DFT-D3 Study of Molecular N₂ and H₂ Activation on Co₃Mo₃N Surfaces

Constantinos D. Zeinalipour-Yazdi,*† Justin S. J. Hargreaves,‡ and C. Richard A. Catlow*†

1Kathleen Lonsdale Materials Chemistry, Department of Chemistry, University College London, London, WC1H 0AJ, United Kingdom
2WestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, United Kingdom

ABSTRACT: Cobalt molybdenum nitride (Co₃Mo₃N) is one of the most active catalysts for ammonia synthesis, although the atomistic details of the reaction mechanism are currently unknown. We present a dispersion-corrected (D3) DFT study of the adsorption and activation of molecular nitrogen and hydrogen on Co₃Mo₃N-(111) surfaces to identify possible activation sites for ammonia synthesis. H₂ was found to adsorb both molecularly on the Mo₃N framework and dissociatively on Co₈ clusters or Mo₃ clusters that were exposed due to N-vacancies. We find that there are two possible activation sites for N₂, where both N₂ and H₂ can coadsorb. The first is a Mo₃ triangular cluster that resides at 3f nitrogen vacancies, and the second is a surface cavity where N₂ is activated by a Co₈ cluster, the second being a more efficient activation site. N₂ was found to adsorb in three adsorption configurations: side-on, end-on, and an unusual tilt end-on (155°) configuration, and the existence of these three adsorption configurations is explained via MP2 calculations and the sphere-in-contact model.

1. INTRODUCTION

Co₃Mo₃N when synthesized using the procedure patented by Topsoe is known to be active for ammonia synthesis at 400 °C and elevated pressures using a 3:1, H₂:N₂ mixture. Indeed, Co₃Mo₃N when doped with Cs is one of the most active catalysts for ammonia synthesis, with turnover-frequencies (TOF) that are remarkably high compared to graphite-nitrogen transfer, which was also suggested that ammonia synthesis may proceed via Mars–Topsøe chemistry and that lattice nitrogen may act in the rate-determining step (RDS). It has been previously shown that ammonia synthesis may proceed via MvK chemistry at low temperatures as there is a large number of nitrogen vacancies (~10¹¹ cm⁻²), which can activate N₂ by weakening of the triple bond. N-vacancies were also found to participate in the mechanism for the electrochemical reduction of ammonia on VN and ZrN and in the two-step solar-energy driven ammonia synthesis on metal nitrides. Here, we extend the earlier study by investigating the adsorption at every possible site compared to the adsorption of molecular hydrogen.

The rest of the paper has the following structure: first we establish the calculation parameters that reproduce well the electronic structure of FeₓCo₃₋ₓMo₃N, where x = 0, 1, 2 and 3; next we describe the method for generating slabs of Co₃Mo₃N-(111) surfaces and apply the calculation parameters to address the question of hydrogen and nitrogen adsorption and activation on Co₃Mo₃N with and without defects. Finally we explain the various bonding configurations of N₂ via molecular orbital (MO) calculations and the sphere-in-contact model.

2. COMPUTATIONAL METHODS

2.1. Methodology. Spin-polarized periodic planewave DFT calculations have been performed with the VASP 5.3.5 code using the revPBE and a 650 eV cutoff for the planewave.
expansion. A detailed description of the computational methodology for the plane wave calculations can be found in ref 13, in which it was found that among various GGA and hybrid-GGA XC functionals, the revPBE yields accurate (to within 1%) bond dissociation enthalpies for N2(g). Here, we further test how well this functional can perform in modeling Fe(3−x)CoMo3N, (x = 0, 1, 2, 3), in a 20 Å periodic unit cell, given by

\[
\Delta E_{\text{ads},D3} = E_{\text{slab}−X2} − E_{\text{slab}} − E_{X2}
\]

where X = N, H. The adsorption energy was also corrected for the dispersion correction using two approaches via the DFT-D3 method as implemented in Gaussian09 code (rev D.01). The first (\(\Delta E_{\text{ads,D3static}}\)) was to fully relax the cluster-adsorbate system, the surface, and the adsorbate separately. The second was by performing a single point energy calculation with the D3-correction at the minimum energy structure obtained from an optimization without the correction (\(\Delta E_{\text{ads,D3relax}}\)). We find that the latter can lead to large errors with respect to the adsorption energies of hydrogen, which was overestimated by 35% in some cases and have therefore applied the former approach.

