Design of a Metal–Organic Framework with Enhanced Back Bonding for Separation of N₂ and CH₄


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Supporting Information

ABSTRACT: Gas separations with porous materials are economically important and provide a unique challenge to fundamental materials design, as adsorbent properties can be altered to achieve selective gas adsorption. Metal–organic frameworks represent a rapidly expanding new class of porous adsorbents with a large range of possibilities for designing materials with desired functionalities. Given the large number of possible framework structures, quantum mechanical computations can provide useful guidance in prioritizing the synthesis of the most useful materials for a given application. Here, we show that such calculations can predict a new metal–organic framework of potential utility for separation of dinitrogen from methane, a particularly challenging separation of critical value for utilizing natural gas. An open V(II) site incorporated into a metal–organic framework can provide a material with a considerably higher enthalpy of adsorption for dinitrogen than for methane, based on strong selective back bonding with the former but not the latter.

INTRODUCTION

Coordination of dinitrogen to transition-metal cations is important both fundamentally and industrially. Dinitrogen is highly inert and generally considered to be a poor ligand. In 1963, however, it was shown that a simple coordination complex, [Ru(NH₃)₅]²⁺, could reversibly bind N₂.¹ In subsequent years, a number of dinitrogen–transition-metal complexes have been isolated for metals in varying oxidation states with various coordination numbers.²,³ These complexes typically feature low-valent, relatively reducing metal cations coordinated to dinitrogen in an end-on binding mode. Activating dinitrogen at a metal center to promote its reduction by hydrogen to ammonia under moderate conditions remains a critical goal for homogeneous catalysis. Somewhat weaker metal–dinitrogen binding, however, may be useful for adsorptive separation of gas mixtures. An example is provided by the need to remove dinitrogen (an omnipresent but noncombustible contaminant) from natural gas or other methane-rich gases. This is an extraordinarily difficult separation based on physical properties alone, as both gases lack a permanent dipole and have similar polarizabilities, boiling points, and kinetic diameters. Although cryogenic distillation is currently utilized for separation of these gases, the cost- and capital-intensive nature of this separation has led to development of a number of competing processes, such as membrane- or kinetics-based separations, which generally suffer from low selectivities.⁴

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Adsorptive separations utilizing porous solids containing transition-metal cations capable of reversibly binding dinitrogen may result in highly selective and efficient dinitrogen/methane separations. Metal–organic frameworks are particularly promising in this regard, as they offer a myriad of materials design opportunities and have already shown great potential for a number of gas separation applications. These materials typically display high internal surface areas that can be decorated with both ligand- and metal-based functionalities.

In principle, this permits rational design of local environments tuned for selective binding of specific gases. The M-MOF-74 series of compounds having formula $M_2$(dobdc)$^-$ (where dobdc$^-$ is 2,5-dioxido-1,4-benzenedicarboxylate) is an especially versatile and intensively studied structure type.\(^{12-15}\) This structure features 12 Å wide hexagonal channels, lined at the cation centers in V(II) adsorbates were investigated theoretically, which suggested dications might be anticipated to have interactions of significant quantum chemistry, which can be used to pinpoint which predictive challenge appropriate for application of computational chemistry. As the synthesis of pure M-MOF-74 phases is often quite challenging, it would be advantageous to know a priori which variations are the best opportunities and have already shown great potential for a number of materials design leads to storage or separation applications. M-MOF-74 structures containing Mg$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ have been synthesized. CH$_4$ and N$_2$ adsorption enthalpies reported for a number of these materials indicate they are likely not useful dinitrogen/methane separation materials. For example, Mg-MOF-74 has CH$_4$ and N$_2$ adsorption enthalpies of 4.4 and 5.6 kcal/mol, respectively. However, in principle, other dicatonic metals could be incorporated into this structure type. The as the synthesis of pure M-MOF-74 phases is often quite challenging, it would be advantageous to know a priori which variations are the best candidates for a given gas separation application. This is a predictive challenge appropriate for application of computational quantum chemistry, which can be used to pinpoint which cations might be anticipated to have interactions of significantly different strengths with competing guests. Interactions between M-MOF-74, corresponding to different M, and various adsorbates are investigated theoretically, which suggested that V-MOF-74 could be promising in N$_2$/CH$_4$ separation. We thus decided to study V-MOF-74 in detail. Here, we show, based on three models (Figure 1a–c) of the MOF, that selective back-bonding interactions\(^{16,17}\) from the vanadium(II) cation centers in V-MOF-74 to the unoccupied $\pi^*$ orbitals of N$_2$ can be used to separate N$_2$/CH$_4$ mixtures. We further use calculations by Kohn–Sham density functional theory\(^{18}\) (DFT) and correlated wave function theory (WFT) to put this prediction on a quantitative basis and compare it with the experimentally characterized Fe-MOF-74.

