higher than those measured, or else hidden by the strong Zn-3 structures assigned to rotational excitations. Spectral structure might also be produced by dynamical coupling between hydrogen at adjacent sites. A para-para sensitive tool such as Raman or IR may shed further light onto the origin of various structures.

![Table I](image_url)

**TABLE I**: Theory vs. experiment (Fig. 3) for the positions (meV) of rotational energy-loss peaks along with the calculated rotational zero point energy. (RZPE).

| # H2/cell | Method | RZPE | Zn-1 | Zn-2 | Zn-3 |
|-----------|--------|------|------|------|------|
| 1         | theory | 10.1 | 10.6 | 14.0 | 21.6 |
| 4.8       | experiment | 8.3 | 11.1 | 20.9 |
| 7         | theory | 13.6 | 9.2  | 13.5 | 26.2 |
| 9.6       | experiment | 8.6 | 10.6 | 23.0 |
| 12        | theory | 12.9 | 9.8  | 12.8 | 26.4 |
|           | O-1    | O-2  | O-3  |
| 9.6       | experiment | 11.2 | 14.5 | 19.2 |
| 12        | theory | 9.6  | 11.0 | 15.6 | 18.5 |

![Fig. 2](image_url)

**FIG. 2**: Orientational dependence of the potential at the Zn site. The spherical coordinates are defined with respect to the axes of Fig. 1. The hydrogen loading is 1 H2/cell.

![Fig. 3](image_url)

**FIG. 3**: Our assignments for the observed energy loss peaks.

The circles and diamonds are the 4 K inelastic neutron scattering data points of Ref. 2 with the ordinate origins shifted arbitrarily. We put cubic splines through the data points as a guide to the eye.
TABLE II: Calculated translational frequencies (meV/\hbar) of adsorbed \text{H}_2.

|    | \# \text{H}_2/cell | n1  | n2  | n3  |
|----|-------------------|-----|-----|-----|
| Zn | 1                 | 7.1 | 15.2| 17.5|
|    | 12                | 9.2 | 12.6| 22.9|
| O  | 12                | 9.5 | 14.5| 21.7|

FIG. 4: The adsorption sites. Left panel: our calculational results for \text{H}_2 or \text{D}_2 without consideration of zero point motions. Right panel: the neutron diffraction results \cite{2} for \text{D}_2 at 4 K. The dihydrogens shown are located at eight different distances perpendicular to the plane of the figure within each primitive cell.

With the rotational and translational energy levels calculated, we are able to obtain the zero point energy corrections to the total binding strength, which are about 10 and 20 meV respectively. Therefore, the effective binding strength at low loading (Zn site) is \(\sim 100\) meV. It is somewhat larger than the experimental value of 91 meV \cite{2}. The slight overestimation of the \text{H}_2 binding energy by vdW-DF is also observed for another MOF \cite{3}. For the O site, our calculated binding including zero point correction is \(\sim 90\) meV. This latter value would probably be smaller relative to the prediction for the Zn site, if it were not for a known inaccuracy of an extremal limit in the exchange part of the functional \cite{10}. The experimental value \cite{2} is \(\sim 50\) meV.

Finally, we discuss the hydrogen uptake in this compound. As shown in Ref. \cite{2}, a total of 24 \text{D}_2/cell can be loaded into the system to form a structure as shown in the right panel of Fig. 4 where each hydrogen molecule is represented by a single point. To make a comparison, we put 24 \text{H}_2 per cell into the MOF and let them relax. To speed up the relaxation, the dihydrogens were initially positioned to satisfy the 3-fold rotation plus inversion symmetry, with 6 near each Zn site, 6 near each O site, 6 around 3 Å from each aromatic ring, and 6 at random in the central region. The final result is shown in the left panel of Fig. 4 where both hydrogen atoms in \text{H}_2 are displayed. Overall agreement is obtained between theory and experiment with the the sorbate-sorbent distances in our calculations deviating from experiment by about 15%.