Molecular calculations for the electronic structure of N2 were performed within restricted density functional theory (DFT) implemented in the Gaussian09 code (rev D.01). The basis set used was the correlation-consistent polarized valence double-\(\xi\) abbreviated as cc-pVDZ. Stationary states were confirmed by the absence of imaginary frequencies in the vibrational analysis. The convergence criteria for the maximum forces and the root-mean-square (RMS) forces were less than 0.01 eV/A and 0.001 eV/A, respectively.

### 2.2. Choice of XC-Functional for FeCoMo3N

We find that the choice of exchange-correlation (XC) functional is critical when addressing the chemistry of N2/H2 with FeCoMo3N, where x = 0, 1, 2, and 3. Although it has been shown for solids that hybrid XC functionals HSE06 functional, we found that the latter underestimates the bandgap by overestimation of the exchange splitting known for the hybrid functional PBE0.23 It has been suggested that the HSE06 functional greatly improves the computer time and resource requirements mostly due the faster convergence of the total energy with respect to k-point mesh, as the bare unscreened exchange operator requires a 12 × 12 × 12 mesh equivalent to a 6 × 6 × 6 mesh for the HSE06 functional.23 However, we found that the latter underestimates by 38 kJ/mol the bond dissociation enthalpy of N2(g), \(\Delta g_0H(N−N)\). Therefore, we have tested the remaining XC-functionals commonly used for solids, PBE, PW91, revPBE, and PBEsol with respect to their accuracies in predicting the lattice constant of FeCoMo3N, where x = 0, 1, 2, and 3 (see Table 1). These alloys contain also iron which makes possible the testing of the computational methodology on other elements for which crystallographic data are available.23−27 Our calculations are based on full optimization of unit cell dimensions and atom positions and the reported mean-average-percent-error (MAPE) value, which indicates to within which percentage the experimental values, are reproduced. The calculated values were compared to two sets of experimental lattice constants: the first comprised solely of PND data obtained at 4.2 K (Exp1) and the second based on combined XRD and temperature-dependent magnetic susceptibility measurements (Exp2). In both sets, we obtained the same trend with respect to the average-MAPE calculated at each functional, which was found to be PBE < revPBE < PW91 < PBEsol. In particular, according to Table 1, an average MAPE of 0.30−0.36% was found for PBE: both revPBE and PW91 gave values of about 0.5−0.6% and PBEsol gave higher average MAPE, of the order of 2%. The results show that with the use of a plane wave code the lattice parameter can be estimated very well both with the PBE and the revPBE functional, which are also computationally less expensive than some of the hybrid GGA functionals tested.

In an earlier account of bond dissociation enthalpy (BDE) of N2 with the use of various XC functional, the % error for the revPBE was found to be the lowest among various GGA and hybrid GGA functionals.15 In particular, we found that the % error was for revPBE = 0.2 < B3LYP = 1.7 < PBE = 3.5 < HSE06 = 4.1 < PBE = 4.9 < PW91 = 7.0. Therefore, all subsequent calculations have been performed with the revPBE functional, which can yield more accurate barrier heights according to the calculated BDE of the N≡N bond.
Various surface compositions of Co₃Mo₃N-(111) surfaces found

- A: CoMo₀.₉N₂.₁ N: 6f
- B: CoMo₁.₂N₀.₄ N: 5f
- C: CoMo₁.₀N₀.₄ N: 3f
- D: CoMo₀.₈N₀.₂ N: 6f
- E: CoMo₀.₇N₀.₃ N: 3f
- F: CoMo₀.₈N₀.₃ N: 3f

Figure 1. 2 × 2 surface supercells of Co₃Mo₃N showing surface terminations of different composition in cobalt molybdenum nitride (111) surfaces. Note that only four out of the six surface compositions expose surface nitrogen (i.e., 5f or 3f). Two surfaces only have subsurface nitrogen (i.e., 6f).