### THEORETICAL METHODS

In order to treat the adsorption process reliably, we need to use electronic structure methods that include dynamical correlation, especially attractive medium-range noncovalent forces. Most exchange-correlation (xc) functionals currently used in DFT do not treat such medium-range correlation energy accurately; however, here we use two kinds of density functionals that overcome this limitation. (1) The Rutgers–Chalmers van der Waals density functionals\(^{19}\) use a nonlocal formulation of the correlation part of the xc functional and can treat attractive van der Waals interactions at medium range and long range. We use the vdW-DF2+U functional\(^{20}\) of this type with Hubbard U corrections,\(^{21}\) where U is a parameter for metal d electrons that is determined to reproduce oxidation energies. (2) The Minnesota functionals\(^{22}\) include the local kinetic energy density in the xc functional and have been shown to yield accurate noncovalent attraction at van der Waals distances;\(^{23}\) we will employ three such functionals, M06-L,\(^{24}\) M06,\(^{25}\) and M11-L,\(^{26}\) because they are based on very different approaches: M06-L is a well-validated\(^{22,23,25}\) local functional with global parameters; M11-L is a recent local functional employing different exchange and correlation parameters for short and long interelectronic distances, and M06 employs 27% Hartree–Fock exchange, as justified by adiabatic connection arguments\(^{27}\) to reduce DFT self-interaction error.

We also employ two WFT methods, in particular, local-pair natural-orbital coupled cluster theory with single and double excitations\(^{28}\) (LPNO-CCSD) and complete active space second-order perturbation theory with counterpoise corrections (CASPT2-CP).\(^{29}\) The latter method has been shown to yield accurate energetics in systems containing transition-metal compounds.\(^{30,31}\)

The DFT and WFT methods used here involve approximations that impose limits on their accuracy. Because they represent very different approaches to the electronic structure problem, confidence in the utility of their quantitative predictions is significantly increased when different models agree, even if the natures of the various approximations employed make it unclear which model is most accurate within the remaining variation.

**Orbitals, Spin States, Cores, Relativistic Effects, and Metal Ions.** In Kohn–Sham calculations and in the reference state for LPNO-CCSD, the V and Fe ions are in high-spin states (quartet and quintet, respectively) and all other orbitals are doubly occupied. For the CASPT2-CP calculation on the 88-atom cluster, we replace the

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**Figure 1.** (a–c) Structural models used in this work. (a) Optimized periodic framework model, based on the symmetry of the experimental primitive cell. (b) Eighty-eight-atom cluster. (c) Small model. Light blue, red, dark gray, and white spheres represent vanadium, oxygen, carbon, and hydrogen atoms, respectively. (d) Three-center bonding diagram between framework O atoms, the metal, and a guest. On the left we show the d subshell occupancy of Fe(II) in both blue and green; V(II) would have only three electrons (green alone) in the d subshell, and the metal d$_z^2$ orbital would be empty. On the right, the middle section shows how the d$_z^2$ orbital splits upon interacting with the four lone pair electrons of two axial Lewis bases; occupancies shown are for Fe(II)—only four electrons would be present for V(II) because the d$_z^2$ orbital of V(II) is unoccupied. The right-most orbital diagram shows the nature of the interaction of the ligand-unoccupied $\pi^*$ orbitals with the occupied $d\sigma$ orbitals of the metal; when the antibonding orbital is occupied, the ligand cannot approach the metal as closely, and this interaction is substantially weaker.
two outer metal ions by closed-shell Zn(II) ions and treat the central metal in the active space. (None of the DFT calculations involve this Zn substitution.) Descriptions of the active spaces used for all species are given in the Supporting Information. The vdW-DF2 calculations with the Hubbard U correction employ the all-electron projector-augmented wave (PAW) method for scalar relativistic core electrons and ionic potentials; all other calculations treat all electrons explicitly. CASPT2-CP calculations use the Douglas–Kroll–Hess relativistic approximation, and the extended transition state (ETS) method for energy decomposition analysis combined with the natural orbitals for chemical valence (NOCV) theory calculations use the ZORA relativistic approximation. All other calculations are nonrelativistic.