In summary, we studied \text{H}_2 adsorbed within the nanopores of a complex metal organic framework material (MOF-74) \cite{8} with vdW-DF calculations. We confirmed the primary and secondary binding sites associated with unsaturated metal atoms and with triangles of O atoms, respectively. The predicted (zero point corrected) binding energy of the primary site is in good agreement with heat of adsorption measurements \cite{2,3} at low \text{H}_2 loading. We also identify a third and fourth type of site, which are fully occupied at an \text{H}_2 concentration of 24 \text{H}_2 per primitive cell, in agreement with experiment \cite{2}. Rotational motion of the adsorbed \text{H}_2 at the primary and secondary sites is analyzed. The dihydrogen behaves as three-dimensional quantum rotor at both sites and the hindered rotation splits the triplet state into three nondegenerate levels. Based on the calculated para–ortho transitions from singlet to triplet, we are able to identify the main features in the INS spectra \cite{2} for different \text{H}_2 concentrations, with agreement on the 20% (5%) level for the primary (secondary) sites.

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[1] M. Dion, H. Rydberg, E. Schoder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. 92, 246401 (2004); Erratum: Phys. Rev. Lett. 95, 109902 (2005); T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard, and D. C. Langreth, Phys. Rev. B 76, 125112 (2007).
[2] Y. Liu, H. Kabour, C. M. Brown, D. A. Neumann, and C. C. Ahn, Langmuir 24, 4772 (2008).
[3] N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O’Keefe, and O. M. Yaghi, J. Am. Chem. Soc. 127, 1504 (2005).
[4] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O’Keefe, and O. M. Yaghi, Acc. Chem. Res. 34, 319 (2001).
[5] W. Zhou, H. Wu, and T. Yildirim, J. Am. Chem. Soc. 130, 15268 (2008).
[6] J. G. Vitillo, L. Regli, S. Chavan, G. Ricchiardi, G. Spoto, P. D. C. Dietzel, S. Bordiga, and A. Zecchina, J. Am. Chem. Soc. 130, 8386 (2008).
[7] S. Hamel and M. Côté, J. Chem. Phys. 121, 12618 (2004).
[8] L. Kong, V. R. Cooper, N. Nijem, K. Li, J. Li, Y. J. Chabal, and D. C. Langreth, Phys. Rev. B 79, 081407(R) (2009).
[9] C. M. Brown, Y. Liu, T. Yildirim, V. K. Peterson, and C. J. Kepert, Nanotechnology 20, 204025 (2009).
[10] G. Román-Pérez and J. M. Soler, arXiv0812.0244. We adapted the Siesta [P. Ordejón, E. Artacho and J. M. Soler, Phys. Rev. B 53, 10441(R) (1996); J. M. Soler et al., J. Phys.: Condens. Matt. 14, 2745 (2002)] vdW code for use within a private version of Abinit [X. Gonze et al., Comp. Mat. Sci. 25, 478 (2002)]. The calculations were made fully self-consistent with the vdW functional, thus enabling efficient force evaluations.
[11] T. Yildirim and M. R. Hartman, Phys. Rev. Lett. 95, 215504 (2005).
[12] I. F. Silvera and M. Nielsen, Phys. Rev. Lett. 37, 1275 (1976).
[13] D. C. Langreth, B. I. Lundqvist, S. D. Chakarova-Käck, V. R. Cooper, M. Dion, P. Hyldgaard, A. Kelkkänen, J. Kleis, L. Kong, S. Li, et al., J. Phys.: Cond. Mat. 21, 084203 (2009).
[14] J. A. Young and J. U. Koppel, Phys. Rev. 135, A603 (1964).
[15] V. F. Sears, in Methods of Experimental Physics, edited by D. Price and K. Skold (Academic Press, New York, 1987), vol. 23a.
[16] E. D. Murray, K. Lee, and D. C. Langreth, J. Chem. Theor. Comp. (to be submitted).