Figure 2. Symmetry unique sites for molecular hydrogen adsorption on Co₃Mo₃N surface C, in the presence of a nitrogen vacancy (site 1 and 2) in (a) top view and (b) perspective view.

- Site 1
- Site 2
- Site 3
- Site 4
- Site 5
- Site 6
- Site 7
- Site 8

The bulk in 0.1 Å increments and generate centro-symmetric slabs of thickness <1 nm for computational efficiency. A top view of these slabs along the c direction is shown in Figure 1 that shows the composition of six distinct surfaces generated, of which four had surface nitrogen (i.e., B, C, E, and F) and two had only a MoCo exposed phase (i.e., A and D) with subsurface nitrogen. The subsurface nitrogen is a 6-fold bound nitrogen (6f) to Mo atoms, whereas surfaces C, D, and F had entirely 3f nitrogens, and one surface (B) had 5f nitrogens. The nitrogen vacancy formation energies (VFE) and concentrations have been previously calculated, and the latter was found to be on the order of 10¹³ per cm² at ambient conditions. We have...
evaluated the surface composition in these slabs and found that it significantly differs among these thin films. It is interesting to note that the surface with the highest surface nitrogen concentration, C had a very low composition of nitrogen based on the normalized stoichiometric coefficient (s.c.) of nitrogen, having set the s.c. of cobalt to 1. These compositions were found to be A = CoMo0.9N0.1, B = CoMo0.8N0.2, C = CoMo0.7N0.3, D = CoMo0.6N0.4, E = CoMo0.5N0.5, and F = CoMo0.4N0.6. For example surface A, which had a complete absence of exposed surface nitrogens, had the highest stoichiometric coefficient for nitrogen (i.e., N_s.c.). This suggests that the exact surface composition of very thin layers of this material may have to be evaluated by topographic techniques, e.g., via scanning probe microscopies that are currently absent in the literature.

In an earlier DFT study with the same methodology used here, we proposed that surface C is the most active surface for Mars–van Krevelen type chemistry for ammonia synthesis. This choice was based on two kinetic factors and an energetic factor: (i) the density of sites that can activate N2 (i.e., N-vacancies), (ii) which surface had the most exothermic adsorption energies for N2 adsorption, and (iii) the surface formation energies (E_s.), which were calculated for the four surface compositions that had exposed surface nitrogen. As the calculation of surface stabilities is not possible for Co3Mo3N, we continue with surface C for calculating the adsorption of N2/H2 on Co3Mo3N.

### 3.2. H2 Adsorption and Activation on Co3Mo3N.

Various phases of atomically adsorbed hydrogen have been observed via scanning-tunnelling microscopy (STM) on Co nanoparticles grown on Cu(111). In a recent DFT study, the adsorption energy of H2 was found to be roughly proportional to the surface energy in the following order Co(100) > Co(110) > Co(111) [13]. The nitrogen vacancy-induced heterogeneity of the surface, offers H2 an additional degree of complexity with respect to the availability of adsorption sites. In this study, we have studied the adsorption of H2 at 8 symmetry unique sites of the C surface of Co3Mo3N shown in Figure 2, with a nitrogen vacancy shown by the yellow circle in Figure 1. This surface is expected to yield a better representation of the actual surface of the catalyst, which we have previously shown to have a large number of nitrogen vacancies (∼10^13 cm^-2) even at ambient temperature. The adsorption energy of H2 was found to be roughly proportional to the percentage of H−H activation defined as the percentage lengthening of the H−H bond, when adsorbed side-on at every adsorption site with an adsorption angle of α(Fe−H−Fe) = 72°−87°. In this adsorption configuration, the adsorbate–surface bonding is interpreted as an interaction between the filled σ MO of H2 with empty π-states of the metal and π-back-donation into the antibonding orbital of H2. Interestingly an end-on adsorption could not be found in agreement with H2 adsorption studies on rhodium clusters. H2 can absorb either molecularly or dissociatively (see Scheme 1) at five distinct adsorption sites after optimization of 8 symmetry unique adsorption sites, which are shown in Figure 2.