**RESULTS AND DISCUSSION**

**Basis Sets.** All vdW-DF2+U calculations employed a plane-wave basis with a 1000 eV kinetic energy cutoff. All other DFT calculations employed the de2-TZVP basis except the ETS-NOCV analysis, which used TZ2P. LPNO-CCSD calculations are extrapolated to a complete basis set from de2-TZVP and de2-QZVP. CASPT2-CP calculations for the small model employed the ANO-RCC-TZVP basis for all atoms, and for the 88-atom cluster they employed the ANO-RCC-DZVP basis for all atoms. References for basis sets are in Supporting Information.

**Coordinates.** We used a triclinic primitive unit cell containing 54 atoms including 6 metal centers and simultaneously optimized the lattice vectors and atomic positions in the unit cell with variable cell dynamics with PBE+U for bare MOFs and with vdW-DF2+U for adsorbates. The 88-atom clusters were taken out of these periodic structures. Optimization of binding geometry of adsorbates in the periodic MOFs and on the 88-atom cluster involved freezing the MOF structures. The structure of the small model was fully optimized by M06-L, and these structures were used for the LPNO-CCSD and CASPT2-CP calculations. Full coordinates and absolute energies in harteens of selected structures are in the Supporting Information.

Starting geometries for the periodic model were based on the experimental structures6–10,12,32 of M-MOF-74 (Figure 1a) and further optimized by DFT; the primitive unit cell of experimental structure contains 54 atoms, including 6 metal centers. We defined two other models of M-MOF-74 to be studied at additional levels of theory. The cluster (Figure 1b) has 88 atoms, including three metal centers, and it was designed43 to retain the local structure of MOF-74 about the central metal ion while remaining small enough for high-level electronic structure calculations. The small model (Figure 1c) has 19 atoms, including one metal center, and is small enough to conduct calculations by expensive wave function methods for comparison. All iron and vanadium ions were modeled in their respective ground state bonding configuration with a 3d electronic configuration of V(II). In this case, the two doubly occupied lone pairs provide four electrons to the three-center bond and the occupation of the metal d orbital provides one electron, for a total of five electrons in the three-center bond; so, one electron is in the antibonding orbital. As the N2 approaches the metal site, it thus experiences unfavorable σ antibonding plus additional exchange repulsion from the occupied nonbonding orbital. Consequently, N2 cannot approach the Fe(II) center closely enough to experience π* back-bonding stabilization as favorable as is present in the V(II)−N2 system.

In subsequent sections of this article, we confirm the differential stabilization effect with local and nonlocal DFT calculations, confirming our molecular orbital prediction that as-yet unsynthesized V-MOF-74 could be used to separate N2 from CH4. We also reinforce our DFT results with correlated wave function calculations to rule out the possibility of artificial back bonding43 owing to the possible underestimation of the energy gap and the delocalization of d electrons in the DFT models. Finally, we analyze single-determinantal Kohn–Sham reference functions to confirm the above explanation of the effect.