![Scheme 1. Simplified Schematic Showing (a) Molecular and (b) Dissociative Adsorption of H2 on Co3Mo3N Surfaces](image)

The molecular adsorption occurred mostly on the MoN framework, where it was bound through the Mo atoms (see Table 2). Dissociative adsorption occurred on exposed Co atoms that belong to the Co9 clusters or Mo9 clusters that were exposed due to N-vacancies.

The adsorption energies without (ΔE_H2) and with (ΔE_H2+D3, ΔE_H2+D3) the inclusion of dispersion interactions via the DFT-D3 method and the optimized structure of the adsorbates (i.e., r(M−H), r(F−M−H), a(M−H−H)) are presented in Table 2. We have also calculated % activation, defined as the percent increase of the H−H bond length during adsorption. It may seem at some point surprising that the addition of the D3 correction can shift the adsorption energy endo- or exothermically; however, for the static calculation, it always adds to a more exothermic adsorption energy, which is what is expected.

The various adsorption sites found had the following characteristics: site 1 the hydrogen was adsorbed side-on to a molybdenum atom that was adjacent to a nitrogen-vacancy site (N_vac) with an adsorption energy of −67 kJ/mol but with only a small activation of the H−H bond.

Site 2 was found to dissociatively chemisorb H2, where it was bound to a molybdenum atom at a nitrogen vacancy site. This site had the largest % activation (i.e., 41%) for molecular hydrogen; sites 3–5 in which hydrogen was adsorbed on a molybdenum atom on the MoN framework with a moderate adsorption energy of −30 to −68 kJ/mol due to the less metallic character of the MoN framework. The strongest adsorption energy for H2 was found on sites 6–7, which corresponds to a corner atom of the Co9 nanoclusters denoted as Co9_top with adsorption energy of −127 and −110 kJ/mol, respectively. At these sites, the H−H bond was also found to be considerably activated (i.e., 23−24%). These results indicate that the Co9 clusters will be saturated with molecular hydrogen at low temperatures under conditions where both N2/H2 are available in the feedstream. Interestingly we find that at site 8, H2 will generally not adsorb at low-T based on the D3-corrected adsorption energy of just 21 kJ/mol, and it is the only site on the Co9Mo3N surface that will not be occupied by hydrogen when it is coadsorbed with N2. Therefore, we consider site 8 as free under conditions of competitive adsorption with N2 at low temperatures (e.g., T < 200 °C).

### 3.3. N2 Adsorption and Activation on Co3Mo3N.

The adsorption of N2 over a range of surfaces has been studied using various surface analytical probes extensively. Both physisorbed and chemisorbed states are identified using a combination of electron spectroscopy and thermal desorption techniques. According to this report and earlier LEED experiments, N2 can chemisorb side-on and end-on on the surfaces of certain metals (e.g., Ni, Fe, Ru, and W). In this study, we find that apart from these two adsorption configurations, N2 can also adsorb in a tilt end-on configuration on Co3Mo3N shown in Scheme 2. This is a well-defined adsorption configuration with a tilt angle equal to 155° in which the dihedral δ(Co−Mo−N−N) of this bond is found to be 0°.

Angle resolved photoemission spectra have identified two phases of N2 adsorbed to Fe(111) surfaces (γ-phase and α-phase). In the first, N2 is adsorbed perpendicularly, and in the latter in a strongly inclined configuration, where N2 was described to form two covalent bonds with Fe atoms. A (c(2 × 2)-N/Fe(110) structure was found to form on Fe(111) and Fe(110) surfaces, whereas two side-on (α and α′) and two end-on (β and γ) adsorbed states have been found via periodic DFT calculations for molecular N2 adsorption on Fe(111). Two
Distinct Adsorption Sites on \( \text{Co}_3\text{Mo}_3\text{N} \) Surface

On the surface of \( \text{Co}_3\text{Mo}_3\text{N} \) (i.e., surface C), we have identified three adsorption configurations for \( \text{N}_2 \), which are shown in Scheme 2. For the eight adsorption sites, we placed \( \text{N}_2 \) either \textit{side-on} or \textit{end-on} at every site shown in Figure 3 and let it optimize without any restrictions. The adsorption energies for \( \text{N}_2 \) without \((\Delta E_{\text{ads}})\) and with \((\Delta E_{\text{ads,relax-D3}})\) the inclusion of dispersion interactions via the DFT-D3 method and the optimized structure of the adsorbates \((i.e., r(H-H), r(M-H))\) are presented in Table 3. The \textit{side-on} configurations stayed either \textit{side-on} or became a \textit{tilt end-on} configuration during relaxation. This change in adsorption configurations was not observed for the \textit{end-on} configuration, which remained \textit{end-on} even after relaxation. This indicates that there is barrier for the \textit{end-on} to \textit{side-on} transformation. Adsorption at some sites would activate nitrogen, but dissociation such as in the case of \( \text{H}_2 \) was not observed, in accord with the large bond dissociation enthalpy of \( \text{N}_2 \) \((i.e., 946 \text{ kJ/mol})\).

The various adsorption sites found had the following characteristics: site 1 the nitrogen was adsorbed in a tilt \textit{end-on} configuration to a molybdenum atom that was adjacent to a nitrogen-vacancy site \((\text{N}_{\text{vac}})\) with an adsorption energy of \(-59 \text{ kJ/mol} \) but with only a small activation of the \( \text{N} \sim \text{N} \) bond. Site 1 was previously identified as \textit{side-on} and \textit{end-on}, based on an extensive collection of surface analytical studies.\(^{33,34} \)

Side-on and \textit{end-on} adsorbed configurations for \( \text{N}_2 \) when it is adsorbed to nickel surfaces have also been found, where the \textit{end-on} adsorption occurs either through a single surface atom on \( \text{Ni}(110) \) surfaces or in a \textit{tilt end-on} configuration through two surface atoms on \( \text{Ni}(110) \) surfaces.\(^{37} \)

An \textit{end-on} adsorbed configuration of \( \text{N}_2 \) as well as \( \text{CO} \), which is isoelectronic, was found via X-ray emission spectroscopy (XES) and DFT calculations on \( \text{Ni}(100) \).\(^{38} \)

An \textit{end-on} adsorbed configuration for \( \text{N}_2 \) has been found on cobalt clusters of the form \( \text{Co}_n(\text{N}_2)^n \), where \( n = 8-17 \) using infrared photon dissociation (IRPD) spectroscopy and DFT calculations of the stretching frequency of the \( \text{N} \sim \text{N} \) bond.\(^{39} \)

Adsorption at some sites would activate nitrogen, but dissociation such as in the case of \( \text{H}_2 \) was not observed, in accord with the large bond dissociation enthalpy of \( \text{N}_2 \) \((i.e., 946 \text{ kJ/mol})\). The various adsorption sites found had the following characteristics: site 1 the nitrogen was adsorbed in a tilt \textit{end-on} configuration to a molybdenum atom that was adjacent to a nitrogen-vacancy site \((\text{N}_{\text{vac}})\) with an adsorption energy of \(-59 \text{ kJ/mol} \) but with only a small activation of the \( \text{N} \sim \text{N} \) bond. Site 1 was previously identified as \textit{side-on} and \textit{end-on}, based on an extensive collection of surface analytical studies.\(^{33,34} \)