**N2 and CH4 Adsorption in V-MOF-74 and Fe-MOF-74.**

The key quantity we calculated is the differential adsorption energy defined by

\[ \Delta E_{\text{ads}} = E_{\text{ads}}(N_2) - E_{\text{ads}}(\text{CH}_4) \]

where \( E_{\text{ads}} \) is the energy of adsorption (here defined as a positive number to denote that desorption is endothermic); thus, \( \Delta E_{\text{ads}} \) is more positive when \( N_2 \) binds more strongly. The results are in Table 1. Across all levels of theory and all models, CH4 binding is comparable between the two metals but N2 is predicted to bind significantly more strongly than CH4 to the coordinatively unsaturated metal site when the metal is V rather than Fe.

We noted above the consistent trend observed for calculated \( \Delta E_{\text{ads}} \) values; the trends in calculated \( \Delta E_{\text{ads}} \) values are also

Table 1. \( \Delta E_{\text{ads}} \) Differences, \( \Delta E_{\text{ads}} \) (in kcal/mol)

<table>
<thead>
<tr>
<th>level of theory</th>
<th>small model</th>
<th>large model*</th>
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<tbody>
<tr>
<td></td>
<td>V</td>
<td>Fe</td>
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<tr>
<td>DFT, vdW-DF2+U</td>
<td>4.9</td>
<td>0.4</td>
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<td>DFT, M06</td>
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<td>0.8</td>
</tr>
<tr>
<td>DFT, LPNO-CCSD/CBS</td>
<td>4.8</td>
<td>0.7</td>
</tr>
<tr>
<td>WFT, CASPT2 CP</td>
<td>3.8</td>
<td>0.3</td>
</tr>
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</table>

*The first row is for the periodic model, and the other large-model calculations are for the 88-atom cluster. 4Impractically computationally intensive.
consistent across the methods. Absolute adsorption energies for the 88-atom cluster and the periodic model are compared in Table 2. We see remarkable agreement between the adsorption

<table>
<thead>
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<th>Table 2. Absolute Binding Energies (kcal/mol)</th>
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<tr>
<td>periodic model</td>
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<tr>
<td>V—N&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>vDW-DF2+U  88-atom cluster</td>
</tr>
<tr>
<td>vDW-DF2+U</td>
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<tr>
<td>M06-L</td>
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<td>M06</td>
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<td>M11-L</td>
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<tr>
<td>CASPT2 CP small model</td>
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<tr>
<td>LPNO-CCSD/CBS</td>
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<td>CASPT2 CP</td>
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energies calculated with the 88-atom cluster and the periodic model and further remarkable agreement between the absolute binding energies calculated by DFT with different functionals and by WFT; the good agreement of results obtained with several methods that incorporate the physics in different ways adds confidence to the predictions. Inspection of Table 2 shows relatively large differences in the absolute binding energies between the large and small clusters. The enhanced attraction in the 88-atom cluster model can partially be attributed to greater medium-range correlation effects. One should also consider that the two models have different ligand coordination environments, and this too has an influence on the absolute binding energies.

In order to further verify the validity of these predictions, isosteric heats of CH<sub>4</sub> and N<sub>2</sub> adsorption in Fe<sub>2</sub>(dobdc) were obtained experimentally from adsorption isotherms at 175 K. (Details of the experiment are in the Supporting Information.) As seen in Figure 2, the uptake of N<sub>2</sub> in Fe-MOF-74 is relatively steep and approaches one N<sub>2</sub> molecule per iron cation site at 1 bar and 175 K. Methane uptake, while similar at low pressure, reaches a higher value of approximately 1.5 CH<sub>4</sub> molecules per iron at 1 bar. These plots yield isosteric heats of adsorption for methane and dinitrogen that are both relatively low and quite similar; in particular, they are 5.3 ± 0.2 and 5.5 ± 0.2 kcal/mol, respectively, which yields an experimental difference of 0.2 ± 0.3 kcal/mol. These results differ from the previously reported values of 4.8 kcal/mol for CH<sub>4</sub> and 8.4 kcal/mol for N<sub>2</sub>, both because of the lower temperature and because of the change in experimental procedure; the present results should be more accurate for the difference because they were done with isotherms at the same temperature on the exact same batch of sample. An attempt to obtain the same information for V-MOF-74 was not successful.

Experimental enthalpies of adsorption should not be compared directly to the energies of adsorption in Table 2. For the 88-atom cluster, however, we computed the enthalpies of adsorption at 175 K by a formula given previously. The M06-L, M06, and M11-L levels of theory give predicted differences in adsorption enthalpy of 1.1, 0.5, and −1.6 kcal/mol, respectively. The average difference in predicted adsorption enthalpy of 0.0 kcal/mol is in good agreement with the 0.2 kcal/mol difference observed experimentally.

Figure 2. (Top) Adsorption of methane (green) and dinitrogen (blue) in Fe<sub>2</sub>(dobdc) at 175 K. (Top inset) Isosteric heats of adsorption. (Bottom) First coordination spheres for the iron centers in the solid-state structures obtained upon dosing Fe-MOF-74 with dinitrogen or methane; orange, red, blue, gray, and light blue represent iron, oxygen, nitrogen, carbon, and deuterium, respectively.

### Structural Parameters, Vibrational Frequencies, and Charges

Table 3 shows that the M—N distance is shorter in V-MOF-74 than in Fe-MOF-74, as anticipated above; there is also a smaller difference in the M—C distances for CH<sub>4</sub>. Neutron powder diffraction experiments on Fe-MOF-74 at 10 K (see figure in the Supporting Information) indicate excellent agreement between the calculated and the experimentally observed structures of methane bound to Fe<sup>2+</sup>. Specifically, the Fe—C distance of 2.98(1) Å is very close to the distance of 2.96 Å calculated for the 88-atom cluster. Differences in M—N
distances are consistent with the energetic results presented above.

The potential energy curves (given in Figure 3) provide further evidence for qualitatively different kinds of interaction;

![Figure 3](image)

**Figure 3.** Potential energy curve as a function of M−N2 distance for the small model as calculated with the M06-L exchange–correlation functional. The curve for M = V(II) is shown as a dashed line with diamond points indicating single-point energies. The curve for M = Fe(II) is shown as a dotted line with square points indicating single-point energies.

we give just one example, the interaction of N2 with M in the small model, calculated by M06-L. Single-point energies were calculated by modifying the M−N2 distance but keeping all other geometrical parameters unchanged from the geometric minima. Interestingly, the predicted interaction energy at 2.8 Å is nearly equivalent for N2 with the Fe and V small models. At an M−N distance of 2.8 Å, the interaction energy is ∼−4 kcal/mol for both V and Fe. As N2 approaches more closely, the potential energy reaches a minimum of −4.3 kcal/mol at 2.73 Å for Fe but goes to a much deeper well at −9.1 kcal/mol at 2.21 Å for V. (This further reinforces the conclusion that the binding interaction to vanadium is quite different from that of other metals studied.) For comparison, the Fe−N distance was determined to be 2.30±0.01 Å for N2 adsorbed within Fe-MOF-74 by neutron diffraction experiments at 9 K. The predicted Fe−N distance for the 88-atom cluster compares favorably with the measured value of 2.30±0.01 Å.

The N−N stretching frequency is a probe of back bonding, because these shifts result from weakening the bond by dx.d to π* back-donation. Periodic vDW-DF2+U calculations show that, as compared to the isolated gas-phase diatomic vibrational frequency (2415 cm⁻¹), N2 bound to V experiences a significant shift in the N−N stretch (−102 cm⁻¹), whereas N2 bound to Fe shows a negligible change (−6 cm⁻¹). In contrast, vibrational frequency shifts for C−H modes in CH₄, where no back bonding is predicted, are negligible. For the 88-atom cluster, M06 calculations for N₂ bound to MOF show similar trends—a 103 cm⁻¹ shift for V and a 4 cm⁻¹ shift for Fe. M11-L also shows similar shifts: 101 and 5, respectively. Table 3 shows a more complete set of results for M06-L, and these too are consistent with our analysis.

Next we examine in more detail the amount of charge transfer between the metal and the N₂ guest. Key charges in atomic units are given in Table 3.