On the surface of \( \text{Co}_3\text{Mo}_3\text{N} \) \((i.e., \text{surface C})\), we have identified three adsorption configurations for \( \text{N}_2 \), which are shown in Scheme 2. For the eight adsorption sites, we placed \( \text{N}_2 \) either \textit{side-on} or \textit{end-on} at every site shown in Figure 3 and let it optimize without any restrictions. The adsorption energies for \( \text{N}_2 \) without \((\Delta E_{\text{ads}})\) and with \((\Delta E_{\text{ads,relax-D3}})\) the inclusion of dispersion interactions via the DFT-D3 method and the optimized structure of the adsorbates \((i.e., r(H-H), r(M-H))\) are presented in Table 3. The \textit{side-on} configurations stayed either \textit{side-on} or became a \textit{tilt end-on} configuration during relaxation. This change in adsorption configurations was not observed for the \textit{end-on} configuration, which remained \textit{end-on} even after relaxation. This indicates that there is barrier for the \textit{end-on} to \textit{side-on} transformation. Adsorption at some sites would activate nitrogen, but dissociation such as in the case of \( \text{H}_2 \) was not observed, in accord with the large bond dissociation enthalpy of \( \text{N}_2 \) \((i.e., 946 \text{ kJ/mol})\). The various adsorption sites found had the following characteristics: site 1 the nitrogen was adsorbed in a tilt \textit{end-on} configuration to a molybdenum atom that was adjacent to a nitrogen-vacancy site \((\text{N}_{\text{vac}})\) with an adsorption energy of \(-59 \text{ kJ/mol} \) but with only a small activation of the \( \text{N} \sim \text{N} \) bond. Site 1 was previously identified as \textit{side-on} and \textit{end-on}, based on an extensive collection of surface analytical studies.\(^{33,34} \)
Table 3. Adsorption Energy ($\Delta E_{ads}$) of N$_2$ Adsorbed to C Surface of Co$_3$Mo$_3$N, N–N Bond Length ($r$ (N–N)), M–N Bond Length ($r$ (M–N)), Tilt Angle ($\alpha$ (M–N–N)), Adsorption Site Composition, and % Elongation for Side-on Adsorption at Various Distinct Adsorption Sites on 2 × 2 Co$_3$Mo$_3$N (Surface C)$^a$

| property                      | site 1 | site 2 | site 3 | site 4 | site 5 | site 6 | site 7 | site 8 | units |
|-------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|-------|
| $\Delta E_{ads}$             | $-58.9$| $-19.6$| $59.8$ | $-33.6$| $-44.3$| $-22.1$| $-18.7$| $79.3$ | kJ/mol |
| $\Delta E_{ads,relax}$       | $-58.9$| $-48.8$| $1.5$  | $-29.9$| $-41.3$| $-38.2$| $-13.6$| $40.2$ | kJ/mol |
| $r$ (N–N)                    | $1.166$| $1.244$| $1.130$| $1.173$| $1.163$| $1.166$| $1.173$| $1.357$| Å     |
| $\alpha$ (M–N–N)            | $154$  | $176$  | $175$  | $152$  | $158$  | $73$   | $75$   | $71$   |       |
| $r$ (M–N)                    | $1.753$| $1.930$| $2.398$| $1.820$| $1.754$| $2.001$| $1.971$| $1.928$| Å     |
| type                         | tilted | tilted | tilted | tilted | tilted | tilted | tilted | tilted |       |
| bound to                     | N$_{vac}$| N$_{vac}$| MoN$_3$| Co$_{top}$| Co$_{top}$| Co$_{top}$| Co$_{top}$| Co$_{side}$|       |
| N$_2$ activation$^b$         | $4$    | $11$   | $1$    | $5$    | $4$    | $5$    | $21$   | $1$    | %     |

$^a$The 32e and 16d Wycko sites of the Co$_3$ in the bulk, have been denoted as Co$_{top}$ and Co$_{side}$ for the surface slabs, respectively. $^b$Percent activation is defined as $[r(N_2, g) - r(N_2, ads)] 	imes 200/[r(N_2, g) + r(N_2, ads)]$.