The total charge on the guest molecule is computed by summing the partial charges of the individual atoms of the guest molecule; this indicates the magnitude and direction of charge transfer between the MOF and the guest. For each of the three functionals, C5 partial atomic charges for the 88-atom cluster indicate donation of negative charge from the central metal ion to the nitrogen molecule and an opposite direction of transfer for methane. This is also reflected in the charge on the metal ion being increased for N₂ adsorption and decreased for CH₄ adsorption when compared to the bare MOF. The increase or decrease in the positive charge of the central metal ion with N₂/CH₄ adsorption does not exactly equal the total charge on the guest molecule. This reflects charge change within the rest of the MOF framework.

We find that the direction of electron transfer from the metal center to the guest molecule for the Fe−N₂ system is opposite to what is observed for V−N₂. Specifically, the partial atomic charge on Fe is 0.66 in the presence of either N₂ or CH₄; these values are the same as the values of 0.66 for the bare Fe-MOF-74 framework. The partial atomic charge on the V ions in V-MOF-74 is significantly higher in all structures, and it is not very sensitive to the adsorbates in the small model, but in the 88-atom cluster the partial atomic charge on V increases by 0.07 upon adsorption of N₂ and decreases by 0.07 upon adsorption of CH₄. Overall, these changes are consistent with our interpretation of increased back bonding in the V−N₂ case.

**Orbital Analysis.** The nature of the M−N₂ bond of the small model was investigated using the extended transition state (ETS) method for energy decomposition analysis combined with the natural orbitals for chemical valence (NOCV) theory. ETS-NOCV analysis separates bond formation energy into distortion of interacting subsystems, steric interaction (with electrostatic and exchange-correlation contributions), and an “orbital” term that represents a combination of the interactions between the occupied molecular orbitals on one bonding partner with the unoccupied molecular orbitals of the other and the intragraftar polarization. ETS-NOCV calculations carried out on the small model with M06-L show (see Figure 4) that both σ donation and π* back-bonding interactions are weaker.
for Fe–N₂ than for V–N₂. Comparing the two largest alpha and beta spin-paired NOCV contributions to the bond energy, the σ interactions are about eight times stronger for V than for Fe and the π* back-bonding-type interactions are about twice as strong, with all other contributions being less than 1 kcal/mol for V and less than 0.5 kcal/mol for Fe. Such analyses of charge rearrangement are not unique, so we also performed natural bond order (NBO) analysis, as described next, to test the robustness of this interpretation.

NBO analysis on the small model identifies a σ bond for V–N₂ but not for Fe–N₂. Second-order perturbation analysis of the Kohn–Sham matrix in the NBO basis shows that back bonding, defined as the interaction between occupied π-type NBO orbitals and unoccupied π*-type NBO orbitals of N₂, is stronger for V than for Fe. Summing the contribution from orbitals with occupations greater than 0.8 electrons, the total back-bonding interaction is 32 kcal/mol for V–N₂ and 13 kcal/mol for Fe–N₂.

Given its predicted N₂/CH₄ separation capabilities rationalized above, we initiated efforts to synthesize V-MOF-74. To date, isolation of crystalline material, rather than amorphous powders (as determined by powder X-ray diffraction), has proven elusive, highlighting another MOF challenge: the need for a greater understanding of the mechanisms by which metal–organic frameworks form. The present computational results strongly motivate continued efforts to realize both of these goals.

**CONCLUSIONS**

We predict that dinitrogen separation from methane can be accomplished by the as-yet-unsynthesized V-MOF-74, because the vanadium ions in this MOF have their interaction energies significantly increased by π back bonding with N₂ but not with CH₄. This provides a new M-MOF-74 target as a challenge to mol for Fe and the π* back-bonding-type interactions are about twice as strong, with all other contributions being less than 1 kcal/mol for V and less than 0.5 kcal/mol for Fe. Such analyses of charge rearrangement are not unique, so we also performed natural bond order (NBO) analysis, as described next, to test the robustness of this interpretation.

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**REFERENCES**

(35) Frisch, M. J.; et al. Gaussian 09, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2010.