2 was found to activate N$_2$, where it was bound end-on at the 3-fold hollow generated by the nitrogen vacancy. This site had the second largest % activation (i.e., 11%) for molecular nitrogen. Site 3 N$_2$ was adsorbed in an end-on configuration on the Mo$_3$N framework with a weak adsorption energy (1.5 kJ/mol) due to the less metallic character of the Mo$_3$N framework. Site 4–5 N$_2$ adsorbs in a tilting end-on at the 32e Wycko site of the (Co$_{top}$) configuration with a 4–5% activation of the N–N bond and an adsorption energy of $-30$ to $-41$ kJ/mol. Site 6–7 N$_2$ adsorbs in a side-on at the 32e Wycko site (Co$_{top}$), with a 4–5% activation of the N–N bond. Interestingly, we find a surface cavity on surface C of Co$_3$Mo$_3$N (site 8), at which there is the largest activation of N–N bond, 21%. This % activation is even larger than the activation that we have found at Sf sites on surface B, which was 19%, in a previous study. Although the adsorption energy at this site maybe positive, if we take into account the entropy change for adsorption at 300 K, which is $-\Delta S = 58$ kJ/mol, the adsorption free energy becomes $-17$ kJ/mol. To summarize, two activation sites for N$_2$ have been found (i) the first at nitrogen vacancies on the Mo$_3$N framework (i.e., site 2) and (ii) the second at surface cavities where it activated on a Co atom at the 16d Wycko sites Co$_3$ (i.e., site 8, Co$_{side}$). The existence of two activation sites for nitrogen clearly suggests that there may be more than one ammonia synthesis mechanism occurring on Co$_3$Mo$_3$N catalysts. In the following section, we explain based on molecular orbital (MO) diagrams why these three adsorption configurations where found, based on the energy and spatial distribution of the frontier orbitals.

### 3.4. Interpretation of the Three N$_2$ Adsorption Configurations on Co$_3$Mo$_3$N

It is intriguing that there are three different low-overlap adsorption configurations for N$_2$ on the surface of Co$_3$Mo$_3$N, which suggests that there are three different adsorbate–surface bonding interactions. We have calculated with MP2/cc-pVTZ the molecular orbitals (MOs) of N$_2$ in order to tentatively offer an interpretation of the three adsorption configurations found. The eigenvalues and eigenfunctions of these calculations are shown in Figure 4, which show that the ordering for the highest-occupied-molecular-orbitals (HOMO: 1$p_x$), which has a $\pi$-symmetry is separated by only 0.7 eV from an MO with $\sigma$-symmetry (HOMO−1: 3$\sigma$). Both these orbitals are expected to undergo bonding interactions. Because these MOs have their lobes pointing along directions perpendicular to the molecular axis (90°) of N$_2$ and along the molecular axis (180°), therefore bonding interactions are expected along these directions. Furthermore, these MOs are not expected to take any charge from the metal atoms, but could possibly donate electron density in the form of $\sigma$-donation and $\pi$-donation, respectively.

Morokuma$^{40}$ in an energy decomposition analysis (EDA) of the bonding in (CO)$_2$Fe–CO and (CO)$_2$Fe–N$_2$ revealed equally strong contributions from $\sigma$-donation and $\pi$-backdonation, results which however may differ for cobalt dimers in which a very strong M–M interaction is present.$^{41}$

The lowest-unoccupied-molecular-orbital (LUMO: 1$\pi^*$) has a degenerate pair of orbitals and is expected to accept electron density from filled d-states of the metal through the $\pi$-back-donation mechanism. The symmetry of the highest occupied-molecular-orbital (LUMO: 1$p_x$) is identical to that of CO(g), although there the lobes of the antibonding orbital are somewhat stronger on the carbon atom.$^{43}$ We have previously shown that carbon monoxide (CO) adsorbs on various d$^7$, d$^8$, and d$^9$ metal nanoclusters in a primarily end-on configuration$^{44,45}$ at an angle of $\alpha$(M–C–O) = 180°. The existence of the end-on configuration was explained by a mechanism in which the filled d-states of the metal (that have $\pi$-symmetry) donate electron density into the empty antibonding state of CO and where the filled HOMO of CO which has $\sigma$-symmetry and resembles the HOMO−1 of N$_2$ undergoes mostly $\sigma$-repulsion. This was in agreement with previous theoretical$^{46}$ and X-ray
CO adsorbed in a tilt configuration has been previously found on Agₙ (n = 1 to 7), which was rationalized on the basis of better orbital overlap of tilt-CO with Agₙ-HOMO of σ-symmetry and of the linear end-on CO with Agₙ-HOMO of π-symmetry. Additionally, a tilt-CO was also found as a result of CO-CO repulsions and adsorption at 4-fold hollow sites. There have been many computational studies of the doping, support and NP-size effects on CO adsorption on various metal and their oxides and as elementary reaction steps in catalytic reactions. In a recent combined DFT and experimental study of the catalytic CO oxidation using bimetallic M₄Au₂₅⁻SC₄H₄Ph clusters, where M = Cu, Au, Ag, the following trend Cu > Au > Ag was found and interpreted as a result of a stronger metal-CO interaction in metals with a smaller covalent radius. Based on these earlier studies and the results found here, we rationalize that the π-back-donation of electron density into the LUMO of both N₂ and CO is expected to result in a linear end-on adsorption. The tilt end-on adsorption configuration of N₂ on Co₅Mo₃N has not been previously reported and is shown in Scheme 2. This is a well-defined adsorption configuration with a tilt angle equal to 155° in which the dihedral angle between the planes of the metal and the N₂ molecule is 0°. In the following section, we provide evidence that there are two bonding interactions that take place based on the sphere-in-contact model. We have taken literature values of 190 and 152 pm, respectively. If we fit a set of atomic radius data of various elements (60 pm) to 155°, the spheres are in contact, which indicates the presence of covalent bonding interactions, and that there is bonding both from the 3πg (HOMO−1) along the molecular axis of N₂ and the 1πg (HOMO) perpendicular to the molecular axis of N₂. This orientation is such that it would additionally undergo interactions between filled d-states of the metal and antibonding 1σ* MO of N₂. The small percentage activation of the N=N bond indicates a potential bonding mechanism where π-back-donation and a tautochronous σ- and π-repulsion are present, which results in this unusual tilt end-on adsorbed configuration of N₂.

### CONCLUSIONS

We present a dispersion-corrected DFT study of the adsorption and activation of molecular nitrogen and hydrogen on cobalt molybdenum nitride (111) surfaces to identify possible activation sites for ammonia synthesis. H₂ was found to adsorb molecularly on the Mo₃N framework and dissociatively on Co₇ clusters or Mo₃ clusters that were exposed due to N-vacancies. N₂ was found to adsorb side-on, end-on, and in an unusual tilt end-on (155°) configuration, which is rationalized via MO diagrams and the sphere-in-contact model. We find that there are two possible activation sites for N₂. The first is a Mo₃ triangular cluster that resides at M nitrogen vacancies and the second is a surface cavity where N₂ is activated by the inner tetrahedral atom of the Co₈ cluster, the second being a more efficient activation site and a particular activation site exposed only in Co₅Mo₃N surfaces with a surface composition of CoMoN₀.₄.

### AUTHOR INFORMATION

**Corresponding Authors**

*E-mail: c.zeinalipour-yazdi@ucl.ac.uk; Tel: +44 207-679-0312.*

*E-mail: c.r.a.catlow@ucl.ac.uk; Tel: +44 207-235-2818.*

**Notes**

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